Studies on the Chemical Analysis of Heavy Metal Ions by Ternary Heteropoly Anions

by

Takao FUKUMOTO

Faculty of Science
Osaka University

1986

Abstract

Heteropoly and isopoly oxometalates have been investigated in various fields, i.e., inorganic stereochemistry, organic chemistry(catalysis), biochemistry(materials), and analytical chemistry. In the field of analytical chemistry, some heteropoly complexes have been used for determination and/or separation of metal and metalloid ions in aqueous solution. The "molybdenum yellow method", which is one of the methods for the determination of phosphorus, was frequently subjected to troubles because of the interferences with coexisting metal ions, which developed the enhanced yellow color in solution. In this connection, Murata et al. have first reported that in the case of group 4A elements the interference is not attributed to any catalytic actions but to the formation of new compounds of molybdophosphate and these elements, which are called as the ternary heteropoly complexes. They have developed first stoichiometrical consideration for formation of ternary heteropoly molybdate from the results of Raman measurement. There are, however, no reports for ternary heteropoly molybdates containing group 5A elements except molybdovanadophosphates, and no attempt has been made to determine simultaneously some metal ions by use of formation of ternary heteropoly molybdate so far.

The purpose of this study is to establish an analytical

method used heteropoly complex as an "analytical reagent", so that the chemical analysis for ternary heteropoly molybdates, i.e., formation, reaction, structure, and chemical properties, by use of various experimental techniques [NMR(liquid and solid), IPRPLC, EXAFS, Raman, and IR] was examined. In this paper, the simultaneous determination of metal ions is carried out by ^{31}P NMR technique and the difference of chemical shift for each ternary heteropoly molybdate is explained well by a simple rigid sphere model. Further the separation and determination of metal ions are also carried out in lower concentrations by IPRPLC technique. In order to interpret the formation of ternary heteropoly molybdate the donor-acceptor interaction is considered and from the extended donor-acceptor interaction new concept for acceptor property of metal ion is introduced.

Finally, the contents in this paper can be summarized as follows:

In Chapter I, "General Introduction" provides the backgrounds of this study, i.e., historical perspective and methods of investigation of heteropoly oxometalates, and the present situation of those in analytical chemistry. In addition, the purpose of this study is described.

In Chapter II, reagents and the preparation of their stock solutions used are described, and general procedures for formation of ternary heteropoly molybdate and for solvent extraction of it are also described.

In Chapter III, the results of near UV spectrophotometric measurement and solvent extraction are reported. The formation of ternary heteropoly molybdates containing group 5A elements was indicated by a change in the absorption spectra. Although no maximum absorption peak was found at the wavelength higher than 250 nm, a smooth degrading curve appeared at the wavelength over 280 - 310 nm.

Solvent extraction of these species is found to be relied upon not only the kinds of oxygenated solvent but also pH value of the solution. In order to interpret the high stability of ternary heteropoly molybdate in aqueous solution, the difference of solvency of water between ternary heteropoly molybdate and 12-molybdophosphate is discussed.

In Chapter IV, ^{31}P NMR measurement is examined for ternary heteropoly molybdates. From the results it is shown that ^{31}P NMR technique leads to the assignment for each ternary heteropoly molybdate and to the quantitative determination of complexed metal ions. Simultaneous determination of these ions is also carried out by use of this technique. In order to interpret the difference of chemical shift a simple rigid sphere model is introduced and an empirical equation offers a reasonable quantitative correlation between calculated and measured results. The further analysis is tried to get the information on the structure of ternary heteropoly molybdate and by EXAFS and XANES analyses it suggests that the structure of these

species in solution must be partially distorted from the Keggin one.

In Chapter V, several chromatographic techniques are carried out to separate these ternary heteropoly molybdates and as a result, IPRPLC technique is adopted to separate them in low ppm level. In order to find out the most suitable separating condition many experiments are performed and, in analogy with NMR study, simultaneous determination and separation of these species are carried out. The interpretation for orders of elution is also reported.

In Chapter VI, according to the results of NMR and EXAFS measurements, donor-acceptor interaction is considered to interpret the formation of ternary heteropoly molybdates having the Keggin like structure. The difference of chemical shift proovides a more quantitative conclusion from the donor-acceptor interaction and leads to the new concept for acceptor property of metal ion.

Contents

Chapter I. General Introduction

In 1826 Berzelius described the yellow precipitate that is produced when ammonium molybdate is added to phosphoric acid(1), which is now known as ammonium 12-molybdophosphate, and this compound was introduced into analytical chemistry by Svanberg and Struve(2) in 1848. However it was not until the discovery of the tungstosilicic acids and their salts by Marignac(3) in 1862 that the analytical compositions of such heteropoly acids were precisely determined. Thereafter the studies on the heteropoly complexes developed rapidly and many different types of heteropoly complexes have been found. Heteropoly anions may incorporate primary(or central) and/or secondary(or peripheral) heteroatoms. The distribution of elements which are known to function as primary and secondary heteroatoms consists of a total of some 67 different elements, although the distinction between primary and secondary heteroatoms are uncertain in a few cases. Thus, in order to study for heteropoly complexes various methods, e.g., polarograpy(4,5), x-ray scattering(6-8), vibrational spectroscopy(9-11), nuclear magnetic resonance(NMR)(12-16), and so on(17-21), have been examined with respect to these primary and secondary elements up to the present. Because the complexity of polyoxometalate systems places extreme demands upon experimental techniques

and upon interpretation of results.

In many experimental techniques structural x-ray crystallography has played a major role. Therefore the structure was first reported by Keggin in 1933 for 12-tungstophosphoric acid, $H_3PW_{12}O_{40}.5H_2O$, by using of x-ray diffraction, and in his paper(22) he showed that the anion was indeed based on WO_6 octahedral units as had been suggested by Pauling(23) and that these octahedra were linked by shared edges as well as corners, which is called the Keggin structure. The majority of polyanions with tetrahedrally-coordinated heteroatoms have structures based on the Keggin anion. Since the publication of Evans' review(24), there has been a considerable increase in numbers of new polyanion structures available. However, major problems remain with the identification and structural characterization of species in solution, since more than one complex may be present, and complexes may undergo rapid(or slow) exchange or exhibit fluxional behavior. In the general case therefore, a set of different experimental techniques is necessary to offer the most promise for the characterization of polyoxometalate solutions. NMR spectroscopy is one of more effective techniques to grant the request, though the reliability and usefulness of heteronuclear NMR spectra of polyoxometalates depend very much upon the stability of its polyanion. Thus, NMR techniques for the isopoly- and heteropoly oxometalates have been already utilized by many

earlier investigators(25-32) and as the application of NMR spectroscopy to polyanions, resonances of about eight nuclei have been observed in solutions up to the present. In the studies on ^{17}O NMR(33-35), as an example, chemical shifts are determined largely by the metal-oxygen bond orders, and it is often possible to assign resonances by inspection of the anion structures. Recently, ^{183}W NMR(36-38) has been directly observed in a number of polytungstates. This nucleus has a very low receptivity, but has I = 1/2, and yields spectra with extremely narrow lines. The chemical shifts are large enough to distinguish between all structurally distinct tungsten atoms in the polyanions so far examined. Numerous heteropoly anions contain phosphorus as a primary heteroatom, and so ^{31}P NMR of such anions has attracted attention. As an example, it was through ^{31}P NMR technique that isomers of mixed heteropoly anions were first shown to exist(39).

In a field of analytical chemistry, heteropoly complexes as analytical reagents have been much valued to analyze various metal or non-metal ion in aqueous solution. For example heteropoly acids, particularly the molybdates and tungstates, have traditionally been utilized for the determination of the central atom(i.e., P, As, Si, or Ge) by means of spectrophotometric methods(40) and recently the separation of molybdophosphate and molybdosilicate by use of HPLC has been achieved by Imanari et al.(41). In addition,

ammonium 12-molybdophosphate has been successfully used as ion exchangers in column chromatographic separations of mono- or divalent cations(42-45).

By the way, in earlier investigations(46-48), it has been reported that the addition of several metal ions causes some interference or catalytic action for determination of a given metal or non-metal ion. For example, "molybdenum yellow method", which is one of the analytical methods for determination of phosphorus in aqueous solution(49-51), was furnished to severe interference with coexisting metal ions, e.g., Ti(IV), Hf(IV), Zr(IV), Th(IV), V(V), and Sb(III)(52-54). Coexistence of these metal ions, that is, developed the enhanced yellow color in solution. With respect to this interference several investigators(55,56) have already reported and in their papers it was described that this interference must result from the formation of '1:1' complexes of $PMo_{12}O_{40}^{3-}$ and $SiMo_{12}O_{40}^{4-}$ with these ions, which is called as the ternary heteropoly complexes. These complexes have been investigated for the interest of almost inorganic, catalytic and stereochemical studies, though little was known of their true stoichiometry and structures. On the other hand, nevertheless the complexes underlay reliable spectrophotometric analytical procedures, no ternary heteropoly complexes was found for the interest in the field of analytical chemistry. In this connection, Murata et al.(57,58) had first reported that with respect to the

formation of ternary heteropoly molybdate a stoichiometrical interpretation was considered by means of Raman scattering measurement and that as the result of elementary analysis the ternary heteropoly molybdate was consisted of a constant molar ratio, P:Me:Mo = 1:1:11, where Me is group 4A elements. Therefore they clarified that in the case of group 4A elements the interference is not attributed to any catalytic actions but to the formation of new compounds of PMo_{12} and these elements in aqueous solution. In addition, they have also found out that the addition of group 4A elements led to the shift for the terminal Mo=O stretching vibration of its complex at less wave number, as compared with that of PMo_{12}, in Raman spectra(59). The existence of ternary heteropoly molybdate in solution can be first confirmed by laser Raman spectroscopy. The assignment of these ternary heteropoly molybdates, however, was very difficult for the close or same wave number of these peaks, though the difference on Raman spectra was more distinct than that in the near ultraviolet spectra.

However, Murata has only discribed on the formation of ternary heteropoly molybdates containing group 4A elements, though heavy metal ions including heteropoly complexes must be exist other than those which have been studied by him, and he has not mentioned about the possibility of formation of ternary heteropoly molybdates containing group 5A elements in his papers. With respect to ternary heteropoly molybdate

containing group 5A elements, molybdovanadophosphates, PV_nMo_{12-n}(n = 1-3), have been known for many years and have often been used for the chemical analysis of phosphorus instead of PMo_{12}(60). For the chemical structure of these complexes, however, in 1959 Ablov et al.(61) had first reported that 10-molybdo-2-vanadophosphate exhibited the same feature with 12-tungstosilicate as the result of x-ray diffraction analysis, and so it was confirmed that its complex has the Keggin like structure. In addition, only recently, it has been possible to verify that discrete complexes of this type could be isolated in pure form by means of voltammetry(62). There is, however, no reports with respect to ternary heteropoly molybdates containing Nb(V) and Ta(V) ions so far. For these reasons, as part of an extensive investigation of ternary heteropoly molybdates containing several metal ions, mainly group 5A elements, it has been studied for formation, reaction, determination, and configuration of these complexes.

In this work, though Murata paid attention to molybdenum atom as secondary element and examined by use of Raman measurement, phosphorus atom as primary element was paid attention and ^{31}P NMR measurement has been first carried out(63,64). It has never been told on the quantitative attempts to determine metal ions by use of NMR technique so far. In addition, the separation of these ternary heteropoly molybdates in lower concentrations has been first

carried out by the application of ion pair reversed phase liquid chromatograpy(IPRPLC)(65). Thus two kinds of new methods for the simultaneous determination and separation of several metal ions were established. In order to study the structure of these ternary heteropoly molybdates in solution extended x-ray absorption fine structure(EXAFS) and x-ray absorption near edge structure(XANES) analyses were measured(66), because it was very difficult to crystallize them. By use of IR, Raman, and ^{31}P solid NMR measurements, the further information was obtained with respect to the structure of ternary heteropoly molybdates in liquid and/or solid states.

Thus, this paper reports the chemical analysis for several metal ions, mainly group 5A elements, by use of heteropoly molybdates as "analytical reagents". Some methods for measurement, e.g., NMR, IPRPLC, EXAFS, and so on, are adopted to investigate with respect to chemical properties of ternary heteropoly molybdates, because it is clearly desirable to make use of independent experimental methods as many as possible in order to construct a comprehensive picture of these species.

I - 2. References

1) J.Berzelius, Pogg.Ann., 6,369,380(1826).

2) L.Svanberg and H.Struve, J.Prakt.Chem., 44,257,291(1848).

3) C.Marignac, C.R.Acad.Sci., 55,888(1862).

4) P.Souchay, Ann.Chim., 19,102(1943).

5) R.Contant, J.M.Fruchart, G.Herve, and A.Teze, C.R.Acad.Sci., Ser.C,278,199(1974).

6) G.Johansson, L.Pettersson, and N.Ingri, Acta Chem. Scand., A28,1119(1974).

7) G.Johansson, L.Pettersson, and N.Ingri, Acta Chem. Scand., A32,407(1978).

8) H.A.Levy, P.A.Agron, and M.D.Danford, J.Chem.Phys., 30,1486(1959).

9) C.Rocchiccioli-Deltcheff and R.Thouvenot, Spectrosc.Lett., 12,127(1979).

10) C.Rocchiccioli-Deltcheff, R.Thouvenot, and M.Dabbabi, Spectrochim.Acta., 33A,143(1977).

11) J.Aveston, E.W.Anacker, and L.S.Johnson, Inorg.Chem., 3,735(1964).

12) S.H.Wasfi, W.Kwak, M.T.Pope, K.M.Barkigia, R.J.Butcher, and C.O.Quicksall, J.Am.Chem.Soc., 100,7786(1978).

13) L.P.Kazanskii and V.I.Spitsyn, Dokl.Phys.Chem., 223,721(1975).

14) O.W.Howarth and M.Jarrold, J.Chem.Soc., Dalton

Trans,503(1978).

15) S.E.O'Donnell and M.T.Pope, J.Chem.Soc., Dalton Trans,2290(1976).

16) R.Acerete, C.F.Hammer, and L.C.W.Baker, J.Am.Chem.Soc., 101,267(1979).

17) H.So and M.T.Pope, Inorg.Chem., 11,1441(1972).

18) L.C.W.Baker and M.T.Pope, J.Am.Chem.Soc., 82,4176(1960).

19) B.Viossat, C.Volfovsky, and M.Cadiot, C.R.Acad.Sci., Ser.C,273,1637(1971).

20) S.Ostrowetsky and D.Labonnette, C.R.Acad.Sci., Ser.C,282,169(1976).

21) S.C.Termes and M.T.Pope, Transit.Met.Chem., 3,103(1978).

22) J.F.Keggin, Nature., 131,908(1933).

23) L.C.Pauling, J.Am.Chhem.Soc., 51,2868(1929).

24) H.T.Jr.Evans, Perspec.Struct.Chem., 4,1(1971).

25) J.P.Launay, M.Boyer, and F.Chauveau, J.Inorg.Nucl.Chem., 38,243(1976).

26) L.P.Kazanskii, M.A.Fedotov, M.N.Ptushkina, and V.I.Spitsyn, Dokl.Phys.Chem., 224,1029(1975).

27) J.V.Hatton, Y.Saito, and W.G.Schneider, Can.J.Chem., 43,47(1965).

28) E.Heath and O.W.Howarth, J.Chem.Soc., Dalton Trans,1105(1981).

29) W.D.Kautt, H.Krueger, O.Lutz, H.Maier, and A.Nolle, Z.Naturforsch., 31a,351(1967).

30) L.I.Lebedeva and E.V.Vanchikova, Russ.J.Inorg.Chem.,

19,1798(1974).

31) M.A.Fedotov, V.N.Molchanov, L.P.Kazanskii, E.A.Torchenkova, and V.I.Spitsyn, Dokl.Chem., 245,122(1979).

32) R.Massart, R.Contant, J.M.Fruchart, J.P.Ciabrini, and M.Fournier, Inorg.Chem., 19,3866(1980).

33) M.Filowitz, R.K.C.Ho, W.G.Klemperer, and W.Shum, Inorg.Chem., 18,93(1979).

34) M.Filowitz, W.G.Klemperer, L.Messerle, and W.Shum, J.Am.Chem.Soc., 98,2345(1976).

35) L.P.Kazanskii, M.A.Fedotov, and V.I.Spitsyn, Dokl.Phys.Chem., 234,617(1977).

36) R.G.Finke, M.Droege, J.R.Hutchinson, and O.Gansow, J.Am.Chem.Soc., 103,1587(1981).

37) J.Lefebvre, F.Chauveau, P.Doppelt, and C.Brevard, J.Am.Chem.Soc., 103,4589(1981).

38) P.R.Sethuraman, M.A.Leparulo, M.T.Pope, F.Zonnevijlle, C.Brevard, and J.Lemerle, J.Am.Chem.Soc., 103,7665(1981).

39) M.T.Pope, S.E.O'Donnell, and R.A.Prados, J.Chem.Soc., Chem Comm,22(1975).

40) G.A.Tsigdinos, Climax monograph: Heteropoly compounds of molybdenum and tungsten. In "Bull.Cdb-12a(Revised)",Nov. 1969.

41) I.Koshiishi and T.Imanari, Anal.Sci., 1,253(1985).

42) C.J.Coetzee and E.F.C.H.Rohwer, J.Inorg.Nucl.Chem., 32,1711(1970).

43) C.J.Coetzee and A.J.Van.Wyk, J.Inorg.Nucl.Chem., 33,1501(1971).

44) J.V.R.Smit, J.J.Jacobs, and W.Robb, J.Inorg.Nucl.Chem., 12,95(1959).

45) M.T.Ganzerli Valentini, V.Maxia, M.A.Rollier, and M.Barbaro Forleo, J.Inorg.Nucl.Chem., 32,671(1970).

46) M.Ishibashi and M.Tabuchi, Bunseki Kagaku., 8,588(1959).

47) R.M.Veitsman, Zavod.Lab., 26,927(1960).

48) A.K.Babko and Yu.F.Shkaravskii, Zh.Neorgen.Khim., 6,2091(1961).

49) F.D.Snell and C.T.Snell, "Colorimetric Methods of Analysis" Vol.II,3rd ed., D.Van Nostrand Co,Inc., Princeton,N.J.(1949).

50) I.M.Kolthoff and E.B.Sandell, "Textbook of Quantitative Inorganic Analysis" 3rd ed., Macmillan, New York(1964).

51) I.M.Kolthoff and P.J.Elving, "Treatise on Analytical Chemistry" Part II,Vol.V, Phosphorus,(W.Rieman III, J.Benken Kamp) (1961).

52) P.Pakalns, Anal.Chim.Acta., 40,1(1968).

53) J.E.Going and S.J.Eisenreich, Anal.Chim.Acta., 70,95(1974).

54) V.F.Barkovskii and T.V.Velikanova, Russ.J.Inorg.Chem., 15,879(1970).

55) V.F.Barkovskii and O.N.Skornyakova, Russ.J.Inorg.Chem., 14,545(1969).

56) Yu.F.Shkaravskii, Russ.J.Inorg.Chem., 8,1399(1963).

57) K.Murata, Y.Yokoyama, and S.Ikeda, Anal.Chim.Acta., 48,349(1969).

58) K.Murata and S.Ikeda, Anal.Chim.Acta., 51,489(1970).

59) K.Murata and S.Ikeda, Anal.Chim.Acta., 151,29(1983).

60) H.C.Baghurst and V.J.Norman, Anal.Chem., 27,1070(1955).

61) A.V.Ablov, T.I.Malinovskii, and V.I.Dedyu, Zh.Neorg.Khim., 4,397(1959).

62) D.P.Smith and M.T.Pope, Inorg.Chem., 12,331(1973).

63) T.Fukumoto, K.Murata, and S.Ikeda, Anal.Chem., 56,929(1984).

64) T.Fukumoto, J.Iyoda, K.Murata, and S.Ikeda, Chem.Lett., 1311(1985).

65) T.Fukumoto, K.Murata, and S.Ikeda, Anal.Sci., in submitted.

66) T.Fukumoto, N.Matsubayashi, K.Murata, and S.Ikeda, INorg.Chem., in submitted.

Chapter II. Experimental

II - 1. Reagents and General Procedure

All solutions were prepared with reagent grade chemicals. A stock solution of molybdate was prepared by dissolving about 121.0 g $Na_2MoO_4.2H_2O$ in water and diluting to 1 dm^3 with water (C_{Mo} = 0.5 mol dm^{-3}). This solution was standardized by the oxine method(1). A stock solution of phosphate was prepared by dissolving precisely 13.609 g KH_2PO_4, after drying overnight at 110 °C, into 1 dm^3 of water (C_P = 0.1 mol dm^{-3}). Stock solutions of Zr(IV) and Hf(IV) were prepared by dissolving $ZrOCl_2.8H_2O$ and $HfOCl_2.8H_2O$ into 1 mol dm^{-3} HNO_3 solution, respectively (C_{Zr} = C_{Hf} = 0.1 mol dm^{-3}). A stock solution of Ti(IV) was prepared by dissolving titanium metal into dil. sulfuric acid and then oxidizing with a small amount of nitric acid (C_{Ti} = 0.1 mol dm^{-3}). A stock solution of Th(IV) was prepared by dissolving $Th(NO_3)_4.4H_2O$ into 1 mol dm^{-3} HNO_3 solution (C_{Th} = 0.1 mol dm^{-3}). Each solution of Zr(IV), Hf(IV), Ti(IV), and Th(IV) was standardized by gravimetric determination with cupferron(2). A stock solution of V(V) was prepared by dissolving NH_4VO_3 in dil. sodium hydroxide (C_V = 0.1 mol dm^{-3}). Stock solutions of Nb(V) and Ta(V) were prepared by dissolving an aliquot amount of the respective metal(purity, 99.9%) with the mixed acid of 47% hydrofluoric acid and

nitric acid(1+1). Sulfuric acid(1+1) was slowly added in the solution and excess hydrofluoric acid was removed by heating to fume. They were finally diluted to the definite volume by sulfuric acid(1+1) ($C_{Ta} = C_{Nb} = 0.1$ mol dm^{-3}). Stock solutions of Ce(III) and Ce(IV) were prepared by dissolving $Ce_2(SO_4)_3$ and $Ce(SO_4)_2$ into 1 mol dm^{-3} HNO_3 solution, respectively ($C_{Ce(III)} = C_{Ce(IV)} = 0.1$ mol dm^{-3}). Stock solutions of Bi(III) were prepared by dissolving $Bi(NO_3)_3.5H_2O$ and BiOCl into 1 mol dm^{-3} HNO_3 and HCl solutions, respectively ($C_{Bi(III)} = 0.1$ mol dm^{-3}). Each metal ion solution, V(V), Nb(V), Ta(V), Ce(III), Ce(IV), and Bi(III), was standardized by use of the published methods(3-6). Stock solutions of As(III) and As(V) were prepared by dissolving As_2O_3 and $Na_2HAsO_4.7H_2O$ into dil. sodium hydroxide, respectively ($C_{As(III)} = C_{As(V)} = 0.1$ mol dm^{-3}). Stock solutions of Se(IV), Se(VI), Te(IV), and Te(VI) were prepared by dissolving Na_2SeO_3, Na_2SeO_4, Na_2TeO_3, and $Na_2H_4TeO_6$ in water, respectively ($C_{Se(IV)} = C_{Se(VI)} = C_{Te(IV)} = C_{Te(VI)} = 0.1$ mol dm^{-3}). Stock solutions of Sb(III) and Sb(V) were prepared by dissolving $COOKCH(OH)CH(OH)COO(SbO).1/2H_2O$ and $SbCl_5$ in water and conc. HCl solution, respectively ($C_{Sb(III)} = C_{Sb(V)} = 0.1$ mol dm^{-3}). Above mentioned non-metal ion solutions, As(III), As(V), Se(IV), Se(VI), Te(IV), Te(VI), Sb(III), and Sb(V), were standardized by use of the published methods(7,8). PAR[4-(2-pyridylazo)-resorcinol] sln. was prepared by dissolving 1 g

of it in dil. sodium hydroxide sln(5%). and diluting to 1 dm^3 with water(0.1% sln.). This colorimetric reagent sln. was stable within one month. L-ascorbic acid(1% sln.) as reductant is not stable for long periods of time at room temperature and so were prepared fresh just prior to use. Stock solutions of six varieties of ion-pair reagents, i.e., guanidine hydrochloride, tetra-n-butylammonium bromide, tetra-ethylammonium bromide, n-dodecyltrimethylammonium bromide, n-cetyltrimethylammonium bromide, and trimethylphenylammonium bromide, were prepared by dissolving aliquot amounts into 1 mol dm^{-3} HNO_3 solution, respectively (C_{IP} = 0.1 mol dm^{-3}). Analytical grade reagents, i.e., acetonitrile, methanol, HCl, HNO_3, ion-pair reagents, and some organic solvents(used solvent extraction) were used without further purification.

The general procedure for the preparation of ternary heteropoly molybdate was as follows: each aliquot of phosphate and molybdate solution was first mixed and an acid was added to it, and so the solution developed a yellow color. An metal ion was slowly added in the solution with vigorous stirring, and water and/or dil. acid solution were used to adjust the acidity of this solution to the adequate value. For EXAFS, ^{31}P solid NMR, IR, and Raman measurements, polymorphs heteropoly molybdates were prepared synthetically by the following procedure. Thus an ion pair reagent solution was slowly added in an above heteropoly molybdate

solution with vigorous stirring, and so a yellow precipitate was found almost immediately. The solution and precipitate were kept at ca.50 °C for 8 h in water bath, and the yellow precipitate was separated from the solution by filtration, after washed with dil. nitric acid and water, and dried under vaccum.

In addition, solvent extraction was carried out according to the following procedure. Thus a centrifuge tube with stopper, 3 cm in diameter and 50 cm^3 in volume, was used as a separatory funnel for extraction. The shaking for extraction was carried out with an autoshaker operating at 200 strokes min^{-1}. A mixed solution of equal volumes of organic solvent and ternary heteropoly molybdate solution was equilibrated at 25 °C by shaking the mixture for 20 min and then allowing it to stand for 5 min for phase separation. Both phases were completely separated by centrifugation. After the extraction, the aqueous phase was separated out and spectrophotometric determination of the metal ion remained in aqueous phase with PAR(9) was done to measure the distribution ratio of metal ion.

By the way, although solutions with various molar ratios of P:Me:Mo and pH values were prepared, the concentration and pH value of liquid samples were varied depending upon the sensitivity of instruments: for NMR(liquid), EXAFS, and Raman measurements, C_p = 1.0 x 10^{-2} mol dm^{-3}, pH 0.5 - 1.0; for IPRPLC measurement and solvent extraction, C_p = 1.0 x 10^{-4}

mol dm^{-3}, pH ~ 2.0; for near UV measurement, C_P = 1.0 x 10^{-5} mol dm^{-3}, pH ~ 3.0.

II - 2. Instrumentation

1) NMR(liquid) measurement

^{31}P NMR spectra were measured with 10 or 15 mm tubes by using both Bruker WM-360WB and JEOL JNM-FX200 spectrometers operating at 145.805 and 80.74 MHz, respectively. Measurement was made at ambient temperature, ca.25 °C. An external ^{2}H lock(D_2O) was employed and proton decoupling was not used. Spectra were obtained by Fourier transform FID with a 45° pulse and repetition time of 3.05 s, and they were accumulated for 1000 - 3000 times. A 0.05 mol dm^{-3} 1-aminoethylidene-bis(phosphonic acid) aqueous solution was used as an external standard in the ^{31}P NMR spectra and the chemical shift of external standard signal is at +14.01 ppm relative to that of 85% H_3PO_4(downfield from H_3PO_4). These operating conditions were selected to obtain the maximum signal-to-noise ratio for the spectrum of 12-molybdophosphate solution(pH 0.8). A typical running time for each NMR measurement was approximately 2 h. Negative value of δ represents a resonance at higher field than that of external standard. These instruments and operating conditions, as above mentioned, are summarized in Table II-1.

2) NMR(solid) measurement

Solid ^{31}P NMR spectra of the static samples were measured with 5 mm tube by using JEOL JNM-FX100 spectrometer operating at 40.30 MHz. The measurement was made at room temperature, ca. 25 °C, and an external ^{2}H lock(D_2O) was employed. Spectra were obtained by single pulse or cross polarization(CP) technique, and 50 - 200 scans at 20 s recycle time were applied. The chemical shift was measured relative to external standard of 85% H_3PO_4. These instrument and operating conditions are summarized in Table II-2.

3) IPRPLC measurement

The high performance liquid chromatographic system of a JASCO Model TRI ROTAR-VI was used(TRI ROTAR HPLC pump, Model VL-614 loop injector, UVIDEC 100-VI spectrometric detector, and Model TU-300 column oven). Reversed phase separations were carried out on Chemcosorb 7-ODS-L, 10-ODS-L, Nucleosil 10C18, and Finepak SIL C_1 (150 mm x 4.6 mm-i.d) columns at 20 - 40 °C. In all the studies the composition of mobile phase consisted of mixed solvents(aceton itrile, dil. nitric acid, and an ion pair reagent sln.) with various volume fractions. In this paper the compositions of mobile phase are given in volume ratio. The mobile phase flow rate was 1.5 - 2.5 ml/min, and UV detector was operated at 300 nm. Sample injection volume was 10 - 30 μl. One IPRPLC run took as little as 30 min or less. These instrument and chromatographic conditions are summarized in Table II-3. Between changes of mobile phases, the chromatographic system,

Table II-1. Instruments and Operating Condition of Liquid NMR Measurement

Instrument	JEOL JNM-FX200 Bruker WM-360WB
^{31}P resonance frequency	80.74 MHz (145.805 MHz)[a]
External standard	1-aminoethylidene bis(phosphonic acid)
Lock	D_2O
Temperature	23 - 25 °C
Accumulated time	1000 - 3000 times
Interval	3.05 s
Pulse sequence	single pulse mode (45° pulse)

[a]Used for Bruker WM-360WB.

Table II-2. Instrument and Operating Condition of Solid NMR Measurement

Instrument	JEOL JNM-FX100
^{31}P resonance frequency	40.30 MHz
Lock(external)	D_2O
Temperature	25 °C
Accumulated time	50 - 200 times
Interval	20 s
External standard	85% H_3PO_4
Pulse sequence	single pulse or cross polarization(CP)

including the column, was washed with 100 ml of acetonitrile and water(1+1).

4) EXAFS and XANES measurements

The x-ray absorption measurement was carried out by use of the EXAFS spectrometer at the Beam Line 10B(BL-10B) of the Photon Factory in the National Laboratory for High Energy Physics(KEK-PF)(10). Synchrotron radiation from the electron storage ring(2.5 GeV, 80 - 150 mA) was monochromatized with a channel-cut Si(311) or Si(111) monochromator. The incident and transmitted beam intensities were measured with N_2 and Ar filled ionization chambers, respectively. A typical running time for each experiment was approximately 30 min. The liquid samples were placed in polyethylene pouches held between two stainless holders having 4 mm x 14 mm window. The thickness of the liquid sample was 0.5 - 3.5 cm. The powdered crystal samples were held on adhesive tape and the thickness was adjusted to obtain the optimum beam intensities. The analysis of data obtained from x-ray absorption measurement was mainly carried out according to the analytical method proposed by Matsubayashi(11).

5) Raman measurement

Raman spectra were measured with a JASCO R750 triple monochromator and JASCO R800, using Ar^+ laser 514.5 nm(300 mW at the laser head) for liquid samples and He-Ne laser 632.8 nm(50 mW) for solid ones as the excitation source, respectively. Entrance, intermediate, and exit slits were at

300, 350, and 300 μm for liquid, and 500, 550, and 500 μm for solid, respectively. About 4 ml of sample solution was taken out in a measured cell and used for measurement. The solid state spectra of heteropoly complexes were measured in sealed glass capillary tubes. In order to avoid the uncertainty in measured wavenumbers due to monochromator drift, the intense and sharp line of NO_3^-, which is observed at 1049 cm^{-1}, was adopted as an internal standard for liquid samples. Besides, the terminal Mo=O stretching vibration of the heteropoly molybdates appears at the wavenumber below 1000 cm^{-1}. This sodium nitrate of a constant concentration(0.08 mol dm^{-3}) is used as an internal standard and added in each sample solution to be measured. Addition of sodium nitrate did not affect Raman spectra. These instrument and operating conditions are summarized in Table II-4.

6) IR and UV measurements

IR spectra(KBr disks) were recorded on a JASCO Model DS-402G infrared spectrometer.

Spectrophotometric measurement was made with a UVID EC-500 spectrophotometer (Nihon Bunko) at the wavelength range 450 - 250 nm using 1.0 cm silica cell, while for solvent extraction at 545 nm using 0.1 - 1.0 cm ones.

Table II-3. Instrument and Chromatographic Condition of IPRPLC

Instrument	JASCO TRI ROTAR-VI
Detector	UVIDEC 100-VI spectrometer
Column	Chemcosorb 7-ODS-L , 10-ODS-L Nucleosil 10C18 (ϕ 4.6 x 150 mm)
Wavelength	300 nm
Flow rate	1.5 - 2.5 ml/min
Temperature	20 - 40 °C
Sample size	10 - 30 µl
Mobile phase	CH_3CN + HNO_3 sln.(pH 2-3) + Ion-pair reagent sln. (DTMA or TBA)

Table II-4. Instrument and Operating Condition of Raman Measurement

Instrument	JASCO R750 monochromator JASCO R800
Excitation source	Ar^+ laser(514.5 nm) He-Ne laser(632.8 nm)[a]
Entrans slit	300 µm (500 µm)[a]
Intermediate slit	350 µm (550 µm)[a]
Exit slit	300 µm (500 µm)[a]
measured wave number	100 - 1100 cm^{-1}
Internal standard	$NaNO_3$(1049 cm^{-1})

[a]Used for solid sample.

II - 3. References

1) N.H.Furman, Ed."Standard Method of Chemical Analysis",6th ed; Van Nostrand: New York, 1962; Vol 1.

2) P.J.Elving and E.C.Olson, Anal.Chem., 27,1817(1955).

3) D.C.G.Pearton, J.D.Taylor, P.K.Faure, and T.S.Steele, Anal.Chim.Acta., 44,353(1968).

4) J.L.Hague and L.A.Machlan, J.Research NBS., 62,11(1959).

5) A.I.Popov and W.W.Wendlandt, Anal.Chem., 26,883(1954).

6) H.Bode and G.Herrich, Z.Anal.Chem., 135,98(1952).

7) W.F.Hillebrand, et al.:"Applied Inorganic Analysis", 2nd Ed. (1953), (John Wiley).

8) L.Erdey.:"Gravimetric Analysis", Part 2 (1965), (Pergamon).

9) R.Belcher, et al. Talanta., 10,1013(1963).

10) H.Oyanagi, T.Matsushita, M.Ito, and H.Kuroda, KEK Report., 83-30(1984).

11) N.Matsubayashi, Ph.D.Thesis, Osaka University,(1986).

Chapter III. Reaction of 12-Molybdophosphate and Group 5A Elements

III - 1. Measurement of Near UV Spectra, Raman Spectra and Solvent Extraction

Although there are many reports for formation, reaction, or chemical properties of binary heteropoly complexes, e.g., 12-molybdophosphate(PMo_{12}), 18-molybdodiphosphate(P_2Mo_{18}), and so on(1-5), a few papers have been reported for those of ternary heteropoly complexes so far. As an example, Murata et al.(6) have succeeded in introduction of group 4A elements into the cluster of heteropoly complex by use of the reaction between its element and 11-molybdophosphate(PMo_{11}), which is one of the lacunary heteropoly complexes. In its paper they have first treated stoichiometrically with respect to the formation of ternary hrteropoly molybdate from the point of view of analytical chemistry. Although they have mainly made their investigation by Raman measurement, the mechanism of formation of these complexes has remained obscure. The present author extended his research on the reaction of group 5A elements with phosphate and molybdate, and found the rapid and quantitative formation of new heteropoly complexes in an aqueous medium. The interpretation for the mechanism of formation of these complexes was firstly examined by use of spectrophotometric and solvent extraction methods.

The formation reactions between Nb(V) and Ta(V) ions and the mixture of phosphate and molybdate were very critical, as compared with the reaction for vanadium(V) ion, so that the quantitative investigation of these complexes in aqueous medium required careful procedures, i.e., adjustment of pH value, slow addition, and continuons stirring, because Nb(V) and Ta(V) ions are subject to hydrolytic change easily.

At first keeping other factors constant, i.e., C_{Nb} = 8 x 10^{-6}, C_P = 1.0 x 10^{-5}, C_{Mo} = 1.5 x 10^{-4} (mol dm^{-3}), pH value was varied from 1.0 to 4.5. Figure III-1 shows the variation of near UV spectra for pH values. As shown in Fig.III-1, the dependence on pH value was represented with respect to the reaction of Nb(V) ion and 12-molybdophosphate. Thus, in the pH range 2.5 - 3.5, a shoulder peak was observed near 300 nm in spectra. This result indicated that the most suitable formation condition for the new heteropoly complex could be gained in this pH range. The formation of the new heteropoly complex, however, depended not only on pH value in solution, but also on the concentration of each component to construct it. Thus the higher concentration of its complex, the lower pH value was required for the acquisition of most suitable formation condition, i.e., C_X ~ 1.0 x 10^{-4} mol dm^{-3} / near pH 2.0, while C_X ~ 1.0 x 10^{-2} mol dm^{-3} / pH 0.5 - 1.0, where C_X refers to Nb(V) ion concentration. In addition, the dependence of the formation of the new compound on Nb(V) ion concentration was examined. Figure III-2 shows the variation

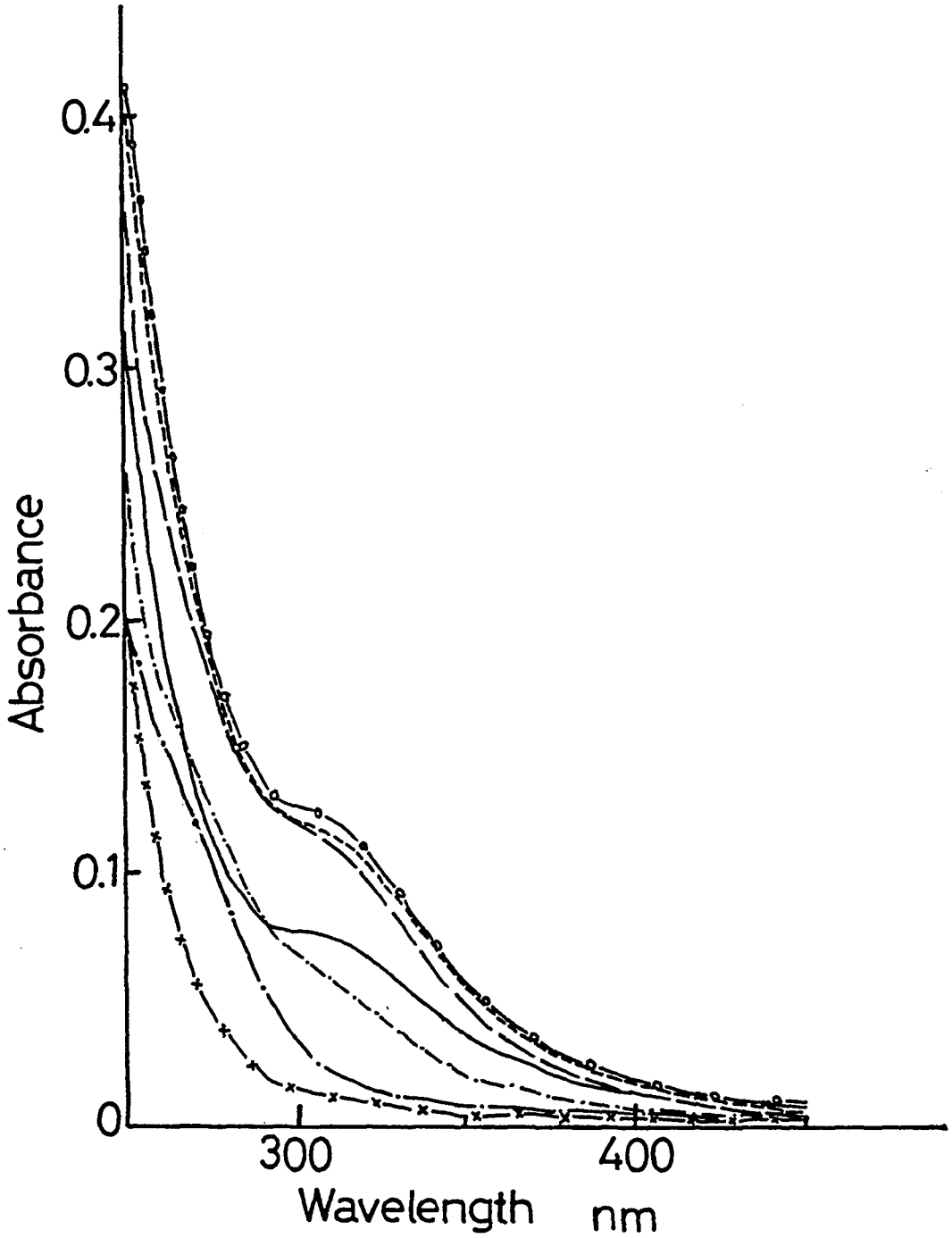


Fig III-1. Dependence of absorbance on pH value in near UV spectra.

$C_P = 1.0 \times 10^{-5}$, $C_{Nb} = 8.0 \times 10^{-6}$, $C_{Mo} = 1.5 \times 10^{-4}$ (mol dm^{-3}) L = 10 mm, ref. H_2O

1) pH 1.0 (—·—) 2) pH 2.0 (-·—·—) 3) pH 2.5 (— — —)
4) pH 3.0 (—o—) 5) pH 3.5 (------) 6) pH 4.0 (———)
7) pH 4.5 (—X—)

of near UV spectra by the addition of Nb(V) ion. A shoulder peak was observed clearly with increasing Nb(V) ion concentration, but in the presence of excess amount of Nb(V) ion a precipitate or turbidity appeared soon. The variation of near UV spectra, while sufficient to confirm the formation of new heteropoly complexes in solution, does not permit the idetification of each species. Therefore three new heteropoly complexes were indistinguishable from each other by the near UV spectra because of the overlapping of the maximum absorption wavelength for each at 302 nm. The stoichiometrical formation of the heteropoly complex, however, could be guessed from near UV spectra and these features of near UV spectra were in good agreement with the case of group 4A elements.

Murata et al.(7) have also reported for the quantitative determination of ternary heteropoly molybdates containing group 4A elements by use of solvent extraction-spectrophotometric method. In the paper, the extraction of excess PMo_{12} from the mixed heteropoly complexes' solution was done with n-butyl acetate and the metal ions remained in aqueous solution were determined by spectrophotometric method. In general, binary heteropoly complexes were virtually extracted with many oxygenated solvents(8), while in the extraction of ternary heteropoly molybdate containing group 4A elements by alcohols, a turbidity was observed in the aqueous phase. In this work, in analogy with the case of

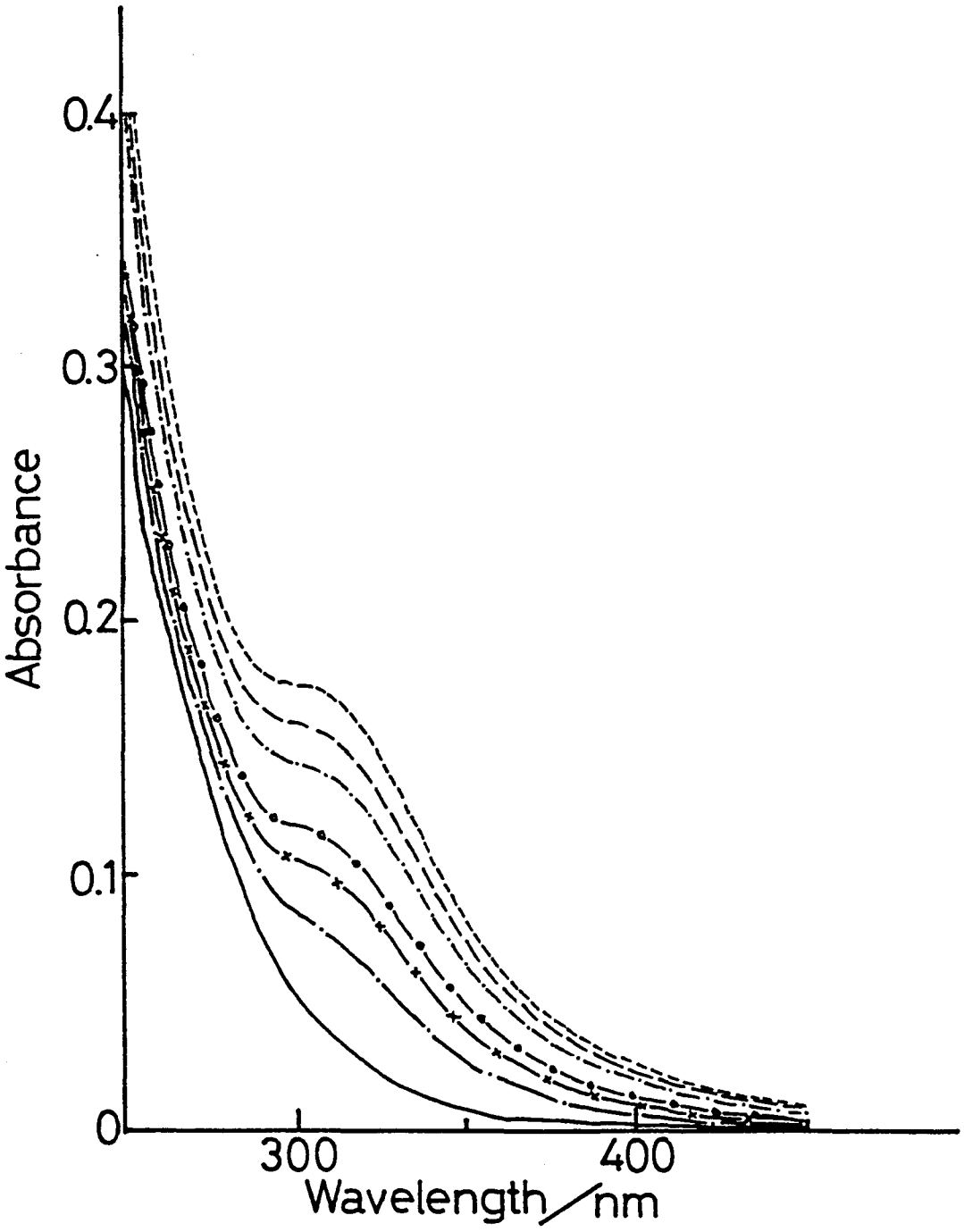


Fig III-2. Dependence of absorbance on the concentration of Nb(V) ion in near UV spectra.

C_P = 1.0 x 10^{-5}, C_{Mo} = 1.5 x 10^{-4} (mol dm^{-3}) pH 3.0

L = 10 mm, ref. H_2O

1) C_{Nb}= 0 (———) 2) C_{Nb}= 2x10^{-6} (—·—) 3) C_{Nb}= 3x10^{-6} (—x—)

4) C_{Nb}= 4x10^{-6} (—o—) 5) C_{Nb}= 6x10^{-6} (—·—·—)

6) C_{Nb}= 8x10^{-6} (— — —) 7) C_{Nb}= 1x10^{-5} (------)

group 4A elements, the extraction of the new compounds by alcohols led to a turbidity in aqueous phase and, as summarized in Table III-1, solvent extraction of the new heteropoly complex formed in aqueous solution was found to be selectively done, and cyclohexanone and propylene carbonate preferentially could extract it in higher yield. These results suggested the formed new heteropoly complexes to be the same type of ternary heteropoly molybdate as the cases for the addition of group 4A elements. In addition, the extraction of the new compounds with cyclohexanone was further carried out to investigate the formation of it. The pH dependence of distribution ratio was determined with various molybdate concentrations. Figure III-3 shows the distribution ratio vs. pH values with respect to the niobium compound. The results obtained show that the niobium compound is formed within the limited pH range and that more narrow range than that of PMo_{12}. Therefore it was shown that the solution acidity as well as the kind of solvent is critical upon extractability and that it is decomposed in either very dilute or very concentrated acid solution. In addition, the dependence of distribution ratios on molybdate concentration was also determined, in which the molybdate concentration was varied from 9.0×10^{-4} to 1.6×10^{-3} mol dm^{-3} by keeping other factors constant, i.e., $C_P = C_{Nb} = C_{Ta} = 1.0 \times 10^{-4}$ mol dm^{-3}, pH 2.0. Figure III-4 shows that the distribution ratios approach almost to constant limiting

Table III-1. Recovery of Molybdoniobophosphate Extracted by Various Solvents

solvent	% recovery[a)]
cyclohexanone	99.1 ± 0.5
propylene carbonate	97.8 ± 0.6
acetyl acetone	86.9 ± 0.5
methyl n-propyl ketone	74.0 ± 0.6
acetophenone	67.5 ± 0.7
methyl ethyl ketone	40.9 ± 0.3
methyl isobutyl ketone	40.8 ± 0.7
isoamyl alcohol	34.6 ± 0.7
n-butyl alcohol	22.1 ± 0.5
methyl tert-butyl ketone	16.6 ± 0.8
nitromethane	6.2 ± 0.6
nitrobenzene	6.0 ± 0.4
ethyl acetate	4.7 ± 0.4
chloroform	3.9 ± 0.5
carbon tetrachloride	3.4 ± 0.6
cyclohexane	1.0 ± 0.6
benzonitrile	1.0 ± 0.8
ethyl n-butyl ketone	----b)
isoamyl acetate	----
diethyl ether	----
diisopropyl ether	----
n-caproic acid	----
n-butyl acetate	----

a) Data are average and average deviation of three replicates.

b) Not detected.

(Sample: $C_P = C_{Nb} = 1.0 \times 10^{-4}$, $C_{Mo} = 1.5 \times 10^{-3}$ mol dm^{-3} pH 2.0)

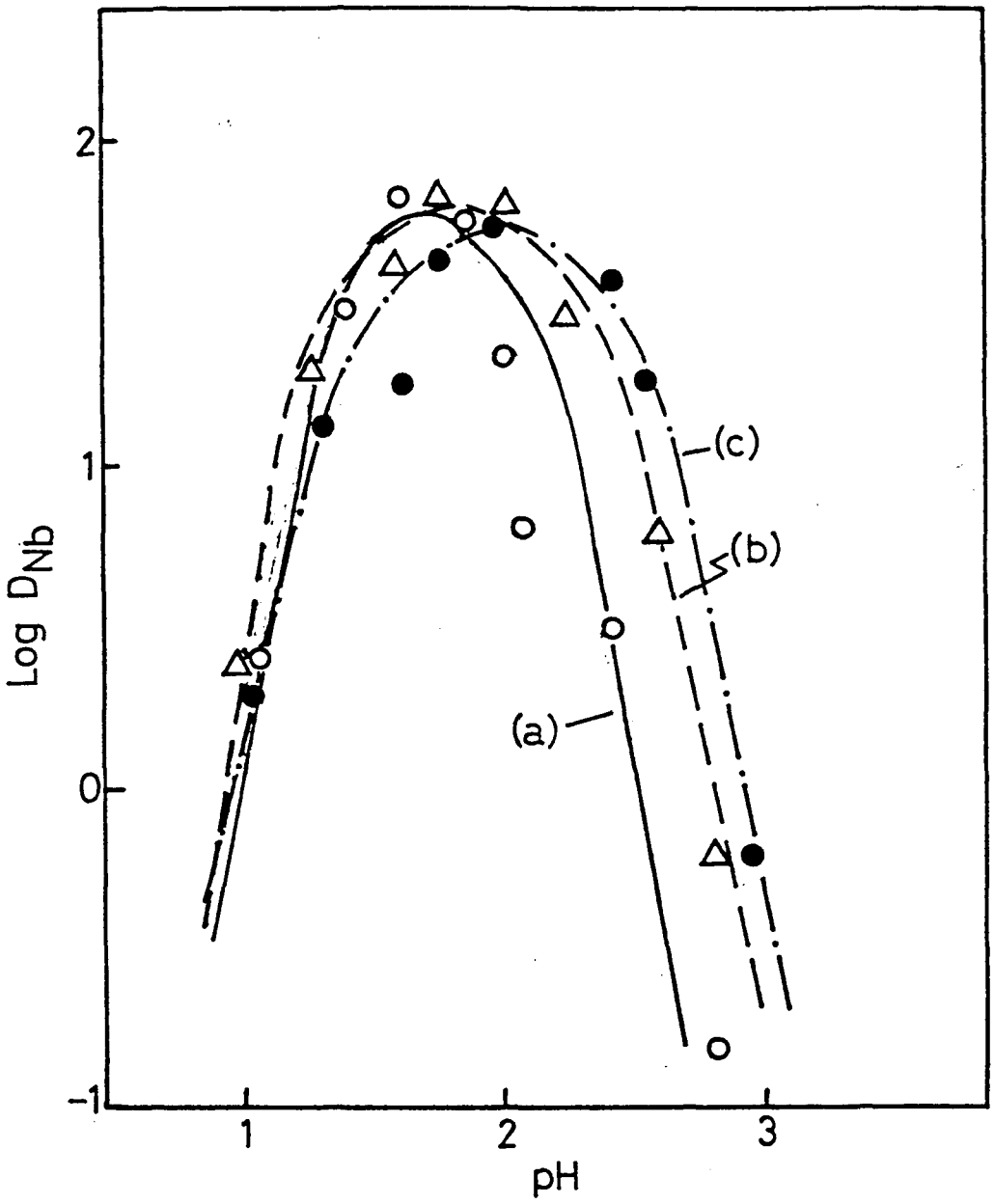


Fig III-3. Dependence of distribution ratios on pH value.

$C_P = C_{Nb} = 1.0 \times 10^{-4}$ (mol dm^{-3})

(a) $C_{Mo} = 1.1 \times 10^{-3}$ (O) (b) $C_{Mo} = 1.2 \times 10^{-3}$ (Δ)

(c) $C_{Mo} = 1.5 \times 10^{-3}$ (●) (mol dm^{-3})

values, the molar ratio(C_{Mo} / C_P) at the intercept of the extrapolation of two lines being 11. This result can be presumed that the excess molybdenum species, though in such a case the complex must be more stable, are not necessarily to produce the complex quantitatively and that it has the composition ratio of P:Me:Mo = 1:1:11, where Me refers to group 5A elements. This result was further supported by the gravimetric analysis experimentally. Although the results of Raman measurement will be reported elsewhere(see Chapter IV) in detail, the shift of the peak pertaining to heteropoly molybdate at less wave number, in analogy with the case of group 4A elements, observed by the addition of group 5A ones. In light of these experimental results it must be noted that the new heteropoly complexes have a similar structure to that of ternary heteropoly molybdate containing group 4A elements, $PXMo_{11}$.

By the way, cyclohexanone dissolved in aqueous phase accelerated the degradation of PAR reagent. The color was stable up to 5 h, so that measurement must be made within this period.

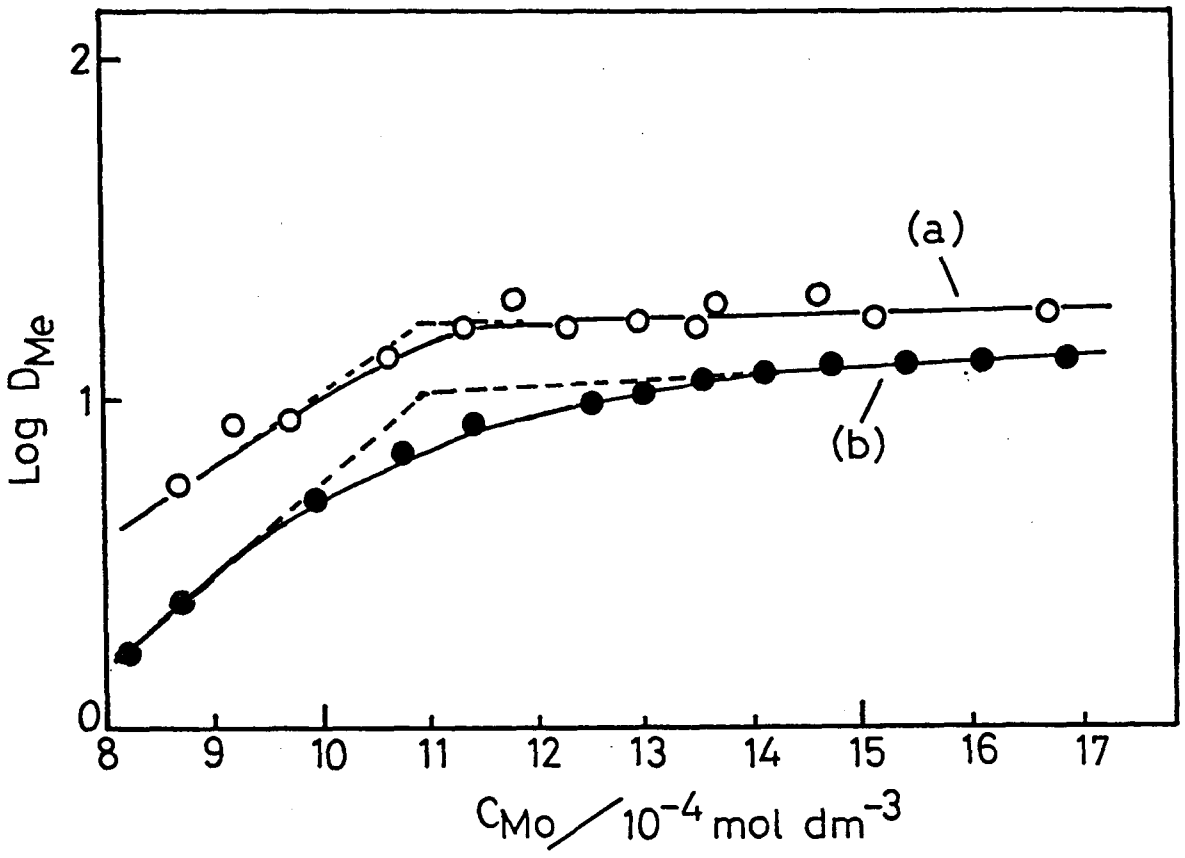


Fig III-4. Dependence of distribution ratios on molybdate concentration.

$C_P = C_{Me} = 1.0 \times 10^{-4}$ (mol dm^{-3}) pH 1.9-2.1

(a) $C_{Me} = C_{Nb}$ (○) (b) $C_{Me} = C_{Ta}$ (●)

III - 2. Interpretation for Formation of Ternary Heteropoly Molybdate

The experimental data to confirm the formation of ternary heteropoly molybdate have been obtained not only from the studies of spectrophotometry but also from those of solvent extraction. In light of the above data of near UV spectra, together with the results of Raman measurement, and solvent extraction the formation of ternary heteropoly molybdate is considered as follows:
in aqueous solution PMo_{12} has a limited stable range for the acid concentration and it is reversibly converted to PMo_{11}. When the excess molybdate is added the equilibrium shifts to the formation of PMo_{12}, whereas X ion is added in this solution the metal ion can react with PMo_{11} to form ternary heteropoly molybdate, $PXMo_{11}$. Apparently the ternary heteropoly molybdate is more stable than PMo_{12} in solution because of the ansymmetrical, with higher charge density, and distorted form. Thus the former woulld have a larger formation constant than the latter. The above reactions are illustrated in Fig.III-5. The high stability of ternary heteropoly molybdate in water is mainly due to the higher solvency of water. By the comparison of the number of water of crystallization in PMo_{12} and that in ternary heteropoly molybdate this is explained well. For these reasons, it was difficult to extract these complexes from aqueous medium.

Fig III-5. Formations of 12-molybdophosphate and ternary heteropoly molybdate.

When viewed further under the microscopic, from the results of x-ray analysis of PMo_{12}(Although the accurate determination of the structure of ternary heteropoly molybdate by x-ray structure analysis has not been succeeded diffraction can not be achieved except PV_nMo_{12-n}(n=1-3) so far, similar features can be considered as to ternary heteropoly molybdate because of the results of Raman spectra and also comparison the structure of molybdovanadophosphate($PVMo_{11}$) and that of PMo_{12}) the stability of ternary heteropoly molybdate in water must be ascribed to the closer packing which is possible when the anions are arranged on a triclinic lattice. Despite the closer packing, however, there is still a considerable volume of unoccupied space because of the shape of the anions. In aqueous solution, PMo_{12} was solvated so as to make the whole structure as homogeneous as possible because the negative charge of PMo_{12} is distributed uniformly over its whole surface. On the other hand, for ternary heteropoly molybdate, the substitution of a complexed metal ion for one molybdemun ion causes the ununiformity(or localization) of the charge density to the surface of heteropoly anion, so that its anion is solvated heterogeneously by water molecule according to the localized electron density. The induced stronger interaction with solvating waters, as compared with PMo_{12}, leads to the stability of ternary heteropoly molybdate in solution. The difference between each ternary heteropoly

molybdate will be reported elsewhere in detail(see Chapter VI).

III - 3. References

1) L.P.Kazansky, I.V.Potapova, and V.I.Spitsyn, Proc.3rd rnat.Conf.Chemistry and Uses of Molybdunum, Arbor,MI, pp.67(1979).

2) L.Pettersson, Chem.Scr., 7,145(1975).

3) L.Lyhamn and L.Pettersson, Chem.Scr., 16,52(1980).

4) B.Hedman, Acta Chem.Scand., 27,3335(1977).

5) M.T.Pope, Inorg.Chem., 15,2068(1976).

6) K.Murata and S.Ikeda, Anal.Chim.Acta., 151,29(1983).

7) K.Murata, Y.Yokoyama, and S.Ikeda, Anal.Chim.Acta., 49(1969).

8) J.F.Keggin, Proc.Roy.Soc.A., 144,75(1934).

Chapter IV. The Analysis of Ternary Heteropoly Molybdate by Use of NMR Technique

IV - 1. Introduction

Nuclear magnetic resonance(NMR) spectroscopy is now so widely applied throughout chemistry. The interaction of the electron cloud surrounding a given nucleus with an external applied magnetic field H_o gives rise to a local magnetic field. This induced field shields the nucleus with the shielding proportional to the field H_o so that the effective field H_{eff} felt by the nucleus is given by

$$H_{eff} = H_o(1 - \sigma) \qquad (1)$$

where σ is the shielding constant. The difference in chemical shift δ between two lines is simple the difference in shielding constants σ of the nuclei giving rise to the two lines and increased shielding corresponds to more negative chemical shifts. For a nonspherical charge distribution about the phosphorus nucleus, the shielding constant largely results from a local diamagnetic shielding contribution δ_d and a local paramagnetic shielding contribution δ_p(1)

$$\delta = \delta_d + \delta_p \qquad (2)$$

However, because the charge distribution in a phosphorus molecule will be far from spherically symmetrical, the major contribution to the ^{31}P chemical shift comes from the paramagnetic term(2). This is a deshielding contribution

originating from the small amount of mixing of paramagnetic excited states into the ground state wave function. The chemical shift will thus be affected by changes in bond overlap and hybridization, changes in atomic charges, as well as changes in the average electronic excitation energy between ground and excited states. The often observed correlation of chemical shifts and charge densities probably derives from the expansion or contraction of the *p* orbitals with charge variations. In earlier investigators, as an example, Gorenstein and Kar noted that ^{31}P chemical shifts in phosphate esters are just as well correlated with calculated phosphorus electron densities as the full paramagnetic contribution(3).

It is certainly safe to say that the use of NMR spectroscopy will have a profound impact upon our knowledge of polyoxometalates, particularly on their structures and dynamics in the solution, although the reliability and usefulness of heteronuclear NMR spectra of polyoxoanions depends very much upon the stability of its polyanion. Numerous heteropoly anions contain phosphorus as a primary heteroatom, and so ^{31}P NMR of such anions has attracted attention(4-9). By Fournier et al.(10), as an example, ^{31}P NMR study had been carried out on 24 kinds of tungstophosphates and molybdophosphates, regarding the structures of which are derived from PM_{12} and P_2M_{18} by the removal or the partial substitution of metallic atoms. In

his paper they have reported that the chemical shift value is correlated with the PO_A bond strength, O_A being the oxygen atom of the central PO_4 tetrahedron. As another example, Pope et al.(11) had reported to the structures of molybdovanadophosphates in combination with vanadium-51 NMR and confirmed the existence of geometrical isomers distinguished by the relative positions of vanadium atoms in the polyanion structure. Recently, Pettersson et al.(12) had studied with respect to the equilibria in the system H^+ - MoO_4^{2-} - HPO_4^{2-} by means of ^{31}P NMR and had shown the dependence of the formation of molybdophosphates on pH value, and the concentration of molybdenum and phosphorus. However, these papers have been reported for the interest of inorganic and stereochemical studies, not analytical one, and no attempt has been made to explain the function and stoichiometry of the complexed metal ions in the formation process by using of NMR technique so far.

In this chapter, it is described the first stoichiometrical attempt to determine complexed metal ions, mainly group 5A elements, based on the formation of ternary heteropoly molybdate in the aqueous solution. In order to interpret the relationship between the chemical shift value δ and the chemical property of complexed metal ion a rigid sphere model is considered and its model gives a reasonable empirical equation. The effect of coexisting metal and non-metal ions is examined and as a result simultaneous

determination of complexed metal ions is carried out by use of this NMR technique. In addition, EXAFS and XANES analyses, instead of x-ray diffraction one, is also carried out to get the structural information of ternary heteropoly molybdate in solution.

IV - 2. NMR Measurement of Ternary Heteropoly Molybdates Containing Group 4A and 5A Elements

In the previous chapter, the variation of near ultraviolet spectra was observed to determine the formation of ternary heteropoly molybdates containing group 5A elements in solution. It is, however, very difficult to identify each ternary heteropoly molybdate from the near UV spectra because of the similarity of each spectrum. Thus, by means of the analytical procedure proposed by Murata et al.(13), Raman spectra measurement was carried out to examine the formation of ternary heteropoly molybdate. As shown in Figs. IV-1 and IV-2, the shifts of Mo=O stretching vibration at lower wave number, in analogy with those of group 4A elements, were observed by the addition of group 5A ones in 12-molybdophosphate(PMo_{12}) solution, although the degree of the shifts for these complexes was less than those for group 4A elements. This difference on Raman spectra is more distinct than that in the near UV spectra. The results obtained in this work, with the addition of previously reported ones(13,14), are listed in Table IV-1. Although some frequencies could be assigned to well-characterized vibrations from a general discussion of Raman spectra of heteropoly complexes(15-17), the identification of these peaks in the mixture was very difficult for the close or same

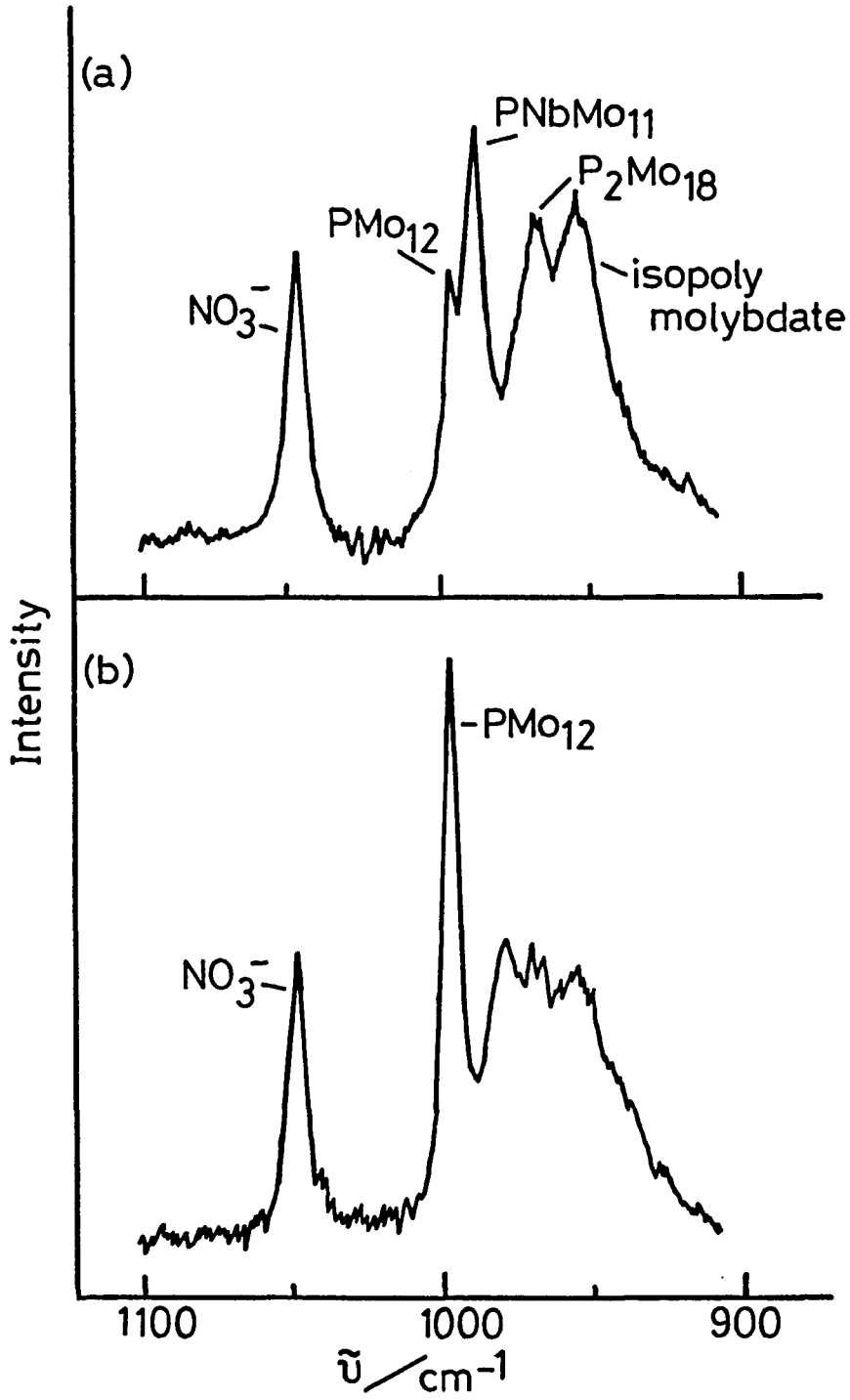


Fig IV-1. Raman spectra of binary- and ternary heteropoly molybdates in solution.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(a) $C_{Nb} = 4.5 \times 10^{-3}$

(b) $C_{Nb} = 0$ (mol dm^{-3}) pH 0.55 - 0.7

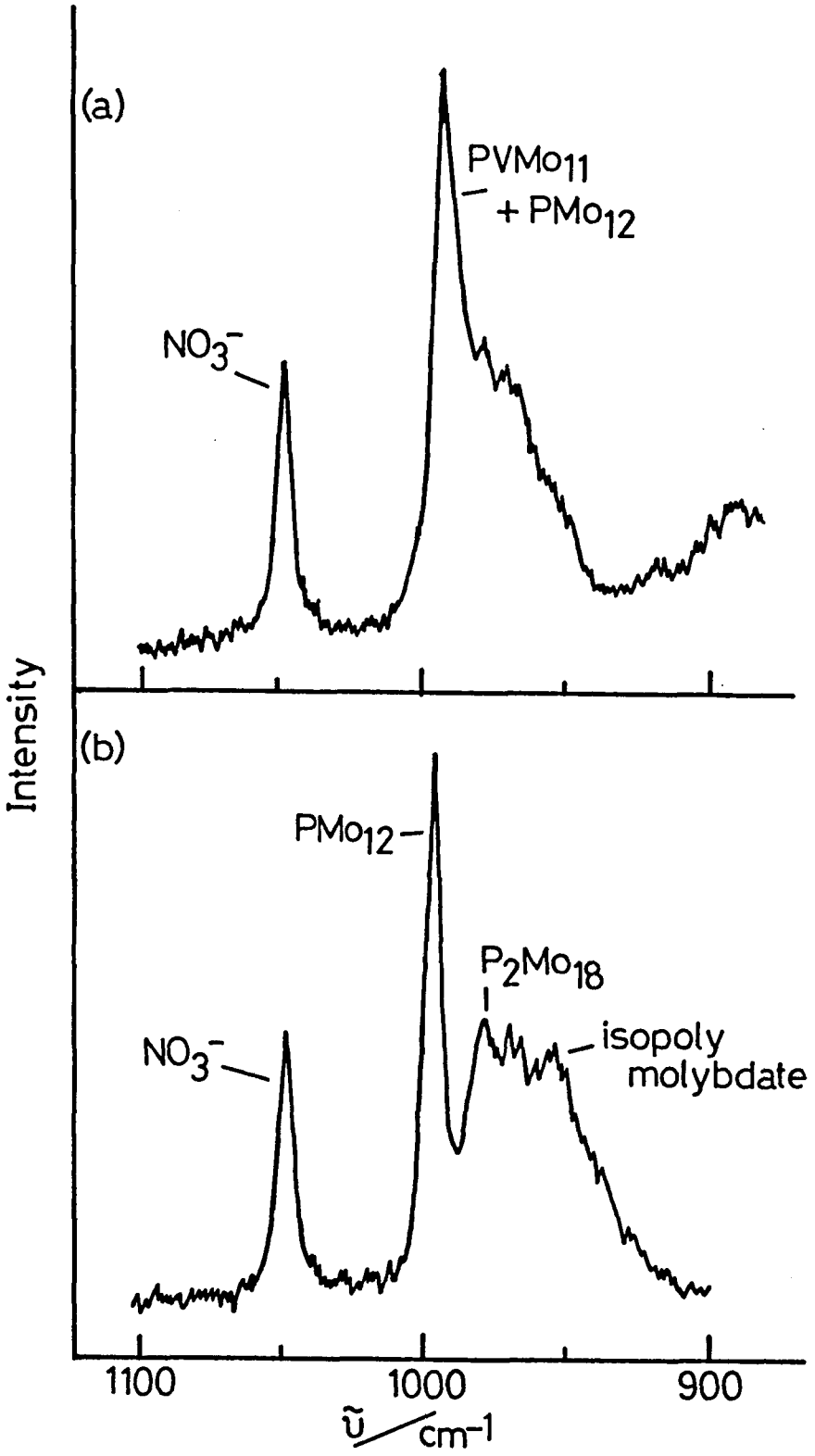


Fig IV-2. Raman spectra of binary- and Ternary heteropoly molybdates in solution.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(a) $C_V = 4.8 \times 10^{-3}$

(b) $C_V = 0$ (mol dm^{-3}) pH 0.6 - 0.7

Table IV-1. Band Positions of Each Heteropoly Molybdate in Raman Spectra

	$\bar{\nu}$ / cm^{-1} [a]
$(P_2Mo_5O_{23})^{6-}$	944 - 946 [b]
$(P_2Mo_{18}O_{62})^{6-}$	972 - 975 [c]
$(PZrMo_{11}O_{40})^{5-}$	980 [c]
$(PHfMo_{11}O_{40})^{5-}$	980 [c]
$(PThMo_{11}O_{40})^{5-}$	980 [d]
$(PCeMo_{11}O_{40})^{5-}$	980 [d]
$(PBiMo_{18}O_{62})^{8-}$	980 - 982 [d]
$(PTeMo_{18}O_{62})^{7-}$	980 - 982 [d]
$(PTiMo_{11}O_{40})^{5-}$	986 [c]
$(PNbMo_{11}O_{40})^{4-}$	990 [d]
$(PVMo_{11}O_{40})^{4-}$	994 [d]
$(PTaMo_{11}O_{40})^{4-}$	990 [d]
$(PMo_{12}O_{40})^{3-}$	996 [b]

a) Normalized wave number, internal standard ($\bar{\nu}_{NO_3^-}$ = 1049 cm^{-1}).

b) See ref.13.

c) See ref.14.

d) This work.

wave number of those in Raman spectra. ^{31}P NMR measurement was attempted to find out the more elaborated way to determine complexed metal ions by use of the formation of ternary heteropoly molybdate in aqueous solution.

Figure IV-3 shows typical ^{31}P NMR spectra of ternary heteropoly molybdates in weak acidic solution containing group 5A elements, i.e., V(V), Nb(V), and Ta(V), respectively. As shown in Fig.IV-3, the peak for each ternary heteropoly molybdate yielded well-defined difference in its chemical shift. In addition, when complexed metal ion was absent, the spectrum exhibited two peaks (see Fig.IV-4): one peak at lower field, near -15.1 ppm, which is rather broad, and the other at -17.33 ppm which is very sharp. The latter was assigned to the phosphorus in PMo_{12} produced by reacting with molybdate and the former to 18-molybdodiphosphate(P_2Mo_{18}) in equilibrium state in solution. No evidence for the peak of 11-molybdophosphate(PMo_{11}) was found in this work, but it must exist as well as P_2Mo_{18} in equilibrium state. The addition of Nb(V) ion, as shown in Fig.IV-4, developed a new peak at -17.11 ppm and further addition of one in the solution progressively led to the decrease of the peak for PMo_{12}, whereas its new peak increased. In the solution having equimolar amounts of phosphate and Nb(V) ion, finally, the peak for PMo_{12} disappeared completely and only single peak at -17.11 ppm remained in NMR spectra. This peak was observed to be

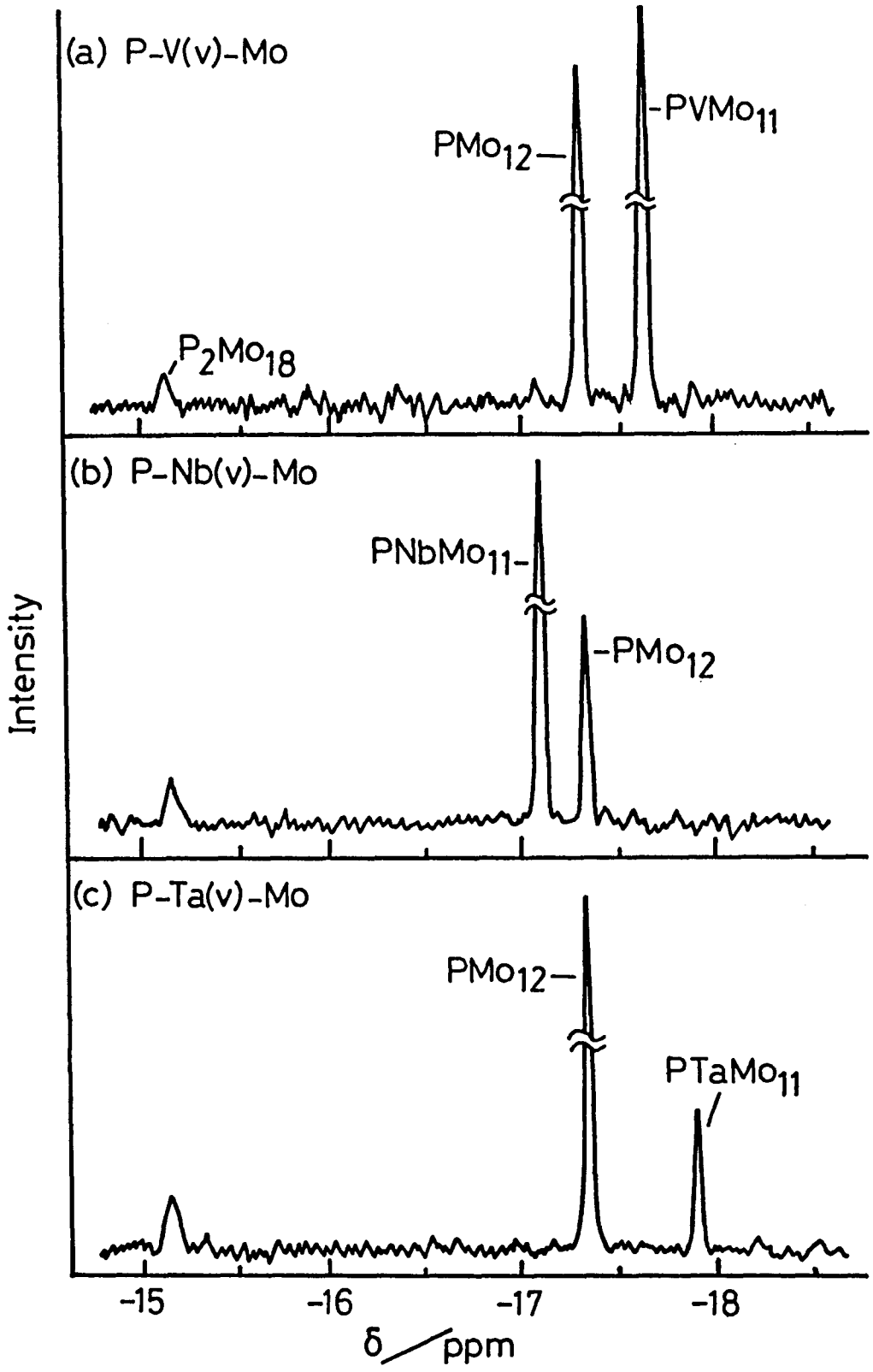


Fig IV-3. ^{31}P NMR spectra of ternary heteropoly molybdates in solution.

$C_P = 1.0 \times 10^{-2}$

(a) $C_V = 4.0 \times 10^{-3}$ $C_{Mo} = 1.5 \times 10^{-1}$

(b) $C_{Nb} = 5.6 \times 10^{-3}$ $C_{Mo} = 3.0 \times 10^{-1}$

(c) $C_{Ta} = 2.6 \times 10^{-3}$ $C_{Mo} = 2.0 \times 10^{-1}$

(mol dm^{-3}) pH 0.6 - 0.8

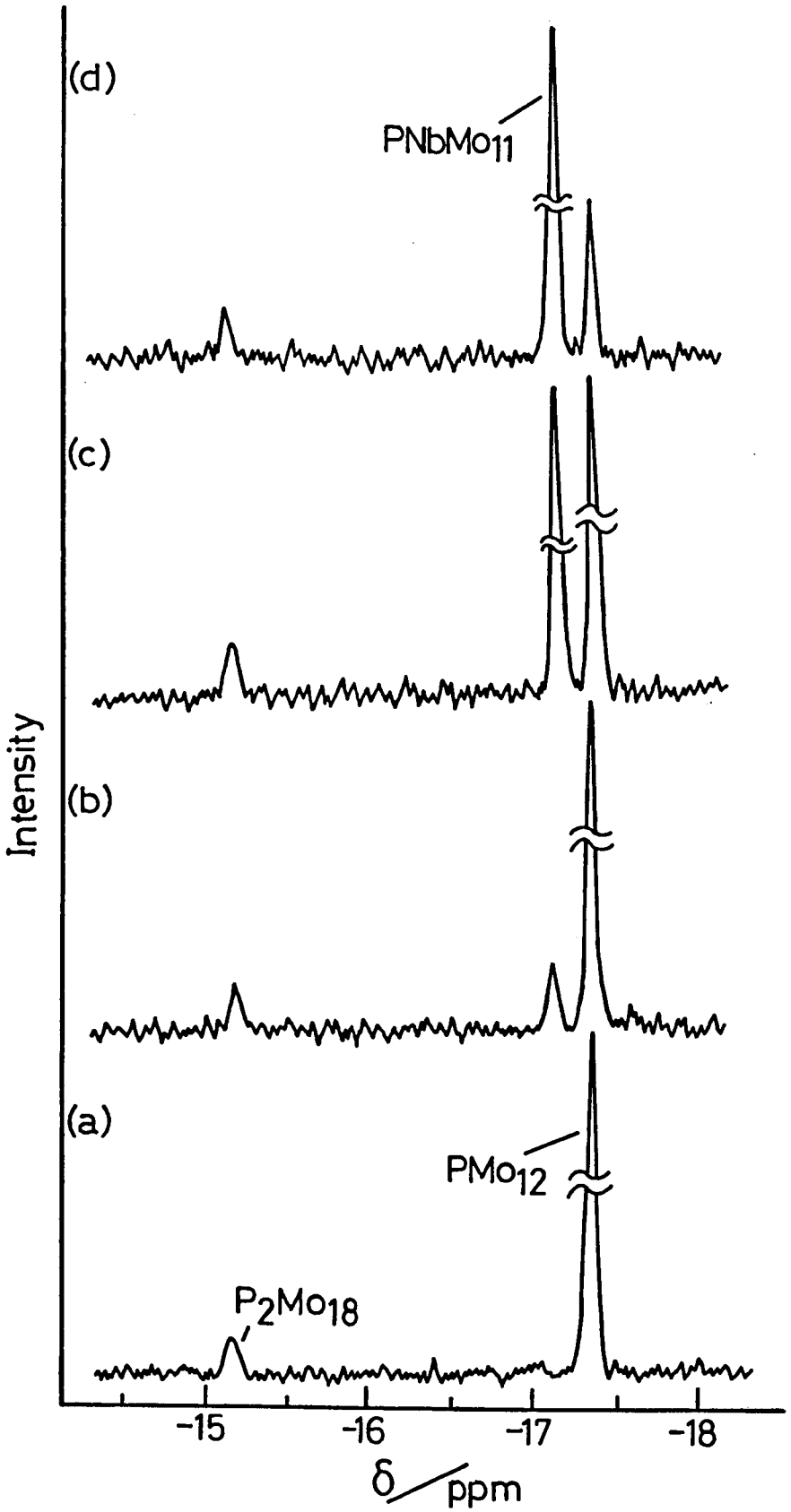


Fig IV-4. ^{31}P NMR spectra of the KH_2PO_4 - Nb(V) - Na_2MoO_4 aqueous system.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(a) $C_{Nb} = 0$ (c) $C_{Nb} = 4.0 \times 10^{-3}$

(b) $C_{Nb} = 6.7 \times 10^{-4}$ (d) $C_{Nb} = 6.5 \times 10^{-3}$

(mol dm^{-3}) pH 0.5 - 0.7

dependent on Nb(V) concentration. No other peak was observed with repetition time of 10.0 s and by the data acquisition with 3.0 s repetition overnight. While determination of relaxation time, T_1, was not stoichiometrically carried out, but each relative peak area was very reproducible with the repetition time of 2.0 s or over. These facts lead to the assignment of the peak at -17.11 ppm to ^{31}P resonance in molybdoniobophosphate, $PNbMo_{11}O_{40}^{4-}$($PNbMo_{11}$) and indicate the absence of any ternary heteropoly molybdates other than 1:1:11 anion in solution. The addition of an excess amount of Nb(V) ion, however, gave rise to the gradual decomposition of $PNbMo_{11}$ and produced a hydrolyzed product or niobium-molybdenum heteropoly complexes(18,19) in solution. Molybdotantalophosphate, $PTaMo_{11}O_{40}^{4-}$($PTaMo_{11}$), is unstable and its hydrolyzed product being similar to that observed in the case of niobium solution precipitated gradually in the range of higher concentration of Ta(V) ion. This result places a restriction on the application of this method for the determination of Ta(V) ion in aqueous solution. To determine the validity of this NMR technique a series of known compounds(i.e., ternary heteropoly molybdates containing group 4A elements) were further studied. As shown in Fig.IV-5, NMR spectrum of each ternary heteropoly molybdate provided a similar feature to that of $PNbMo_{11}$, and that the peak for each complex was developed with characteristic chemical shift. The addition of an excess

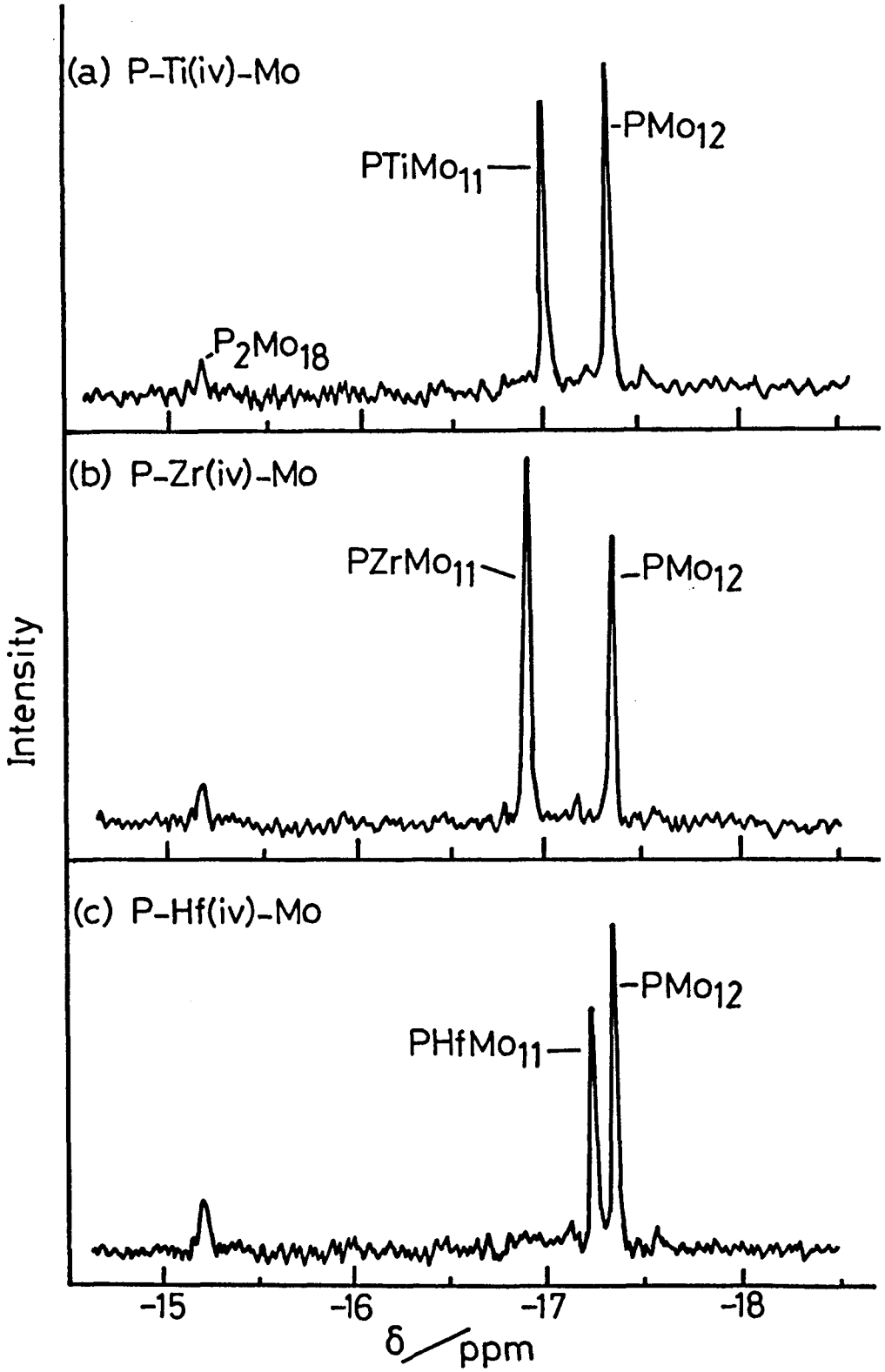


Fig IV-5. ^{31}P NMR spectra of ternary heteropoly molybdate in solution.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(a) $C_{Ti} = 3.3 \times 10^{-3}$ (c) $C_{Hf} = 3.4 \times 10^{-3}$

(b) $C_{Zr} = 5.2 \times 10^{-3}$ (mol dm^{-3})

pH 0.6 - 0.7

amount of metal ion, in analogy with Nb(V) ion, led to the gradual decomposition of the complex. Thus it would not be probable that the secondary metal ion substituted for another molybdenum atom, even in the presence of excess, in heteropoly cage. The values of the chemical shift for binary and ternary heteropoly molybdates obtained in this work are listed in Table IV-2. The NMR spectra showed that the peak for each ternary heteropoly molybdate appeared at a different chemical shift and that the relative peak area for it, with the exception of tantalum, was proportional to the concentration of each metal ion. It is possible to determine each metal ion over range of 7.0×10^{-4} to 8.0×10^{-3} mol dm^{-3} with the standard deviations of 5 ± 8% and these calibration curves, as shown in Figs.IV-6, IV-7, and IV-8, gave the approximate same slopes.

On the other hand, in contrast to the results of other group 4A and 5A elements, the addition of an excess amount of vanadium(V) ion did not cause the decomposition of $PVMo_{11}$ but produced poly-substituted molybdovanadophosphates, i.e., PV_2Mo_{10} or PV_3Mo_9, in the solution(20). Several new peaks were developed at higher field than that for PMo_{12} in NMR spectra, as shown in Fig.IV-9. Whereas as shown in Fig.IV-10, it was impossible to confirm the formation of these compounds from only the result of Raman measurement. As to poly-substituted ternary heteropoly molybdates, Hallada et al.(21) have reported that the free heteropoly acid,

Table IV-2. ^{31}P NMR Chemical Shifts of Binary- and Ternary Heteropoly Molybdates in Solution

	δ / ppm [a]
$(P_2Mo_5O_{23})^{6-}$	-13.67
$(P_2Mo_{18}O_{62})^{6-}$	-15.10
$(PBiMo_{18}O_{62})^{8-}$	-15.50
$(PThMo_{11}O_{40})^{5-}$	-16.25
$(PTeMo_{18}O_{62})^{7-}$	-16.30
$(PCeMo_{11}O_{40})^{5-}$	-16.33
$(PZrMo_{11}O_{40})^{5-}$	-16.88
$(PTiMo_{11}O_{40})^{5-}$	-16.99
$(PNbMo_{11}O_{40})^{4-}$	-17.11
$(PHfMo_{11}O_{40})^{5-}$	-17.25
$(PMo_{12}O_{40})^{3-}$	-17.33
$(PVMo_{11}O_{40})^{4-}$	-17.66
$(PTaMo_{11}O_{40})^{4-}$	-17.90
$(PV_2Mo_{10}O_{40})^{5-}$	-17.45
	-17.49
	-17.54
	-17.72
	-17.74

[a] Relative to 1-aminoethylidene bis(phosphonic acid).

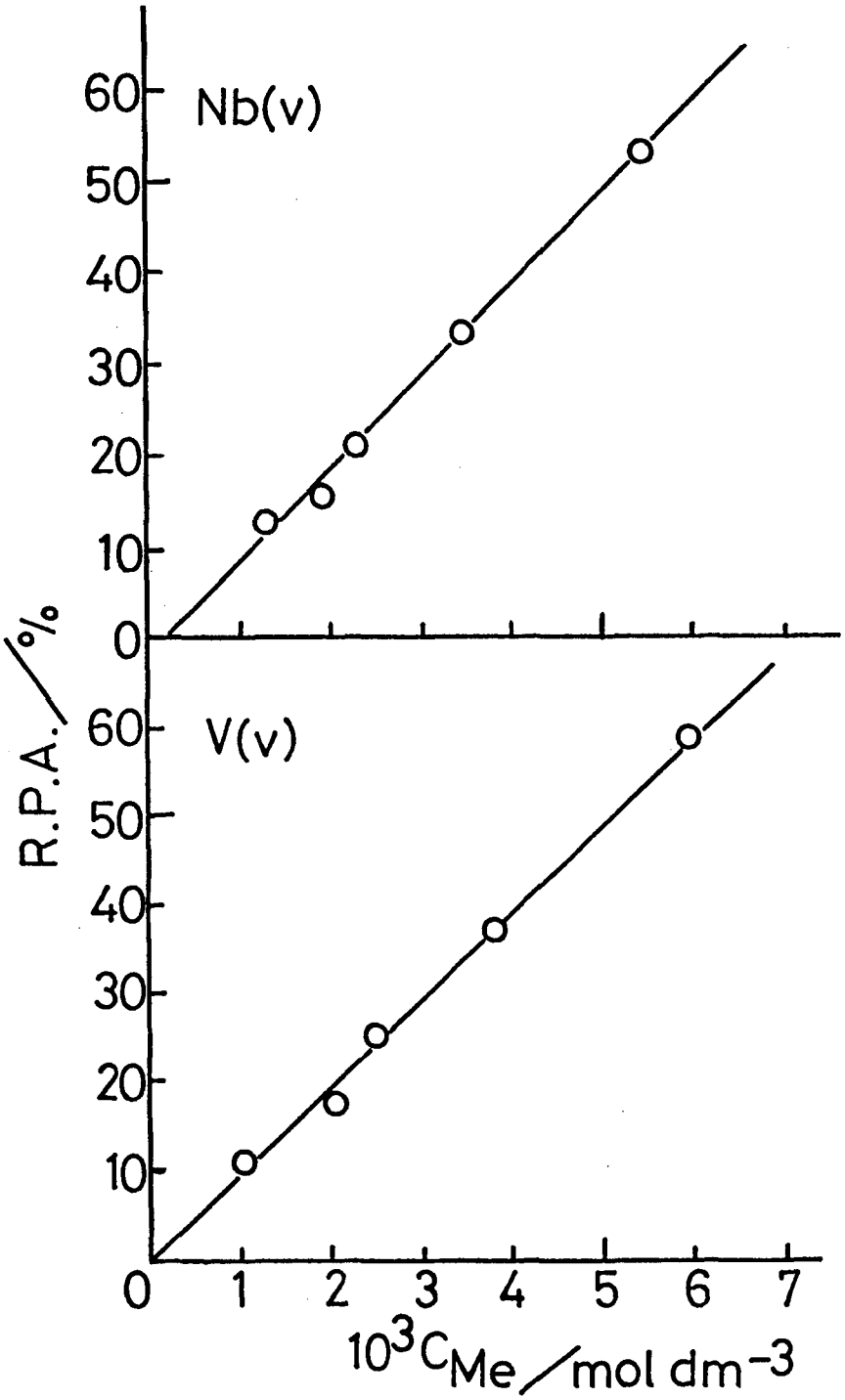


Fig IV-6. Calibration curves of Nb(V) and V(V) ions obtained from NMR signal.

C_P = 1.0 x 10^{-2} (mol dm^{-3}) C_{Mo} = 1.5 x 10^{-1} pH 0.5 - 0.7

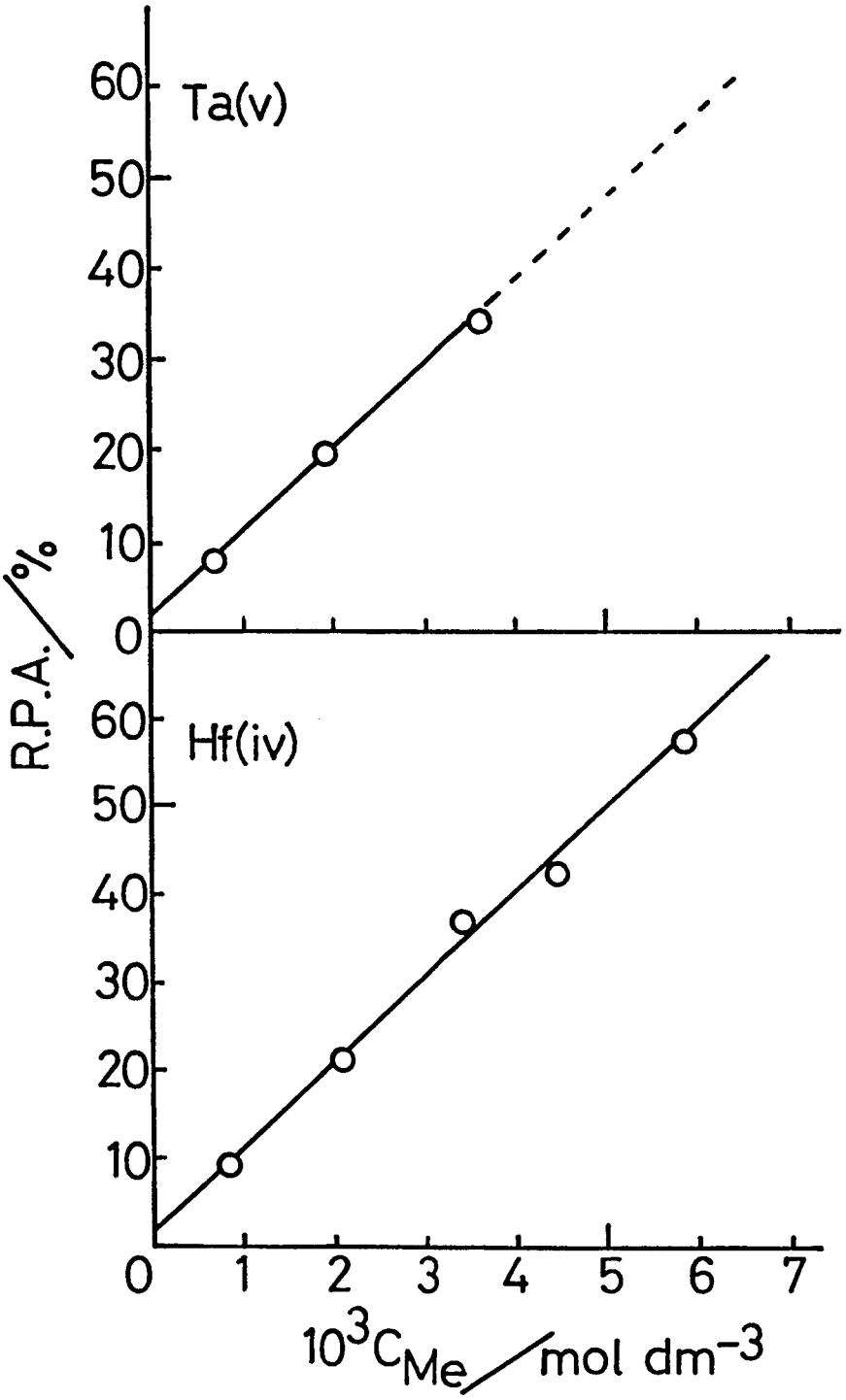


Fig IV-7. Calibration curves of Ta(V) and Hf(IV) ions obtained from NMR signal.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$ (mol dm^{-3})

pH 0.5 - 0.8

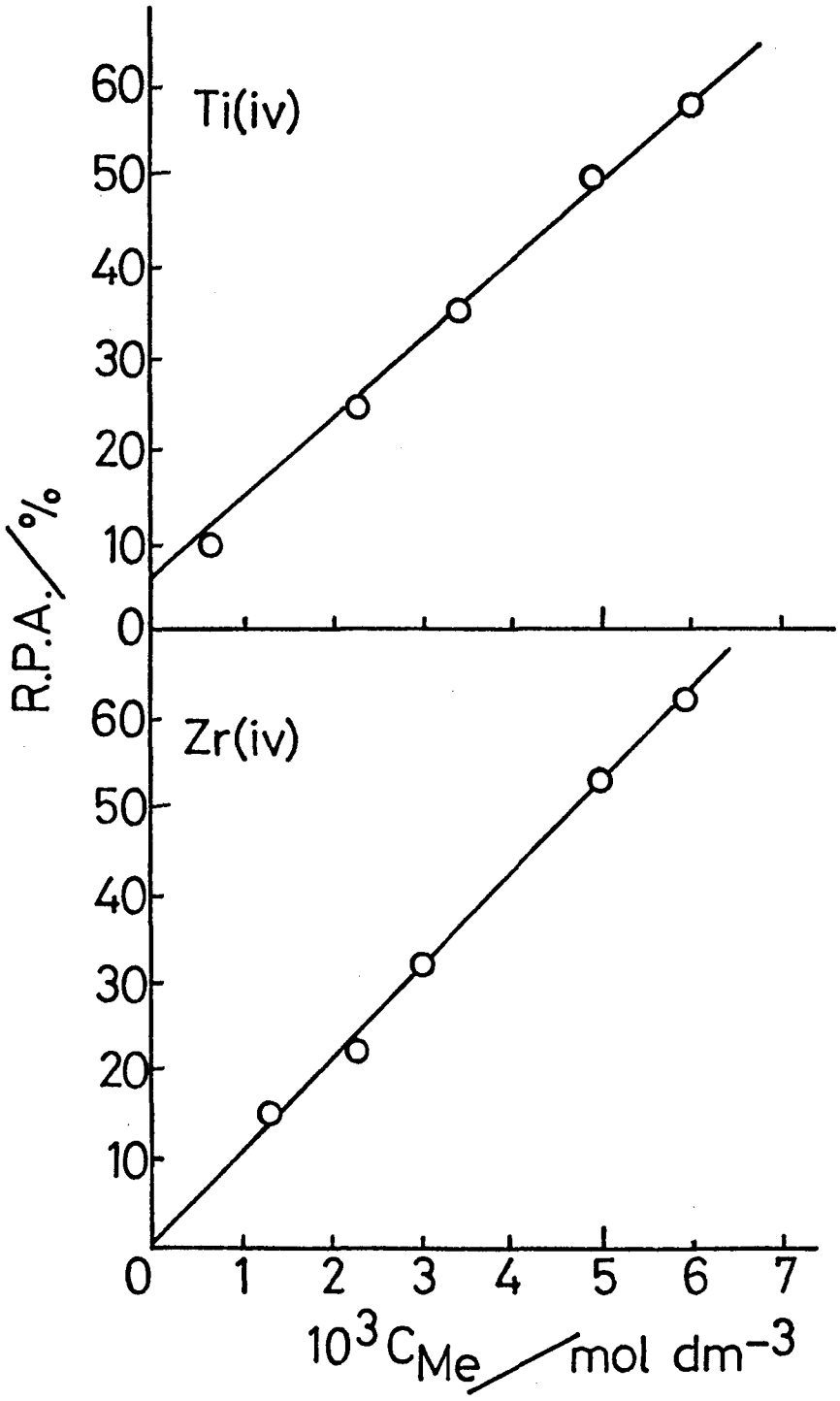


Fig IV-8. Calibration curves of Ti(IV) and Zr(IV) ions obtained from NMR signal.

$C_P = 1.0 \times 10^{-2}$ (mol dm^{-3}) $C_{Mo} = 1.5 \times 10^{-1}$ pH 0.5 - 0.8

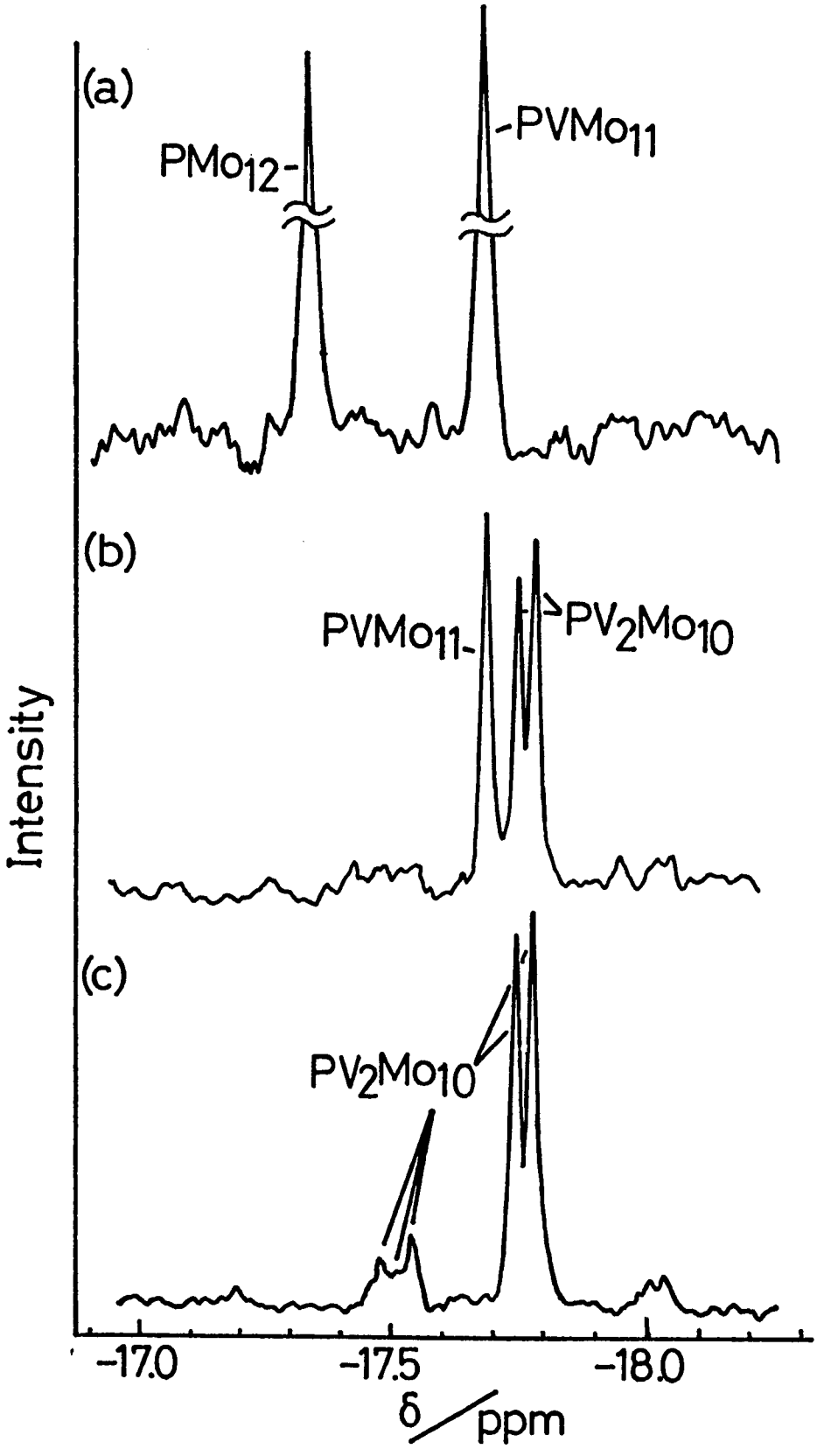


Fig IV-9. ^{31}P NMR spectra of poly-substituted molybdovanadophosphates in solution.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(a) $C_V = 5.0 \times 10^{-3}$ (b) $C_V = 1.6 \times 10^{-2}$

(c) $C_V = 2.4 \times 10^{-2}$ (mol dm^{-3}) pH 0.8 - 1.0

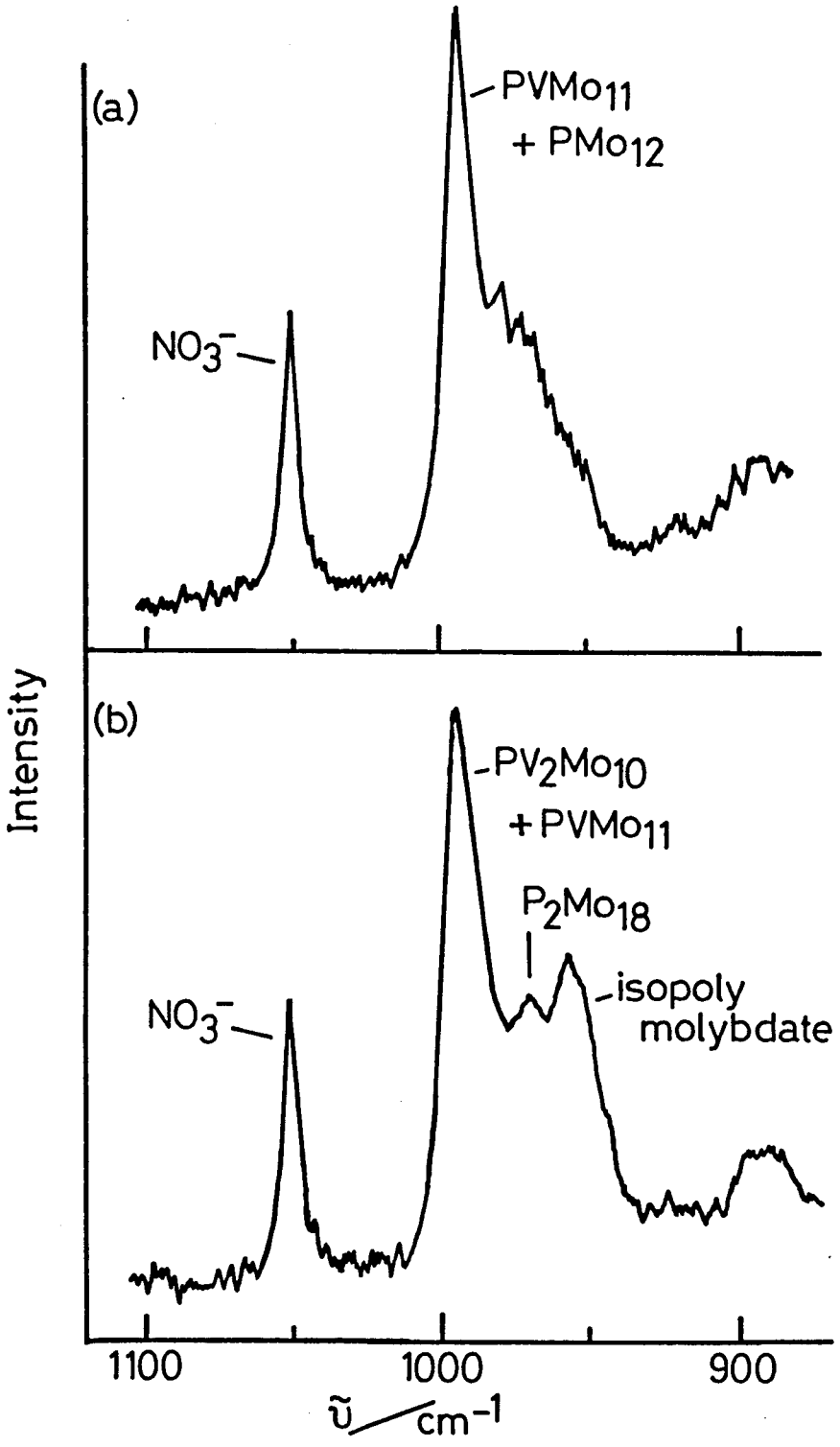


Fig IV- 10. Raman spectra of poly-substituted molybdovanadophosphates in solution.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(a) $C_V = 5.0 \times 10^{-3}$ (b) $C_V = 1.6 \times 10^{-2}$

(mol dm^{-3}) pH 0.8

$H_5PV_2Mo_{10}O_{40}.32H_2O$ and $H_6PV_3Mo_9O_{40}.34H_2O$, were measured by use of potentiometric titration, differential thermal analysis, and thermogravimetric analysis. Further Pope et al.(22,23) have demonstrated that such complexes should be capable of existing in isomeric forms according to the different ways of arranging the two kinds of metal atom within the Keggin structure. In the paper they state that $H_5PV_2Mo_{10}O_{40}$ complex has the five possible isomers with relative statistical weights of 2(1,2), 2(1,4), 4(1,5), 2(1,6), and 1(1,11), where the values in parentheses show the position of vanadium atoms in the Keggin like structure. They also got a poorly resolved spectrum, which is consistent with the presence of all five isomers with their expected relative abundance. In a series of NMR measurement, however, a somewhat different spectrum from Pope's one was obtained. Five peaks at very narrow frequency intervals were clearly confirmed in higher resolved spectra, which partially supported Pope's result, but it showed a significant difference in the integrated intensity as compared with Pope's one. The values of the chemical shift for these five peaks are also given in Table IV-2. Most intense peak is observed at higher field, while very weak three peaks at lower field, respectively. This result shows that the secondary vanadium atom introduced by the substitution of molybdenum atom is arranged to the different ways. Thus it must be attacked preferentially a readily substitutable

position within the Keggin like structure, and not a position governed by the statistical low. In ^{31}P solid NMR measurement, as shown in Fig.IV-11, di-substituted ternary heteropoly molybdate(PV_2Mo_{10}) gave a more broaden peak than that of mono-substituted one($PVMo_{11}$) and apparently the formation of PV_2Mo_{10} decreases the chemical shift anisotropy owing to the average of the chemical shift tensor surrounding phosphorus atom for the coexistence of five isomers. For liquid sample, NMR chemical shift of a central phosphorus atom is sufficiently dependent upon the nature and disposition of environment surrounding it to permit distinction between isomers, but unambiguous assignment of these five peaks is very difficult to make from only NMR measurement at present.

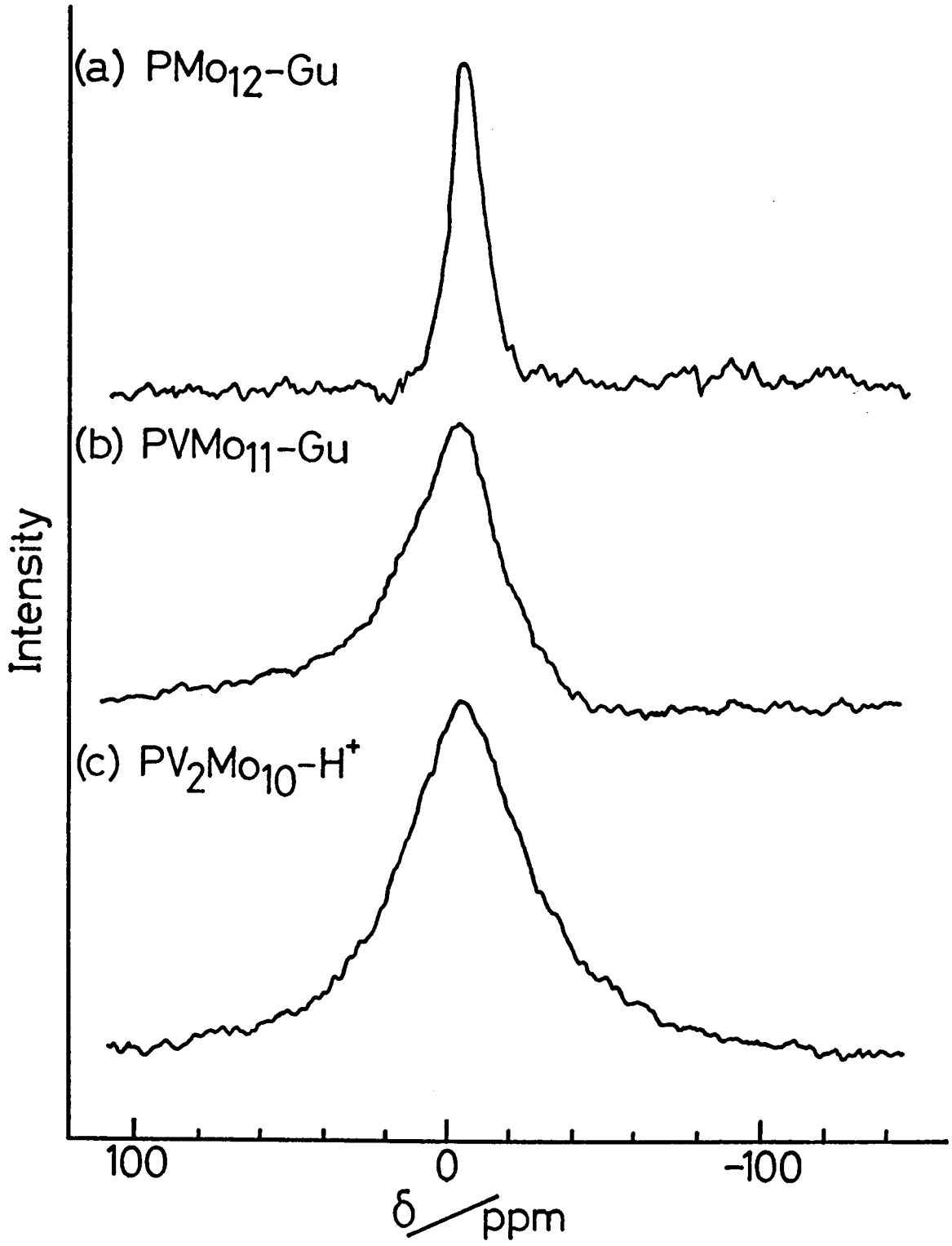


Fig IV-11. ^{31}P solid NMR spectra of poly-substituted heteropoly molybdate.

IV - 3. Interpretation with A Rigid Sphere Model

At first, taking into account the data of other experiments, ^{31}P NMR chemical shifts of ternary heteropoly molybdates containing group 4A and 5A elements in aqueous solution were expected to be found at lower field from that of 12-molybdophosphate(PMo_{12}). Because the structural deformation of ternary heteropoly molybdate caused the deviation from the Keggin structure and so induced the deshielding effect on the phosphorus atom due to the rearrangement of electron density distribution around it. Contrary to the expectation, however, the peaks of molybdovanadophosphate($PVMo_{11}$) and molybdotantalophosphate($PTaMo_{11}$) were observed in higher field than that of PMo_{12}. This phenomenon indicated that the difference of chemical shift must be derived from the difference of character of substituted metal ions. The attempt to interpret the difference of chemical shift by ionic potential, which is frequently used to explain the strength of acid or base, the trend of amphoteric property, and so on, was failed, although it could be partially true. This result could be presumed that a more rigorous relation between the value of chemical shift and the character of each element should be existed.

In general, the difference of chemical shift reflects the magnitude of electron density around the atom to be measured,

and so a rigid sphere model for heteropoly cage was considered to interpret it by means of the extended concept of electron density. The Keggin structure, in which each oxygen atom was taken out of the consideration for the sake of simplisity, was illustrated graphically in Fig.IV-12; where a dotted circle denotes phosphorus atom, and eleven unshaded and one shaded spheres represent molybdenum and substituted metal ions in the outer shell, respectively. Thus it was regarded that the ion is impenetrable rigid sphere of ionic radius r and charge z, and that "the electron density around phosphorus atom" is defined in terms of the size and electron number of these spheres. The results of the data treated in this manner are summarized in Table IV-3, where I.r and e^- refer to the ionic radius and electron number of X ion, respectively, Σe^- and V are the sums of electron and volume of twelve spheres, which consist of one X plus eleven Mo ions, respectively, d refers to a parameter for the electron density around phosphorus atom which comes from the values Σe^- over V, and Δd and $\Delta\delta$ are the differences of the electron density parameter and chemical shift of ^{31}P NMR spectra between PMo_{12}(binary heteropoly molybdate) and ternary heteropoly molybdates, respectively. Based on the data in Table IV-3, an empirical relationship was established between the chemical shift and electron density parameter around phosphorus atom. In this manner a fairly good linear relation was obtained as given in the

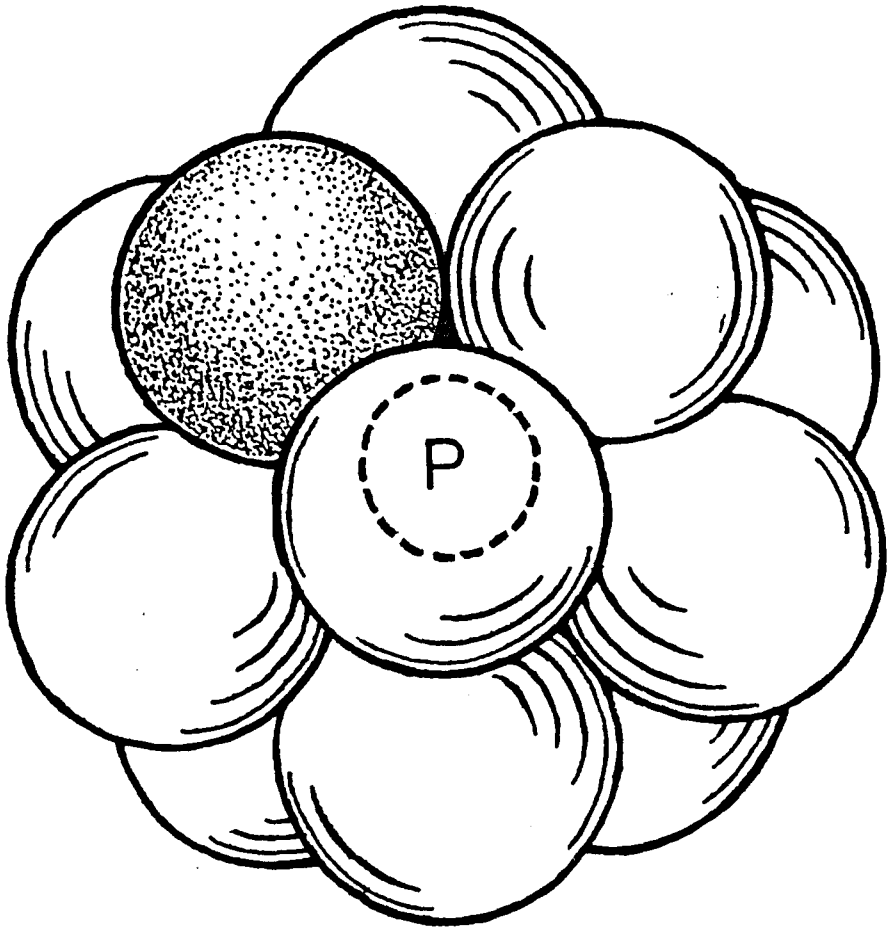


Fig IV-12. A rigid sphere model of ternary heteropoly molybdate.

phosphorus atom (dotted circle)
molybdenum atom (unshaded sphere)
substituted atom (shaded sphere)

Table IV-3. Calculated "Electron Density around P Atom" and Chemical Shift for Ternary Heteropoly Molybdates

X	I.r	e^-	Σe^-	V	$\Sigma e^-/V = d$	Δd	$\Delta\delta$
Th(IV)	1.02	86	482	15.43	31.24	4.82	-1.08
Zr(IV)	0.79	36	432	13.05	33.11	2.95	-0.45
Ti(IV)	0.68	18	414	12.30	33.66	2.40	-0.34
Nb(V)	0.69	36	432	12.36	34.96	1.10	-0.22
Hf(IV)	0.78	68	464	12.97	35.78	0.28	-0.08
(Mo(VI)	0.62	36	432	11.98	36.06		)
V(V)	0.59	18	414	11.84	34.96	1.10	0.33
Ta(V)	0.68	68	464	12.30	37.73	-1.67	0.57
Ce(IV)	0.92	54	450	14.24	31.59	4.47	-1.00
Bi(III)	0.96	80	476	14.69	32.41	3.65	-1.83
Te(IV)	0.70	48	444	12.42	35.76	0.30	-1.03

I.r : Ionic radius

e^- : Electron number of X ion

Σe^- : Sum of electron number in one X plus eleven Mo ions

V : Sum of volume of twelve spheres

$= 4\pi/3(I.r_X^3 + 11\ I.r_{Mo}^3)$

Δd : Difference of electron density

$= d_{Mo} - d_X$

$\Delta\delta$: Difference of chemical shift

$= \delta_{Mo} - \delta_X$

following equation:

$$\Delta\delta(\text{ppm}) = -0.24\Delta d + 0.16 \qquad (r^2 = 0.88)$$

As shown in Fig.IV-13, a reasonable quantitative correlation between calculated and measured results was obtained. This result, that is, leads to the parametric description of the chemical shift in NMR spectra. Vanadium(V) ion, however, shows a slight deviation from the line. This must be due to the underestimation of the electron density around phosphorus in $PVMo_{11}$. Vanadium(V) ion may be situated in positions at the closer site to phosphorus atom because of its smaller ionic radius on comparing to that for molybdenum(VI) ion, and then may give rather larger electrostatic contribution to phosphorus than other substituted metal ions. However, in spite of such a speculative approximation, this model provided the fairly good reproducibility of the experimental data with respect to the structure of ternary heteropoly molybdate in solution. By the way, this NMR measurement suggested indirectly that the structure of ternary heteropoly molybdate might be distorted from the Keggin structure and the paper supported this idea was reported by Yurchenko et al.(24) in 1980. They described as follows: "A number of the Keggin anions crystallize in the tetragonal space group $P_{4/mnc}$ which imposes a higher symmetry(4/m) upon the anion.- - - - - - As the results of structural investigations of poly-substituted molybdovanadophosphoric acid i.e., $H_5PV_2Mo_{10}O_{40}\cdot nH_2O$ and $H_6PV_3Mo_9O_{40}\cdot nH_2O$ which crystallize in

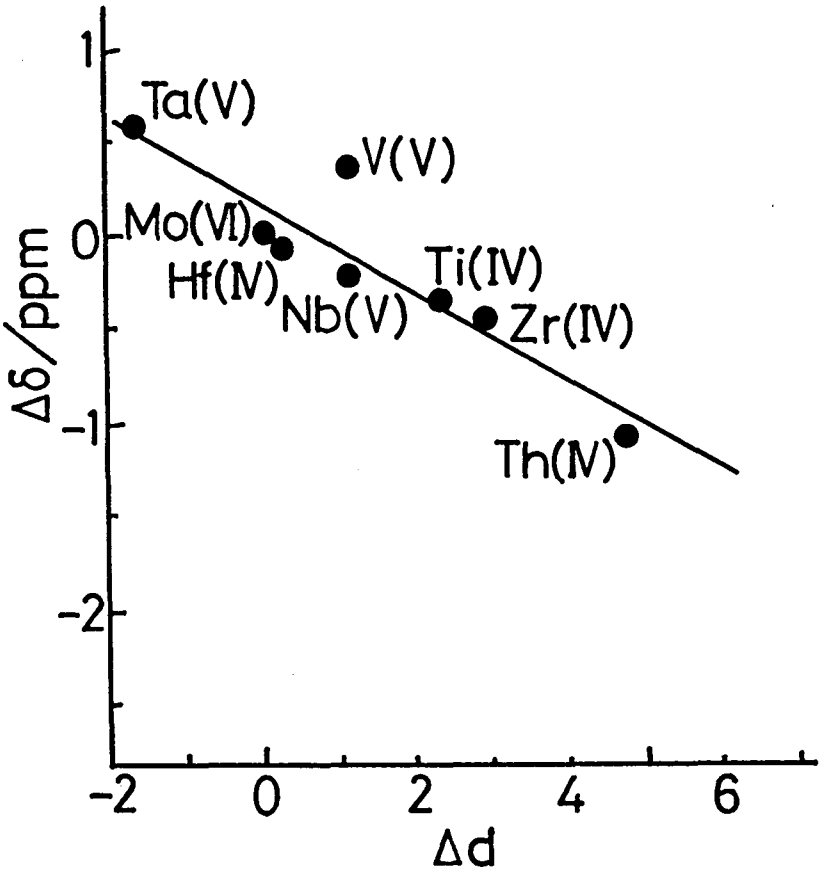


Fig IV-13. Relationship between 'electron density around P atom' and chemical shift for group 4A and 5A elements.

this space group these two heteropoly complexes were revealed as anions disordered not only with respect to the vanadium- or molybdenum-occupancy of the MO_6 octahedra, but also with respect to the orientation of the PO_4 groups." In general, x-ray diffraction was utilized to study for the structural analysis of heteropoly complexes, but the accurate determination of the structure of ternary heteropoly molybdate by x-ray diffraction could not be applied, except PV_nMo_{12-n}(n=1-3)(24), because the preparation of single crystal has not been succeeded yet in spite of the repeated trials. For these reasons, in order to estimate the structure of ternary heteropoly molybdate in aqueous medium, extended x-ray absorption fine structure(EXAFS) and x-ray absorption near edge structure(XANES) measurements were carried out. The results obtained are summarized, together with the data of x-ray diffraction analysis of PMo_{12}(25) and $PVMo_{11}$(24), in Table IV-4. Fourier transforms of EXAFS of Mo atom for binary and ternary heteropoly molybdates, together with its MEM analysis, are shown in Fig.IV-14. In this paper, each figure for the present EXAFS results contains both FT and MEM spectra on the left and the right side, respectively. As shown in Fig.IV-14, both FT and MEM spectra of ternary heteropoly molybdates were very similar to those of PMo_{12}. Likewise, XANES spectrum for Mo atom in each ternary heteropoly molybdate was also very similar to that of PMo_{12}(see Fig.IV-15). The obtained results indicates that

Table IV-4. Comparison of EXAFS Analysis(FT and MEM) and X-Ray Diffraction

---- The Keggin like structure ----

	EXAFS				x-ray diffraction	
	X-O		X-Mo			
	FT	MEM	FT	MEM	X-O	X-Mo
Mo/PMo_{12}	1.58 1.88 2.22	1.51 1.81 2.25	3.37	3.31 3.63	1.68 1.92 2.43	3.42[a] 3.70
$Mo/PZrMo_{11}$	1.57 1.86 2.20 2.47	1.63 2.13 2.45	3.32 3.75	3.29 3.76		
$V/PVMo_{11}$	1.99	1.47 1.92	2.62	2.59 2.88	1.63 1.97	2.62[b] 2.65
$Nb/PNbMo_{11}$	1.67 1.99 2.41	1.97	3.52	3.49	(2.05 2.31	------)[c]
$Hf/PHfMo_{11}$	1.71 2.07	1.71 2.08	3.52	3.36 3.64		
$Zr/PZrMo_{11}$	1.78 2.10 2.36	2.10 2.42	3.36 3.81	3.43 3.79	(2.14	3.87)[d]
$Th/PThMo_{11}$	1.97 2.26 2.45	1.94 2.33 2.58	3.68 3.92 4.16	3.93 4.32	(2.36	3.92)[e]

a) See ref. 25.

b) See ref. 24.

c) Data for Nb_2O_5.

d) Data for $Zr(MoO_4)_2$.

e) Data for $Th(MoO_4)_2$.

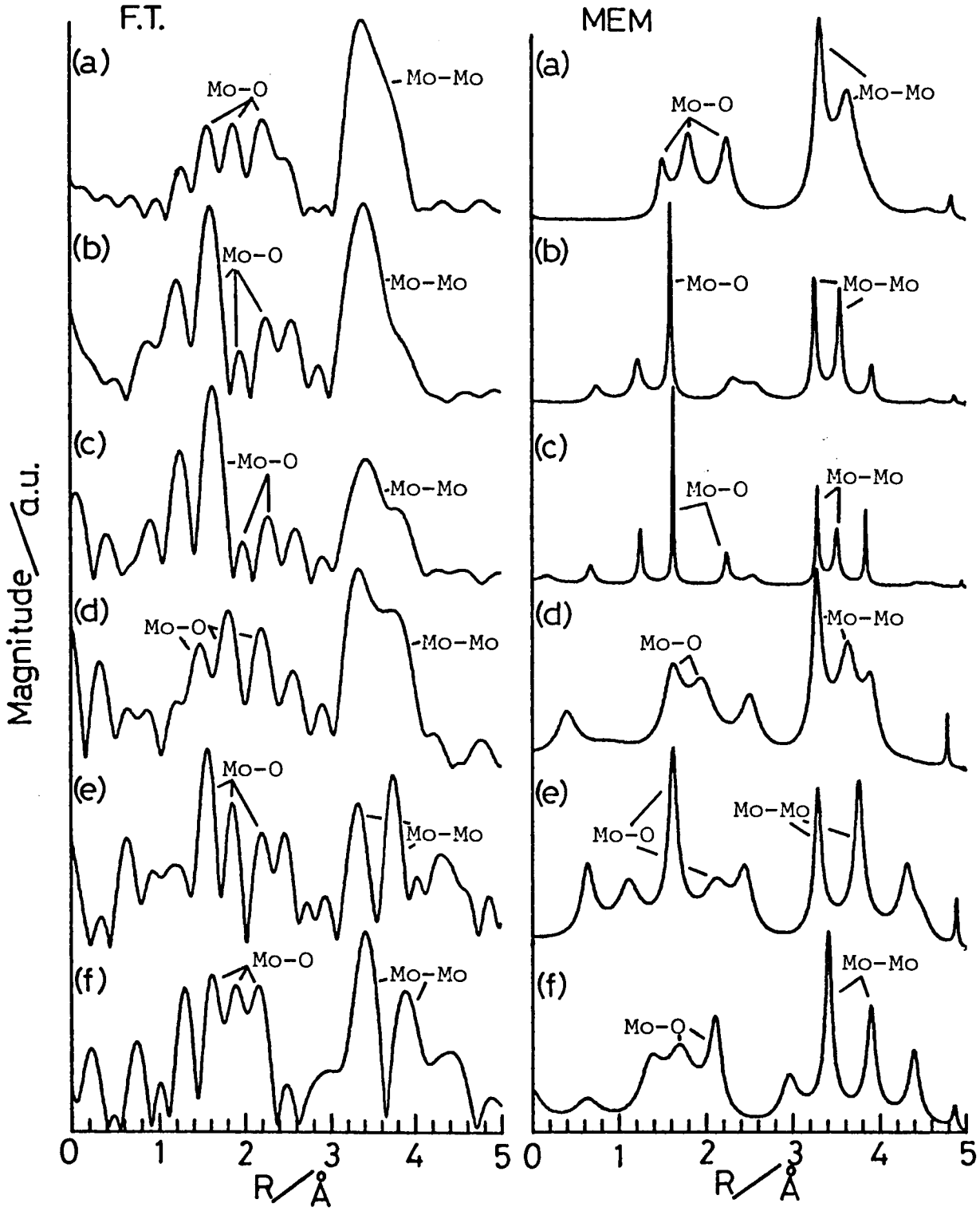


Fig IV-14. Fourier transform(left) and MEM(right) spectra of EXAFS of Mo atom for ternary heteropoly molybdates.

(a) PMo_{12} sln. (b) $PVMo_{11}$ sln. (c) $PNbMo_{11}$ sln.

(d) $PHfMo_{11}$ sln. (e) $PZrMo_{11}$ sln. (f) $PThMo_{11}$ sln.

$C_P = C_{Me} = 1.5 \times 10^{-2}$ $C_{Mo} = 2.0 \times 10^{-1}$ (mol dm^{-3})

pH 0.5 - 0.7

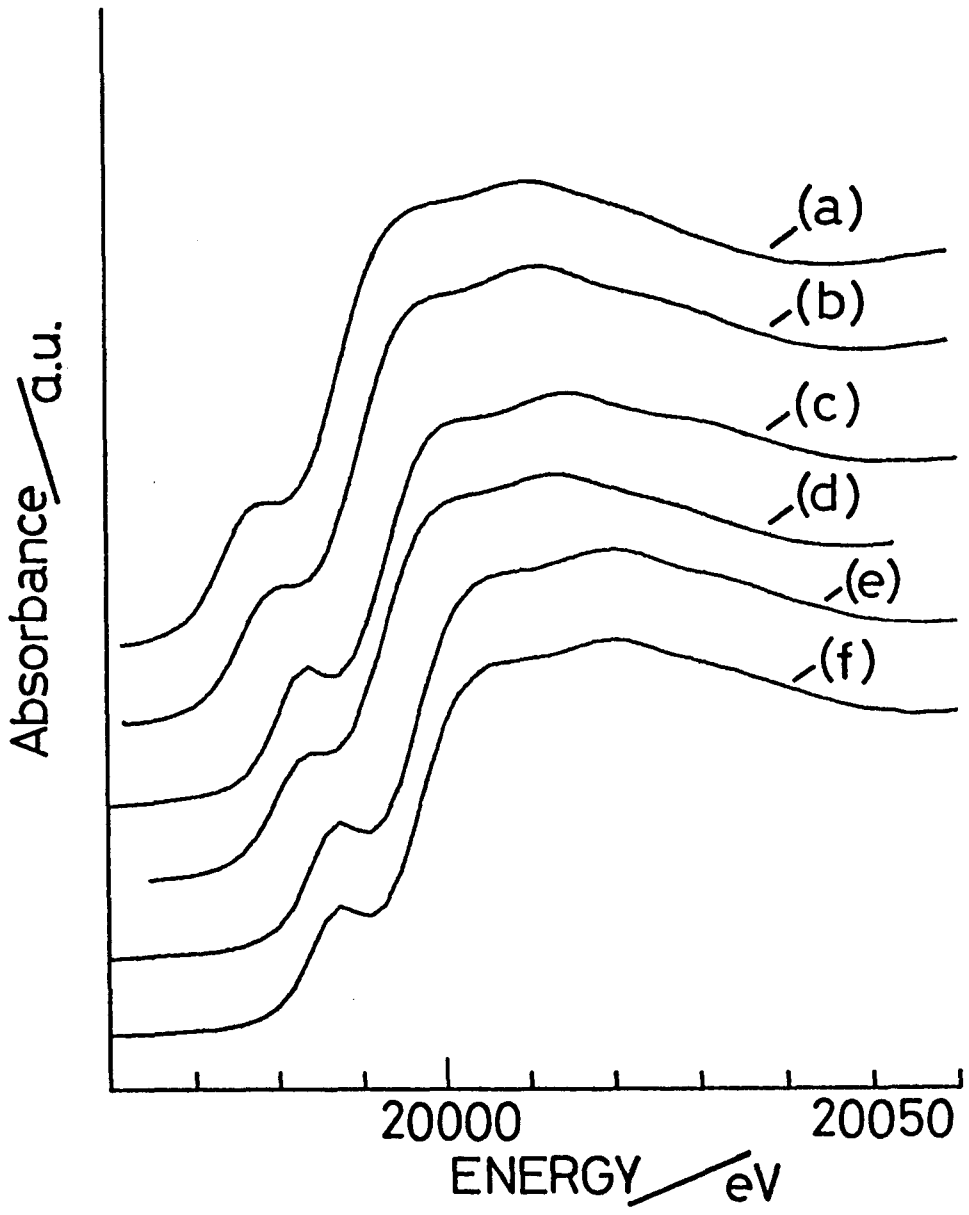


Fig IV-15. Mo K-edge XANES spectra of ternary heteropoly molybdates.

(a) PMo_{12} sln. (b) $PVMo_{11}$ sln. (c) $PNbMo_{11}$ sln.

(d) $PHfMo_{11}$ sln. (e) $PZrMo_{11}$ sln. (f) $PThMo_{11}$ sln.

$C_P = C_{Me} = 1.5 \times 10^{-2}$ $C_{Mo} = 2.0 \times 10^{-1}$ (mol dm^{-3})

pH 0.5 - 0.7

the formation of ternary heteropoly molybdate does not cause the conversion of the Keggin structure into the different form, but leads to the distorted Keggin like structure in solution, and this result agreed with Yurchenko's one. Because these ternary heteropoly molybdates had analogous structure to that of PMo_{12}, it was difficult to distinguish between each other from the results of EXAFS analysis of Mo atom. On the contrary, Fourier transforms of EXAFS of substituted atoms, X, in ternary heteropoly molybdate gave clear differences on X-O and X-Mo distances, respectively. As shown in Fig.IV-16, each X-O distance except V-O one is longer than Mo-O one(1.58 Å), i.e., Nb-O(1.67 Å), Hf-O(1.71 Å), Zr-O(1.78 Å), and Th-O(1.94 Å). However, each X-O distance was shorter compared with that for octahedral coordinated aquo complex. This result indicates that metal ion, X, which bonds to the oxygen atoms in heteropoly cage is more stable than the hydrated one which bonds with oxygen atoms of coordinated water molecules. On the other hand, for X-Mo distances they were longer than Mo-Mo one(3.4 Å), as well as X-O ones. With respect to the structure of $PVMo_{11}$, both V-O(1.47 Å) and V-Mo(2.88 Å) distances were conversely shorter than those of PMo_{12}. From these data, it can be presumed that the deviation from the Keggin structure arises in this order in solution.

In addition, with respect to the poly-substituted ternary heteropoly molybdates, EXAFS and XANES measurements were

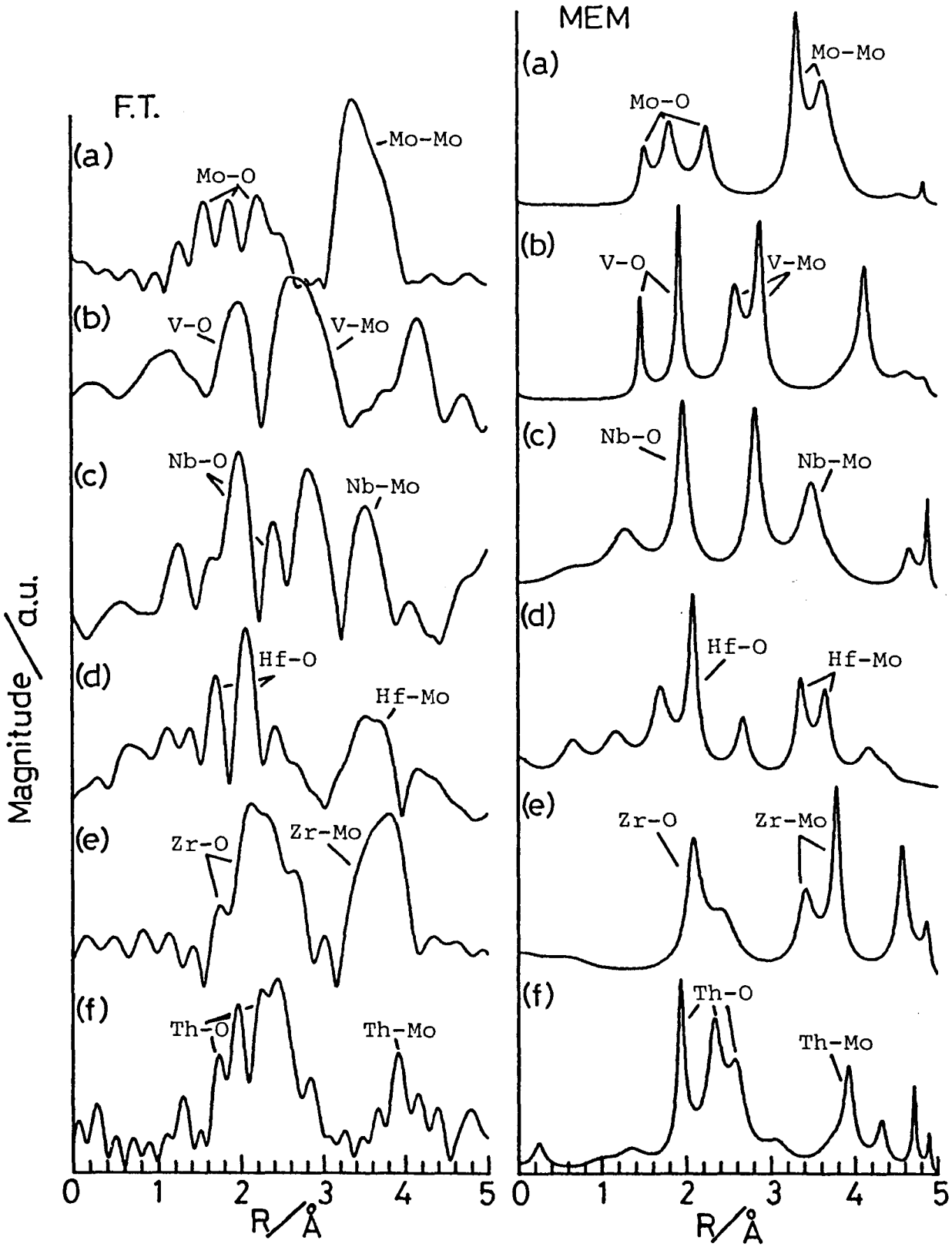


Fig IV-16. Fourier transform(left) and MEM(right) spectra of EXAFS of substituted metals for ternary heteropoly molybdates.

(a) PMo_{12} sln.(Mo) (b) $PVMo_{11}$ sln.(V) (c) $PNbMo_{11}$ sln.(Nb)

(d) $PHfMo_{11}$ sln.(Hf) (e) $PZrMo_{11}$ sln.(Zr) (f) $PThMo_{11}$ sln.(Th)

$C_P = C_{Me} = 1.5 \times 10^{-2}$ $C_{Mo} = 2.0 \times 10^{-1}$ (mol dm^{-3})

pH 0.5 - 0.7

carried out. Figure IV-17 shows the variation of FT and MEM spectra for Mo atom with the increase of substituted number of vanadium(V). No clear difference for Mo-O distances was observed in EXAFS spectra, while for Mo-Mo distances there was some differences between each other. Thus the trend of decreasing Mo-Mo distance, from 3.47 to 3.41 Å, with increasing the substituted number was found in these spectra. In FT spectra it was observed that most intense peak near 3.4 Å corresponding to the Mo-Mo distance sweeped for shorter distance. This is predicted that its peak may be separable two parts. In fact, it could be seen obviously in the variation of MEM spectra. Two peaks, one at 3.2 Å and the other at 3.5 Å, were observed in MEM spectra and with increasing substituted number, the strength of former increased while that of latter decreased by degrees. These results are shown that the former corresponds to Mo-V distance and latter to Mo-Mo one. XANES spectra, as shown in Fig.IV-18, are also indicated that molybdenum atoms in poly-substituted heteropoly molybdates retain the MoO_6 octahedron structure.

These EXAFS and XANES measurements, instead of x-ray diffraction analysis, gave the information regarding the structure of ternary heteropoly molybdate and further supported resultingly the empirical equation based on the rigid sphere model.

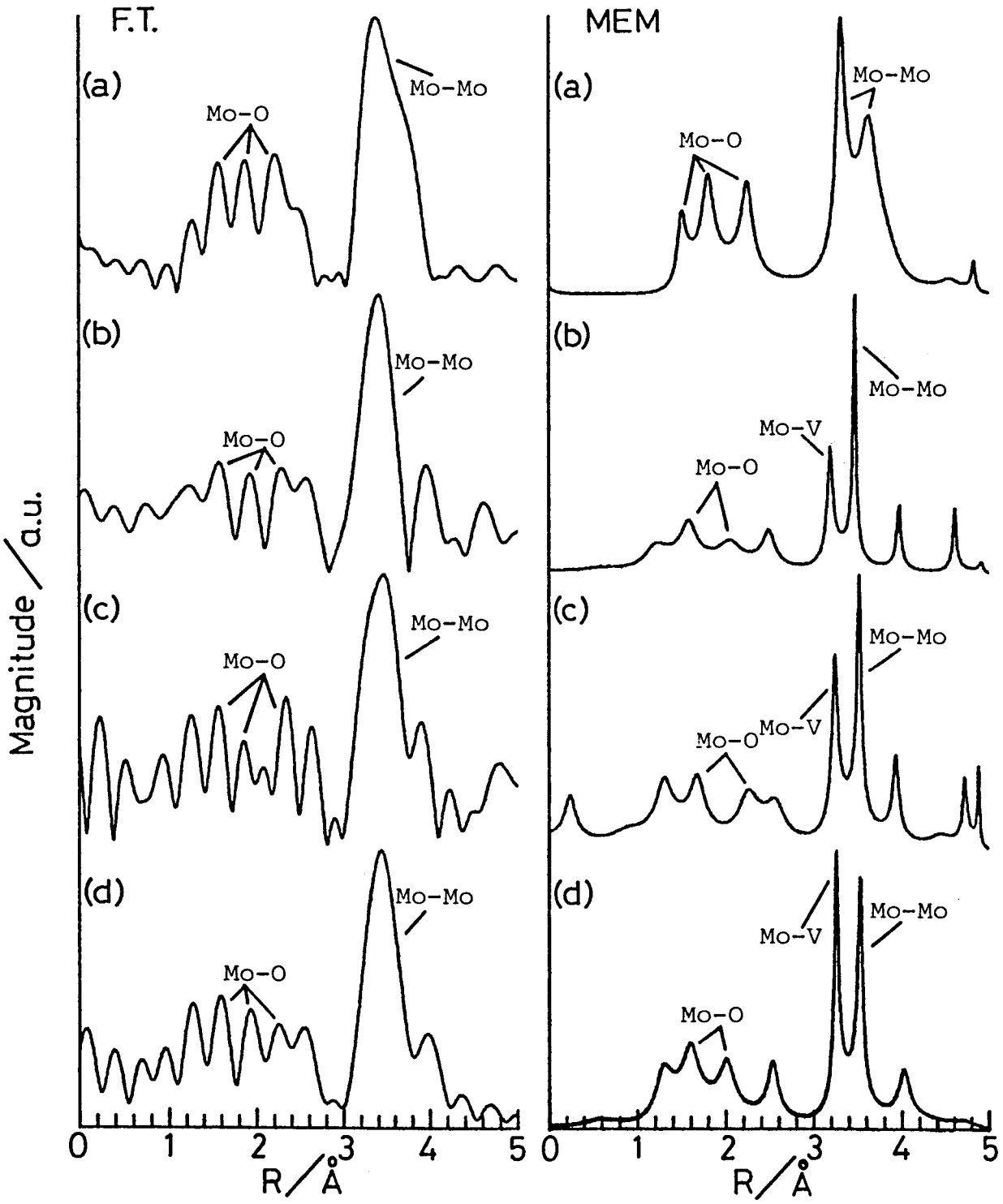


Fig IV-17. Fourier transform(left) and MEM(right) spectra of EXAFS of Mo atom for poly-substituted molybdovanadophosphates in solid state.

(a) PMo_{12} sln. (b) $PVMo_{11}$-H^+

(c) PV_2Mo_{10}-H^+ (d) PV_3Mo_9-H^+

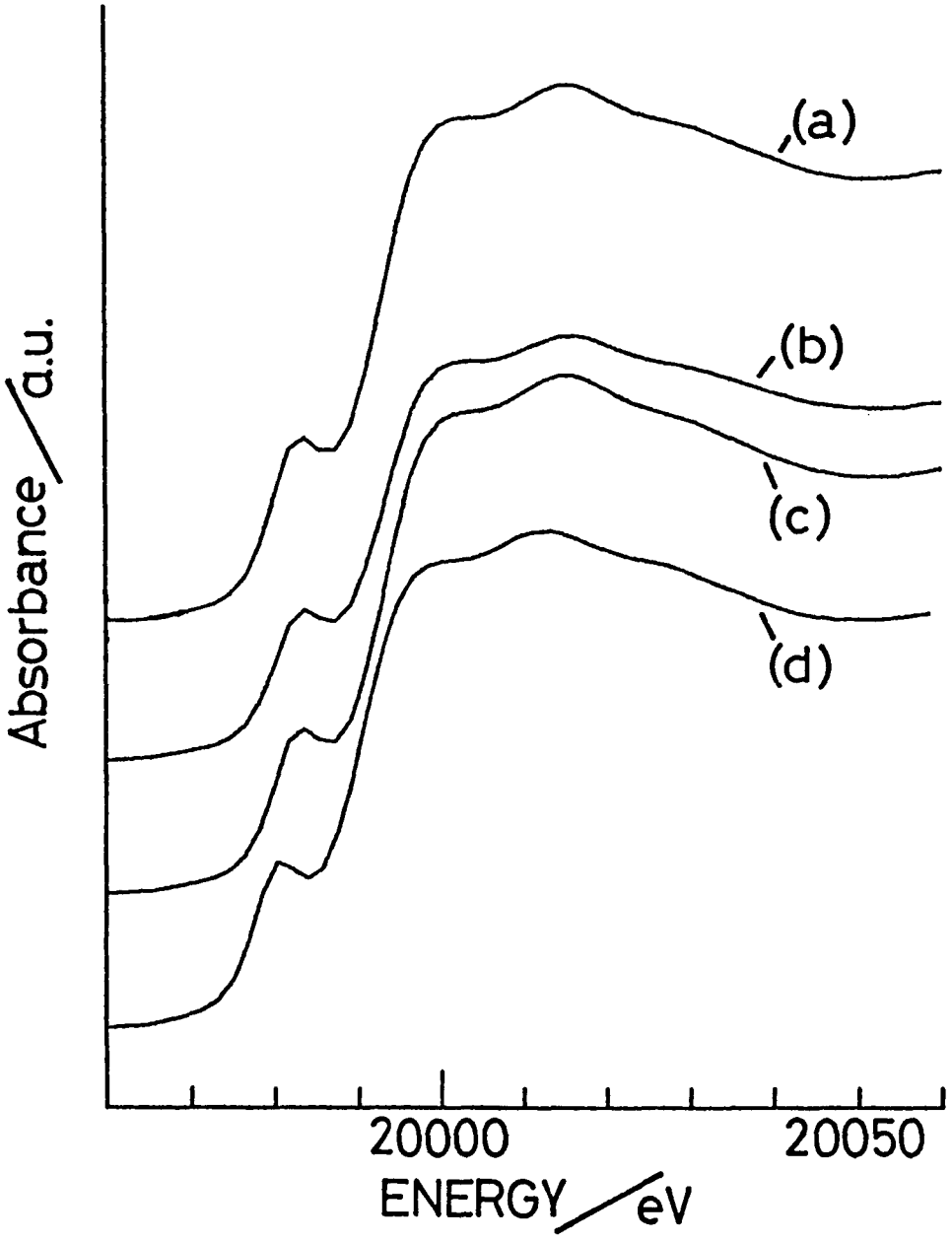


Fig IV-18. Mo K-edge XANES spectra of poly-substituted molybdovanadophosphates in solid state.

(a) $PV_3Mo_9-H^+$ (b) $PV_2Mo_{10}-H^+$

(c) $PVMo_{11}-H^+$ (d) PMo_{12} sln.

IV - 4. Simultaneous Determination of Complexed Metal Ions in Aqueous Solution

The separation of very similar species in chemical properties occupies an important part in analytical chemistry. Therein, particularly Zr(IV) and Hf(IV) ions, and Nb(V) and Ta(V) ones, are these pair ions which encounters the difficult to achieve the separation and/or the determination of each ion simultaneously without any pre-mass separation, because two pairs of ions have very close atomic and ionic radii by the effect of so-called the lanthanide contraction. For the quantitative determination of each ion, although it needs a few steps of very complicated procedures, it has been possible to achieve up to the present(26-32). Recently, for example, the development of ICP emission spectrochemical analysis has led to the simultaneous determination of these ions at low ppm level(33). On the other hand, as for the separation of each ion respectively, elavorated works(34-36) have been devoted, but at present we must rely upon an interminable ion exchange method so as to obtain in reasonable yield. It is clear, though it is desirable, that the experimental procedures can be indeed simple and reliable one, which is applied to determine simultaneously without any or with a minimum of preliminary treatment after dissolving a sample in acidic solution, and not subject to complicated and delicate process. For these

reasons, the simultaneous determination of complexed metal ions in aqueous solution has been examined by use of NMR technique, based on the following results obtained by means of ^{31}P NMR measurement:

1) each ternary heteropoly molybdate gives a peak identified by its specific chemical shift.
2) there is a linear relationship between its relative peak area and the metal ion concentration.

In addition, the effect of coexistence of inert metal ions has been also investigated.

At first, in order to compare this NMR method with the Raman one both measurements were examined for same sample solution. The results obtained were shown in Fig.IV-19. As shown in Fig.IV-19b, only Raman measurement provided very poor resolution in its spectra, while the reasonable result was shown in NMR spectra. Six peaks pertaining to ternary heteropoly molybdates were observed in Fig.IV-19a, and each peak was identified by its specific chemical shift which is listed in Table IV-2. In addition, it was also established a good correlation between the relative peak area and each metal ion concentration in solution. Only result of one sample solution was dealt in this paper, but the results obtained with the others gave a good reproducibility within experimental error of $\pm$ 5% and the detection limit for each metal ion was at ppm level.

Next, a further study was made to examine the effect of

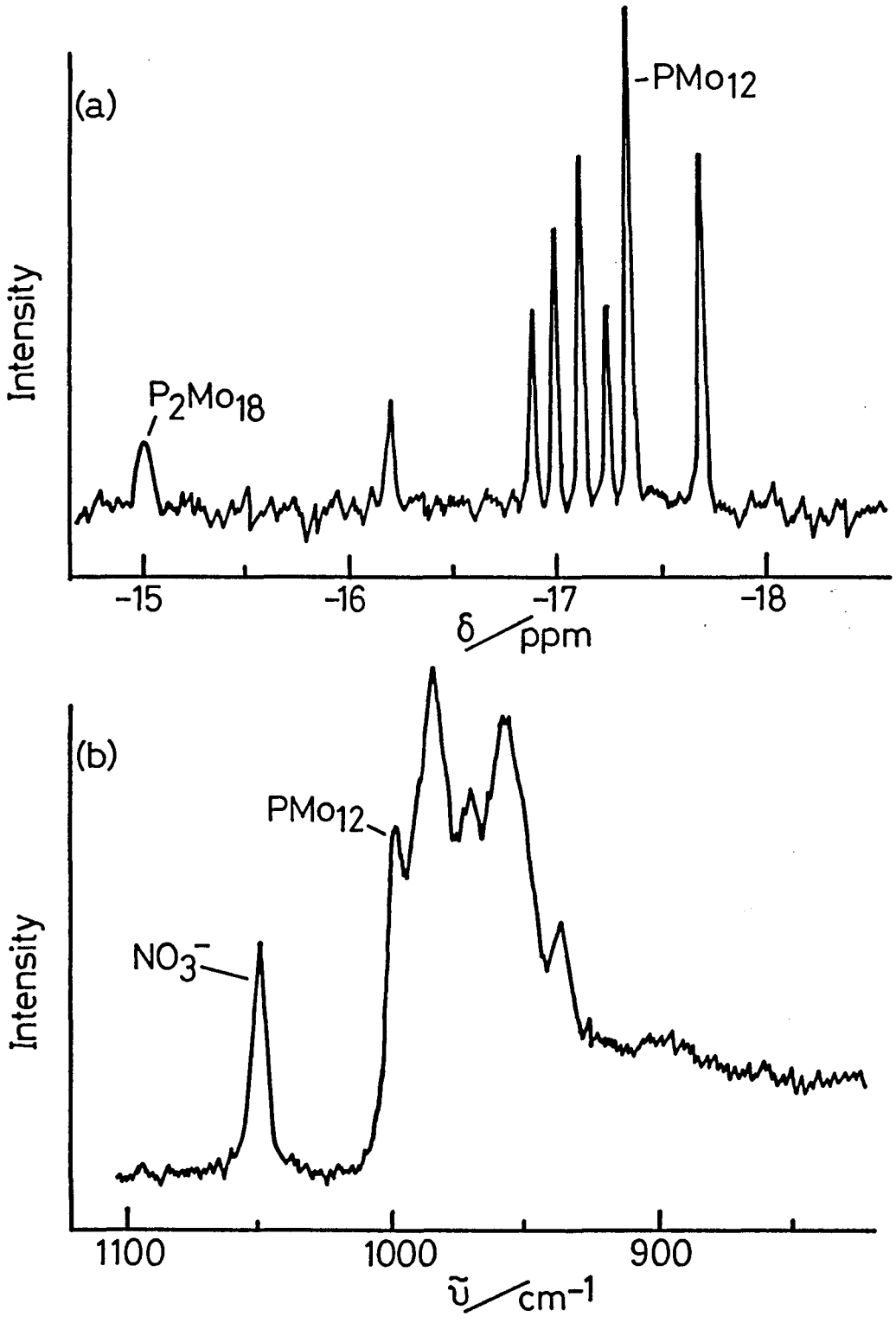


Fig.IV-19 Comparison of (a) ^{31}P NMR method and (b) Raman one for simultaneous determination.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

$C_{Me} = 7.0 \times 10^{-3}$ (mol dm^{-3}) pH 0.55

50 - 60 folds weight excess of various inert metal ions on the determination of coexisting complexed metal ions by the recommended procedure. The result obtained, as an example, was shown in Fig.IV-20 and each peak is labeled alphabetically in sequence from low to high field for assignment to the corresponding species in it. In the solution the following metal ions were contained, thus as complexed metal ions are Ce(IV), Th(IV), Zr(IV), Ti(IV), Hf(IV), V(V), and Nb(V) ones, while as inert metal ions Zn(II), Cu(II), Y(III), Fe(III), and Cr(VI) ones. The spectrum obtained is shown a similar result to that of free solution. For complexed metal ions, that is, it was established a good coincidence of calculated and observed results. On the contrary, inert metal ions developed no peak in the NMR spectra and they did not interfere with the determination of complexed metal ions. Even though existing conditions the limitation of the applicability of this method which the total metal ion concentration must be equal to or less than of phosphate in aqueous solution, this method can be widely employed for the simultaneous determination of the complexed metal ions without their mutual interaction and the interference of coexisting inert metal ions in solution. However a few non-metal ions, e.g., As(V), Se(IV), and Te(VI) ones, which react with the excess molybdate, interfered with the determination of complexed metal ions.

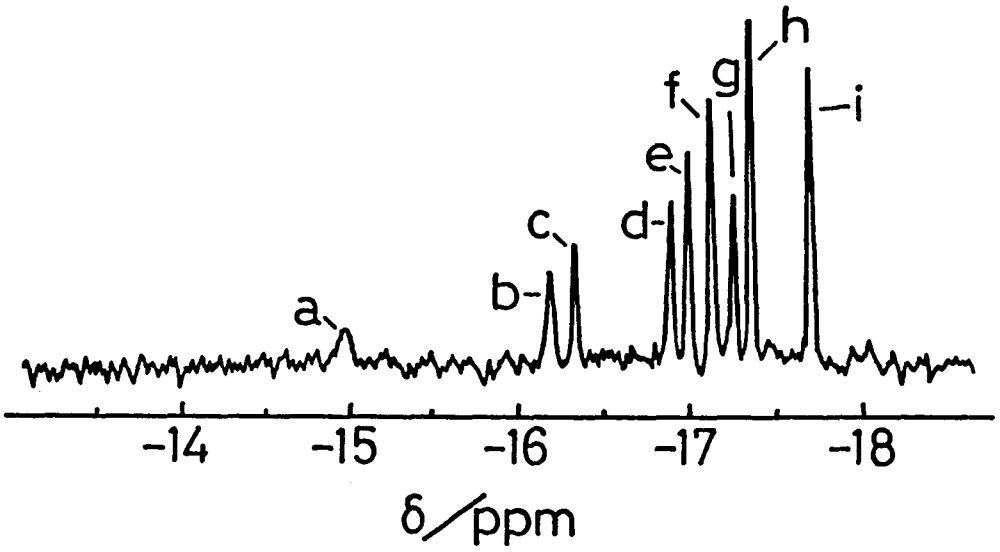


Fig.IV-20 Simultaneous determination by ^{31}P NMR measurement.

a - $(P_2Mo_{18}O_{62})^{6-}$

b - $(PThMo_{11}O_{40})^{5-}$

c - $(PCeMo_{11}O_{40})^{5-}$

d - $(PZrMo_{11}O_{40})^{5-}$

e - $(PTiMo_{11}O_{40})^{5-}$

f - $(PNbMo_{11}O_{40})^{4-}$

g - $(PHfMo_{11}O_{40})^{5-}$

h - $(PMo_{12}O_{40})^{3-}$

i - $(PVMo_{11}O_{40})^{4-}$

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 2.0 \times 10^{-1}$

$C_M = 0.8\text{-}1.3 \times 10^{-3}$ (mol dm^{-3}) pH 0.58

IV - 5. Formation of Ternary Heteropoly Molybdates Containing Metal and Metalloid Ions Other than Group 4A and 5A Elements

As mentioned previous section, group 4A and 5A elements reacted with 12-molybdophosphate and produced ternary heteropoly molybdate in solution. Each ternary heteropoly molybdate provided the different chemical shift in NMR spectra. In order to interpret the difference of chemical shifts a rigid sphere model was introduced and established a linear relationship between the chemical shift and the derived electron density parameter around phosphorus nucleus. In this chapter, studies on the effect of addition of metal and metalloid ions other than group 4A and 5A elements using of NMR technique was described, and the validity of the empirical rule was ascertained. The results obtained are also listed in Table IV-2(see section IV-2).

(A) Rare earth[Lu(III),Ce(III),Ce(IV),Sm(III),Gd(III), Ho(III),Yb(III), and Lu(III)], Th(IV), and U(VI).

Heteropoly complexes containing several rare earth, thorium, and uranium atoms, which have been seen the published reports so far, have these elements in the center of the compounds as tetrahedral oxoanions. Weakley et al.(37,38), for example, first characterized structurally salts of such anions as $(XW_{10}O_{36})^{n-}$ where X is a variety of

tri- and tetravalent metals(39,40). It appears very probable that tungstate complexes of Ce(III),Ce(IV),Th(IV), and U(IV) originally formulated as 1:8 species(41,42) belong to the same series. Further dodecamolybdometalates, $(XMo_{12}O_{42})^{n-}$, were proposed as one of other structures and salts of Ce(IV) and Th(IV) complexes were first prepared by Barbieri(43), and the free acid was later shown to be octabasic(44). The vibrational(45) electronic(46,47), broadline NMR spectra(48), and XPES(49) of the Ce, Th, and U complexes have been reported and discussed.

The addition of U(VI) ion revealed no new peak in NMR spectra, while a new peak at -16.25 ppm was observed by the addition of Th(IV) ion in 12-molybdophosphate(PMo_{12}) solution(see Fig.IV-21). Therefore Th(IV) ion reacted with PMo_{12} and a ternary heteropoly molybdate was found in solution. This is the evidence of the formation of molybdothorophosphate($PThMo_{11}$) in solution. The peak for $PThMo_{11}$ developed at the very similar feature to that for molybdoniobophosphate($PNbMo_{11}$) in NMR spectra. Its relative peak area, that is, increased with the increase of Th(IV) ion concentration. When Th(IV) concentration is attained to equimolar amounts of phosphate one, the peak for PMo_{12} disappeared and only single peak which is assigned to the thorium-phosphorus heteropoly molybdate remained. Under the condition of the presence of excess Th(IV) ion, it was gradually decomposed and produced its hydrolysis or the

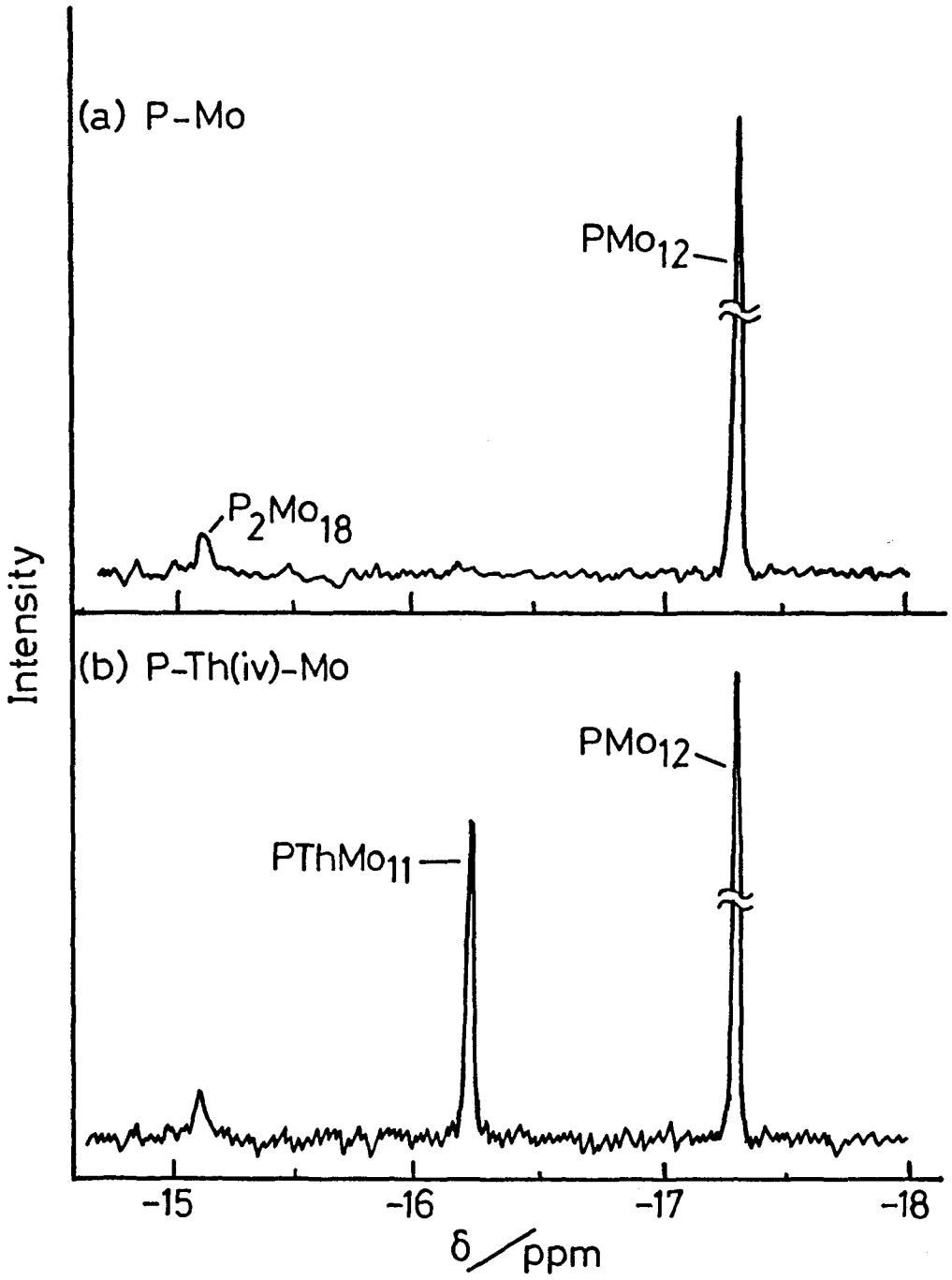


Fig.IV-21 ^{31}P NMR spectra of 12-molybdophosphate and ternary heteropoly molybdate in solution.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(a) $C_{Th} = 0$ (b) $C_{Th} = 3.2 \times 10^{-3}$

(mol dm^{-3}) pH 0.7 - 0.8

precipitate of thorium-molybdenum heteropoly complexes.

In rare earth elements, only cerium(IV) ion produced a ternary heteropoly molybdate in solution(see Fig.IV-22c). On the other hand, the addition of Ce(III) ion, as shown in Fig.IV-22b, did not give any effect on NMR spectra. The peak for cerium(IV)-phosphorus heteropoly molybdate at -16.33 ppm also developed at similar feature to that for $PNbMo_{11}$. As the result, it was possible to determine two metal ions, i.e., Th(IV) and Ce(IV) ones, over range of 6.5×10^{-4} to 8.0×10^{-3} mol dm^{-3}(see Fig.IV-23). The effect of the addition of Ce(III) and Ce(IV) ions was also confirmed by Raman measurement, as shown in Fig.IV-24. When Ce(III) ion was added in PMo_{12} solution, the Raman spectrum exhibited almost similar one to that of PMo_{12}, while the addition of Ce(IV) ion led to appearance of a new peak at 980 cm^{-1}. This value of wave number was quite the same one as those of $PZrMo_{11}$ and $PHfMo_{11}$.

In order to examine the applicability of the empirical equation described in the previous section, the comparison of the predicted difference of chemical shift,$\Delta\delta_{calcd.}$, which is estimated from the ionic radius of cerium(IV) ion and its electron number, with the observed one actually,$\Delta\delta_{obsd.}$, was carried out and it was confirmed to be useful for the identification of the Keggin like structures. Thus, under the assumption of the presence of the Keggin like structure, $PCeMo_{11}O_{40}^{5-}$, the difference of the chemical shift from that

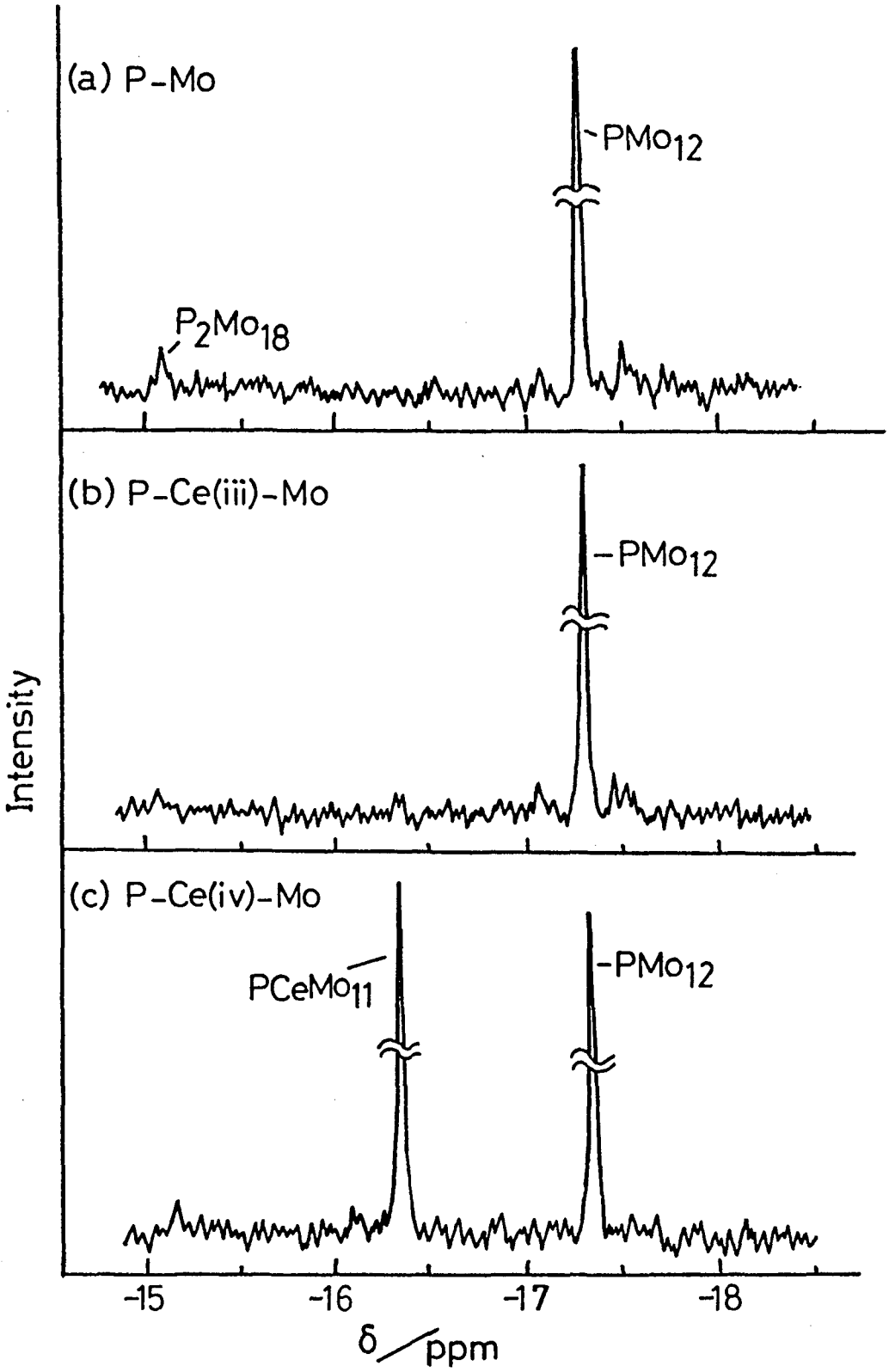
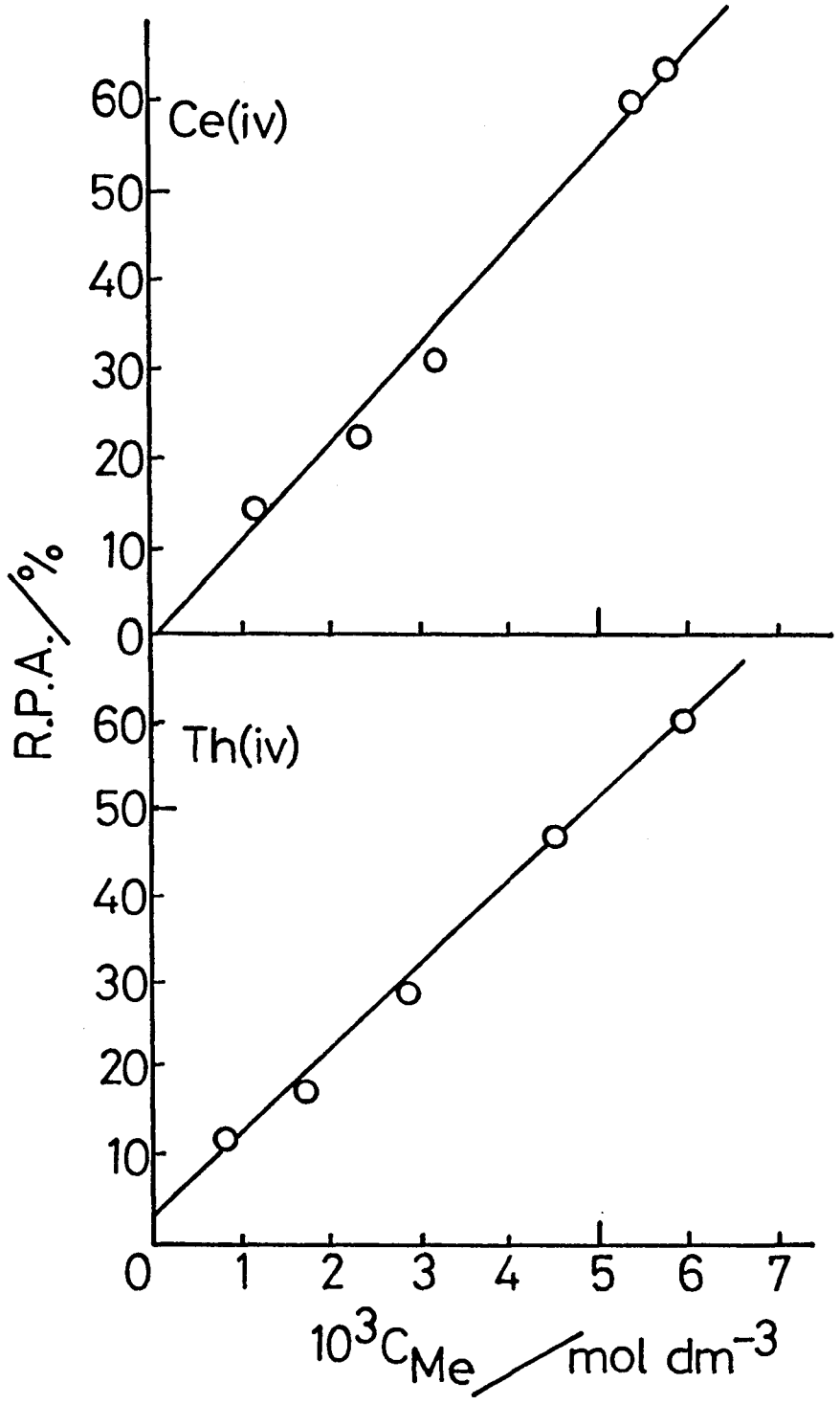


Fig. IV-22 Effect of Ce(III) and Ce(IV) ions by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(b), (c) $C_{Ce} = 6.0 \times 10^{-3}$ (mol dm^{-3})

pH 0.7 - 0.9



Fig,IV-23. Calibration curves of Ce(IV) and Th(IV) ions obtained from NMR signal.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$ (mol dm^{-3})

pH 0.5 - 0.7

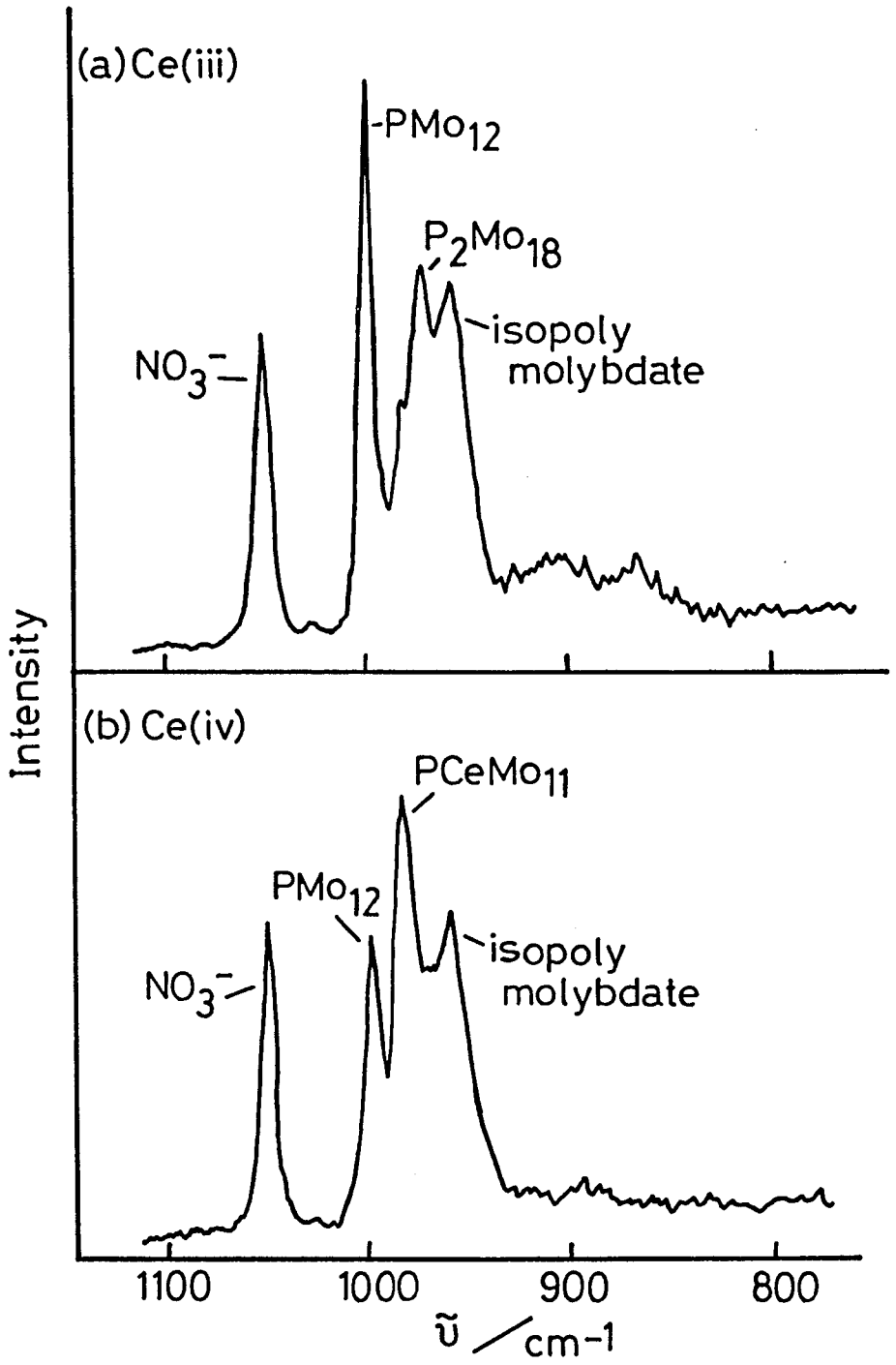


Fig .IV-24 Effect of Ce(III) and Ce(IV) ions by Raman spectra.

C_P = 1.0 x 10^{-2} C_{Mo} = 1.5 x 10^{-1}

C_{Ce} = 6.0 x 10^{-3} (mol dm^{-3})

pH 0.7 - 0.9

for PMo_{12} was plotted against that of electron density parameter in the manner previously described. As shown in Fig.IV-25, the point of Ce(IV) lies so close to the straight line as to give a good relationship. In light of the above data, the phosphorus-cerium(IV) heteropoly molybdate may be regarded as the Keggin like structure, although precise x-ray diffraction analysis has not been done yet. By the way, the formation and stability of phosphorus-cerium(IV) heteropoly molybdate has been already investigated by several workers(50,51), and the methods for the determination of cerium by combined solvent extraction, and spectrophotometry or atomic absorption spectroscopy based on the formation of heteropoly complex have been also reported(52,53). Whitehouse et al. has reported, in distinction to this conclusion, the composition molar ratio of P:Ce:Mo = 1:2:12. They might not separate completely the binary molybdoceric acid complex(54) formed simultaneously, because it is necessary to present a large excess of molybdate to ensure complete formation of PMo_{12} and these procedures are all, at some point, based upon the extraction of excess PMo_{12} from the mixed heteropoly complexes solutions. This result represented the possibility to determine Ce(IV) ion under the condition of coexistence of Ce(III) one by use of NMR technique.

(B) Bi(III) ion.

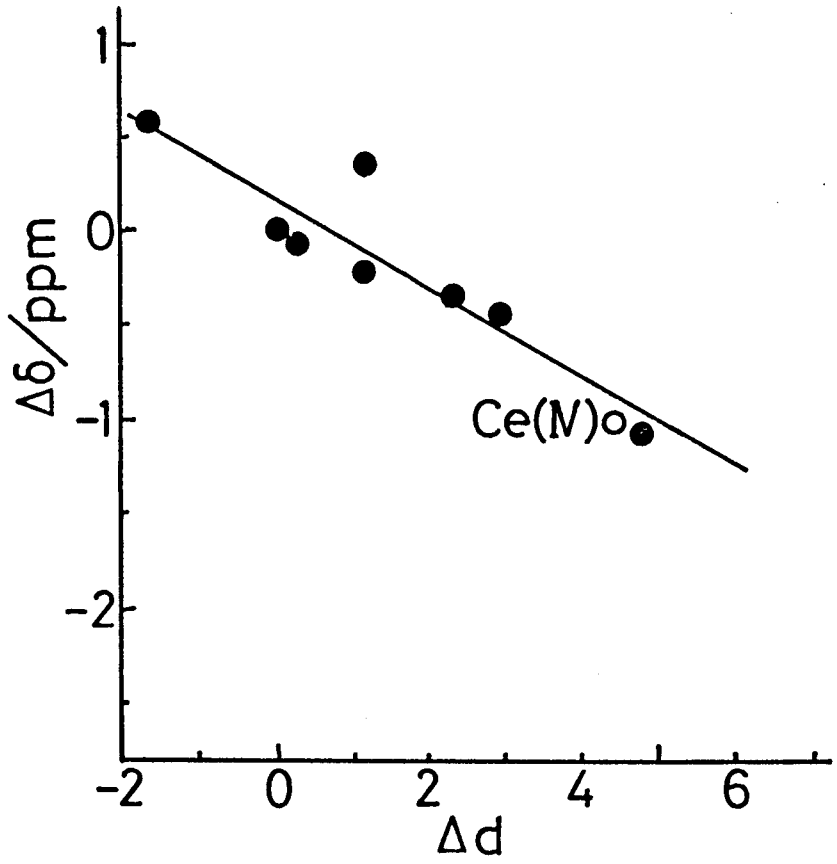


Fig.IV-25 Relationship between 'electron density around P atom' and chemical shift for Ce(IV) ion.

It has been reported by earlier investigators(55,56) that bismuth(III) affected the reduction of 12-molybdophosphate(PMo_{12}) to the corresponding heteropoly blue. At first, however, the investigations concerning the nature of the effect were unable to determine if the effect was catalytic or the result of complex formation involving Bi(III) ion. By means of a spectrophotometric study, Goldman and Hargis showed for the first time that a discrete phosphorus-bismuth heteropoly molybdate can be formed in solution which reduces considerably more rapidly than PMo_{12}(57). A further detailed reports with respect to phosphorus-bismuth heteropoly molybdate, however, have not been presented up to now. Thus to study the role of Bi(III) ion in the formation and reduction processes, NMR and EXAFS measurements were carried out.

The phosphorus-bismuth heteropoly molybdate, as compared with other ternary heteropoly molybdates, offered a slight different feature in NMR spectra. With respect to complexed metal ions, i.e., group 4A and 5A elements, each peak for ternary heteropoly molybdate was sharply and in equimolar amounts of phosphate and its metal ion the peak for PMo_{12} disappeared, though a single peak pertaining to ternary heteropoly molybdate remained, from NMR spectra. The phosphorus-bismuth heteropoly molybdate, however, gave a broaden peak like 18-molybdodiphosphate(P_2Mo_{18}) one and even in the presence of excess Bi(III) ion the peak for PMo_{12} did

not disappear. It was also provided an upper convexed calibration curve, as shown in Fig.IV-26. Thus the empirical equation was applied for the phosphorus-bismuth heteropoly molybdate as well as the case of Ce(IV) ion. Under the assumption of the presence of Keggin like structure, $PBiMo_{11}O_{40}^{6-}$, the difference of the chemical shift from that of PMo_{12} was plotted against the difference of electron density from that. It is noteworthy that the point of Bi(III) ion, as shown in Fig.IV-27, deviates appreciably from the straight line. These results imply two facts as follows:

(i) phosphorus-bismuth heteropoly molybdate has a different structure from the Keggin one.

(ii) it has a smaller equilibrium constant than those of other ternary heteropoly molybdates.

However, Hargis et al. did not shed any lights on the nature of this reaction for they used perchloric acid to adjust the pH value, could be encountered in adjustment the pH value with hydrochloric acid. Contrary to using nitric acid, it was not shown the peak for phosphorus-bismuth heteropoly molybdate, at -15.50 ppm, but similar spectra to that of PMo_{12} in NMR measurement, as shown Fig.IV-28. Similar evidence could be seen in Raman spectra(see Fig.IV-29). The sample solution which was adjusted the pH value with hydrochloric acid, that is, was not revealed the peak for phosphorus-bismuth heteropoly molybdate in its spectra and gave the similar to that of PMo_{12} solution(see Fig.IV-

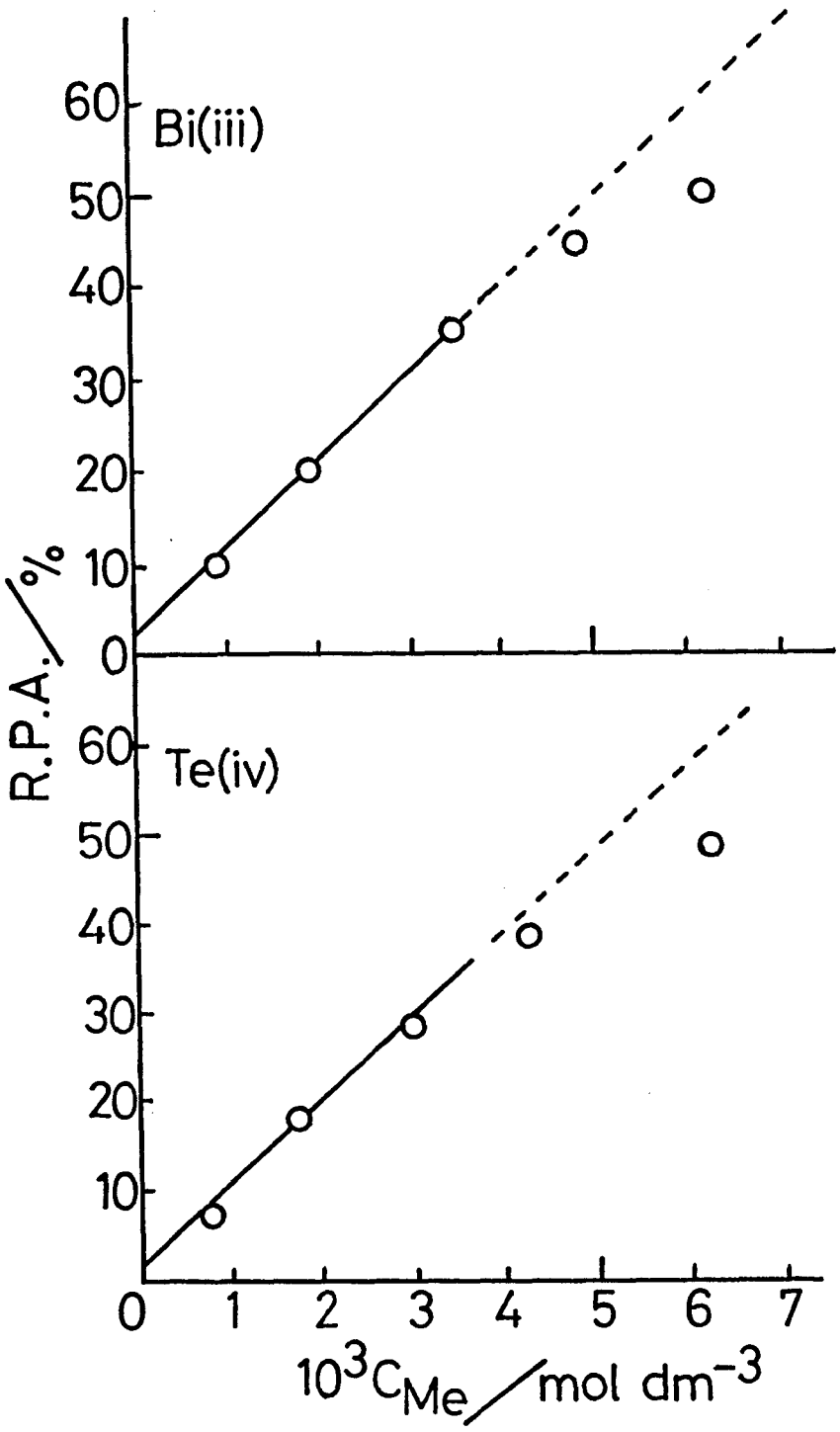


Fig. IV-26 Calibration curves of Bi(III) and Te(IV) ions obtained from NMR signal.

C_P = 1.0 x 10^{-2} C_{Mo} = 2.0 x 10^{-1}

(mol dm^{-3}) pH 0.5 - 0.8

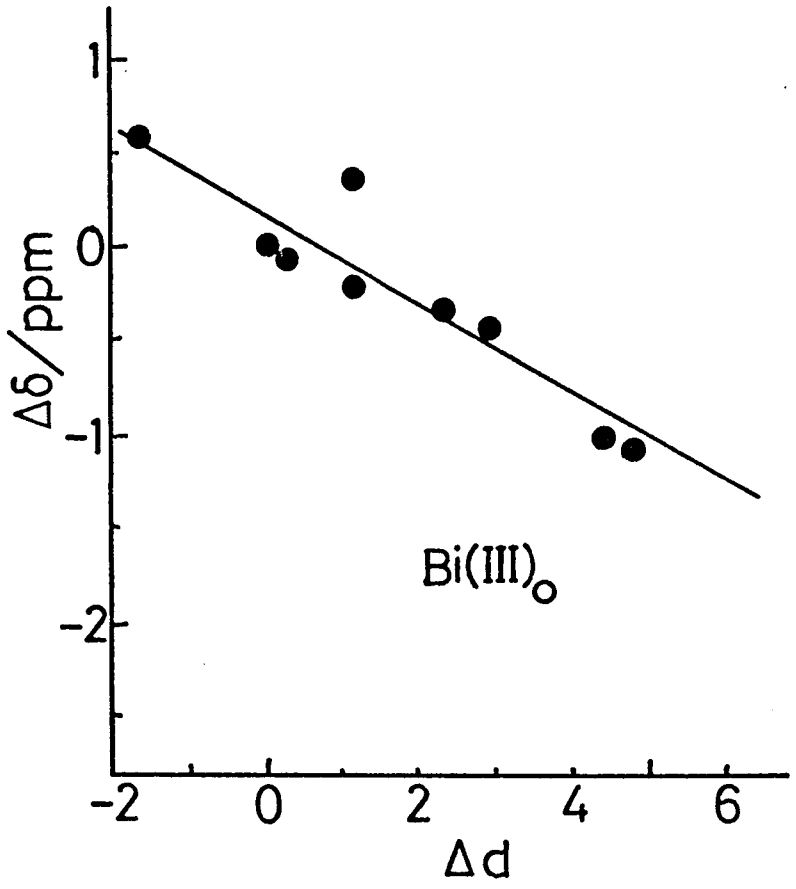


Fig.IV-27 Relationship between 'electron density around P atom' and chemical shift for Bi(III) ion.

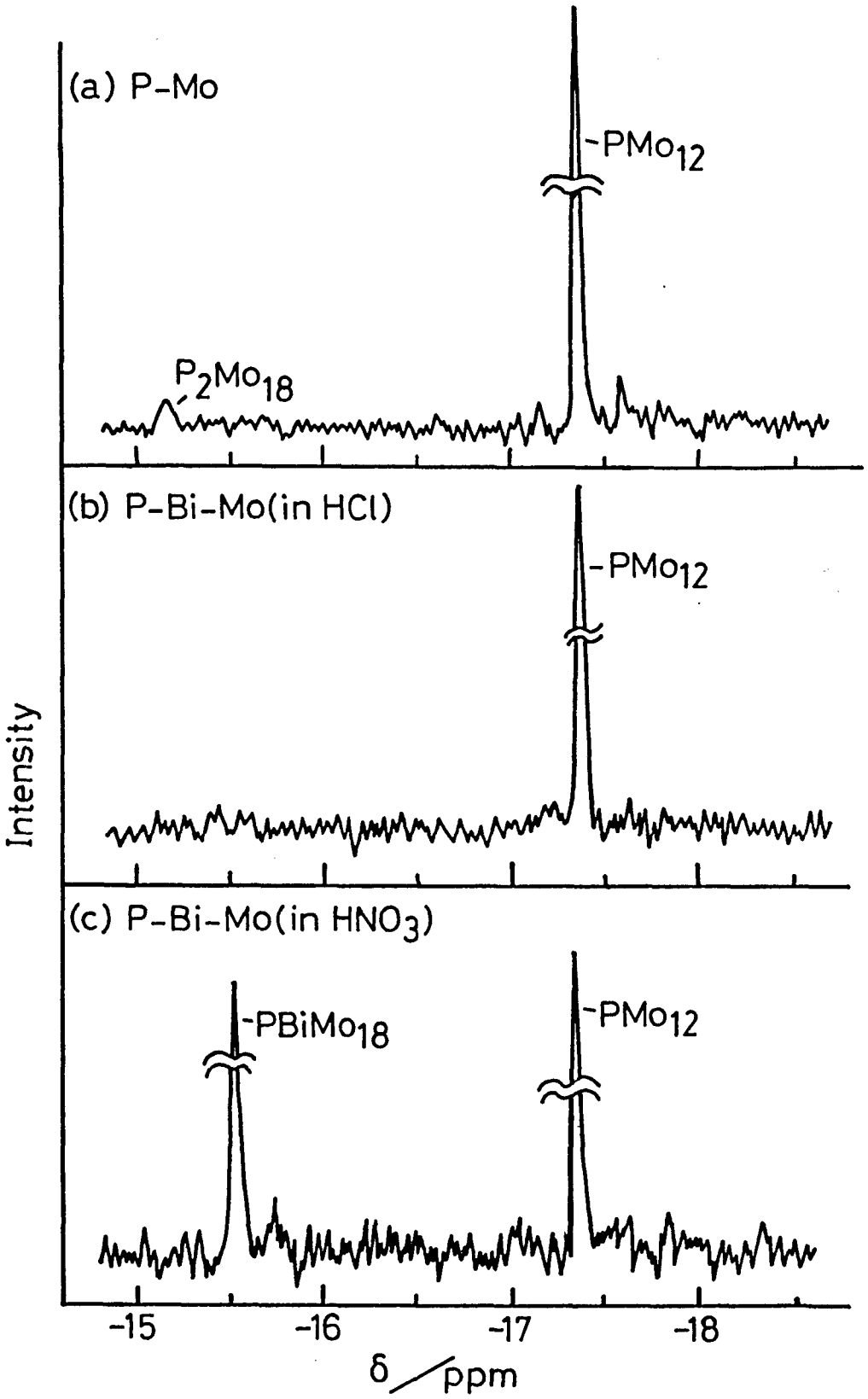


Fig .IV-28 Effect of HCl sln. and HNO_3 sln. in the KH_2PO_4 - Bi(III) - Na_2MoO_4 aqueous system by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 2.0 \times 10^{-1}$

(b),(c) $C_{Bi} = 7.0 \times 10^{-3}$ (mol dm^{-3})

pH 0.7 - 0.8

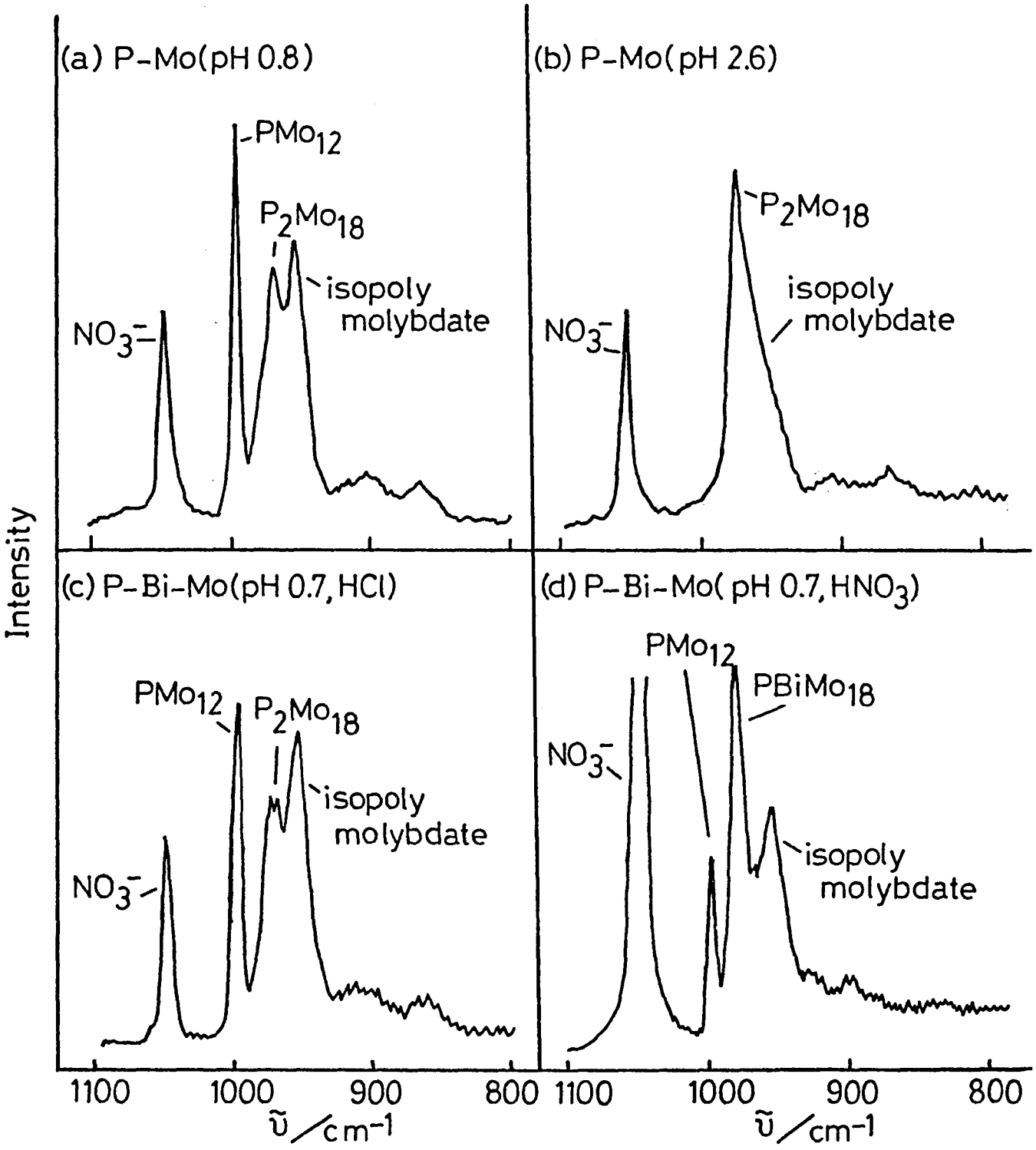


Fig .IV-29 Effect of HCl sln. and HNO_3 sln. in the KH_2PO_4 - Bi(III) - Na_2MoO_4 aqueous system by Raman spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 2.0 \times 10^{-1}$

(c), (d) $C_{Bi} = 7.0 \times 10^{-3}$ (mol dm^{-3})

29c). It was observed to be independent of Bi(III) ion concentration. On the other hand, dil. nitric acid solution, as shown in Fig.IV-29d, provided a somewhat broaden peak near 980 cm^{-1}. These experimental results were sufficient to confirm that Bi(III) ion does not form the phosphorus-bismuth heteropoly molybdate in dil. hydrochloric acid solution, while does in dil. nitric acid solution. By only NMR measurement, however, a tentative conclusion must be reached for the structure of phosphorus-bismuth heteropoly molybdate in solution. Thus a series of EXAFS and XANES measurements were carried out to follow up this unexpected observation and to make clear the difference between two acidic solutions. These EXAFS and XANES spectra are shown in Figs.IV-30,31,32, and 33, with the addition of those for bismuth oxychloride(BiOCl) in dil. hydrochloric acid solution. In addition, the results of the data treated in this manner, together with x-ray diffraction data(58), are summarized in Table IV-5. Fourier transforms of EXAFS of Mo atom for heteropoly molybdate in dil. hydrochloric acid solution, as shown in Fig.IV-30c, gave a similar spectrum to that of P_2Mo_{18}(Fig.IV-30b), while that of heteropoly molybdate in dil. nitric acid solution gave two more intense peaks corresponding to Mo-Mo distances (near 3.3 and 3.8 Å), as shown in Fig.IV-30d. From the results of XANES spectra, however, it was found that these heteropoly molybdates retained a similar structure consisted of MoO_6 octahedron

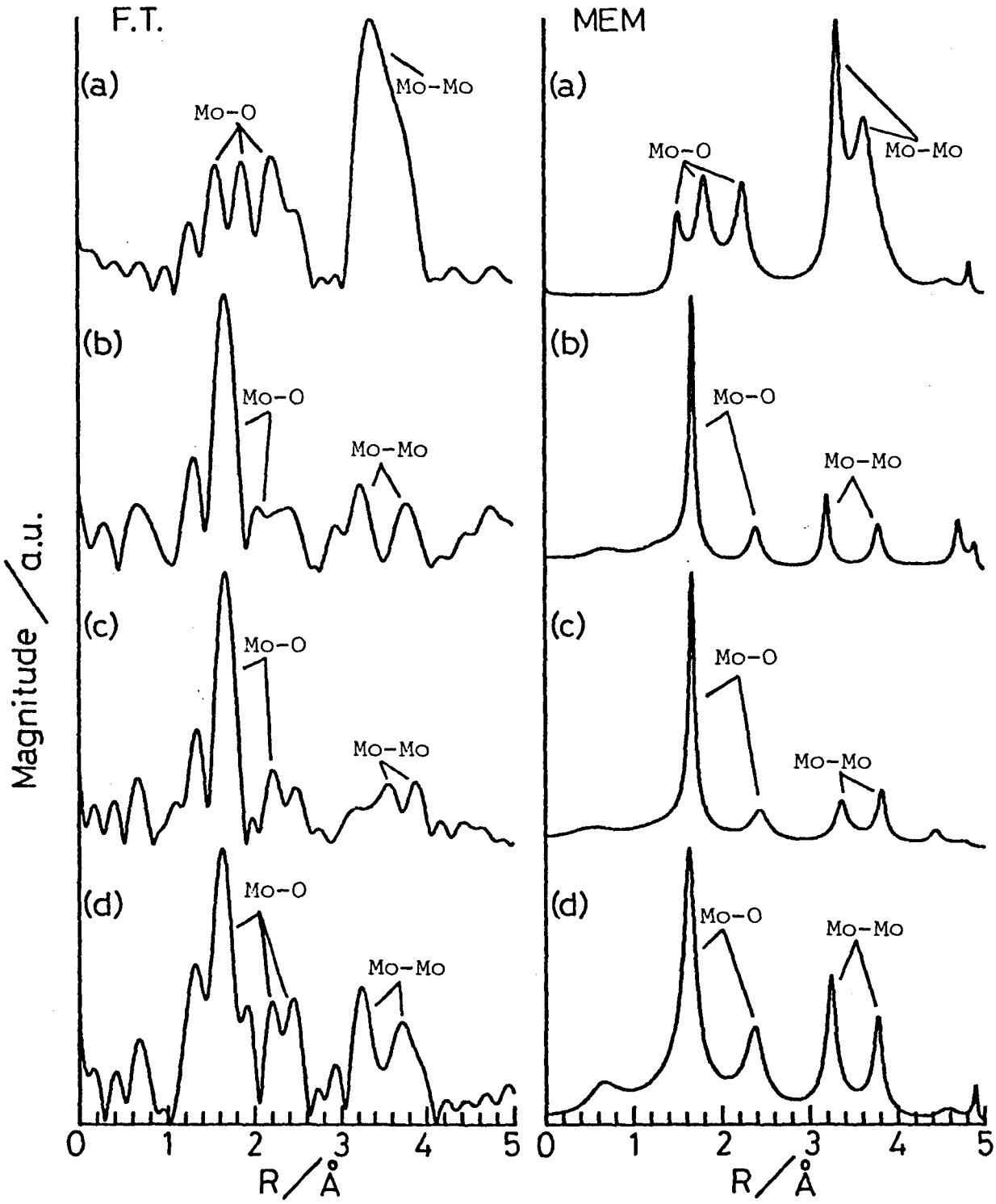


Fig.IV-30 Fourier transform(left) and MEM(right) spectra of EXAFS for Mo atom.

(a) PMo_{12} sln. (b) P_2Mo_{18} sln.

(c) P-Bi-Mo system in dil. HCl sln.

(d) P-Bi-Mo system in dil. HNO_3 sln.

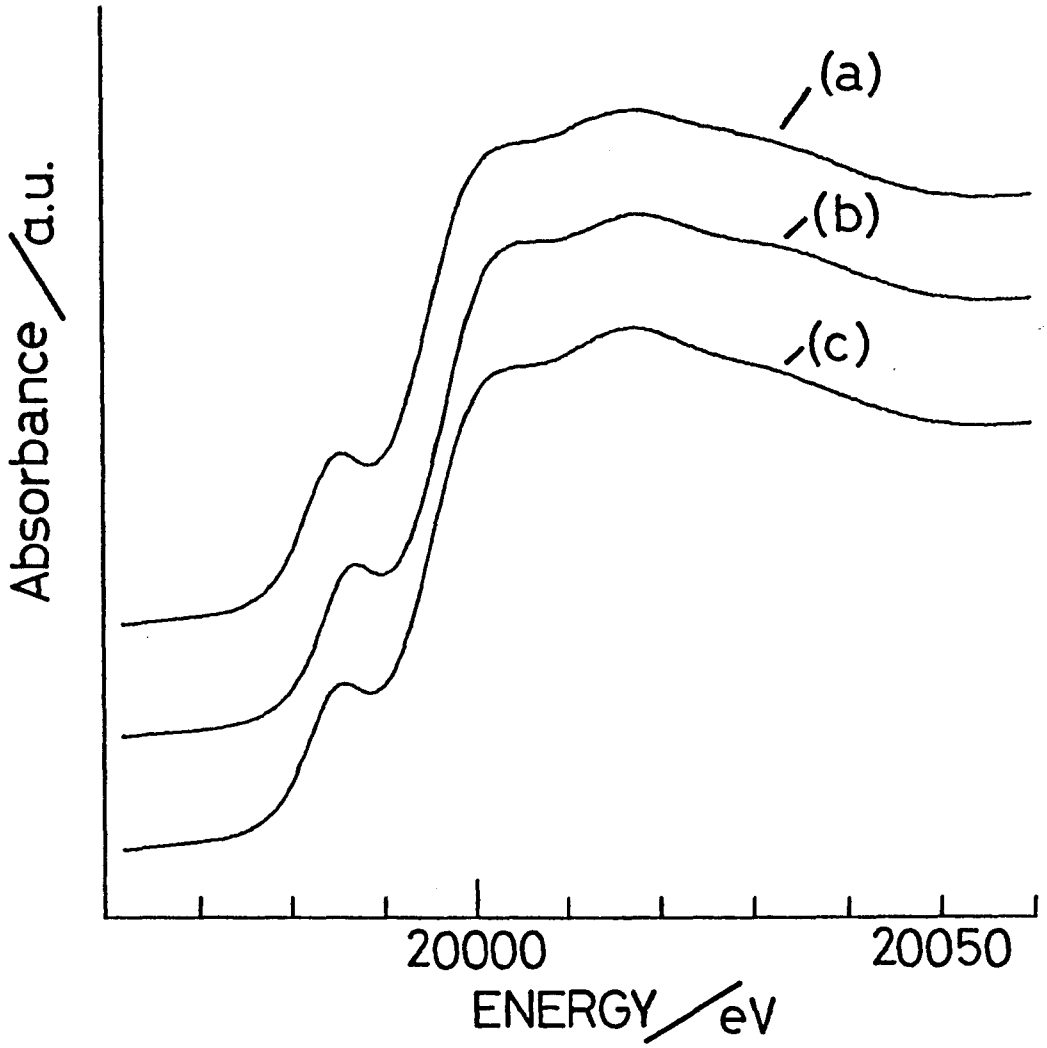


Fig. IV-31 Mo K-edge XANES spectra.

(a) P_2Mo_{18} sln.

(b) P-Bi-Mo system in dil. HCl sln.

(c) P-Bi-Mo system in dil. HNO_3 sln.

units(see Fig.IV-31). As a result, it can be presumed that these heteropoly molybdates in two acidic solutions have the Dawson or Dawson like structure. A more clear difference was observed in Fourier transform spectra of Bi(III) atom for heteropoly molybdate, as shown in Fig.IV-32. Thus Fourier transforms of Bi(III) atom for heteropoly molybdate in hydrochloric acid solution gave a similar spectrum to that of BiOCl and no peak corresponding to Bi-Mo distance was observed in its spectra. Fourier transforms of Bi(III) atom for BiOCl showed a good agreement with the x-ray diffraction data by Bannister(59). This result shows that Bi(III) ion does not form phosphorus-bismuth heteropoly molybdate but does bismuth oxychloride in dil. hydrochloric acid solution. On the other hand, Fourier transform of Bi(III) atom in nitric acid solution, differently from hydrochloric acid, developed a few peaks corresponding to Bi-Mo distances in its spectra(see Fig.IV-32c). These peaks were subdivided into two groups: one denotes the distance from Mo atom in the identical half anion (near 3.4-3.7 Å), and the other in the adjacent one (near 4.4 Å). This difference was obviously observed in XANES spectra, as shown in Fig.IV-33. With respect to the phosphorus-bismuth heteropoly molybdate Hargis et al. have been also reported that its heteropoly molybdate gave a molar ratio P:Bi:Mo = 1:1:18, as the result of a stoichiometric study(60). However, they have not given the data to confirm an appropriate configuration for its

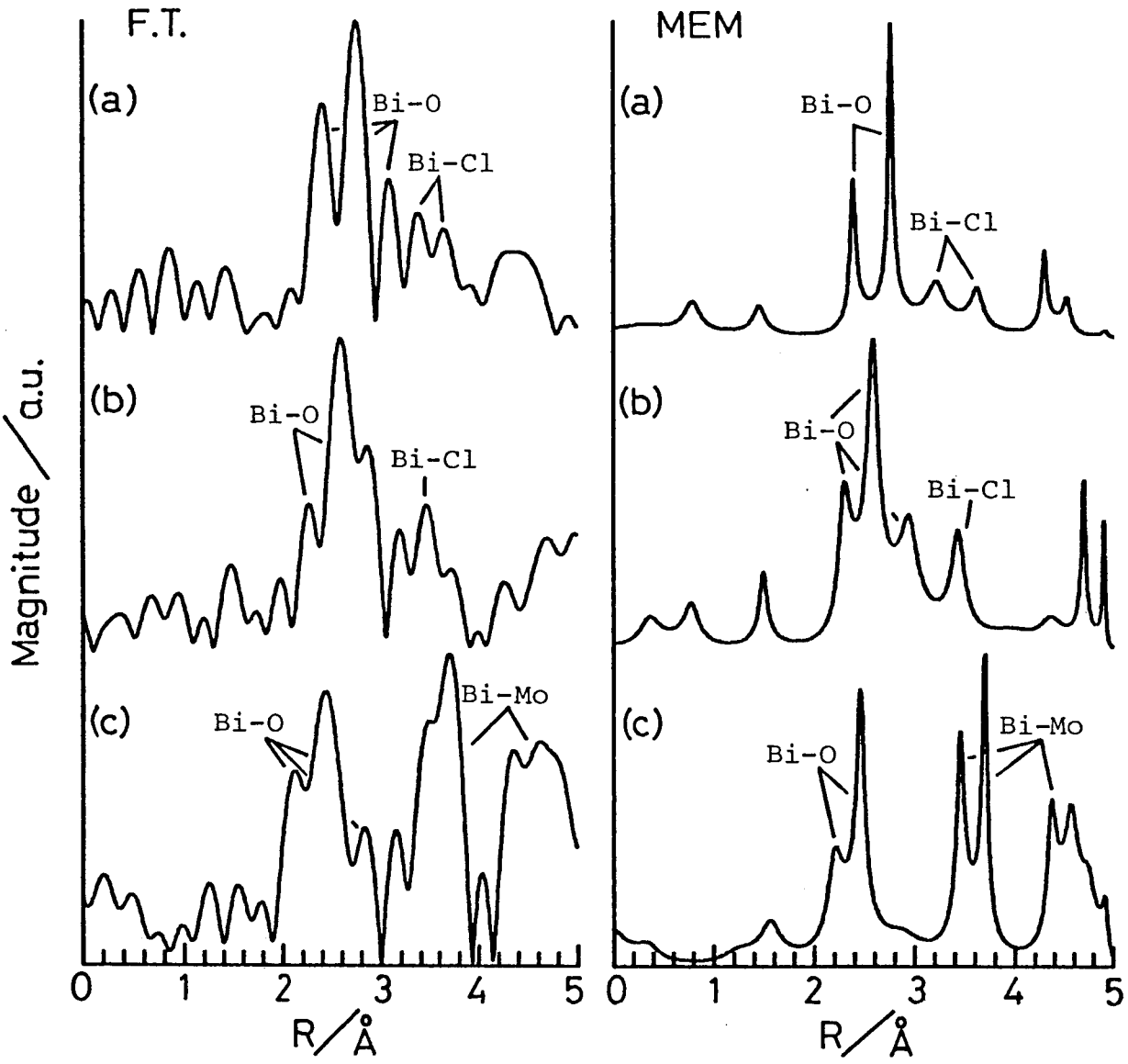


Fig.IV-32 Fourier transform(left) and MEM(right) spectra of EXAFS of Bi atom.

(a) BiOCl in dil. HCl sln.

(b) P-Bi-Mo system in dil. HCl sln.

(c) P-Bi-Mo system in dil. HNO_3 sln.

C_{Bi} = 7.0 x 10^{-3} mol dm^{-3}

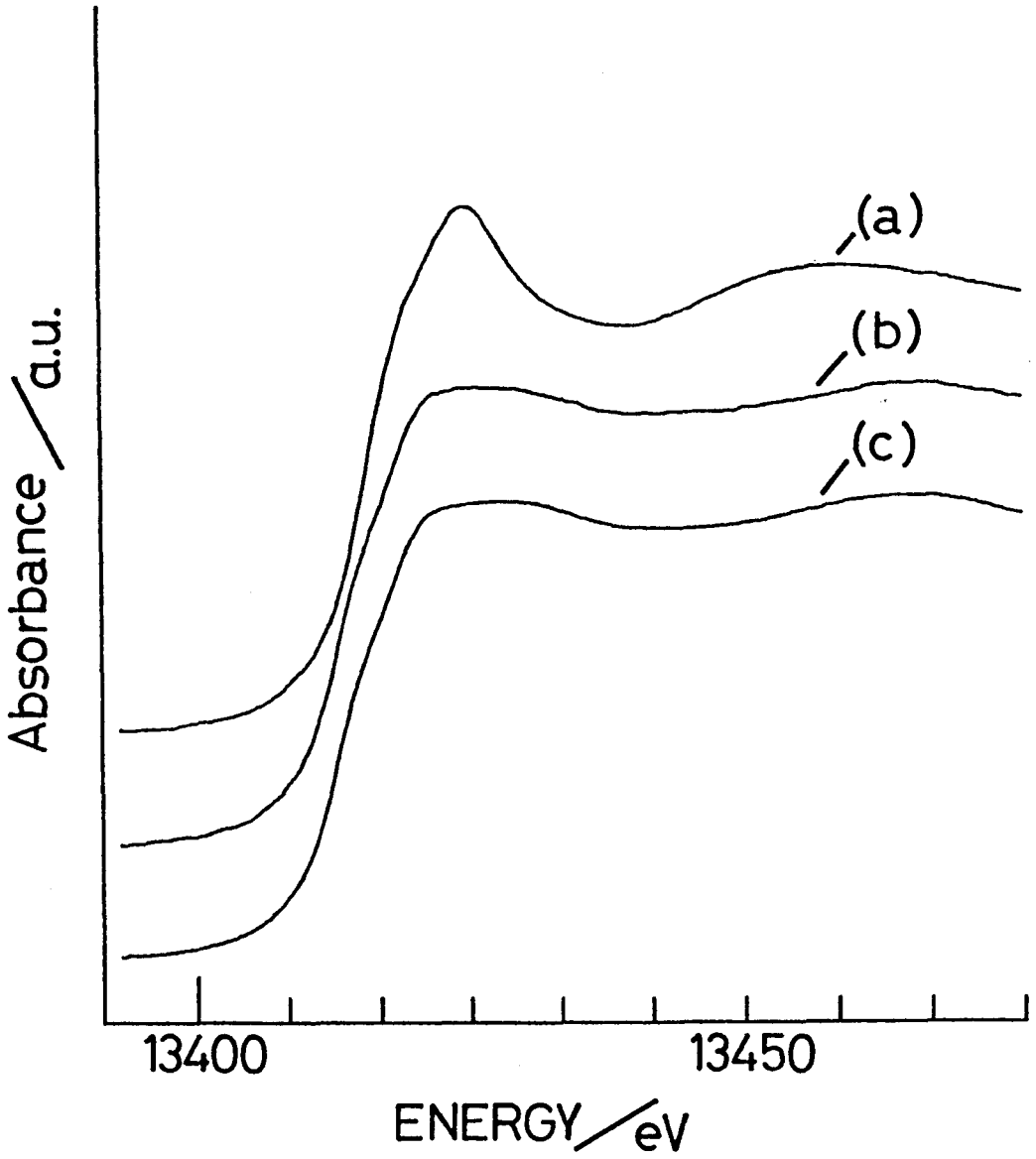


Fig.IV-33 Bi L_3-edge XANES spectra.

(a) P-Bi-Mo system in dil. HNO_3 sln.

(b) P-Bi-Mo system in dil. HCl sln.

(c) BiOCl in dil. HCl sln.

Table IV-5. Comparison of EXAFS Analysis(FT and MEM) and X-Ray Diffraction

---- The Dawson like structure ----

	EXAFS				x-ray diffraction	
	FT		MEM			
Mo/P_2Mo_{18}	Mo-O 1.68 2.05 2.41	Mo-Mo 3.24 3.78	Mo-O 1.67 2.40	Mo-Mo 3.19 3.78	P-O 1.53 2.51 P-Mo 3.46 3.51 P-P 4.15	Mo-O a) 1.70 1.85 2.33 2.38 Mo-Mo 3.66 3.83
Mo/P-Bi-Mo (in HCl)	Mo-O 1.67 2.22 2.48	Mo-Mo 3.19 3.57 3.88	Mo-O 1.66 2.44	Mo-Mo 3.36 3.82		
Mo/P-Bi-Mo (in HNO_3)	Mo-O 1.64 2.20 2.45	Mo-Mo 3.24 3.72	Mo-O 1.63 2.37	Mo-Mo 3.24 3.77	Bi-O b,c) 2.1 - 2.8 Bi-Cl 3.0 - 3.5 b) Bi-Mo 4.5 - 5.0 c)	
Bi/BiOCl	Bi-O 2.41 2.75	Bi-Cl 3.09 3.38	Bi-O 2.39 2.76	Bi-Cl 3.21 3.62		
Bi/P-Bi-Mo (in HCl)	Bi-O 2.27 2.59 2.87	Bi-Cl 3.19 3.47	Bi-O 2.31 2.59 2.95	Bi-Cl 3.44		
Bi/P-Bi-Mo (in HNO_3)	Bi-O 2.12 2.44 2.84	Bi-Mo 3.50 3.71 4.12	Bi-O 2.22 2.46	Bi-Mo 3.40 3.71 4.08		

a) See ref. 58.

b) Data for BiOCl.

c) Data for $Bi_2(MoO_4)_3$.

heteropoly molybdate. In light of the above data, its heteropoly molybdate seems plausible to consist of a dimeric heteropoly species containing one bismuth and one phosphorus as central positions, coordinated with the structure of P_2Mo_{18}, $H_aPBiMo_{18}O_{62}^{(8-a)-}$, in solution. The data of NMR and Raman measurements further support this view resultingly. In x-ray diffraction data of P_2Mo_{18}, P-O and P-Mo distances are near 1.5 and 3.5 Å, respectively. In Fourier transform of Bi(III) atom for phosphorus-bismuth heteropoly molybdate, however, Bi-O and Bi-Mo distances give longer ones, which are 2.2 - 2.4 Å and 3.4 - 3.8 Å, respectively. Presumably, phosphorus-bismuth heteropoly molybdate may be deformed seriously from the structure of P_2Mo_{18}.

(C) Other Metalloid Elements

It was tried to investigate the effect of the addition of metalloid ions, i.e., As(III), As(V), Sb(III), Sb(V), Se(IV), Se(VI), Te(IV), and Te(VI) ones, in 12-molybdophosphate(PMo_{12}) solution by ^{31}P NMR measurement. It has already been reported that these ions form numerous heteropoly anions, mainly with tungstate, many of which appear to have structure based on fragment of the Keggin anion(61-68). However, in only a few cases have structural determination been made, and much of the published work are in the form of preliminary communications. In addition, the compounds prepared were not fully characterized and no

analytical data were given. Although this area of polyanion chemistry has not been extensively explored, with the exception of As(V) ion, to obtain a new evidence for ternary heteropoly molybdates NMR measurement has been carried out.

(a) As(III) and As(V)

As(III) and As(V) ions were added in PMo_{12} solution and the results obtained are shown in Fig.IV-34. The addition of As(III) ion, as shown in Fig.IV-34b, gave an almost similar spectrum to that of PMo_{12} and this result indicated that in aqueous solution As(III) ion did not react with PMo_{12}. On the other hand, the addition of As(V) ion, as compared with As(III) one, gave apparently a different spectrum which is obtained under the condition similar to lower molybdate concentration (C_P : C_{Mo} ~ 1:8). This result also indicated that As(V) ion reacted with excess molybdate which is present in equilibrium state with PMo_{12}, and must produce molybdoarsenates in the solution. No ternary heteropoly molybdate, however, was observed in NMR spectra.

(b) Sb(III) and Sb(V)

A procedure for the trace analysis of phosphate which incorporates the use of Sb(III) ion to increase the rate of reduction of the heteropoly acid, was reported by Murphy and Riley(69). In the paper they described that Molybdoantimonylphosphate initially formed and that it was reduced easily by ascorbic acid. In this work, however, addition of Sb(III) ion caused immediately the reduction of

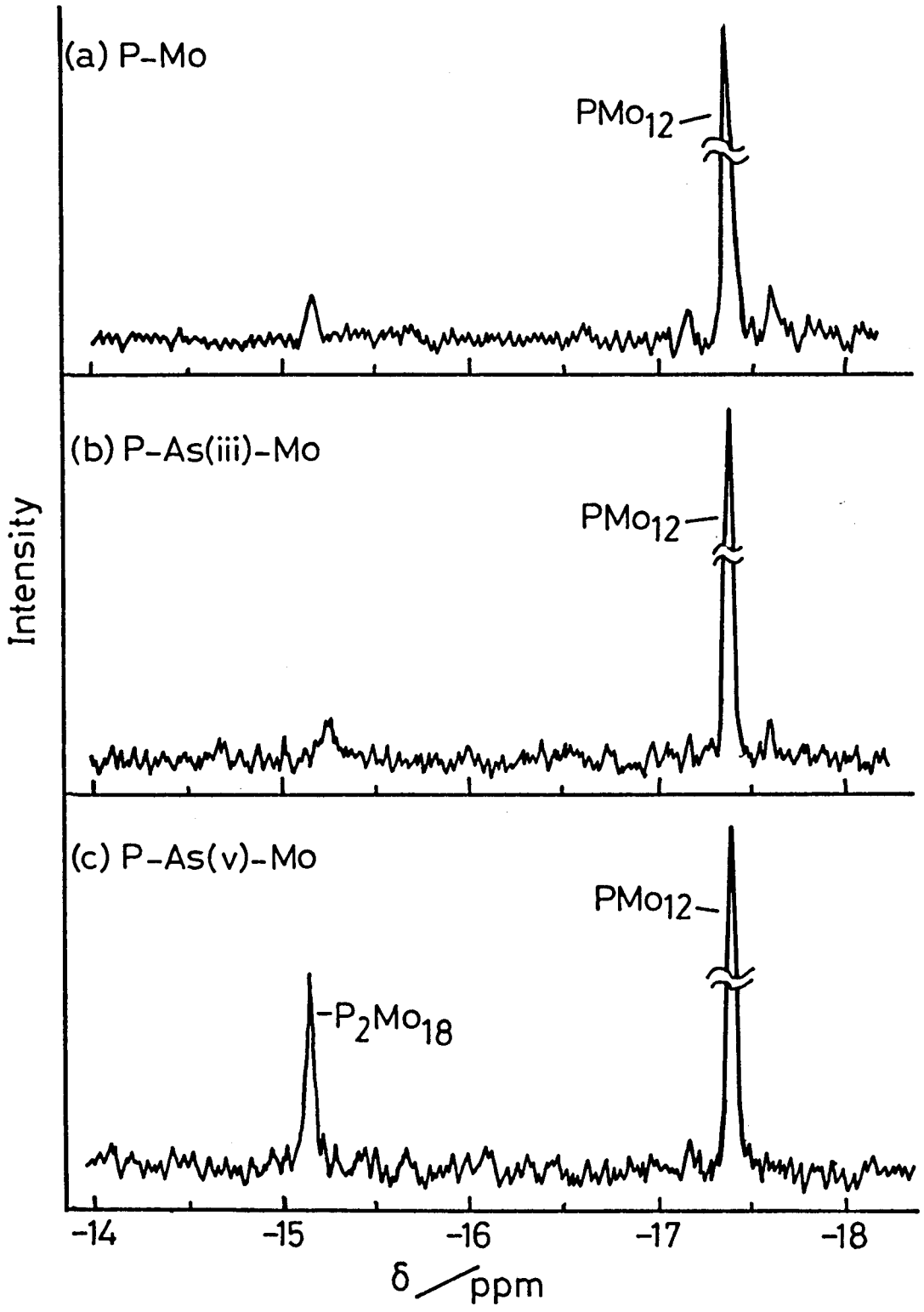


Fig .IV-34 Effect of As(III) and As(V) ions by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(b) $C_{As(III)} = 3.5 \times 10^{-3}$ (c) $C_{As(V)} = 3.0 \times 10^{-3}$

(mol dm^{-3}) pH 0.5 - 0.7

PMo_{12} and yielded so-called "heteropoly blue". In NMR spectra, as shown in Fig.IV-35b, an extremely broaden peak assigned to the heteropoly blue was obtained at downfield. A peak pertaining to H_3PO_4 was observed,too. This result indicates that PMo_{12}, as compared with 18-molybdodiphosphate(P_2Mo_{18}), is easily subject to reduction and that the reduced molybdophosphate(heteropoly blue) is gradually decomposed to "molybdenum blue". Thus it could not confirm the formation of molybdoantimonylphosphate in solution. Addition of Sb(V) ion, in analogy with As(III) one, gave a similar spectrum to that of PMo_{12} and this result showed that Sb(V) ion did not react with PMo_{12} in solution.

(c) Se(IV) and Se(VI)

Se(IV) and Se(VI) ions were added in PMo_{12} solution. The addition of Se(IV) ion, being similar to that of As(V) one, caused the decomposition of PMo_{12} and formed new heteropoly complexes, molybdoselenites(70), in solution(see Fig.IV-36b). However, it was not observed a new peak pertaining to ternary heteropoly molybdate in NMR spectra. On the contrary, the addition of Se(VI) ion gave a similar spectrum to that of PMo_{12}. This result indicates that Se(VI) ion does not react with PMo_{12} or excess molybdate in solution.

(d) Te(IV) and Te(VI)

Addition of Te(IV) ion, at variance with Se(IV) one, developed a new peak pertaining to ternary heteropoly molybdate in NMR spectra, as shown in Fig.IV-37b. There is

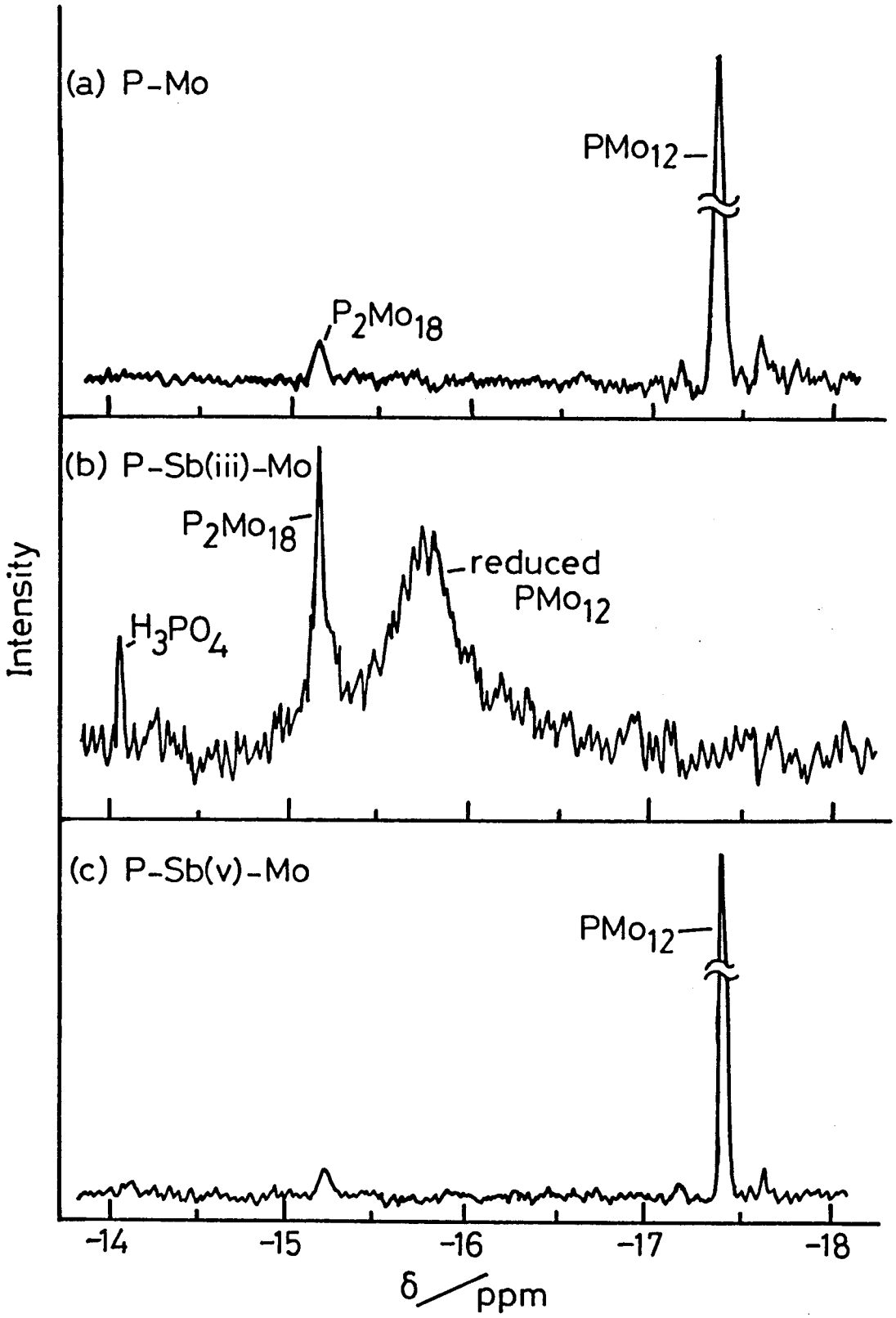


Fig.IV-35 Effect of Sb(III) and Sb(V) ions by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(b) $C_{Sb(III)} = 3.2 \times 10^{-3}$ (c) $C_{Sb(V)} = 2.5 \times 10^{-3}$

(mol dm^{-3}) pH 0.5 - 0.8

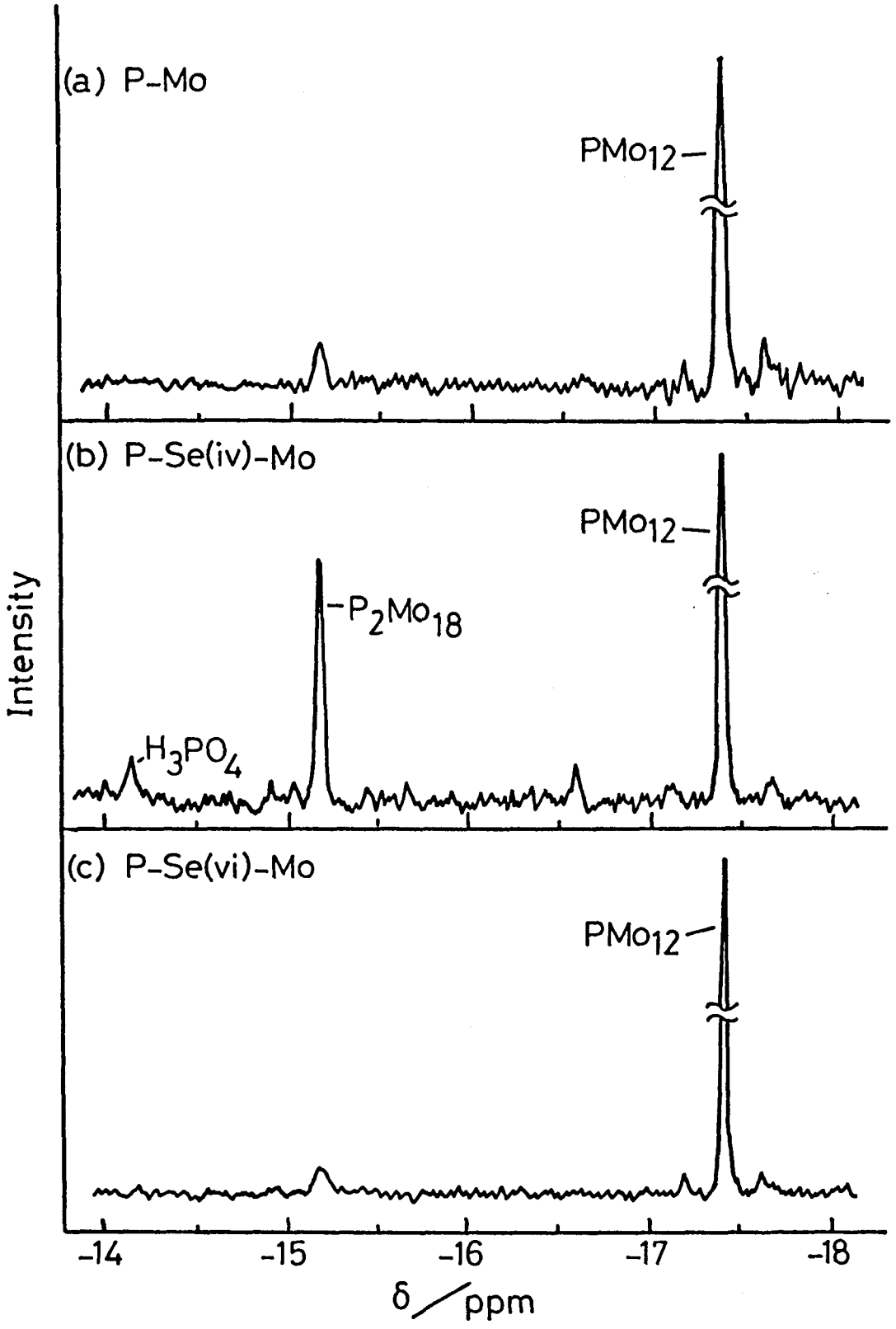


Fig.IV-36 Effect of Se(IV) and Se(VI) ions by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(b) $C_{Se(IV)} = 3.1 \times 10^{-3}$ (c) $C_{Se(VI)} = 3.6 \times 10^{-3}$

(mol dm^{-3}) pH 0.6 - 0.7

no reports with respect to the ternary heteropoly molybdate containing Te(IV) ion so far. This new peak provided a very similar behavior to that of phosphorus-bismuth heteropoly molybdate($PBiMo_{18}$) in a series of experiment. Thus its peak was a broaden one, as compared with other ternary heteropoly molybdates, and even in the presence of excess Te(IV) ion the peak of PMo_{12} did not disappear. As shown in Fig.IV-26, it is also provided an upper convexed calibration curve as well as Bi(III) ion. In addition, under the assumption of the presence of the Keggin like structure, $PTeMo_{11}O_{40}^{5-}$, according to the empirical equation described previously, the difference of the chemical shift was plotted against that of electron density parameter. The point of Te(IV) ion, like that of Bi(III) one, deviated appreciably from the straight line, as shown in Fig.IV-38. Although it has not been carried out to confirm by use of other measurement, it could be expected that the phosphorus-tellurium(IV) heteropoly molybdate consists of a similar structure to that of $PBiMo_{18}$, judging from the results of NMR measurement. On the other hand, addition of Te(VI) ion gave a similar spectrum to that of Se(IV) one. There is also no reported with respect to the formation of binary heteropoly molybdate containing Te(VI) ion in solution. As shown in Fig.IV-37c, for the minor formation of its complex, it could not be obtained the finding of its complex obviously.

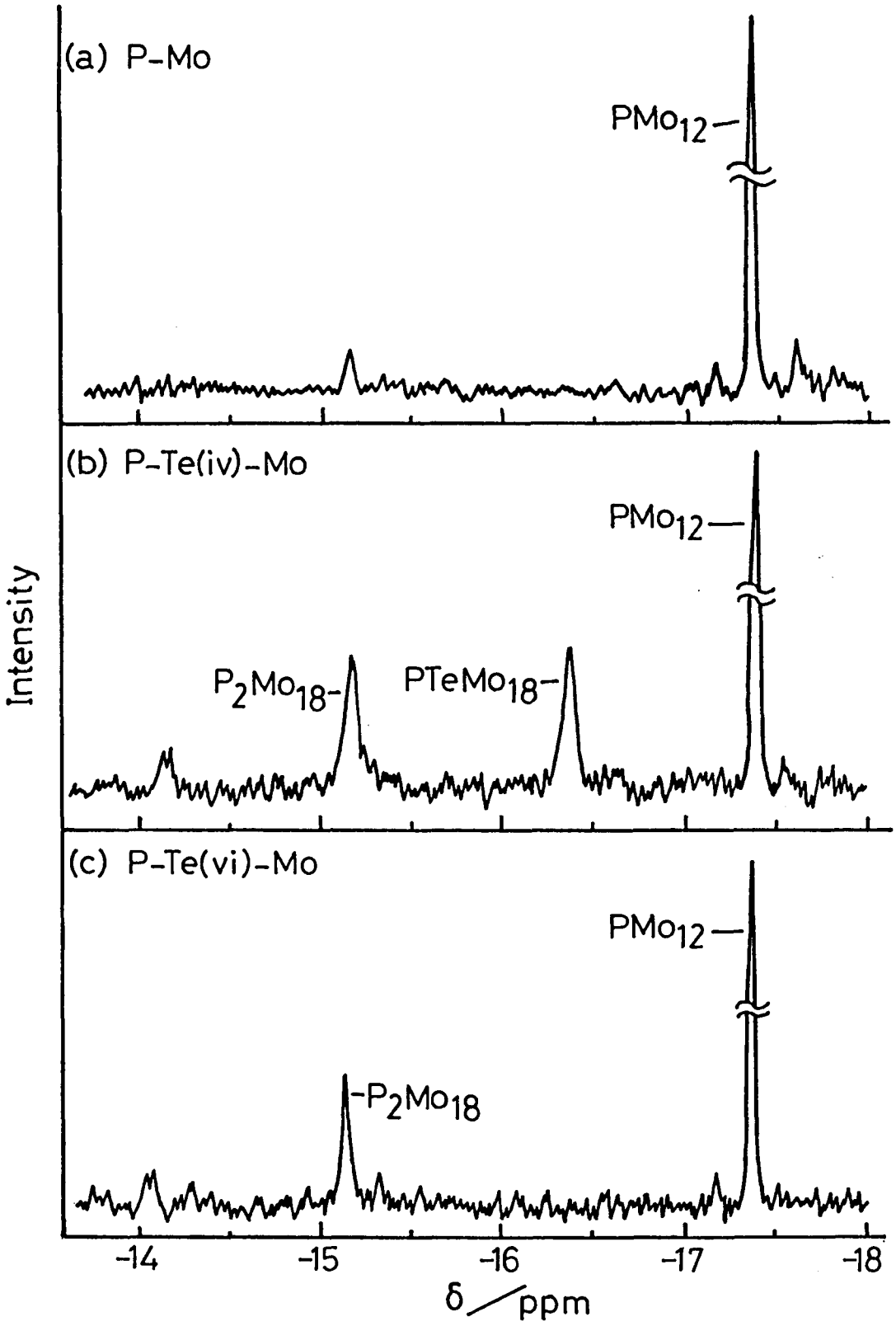


Fig.IV-37 Effect of Te(IV) and Te(VI) ions by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$

(b) $C_{Te(IV)} = 3.3 \times 10^{-3}$ (c) $C_{Te(VI)} = 3.5 \times 10^{-3}$

(mol dm^{-3}) pH 0.6 - 0.8

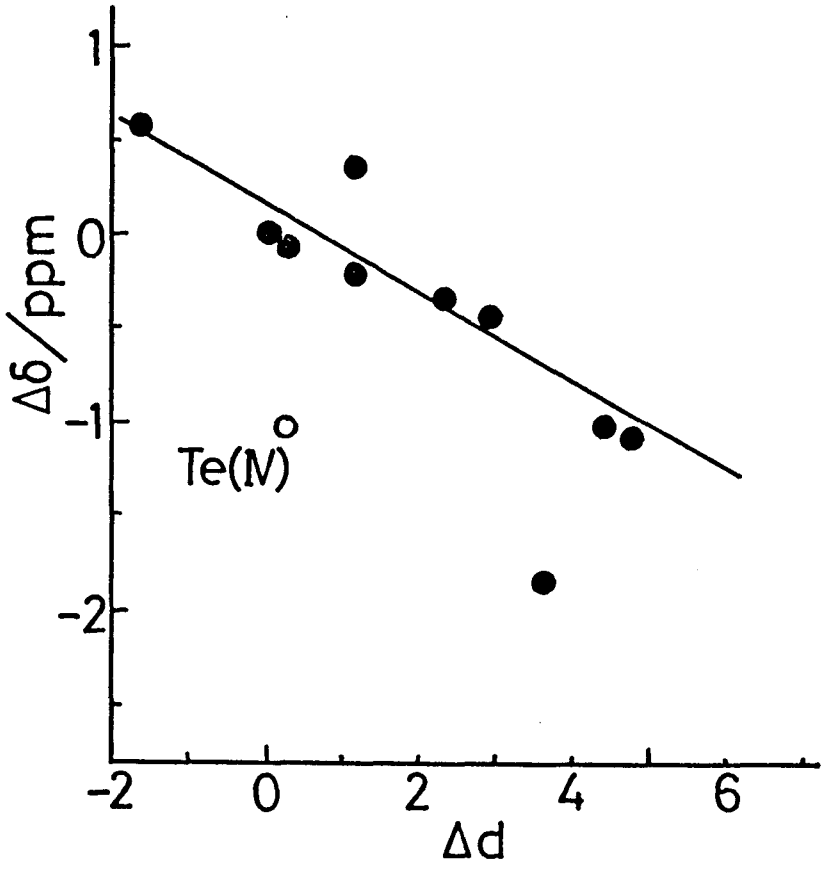


Fig. IV-38 Relationship between 'electron density around P atom' and chemical shift for Te(IV) ion.

The application of the heteropoly molybdates as "analytical reagents" was researched by use of NMR and EXAFS techniques with respect to some metal and metalloid ions, and results obtained are summarized in Table IV-6. As shown in Fig.IV-39, eight kinds of metal ions reacted with 12-molybdophosphate and produced ternary heteropoly molybdates which had the Keggin like structure, $PXMo_{11}$, while Bi(III) and Te(IV) ions did another type's heteropoly molybdate which had the Dawson like structure, $PX'Mo_{18}$. On the other hand, Sb(III) and Sn(II) ions caused a negative interference, for these two ions reduced 12-molybdophosphate and produced the "molybdenum blue". Se(IV), As(V), Te(VI), and W(VI) ions, though there is the limit, also caused negative interferences, because selenite, arsenate, tellurate, and tungstate reacted with excess molybdate and produced binary heteropoly molybdate, e.g., molybdoarsenate. The others, i.e., Ni(II), Cu(II), Fe(III), and so on, did not form any ternary heteropoly molybdate and no peak was observed in NMR spectra.

Fig .IV-39 Structures of binary- and ternary heteropoly molybdates.

(a) The Keggin structure (b) The Keggin like structure

(c) The Dawson like structure

Table IV-6. Effect of Metal and Non-Metal Ions for Formation of Ternary Heteropoly Molybdates [a)]

Complexed :	Ti(IV, 0.68)	Hf(IV, 0.78)	Zr(IV, 0.79)
	Ce(IV, 0.92)	Th(IV, 1.02)	V(V, 0.59)
	Nb(V, 0.69)	Ta(V, 0.68)	
	Bi(III, 0.96)	Te(IV, 0.70)	
Inerted :	Ni(II, 0.69)	Cu(II, 0.72)	Zn(II, 0.74)
	Co(II, 0.72)	Cr(III, 0.63)	Fe(III, 0.64)
	Y(III, 0.89)	Sm(III, 0.96)	La(III, 1.02)
	Ce(III, 1.03)	As(III, 0.58)	Sb(V, 0.62)
	Cr(VI, 0.52)	U(VI, 0.80)	Se(VI, 0.42)
	Mn(VII, 0.46)		
Disturbed :	Sn(II, 0.93)	Sb(III, 0.76)	Se(IV, 0.50)
	As(V, 0.46)	Te(VI, 0.56)	W(VI, 0.62)
	NH_4(I, 1.43)		

[a)] Values in parentheses denotes radii in Å.

IV - 6. References

1) J.A.Pople, W.G.Schneider, and H.J.Bernstein, "High Resolution Nuclear Magnetic Resonance". McGraw-Hill, New York(1959).

2) F.R.Prado, C.Geissner-Prettre, B.Pullman, and J.P.Daudey, J.Am.Chem.Soc., 101,1737(1979).

3) D.G.Gorenstein and D.Kar, Biochem.Biophys.Res.Common., 65,1073(1975).

4) L.P.Kazanskii, M.A.Fedotov, M.N.Ptushkina, and V.I.Spitsyn, Dokl.Chem., 244,1029(1975).

5) S.E.O'Donnell and M.T.Pope, J.Chem.Soc., Dalton Trans,2290(1976).

6) R.Massart, R.Contant, J.M.Fruchart, J.P.Ciabrini, and M.Fournier, Inorg.Chem., 16,2916(1977).

7) L.P.Kazanskii, V.F.Chuvaev, and V.I.Spitsyn, Bull.Acad.Sci,USSR, Div.Chem.Soc., 242(1976).

8) L.P.Kazanskii, M.A.Fedotov, I.V.Potapova, and V.I.Spitsyn, Dokl.Chem., 244,36(1979).

9) M.T.Pope, S.E.O'Donnell, and R.A.Prados, J.Chem.Soc., Chem Comm,22(1975).

10) R.Massart, R.Contant, J.Fruchart, J.Ciabrini, and M.Fournier, Inorg.Chem., 16,22916(1977).

11) S.E.O'Donnell and M.T.Pope, J.Chem.Soc., Dalton Trans.,2290(1976).

12) L.Pettersson, I.Andersson, and L.Ohman, Acta.Chem.Scand., A39,53(1985).
13) K.Murata and S.Ikeda, Anal.Chim.Acta., 151,29(1983).
14) K.Murata and S.Ikeda, Polyhedron., 2,1005(1983).
15) L.Lyhamn and L.Pettersson, Chemica.Scripta., 12,142(1977).
16) C.Rocchiccioli-Deltcheff, R.Thouvenot, and R.Franck, Spectrochim.Acta., 32A,587(1976).
17) J.Fuchs and E.P.Flindt, Z.Naturforsch., 34b,412(1979).
18) M.Dabbabi, M.Boyer, J.P.Launay, and Y.Jeannin, J.Electroanal.Chem., 76,153(1977).
19) G.Morwitz and M.Codell, Anal.Chem., 28,1230(1954).
20) P.Courtin, Bull.Soc.Chim., France,4799(1968).
21) G.A.Tsigdinos and C.J.Hallada, Inorg.Chem., 7,437(1968).
22) M.T.Pope, S.E.O'Donnell, and R.A.Prado, J.Chem.Soc., Chem Commun., 22(1975).
23) M.T.Pope and T.F.Scully, Inorg.Chhem., 14,953(1975).
24) V.S.Sergienko, N.A.Porai-Koshits, and E.N.Yurchenko, Russ.J.Struct.Chem,21,87(1980).
25) R.Strandberg, Acta Chem.Scand., A29,359(1975).
26) C.J.Rodan, "Analytical Chemistry of the Manhattan Project" McGraw-Hill, New York(1950).
27) Y.Goshi, "Advances in X-Ray Analysis" Vol.11,pp.518, Plenum(1969).
28) P.Lubin, "Advances in X-Ray Analysis" Vol.2,pp.229, Plenum(1960).

29) K.Steet and G.T.Seaborg, J.Am.Chem.Soc., 70,4268(1948).

30) J.H.Hill, Analyst., 91,659(1966).

31) J.P.Faris, Anal.Chem., 32,1185(1960).

32) E.A.Huff, Anal.Chem., 36,1921(1964).

33) Y.Nakamura and Y.Noto, Bunseki Kagaku., 31,413(1982).

34) F.W.E.Strelow and C.J.C.Boyhema, Anal.Chem., 39,595(1967).

35) E.Cerrai and C.Testa, Anal.Chim.Acta., 26,204(1962).

36) R.B.Hahn, Anal.Chem., 23,1259(1951).

37) J.Iball, J.N.Low, and T.J.R.Weakley, J.Chem.Soc., Dalton Trans,2021(1974).

38) R.D.Peacock and T.J.R.Weakley, J.Chem.Soc., A,1836(1971).

39) L.P.Kazanskii, M.A.Fedotov, and V.I.Spitsyn, Dokl.Phys.Chem., 234,617(1977).

40) A.M.Golubev, L.P.Kazanskii, E.A.Torchenkova, V.I.Simonov, and V.I.Spitsyn, Dokl.Chem., 221,198(1975).

41) R.Ripan and A.Botar, Rev.Roum.Chim., 15,1529(1970).

42) R.Ripan and I.Todorut, Rev.Roum.Chim., 11,691(1966).

43) G.A.Barbieri, Atti Accad.Naz.Lincei., 22,781(1913).

44) L.C.W.Baker, G.A.Gallagher, and T.P.McCutcheon, J.Am.Chem.Soc., 75,2493(1953).

45) L.P.Kazanskii, E.A.Torchenkova, and V.I.Spitsyn, Dokl.Phys.Chem., 209,208(1973).

46) L.P.Kazanskii, E.A.Torchenkova, and V.I.Spitsyn, Dokl.Phys.Chem., 213,932(1973).

47) S.C.Termes and M.T.Pope, Transit.Met.Chem., 3,103(1978).

48) A.M.Golubev, L.P.Kazanskii, V.F.Chhuvaev, E.A.Torchenkova, and V.I.Spitsyn, Dokl.Chem., 209,326(1973).

49) I.V.Tat'janina, E.A.Torchenkova, L.P.Kazanskii, and V.I.Spitsyn, Dokl.Phys.Chem., 234,597(1977).

50) Yu.F.Shkaravskii, Ukr.Khim.Zh., 30,241(1964).

51) V.F.Barkovskii and T.V.Velikanova, Russ.J.Inorg.Chem., 15,879(1970).

52) V.F.Barkovskii and T.V.Velikanova, Russ.J.Inorg.Chem., 15,385(1970).

53) H.N.Johnson, G.F.Kirkbright, and R.J.Whitehouse, Anal.Chem., 45,1603(1973).

54) Z.F.Shakhova and S.A.Gavriova, Zh.Anal.Khim., 13,211(1958).

55) D.F.Boltz and M.G.Mellon, Anal.Chem., 20,749(1948).

56) R.H.Campbell and M.G.Mellon, Anal.Chem., 32,54(1960).

57) H.D.Goldman and L.G.Hargis, Anal.Chem., 41,490(1969).

58) H.D'Amour and R.Allmann, Naturwiss., 61,34(1974).

59) F.A.bannister and M.H.Hey, Mineralog.Mag., 24,49(1935).

60) C.Tourne, A.Revel, G.Tourne, and M.Vendrell, C.R.Acad.Sci., Ser.C,277,643(1973).

61) G.Petrini, O.Pilati, and N.Giordano, Chem.Ind., 50,1002(1968).

62) Z.F.Shakhova, S.A.Morosanova, and V.F.Zakharova, Russ.J.Inorg.Chem., 14,1609(1969).

63) E.G.Ganelina, Russ.J.Inorg.Chem., 7,812(1962).

64) P.Souchay, M.Leray, and G.Herve, C.R.Acad.Sci.,Ser.C, 271,1337(1970).

65) A.Rosenheim and A.Wolff, Z.Anorg.Chem., 64,193(1930).

66) M.Michelon and G.Harve, C.R.Acad.Sci.,Ser.C, 274,209(1972).

67) J.Fischer, L.Richard, and R.Weiss, J.Am.Chem.Soc., 98,3050(1976)

68) J.Murphy and J.P.Riley, Anal.Chim.Acta., 27,31(1962).

69) K.Y.Matsumoto, M.Kato, and Y.Sasaki, Bull.Chem.Soc.Jpn., 49,106(1976)

Chapter V. Separation of Ternary Heteropoly Molybdate by Use of HPLC Technique

V - 1. Introduction

At the initial stages of chromatography, most of the development in chromatography was for the separation of organic compounds. On the other hand, the separation of inorganics and organometallics by gas chromatography is limited by compound vapor pressures and temperature instabilities. The first application of column chromatography in inorganic chemistry is attributed to Schwab in Munich(1,2). In the case of analysis of ionized compounds, it has some problems for the retention of solutes, the symmetry of peak shape, and the separating efficiency. If the adsorption chromatography is carried out by polar solvents, an enormous tailing of peaks derived from ununiformity of the adsorbent surface occurs and unsymmetry of the peaks depends on the conversion of the extent of ionized solutes in the band of chromatography. For these reasons, an ion exchange chromatography(IEC) has been the major technique to separate the ionized species for a long time. The application of IEC, however, has some disadvantages. In IEC, that is, it is actually impossible to analyse ionized and non-ionized species simultaneously and the separating efficiency of the column is low. The

application of the reversed phase liquid chromatography(RPLC) originates in the fundamental studies of Howard and Martin(3) and a large portion of chromatographic separation is now subjected to this technique. RPLC is just appropriate method to separate either non-polar or light polar compounds ideally, and has some characteristics, e.g., usefulness, high separating efficiency, high stability of column. Some advantages also have been improved by many investigators in the fields of biochemistry(4-8), medical chemistry(9-12), medicinal chemistry(13-15), and so on. The first attempt of ion-pair reversed phase liquid chromatography(IPRPLC) was carried out by Horvath and Lipsky(16) in 1966. In this method, the retentions of the higher polar compounds and ionized ones are drastically changed under the condition of the presence of ion pair reagents which contain a hydrophobic group. Since this method was applied to the systems of RPLC by Wahlund(17) in 1975, it was applied in various fields of the separation science(18-21).

Regardless the mechanism of retention, taking into account the thermodynamic equilibrium, the following simple equation can be given in IPRPLC,

$$R_{aq}^{+} + I_{aq}^{-} \rightleftharpoons [RI]_{org} \qquad (1)$$

where R_{aq}^{+} and I_{aq}^{-} refer to the sample ion and the ion pair reagent, respectively, and $[RI]_{org}$ refers to the ionic association molecule, where the subscripts aq and org refer to the aqueous and organic phases, respectively. In

addition, the following relation is applied

$$t_R = L(1 + K_{IA}\phi[I_{aq}^-])/u \qquad (2)$$

where t_R is the retention time, L is the column length, u is the linear velocity, K_{IA} is the equilibrium constant of all ionic association processes, ϕ is the volume fraction of the solvent, and $[I_{aq}]$ is the concentration of a hydrophobic ion pair reagent in aqueous solution. It is clear that the retention is governed by the extent of coupling constant and the concentration of the ion pair reagent. However, the factors influencing the distribution between two phases are very complicated and with respect to the condition of ionic association in the column several investigators(22-25) have presented different kinds of process on the thermodynamic and/or kinetic equilibria. Thus, inherent in the chromatography are equilibrium thermodynamic factors that govern solute/ion pair reagent, ion pair/solvent, and ion pair/system interactions and also, kinetic factors that enter into the transport of solutes between the mobile and stationary phases as well as contribute to the overall rate of solute longitudinal migration. In general, it is said that the following factors play the important role of the separation by use of IPRPLC:

1) the variety and the magnitude of interaction with solute of ion pair reagent
2) the size of ion pair reagent
3) the concentration of ion pair reagent

4) pH value of the elute

5) the variety and the concentration of organic solvents in the mobile phase

6) temperature

7) the degree of the coating in the stationary phase.

However, a more exact mechanism of retention of IPRPLC has not been established yet.

In this chapter, several kinds of chromatographic separation methods are first examined for the separation of each ternary heteropoly molybdate. In order to apply the IPRPLC the examinations for experimental conditions are carried out. By IPRPLC technique the simultaneous determination and separation of complexed metal ions are studied in the low concentration, i.e., in the low-to-mid ppb level. In addition, the effect of coexisting inert metal ions is also investigated.

V - 2. Preliminary Investigations by Several Chromatographic Techniques

By means of ^{31}P NMR technique, as mentioned previous chapter, the method for the simultaneous determination of group 4A and 5A elements was established. Nonetheless the application of NMR one had two inevitable limits: first, it can not isolate each ternary heteropoly molybdate from the mixture, and second, detection limits are rather high in concentration. Solvent extraction was examined to separate each ternary heteropoly molybdate, but the separation of each chemical species by the method was out of the discussion because of the very closed character of the solute-solvent interaction (it has been reported in Chapter III in detail). In such case of the separation of chemical species with the very similar solute-solvent interaction character in the liquid medium, multistep methods are considered to be the most promised technique for the mutual separation. Chromatograpy is a method of chemical separations by multistep technique. Chemical separations commonly occur as a result of the distribution of chemical components between two phases. One phase is, that is, fixed in place and is called the stationary phase, while the other flows over this stationary phase and is called the mobile phase. The thin layer chromatography(TLC) was adopted at first to examine the condition to separate each chemical species, because it has

the unique advantage of allowing analyses in parallel. All the other chromatographies offer only serial analyses. Under some conditions, although this phenomenon is applicable for every chromatographic method in principle, silica gel can act as a cation exchanger(26,27), and the selectivity of the exchanger and the resultant migration of solutes will be influenced by the nature of the mobile phase and the charge of the ions(28). On the basis of this property, theoretical aspects of inorganic TLC have been studied and Takitani(29), who developed a scheme for separating 20 common metal ions with three mobile phases as well as the separation of different valency states of the same elements, studied the relation between R_F and solvent composition.

The chromatographic technique can be classified into two modes, according to the difference of characteristic of the two phases. One, non-polar substances as the mobile phase and polar ones as the stationary phase, being called the normal phase mode, and the other being applied by the reverse, which is called the reversed phase mode. In a series of TLC, 12-molybdophosphate(PMo_{12}) developed well in normal phase TLC, whereas ternary heteropoly molybdates scarcely developed and remained near the original spot. On the other hand, in reversed phase TLC the opposite results were obtained. The method of TLC, however, led to only the incomplete separation, as shown in Fig.V-1. In light of the data of TLC measurement the reversed phase liquid

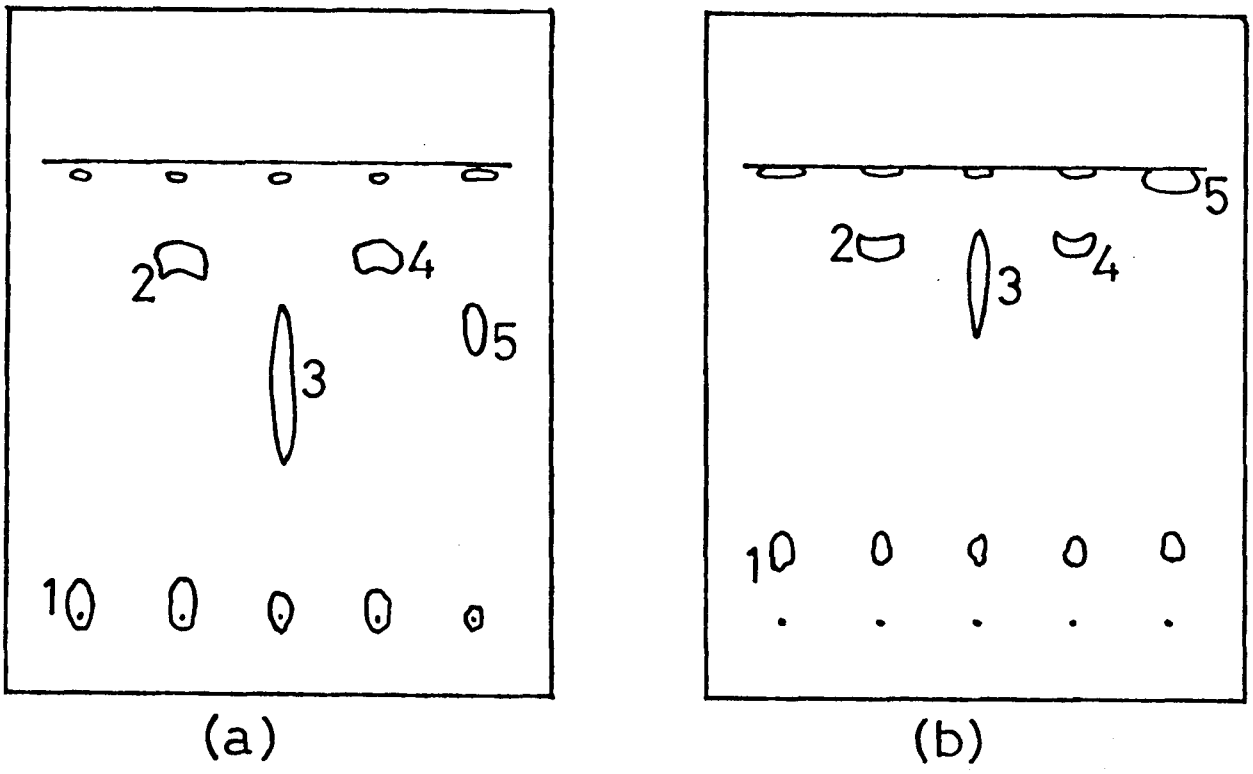


Fig V-1. Chromatograms of some heteropoly molybdates on reversed phase pre-coated TLC plates($RP\text{-}18F_{254}s$).

C_P = 1.0 x 10^{-2} C_{Me} = 3-6 x 10^{-3} C_{Mo} = 1.5 x 10^{-1} (mol dm^{-3}) pH 0.5 - 0.9

eluent: (a) HNO_3 sln.(pH 1.0) : CH_3CN = 3 : 1
(b) HNO_3 sln.(pH 1.0) : CH_3CN = 1 : 3

(1) PMo_{12} (2) $PZrMo_{11}$ (3) $PTiMo_{11}$ (4) $PHfMo_{11}$
(5) $PVMo_{11}$

chromatography(RPLC) is more appropriate to separate these ternary heteropoly molybdates than the normal phase liquid chromatography(NPLC) and thus RPLC method was examined consequently. RPLC has two advantages as follows: first, ionic and non-ionic samples can be analyzed simultaneously, and second, selection of the mobile phase is very easy. Further RPLC can be classified into two types: one is the ion suppression liquid chromatography(ISLC), and the other ion pair liquid chromatography(IPLC). ISLC is effective for the separation of weak acidic sample, while IPLC for the separation of strong acidic sample and basic one. Thus, if weak inorganic acids are chromatographed in a mobile phase containing a more strong acid, the undissociated acid will be formed and retained in the column to separate from other concomitants in ISLC, as delineated in Fig.V-2. Attempts to separate each ternary heteropoly molybdate by use of ISLC, as shown in Fig.V-3a, produced the serious tailing of peaks for heteropoly molybdates and as a result it was very difficult to separate these peaks actually. As compared with ISLC, IPLC yielded higher separating efficiency for ternary heteropoly molybdates depending upon the selection of ion pair reagent(see Fig.V-3b). For these reasons, the application of IPRPLC has been carried out to separate these ternary heteropoly molybdates in lower concentrations.

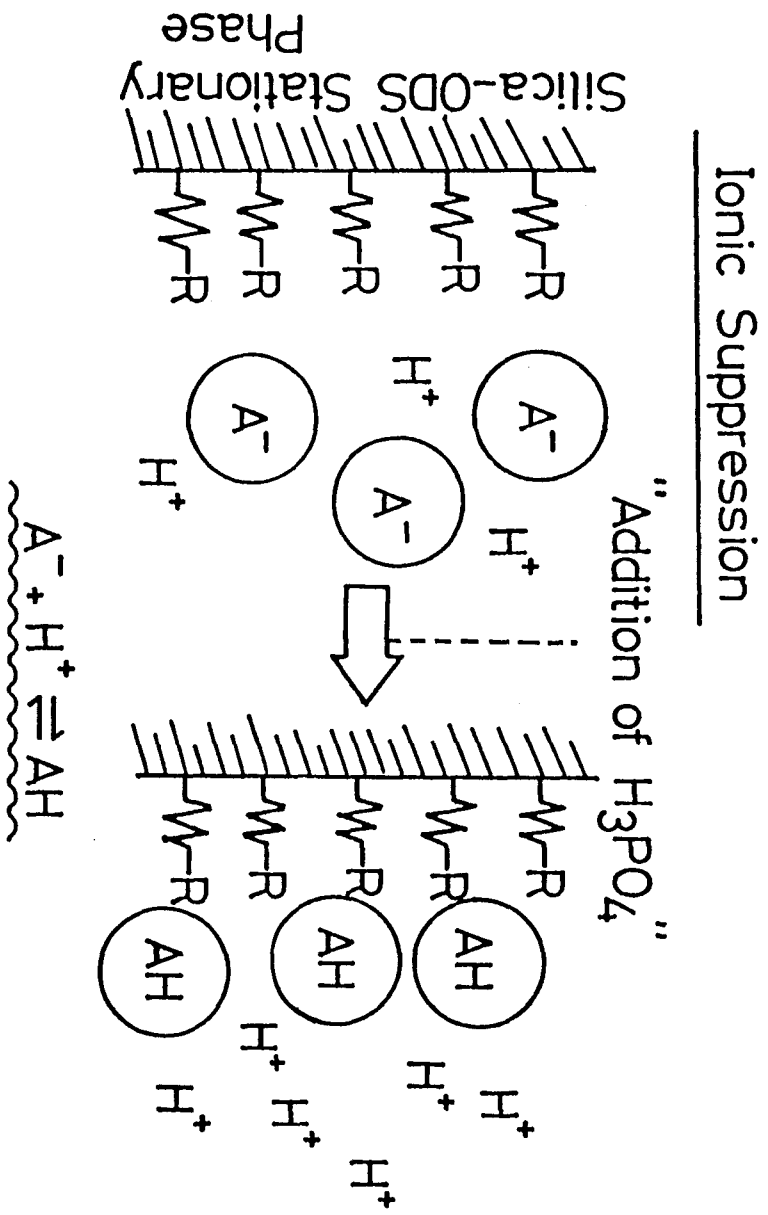


Fig V-2. Schematic of ion suppression RPLC mechanism.

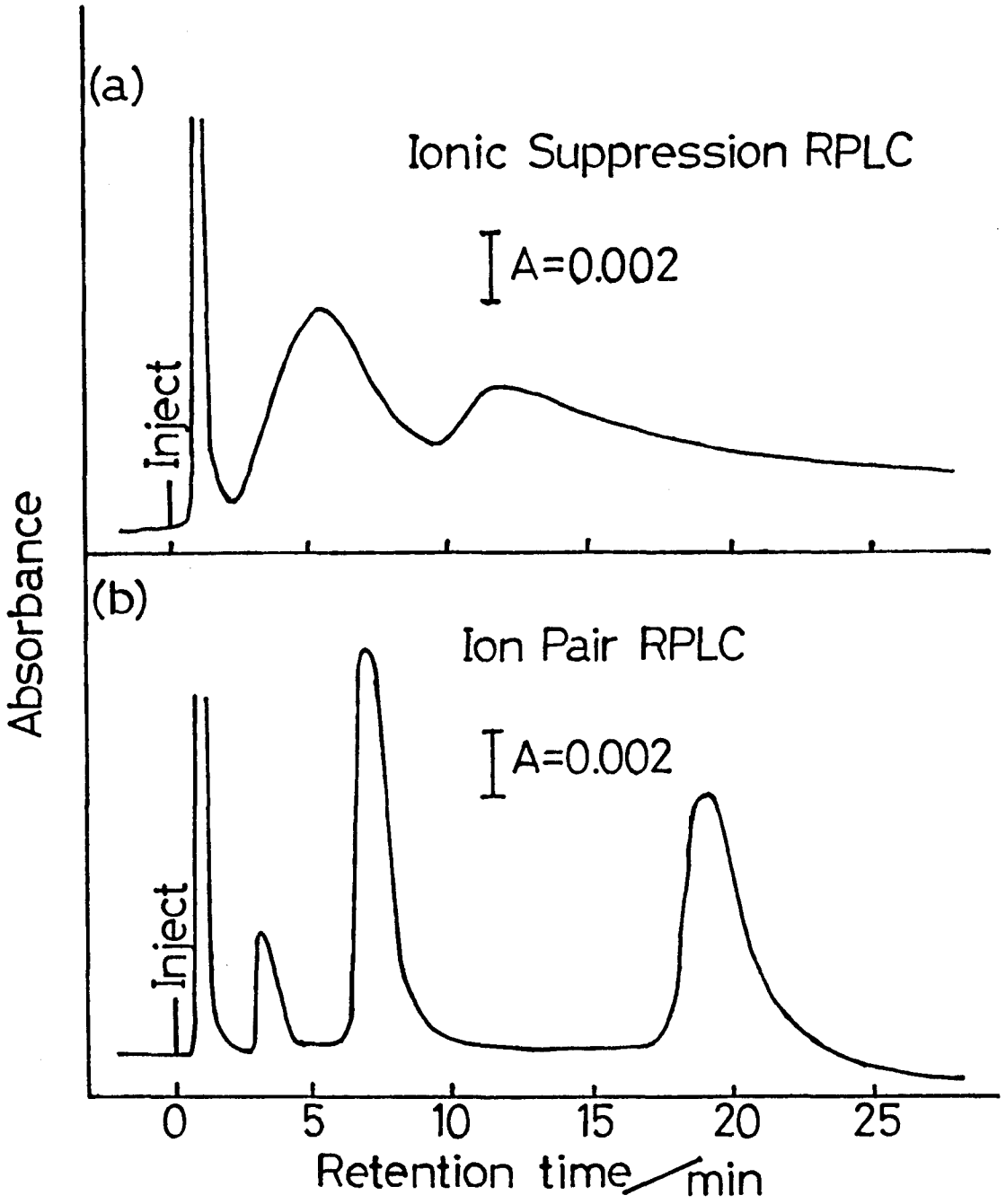


Fig V-3. Comparison of (a) Ionic suppression RPLC and (b) Ion pair RPLC.

sample: $C_P = 1.0 \times 10^{-4}$ $C_{Zr} = 4.0 \times 10^{-5}$

$C_{Mo} = 2.0 \times 10^{-3}$ (mol dm^{-3}) pH 2.1

eluent: (a) 1% CH_3COOH sln. : CH_3CN = 60:40

(b) HNO_3 sln. (pH 2.0) : CH_3CN : DTMA sln.= 60:150:10

20 µl injected. column; Nucleosil 10C18 λ; 300 nm

flow rate; 2.44 ml min^{-1}

V - 3. Examination for Experimental Conditions

In ion pair reversed phase liquid chromatograpy(IPRPLC) the composition of the mobile phase is the key to the successful separation. As practical problem it is frequently told as follows:
"the eventual analysis may take only half an hour, but it is no exception when many days were needed to achieve the first adequate separation." Likewise the separation of ternary heteropoly molybdates by IPRPLC was dependent on the selection of the mobile phase and the settlement of the environmental conditions for phase distribution, i.e., variety of ion pair reagent, pH value, molar ratio of solvent, and species of column.

(a) selection of ion pair reagents

The retention mechanism severely depends on the variety of ion pair reagent and its concentration. In general, for separation of acidic solutes tetraalkyl ammonium salts as ion pair reagents are used, whereas for basic ones sulfate esters are used. Tetraalkyl ammonium salts are also used to obtained the precipitate of isopoly or heteropoly oxometalate from solution. In earlier investigations(30-33), the following proposals have been reported with respect to the mechanism of ionic association in column:
1) the mechanism of retention would be varied with the type

of ionic association and by the hydrophobic character of the ion pair reagent, i.e., the number of methylene group in alkyl chain.

2) the ionic association is not produced in the mobile phase if used the ion pair reagent with long alkyl chain.

3) the force of retention is directly proportional to the charge density of packing surface in column, which is ascribed to the adsorption of ion pair reagent on the packing.

Therefore the mechanism of separation in IPRPLC is governed by the size of ion pair reagent, because it changes the hydrophobic property of "paired" species drastically, and is very effective to separate the chemical species having similar property and configuration. In this work six varieties of ion pair reagents were examined to separate ternary heteropoly molybdates on an ODS column.

The six varieties of ion pair reagents used are as follows; guanidine hydrochloride(noted as Gu), tetraethylammonium bromide(TEA), tetra-n-butylammonium bromide(TBA), dodecyltrimethylammonium bromide(DTMA), cetyltrimethylammonium bromide(CTMA), and trimethylphenylammonium bromide(TMPA). These results obtained are shown in Table V-1. Further, as noted the footnote in Table V-1, each ion pair reagent was prepared in the concentration range 0.003 - 0.015 mol dm^{-3} in all subsequent work. As might have been expected, there appeared

Table V-1. Effect of Ion-Pair Reagents for IPRPLC [a)]

Guanidine hydrochloride (Gu)	(Not retained)
Tetramethylammonium bromide (TEA)	(Not retained)
Tetrabutylammonium bromide (TBA)	○
Dodecyltrimethylammonium bromide (DTMA)	○
Cetyltrimethylammonium bromide (CTMA)	(Long retention time)
Trimethylphenylammonium bromide (TMPA)	(Caused tailing)

a) Prepared in the concentration range 0.003-0.015 mol dm^{-3}

to be a general trend of increasing the retention time with increasing the carbon chain in alkyl group. The retention was little affected by the addition of Gu and TEA, almost the same with that for the free solution from ion pair reagent. The addition of TBA or DTMA, even though observed a little tailing of peaks in chromatogram, caused the separation of peaks and exhibited a differentiation of the retention time for each respective solute. Large tailing of peaks were observed by the addition of TMPA and from this result it could be considered that the concentration of the paired species in the column is, compared with that in the stationary phase, rather higher in the mobile phase. Therefore, because of smaller ionic association constant of TMPA and heteropoly complexes, the solute-solvent(i.e., heteropoly complexes - eluent) interaction is larger than the solute-solute(i.e., heteropoly complexes - ion pair reagent). The addition of CTMA, on the contrary to TMPA, gave extremely broadening peaks and thus the reverse feature was found here for retention. CTMA provided the longer retention time, because of the formation of a rigid ion paired species with heteropoly complexes, which is difficult to be eluted in the mobile phase. In light of the above data, TBA and DTMA were used as ion pair reagent in all subsequent work. As compared of TBA and DTMA, DTMA had longer retention time than TBA. It was also examined the effect of concentration of ion pair reagent, keeping other factors constant; pH value, volume

fraction of acetonitrile, temperature, and species of column. Capacity factors of ternary heteropoly molybdates increased with the increase in the concentration of ion pair reagent and that of molybdozirconophosphate($PZrMo_{11}$) reached a maximum at 4.5 x 10^{-3} mol dm^{-3} DTMA, while that of molybdovanadophosphate($PVMo_{11}$) at 4.2 x 10^{-3} mol dm^{-3} TBA.

(b) Effect of pH value

The pH of the mobile phase affects the capacity factor for ternary heteropoly molybdate, because it decides the promotion or depression of ionization of solute molecule, and most suitable condition of ionic association. In this work several kinds of acid, e.g., HNO_3, HCl, H_2SO_4, and CH_3COOH, were examined to control the pH of eluent. Each acid exhibited an almost similar chromatogram with same pH value and the difference of chromatogram as a function of acid was not observed. The capacity factor of 12-molybdophosphate decreased significantly with the increase of concentration of acid, but those of ternary heteropoly molybdates were scarcely affected by the concentration of acid. According to the results of near UV measurement described previously(see Chapter III), the eluent was adjusted the pH to 2~3 by nitric acid.

(c) selection of organic solvent

In general, the chromatographic separation is governed by

the force of solute-solvent interaction in the stationary phase and the polarity of solvent has an important factor to achieve the separation of solutes. In RPLC polar solvents are used as the mobile phase and so water plays a most active part in eluents. In addition, to control the polarity of eluent a few organic solvents, which have relative lower polarity and are highly soluble in water, are added in the eluent. Thus acetonitrile and methanol were examined as organic solvent. At the same volume fraction, methanol gave a somewhat longer retention time than acetonitrile. The use of methanol, however, was experimentally limited in fact, because the pressure in column increased with increasing the volume fraction of methanol and reached easily the limiting pressure of its column. For the reason, acetonitrile was used in this work.

The acetonitrile concentration affected the capacity factor for both binary and ternary heteropoly molybdates. The capacity factor of 12-molybdophosphate decreased significantly with the increase of acetonitrile content in the eluent, but the degradation was small in the case of ternary heteropoly molybdates.

For these reasons, the eluent consisted of mixed solvents{acetonitrile-dil.HNO_3-TBA(or DTMA)} was used in this work. However, attempting to develop and optimize a separation empirically with such a large number of variables becomes quite complex, with a diminished probability of

randomly finding an eluent. The eluent to such an "optimization" problem will remain unaltered.

(d) column, detector, and temperature

Four varieties of columns as the reversed phase mode were examined to separate ternary heteropoly molybdates with the eluent of same composition. Four columns used are as follows; Chemcosorb 10-ODS-L(noted as 10-ODS), Chemcosorb 7-ODS-L(7-ODS), Nucleosil 10C18(10C18), and Finepak SIL-C1(SIL-C1). All columns are commercially available. For retention of solutes few differences observed between three columns(10-ODS, 7-ODS, and 10C18), however, only SIL-C1 gave very short retention time. As compared of these three columns, 7-ODS gave a largest capacity factor for ternary heteropoly molybdate. The order of elution of solutes was no difference between three columns.

The near UV spectrophotometer as detector was used. The UV absorption spectra were examined to select the most suitable wavelength and these spectra are shown in Fig.V-4. A smooth bend was observed at the wavelength over 280 -310 nm in spectra. Although no absorption maximum was observed, these spectra gave satisfied results for measurement in modern detectors set at wavelength higher than 190 nm. Thus UV absorbance was measured at 300 nm to analyze the eluted species in all subsequent work.

The effect of temperature variation to separate the

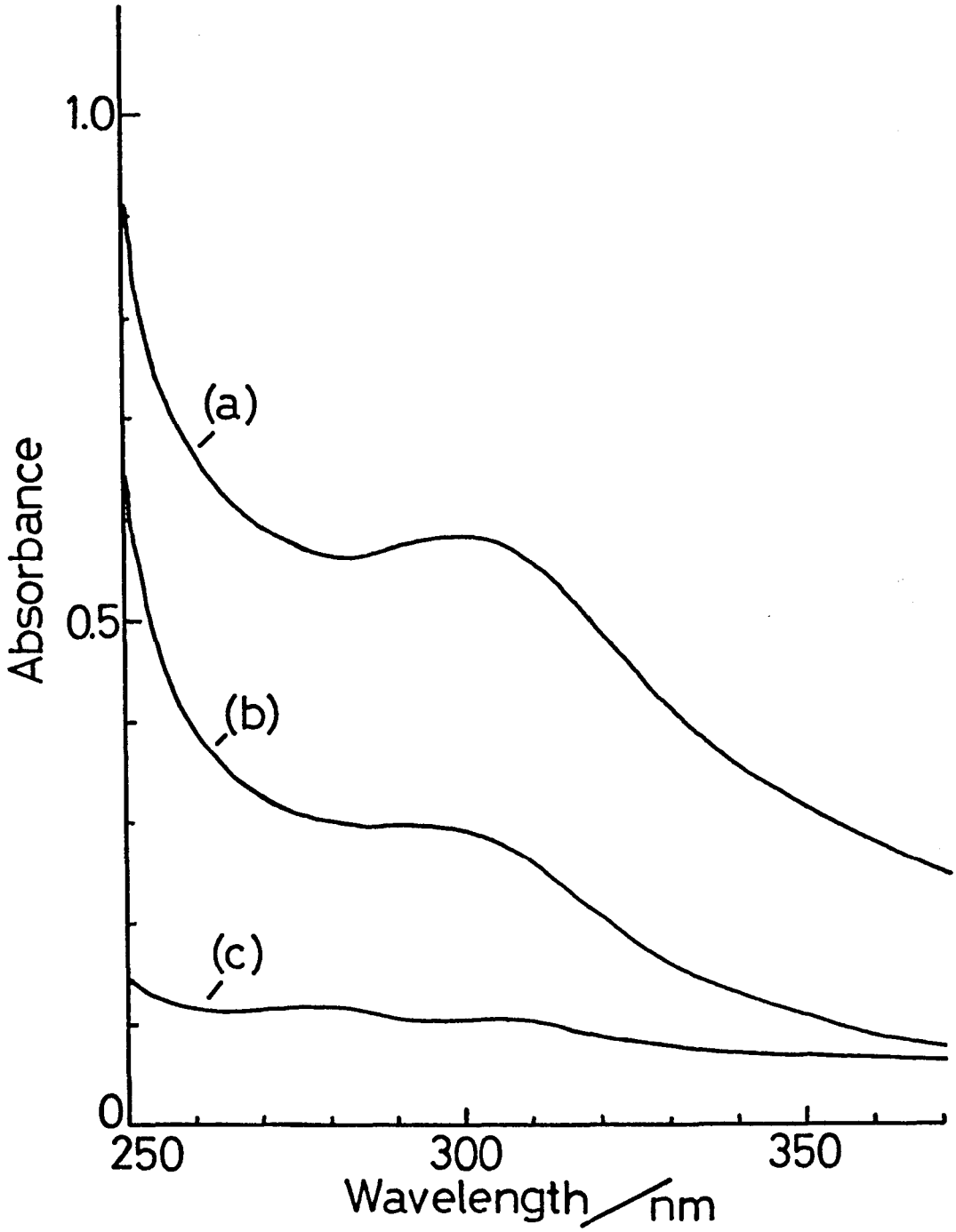


Fig V-4. UV absorption spectra.

(a) sample sln. + mobile phase

(b) sample sln. (C_P = 1.0 x 10^{-4}, C_{Mo} = 2.0 x 10^{-3} C_{Zr} = 5.0 x 10^{-5} mol dm^{-3}, pH 2.1)

(c) mobile phase (HNO_3 sln. + CH_3CN + DTMA sln.)

(a),(c): L = 10 mm, (b): L = 1 mm

ternary heteropoly molybdates was examined. The retention time shortened with the increase of temperature, but the capacity factors of ternary heteropoly molybdates decreased with it. Thus the measurement of IPRPLC was carried out at room temperature.

V - 4. Simultaneous Determination and Separation of Complexed Metal Ions

At first, the separating conditions were examined for each ternary heteropoly molybdate in IPRPLC and the most suitable condition(i.e., ion pair reagent, pH value, volume fraction of acetonitrile, and so on) for each species was found out. The chromatograms obtained are shown in Figs. V-5 and V-6. It should be noted that the composition of the mobile phase, ion pair reagent, and flow rate are somewhat different from one another. Although these chromatograms gave poor resolution of peaks, those of ternary heteropoly molybdates were well base-line resolved to estimate the peak areas. As shown in Fig.V-6, however, $PZrMo_{11}$ and $PHfMo_{11}$ gave almost the same retention time in all subsequent work and so it was very difficult to distinguish these two species from the chromatogram. The agreement of retention must be derived from the similarity of chemical property between two species. This result indicates that the retention mechanism of ternary heteropoly molybdates in IPRPLC must be governed by the solute-solute interaction, rather than the solute-solvent one in the stationary phase. Thus the following interpretation is considered:

At first, the ion pair reagent in the mobile phase is strongly adsorbed by the non-polar packing material in the stationary phase and formed the charged layers of ion pair

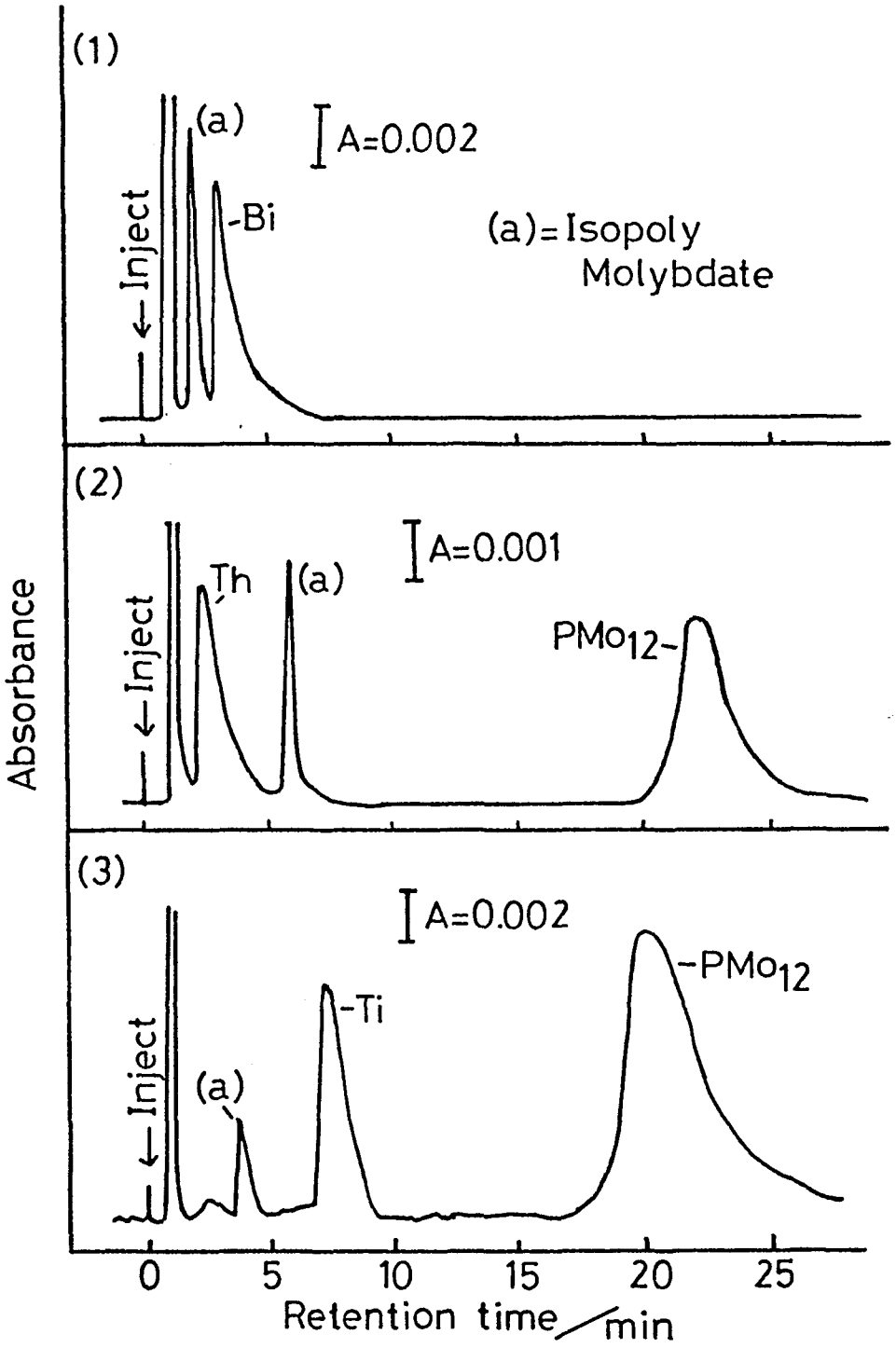


Fig V-5. Separation of each ternary heteropoly molybdate by IPRPLC.

$C_P = 1.0 \times 10^{-4}$ $C_{Mo} = 2.0 \times 10^{-3}$

$C_{Me} = 1.5\text{-}3.0 \times 10^{-5}$ (mol dm^{-3}) pH 1.8 - 2.4

20 µl injected. column, Nucleosil 10C18 λ, 300 nm

mobile phase,

(1) HNO_3 sln.(pH 3.0): CH_3CN: DTMA sln. = 30:150:10

(2) HNO_3 sln.(pH 2.0): CH_3CN: TBA sln. = 70:150:8

(3) HNO_3 sln.(pH 3.0): CH_3CN: DTMA sln. = 60:150:5

flow rate, (1) 1.57 (2) 1.72 (3) 1.65 (ml/min)

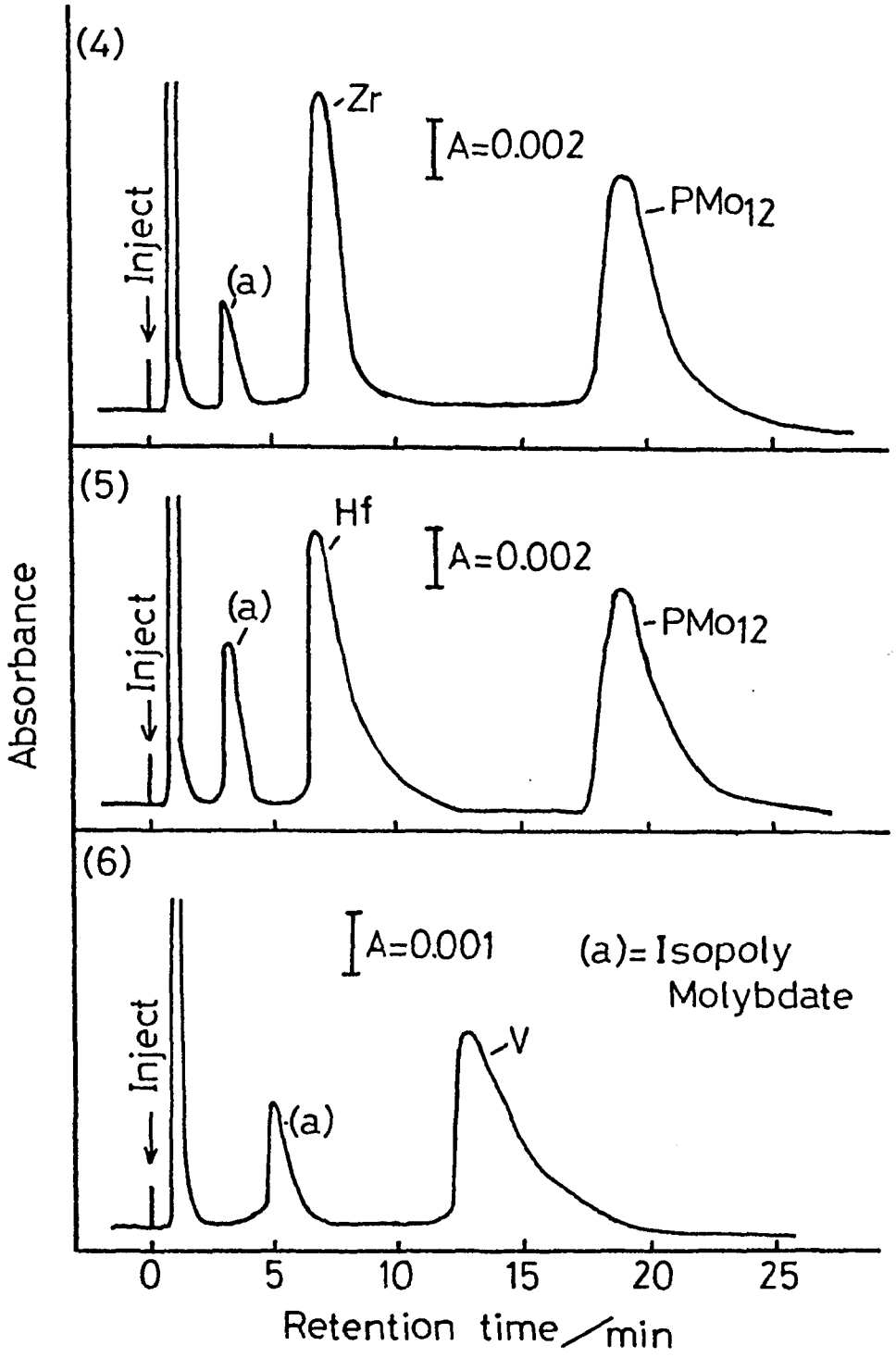


Fig V-6. Separation of each ternary heteropoly molybdate by IPRPLC.

$C_P = 1.0 \times 10^{-4}$ $C_{Mo} = 2.0 \times 10^{-3}$

$C_{Me} = 3.2\text{-}4.0 \times 10^{-5}$ (mol dm^{-3}) pH 2.0 - 2.2

20 µl injected. column, Nucleosil 10C18 λ, 300 nm

mobile phase,

(4),(5) HNO_3 sln.(pH 2.0): CH_3CN: DTMA sln. = 60:150:10

(6) HNO_3 sln.(pH 3.0): CH_3CN: TBA sln. = 80:150:10

flow rate, (4),(5) 2.44 (6) 1.54 (ml/min)

reagent on packing surface. Next, the solute(heteropoly complexes) is retained by the charged layers as a result of electrostatic force of attraction. Thus the retention time may be established by the electrostatic interaction, i.e., Coulomb's force, between the solute ion and the modified packing. This is delineated in Fig.V-7. This is supported further from the following two results. One is that the greater is the charge on the anion, the shorter the retention time is, and second, although the result is not shown in this paper, when TBA was used as ion pair reagent, compared with the result of DTMA, the retention time of $PVMo_{11}$ was reversed against that of PMo_{12}. The order of eluted species must be, that is, in agreement with the magnitude of interaction between each ternary heteropoly molybdate and the packing material modified by ion pair reagent in the stationary phase. The peak area calibration was linear over the concentration range of metal ions, 0.5 - 10 ppm, as shown in Fig.V-8. The lower limit of detection is at a concentration which gives a signal three times the peak-to-peak base line noise. The analytical precision of this method was tested by analysing 10 identical samples of solutions containing 3 ppm of zirconium and 2 ppm of vanadium ions, respectively. According to the results of these experiments, the coefficient of variation of the former was 4.6%, while that of the latter was 3.4%. The accuracy of this method was also evaluated by adding different amounts of zirconium and

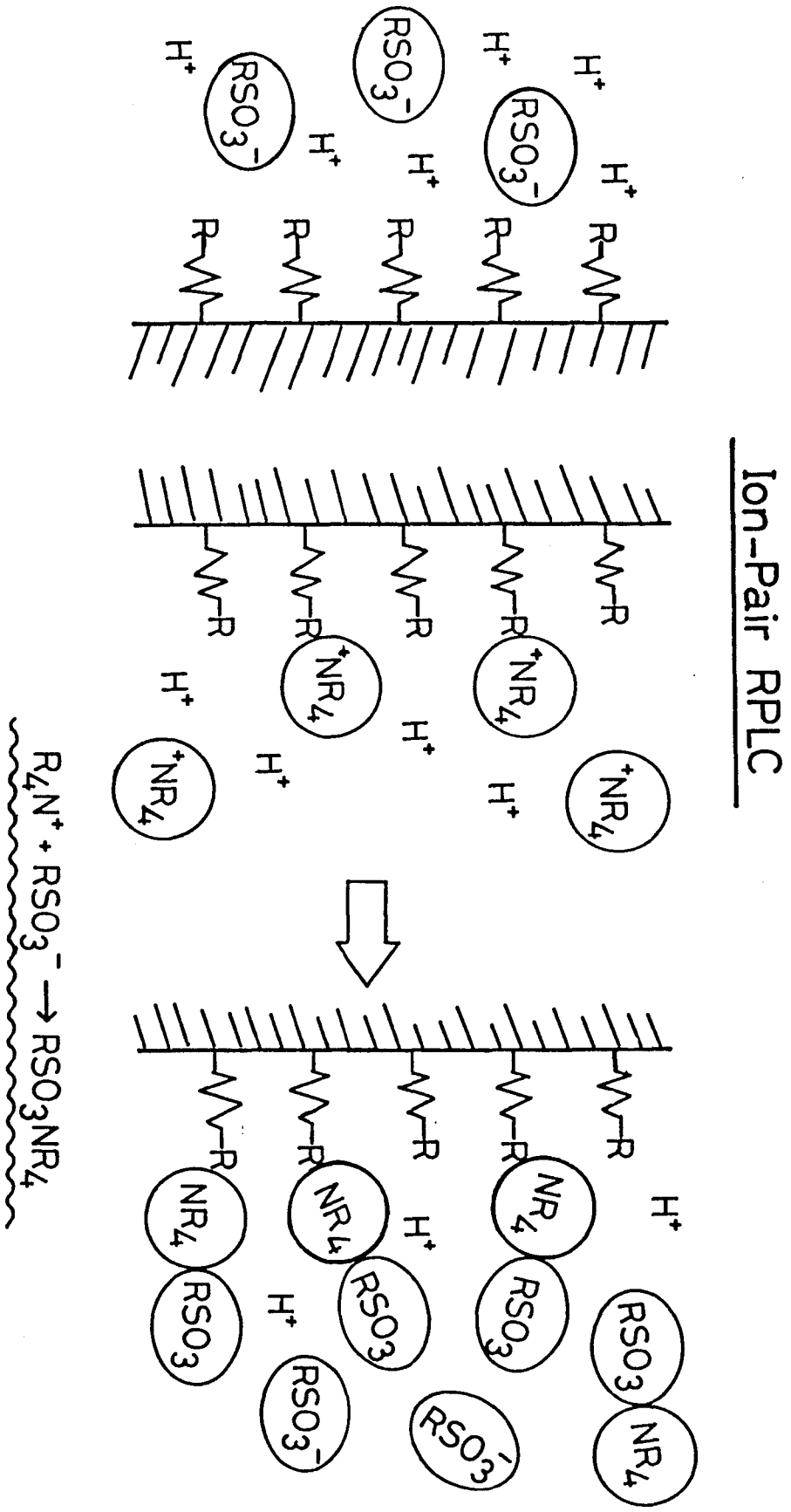


Fig V-7. Schematic of ion pair RPLC mechanism.

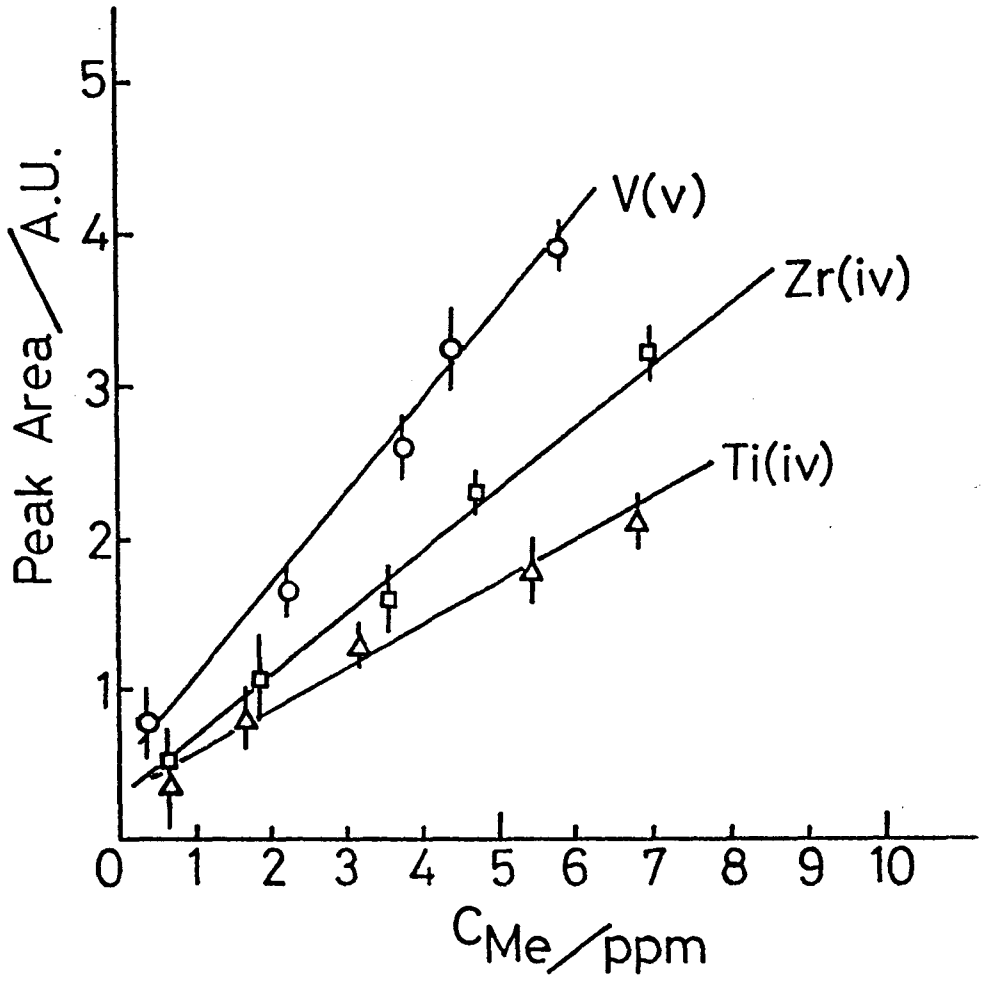


Fig V-8. Relationships between the metal ion concentration and peak area of each ternary heteropoly molybdate in IPRPLC.

C_P = 1.0 x 10^{-4} C_{Mo} = 2.0 x 10^{-3} (mol dm^{-3}) pH 1.8-2.4

20 µl injected. column, Nucleosil 10C18 λ, 300 nm

mobile phase,

Zr(IV); HNO_3 sln.(pH2.0): CH_3CN: DTMA sln. = 60:150:10

Ti(IV); HNO_3 sln.(pH3.0): CH_3CN: DTMA sln. = 60:150:5

V(V) ; HNO_3 sln.(pH2.0): CH_3CN: TBA sln. = 80:150:10

flow rate, Zr(IV) 1.5, Ti(IV) 1.7, V(V) 2.1 (ml/min)

vanadium ions to identical 12-molybdophosphate solution, respectively and measuring this recoveries by the proposed analytical procedure. The results obtained were indicated that this IPRPLC measurement could give a good recovery within the standard deviation of 4.3%.

In addition, in analogy with NMR measurement, the effect of coexisting inert metal ions was examined. Thus five kinds of inert metal ions in the range of 50 - 120 folds (i.e., Cu(II), Ni(II), Co(II), Fe(III), and Cr(VI) ions) were added in each ternary heteropoly molybdate solution and the recovery of complexed metal ion was measured in chromatogram. The results obtained, with respect to Zr(IV) and Bi(III) ions, are summarized in Table V-2 and they gave good recoveries for these two ions. Under the experimental conditions(they are noted in the footnote of Table V-2), these inert metal ions were no retained and that solvent peak including these ions was observed. For Bi(III) ion, that is, positive errors have been undergone slightly by the overlap between the edge of solvent peak and that of $PBiMo_{18}$. This errors are, however, negligibly affected on the determination of complexed metal ions by this technique. Judging from these experimental results, although the further studies for other inert metal ions have not been carried out, it could be expected that no interference is observed even in the presence of several inert metal ions at high ppm level. In analogy with the results of NMR measurement, however,

Table V-2. Effect of Coexisting Metal Ions for IPRPLC Measurement

Metal ion	C_{Me}/ppm	C_{Zr}/ppm[a)]	Recovery/%	C_{Bi}/ppm[b)]	Recovery/%
———	———	3.65 ± 0.20	———	4.27 ± 0.06	———
Cu(II)	500	3.59 ± 0.17	98	4.53 ± 0.14	106
Ni(II)	400	3.69 ± 0.11	101	4.60 ± 0.29	108
Co(II)	200	3.59 ± 0.11	98	4.37 ± 0.05	102
Fe(III)	300	3.68 ± 0.13	101	4.34 ± 0.15	102
Cr(VI)	250	3.57 ± 0.20	98	4.53 ± 0.31	106

30 µl injected. column, Nucleosil 10C18
mobile phase
a) HNO_3 sln.(pH 2.0): CH_3CN: DTMA sln. = 60:150:10
b) HNO_3 sln.(pH 3.0): CH_3CN: DTMA sln. = 30:150:10
flow rate, a) 1.50 ml/min b) 1.71 ml/min λ, 300 nm

remarkable interferences were caused in the presence of a few metalloid ions, e.g., As(V), Se(IV), and W(VI) ones, because these ions reacted with excess molybdate and produced another binary heteropoly molybdates in solution.

As noted above, there were a few differences of elution conditions regarding with ternary heteropoly molybdates. This result indicates the possibility of simultaneous determination of complexed metal ions, in analogy with NMR technique, by IPRPLC one, if more suitable separating condition is selected. Systematic separating conditions for ternary heteropoly molybdates were examined in a series of experiment. A chromatogram obtained under the most suitable separating condition is shown in Fig.V-9, and the result is summarized in Table V-3. The chromatogram, if not thoroughly, indicates that it is possible to separate these ternary heteropoly molybdates within 30 min. The separation of $PZrMo_{11}$ and $PHfMo_{11}$, however, could not be achieved in all subsequent work. The overlapping with the peak of isopoly Mo(VI) species caused the positive errors for determination of Th(IV) and Ti(IV) ions. However, there was well base-line resolved even if metal ion concentration was below low ppm. Under this separating condition the order and the retention time of these ternary heteropoly molybdates were as follows: $PBiMo_{18}$(2.2 min), $PThMo_{11}$(4.5 min), $PTiMo_{11}$(7.1 min), $PHfMo_{11}$ and $PZrMo_{11}$(9.7 min), and $PVMo_{11}$(17.8 min). In this work, although the separation of Zr(IV) and Hf(IV) ions was

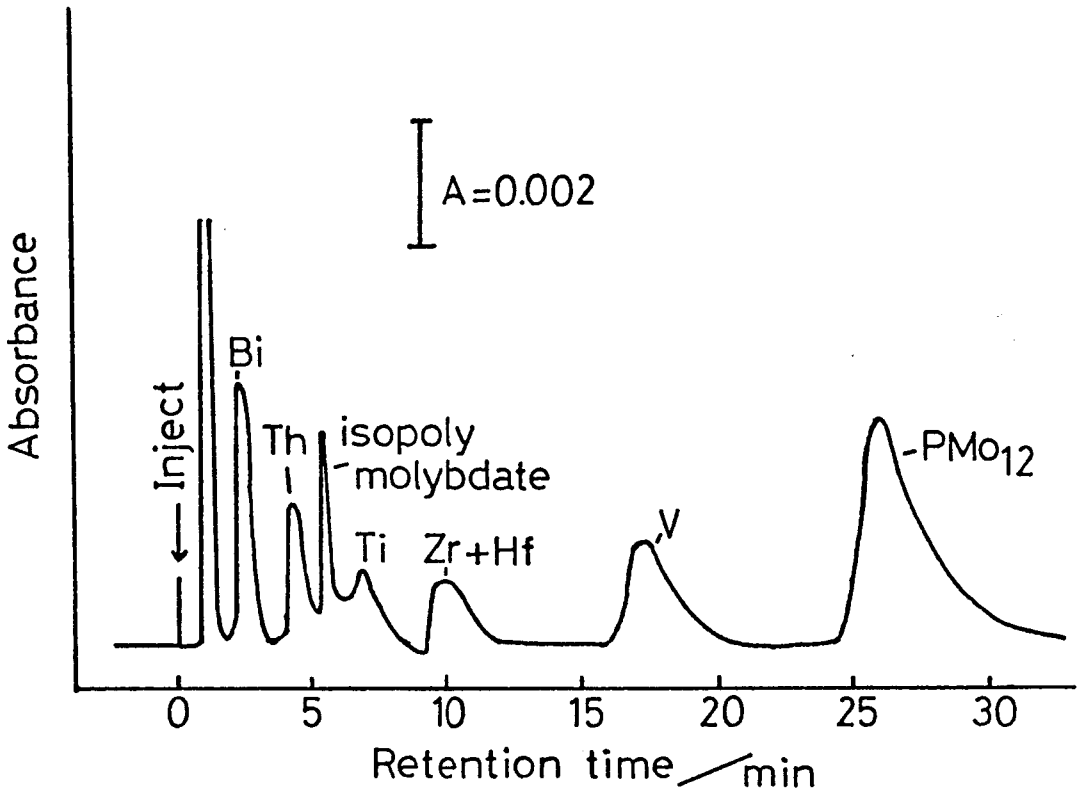


Fig V-9. Simultaneous determination of each metal ion by IPRPLC.

$C_P = 1.0 \times 10^{-4}$ $C_{Mo} = 2.0 \times 10^{-3}$

$C_{Me} = 0.8\text{-}1.2 \times 10^{-5}$ (mol dm^{-3}) pH 1.8

20 µl injected. column, Nucleosil 10C18

mobile phase,

HNO_3 sln.(pH 2.0): CH_3CN: TBA sln. = 80:150:10

flow rate 1.64 ml/min, λ, 300 nm

Table V-3. Results of Simultaneous Determination of Several Metal Ions by IPRPLC

Metal ion	Retention time[a] /min	Detection limit /ppm	R.S.D./%
Bi(III)	2.2	1.2	2.7
Th(IV)	4.5	1.5	2.5
Ti(IV)	7.1	0.5	8.7
Zr(IV)	9.7	0.5	4.4
Hf(IV)	9.7	1.0	3.9
V(V)	17.8	0.5	5.4

a) $C_P = 1.0 \times 10^{-4}$ $C_{Mo} = 2.0 \times 10^{-3}$

$C_{Me} = 0.8\text{-}1.2 \times 10^{-5}$ (mol dm^{-3}) pH 1.8

20 µl injected. column, Nucleosil 10C18

mobile phase,

HNO_3 sln.(pH 2.0): CH_3CN: TBA sln. = 80:150:10

flow rate, 1.64 ml/min λ, 300 nm

incomplete, it was possible to determine each metal ion at high ppb level.

Separation of chemical species with the very closed properties is one of the most important problems in analytical chemistry. As previously mentioned, the solvent-solvent distribution analysis was first examined to separate these complexes, although cyclohexanone was found to be the best organic solvent to extract each compound from aqueous medium, but the separation of each chemical species by solvent extraction was out of the discussion because of the very closed character of the solute-solvent interaction. On the other hand, in liquid chromatography the separating technique is fundamentally the same that of solvent extraction, which is based on the distribution between two phases. However, the mechanism of separation by IPRPLC is governed by more complicated interactions, i.e., between ternary heteropoly molybdate and ion pair reagent, ion pair reagent and packing material, eluent and the paired chemical species, etc. Therefore to interpret the order of eluted species, it is necessary to take into account not only the difference of chemical property of each ternary heteropoly molybdate but also the force of interaction between its species and ion pair reagent. Thus the order of eluted species is considered as follows: for $PBiMo_{18}$, which has the Dawson like structure, it was scarcely retained in column because of the smaller formation constant of the ion paired

species. This is guessed from the fact that it is very difficult to obtain the precipitate of P_2Mo_{18} with tetraalkyl ammonium salts. For PMo_{12}, which gives rise to the longest retention time in this work, this species has a hydrophobic property and exhibits stronger interaction with the ion pair reagent, because the charge density is distributed uniformly on the large surface area of PMo_{12} anion. $PVMo_{11}$ has also relative large hydrophobic property, as compared with other ternary heteropoly molybdates, so that this species is extracted by several oxygenated solvents(34), e.g., MIBK, i-butyl alcohol, etc. For the reason, in ternary heteropoly molybdates it was the slowest eluted species, though it was more rapidly than PMo_{12}. In comparison between four species, i.e., $PTiMo_{11}$, $PThMo_{11}$, $PZrMo_{11}$, and $PHfMo_{11}$, the order of elution seems to depend not on the electrostatic contribution(based on the difference of chemical properties), but on the magnitude of formation constant of ion paired species(based on the structural difference) between ternary heteropoly molybdates and ion pair reagent. Although further investigations to confirm this result have not been carried out yet, the order of elution must be consistent with that of interaction with ion pair reagent.

Finaly, near UV absorption spectra of ternary heteropoly molybdate solution gives a smooth degradation curve at around 300 nm and it was established an almost linear relationship between the metal ion concentration and its absorbance. Thus

on the basis of this findings, a rapid and highly selective IPRPLC / photometric detection system has been developed for the determination of these complexed metal ions. Since UV spectrophotometer was applied to a detector in all runs now, the detection limits of these metal ions are due to the molar extinction coefficient of ternary heteropoly molybdates at 300 nm. As far as the detection limits are concerned, that is, a restriction is placed on the analytical usefulness when the UV spectrophotometer is combined with a separation technique such as IPRPLC. The analytical sensitivity can be further increased by use of more sensitive photometric detectors. In one of these detectors, inductively coupled plasma(ICP) technique has been coupled to HPLC(35) and is being used for trace analysis by Krull and his co-workers(36). That work used IPRPLC with a tetraalkylammonium salt as the ion pair reagent to separate arsenite, dimethyl arsenate, and arsenate. The ICP detector gave calibration curves after hydride formation that were linear over several orders of magnitude with detection limits at 100 - 200 ppb or less. By use of more sensitive detectors, e.g., ICP one, it could expected that the estimated detection limits are in the low-to-mid ppb level.

V - 5. References

1) G.M.Schwab and K.Jockers, Angew.Chem., 50,546(1937).

2) G.M.Schwab and G.Dattler, Angew.Chem., 50,691(1937).

3) G.A.Howard and A.J.P.Martin, Biochem.J., 46,532(1950).

4) E.Grushka and R.P.W.Scott, Anal.Chem., 45,1626(1973).

5) A.M.Krstulovic, M.Zakaria, K.Lohse, and L.B.Dziedzic, J.Chromatogr., 186,733(1979).

6) R.M.Riggin and P.T.Kissinger, Anal.Chem., 49,2109(1977).

7) R.A.Hartwick, A.Jeffries, A.M.Krstulovic, and P.R.Brown, J.Chromatogr.Sci., 16,427(1978).

8) N.A.Porter, R.A.Wolf, and J.R.Nixon, Lipids., 14,20(1979).

9) F.A.Fitzpatrick, S.Siggia, and J.C.Dingman, Anal.Chem., 44,2211(1972).

10) R.A.Hartwick, A.M.Krstulovic, and P.R.Brown, J.Chromatogr., 186,659(1979).

11) R.A.Hartwick and P.R.Brown, J.Chromatogr.Biomed.Appl., 143,383(1977).

12) S.Assenza and P.R.Brown, J.Chromatogr.Biomed.Appl., 181,169(1980).

13) R.F.Adams, Adv.Chromatogr., 15,131(1977).

14) G.R.Gotelli, P.M.Kabra, and L.J.Marton, Clin.Chem., 23,957(1977).

15) R.K.Desiraju and E.T.Sugita, J.Chromatogr.Sci.,

15,563(1977).

16) C.G.Horvath and S.R.Lipsky, Nature., 211,748(1966).

17) K.G.Wahlund, J.Chromatogr., 115,411(1975).

18) B.Fransson, K.G.Wahlund, I.M.Johansson, and G.Schill, J.Chromatogr., 125,327(1976).

19) J.C.Kraak, K.M.Jonker, and J.F.K.Huber, J.Chromatogr., 142,671(1977).

20) C.P.Terweij-Groen, S.Heemstra, and J.C.Kraak, J.Chromatogr., 161,69(1978).

21) E.Tomlinson, T.M.Jeffries, and C.M.Riley, J.Chromatogr., 159,315(1978).

22) C.Horvath, W.Melander, I.Molnar, and P.Molnar, Anal.Chem., 49,2295(1977).

23) J.H.Knox and J.Jurand, J.Chromatogr., 125,89(1976).

24) P.T.Kissinger, Anal.Chem., 49,877(1977).

25) D.Westerlund and A.Theodorsen, J.Chromotogr., 144,27(1977).

26) F.Umland and K.Kirchner, Z.Analog.Allgem.Chem., 280,211(1955).

27) H.Seiler, Helv.Chim.Acta., 45,381(1962).

28) B.Sansoni, Z.Naturforsch., 11b,117(1956).

29) S.Takitani, Bunseki Kagaku., 12,1156(1963).

30) J.H.Knox and J.Jurand, J.Chhromatogr., 125,89(1976).

31) J.H.Knox and R.A.Hartwick, J.Chromatogr., 204,3(1981).

32) C.Horvath, W.Melander, I.Molnar, and P.Molnar, Anal.Chem., 49,2295(1977).

33) D.Westerlund and A.Theodorsen, J.Chromatogr., 144,27(1977).

34) K.Kitagawa and N.Shibata, Bunsseki Kagaku., 8,302(1959).

35) D.Bushee, I.S.Krull, R.N.Savage, and S.B.Smith Jr, J.Liquid.Chrom., 5(3),463(1982), 5(4),693(1982).

36) I.S.Krull, D.Bushee, R.N.Savage, R.C.Schleicher, and S.B.Smith Jr, Anal.Letters., 15(A3),267(1982).

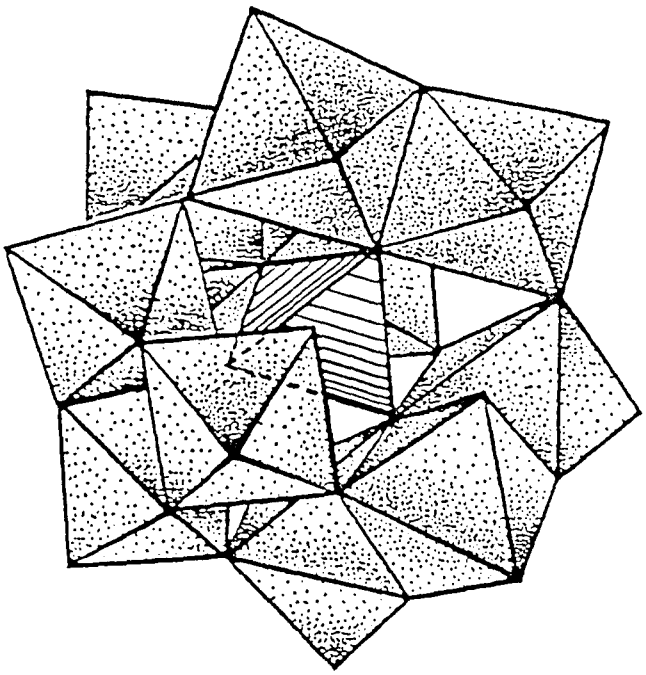
Chapter VI. Consideration on Chemical Properties of Ternary Heteropoly Molybdates

VI - 1. Interpretation of Formation of Ternary Heteropoly Molybdate(the Keggin Like Structure) from Donor-Acceptor Interaction

The formation of new ternary heteropoly molybdates by the addition of several metal and metalloid ions in 12-molybdophosphate(PMo_{12}) solution was described. As a result, the di- and trivalent states of metal ions, e.g., Cu(II), Zn(II), and Fe(III) ions, could not be formed the ternary heteropoly molybdate, in contrast to the tetra- and pentavalent ions. This was also seen clearly in the fact that Ce(III) ion could not be formed ternary heteropoly molybdate, while Ce(IV) one could. It can therefore be presumed that the formation of ternary heteropoly molybdate is not due to the geometric size in configuration, i.e., ionic radius, so much as electrostatic interaction between the complexed metal ion and heteropoly molybdate in solution. For these reasons, to interpret the formation of ternary heteropoly molybdate the concept of donor-acceptor interaction was considered. A donor-acceptor interaction leads to increasing polarities of the bonds originating from the donor and acceptor atoms, respectively. Increasing polarity is related to an increase in fractional positive

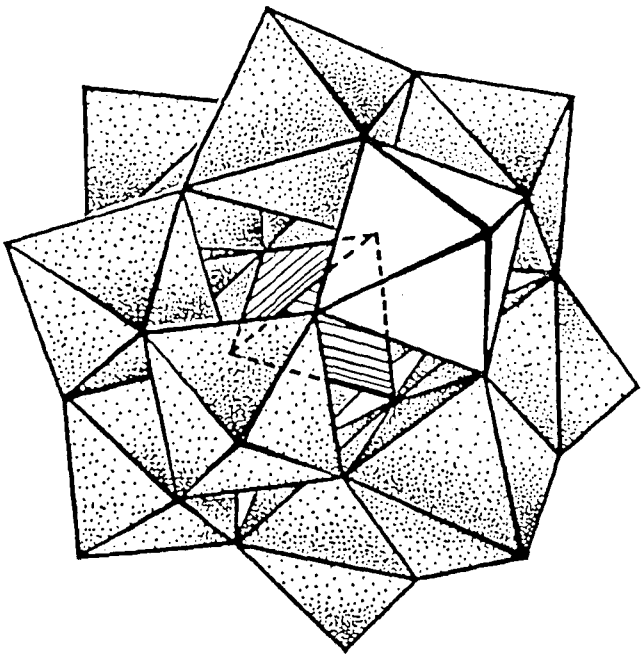
charge at the acceptor atom and an increase in fractional negative charge at the donor atom. On the consideration of donor-acceptor approach, it should be noted the role of 11-molybdophosphate(PMo_{11}), which is one of the lacunary heteropoly molybdates, for formation of ternary heteropoly molybdate. As previously mentioned, PMo_{12} has a limited stable range as for the acid concentration and it is reversibly converted to PMo_{11} in aqueous solution. When a complexed metal ion is added in this solution, the metal ion reacts with PMo_{11} and produces a ternary heteropoly molybdate(these two species are illustrated graphically in Fig.VI-1). Thus PMo_{11} might be the essential basis of the formation of ternary heteropoly molybdate. When viewed under the more microscopic observations regarding the structure of PMo_{11}, by some very active oxygen atoms, which have an abundance of electron donor ability, the lacuna is surrounded. When an added metal ion encloses in the lacuna, the larger electron acceptor property the metal ion has, as compared with that of molybdenum atom, the stronger donor-acceptor interaction it yields between the metal ion and PMo_{11}. As an another example for donor-acceptor interaction, it could be seen not only between the complexed metal ion(solute) and PMo_{11}(solute) but also between heteropoly molybdates(solute) and water molecules(solvent) in solution. Thus in general, PMo_{12} was virtually extracted with many oxygenated organic solvents. On the contrary, solvent

(a)



$PMo_{11}O_{39}^{7-}$

(b)



$PXMo_{11}O_{40}^{n-}$

Fig VI-1. Structures of heteropoly anions.

(a) lacunary structure

(b) ternary heteropoly molybdate

extraction of ternary heteropoly molybdates was found to be selectively. This indicates that ternary heteropoly molybdate becomes more stable for its hydrophilic property than PMo_{12} in acidic solution and that the high stability of it is mainly due to the higher solvency of water. This has also been implied by the fact that the near UV spectra of ternary heteropoly molybdate in solution show a characteristic absorption maximum at 302 nm. While in the case of PMo_{12} the obscurity for it remains, the presence of this absorption band is associated with the rigid formation of ternary heteropoly molybdate in a liquid medium. Since water is by far the commonest solvent for heteropoly molybdates, it could be discussed how solvation are subjected to heteropoly molybdates in water according to the comparison of the Raman spectra between in solid and in liquid states. As shown in Figs.VI-2 and VI-3, no peak shift was observed in solid state, in contrast to the results in liquid state. Therefore the peak of $PZrMo_{11}$, in analogy with that of $PVMo_{11}$, was shown almost similar position to that of PMo_{12} in solid state. The shift of Mo=O stretching vibration for ternary heteropoly molybdate in solution does not arise from the effect of complexed metal ion so much as the interaction between oxygen atoms(donor) combined with molybdenum atom and hydrogen atoms(acceptor) in the solvated water molecules, although the increasing polarity based on the rearrangement of electron density by the substitution of metal ion causes

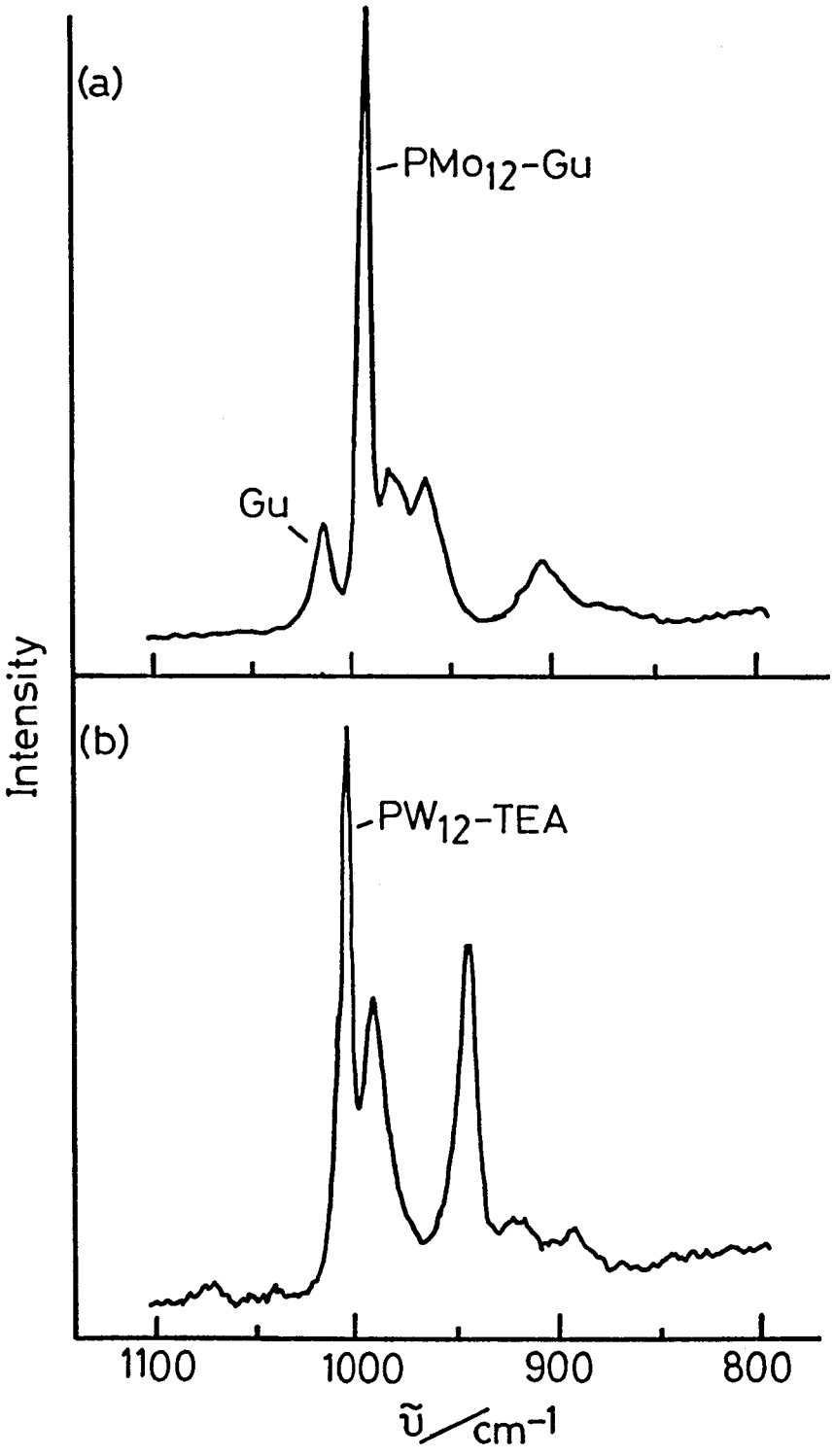


Fig VI-2. Raman spectra of PMo_{12} and PW_{12} in solid state.

(a) PMo_{12} - Gu (b) PW_{12} - TEA

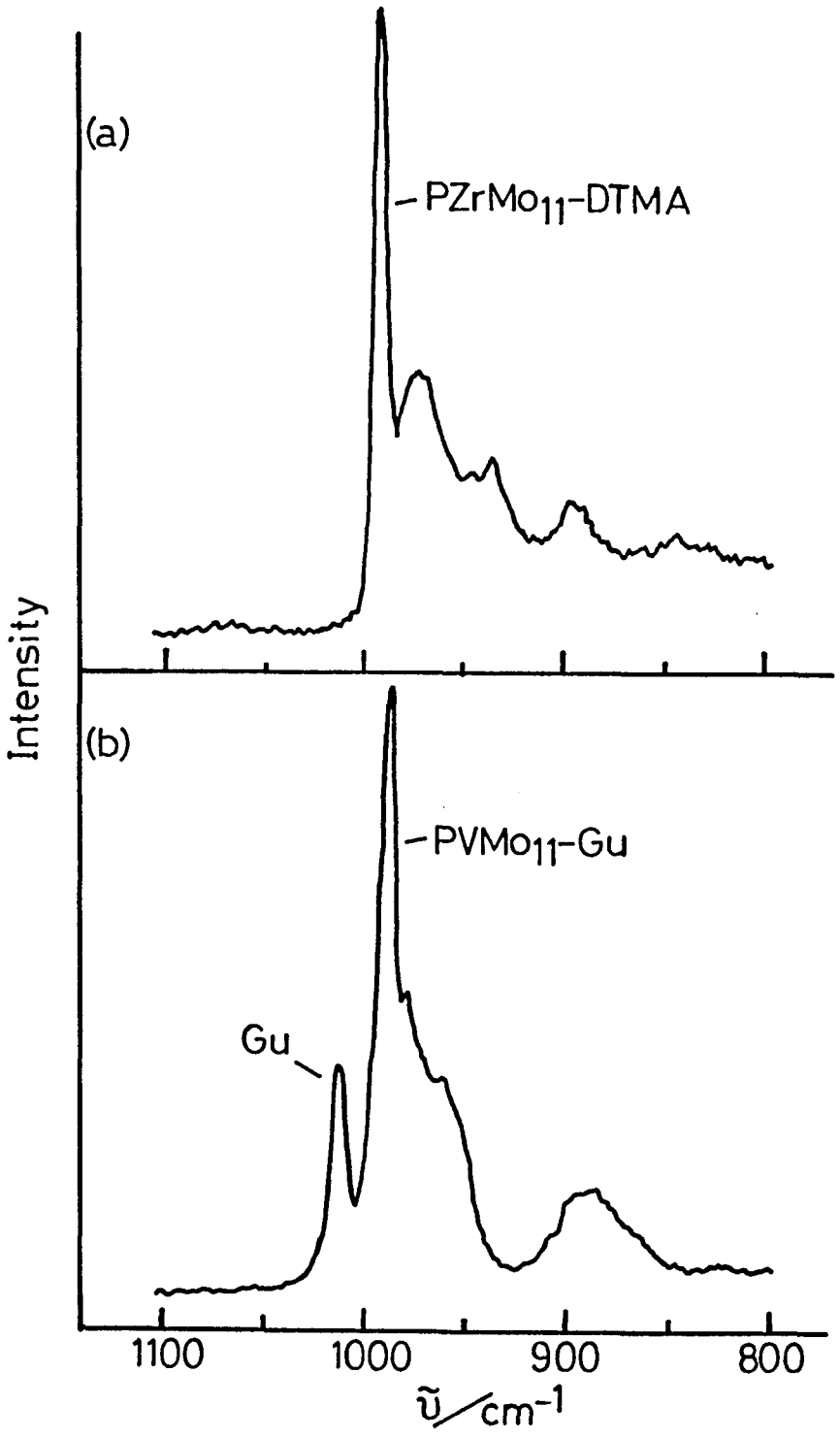


Fig VI-3. Raman spectra of ternary heteropoly molybdates in solid state.

(a) $PZrMo_{11}$ - DTMA (b) $PVMo_{11}$ - Gu

its interaction indirectly. In light of the results of Raman measurement, it could be presumed that the stronger hydration of ternary heteropoly molybdate, compared with that of PMo_{12}, induces the shift of Mo=O vibration at lower wave number and leads the stability of the species in solution. Thus whether the ternary heteropoly molybdate can form or not must be governed by the following chemical properties:

1) donor-acceptor interaction between the oxygen atoms around the lacuna in PMo_{11} and the added metal ion.
2) solvency of water: the interaction between the ternary heteropoly molybdate induced polarity and the solvated water molecules.

VI - 2. New Concept of Acceptor Properties of Group 4A and 5A Elements

As described in the previous Chapter IV, by the concept of a simpler rigid sphere model the differences of chemical shifts of ^{31}P NMR were interpreted very well. The chemical shift variations, however, must be essentially explained in terms of changes in electron density surrounding the phosphorus atom. The oxygen atoms of the central PO_4 tetrahedron, although its model was allowed only twelve metal ions for calculation, may be assumed to have the largest contribution to this electron density. In spite of such a speculative approximation, its model provided the fairly good reproducibility of the experimental data. Thus this empirical equation does not express only the formal electron density, beyond this expression, and it might reflect the difference between the chemical property of each complexed metal ion.

Several authors have attempted to develop a unified theoretical foundation for ^{31}P chemical shifts of phosphorus compounds(1-4). In one of the more successful theoretical approaches, Letcher and Van Wazer(5,6), for example, using approximate quantum-mechanical calculations, demonstrated that three factors appear to dominate ^{31}P chemical shift differences $\Delta\delta$, as shown by

$$\Delta\delta = -C\Delta\chi_x + k\Delta n_\pi + A\Delta\theta$$

where $\Delta\chi_x$ is the difference in electronegativity in the P-X bond, Δn_π the change in the π-electron overlap, $\Delta\theta$ the change in the σ-bond angle, and C, k, and A are constants. The Letcher and Van Wazer's theories, which relate ^{31}P NMR shift changes to structural and electronic parameters, was applied to discuss the wide variation of ^{31}P chemical shifts. Since binary and ternary heteropoly molybdates in this work consist of a central PO_4 tetrahedron surrounded by twelve oxometalates cage, the difference in electronegativity of the P-O bond is negligible, $\Delta\chi_x \sim 0$. In addition, the central P atom is encircled by very stable frames in the Keggin like structure and so it can be expected that the change in the σ-bond angle is very small, $\Delta\theta \sim 0$. From these reasons, the difference of chemical shift must be ascribed to the change in the π-electron overlap, Δn_π. The substitution of a complexed metal ion for one molybdenum ion induces the changes in the π-electron overlap with phosphorus atom through the oxygen atom combined with the complexed metal ion. The result which supports this idea was obtained from ^{31}P NMR(solid) measurement. A powder pattern of ^{31}P NMR for PMo_{12} was very sharp and axially symmetrical. For the Keggin structure there is no local overlap of π bond in either one of the four P-O bonds. On the other hand, as shown in Fig.VI-4, the powder patterns of ternary heteropoly molybdates exhibited skewed peaks, in which a small hump was shown at higher field for $PZrMo_{11}$ and $PHfMo_{11}$, while for

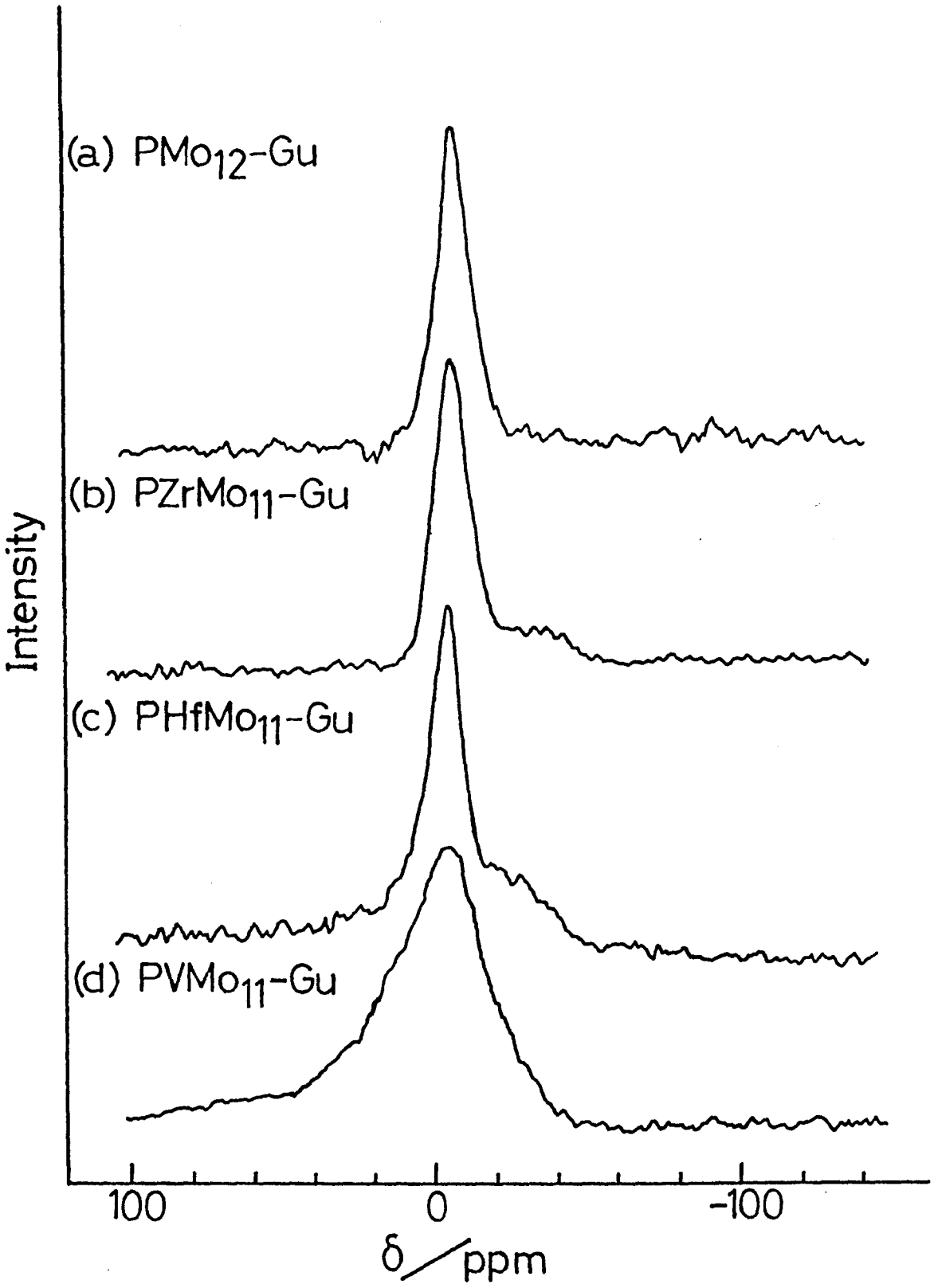


Fig VI-4. ^{31}P solid NMR spectra of binary- and ternary heteropoly molybdates.

$PVMo_{11}$ at lower field. Thus the chemical shift anisotropy was observed clearly with regard to ternary heteropoly molybdates. This could be explained as follows: neglecting the σ bonds, the each different value of the anisotropy is related to the π-bond character of the P-O bonds induced by the formation of ternary heteropoly molybdate. The axis of symmetry of axially symmetric shielding tensor, as illustrated in Fig.VI-5, could coinside with the P-O' bond of central PO_4 tetrahedron in ternary heteropoly molybdate. Therefore two types of axially symmetric shielding tensors could be considered. In type (A) the maximum shielding direction is along the P-O' bond, and in this case the powder pattern of type (a) is obtained. On the contrary, in the case of type (B) the least shielded direction is along the P-O' bond, and the powder pattern should be of the type (b). With respect to $PVMo_{11}$, decreasing π bond character along the three-fold axis(P-O' bond) is correlated with decreasing shielding of the phosphorus in this direction. Similar evidence could be seen in IR spectra, too. While the P-O stretching band was observed at 1062 cm^{-1} for PMo_{12}, as shown in Fig.VI-6, the formation of ternary heteropoly molybdates led to the band shift. Thus the P-O band shifted at higher wave number(1082 cm^{-1}) for $PVMo_{11}$, whereas for $PZrMo_{11}$ at lower wave number(1048 cm^{-1}) in IR spectra. This indicates that the electron density around P atom is increasing for $PVMo_{11}$, and that, on the contrary, for $PZrMo_{11}$ decreasing.

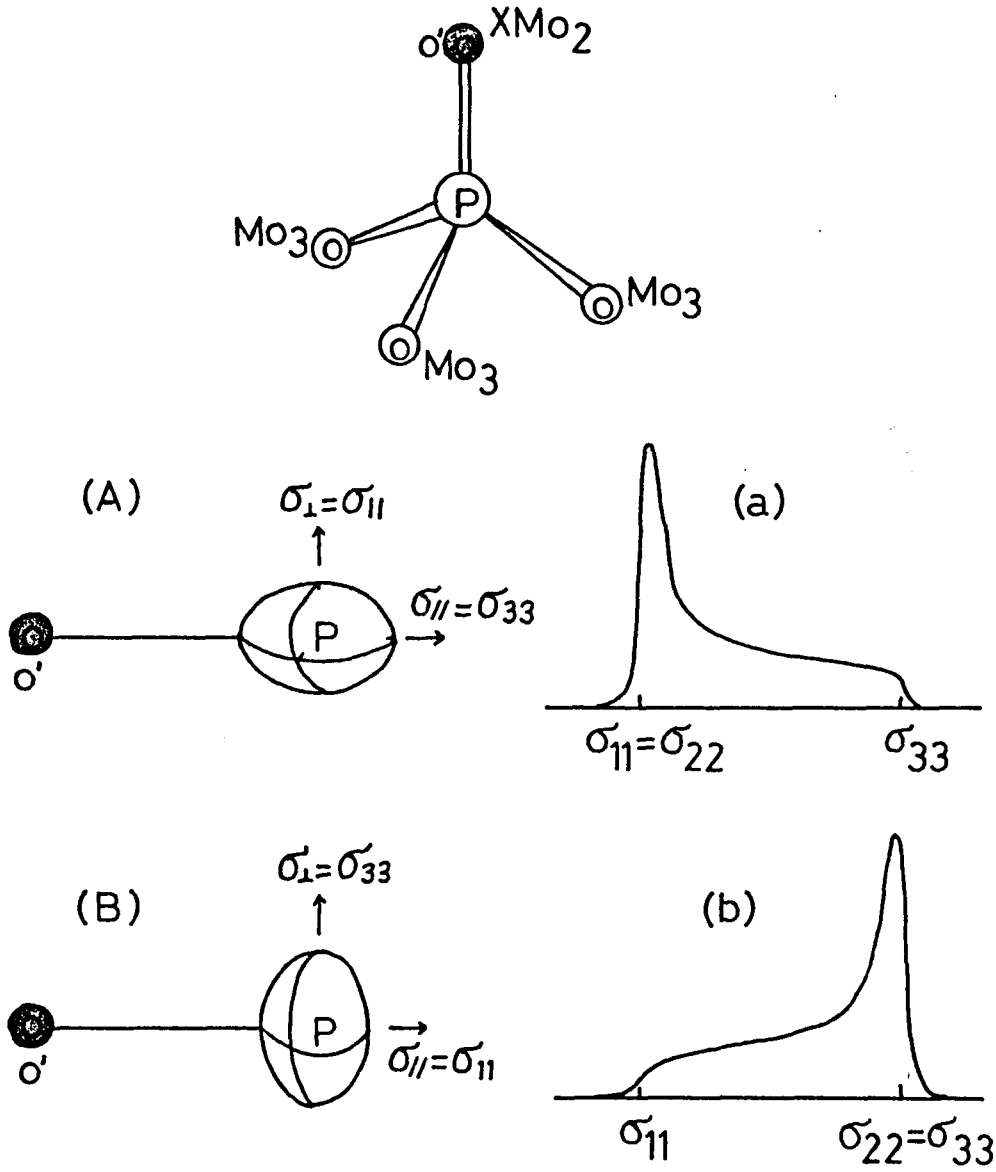


Fig VI-5. Axially symmetric shielding tensor models and their powder pattern.

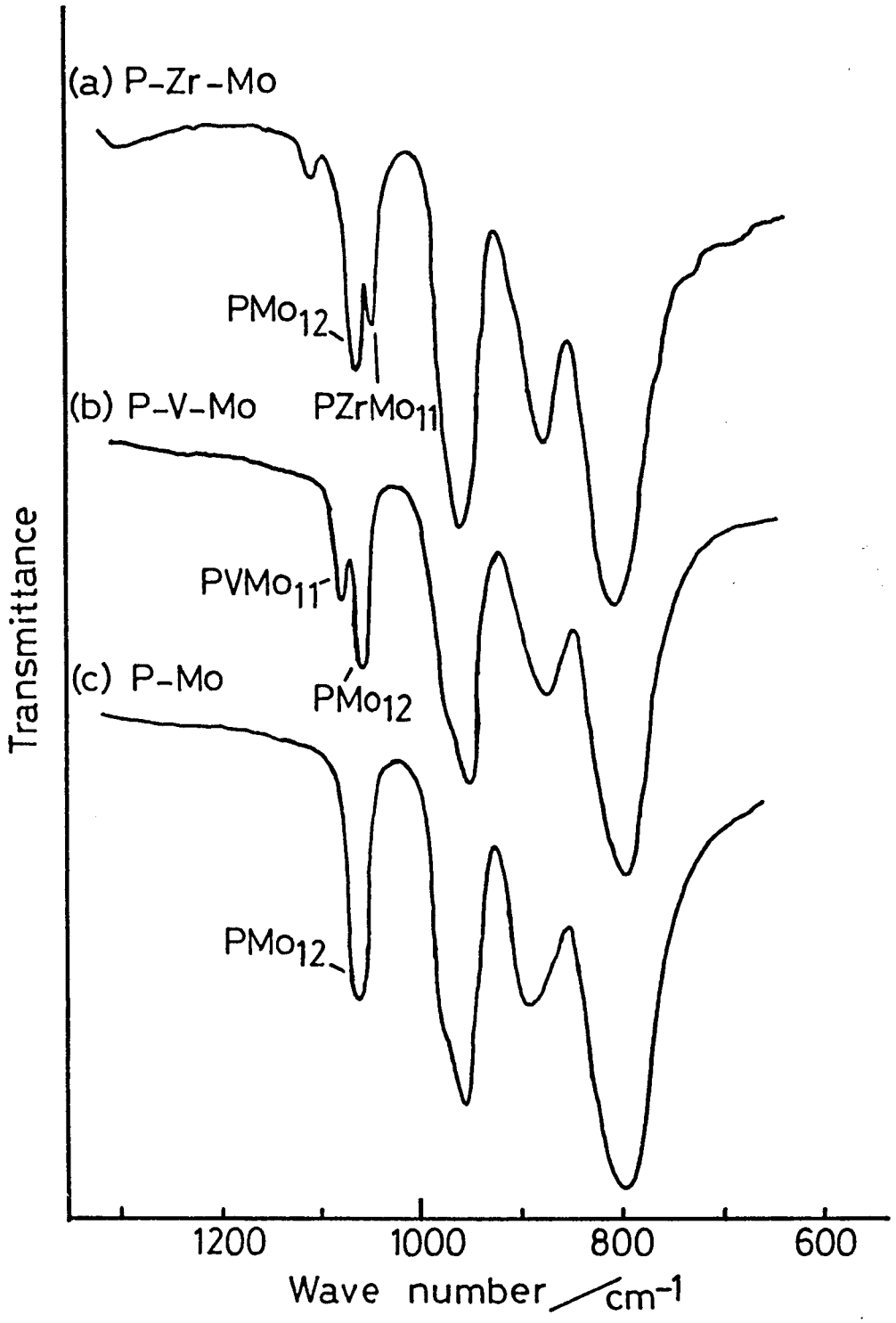


Fig VI-6: IR spectra of binary- and ternary heteropoly molybdates.

(a) $PZrMo_{11}$-DTMA (b) $PVMo_{11}$-Gu

(c) PMo_{12}-Gu

These results of a series of experiments, i.e., Raman(liquid and solid), IR, and NMR(liquid and solid) measurements, are summarized in Table VI-1. In spite of a similar general formula, $PXMo_{11}O_{40}^{n-}$, some differences were observed obviously between the results of $PZrMo_{11}$ and those of $PVMo_{11}$. Since one phosphorus, eleven molybdenum , and forty oxygen atoms are present in both compounds, these differences must be due to the difference of chemical property between the complexed metal ions, i.e., Zr(IV) and V(V), which introduced into the Keggin structure. In earlier studies on the stability, reactivity, and formation of heteropoly complexes, some investigators(7,8) have also reported on them in connection with the chemical properties of metal ions. As an example, The ionization potential of an element was at first related to the ability of the element to form binary heteropoly molybdates by Serebrennikov. In his paper for studies on the properties of heteropoly complexes formed by quadrivalent elements, their ability to form binary heteropoly molybdates decreases in the order Si > Ge > Ti > Zr > Ce > Th. This also coincides with the order of increase in ionic radius or decrease in ionization potential.

In the previous section, in order to interpret the formation of ternary heteropoly molybdate the concept of donor-acceptor interaction was introduced. At that time, the interaction between the oxygen atoms(donor) around a lacuna in PMo_{11} and the complexed metal ion(acceptor) was

Table Results of Raman, IR, and NMR Measurements

	Raman (Mo=O) $\bar{\nu}$ / cm^{-1}	I.R (P-O) $\bar{\nu}$ / cm^{-1}	NMR (^{31}P) δ / ppm	Solid NMR (^{31}P) δ / ppm
$PVMo_{11}$	994 (990)[a]	1082	-17.66 [b]	-4.96 [c]
PMo_{12}	996 (992)	1062	-17.33	-6.35
$PZrMo_{11}$	980 (992)	1048	-16.88	-6.55

a) The values in parentheses were obtained in solid state.

b) Relative to 1-aminoethylidene bis(phosphonic acid).

c) Relative to 85% H_3PO_4 sln.

considered. One can further be expected some correlation between the order of chemical shift and acceptor property for each complexed metal ion. However, the phosphorus atom is surrounded by four oxygen atoms equivalently. Therefore, the complexed metal ion can never approach close enough to cause any marked shielding or deshielding, because it is shielded directly by tetrahedron of oxygen atoms. But this could be interpreted well in terms of the "pileup effect" of negative charge on the donor atom(9). The original loss of negative charge at the donor atom by charge transfer toward the acceptor molecule is overcompensated by attracting electronic charge from other parts of the donor molecule to the donor atom. In this way the electron density at the donor atom is increased with appropriate changes of fractional nuclear charges in other areas of the donor component. As delineated in Fig.VI-7, the oxygen atoms around lacuna in PMo_{11} fill with the electron donor ability and by means of taking in(or off) one molybdenum ion, PMo_{11} being in equilibrium state with PMo_{12}. When a complexed metal ion is enclosed in the lacuna, it is combined with "unsaturated" oxygen atoms and so the electronic charge tranfer reaction goes from donor atom to acceptor one through the X-O bond. Then, the electron density at O_A atom, O_A being the oxygen atom of the central PO_4 tetrahedron, is increased by the pileup effect and thereby the remaining three oxygen atoms of tetrahedron are also subjected to the induced secondary effect. The larger

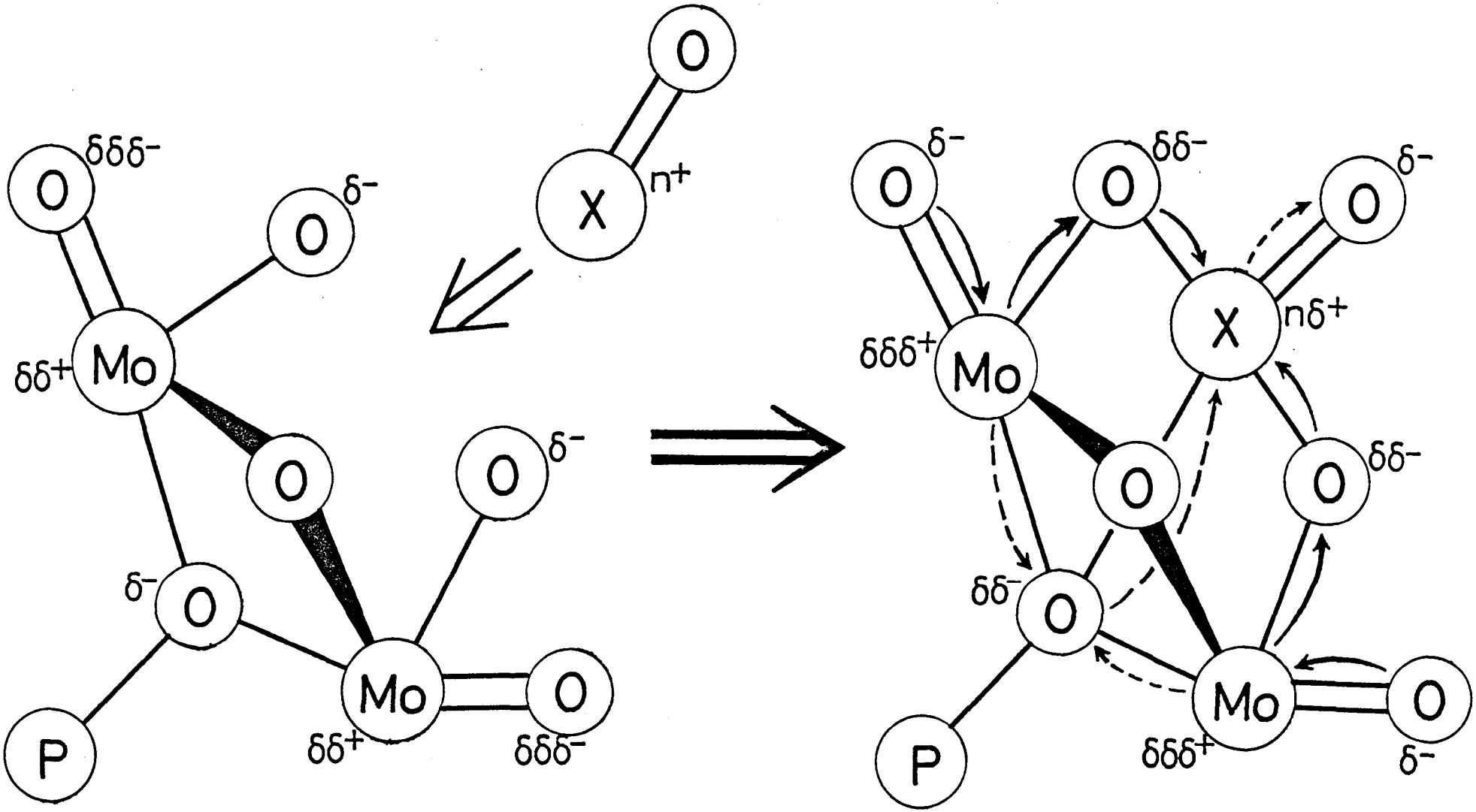


Fig VI-7. Schematic diagram of the 'pileup effect'.

electron acceptor property the complexed metal ion has, the stronger donor-acceptor interaction it induces and as the result, the larger the pileup effect is caused the oxygen atoms surrounding phosphorus one. As far the quantitative characterization of acceptor properties of cations, however, it is very difficult to measure directly because these depend to a great extent on their specific solvation. The stronger the cation is coordinated either by solvent molecules or by solutes, the weaker the acceptor property of the cation. In the past, it has been said that the general trend of acceptor properties of cations in a given medium might be derived approximately by comparing hydration energies and acidity constants of the hydrated cations in water. In 1973, Schlosser(10) had reported, from various chemical observations, that there was much agreement with the following order of acceptor properties for uni- and divalent cations:

$$Bu_4N^+ < Pr_4N^+ < Et_4N^+ < Me_4N^+ < Cs^+ < Rb^+ < K^+ < Ba^{2+} < Sr^{2+} < Na^+ < Ca^{2+} < Li^+ < Mg^{2+} < Be^{2+} < Zn^{2+} < Cu^{2+}$$

The present results obtained by NMR technique are listed in Table VI-2, in which these elements are numbered in sequence to indicate the order of chemical shift from low to high field. Taking into account his proposal, it could be safe to say that the order of chemical shifts agrees with that of acceptor properties for group 4A and 5A elements. Nevertheless Hf(IV) and Ta(V) have similar ionic and atomic

radii to those of Zr(IV) and Nb(V) respectively, the peak shifts for $PHfMo_{11}$ and $PTaMo_{11}$ at higher field, compared with those for $PZrMo_{11}$ and $PNbMo_{11}$, are ascribed to increasing the acceptor properties of Hf(IV) and Ta(V) ions by the effect of the lanthanide contraction.

Table VI-1. Correlation between Chemical Shift and The Periodic Table

	4A	5A	6A
	4 Ti(0.68)	8 V(0.59)[a]	
	3 Zr(0.79)	5 Nb(0.69)	7 Mo(0.62)
2 Ce(0.92)	6 Hf(0.78)	9 Ta(0.68)	W(0.62)
	1 Th(1.02)		

a) Radius in Å

The order of acceptor properties for cations;

Th(IV) < Ce(IV) < Zr(IV) < Ti(IV) < Nb(V) < Hf(IV)
< Mo(VI) < V(V) < Ta(V)

*Cs(I) < Rb(I) < K(I) < Ba(II) < Sr(II) < Na(I) < Ca(II)
< Li(I) < Mg(II) < Be(II) < Zn(II) < Cu(II)

(Schlosser, 1973)

VI - 3. References

1) N.Muller, P.C.Lauterbur, and J.Goldenson, J.Am.Chem.Soc., 78,3557(1955).

2) R.Wolff and V.R.Radeglia, Z.Phys.Chem.,(Leipzig) 261,726(1980).

3) T.Weller, D.Deininger, and R.Lochman, Z.Chem., 21,105(1981).

4) V.R.Radeglia and A.R.Grimmer, Z.Phys.Chem.,(Leipzig) 263,204(1982).

5) J.H.Letcher and J.R.Van Wazer, J.Chem.Phys., 44,815(1966).

6) J.H.Letcher and J.R.Van Wazer, Top.Phosphorus Chem., 5,75(1967).

7) V.V.Serebrennikov, Soobshch.oNauchn.Rabotakh Chlenov Vses. Obshchestva im D.I.Mendeleeva, No.1,50(1953).

8) I.P.Alimarin, Z.F.Shakhova, and F.P.Sudakov, "Omaglu acad. prof Raluca Ripon", Ed. Academiei Republicii Socialiste Romania. pp.37(1966).

9) V.Gutmann, Rev.Ronm.Chim., 22,619(1977).

10) M.Schlosser, "Struktur und Reaktivitat polarer Organometalle", Springer, Berlin/Heidelberg/New York.

Acknowledgement

The author would like to express his sincere gratitude to Professor Shigero Ikeda for his cordial guidance, discussion, and support in coordinating this work.

The author also wishes to express his sincere thanks to Dr. Katsuo Murata for helpful suggestion and encouragement.

The author wishes to express his thanks to Jun Iyoda of Government Industrial Research Institute Osaka for his help with NMR measurement.

The author is grateful to many members of Ikeda Laboratory for their useful discussions and encouragements.

The author would also like to thank all his friends for their considerate encouragements.

Finally, the author would like to dedicate to his father and mother.

List of Publications

1. "Simultaneous Determination of Titanium, Zirconium, and Hafnium in Aqueous Solution by Phosphorus-31 Nuclear Magnetic Resonance Spectrometry"
   T.Fukkumoto, K.Murata, and S.Ikeda, Anal.Chem., 56,929(1984).
2. "Simultaneous Determination of Group 5A Elements in Aqueous Solution by Phosphorus-31 Nuclear Magnetic Resonance Spectrometry"
   T.Fukumoto, J.Iyoda, K.Murata, and S.Ikeda, Chem.Lett., 1311(1985).
3. "Simultaneous Determination of Metal Ions by Phosphorus-31 Nuclear Magnetic Resonance Spectrometry -2. Determination of Group 5A Elements and Interpretation of Chemical Shifts"
   T.Fukumoto, J.Iyoda, K.Murata, and S.Ikeda, Anal.Chem., in submitted.
4. "Studies on Ternary Heteropoly Molybdates by Extended X-Ray Absorption Fine Structure Analysis"
   T.Fukumoto, N.Matsubayashi, K.Murata, and S.Ikeda, Inorg.Chem., in submitted.
5. "Separation of Ternary Heteropoly Molybdates by Ion-Pair Reversed Phase Liquid Chromatography"
   T.Fukumoto, K.Murata, and S.Ikeda, Anal.Sci., in submitted.

Appendix

Qualitative Studies on the Phosphate - Molybdate Systems in Aqueous Medium

I. pH Dependence of Formation

To elucidate the formation process of 12-molybdophosphate(noted as PMo_{12}), pH dependence of mixed solution(phosphate plus molybdate) was examined by use of ^{31}P NMR technique. In earlier investigations, the stoichiometric and continuous variations experiment on the PMo_{12} equilibrium were performed by Crouch et al.(1,2). They had studied the kinetics of the formation and decomposition of PMo_{12} by use of the stopped-flow method. For kinetics of the formation of PMo_{12}, the maximum PMo_{12} formation rate varied with H^+ and Mo(VI) species concentrations larger than with C_H or C_{Mo} in a complex manner, even though the dependence of the rate on the phosphate concentration was a simple first-order dependence. In addition, they had determined the PMo_{12} equilibrium constant from experimental data obtained with Job's method of continuous variation and from computer simulation, and obtained a good match between the experimental data and calculations by the postulation of the occurrence of two additinal molybdophosphates, 11-molybdophosphate(PMo_{11}) and 9-molybdophosphate(PMo_9), in equilibrium state with PMo_{12}. In this work, in weak acidic solution(pH near 2.5) only one

peak was observed, while the peak for PMo_{12} could not been observed at the pH, and as the result of stoichiometrical analysis its heteropoly molybdate was found to consist of a molar ratio, P:Mo = 1:9. The PMo_9 readily dimerized(3) and produces 18-molybdodiphosphate(P_2Mo_{18}), which is called the Dawson structure(4), in acidic solution;

$$2[PMo_9O_{31}(OH_2)_3]^{3-} \rightleftharpoons P_2Mo_{18}O_{62}^{6-} + 6H_2O$$

For these reasons, its peak was assigned to P_2Mo_{18} and its heteropoly molybdate, instead of PMo_9, was used to elucidate the formation process in this work. A series of experiments with the variation of temperature provided only the changes of the integral intensity of two peaks, which are assigned to P_2Mo_{18} and PMo_{12}, and not the shift of peak position and the occurrence of a new peak in NMR spectra. No evidence for such dimeric reaction was found in this work, although PMo_9 anion may well exist. The peak of P_2Mo_{18} was shown a slight broadening one compared with that of PMo_{12}. Since P_2Mo_{18} consists of two PMo_9 half anions, two phosphorus atoms may have slightly different chemical shifts. However, it was impossible to separate each other in this NMR instrument.

In near neutral solution, as shown in Fig.VII-1a, phosphate did not react with isopoly molybdate and no molybdophosphate was observed yet. When an acid was added, near pH 5, two kinds of molybdophosphate formed, which are assigned to 5-molybdodiphosphate(P_2Mo_5), -13.6 ppm, and to P_2Mo_{18}, -15.0 ppm. Upon continued addition the peak for

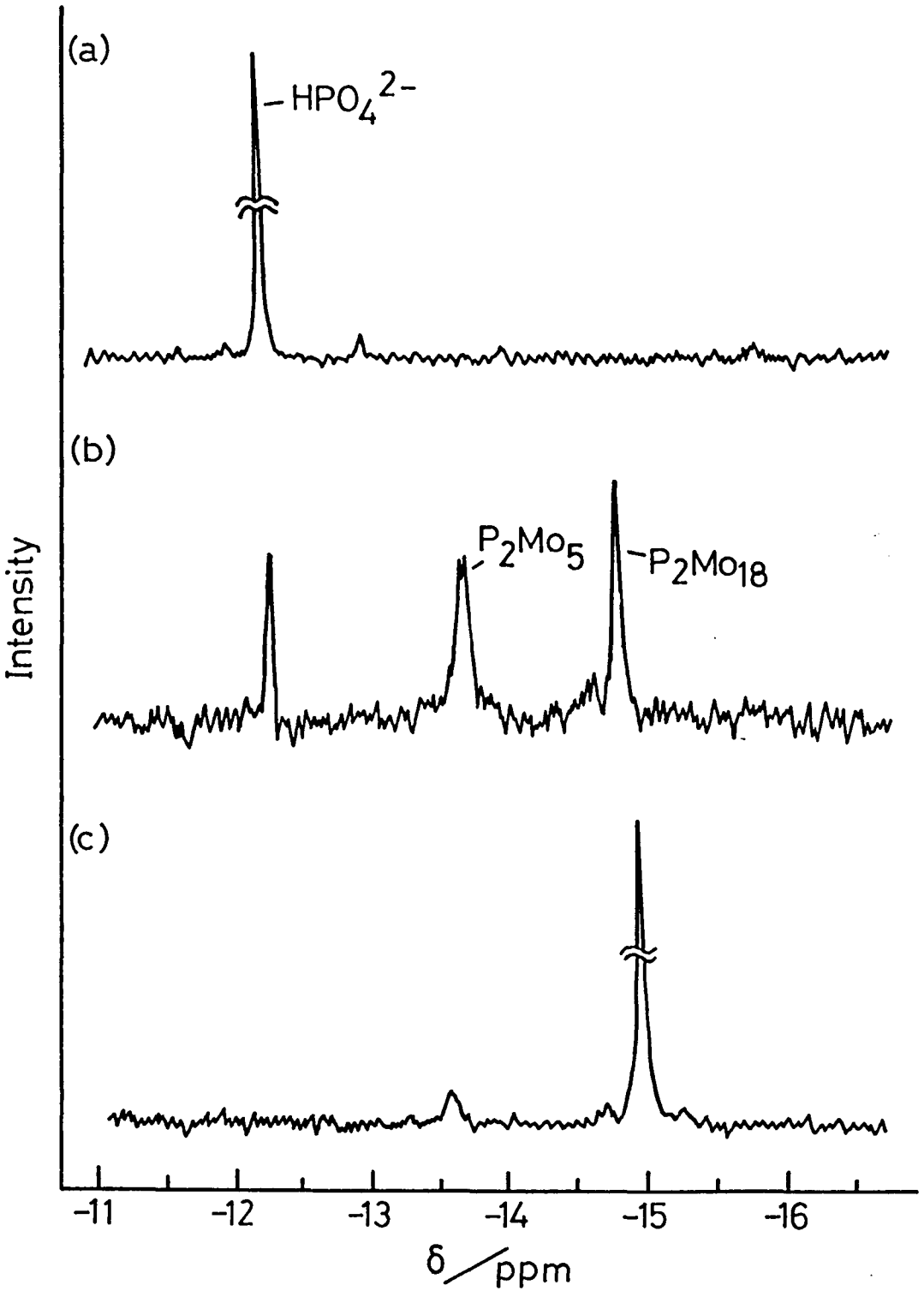


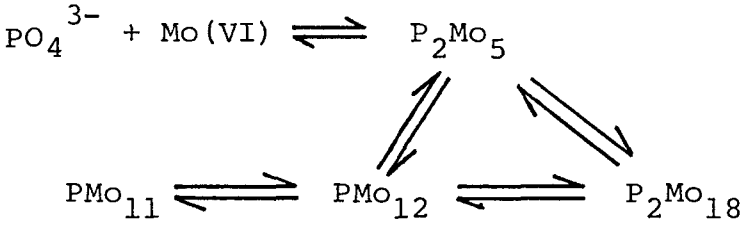
Fig VII-1. Effect of pH of the KH_2PO_4 - Na_2MoO_4 aqueous system by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$ (mol dm^{-3})

(a) pH 5.95 (b) pH 4.94 (c) pH 3.64

P_2Mo_5 disappeared and only one peak assigned to P_2Mo_{18} was observed at pH 2.72 (see Fig.VII-2d). When the acid was further added, new two peaks were observed, which are assigned to H_3PO_4 at lower field and to PMo_{12} at higher field (see Fig.VII-2e). The peak for P_2Mo_{18} decreased gradually with increasing acidity and the peak for PMo_{12} was observed intensely at pH 1-0.5 (see Figs.VII-3g and VII-3h). With increasing acidity, however, it was caused the decomposition of PMo_{12} and promoted the appearance of P_2Mo_5 again(see Fig.VII-3i).

In light of the above data, with addition of the results of Raman measurement(5), the formation of 12-molybdophosphate could be considered as follows: at first, by addition of an acid polymerization of molybdate is caused and several isopoly molybdates are produced in solution. One or more kinds of isopoly molybdates [Mo(VI) species] are labilized with phosphate and some heteropoly molybdates are formed.



The stability of each heteropoly molybdate was observed to depend on the concentration of H^+, under the condition of

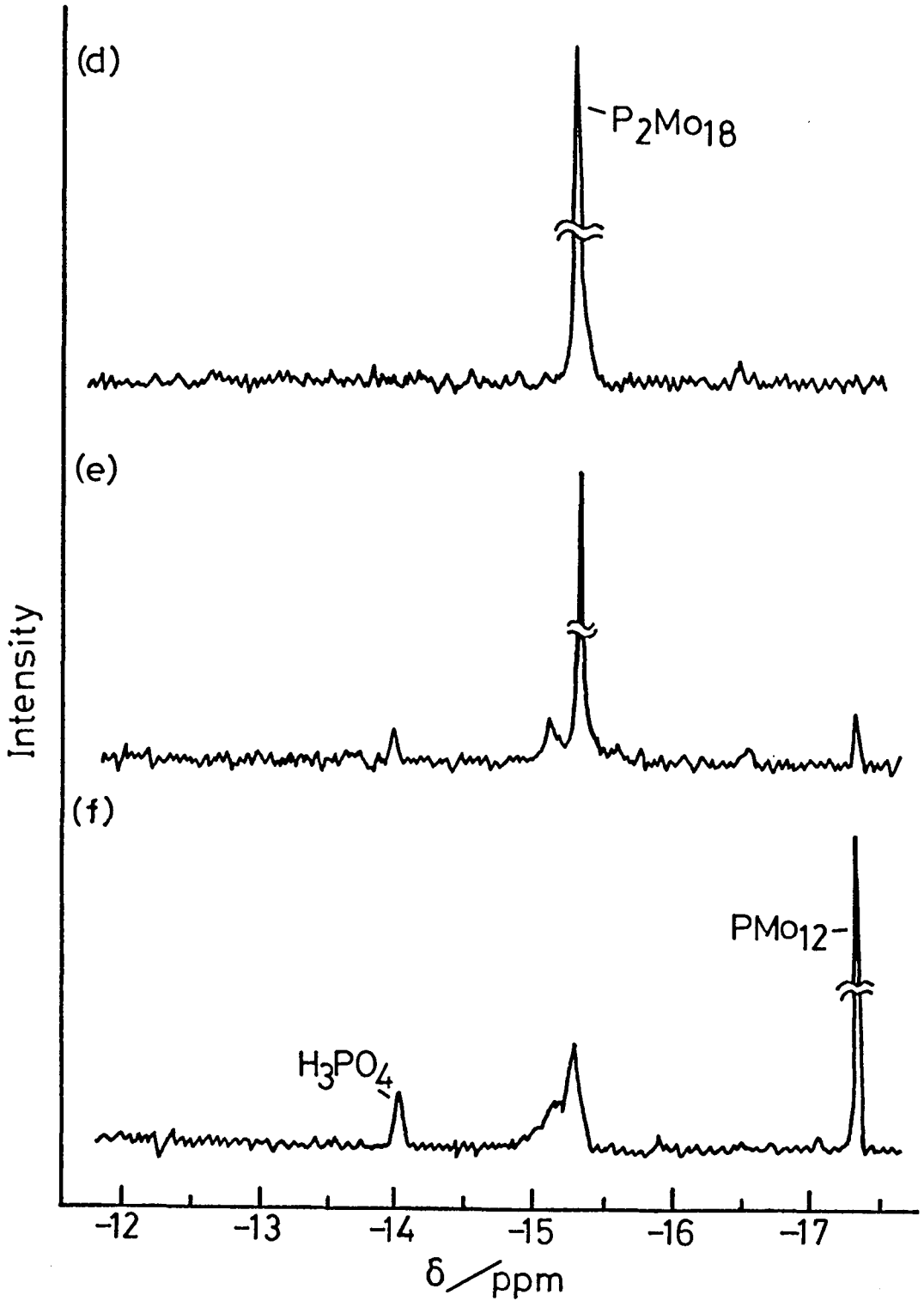


Fig VII-2. Effect of pH of the KH_2PO_4 - Na_2MoO_4 aqueous system by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$ (mol dm^{-3})

(d) pH 2.72 (e) pH 1.63 (f) pH 1.26

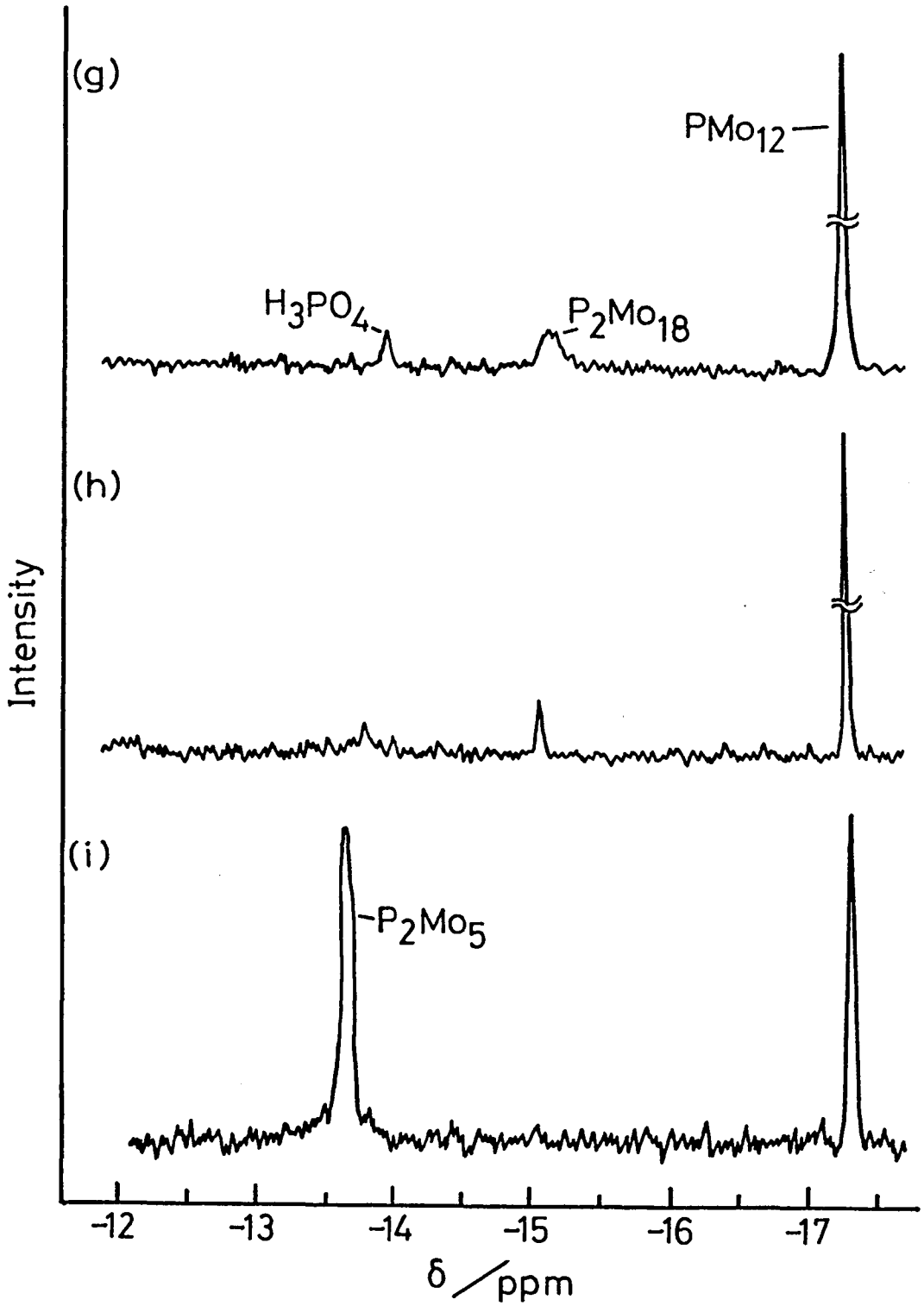


Fig VII-3. Effect of pH of the KH_2PO_4 - Na_2MoO_4 aqueous system by ^{31}P NMR spectra.

$C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.5 \times 10^{-1}$ (mol dm^{-3})

(g) pH 1.07 (h) pH 0.60 (i) pH 0.36

constant concentrations of phosphate and molybdate.

II. Formation of Colorless Molybdophosphate

The formation of molybdophosphate was examined at a constant pH of 1.0 and molybdate concentration of 1.2×10^{-1} mol dm^{-3}, the phosphate concentration being changed from 1.0×10^{-2} to 1.7×10^{-1} mol dm^{-3}. As a result, it was found that excess phosphate reacted with 12-molybdophosphate(PMo_{12}) to yield colorless complex. Thus, as shown in Fig.VII-4, at first the peak for PMo_{12} decreases gradually with increasing the phosphate concentration, while that for 18-molybdodiphosphate(P_2Mo_{18}) increases and a new broaden peak at -13.7 ppm, which is assigned to colorless heteropoly molybdate, appears in NMR spectra. Continuous addition of phosphate led to decreasing P_2Mo_{18} and to remarkable increasing of the new peak. In earlier investigations, it has been pointed out that some colorless molybdophosphate complexes may exist in equilibrium with PMo_{12} in aqueous solution(6-9). In parallel with these studies in solution, colorless molybdate complexes have been investigated in the solid state(10,11) and the crystal structure of 5-molybdodiphosphate(P_2Mo_5), $P_2Mo_5O_{23}^{6-}$, had been first reported by Strandberg(12). In light of the above results, a new peak was assigned to P_2Mo_5 and from the established NMR spectra, a reasonable interpretation could be deduced regarding with the formation of the colorless molybdophosphate. In aqueous solution the following

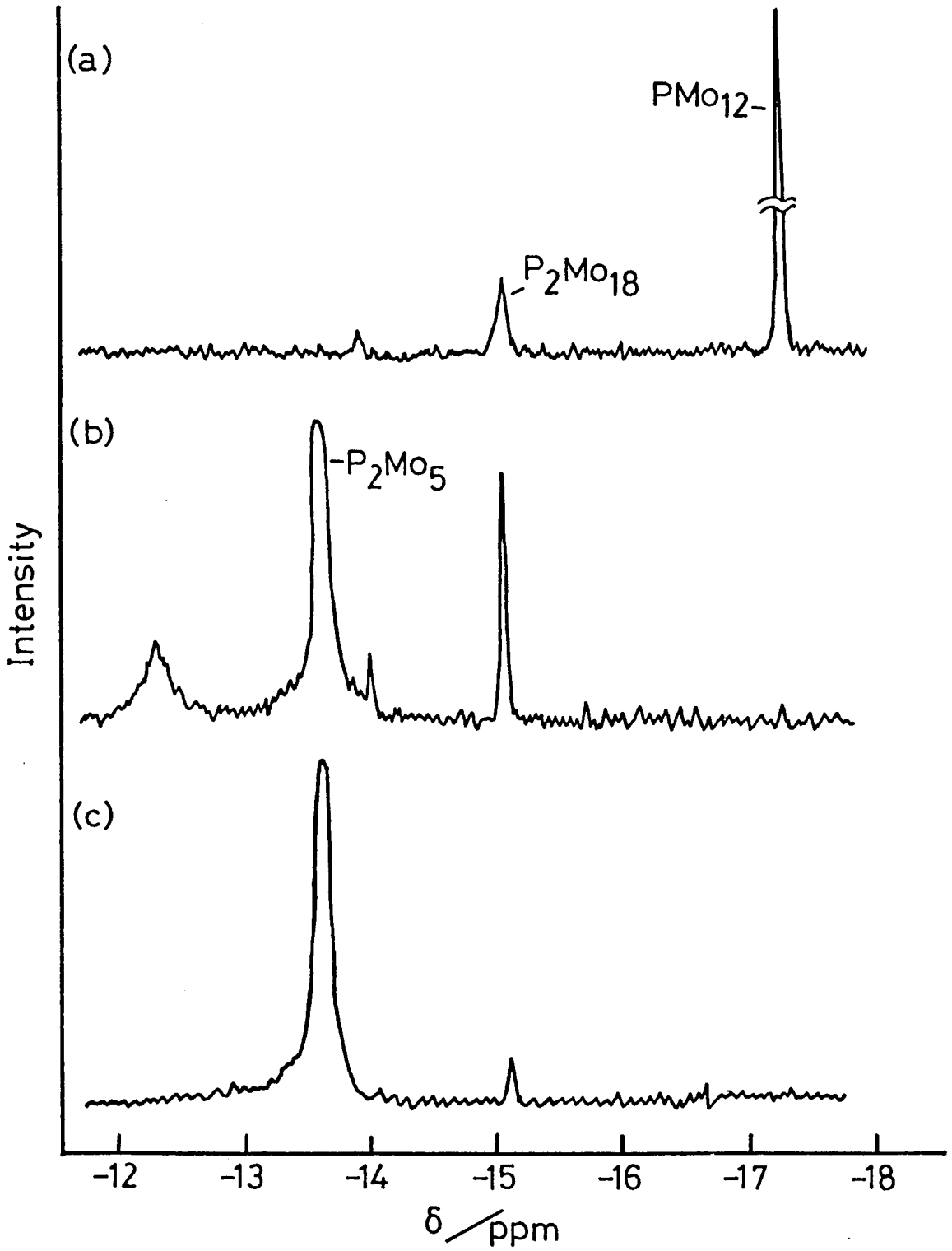


Fig VII-4. Effect of an excess of phosphate in ^{31}P NMR spectra.

(a) $C_P = 1.0 \times 10^{-2}$ $C_{Mo} = 1.2 \times 10^{-1}$

(b) $C_P = 6.0 \times 10^{-2}$ $C_{Mo} = 1.0 \times 10^{-1}$

(c) $C_P = 7.0 \times 10^{-2}$ $C_{Mo} = 5.0 \times 10^{-2}$

(mol dm^{-3}) pH 0.9 - 1.0

subsequent reaction steps are considered:

$$P_2Mo_{18}O_{62}^{6-} + Mo(VI) \rightleftharpoons PMo_{12}O_{40}^{3-} \quad (1)$$

$$PO_4^{3-} + 3PMo_{12}O_{40}^{3-} \rightleftharpoons 2P_2Mo_{18}O_{62}^{6-} \quad (2)$$

$$26PO_4^{3-} + 5P_2Mo_{18}O_{62}^{6-} \rightleftharpoons 18P_2Mo_5O_{23}^{6-} \quad (3)$$

Thus the formation of colorless molybdophosphate does not occur directly from the dissociation of PMo_{12}, but does through the formation of P_2Mo_{18} intermediate.

III. EXAFS Measurement

Fourier transforms of EXAFS of Mo atom for isopoly and heteropoly molybdates, with the addition of its MEM analysis are shown in Fig.VII-5. Each figure for the present EXAFS results contains both FT and MEM spectra on the left and the right side, respectively. Near neutral solution, at pH 5.2, the polymerization of molybdates was not found and only monomer one was observed. The peak at 1.75 Å corresponds to the Mo-O distance in MoO_6 octahedron. Increasing acidity, the polymerization of molybdates led to a few new peaks and these peaks indicated Mo-Mo distances, about 3.1 - 3.5 Å. Since in acidic solution octamer or heptamer isopoly molybdate may be perhaps formed, these peaks were pertained to them. On the other hand, with respect to heteropoly molybdates P_2Mo_{18} was formed in weak acidic solution. As shown in Fig.VII-5c, Fourier transform of Mo atom for P_2Mo_{18} which consists of two PMo_9 half anions was shown a similar spectrum to that of the above isopoly molybdate, but the Mo-O distance of P_2Mo_{18}(1.68 Å) was shorter than that of isopoly molybdate(1.74 Å). This indicates that the formation of heteropoly molybdate leads to more stable framework, compared with isopoly molybdate one. This is also confirmed with the results of Raman measurement(13), in which Mo=O stretching vibration shifts to higher wave number as the formation of ternary heteropoly molybdate. The EXAFS spectra also gave a

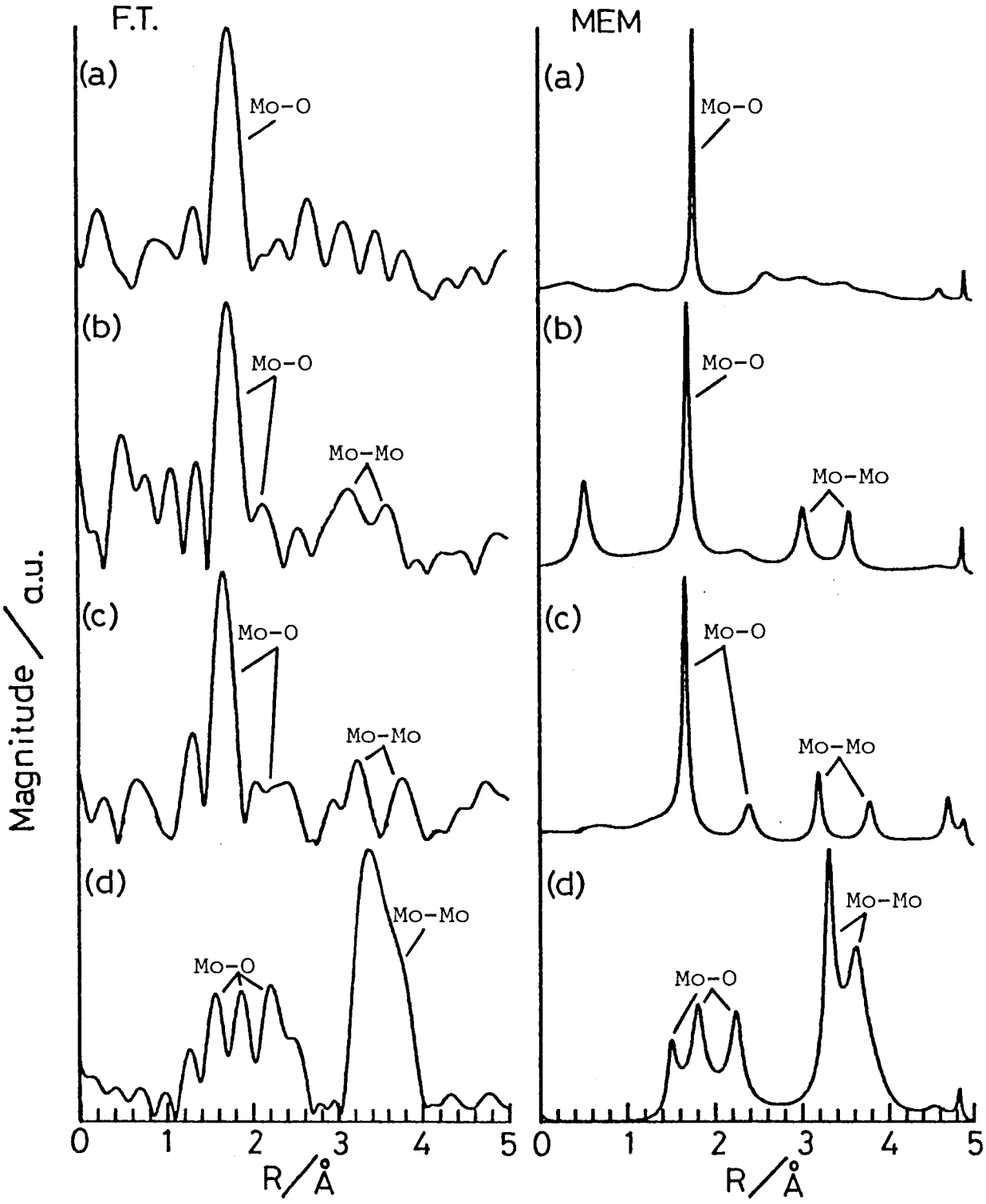


Fig VII-5. Fourier transform(left) and MEM(right) spectra of EXAFS of Mo atom.

(a) Na_2MoO_4 sln(pH 5.2). (b) Na_2MoO_4 sln(pH 1.0).

(c) P_2Mo_{18} sln. (d) PMo_{12} sln.

(c),(d) $C_P = 1.5 \times 10^{-2}$ (a)-(d) $C_{Mo} = 2.0 \times 10^{-1}$ (mol dm^{-3})

result to reproduce the x-ray diffraction data by Strandberg(14). In more acidic solution, P_2Mo_{18} is gradually converted into PMo_{12} as shown in above NMR measurement. Fourier transform of Mo atom for PMo_{12}, which has the Keggin structure, is shown in Fig.VII-5d. The obtained results are very similar to those of x-ray diffraction analysis(15). Thus in edge-sharing MoO_6 octahedra the Mo-Mo distances are about 3.4 Å, while in corner-sharing octahedra the distances increase to near 3.7 Å. The peaks of Mo-O distances can be divided into three groups. According to x-ray analysis, based on the number of atoms to which the oxygen atom is coordinated, these groups were assigned as follows:

1) about 1.58 Å, to only one Mo atom($O_{terminal}$)

2) 1.85 - 1.95 Å, to two Mo atoms(O_{cis})

3) about 2.4 Å, to P atom and to three Mo atoms(O_{trans}).

This agreement supports experimentally that a given species in solution, nevertheless it is solvated, keeps the same or similar structure to that in crystal. In addition, XANES spectra are shown that in heteropoly molybdates as well as isopoly those consist of same MoO_6 octahedron units (see Fig.VII-6). The spectrum of P_2Mo_{18}, however, gives a somewhat different feature, as compared with that of PMo_{12}, in spite of the constitution of same MoO_6 octahedron unit shown in XANES spectra. Thus the peak at near 1.6 Å corresponding to the Mo-$O_{terminal}$ shows stronger intensity, while the peaks at near 3.4 and 3.7 Å corresponding to the

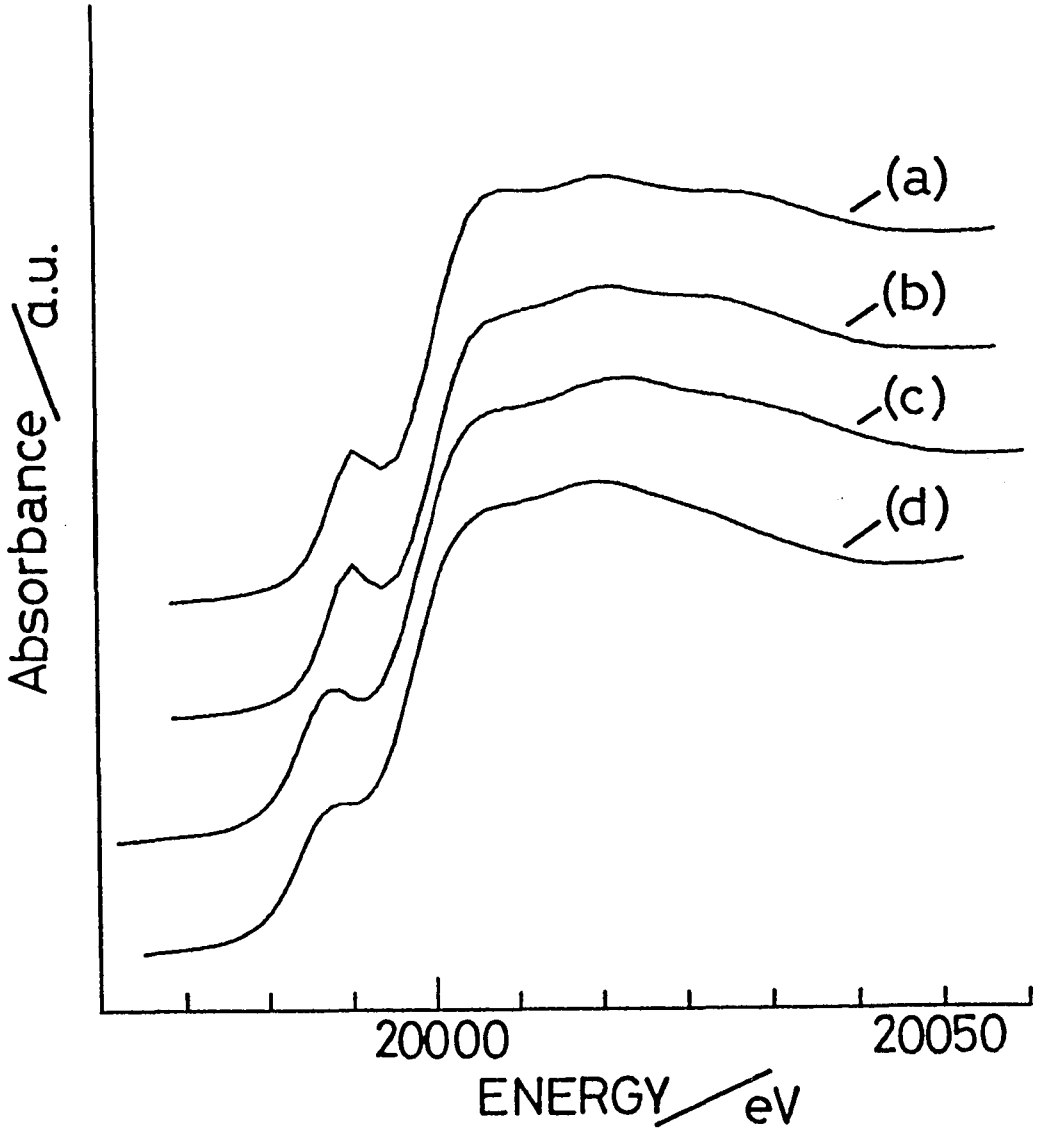


Fig VII-6. Mo K-edge XANES spectra.

(a) Na_2MoO_4 sln(pH 5.2). (b) Na_2MoO_4 sln(pH 1.0).

(c) P_2Mo_{18} sln. (d) PMo_{12} sln.

(c),(d) $C_P = 1.5 \times 10^{-2}$ (a)-(d) $C_{Mo} = 2.0 \times 10^{-1}$ (mol dm^{-3})

Mo-Mo distances are weaker. These results are reverse to that of PMo_{12}. According to x-ray structural analysis of $Na_6P_2Mo_{18}O_{62}.24H_2O$, P_2Mo_{18} retains the structure consisted of the distorted monomer units and has the Dawson structure. However, it is impossible to interpret this difference reasonably at present.

IV. References

1) S.R.Crouch and H.V.Malmstadt, Anal.Chem., 39,1084(1967).

2) C.C.Kircher and S.R.Crouch, Anal.Chem.,54,879(1982).

3) L.Pettersson, Acta.Chem.Scand.,A29,677(1975).

4) B.Dawson, Acta.Cryst.,6,113(1953).

5) K.Murata and S.Ikeda, Polyhedron.,2,1005(1983).

6) A.Miolati and R.Pizzighelli, J.Pract.Chem., 77,417(1908).

7) P.Souchay and J.Faucherre, Bull.Soc.Chim.,355(1951).

8) C.Ferrari, Mikrochim Acta., 551(1956).

9) K.Murata and T.Kiba, J.Inorg.Nucl.Chem., 32,1667(1970).

10) C.Friedheim and J.Meschoirer, Z.Anorg.Allg.Chem., 6,27(1894).

11) J.W.Mellor, "A Comprehensive Treaties on Inorganic and Theoretical Chemistry" Vol.11,pp.659, Longmans, London (1931).

12) R.Strandberg, Acta.Chem.Scand., 27,1004(1973).

13) K.Murata, Ph.D.Thesis, Osaka University,(1982).

14) R.Strandberg, Acta.Chem.Scand., A29,350(1975).

15) R.Strandberg, Acta.Chem.Scand., A29,359(1975).