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Stereoisomers of Cobalt(III) Complexes with the Bi- or Tridentate Ligands Containing a Thioether Donor Atom

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Contents

Introduction

A large number of cobalt(III) complexes which contain halogeno[1)] or cyano[2)] ligands, or ligands having the oxygen[3)] or nitrogen[4)] donor atoms have been prepared, and their absorption (AB) and circular dichroism (CD) spectra have been investigated in detail, whereas a little has been known for the cobalt(III) complexes having the sulfur[5-33)] donor atoms, especially the complexes having thioethers.[5-8, 14-20, 23-33)] This is partly because thioethers do not coordinate very strongly to metals, apart from Pt(II), Pd(II), Ir(III), Rh(III) and Hg(II) which are so-called class (b) metals[34)] and form the most stable complexes with the second or subsequent ligating atoms of the Periodic Table, and partly because the available ligands[35-37)] are also less than those containing oxygen or nitrogen atoms.

For the complexes containing sulfur donor atoms, there are some characteristics, compared with those having nitrogen or oxygen donor atoms. Firstly, sulfur has vacant d_π orbitals which can be used for d_π-d_π bonding with the later transition metals in their normal oxydation states, while, except for special cases, oxygen and nitrogen have no orbitals available to accept electrons from suitably placed filled d-orbitals on the central metal atom. Secondary, in the spectrochemical series, sulfur seems to have a wide range of ligand field strength[38)]; sulfite ion (SO_3^{2-}) has a rather high position in the series near NO_2^-, thioether (R_2S) is between H_2O and NH_3, and mercaptide ion (RS^-) falls close to iodide. The principal difference between thiols and thioethers as ligands has been considered to be that the former are more highly polarisable but not as effective d_π electron acceptors as the latter.39,40) Thirdly, extreme geometric specificity has been found for the complexes with sulfur donor atoms.15,17-19,33) Fourthly, the sulfur donor atom has a single lone-pair which can give a fixed configuration for the asymmetric donor center at ordinary temperature. This was shown by the optical resolution of $[Pt(IV)(NH_2CH_2CH_2SCH_2CH_2NH_2 \cdot HCl)Cl_4]$ which has the asymmetry solely arising from the sulfur donor atom.41) No tertiary amine has been resolved because of the very rapid interconversion and therefore asymmetric nitrogen atom exists only as quaternary ammonium form.

The present work is concerned with the cobalt(III) complexes containing a thioether donor atom. So far, some dozen cobalt(III) complexes containing thioethers have been prepared but the presence of thioether donors appears to induce an extreme geometric specificity, even in such cases that some geometrical isomers are theoretically possible. Recently, bis(tridentate) type cobalt(III) complexes with L-methioninate29) or S-methyl-L-cysteinate30) were prepared and three geometrical isomers have been obtained by J. Hidaka et al., which is first example for the isolation of all possible isomers. Therefore, the absorption spectral investigation for the various cobalt(III) complexes with thioether donors are still insufficient.

Furthermore, in most complexes containing thioethers, the sulfur atoms become asymmetric by coordination to the Co(III) ion. However, the CD contribution due to the asymmetric sulfur donor atom has never been studied for the cobalt(III) complexes. On the other hand, investigations for the vicinal CD due to the asymmetric carbon$^{42-47)}$ and nitrogen atoms$^{48-53)}$ have been considerably undertaken and these results have indicated that the vicinal dissymmetry make a relatively smaller CD contribution than the configurational one. Therefore, it is worthy to investigate this respect for the cobalt(III) complexes containing thioethers.

In this work, the complexes of $[Co(N)_5(S)]$, $[Co(N)_4(S)(O)]$ and $[Co(N)_2(S)_2(O)_2]$ types were prepared, optically resolved and/or separated into the geometrical isomers, and their absorption, circular dichroism, infrared and pmr spectra were discussed.

Purpose of this work:

(1) to prepare new cobalt(III) complexes containing thioether ligands (especially N,S,O-tridentate one), to separate as many isomers as possible, to resolve them into optical antipodes, and to decide their structures,

(2) to study their absorption and CD spectra in the first absorption band region and thioether charge transfer band region, to relate AB and CD spectra to their geometrical structures, and to decide their absolute configurations,

(3) to explore the stereochemistry of the N,S,O-tridentate ligands producing a five-membered chelate ring or a six-membered one,

(4) to isolate diastereomers arising from the asymmetric sulfur donor and to estimate the vicinal CD contribution due to the sulfur donor atom.

Abbreviations of Ligands.

en··········ethylenediamine, $H_2NCH_2CH_2NH_2$
tame·······1,1,1-tris(aminomethyl)ethane, $CH_3C(CH_2NH_2)_3$
mea·H ·····2-mercaptoethylamine, $HSCH_2CH_2NH_2$
ams·········2-aminoethyl methyl sulfide, $CH_3SCH_2CH_2NH_2$
aes·········2-aminoethyl ethyl sulfide, $CH_3CH_2SCH_2CH_2NH_2$
mms·H ·····carboxymethyl methyl sulfide, $CH_3SCH_2CO_2H$
ems·H ·····carboxyethyl methyl sulfide, $CH_3SCH_2CH_2CO_2H$
acms·H ····2-aminoethyl carboxymethyl sulfide,
$NH_2CH_2CH_2SCH_2CO_2H$
aces·H ····2-aminoethyl carboxyethyl sulfide,
$NH_2CH_2CH_2SCH_2CH_2CO_2H$
L-smc·H ···S-methyl-L-cysteine, $CH_3SCH_2CH(NH_2)CO_2H$
L-met·H ···L-methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$
edth·H_2 ···(ethylenedithio)diacetic acid,
$HO_2CCH_2SCH_2CH_2SCH_2CO_2H$.

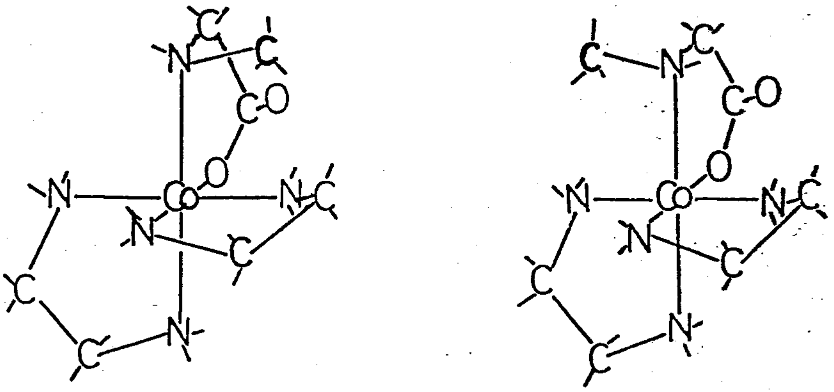
I. A General Consideration of Steric Isomers of Complexes

I-A. Stereochemistry of $[Co(en)_2(\overline{ab})]^{n+}$ Complexes

Absorption and CD spectra for the complexes of the general type $[Co(en)_2(\overline{ab})]^{n+}$, where $\overline{ab}$ is a unsymmetrical bidentate ligand, have been studied extensively.48,54,55) The unsymmetrical bidentate ligands used in this work are classified into two groups. The first one is mea (2-mercaptoethylamine), which contains a thiolo group. For a complex of this ligand, there is a chirality due to the skew pair of chelate rings (=configurational dissymmetry). The second group is ams(2-aminoethyl methyl sulfide), aes (2-aminoethyl ethyl sulfide), mms(carboxymethyl methyl sulfide) and ems(carboxyethyl methyl sulfide), which possess a thioether donor. When these ligands coordinate to a Co(III) ion, it is formally expected that the sulfur atom of the ligand becomes optically active (=vicinal dissymmetry). Therefore, both the dissymmetry about the Co(III) ion and about the coordinated sulfur atom contribute to the CD spectra.

The similar problem raises to the complexes with the asymmetric donor nitrogen atom. In the $(+)_{589}$-$[Co(en)_2(sar)]^+$ system48), where sar is N-methylglycinate, D. A. Buckingham et al. found that sarcosonate is coordinated stereospecifically (Λ-R for $(+)_{589}$-complex); namely, molecular models show that Λ-S configuration, where the methyl group interacts strongly with the adjasent en-ring, should be configurationally less stable than the Λ-R form, where the methyl group is positioned between the two rings and the nonbonded atomic interaction are thereby reduced (Figure 1).

These circumstances are the same for the present complexes containing a thioether donor atom. Therefore, it is worthy to investigate whether the ligands containing a thioether donor atom are coordinated stereospecifically or not.



Λ-S

Λ-R

Figure 1. The configurations of coordinated sarcosinate in the Λ-$[Co(en)_2(sar)]^{2+}$ ion, where absolute configurations, Δ or Λ , are assigned according to the IUPUC rules as described in *Inorg. Chem.*, 9, 1(1970).

I-B. Stereochemistry of [Co(tame)(N,S,O-tridentato)] Type Complexes

1,1,1-Tris(aminomethyl)ethane (tame) is a typical tripod ligand and coordinates facially to a Co(III) ion. When three remaining coordination site is occupied by the N,S,O-tridentate ligand, another kind of chirality due to the arrangement of three different donor atoms is expected

(=configurational dissymmetry, Figure 2). This kind of chirality was already reported by the author et al.56) and Hosokawa et al.57)

In the present system, however, further origin of optical activity is added: for the complex with 2-aminoethyl carboxymethyl sulfide (acms) or 2-aminoethyl carboxyethyl sulfide (aces), important contribution to optical activity due to the coordinated asymmetric sulfur atom (=vicinal dissymmetry) is expected, though this effect is associated with configurational one and cannot be separable with it. These results will be compared with the related complex $[Co(tame)(L\text{-}smc)]^{2+}$, which shows absolute stereospecificity because of the S-methyl-L-cysteinate (L-smc) ligand.

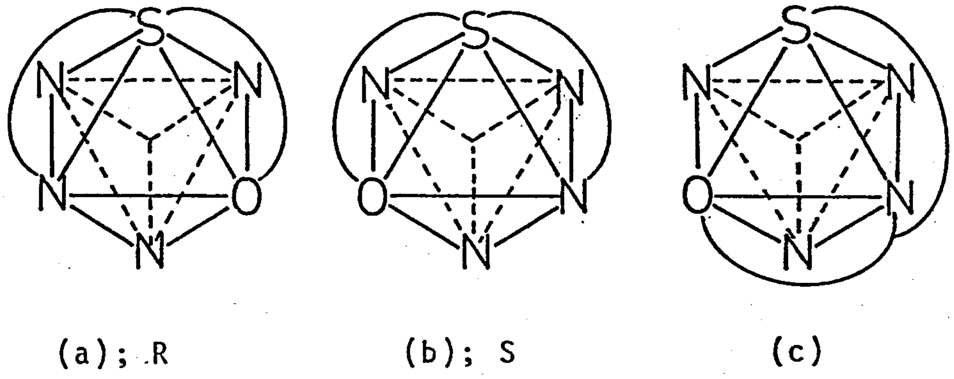
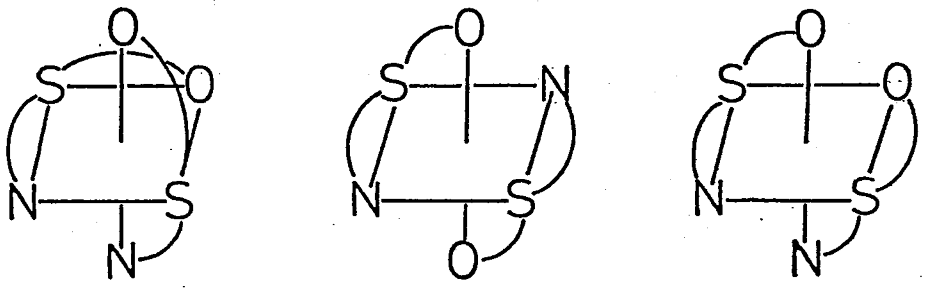


Figure 2. Optical isomers of $[Co(tame)(N,S,O\text{-tridentato})]^{2+}$ [(a) and (b)], and the structure of $[Co(tame)(L\text{-}smc)]^{2+}$ [(c)].

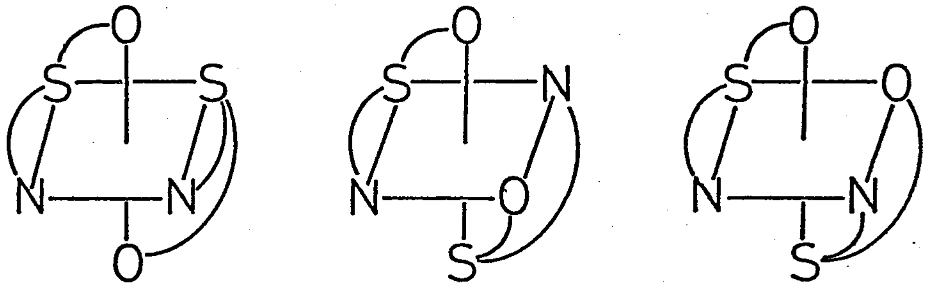
I-C. Stereochemistry of $[Co(N,S,O\text{-tridentato})_2]^+$ Type Complexes

For the complexes of $[Co(L\text{-}met)_2]^+$ (L-met = L-methio L-methioninate) and $[Co(L\text{-}smc)_2]^+$, three geometrical isomers, trans(S), trans(O) and trans(N), are possible, because the optically active tridentate aminoacid can span only a face.

In the complexes containing linear N,S,O-tridentate ligands (acms·H or aces·H), six geometrical isomers, mer-trans(S), tr.tr.tr., trans(S), trans(O), trans(N) and cisciscis, are possible as is seen in Figure 3.



mer-trans(S) tr.tr.tr. trans(S)



trans(O) trans(N) cisciscis

Figure 3. Six possible geometrical isomers for $[Co(N,S,O\text{-}tridentato)_2]^+$ type complexes.

Of these geometrical isomers, optical antipode exists for five isomers except tr.tr.tr. one which has a inversion center. In addition, two sulfur centers of the N,S,O-tridentate ligands become asymmetric on coordination, though this donor asymmetry depends upon the geometrical structure. That is, trans(S), trans(O) and trans(N) isomers have RR or SS configuration but cisciscis one only RS configuration.

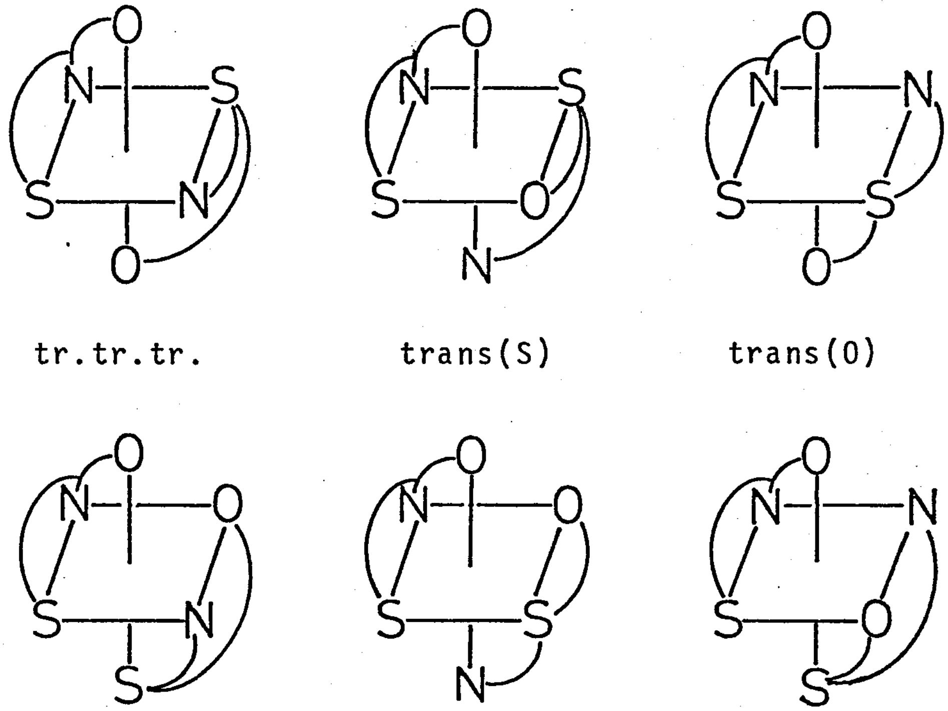
A molecular model examination reveals that acms ligand, which forms two five-membered chelate rings by coordination, strongly prefers the facial coordination, whereas aces one, which forms a five- and a six-membered chelate rings, will enable the existence of meridionally coordinated form. These circumstances seem to be common with the bis(tridentate) type cobalt(III) complexes containing linear O,N,O-tridentate ligands, because meridional isomer has been unknown for the complexes with the two five-membered chelate rings.52,58-60)

I-D. Stereochemistry of [Co(L-met)(N,S,O-tridentato)]$^+$ Type Complexes

In the mixed type complexes, six geometrical isomers, tr.tr.tr., trans(S), trans(O), trans(N), cisciscis-I and cisciscis-II, are possible as is seen in Figure 4. Compared with [Co(N,S,O-tridentato)$_2$]$^+$ complexes, meridional isomer becomes impossible and two cisciscis isomers, cisciscis-I and cisciscis-II, appears for the present mixed type complexes.

In addition, for each of the six geometrical isomers another type of two isomers with respect to the absolute configuration (R or S) of the sulfur donor atom of the L-methioninate moiety are formally expected. This kind of optical isomers have not been isolated. These diastereomeric pairs would be used to investigate the CD contribution due to the asymmetric sulfur donor atom.

For the three geometrical isomers of $[Co(L\text{-}met)_2]^+$ 29) further three isomers, RR, RS and SS, are formally expected because of the same reason. Model construction reveals that the SS-configuration is most probable for trans(S)



tr.tr.tr. trans(S) trans(O)

trans(N) cisciscis-I cisciscis-II

Figure 4. Six possible isomers for $[Co(L\text{-}met)(N,S,O\text{-}tridentato)]^+$ type complexes.

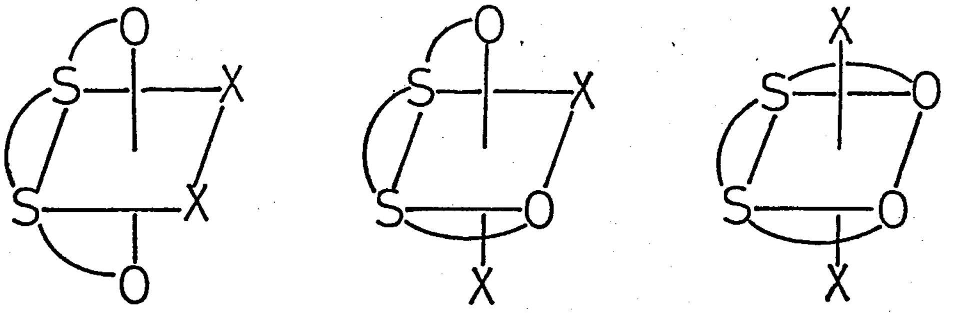
isomer, SS- and SR-configurations for trans(N) isomer, and RR-, SS- and SR-configurations for trans(O) isomer, respectively. The pmr spectra agreed with this expectation.

In the present two mixed complexes, model examination shows that five isomers except for tr.tr.tr. one are expected to prefer S-configuration because of the interaction with the chelate ring of another ligand and tr.tr.tr. one either configuration, though these differences are not very large.

I-E. Stereochemistry of $[Co(edth)(en)]^+$ Complex

The flexible quadridentate ligand (ethylenedithio)diacetic acid ($edth{\cdot}H_2$) having the donor atom sequence oxygen-sulfur-sulfur-oxygen, form monomeric octahedral complexes with Co(III). In principle, metal complexes derived from this ligand can exist in three geometrically isomeric form forms.61,62) These can be designated trans(O), cis(O) and trans(X) (Figure 5). The oxygen atoms are trans to each other in the trans(O) arrangement (I) and cis to each other in the cis(O) configuration (II). In the trans(X) geometry, all four donor atoms of the fused chelate ring system lie in the same plane (III).

In the present work, the only one complex of $[Co(edth)(en)]^+$ was prepared, and its absorption spectrum was used to aid the assignments of the geometrical isomers for the bis(tridentate) or mixed type complexes.



I. trans(O) II. cis(O) III. trans(X)

Figure 5. Three possible isomers for a [Co(edth)(en)] type complex.

II. Experimental

II-A. Preparation of Ligands

(1). 1,1,1-Tris(aminomethyl)ethane (tame)

$CH_3C(CH_2NH_2)_3$: This ligand was prepared by the method of Fleischer et al.63)

Anal. Found: C,26.61; H,8.19; N,18.34%. Calcd for $C_5H_{15}N_3\cdot3HCl$: C,26.51; H,8.01; N,18.55%.

(2). 2-Aminoethyl methyl sulfide (ams)

$CH_3SCH_2CH_2NH_2$: To the alcoholic solution of sodium ethoxide (1 mole) which was prepared by the method of Fieser and Fieser,64) 42 g of 2-aminoethanethiol was dissolved and then 80 g of methyl iodide was successively added dropwise. The mixed solution was refluxed for half an hour and then cooled to a room-temperature. To this reaction mixture, 19 g of water was added to decompose the excess sodium ethoxide. After the several extraction by ether, the collected solution was evaporated to dryness and the remained oil was acidified with 12M HCl. This solution was again evaporated to dryness. The precipitate crystallized in the form of flat plates by adding 12M HCl. The product was very hygroscopic and reserved in a vacuum desiccator over $CaCl_2$.

Anal. Found: C,28.03; H,7.82; N,10.82%. Calcd for $C_3H_9NS\cdot HCl$: C,28.23; H,7.90; N,10.97%.

(3). 2-Aminoethyl carboxymethyl sulfide (acms·H)

$NH_2CH_2CH_2SCH_2CO_2H$: A solution of 77.2 g of

2-aminoethanethiol in 250 ml of water was mixed with the solution of 94.5 g of monochloroacetic acid and 56.1 g of potassium hydroxide in 200 ml of water with vigorous stirring at 80-85°C on a water bath. The mixed solution was further stirred for about 1 hr and cooled in an ice bath. Then 185 ml of 60% perchloric acid was added to it and the deposit, $KClO_4$, was filtered off. The filtrate was concentrated in a vacuum evaporator until it became oily and the deposit, $KClO_4$, was again filtered off. This filtrate was cooled in a refrigerator overnight. The white needles precipitated (=first crop) were recrystallized from a small amount of ethanol and dried in a vacuum desiccator over $CaCl_2$. Further second crop was obtained from the filtrate by standing it in a refrigerator for several weeks. The yield was 110 grams.
Anal. Found: C,30.71; H,6.28; N,9.09; S,20.41; Cl,11.55%. Calcd for $C_4H_9NSO_2$1/2HCl: C,30.52; H,6.08; N,8.90; S,20.37; Cl,11.26%.

(4). 2-Aminoethyl carboxyethyl sulfide (aces·H)

$NH_2CH_2CH_2SCH_2CH_2CO_2H$: This ligand was prepared by the similar procedure described above, except that 3-bromopropionic acid was used instead of monochloroacetic acid.

This ligand easily crystallized at a room-temperature. The yield was 180 grams.
Anal. Found: C,25.52; H,5.39; N,5.87; S,13.07; Br,33.84%. Calcd for $C_5H_{11}NSO_2\cdot HBr\cdot 1/2H_2O$: C,25.11; H,5.48; N,5.86;

S,13.41; Br,33.41%.

(5). (Ethylenedithio)diacetic acid (edth·H_2)

$HO_2CCH_2SCH_2CH_2SCH_2CO_2H$: A solution of 24.5 g of 96% 1,2-ethanedithiol in 100 ml of methanol was mixed with the solution of 47.1 g of monochloroacetic acid and 28 g of potassium hydroxide dissolved in 150 ml of water. To this mixture was added drop by drop 28 g of potassium hydroxide in 60 ml of water with mechanically stirring at 80-85°C on a water bath. The mixture was further stirred for about 2 hr and then cooled in an ice bath. 50 ml of 60% perchloric acid was added to it and the deposit, $KClO_4$, was filtered off. The filtrate was concentrated in a vacuum evaporator until it became oily and the deposit, $KClO_4$, was again filtered off.

This oil was used for the synthesis of the desired complex without crystallization.

II-B. Preparation of Complexes

(1). Preparation and Resolution of Bis(ethylenediamine)-(2-mercaptoethylamino)cobalt(III) Complex

$[Co(en)_2(mea)]Cl_2$: This complex was prepared by the method of K. Hori.23)

$(-)_{589}$-$[Co(en)_2(mea)](ClO_4)_2$: The racemic chloride monohydrate (1 g) and the resolving agent $K_2[Sb_2(d\text{-}tart)_2]\cdot 3H_2O$ (0.99 g) were dissolved in 10 ml of water at 60°C. On scratching the side of the flask with a glass rod, the brown diastereomer $(-)_{589}$-$[Co(en)_2(mea)][Sb_2(d\text{-}tart)_2]\cdot 2H_2O$ was separated. The solution was cooled in an ice bath for about ten minutes and then filtered off. The precipitate was washed with ice cold water, ethanol and acetone.

Anal. Found: C,20.05; H,3.71; N,8.66%. Calcd for $(-)_{589}$-$[Co(en)_2(mea)][Sb_2(d\text{-}tart)_2]\cdot 2H_2O$ = $C_{14}H_{26}N_5SO_{12}CoSb_2$: C,20.34; H,3.66; N,8.47%.

The diastereomer (0.8 g) above was ground in a mortar, water (60 ml) was added and then excess sodium perchloride (5 g), and the mixture was stirred for ten minutes. After filtration, the solution was evaporated to 10 ml and cooled in an ice bath. The needlish crystals were then removed by filtration and washed with 50% ethanol and acetone. The yield was 0.3 grams.

Anal. Found: C,15.96; H,4.91; N,15.31%. Calcd for $(-)_{589}$-$[Co(en)_2(mea)](ClO_4)_2$ = $C_6H_{22}N_5SO_8Cl_2Co$: C,15.87; H,4.88; N,15.42%.

(2). Preparation and Resolution of Bis(ethylenediamine)-(2-aminoethyl methyl sulfide)cobalt(III) Complex

$[Co(en)_2(ams)]Cl_3 \cdot H_2O$: The racemic compound was derived from the reaction of bis(ethylenediamine)-(2-mercaptoethylamino)cobalt(III) complex, $[Co(en)_2(mea)]Cl_2 \cdot H_2O$, and methyl iodide according to the method of K. Hori.[23)]

$(+)_{589}$-$[Co(en)_2(ams)]Cl_3 \cdot H_2O$: The racemic chloride monohydrate (1.91 g) and the resolving agent $Na_2[Sb_2(d\text{-}tart)_2] \cdot 2H_2O$ (1.54 g) were dissolved in 10 ml of water at 50°C. After cooling to a room-temperature, the mixed solution was allowed to stand overnight in a refrigerator. The less soluble diastereomer deposited as orange precipitate was recrystallized from a small amount of hot water.

Anal. Found: C,20.40; H,3.83; N,8.06%. Calcd for $(+)_{589}$-$[Co(en)_2(ams)]Cl[Sb_2(d\text{-}tart)_2] \cdot 2H_2O$ = $C_{15}H_{33}N_5SO_{14}ClCoSb_2$: C,20.53; H,3.79; N,7.98%.

The diastereomer was converted to the optically active chloride by using an anion exchange resin (Dowex 1x8, Cl^- form).

Anal. Found: C,22.47; H,7.24; N,17.20%. Calcd for $(+)_{589}$-$[Co(en)_2(ams)]Cl_3 \cdot H_2O \cdot 1/3C_2H_5OH$ = $C_6H_{27}N_5SOCl_3Co \cdot 1/3C_2H_5OH$: C,22.46; H,7.13; N,17.08%.

(3). Preparation and Resolution of Bis(ethylenediamine)-(2-aminoethyl ethyl sulfide)cobalt(III) Complex

$[Co(en)_2(aes)]Cl_3 \cdot 2H_2O$: This complex was similarly obtained according to above procedure by using ethyl iodide instead of methyl iodide.

$(+)_{589}$-$[Co(en)_2(aes)]^+$: This complex was resolved using $Na_2[Sb_2(d\text{-}tart)_2]\cdot 2H_2O$ as a resolving agent. The resolution procedure was similar with that of $[Co(en)_2(ams)]Cl_3\cdot H_2O$.

Anal. Found: C,20.54; H,4.33; N,7.28%. Calcd for $(+)_{589}$-$[Co(en)_2(aes)]Cl[Sb_2(d\text{-}tart)_2]\cdot 4.5H_2O$ = $C_{16}H_{40}N_5SO_{16.5}ClCoSb_2$: C,20.52; H,4.31; N,7.48%.

The optically active chloride form was obtained by using an anion exchange resin (Dowex 1x8, Cl^- form). The CD spectrum of this complex was measured with the eluate and the concentration was calculated from the determination of the CD intensity referring that of the diastereomer.

(4). Preparation and Resolution of Bis(ethylenediamine)-(carboxymethyl methyl sulfido)cobalt(III) Complex

$[Co(en)_2(mms)]Cl_2$: This complex was prepared by the reaction of methyl iodide and bis(ethylenediamine)-(2-mercaptoacetato)cobalt(III) chloride, $[Co(en)_2(SCH_2CO_2)]Cl$, which was prepared according to the literature.$^{25)}$

$(+)_{589}$-$[Co(en)_2(mms)]Cl_2$: The racemic chloride monohydrate (0.71 g) was dissolved in 2 ml of water at 40°C. Freshly precipitated silver tartarate (0.37 g) was added and the mixture was stirred for ten minutes. The silver halides were filtered off, washed with water (1 ml) and then tartaric acid (0.15 g) was added to the filtrate. The mixed solution was cooled in an ice bath. The reddish diastereomer thus precipitated was recrystallized from 2 ml of hot water by adding ethanol.

Anal. Found: C,29.45; H,5.76; N,9.02%. Calcd for $(+)_{589}$-$[Co(en)_2(mms)](H\cdot d\text{-}tart)_2\cdot 2H_2O$ = $C_{15}H_{35}N_4SO_{16}Co$: C,29.13; H,5.70; N,9.06%.

The diastereomer was converted to the optically active chloride by using an anion exchange resin (Dowex 1x8, Cl^- form).

Anal. Found: C,21.93; H,6.25; N,14.85%. Calcd for $(+)_{589}$-$[Co(en)_2(mms)]Cl_2\cdot 1.5H_2O$ = $C_7H_{24}N_4SO_{3.5}Cl_2Co$: C,22.00; H,6.33; N,14.66%.

(5). Preparation and Resolution of Bis(ethylenediamine)-(carboxyethyl methyl sulfido)cobalt(III) Complex

$[Co(en)_2(ems)]Cl_2^2$: This complex was prepared by the method similar to that described above, except for that $[Co(en)_2(SCH_2CH_2CO_2)]Cl$ was used as a starting material instead of $[Co(en)_2(SCH_2CO_2)]Cl$.

$(-)_{589}$-$[Co(en)_2(ems)]Cl_2\cdot 0.5H_2O$: The racemic chloride (1.16 g) and the resolving agent $Na_2[Sb_2(d\text{-}tart)_2]\cdot 2H_2O$ (0.93 g) were dissolved in 4 ml water at 50°C. After the solution was cooled to a room-temperature, the diastereomer deposited was filtered and recrystallized from a small amount of hot water by adding ethanol.

Anal. Found: C,20.48; H,4.03; N,6.29%. Calcd for $(-)_{589}$-$[Co(en)_2(ems)][Sb_2(d\text{-}tart)_2]\cdot 5H_2O$ = $C_{16}H_{37}N_4SO_{19}CoSb_2$: C,20.80; H,4.04; N,6.06%.

The optically active chloride was obtained by using an anion exchange resin (Dowex 1x8, Cl^- form).

Anal. Found: C,25.33; H,6.44; N,14.92%. Calcd for $(-)_{589}$-$[Co(en)_2(ems)]Cl_2 \cdot 0.5H_2O$ = $C_8H_{24}N_4SO_{2.5}Cl_2Co$: C,25.41; H,6.40; N,14.81%.

(6). Preparation and Resolution of [1,1,1-Tris(aminomethyl)-ethane](2-aminoethyl carboxymethyl silfido)cobalt(III) Complex

$[Co(tame)(acms)]Cl_2$: To a green solution of tricarbonatocobaltate(III) ($CoCl_2 \cdot 6H_2O$, 3.6 g scale) prepared by the method of Shibata,65) 1.1.1-tris(aminomethyl)-ethane (3.4 g) and sodium hydroxide (1.8 g) were added at 0°C. The mixture was then heated to 40°C and stirred for 1.5 hr. After adding 3 g of 2-aminoethyl carboxymethyl sulfide hemihydrochloride, the solution was stirred at ca.60°C for 3 hr, whereupon the solution turned from violet to red. Then 6M acetic acid was added until gas evolution ceased, and the reaction was continued for more 2 hr at 80°C. The resulting red solution was evaporated in vacuum and then cooled. The chloride salt thus precipitated was recrystallized from a small volume of water by adding ethanol.

Anal. Found: C,27.52; H,6.25; N,14.77%. Calcd for $[Co(tame)(acms)]Cl_2 \cdot 0.5H_2O$ = $C_9H_{24}N_4SO_{2.5}Cl_2Co$: C,27.70; H,6.20; N,14.35%.

$(+)_{589}$-$[Co(tame)(acms)]Cl_2$: The racemic chloride (0.39 g) was dissolved in 5 ml of water ay 40°C, and potassium tris[L-cysteinesulfinato-(SN)]cobaltate(III)

$K_3[Co(L\text{-}cysu)_3]\cdot 6H_2O$ 66) (0.22 g) dissolved in 5 ml of water was added to it with stirring. The mixed solution was kept in a refrigerator for about one hour. Orange yellow diastereomer precipitated was filtered and then recrystallized from a large amount of water owing to poor solubility.

Anal. Found: C,23.73; H,5.59; N,11.28%. Calcd for $(+)_{589}\text{-}[Co(tame)(acms)]_3[Co(L\text{-}cysu)_3]_2\cdot 14H_2O\cdot 2KCl$ = $C_{45}H_{127}N_{18}S_9O_{44}Cl_2Co_5K_2$: C,23.91; H,5.66; N,11.15%.

Optically active chloride was obtained by using an anion exchange resin (Dowex 1x8, Cl^- form).

Anal. Found: C,24.97; H,6.20; N,13.18%. Calcd for $(+)_{589}\text{-}[Co(tame)(acms)]Cl_2\cdot 1.5H_2O\cdot 1/4KCl$ = $C_9H_{26}N_4SO_{3.5}Cl_2Co\cdot 1/4KCl$: C,25.32; H,6.14; N,13.13%.

(7). Preparation and Resolution of [1,1,1-Tris(aminomethyl)-ethane](2-aminoethyl carboxyethyl sulfido)cobalt(III) Complex

$[Co(tame)(aces)]Br_2$: This complex was prepared by the same method described above, by using 2-aminoethyl carboxyethyl sulfide monohydrobromide instead of 2-aminoethyl carboxymethyl sulfide hemihydrochloride.

Anal. Found: C,23.45; H,5.90; N,11.35%. Calcd for $[Co(tame)(aces)]Br_2\cdot 1.5H_2O$ = $C_{10}H_{28}N_4SO_{3.5}Br_2Co$: C,23.48; H,5.52; N,10.96%.

$(-)_{589}\text{-}[Co(tame)(aces)]^+$: This complex was resolved by the same method as that of $[Co(tame)(acms)]Cl_2$. The CD spectrum of this complex was measured with the eluate and the concentration was calculated from the determination of the optical density referring that of the racemate.

(8). Preparation of fac-Trinitro[1,1,1-tris(aminomethyl)-ethane]cobalt(III) Complex

fac-$[Co(tame)(NO_2)_3]$: 1,1,1-Tris(aminomethyl)ethane trihydrochloride (4.5 g) and sodium hydroxide(2.4 g) were dissolved in 15 ml of water and the mixture transferred to a separatory funnel. This solution was added dropwise to a solution of $Na_3[Co(NO_2)_6]$ (8.1 g)[67] in 20 ml of water at 70°C. The yellow precipitate was formed readily and removed by filtration. The crude product was recrystallized from a small amount of hot water. The yield was 2 grams.

Anal. Found: C,19.05; H,4.92; N,26.78%. Calcd for fac-$[Co(tame)(NO_2)_3]$ = $C_5H_{15}N_6O_6Co$: C,19.12; H,4.81; N,26.75%. N,26.75%

The synthetic method from cobalt(II) nitrate,[68] which was used to prepare trinitro(diethylenetriamine)-cobalt(III), was unsuccessfully attempted.

(9). Preparation of fac-Trichloro[1,1,1-tris(aminomethyl)-ethane]cobalt(III) Complex

fac-$[Co(tame)Cl_3]$: fac-Trinitro-[1,1,1-tris(aminomethyl)ethane]cobalt(III) complex, fac-$[Co(tame)(NO_2)_3]$ (2.5 g) was added to the alcoholic solution (80 ml) saturated with hydrochloric gas and gently stirred until nitrogen oxide evolution ceased.

This solution was kept standing overnight at a room-temperature. The deep blue precipitate of trichloro[1,1,1-tris(aminomethyl)ethane]cobalt(III) was filtered off and washed with ethanol and ether repeatedly until the washings was colorless. This reaction proceeds almost quantitatively. The yield was 1.9 grams.

Anal. Found: C,20.13; H,5.43; N,14.25%. Calcd for fac-[Co(tame)Cl_3]·3/4H_2O = $C_5H_{16.5}N_3O_{0.75}Cl_3Co$: C,20.29; H,5.62; N,14.20%.

(10). Preparation and Separation of [1,1,1-Tris(aminomethyl)-ethane](S-methyl-L-cysteinato)cobalt(III) Complex

[Co(tame)(L-smc)]Cl_2: Trichloro[1,1,1-tris(aminomethyl)ethane]cobalt(III), [Co(tame)Cl_3] (0.9 g) was suspended in water (10 ml); silver perchloride (1.98 g) was added and the mixture was shaken for ten minutes. The resulting solution was filtered to remove the silver halides. Then S-methyl-L-cysteine (0.41 g) and sodium hydroxide (0.13 g) dissolved in 10 ml of water was added. The mixed solution was heated to 70°C and stirred for 3 hr. The reaction mixture was poured into a column of Sp-Sephadex C-25 (3x40 cm, Na^+ form). The adsorbed band was eluted with 0.15M NaCl solution at a rate of about 0.5 ml/min. The second fine orange red eluate was evaporated and then the deposit, NaCl, was filtered off. To the filtrate was added a large amount of ethanol. The crude product thus abtained was recrystallized from as little water as possible by adding ethanol, and washed with ethanol and then acetone, and dried in a vacuum desiccator.

Anal. Found: C,21.09; H,4.65; N,11.31%. Calcd for $[Co(tame)(L\text{-}smc)]Cl_2 \cdot 2NaCl = C_9H_{23}N_4SO_2Cl_2Co \cdot 2NaCl$: C,21.70; H,4.65; N,11.25%.

(11). Preparation, Separation and Resolution of Isomers of Bis(2-aminoethyl carboxymethyl sulfido)cobalt(III) Complex

$[Co(acms)_2]Cl$: To a hot solution (ca.75°C) of 9 g of cobalt(II) chloride hexahydrate in 80 ml of water was added 9.35 g of 2-aminoethyl carboxymethyl sulfide hemihydrochloride and 1.51 g of sodium hydroxide dissolved in 80 ml of water. Then fifteen grams of PbO_2 was added to the mixed solution on a water bath, whereupon the solution becomes violet. The mixture was stirred for about 40 min. at 70°C. The reaction mixture was filtered to remove an excess of lead dioxide after cooling in an ice bath. After this operation, a considerable amount of brownish violet precipitate (crude A-1) was appeared and then filtered off again.

This filtrate was poured into an ion exchange column containing Dowex 50Wx8 resin (200-400 mesh, Na^+ form, 4.5x40 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.15M aqueous solution of NaCl at a rate of 1 ml per min. Five colored bands, a brownish violet one (A-1), a purple one (A-2), a red one (A-3), a red one (A-4) and a reddish purple one (A-5), were eluted in this order. These were separately concentrated in a vacuum evaporator and then the deposit, NaCl, was filtered off. To each of the filtrates was added a large amount of ethanol. The complexes thus obtained were recrystallized from as little water as possible by adding ethanol and then acetone, and dried in a vacuum desiccator over $CaCl_2$. These five isomers were obtained in comparable yield.

Anal. Found for A-1: C,25.76; H,4.44; N,7.71%. Calcd for $[Co(acms)_2]Cl = C_8H_{16}N_2S_2O_4ClCo$: C,26.49; H,4.45; N,7.72%. Found for A-2: C,26.28; H,4.62; N,7.82%. Calcd for $[Co(acms)_2]Cl = C_8H_{16}N_2S_2O_4ClCo$: C,26.49; H,4.45; N,7.72%. Found for A-3: C,25.04; H,4.83; N,7.81%. Calcd for $[Co(acms)_2]Cl\cdot H_2O = C_8H_{18}N_2S_2O_5ClCo$: C,25.24; H,4.77; N,7.36%. Found for A-4: C,24.46; H,5.10; N,7.56%. Calcd for $[Co(acms)_2]Cl\cdot 1.5H_2O = C_8H_{19}N_2S_2O_{5.5}ClCo$: C,24.65; H,4.91; N,7.15%. Found for A-5: C,24.80; H,4.85; N,7.75%. Calcd for $[Co(acms)_2]Cl\cdot H_2O = C_8H_{18}N_2S_2O_5ClCo$: C,25.24; H,4.77; N,7.36%.

Of these five isomers, four isomers except A-1 were optically resolved.

A-2; $(-)_{589}$-$[Co(acms)_2]Cl$,(trans(O)): This isomer was resolved by using $(-)_{589}$-$K[Co(edta)]\cdot 2H_2O$ as a resolving agent. The racemic chloride (0.36 g) and the resolving agent (0.21 g) were dissolved in 2 ml of water at 40°C. After cooling to a room-temperature, the mixed solution was allowed to stand overnight in a refrigerator. The less soluble diastereomer was deposited as violet

needles. The diastereomer was recrystallized from a small amount of hot water. The yield was 0.25 grams.
Anal. Found: C,27.91; H,4.87; N,7.33%. Calcd for $(-)_{589}$-$[Co(acms)_2][Co(edta)]\cdot 5H_2O$ = $C_{18}H_{38}N_4S_2O_{17}Co$: C,28.27; H,5.01; N,7.33%.

Optically active chloride was obtained by using an anion exchange resin (Dowex 1x8, Cl^- form).
Anal. Found: C,26.23; H,4.49; N,7.71%. Calcd for $(-)_{589}$-$[Co(acms)_2]Cl$ = $C_8H_{16}N_2S_2O_4ClCo$: C,26.49; H,4.45; N,7.72%.

A-3; $(-)_{589}$-$[Co(acms)_2]Cl\cdot H_2O$, (trans(S)): The optical resolution of this isomer was unsuccessfully attempted using several resolving agents such as $Na_2[Sb_2(d\text{-}tart)_2]\cdot 2H_2O$, $Ag_2(d\text{-}tart)$, $(-)_{589}$-$K[Co(edta)]\cdot 2H_2O$ and $(+)_{589}$-$Na[Co(en)(ox)_2]\cdot H_2O$. However, the spontaneous resolution was observed for the crystals prepared as follows; 0.5 g of the racemic chloride monohydrate was dissolved in 5 ml of water at 40°C and the solution was kept standing in refrigerator for several days for crystallization. Then the crystal which was arbitralily chosen showed the optical activity. This result, therefore, indicates that the solubility of the spontaneously resolved racemic salt is $\sqrt{2}$ or more times larger than that of the corresponding optically active salt.$^{69)}$ No hemihedral facets, however, were found for the crystals.
Anal. Found; C,24.93; H,4.83; N,7.45%. Calcd for $(-)_{589}$-$[Co(acms)_2]Cl\cdot H_2O$ = $C_8H_{18}N_2S_2O_5ClCo$: C,25.24;

H,4.77; N,7.36%.

A-4; $(+)_{589}$-$[Co(acms)_2]^+$, (cisciscis): The racemic chloride (0.39 g), dibenzoyl tartaric acid (0.38 g) and sodium hydroxide (0.08 g) were dissolved in 10 ml of water at 40°C. Then the mixed solution was evaporated to 2 ml and cooled in a refrigerator overnight. The red diastereomer deposited was recrystallized form 2 ml of hot water by adding acetone.

Anal. Found: C,36.47; H,4.75; N,4.92%. Calcd for $(+)_{589}$-$[Co(acms)_2]_2DBT\cdot 5.5H_2O$ = $C_{34}H_{55}N_4S_4O_{21.5}Co_2$: C,36.79; H,4.99; N,5.05%.

The optically active chloride form was obtained by using an anion exchange resin (Dowex 1x8, Cl^- form). The CD spectrum of this complex was measured with the eluate, and the concentration was calculated from the determination of the CD intensity referring that of the diastereomer.

A-5; $(-)_{589}$-$[Co(acms)_2]Cl\cdot 2.25H_2O$, (trans(N)): Racemic chloride (0.39 g) and the resolving agent $Na_2[Sb_2(d\text{-}tart)_2]\cdot 2H_2O$ (0.16 g) was dissolved in 3 ml of water at 40°C. The mixed solution was allowed to stand for a few days in a refrigerator to crystallize. The less soluble reddish purple diastereomer precipitated was filtered off and recrystallized from 2 ml of hot water by adding ethanol.

This less soluble diastereomer was converted to the optically active chloride by using an anion exchange resin (Dowex 1x8, Cl^- form).

Anal. Found: C,23.46; H,4.94; N,6.90%. Calcd for $(-)_{589}$-$[Co(acms)_2]Cl\cdot 2.25H_2O$ = $C_8H_{20.5}N_2S_2O_{6.25}ClCo$: C,23.83; H,5.12; N,6.95%.

(12). Preparation, Separation and Resolution of Isomers of Bis(2-aminoethyl carboxyethyl sulfido)cobalt(III) Complex

$[Co(aces)_2]Cl$: This complex was prepared and separated by the same method as that of $[Co(acms)_2]Cl$ using 2-aminoethyl carboxyethyl sulfide instead of 2-aminoethyl carboxymethyl sulfide.

Five colored bands, a brownish violet (B-1), a purple one (B-2), a purple one (B-3 + B-4), a reddish purple one (B-5) and a violet one (B-6), were eluted in this order. The yields for the B-1 and B-2 isomers were very low. It was confirmed by the absorption spectral behavior in the thioether charge transfer band region that the third eluate consists of two isomers, and that B-1, B-2 and one of the third eluate (B-4) have the S-trans configuration. The eluates were separately concentrated in a vacuum evaporator and the deposit, NaCl, was filtered off. To each of the concentrated solution was added a large amount of ethanol. The desired complex was collected by filtration and recrystallized from a small amount of water by adding ethanol and acetone, and then dried in a vacuum desiccator over $CaCl_2$. However, the complete separation of B-3 and B-4 isomers using an ion exchange resin (Dowex 50Wx8 or SP-Sephadex C-25) was unsuccessfully attempted. The pure products of these two isomers were obtained as follows: after removal of excess lead dioxide, the reaction mixture was evaporated to 50 ml and cooled in an ice bath, and then B-3 isomer crystallized was obtained as the bromide salt. On the other hand, the pure product of B-4 isomer was able to be fractionally crystallized from the mixed eluate of B-3 and B-4 isomers because of its relatively lower solubility but that of B-3 isomer was not.

Anal. Found for B-1: C,27.52; H,5.70; N,6.44%. Calcd for $[Co(aces)_2]Cl \cdot 2.5H_2O$ = $C_{10}H_{25}N_2S_2O_{6.5}ClCo$: C,27.56; H,5.78; N,6.43%. Found for B-2: C,26.76; H,6.14: N,5.90%. Calcd for $[Co(aces)_2]Cl \cdot 4H_2O$ = $C_{10}H_{28}N_2S_2O_8ClCo$: C,25.95; H,6.10; N,6.05%. Found for B-3: C,21.74; H,5.06; N,5.23%. Calcd for $[Co(aces)_2]Br \cdot 3.5H_2O \cdot 1/2NaBr$ = $C_{10}H_{27}N_2S_2O_{7.5}BrCo \cdot 1/2NaBr$: C,21.85; H,4.95; N,5.10%. Found for B-4: C,27.96; H,5.43; N,6.58%. Calcd for $[Co(aces)_2]Cl \cdot 2H_2O$ = $C_{10}H_{24}N_2S_2O_6ClCo$: C,28.14; H,5.67; N,6.56%. Found for B-5: C,29.18; H,5.50; N,6.90%. Calcd for $[Co(aces)_2]Cl \cdot H_2O$ = $C_{10}H_{22}N_2S_2O_5ClCo$: C,29.38; H,5.42; N,6.85%. Found for B-6: C,27.60; H,5.73; N,6.47%. Calcd for $[Co(aces)_2]Cl \cdot 2.5H_2O$ = $C_{10}H_{25}N_2S_2O_{6.5}ClCo$: C,27.56; H,5.78; N,6.43%.

B-3; $(-)_{589}$-$[Co(aces)_2]Cl \cdot 2H_2O$; (trans(O)): The racemic bromide (0.55 g) and the resolving agent $K_2[Sb_2(d\text{-}tart)_2] \cdot 3H_2O$ (0.32 g) were dissolved in 5 ml of water at 50°C. After cooling to a room-temperature, the mixed solution was allowed to stand for a week in a refrigerator. The less soluble diastereomer deposited was recrystallized from a small amount of water, and converted to the chloride salt by using an anion axchange resin (Dowex 1x8, Cl^- form).

Anal. Found: C,23.47; H,4.68; N,5.40%. Calcd for $(-)_{589}$-[Co(aces)$_2$]Cl·2H_2O·1.2KCl = $C_{10}H_{24}N_2S_2O_6ClCo$·1.2KCl: C,23.26; H,4.69; N,5.43%.

B-2; $(+)_{589}$-[Co(aces)$_2$]$^+$ (mer-trans(S)), B-4; $(+)_{589}$-[Co(aces)$_2$]$^+$ (trans(S)), B-5; $(+)_{589}$-[Co(aces)$_2$]$^+$ (cisciscis), and B-6; $(+)_{589}$-[Co(aces)$_2$]$^+$ (trans(N)): These four isomers were partially or completely resolved into their optical antipodes by chromatographic technique.

Aqueous solution containing 0.1 g of the complex was poured into a column of SP-Sephadex C-25 (Na^+ form, 3x120 cm). The adsorbed band was eluted with a 0.1M aqueous solution of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ at a rate of 0.3 ml/min. Under these conditions, 7-10 days were required for the complete elution of the complex, which produced a broad band. The eluent was separated into fractions of 5 ml each. A few fractions eluted firstly, which showed the completely enantiomeric CD spectra compared with those of the last fractions, were collected and after removal of the excess elution agents converted to the chloride salt by using an anion exchange resin (Dowex 1x8, Cl^- form). This eluate was used to measure the CD spectrum, and its concentration was calculated from the determination of the optical density referring that of the racemate.

In all of the four isomers , these first eluates were plus for the Na-D line. The complete band separation into their antipodes was only observed for the B-4 isomer.

(13). Preparation and Separation of Isomers of (L-methioninato)(2-aminoethyl carboxymethyl sulfido)-cobalt(III) Complex

[Co(L-met)(acms)]Cl: This complex was prepared according to a similar procedure with that for $[Co(acms)_2]^+$, using acms·H·1/2HCl and L-met·H. The prepared isomers were separated by using a cation exchange column (Dowex 50Wx8, 200-400 mesh, Na^+ form, 4.5x40 cm) with a 0.15M aqueous solution of NaCl as the eluent. Seven colored bands were eluted. It was confirmed by the mesurem nts of the CD and electronic absorption spectra of these eluates, that the second eluate (brownish violet) was tr.tr.tr.-$[Co(acms)_2]^+$, the third one (purple) trans(S)-$[Co(L\text{-}met)_2]^+$, the fourth one (purple) trans(O)-$[Co(acms)_2]^+$, and the seventh one (red) trans(N)-$[Co(acms)_2]^+$, and that the desired compounds, therefore, existed in the remaining three eluates (first, fifth and sixth eluates). It was also found that the first eluate (dark violet, C-1) was single band, but the fifth one (reddish purple) and the sixth one (reddish purple) consisted of some bands more than two. These eluates were concentrated separately with a vacuum evaporator, and then the reposit, NaCl, was filtered off. The complex in the first eluate was obtained by adding a large amount of ethanol to the concentrated solution and recrystallized from a small amount of water.

Each of the concentrated solution of the fifth and sixth eluated were again poured into a column of

SP-Sephadex C-25 (K^+ form, 4.5x120 cm). The adsorbed band was eluted with a 0.05M aqueous solution of $K_2[Sb_2(d\text{-}tart)_2]\cdot 3H_2O$ at a rate of about 0.5 ml/min. For the column of the fifth eluate, five colored bands, a brown red one (C-2), a violet one which was trans(O)-$[Co(L\text{-}met)_2]^+$, a reddish purple one (C-3), a brown red one (C-4) and a brown red one which was trans(N)-$[Co(L\text{-}met)_2]^+$, were eluted in this order. On the other hand, for the column of the sixth eluate four colored band, a brown red one (C-2), a red one (C-5), a red one (C-6) and a violet one (C-7), were eluted in this order. The CD measurements of the fractions of each eluate showed that these bands consisted of the single one. The desired eluates were concentrated separately with a vacuum evaporator, and then the deposit, $K_2[Sb_2(d\text{-}tart)_2]\cdot 3H_2O$, was filtered off. Each of the concentrated eluates was poured into a anion exchange column of Dowex 1x8 (Cl^- form) to convert the chloride salt. The desired complexes were obtained by adding a large amount of ethanol to the eluates. Each of the isomers was recrystallized from as little water as possible by adding a small amount of ethanol and washed with ethanol and then acetone, and dried in a vacuum desiccator over $CaCl_2$.

Anal. Found for C-1: C,28.09; H,4.79; N,7.34%. Calcd for $[Co(L\text{-}met)(acms)]Cl$ = $C_9H_{18}N_2S_2O_4ClCo$: C,28.69; H,4.82; N,7.44%. Found for C-2: C,27.69; H,4.76 N,7.09%. Calcd for $[Co(L\text{-}met)(acms)]Cl\cdot 0.5H_2O\cdot 1/10KCl$ = $C_9H_{19}N_2S_2O_{4.5}ClCo\cdot 1/10KCl$: C,27.49; H,4.87; N,7.12%. Found for C-3:

C,25.79; H,5.30; N,6.54%. Calcd for [Co(L-met)(acms)]Cl·$2H_2O$·1/10KCl = $C_9H_{22}N_2S_2O_6ClCo$·1/10KCl: C,25.72; H,5.28; N,6.67%. Found for C-4: C,26.42; H,5.35; N,6.60%. Calcd for [Co(L-met)(acms)]Cl·$2H_2O$ = $C_9H_{22}N_2S_2O_6ClCo$: C,26.17; H,5.37; N,6.79%. Found for C-5: C,25.33; H,4.89; N,6.75%. Calcd for [Co(L-met)(acms)]Cl·$1.5H_2O$·3/10KCl = $C_9H_{21}N_2S_2O_{5.5}ClCo$·3/10KCl: C,25.37; H,4.97; N,6.57%. Found for C-6: C,24.99; H,4.94; N,6.86%. Calcd for [Co(L-met)(acms)]Cl·$1.5H_2O$·3/10KCl = $C_9H_{21}N_2S_2O_{5.5}ClCo$·3/10KCl: C,25.37; H,4.97; N,6.57%. Found for C-7: C,26.15; H,5.36; N,6.93%. Calcd for [Co(L-met)(acms)]Cl·$2H_2O$ = $C_9H_{22}N_2S_2O_6ClCo$: C,26.19; H,5.37; N,6.79%.

(14). Preparation and Separation of Isomers of (L-methioninate)(2-aminoethyl carboxymethyl sulfido)-cobalt(III) Complex

[Co(L-met)(aces)]Cl: The preparation of this complex and separation of isomers were carried out by a similar method with that for the corresponding [Co(L-met)(acms)]Cl complex, using aces·HBr·1/$2H_2O$ instead of acms·1/2HCl.

Nine colored bands were eluted. By the measurements of the electronic absorption and CD spectra of these eluates, it was confirmed that the first eluate (brownish violet) was tr.tr.tr.-$[Co(aces)_2]^+$, the third one (purple) trans(S)-$[Co(L\text{-}met)_2]^+$, the fourth one (purple) trans(O)-$[Co(aces)_2]^+$, and the sixth one (brownish red) trans(N)-$[Co(aces)_2]^+$, and that the second eluate (dark violet, D-1), the fifth one (purple, D-2), the seventh one (reddish purple, D-3 + D-4), the eighth one (purple, D-5) and the ninth one (red, D-6) were the desired isomers. These eluates were concentrated separately with a vacuum evaporator, and then the deposit, NaCl, was filtered off.

Each of the concentrated filtrates was again poured into a column containing SP-Sephadex C-25 (K^+ form, 4.5x120 cm), respectively. The adsorbed band was eluted with a 0.05M aqueous solution of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ at a rate of about 0.5 ml/min. For the column of the seventh eluate, three bands, a brownish red one (D-3), a purple one which was trans(O)-$[Co(L\text{-met})_2]^+$, and a red one (D-4), were eluted in this order, and for the others there was apparently a single band. However, the careful CD measurements showed that D-4 and D-6 bands consisted of two bands, which were designated as D-4a and D-4b for D-4 eluate, and D-6a and D-6b for D-6 one according to the elution order, though the further separation was impossible even by the repeated chromatography. These desired eluates were concentrated separately with a vacuum evaporator and then the deposit, $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$, was filtered off and converted to the chloride salt by using an anion exchange resin (Dowex 1x8, Cl^- form). To each of the eluate was added a large amount of ethanol and acetone. The products thus obtained were recrystallized from as little water as possible by adding ethanol and acetone, and washed with acetone and then ether, and dried in a vacuum desiccator over $CaCl_2$.

These isomers were contaminated with a small amount of potassium chloride or sodium chloride because of the relatively lower yields, compared with those of $[Co(L\text{-}met)_2]^+$ and $[Co(aces)_2]^+$ complexes. The CD spectra of D-4a and D-4b (or D-6a and D-6b) isomers were measured with the eluates, and their concentrations were calculated from the determination of the optical densities referring that of the mixture.

Anal. Found for D-1: C,23.88; H,4.72; N,5.49%. Calcd for $[Co(L\text{-}met)(aces)]Cl \cdot 2H_2O \cdot 1.4NaCl = C_{10}H_{24}N_2S_2O_6ClCo \cdot 1.4NaCl$: C,23.61; H,4.76; N,5.51%. Found for D-2: C,27.76; H,5.36; N,6.47%. Calcd for $[Co(L\text{-}met)(aces)]Cl \cdot 2H_2O \cdot 1/5KCl = C_{10}H_{24}N_2S_2O_6ClCo \cdot 1/5KCl$: C,27.19; H,5.48; N,6.34%. Found for D-3: C,29.38; H,5.12: N,6.84%. Calcd for $[Co(L\text{-}met)(aces)]Cl \cdot 1/2H_2O \cdot 0.13KCl = C_{10}H_{21}N_2S_2O_{4.5}ClCo \cdot 0.13KCl$: C,29.33; H,5.17; N,6.84%. Found for D-4 (D-4a + D-4b): C,27.68; H,5.61; N,5.89%. Calcd for $[Co(L\text{-}met)(aces)]Cl \cdot 3/2H_2O \cdot CH_3OH \cdot 2/5KCl = C_{10}H_{23}N_2S_2O_{5.5}ClCo \cdot CH_3OH \cdot 2/5KCl$: C,27.54; H,5.67; N,5.84%. Found for D-5: C,28.01; H,5.08; N,6.56%. Calcd for $[Co(L\text{-}met)(aces)]Cl \cdot H_2O \cdot 3/10NaCl = C_{10}H_{22}N_2S_2O_5ClCo \cdot 3/10NaCl$: C,28.17; H,5.20; N,6.57%. Found for D-6 (D-6a + D-6b): C,26.17; H,5.23; N,6.13%. Calcd for $[Co(L\text{-}met)(aces)]Cl \cdot 2H_2O \cdot 2/5KCl = C_{10}H_{24}N_2S_2O_6ClCo \cdot 2/5KCl$: C,26.30; H,5.30; N,6.13%.

(15). Preparation and Separation of [(Ethylenedithio)diacetato]ethylenediaminecobalt(III) Complex

[Co(edth)(en)]Cl: This complex was prepared by a similar procedure to that for s-cis-[Co(edda)(en)]NO_3.[61)]

A suspension of 2.62 g of cobaltous carbonate and 5 g of (ethylenedithio)diacetic acid which is oily, in 50 ml of water was heated at 60°C for an hour with mechanically stirring until the carbon dioxide evolution ceased. To the solution were added successively 10 ml of 2M nitric acid, 1 g of activated charcoal, and 1.22 g of 98% ethylenediamine in 8 ml of water. The oxidation was carried out by the dropwise addition of 2.2 g of 30% H_2O_2 in 30 ml of water with stirring. The solution was evaporated to 20 ml and poured into a column containing atrong cation-exchange resin (Dowex 50Wx8, Na^+ form, 3x30 cm). The adsorbed band was eluted with a 0.2M aqueous solution of sodium chloride at a rate of 1 ml/min. Two colored bands, a purple one and a reddish one, were eluted in this order. These bands were separately concentrated in a vacuum evaporator and then the deposit, NaCl, was filtered off. To each of the filtrates was added a large amount of ethanol. The complex thus obtained were recrystallized from as little water as possible. The purple compound was obtained in the form of flat plates, while the reddish one was contaminated with a serious amount of sodium chloride because of its low yield and remained unidentified.

Anal. Found: C,23.92; H,4.80; N,7.30%. Calcd for

$[Co(edth)(en)]Cl\cdot 1.5H_2O = C_8H_{19}N_2S_2O_{5.5}ClCo$: C,24.65; H,4.91; N,7.19%.

(16). Preparation and Separation of Isomers of Bis(L-methioninato)cobalt(III) Complex

$[Co(L\text{-}met)_2]Cl$: This complex was already prepared and separated into three geometrical isomers as the bromide salts by J. Hidaka et al.$^{29)}$ However, in order to compare their absorption and CD spectra with those of the present many isomers which are almost chloride salts, this complex was also prepared and separated into three isomers which were obtained as the chloride salts. The experimantal procedure used was similar to that reported except for that the sodium chloride was used as a elution agent instead of the sodium bromide.

Anal. Found for trans(S): C,30.34; H,5.24: N,7.11%. Calcd for $[Co(L\text{-}met)_2]Cl\cdot 1/4H_2O = C_{10}H_{20.5}N_2S_2O_{4.25}ClCo$: C,30.39; H,5.23; N,7.09%. Found for trans(N): C,30.34; H,5.27; N,7.17%. Calcd for $[Co(L\text{-}met)_2]Cl\cdot 1/4H_2O = C_{10}H_{20.5}N_2S_2O_{4.25}ClCo$: C,30.39; H,5.23; N,7.09%. Found for trans(O): C,29.83; H,5.07; N.6.92%. Calcd for $[Co(L\text{-}met)_2]Cl\cdot 1/2H_2O = C_{10}H_{21}N_2S_2O_{4.5}ClCo$: C,30.04; H,5.29; N,7.01%.

By the chromatographic technique, it has become apparent that the elution order is changed; namely, the order is trans(S), trans(N) and trans(O) by using a column of Dowex 50Wx8 (Na^+ form), while the order is trans(O), trans(S) and trans(N) by using a column of SP-Sephadex

C-25 (K^+ form), and that further separation of the isomers due to the absolute confidurations of the coordinated two sulfur atoms was unsuccessfully attempted even by using a column of SP-Sephadex C-25.

The chloride salts show the same CD and absorption spectra as those of the bromide salts but there are some differences in details. The thioether charge transfer bands of the chloride salts are intensified for all of three isomers and this band of the trans(S) chloride form is twice in its intensity than that of the trans(S) bromide one.

II-C. Measurements

The electronic absorption spectra were measured by a Shimadzu UV-200 spectrophotometer in aqueous solution. The CD spectra were recorded with a Jasco MOE-1 spectropolarimeter, using the cell with 1 cm pathlength. A Jasco DIP-4 digital polarimeter was used to check the optical rotations. The proton magnetic resonance spectra were measured in deuterium oxide with a Varian XL-100-15 NMR spectrophotometer, using DSS $[(CH_3)_3SiCH_2CH_2CH_2SO_3Na]$ as an internal reference. The infrared spectra were obtained with a Jasco DS-402G spectrophotometer with NaCl prism using nujol mull or KBr disk. All measurements were made at a room-temperature.

III. Results and Discussion

III-A. $[Co(en)_2(\overline{ab})]^{n+}$ Type Complexes

III-A-1. Preparation of the Complexes

2-Aminoethanethiol is the simplest representative of sulfur-nitrogen chelates having a thiolo group, and Jensen[70)] first observed the formation of two nickel complexes of 2-aminoethanethiol in solution. As is shown from the fact[14)] that this ligand displaces $edta^{4-}$ from the hexadentate complex $[Co(edta)]^-$, the thiolo groups have a high coordinating ability for Co(III) ion in spite of the low position of mercaptide ion in the spectrochemical series. This trend was observed for the present preparation of the complexes of $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, $[Co(en)_2(SCH_2CO_2)]^+$ and $[Co(en)_2(SCH_2CH_2CO_2)]^+$: that is, many by-products, tris(ethylenediamine)cobalt(III) and polynuclear species containing thiolo groups, were substantially formed and therefore the yield of the desired material was very low.

On the other hand, there have been some difficulties for the preparation of the corresponding cobalt(III) complexes containing thioether donor atoms because of its weak coordinating ability towards a boderline or rather hard metal as the Co(III) ion. For example, it was reported[22)] that by the reaction of trans-$[Co(en)_2X_2]X$ (X = Cl or Br) and 2-aminoethyl methyl sulfide, cis-$[Co(en)_2(NH_2CH_2CH_2SCH_3)X]X_2$ (X = Cl or Br) was prepared and 2-aminoethyl methyl sulfide did not functionate as a bidentate ligand. The similar study have been made in the system of trans-$[Co(en)_2Cl_2]Cl$ and S-methyl-L-cysteine.[21)]

However, the suggestion to remove these difficulties have been given by the systematic studies of D. H. Busch and his co-workers.71-73) They have reported that the nickel complex with the thiolo group reacts with alkyl halides in demethyl formamide solution to give a complex of the S-alkylated ligand and this reaction proceeds without the Ni-S bond rupture. A typical reaction is

$$\underset{\text{square-planar diamagnetic}}{Ni(SCH_2CH_2NH_2)_2} + 2CH_3I \longrightarrow \underset{\text{octahedral paramagnetic}}{Ni(CH_3SCH_2CH_2NH_2)_2I_2}$$

The same reaction described above was applied for the cobalt(III) complexes23); that is, $[Co(en)_2(CH_3SCH_2CH_2NH_2)]Cl$ was able to be prepared by the reaction of $[Co(en)_2(SCH_2CH_2NH_2)]Cl$ and CH_3I in methanol and water.

In the present work, four complexes containing a thioether donor atom were prepared by the same procedure.

III-A-2. Absorption and Circular Dichroism Spectra of the Containing a Mercaptide Group; $[Co(en)_2(mea)]^{2+}$

The absorption and CD spectra of this complex are shown in Figure 6. The first d-d absorption band maximum appears at 20800 cm^{-1}($\log\varepsilon$=2.31) and a shoulder occurs on the low-energy side of the principal band (ca. 17000 cm^{-1}, $\log\varepsilon$ = 1.85). This absorption spectrum is very similar with to those of $[Co(en)_2(L\text{-cyst})]I$, $[Co(en)_2(L\text{-cyst}\cdot H)]I\cdot Cl$ and $[Co(en)_2(L\text{-cystee})]I_2$21) ($L\text{-cyst}\cdot H_2$ = L-cysteine and L-cystee = L-cysteine ethyl ester), in which the ligands are coordinated through the amino and mercaptide groups. Consequently, based on the approximate C_{4v} symmetry, the

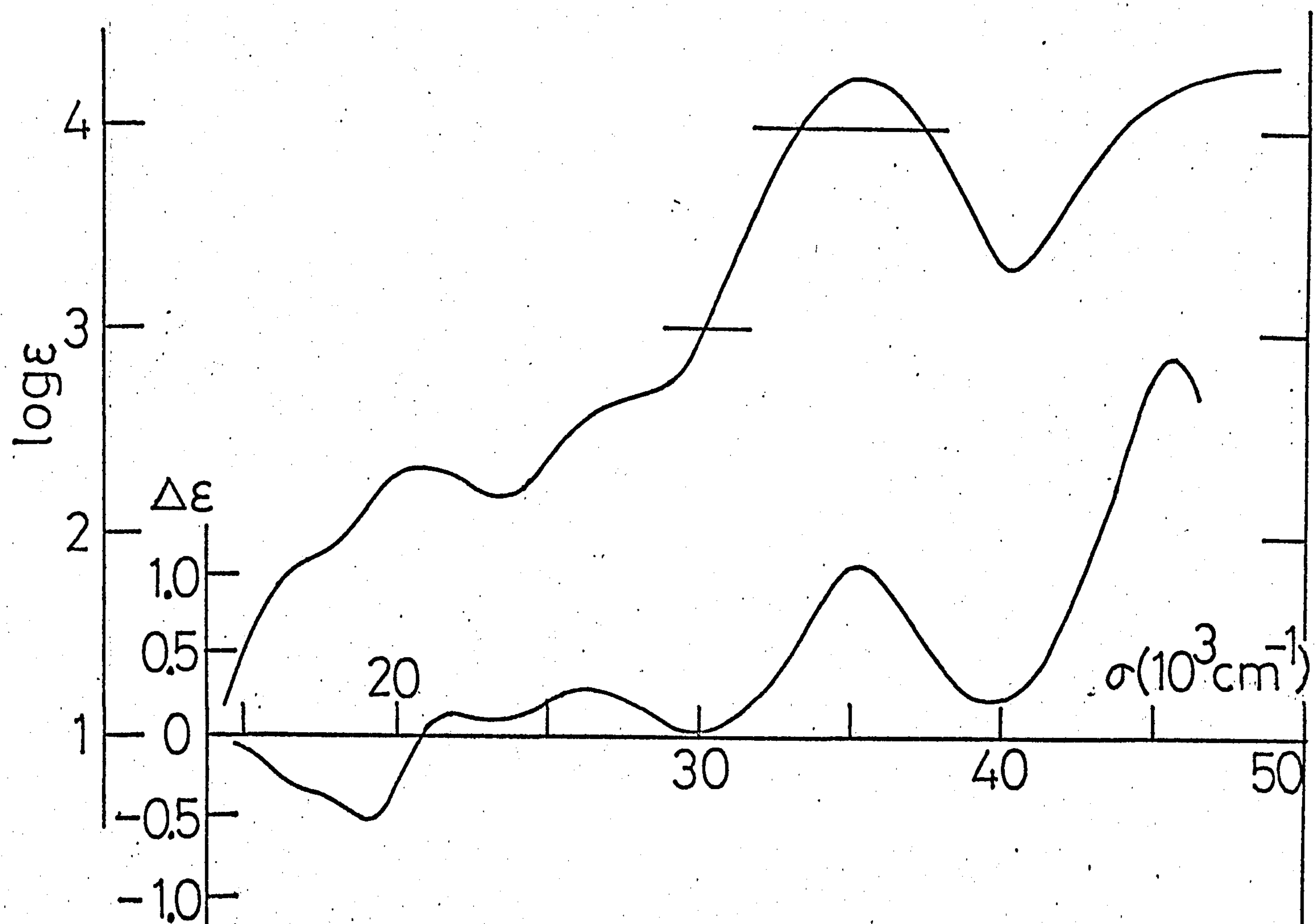


Figure 6. AB and CD spectra of

$(-)_{589}$-[Co(en)$_2$(mea)](ClO$_4$)$_2$.

low-energy band was assigned to the transition $^1A_1 \rightarrow {}^1E$, while the band at higher energy is assigned to $^1A_1 \rightarrow {}^1A_2$. The ligand field strength of the mercaptide group is quite low and falls close to iodide in the spectrochemical series.

The optical isomer, $(-)_{589}$-$[Co(en)_2(mea)](ClO_4)_2$ which was obtained from the less soluble diastereomer, exhibits weak three CD bands in the first absorption band region ($\Delta\varepsilon$=-0.36 at 17000 cm^{-1}(sh), $\Delta\varepsilon$=-0.54 at 19100 cm^{-1} and $\Delta\varepsilon$=+0.12 at 21800 cm^{-1}). Therefore, two low-energy negative bands can be assigned to be $^1A_1 \rightarrow {}^1E$ and a higher energy positive one to be $^1A_1 \rightarrow {}^1A_2$. The absolute configuration of this complex can be assigned as Δ configuration on the basis of the sign of $^1A_1 \rightarrow {}^1E$ band.

III-A-3. Absorption and CD Spectra of the $[Co(en)_2(\overline{ab})]^{n+}$ Type Complexes Containing a Thioether Donor Atom

The electronic absorption and CD spectra of these complexes are shown in Figures 7 and 8 and Table 1. The first absorption bands of $[Co(en)_2(ams)]^{3+}$ and $[Co(en)_2(aes)]^{3+}$ which are a $[Co(N)_5(S)]$ type, appear at 20500 cm^{-1} with only a slight unsymmetrical shape for both complexes. These maxima correspond well to those of $[Co(en)_2(gly)]^{2+}$, $[Co(en)_2(L\text{-}ala)]^{2+}$ and $[Co(en)_2(sar)]^{2+}$ which are a $[Co(N)_5(O)]$ type (gly = glycinate, L-ala = L-alaninate). For the complexes of $[Co(en)_2(mms)]^{2+}$ and $[Co(en)_2(ems)]^{2+}$ which are a $[Co(N)_4(S)(O)]$ type, maxima of the first absorption band lie at 20000 and 20100 cm^{-1}, respectively, and are in good accordance with that of

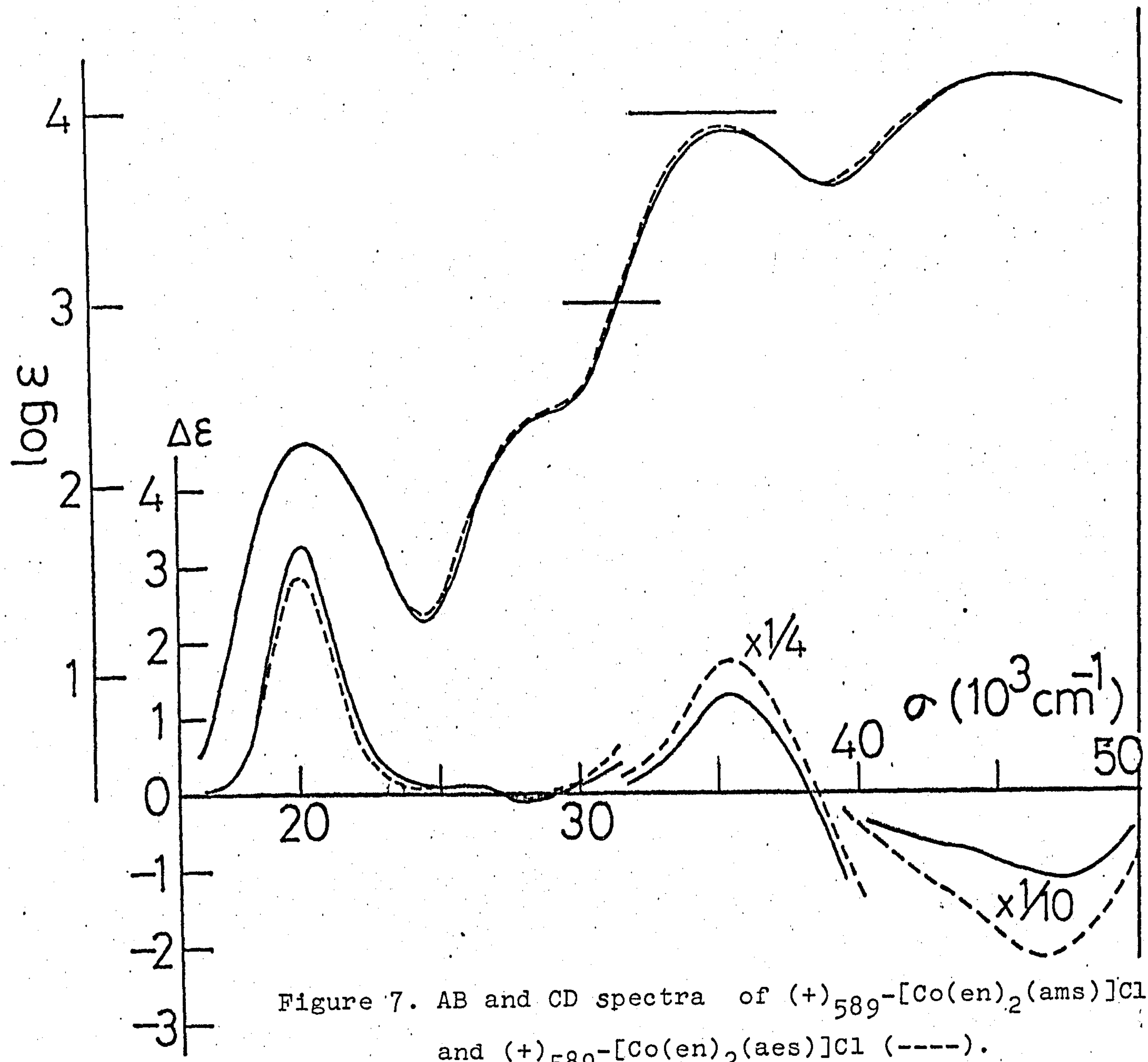


Figure 7. AB and CD spectra of $(+)_{589}$-$[Co(en)_2(ams)]Cl_3$(——) and $(+)_{589}$-$[Co(en)_2(aes)]Cl$ (----).

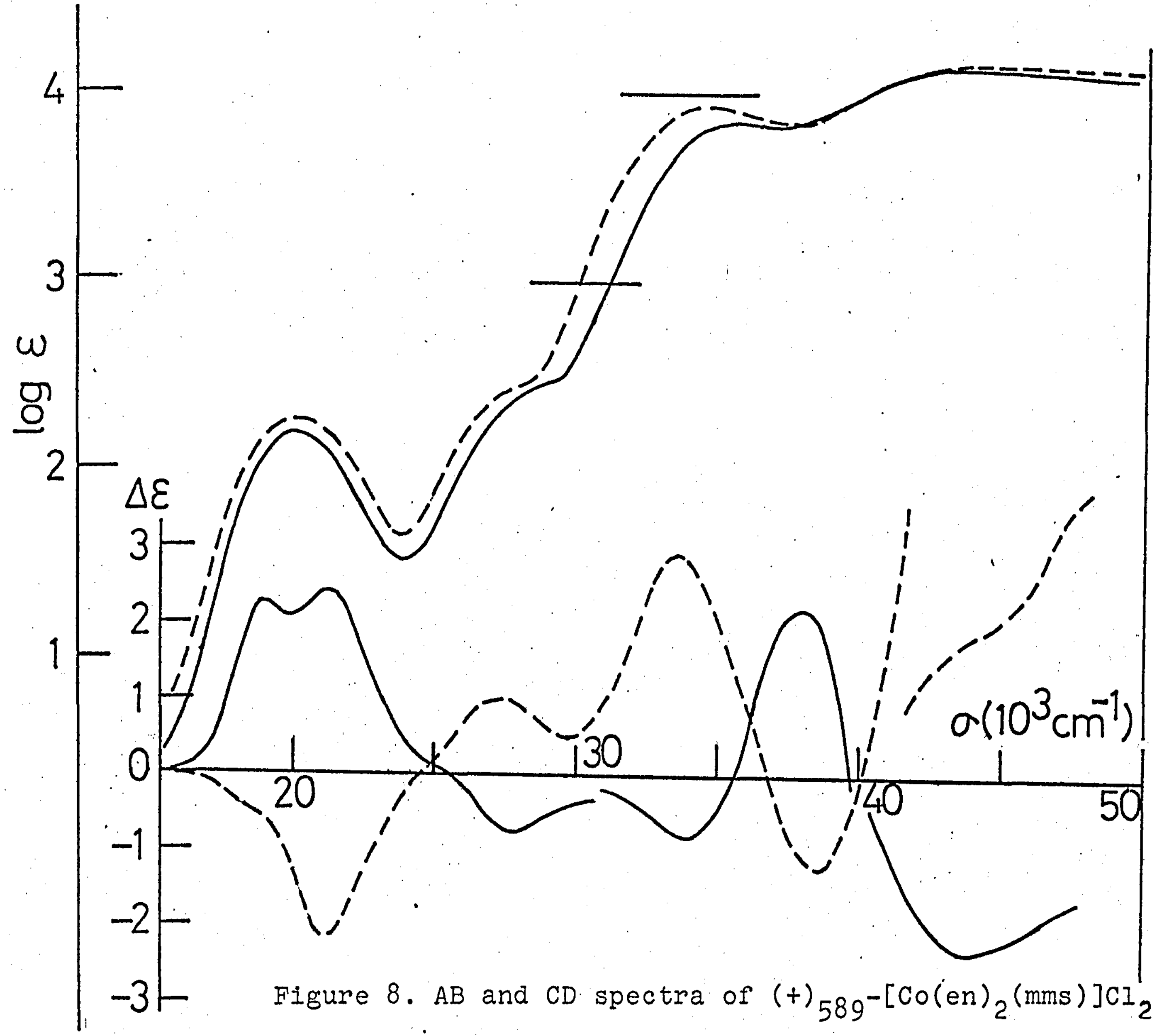


Figure 8. AB and CD spectra of $(+)_{589}$-$[Co(en)_2(mms)]Cl_2$ (——) and $(-)_{589}$-$[Co(en)_2(ems)]Cl_2$(----).

Table 1

AB and CD Data of $[Co(en)_2(\overline{ab})]^{n+}$ Type Complexes

Complex	AB σ_{max}(log ε)	CD σ_{ext}(Δε)
$(-)_{589}$-$[Co(en)_2(mea)](ClO_4)_2$	17 (1.85)*	17.0 (-0.36)*
	20.8 (2.31)	19.1 (-0.54)
	27 (2.62)*	21.8 (+0.12)
	35.4 (4.24)	26.5 (+0.28)
		35.1 (+2.12)
		45.7 (+4.70)
$(+)_{589}$-$[Co(en)_2(ams)]Cl_3$	20.5 (2.25)	20.1 (+3.22)
	28 (2.35)*	26.0 (+0.06)
	35.5 (3.92)	28.1 (-0.13)
	45.8 (4.21)	35.5 (+5.09)
		47.2 (-11.2)
$(+)_{589}$-$[Co(en)_2(aes)]^{+}$ a)	20.5 (2.25)	20.0 (+2.84)
	28 (2.37)*	26.0 (-0.05)
	35.5 (3.94)	28.0 (-0.08)
	45.3 (4.22)	35.4 (+6.73)
		46.4 (-22.2)
$(+)_{589}$-$[Co(en)_2(mms)]Cl_2$	20.0 (2.20)	18.9 (+2.28)
	28 (2.35)*	21.1 (+2.43)
	35.7 (3.85)	27.5 (-0.77)
	43.7 (4.14)	33.9 (-1.59)
		38.0 (+4.44)
		43.9 (-23.4)

Table 1 (continued)

$(-)_{589}$-$[Co(en)_2(ems)]Cl_2$	20.1 (2.27)	19 (-0.65)*
	27 (2.36)*	21.2 (-2.15)
	34.6 (3.93)	27.2 (+0.99)
	44.5 (4.15)	33.7 (+2.93)
		38.6 (-1.23)

* This band is a shoulder.

a) AB spectrum of this complex is that of the racemate.

The wave numbers are given in 10^3 cm^{-1} unit.

Table 2. AB Data of the First Absorption Bands of the $[Co(en)_2(\overline{ab})]^{n+}$, $[Co(tame)(N,S,O\text{-tridentato})]^{2+}$ and Related Complexes

Complex	Type	$\sigma_{max}(\log\varepsilon)$	$\delta^{a)}$	refs.
$[Co(tame)_2]^{3+}$	$[Co(N)_6]$	21.32(1.95)		74
$[Co(en)_3]^{3+}$		21.28(1.92)		75
$[Co(en)_2(NH_3)_2]^{3+}$		21.28(1.86)		76
$[Co(en)_2(gly)]^{2+}$	$[Co(N)_5(O)]$	20.53(1.99)		55
$[Co(en)_2(L\text{-}ala)_2]^{2+}$		20.52(2.04)		55
$[Co(en)_2(sar)]^{2+}$		20.5 (2.00)		48
$[Co(en)_2(ams)]^{3+}$	$[Co(N)_5(S)]$	20.5 (2.25)	3.39	
$[Co(en)_2(aes)]^{3+}$		20.5 (2.25)	3.40	
$[Co(tame)(acms)]^{2+}$	$[Co(N)_4(S)(O)]$	20.3 (2.12)	3.75	
$[Co(tame)(aces)]^{2+}$		20.3 (2.24)	4.12	
$[Co(tame)(L\text{-}smc)]^{2+}$		20.4 (2.05)	4.00	
$[Co(en)_2(mms)]^{2+}$		20.0 (2.20)	3.75	
$[Co(en)_2(ems)]^{2+}$		20.1 (2.27)	3.97	
$[Co(en)_2(H_2O)_2]^{3+}$	$[Co(N)_4(O)_2]$	20.2 (1.92)		76
$[Co(en)_2(ox)]^{+}$		20.0 (2.01)		76
$[Co(en)_2CO_3]^{+}$		19.49(2.16)		76

a) is half-width in the first absorption band.

The wave numbers are given in 10^3 cm^{-1} unit.

$[Co(en)_2(ox)]^+$ which is a $[Co(N)_4(O)_2]$ type (ox=oxalate). Table 2 shows the energies, intensities and half-widths of the first absorption bands for the present and related complexes. This indicates that the thioether group of the bidentate ligands, $-CH_2-S-R$ ($R=CH_3$ for ams, mms and ems ligands; $R=C_2H_5$ for aes ligand) seems to lie close to the COO^- group in the spectrochemical series, and that the first absorption bands of the $[Co(N)_4(S)(O)]$ type complexes occur in the lower energy side and have larger half-widths (δ-values) than those of the $[Co(N)_5(S)]$ type complexes, which are the same for the second d-d absorption bands.

In the near-ultraviolet region, each of the present complexes shows a intense band ($\log\varepsilon$=ca. 4.0). This band appears characteristically for the complexes containing thioethers, which is considered to be the charge transfer transition of the lone-pair sulfur electrons to one of the metal d-orbitals. These bands located at similar with each other not only in the position but also in the intensity for both type complexes.

Both optical isomers of a $[Co(N)_5(S)]$ type, $(+)_{589}$-$[Co(en)_2(ams)]^{3+}$ and $(+)_{589}$-$[Co(en)_2(aes)]^{3+}$ which were obtained from less soluble diastereomer, show one strong CD band in the first absorption band region ($\Delta\varepsilon$=+3.22 at 20100 cm^{-1} for ams complex and $\Delta\varepsilon$=+2.84 at 20000 cm^{-1} for aes one) and two weak CD bands in the second d-d absorption band region ($\Delta\varepsilon$=+0.06 at 26000 cm^{-1} and $\Delta\varepsilon$=-0.13 at 28100 cm^{-1} for ams complex, and $\Delta\varepsilon$=+0.05 at

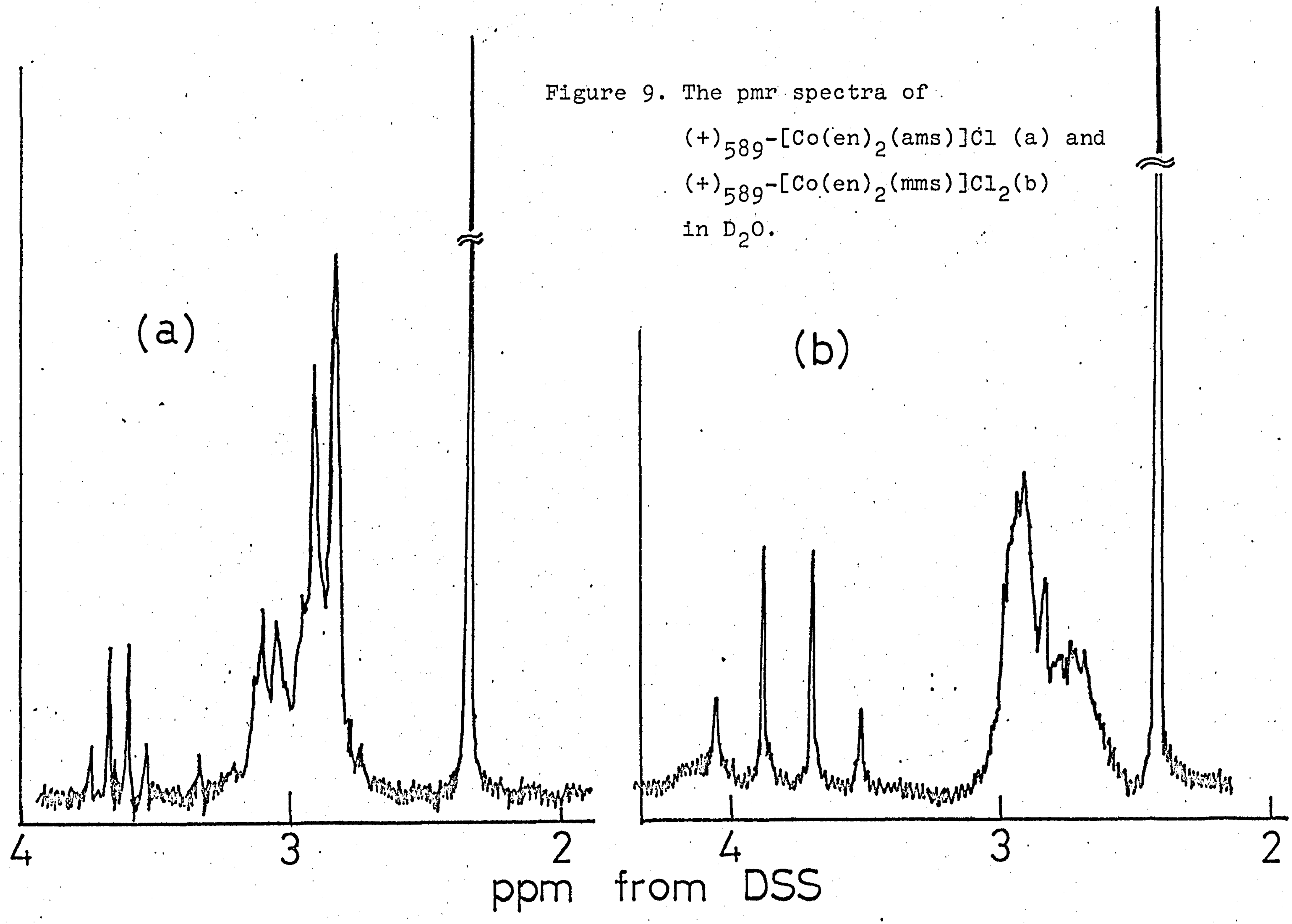
26000 cm^{-1} and $\Delta\varepsilon$=-0.08 at 28000 cm^{-1} for aes one). These CD spectral behaviors are strikingly similar with each other and therefore indicate that the substitution effect of alkyl group has comparatively small CD contribution since the immediate environment about the sulfur atom is the same for both complexes. These trends were also found for the dialkyl-edda complexes which have two asymmetric nitrogens.77)

Of the [Co(N)$_4$(S)(O)] type complexes, both complexes, $(+)_{589}$-[Co(en)$_2$(mms)]$^{2+}$ and $(-)_{589}$-[Co(en)$_2$(ems)]$^{2+}$, show two CD bands in the first absorption band region ($\Delta\varepsilon$=+2.28 at 18900 cm^{-1} and $\Delta\varepsilon$=+2.43 at 21100 cm^{-1} for mms complex and $\Delta\varepsilon$=-0.65 at 19000 cm^{-1}(sh) and $\Delta\varepsilon$=-2.15 at 21200 cm^{-1} for ems one) and one band in the second absorption band region ($\Delta\varepsilon$=-0.77 at 27500 cm^{-1} for mms complex and $\Delta\varepsilon$=+0.99 at 27200 cm^{-1} for ems one). These CD spectral behaviors are considered to reflect the lowering the symmetry compared with those for the [Co(N)$_5$(S)] type complexes and correlate also with the larger half-widths of the first absorption bands.

The absolute configurations of the present four complexes can be assigned on the basis of the sign dominated under the T_{1g}78); namely,,$(+)_{589}$-[Co(en)$_2$(ams)]$^{3+}$, $(+)_{589}$-[Co(en)$_2$(aes)]$^{3+}$, $(+)_{589}$-[Co(en)$_2$(mms)]$^{2+}$ and $(-)_{589}$-[Co(en)$_2$(ems)]$^{2+}$ are Λ, Λ, Λ and Δ configurations, respectively.

As was mentined in Section I-A, for the present four complexes another CD contribution due to the coordinated

Figure 9. The pmr spectra of $(+)_{589}$-$[Co(en)_2(ams)]Cl$ (a) and $(+)_{589}$-$[Co(en)_2(mms)]Cl_2$(b) in D_2O.



asymmetric sulfur atom is formally expected. NMR spectra of these complexes show that there is a single peak in the S-methyl proton region (Figure 9). Futhermore, the chromatographic separation showed that all the fractions gave the same CD spectra for each of the four complexes. These results and model examination suggest that the thioether ligands are coordinated stereospecifically (Δ-S or Λ-R) as was so for sarcosinate complex (Figure 1).

In the region of the thioether charge transfer band, ams and aes complexes show a positive CD band ($\Delta\varepsilon$=+5.09 at 35500 cm^{-1} and $\Delta\varepsilon$=+6.73 at 35400 cm^{-1}, respectively), which corresponds well with the absorption maximum of each complex in position. On the other hand, mms and ems complexes show apparently two bands of opposite sign ($\Delta\varepsilon$=-1.59 at 33900 cm^{-1} and $\Delta\varepsilon$=+4.44 at 38000 cm^{-1} for mms complex; $\Delta\varepsilon$=+2.93 at 33700 cm^{-1} and $\Delta\varepsilon$=-1.23 at 38600 cm^{-1} for ems one). The sign of these bands may be related to the absolute configuration of the complex or the coordinated asymmetric sulfur atom; namely, Λ-R configuration show (+) and Δ-S one (-) band for the $[Co(N)_5(S)]$ type complexes, and Λ-R configuration shows (-) and (+) bands from lower energy side and Δ-S one (+) and (-) for the $[Co(N)_4(S)(O)]$ type complexes.

III-B. Absorption and CD Spectra of the $[Co(tame)(N,S,O\text{-tridentato})]^{2+}$ Type Complexes

As was mentioned already in Section I-B, 1,1,1-tris(aminomethyl)ethane is a typical tripod ligand

and coordinates facially to a Co(III) ion and therefore there is no geometrical isomer for the $[Co(tame)(N,S,O\text{-tridentato})]^{2+}$ type complexes which are a $[Co(N)_4(S)(O)]$ type.

The absorption and CD spectra of the present three complexes are shown in Figure 10 and Table 3. The first d-d absorption bands occur at 20300 or 20400 cm^{-1} with only a slight unsymmetrical shape. These maxima are shifted to the higher energy side than those of the corresponding complexes, $[Co(en)_2(mms)]^{2+}$ and $[Co(en)_2(ems)]^{2+}$, which are also a $[Co(N)_4(S)(O)]$ type. This indicates that the thioether group of the N,S,O-tridentate ligand has the larger Δ-value than that of the S,O-bidentate ligand.

These three complexes, $(+)_{589}$-$[Co(tame)(acms)]^{2+}$, $(-)_{589}$-$[Co(tame)(aces)]^{2+}$ and $(+)_{589}$-$[Co(tame)(L\text{-}smc)]^{2+}$, exhibit two CD bands of opposite sign in the first absorption band region ($\Delta\varepsilon$=+1.46 at 18800 cm^{-1} and $\Delta\varepsilon$=-1.75 at 21300 cm^{-1} for acms complex; $\Delta\varepsilon$=-0.66 at 18700 cm^{-1} and $\Delta\varepsilon$=+0.99 at 21400 cm^{-1} for aces one;$\Delta\varepsilon$=-1.39 at 18700 cm^{-1} and $\Delta\varepsilon$=+1.08 at 21200 cm^{-1} for L-smc one) and one CD band in the second d-d absorption band region ($\Delta\varepsilon$=+0.61 at 28800 cm^{-1} for acms complex; $\Delta\varepsilon$=-0.40 at 28300 cm^{-1} for aces one; $\Delta\varepsilon$=-0.78 at 28400 cm^{-1} for L-smc one). By the analogy of the CD patterns of the present three complexes, the absolute configurations of the acms and aces complexes can be related with that of L-smc one, which has the structure of (c) (Figure 2) due to the absolute stereospecificity of its ligand. Accordingly,

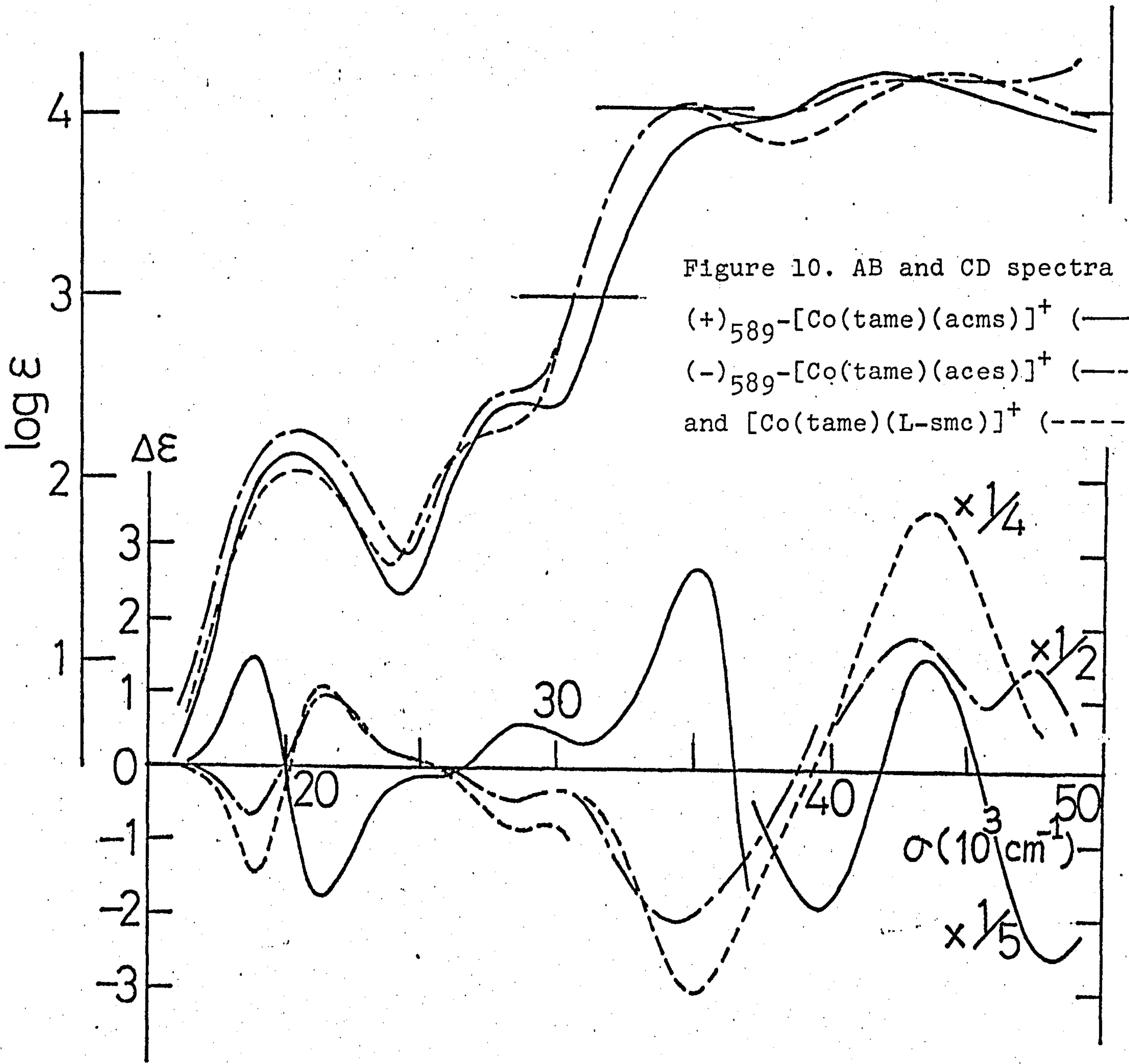


Figure 10. AB and CD spectra of $(+)_{589}$-$[Co(tame)(acms)]^+$ (———), $(-)_{589}$-$[Co(tame)(aces)]^+$ (—·—·—), and $[Co(tame)(L\text{-}smc)]^+$ (- - - - -).

Table 3

AB and CD Data of $[Co(tame)(N,S,O\text{-tridentate})]^+$ Type Complexes

Complex	AB σ_{max} (log ε)	CD σ_{ext} (Δε)
$(+)_{589}$-$[Co(tame)(acms)]Cl_2$ $^{a)}$	20.3 (2.12)	18.8 (+1.46)
	28.6 (2.41)	21.3 (-1.75)
	35.7 (3.93)*	28.8 (+0.61)
	42.4 (4.22)	35.1 (+2.79)
		39.6 (-9.08)
		43.7 (+7.89)
		48.1 (-12.7)
$(-)_{589}$-$[Co(tame)(aces)]^{+}$ $^{a)}$	20.3 (2.24)	18.7 (-1.39)
	28 (2.43)*	21.4 (+0.99)
	35.0 (4.03)	28.3 (-0.40)
	44.0 (4.18)	34.7 (-2.03)
		42.9 (+3.76)
		47.5 (+3.14)
$(\underline{-})_{589}$-$[Co(tame)(L\text{-}smc)]Cl_2$	20.4 (2.05)	18.7 (-1.39)
	28 (2.25)*	21.2 (+1.08)
	34.7 (4.02)	28.4 (-0.79)
	44.4 (4.21)	34.8 (-11.9)
		43.5 (+14.3)

* This band is a shoulder.

a) AB spectrum is that of the racemate.

The wave numbers are given in 10^3 cm^{-1} unit.

the absolute configuration is assigned as R-(S) for $(+)_{589}$-$[Co(tame)(acms)]^{2+}$ and as S-(S) for $(-)_{589}$-$[Co(tame)(aces)]^{2+}$, where the former letter, R- or S-, represents the chirality due to the arrangement of three different donor atoms (=configurational dissymmetry), and the latter one, -(S), designates the chirality due to the asymmetric sulfur atom (=vicinal dissymmetry) and is reversed between acms and aces complexes with the same configuration of the former kind.

In the present type complexes, there is two CD contributions due to the coordinated asymmetric sulfur atom and due to the arrangement of three different donors, but these two contribution cannot be separable with each other. In the thioether charge transfer band region, $(+)_{589}$-acms and $(-)_{589}$-aces complexes show a positive and a negative band, respectively ($\Delta\varepsilon$=+2.79 at 35100 cm^{-1} for acms complex; $\Delta\varepsilon$=-2.03 at 34700 cm^{-1} for aces one), which corresponds well with that these two complexes have the opposite absolute configuration, and that they show opposite CD pattern not only in the first absorption band region but also in the thioether charge transfer band region, even if the formal notation with respect to the asymmetric sulfur atom becomes equal for both complexes.

III-C. Absorption Spectra of $[Co(N,S,O\text{-tridentato})_2]^+$ and $[Co(L\text{-met})(N,S,O\text{-tridentato})]^+$ Type Complexes

III-C-1. General Consideration of the Absorption Spectra

In the present $[Co(N)_2(S)_2(O)_2]$ type complexes, the geometrical isomers should be expected to have different electronic absorption spectra. In particular the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition should split differently. So far, for the octahedral and the lower symmetry complexes belonging to the d^3 and d^6 system, their energy levels have been discussed by many authors,79-83) using several kinds of semiempirical parameters. For the present systems the expected splittings can be calculated semiempirically79) in terms of the spectrochemical effect of the donor atoms which are arranged in octahedral coordination sites in each of the isomers. Table 4 shows the results of such a calculation for the isomers of the $[Co(N)_2(S)_2(O)_2]$ type complexes. In this Table, the effect of π-bonding has been ignored and only the σ-bonding contributions to the spectral shifts are given. The position of $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition of the $[Co(N)_6]$ was used as a reference, and $\delta(S)$ and $\delta(O)$ refer, respectively, to the energy difference between the transition of reference complex and those of the complex $[Co(S)_6]$ and $[Co(O)_6]$. In the spectrochemical series, thioether group is between the oxygen of the carboxyl group and the nitrogen of the amine group.38-40,84)

Thus, it is expected that the tr.tr.tr. and trans(N) isomers shoud have the most shifted component towards the red region, tr.tr.tr. and trans(O) isomers one component

Table 4. Predicted Shifts of the First Absorption Band of $[Co(N)_2(S)_2(O)_2]$ Type Complex

Isomer		Components of I-Band
tr.tr.tr.		$1/2\delta(S) + 1/2\delta(O)$
		$1/2\delta(S)$
		$1/2\delta(O)$
trans(S)	a	$1/2\delta(S) + 1/4\delta(O)$
	b	$1/2\delta(O)$
trans(O)	a	$1/4\delta(S) + 1/2\delta(O)$
	b	$1/2\delta(O)$
trans(N)	a	$1/4\delta(S) + 1/4\delta(O)$
	b	$1/2\delta(S) + 1/2\delta(O)$
cisciscis		$1/2\delta(S) + 1/4\delta(O)$
		$1/4\delta(S) + 1/4\delta(O)$
		$1/4\delta(S) + 1/2\delta(O)$

* When an absorption band is split into two components, the degenerate one (truly or accidentally) is labeled a and another non-degenerate one b.

closest to the transition of reference, and the splitting amount for the tr.tr.tr. isomer is greater than those for the trans(N) and trans(O). Whereas the trans(S) and cisciscis isomers have two and three components about the same region, respectively, and therefore the splitting amount for both isomers is small compared with the three isomers mentined above.

Another absorption spectral criterion to distinguish between the geometrical isomers is given from the thioether charge transfer transition, which is located at 30000-35000 cm^{-1} region for the cobalt(III) complexes and occurs at lower energy side for the complexes with the S-trans geometry than for the corresponding complexes with the S-cis one. In the case of $[Co(L\text{-}met)_2]^+$, the one and the other two isomers have been assigned to trans(S) and cis(S) forms, respectively, according to the characteristic spectral behavior of the thioether charge transfer band (28500 cm^{-1} for trans(S); 32600 cm^{-1} for trans(N); 32700 cm^{-1} for trans(O)).29)

Recently, the crystal and molecular structure of trans(S)-bis(S-methyl-L-cysteinato)cobalt(III) perchlorate monohydrate has been determined by the X-ray diffraction method85) and the geometry of this isomer is consistent with that deduced from the above thioether charge transfer band. Thus, the distinction between the S-trans geometry and the S-cis one is possible on the basis of the thioether charge transfer band.

III-C-2. Absorption Spectra of $[Co(N,S,O\text{-tridentato})_2]^+$ Type Complexes

For the $[Co(N,S,O\text{-tridentato})_2]^+$ type complexes, six geometrical isomers, tr.tr.tr., trans(S), trans(O), trans(N), cisciscis and mer-trans(S), are possible as is shown in Figure 3. Of these isomers, five geometrical isomers were obtained for $[Co(acms)_2]Cl$. The absorption spectra are shown in Figure 11 and summarized in Table 5. The thioether charge transfer bands for A-1 isomer (30900 cm^{-1}, $\log\varepsilon=4.04$) and A-3 one (31200 cm^{-1}, $\log\varepsilon=4.04$) locate at lower energy side than those for the other three isomers (sh.35100 cm^{-1}, $\log\varepsilon=4.09$ for A-2 isomer; 33700 cm^{-1}, $\log\varepsilon=3.98$ for A-4 one; 32400 cm^{-1}, $\log\varepsilon=3.97$ for A-5 one). Therefore, A-1 and A-3 isomers can be assigned to S-trans structure and the others S-cis one. In the first absorption band region, A-1 isomer exhibits two splitting components with the same molar extinction coefficients at 18400 and 20400 cm^{-1}, while A-3 isomer shows apparently a sharp band at 19200 cm^{-1} ($\log\varepsilon=2.10$). These facts indicate that A-1 isomer is tr.tr.tr. and A-3 one trans(S).

On the other hand, of three isomers with the S-cis configuration, A-2 isomer exhibits an explicit shoulder at the high energy side of the major peak of 18100 cm^{-1} ($\log\varepsilon=2.24$) in the first absorption band region, while both A-4 and A-5 isomers show a sharp peak at 19200 cm^{-1} ($\log\varepsilon=2.27$) and 19200 cm^{-1} ($\log\varepsilon=2.31$), respectively. Accoding to the splitting patterns calculated from the semiempirical theory described above, marked splitting

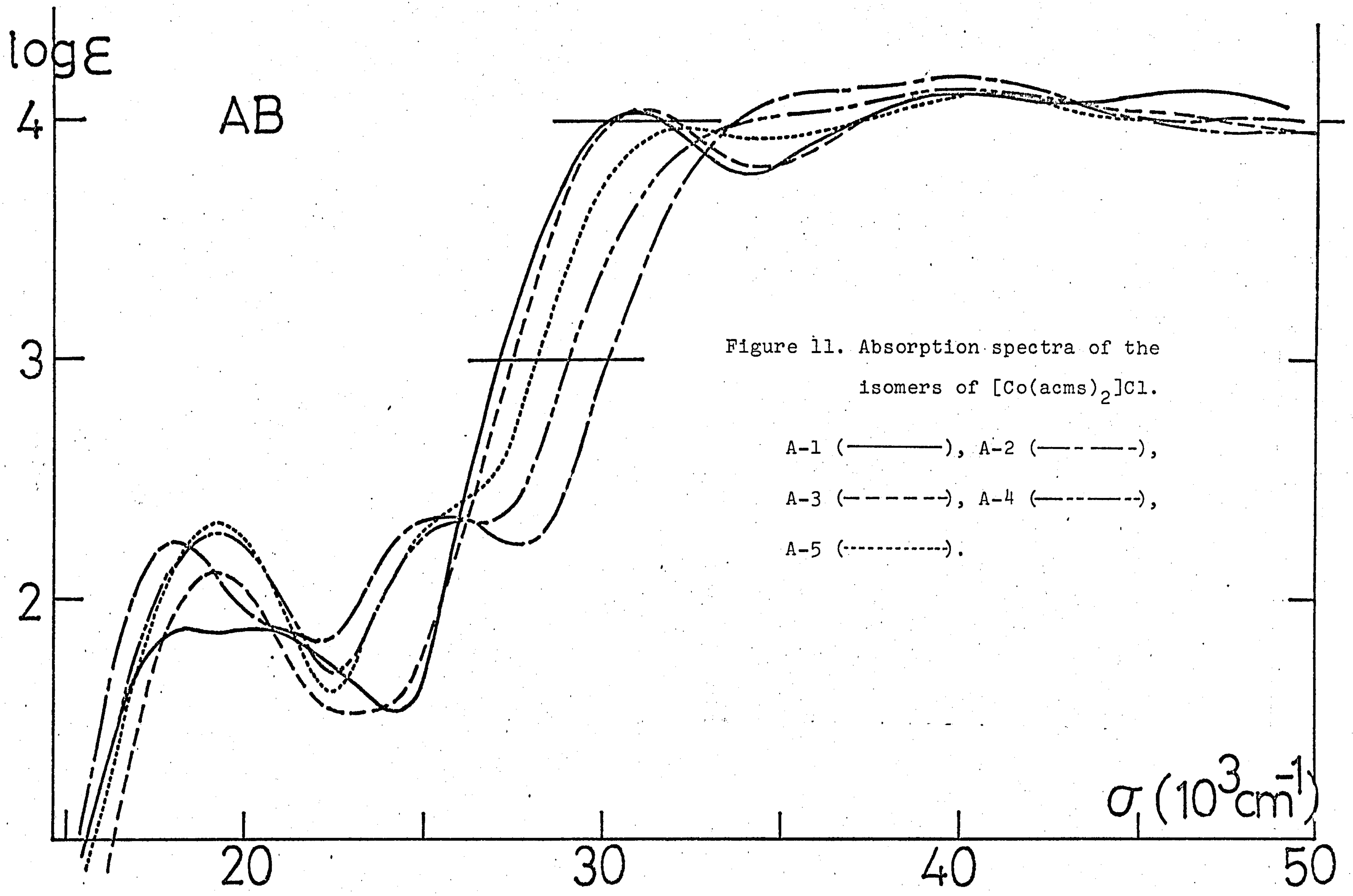


Figure 11. Absorption spectra of the isomers of $[Co(acms)_2]Cl$.

A-1 (————), A-2 (—- - ——-),

A-3 (- - - - - - -), A-4 (——- - - ——),

A-5 (··········).

Table 5

AB Data of Isomers of [Co(acms)$_2$]Cl and [Co(aces)$_2$]Cl

[Co(acms)$_2$]Cl a)		σ_{max} (log ε)		
Isomer	I-Band	II-Band	CT-Band	Assignment
A-1	18.4 (1.87)		30.9 (4.04)	
	20.4 (1.87)		40.1 (4.11)	tr.tr.tr.
			46.3 (4.11)	
A-2	18.1 (2.24)	25.3 (2.34)	35.1 (4.09)*	
	20.8 (1.88)*		40.0 (4.17)	trans(O)
			48.3 (4.04)	
A-3	19.2 (2.10)		31.2 (4.04)	trans(S)
			40.2 (4.12)	
A-4	19.2 (2.27)	26.1 (2.32)	33.7 (3.98)*	cisciscis
			40.0 (4.12)	
A-5	19.2 (2.31)	25.5 (2.36)*	32.4 (3.97)	trans(N)
			40.7 (4.11)	
			47.8 (4.01)	
[Co(aces)$_2$]Cl a)				
B-1	17.5 (1.92)		29.2 (4.13)	
	20.7 (2.02)		39.1 (4.02)	tr.tr.tr.
			4.72 (4.13)	
B-2	18.9 (2.59)	25.3 (2.55)*	31.2 (4.26)	mer-trans(S)
			39.7 (4.04)	

Table 5 (continued)

B-3 c)	17.8 (2.32)	26.4 (2.40)*	34.2 (4.19)	trans(O)
	21.1 (2.05)		40.5 (4.00)	
B-4	18.8 (2.60)		29.7 (4.15)	trans(S)
			39.3 (4.03)	
			47.4 (4.08)	
B-5	19.0 (2.42)	25.6 (2.46)*	33.0 (4.15)	cisciscis
			42.1 (4.06)	
B-6	sh b)	25.3 (2.62)*	31.8 (4.10)	trans(N)
	18.8 (2.60)		40.9 (4.08)	

* This band is a shoulder.

a) AB spectra are those of the racemates.

b) The wave number cannot be decided.

The wave numbers are given in 10^3 cm^{-1} unit.

c) This isomer is the bromide salt.

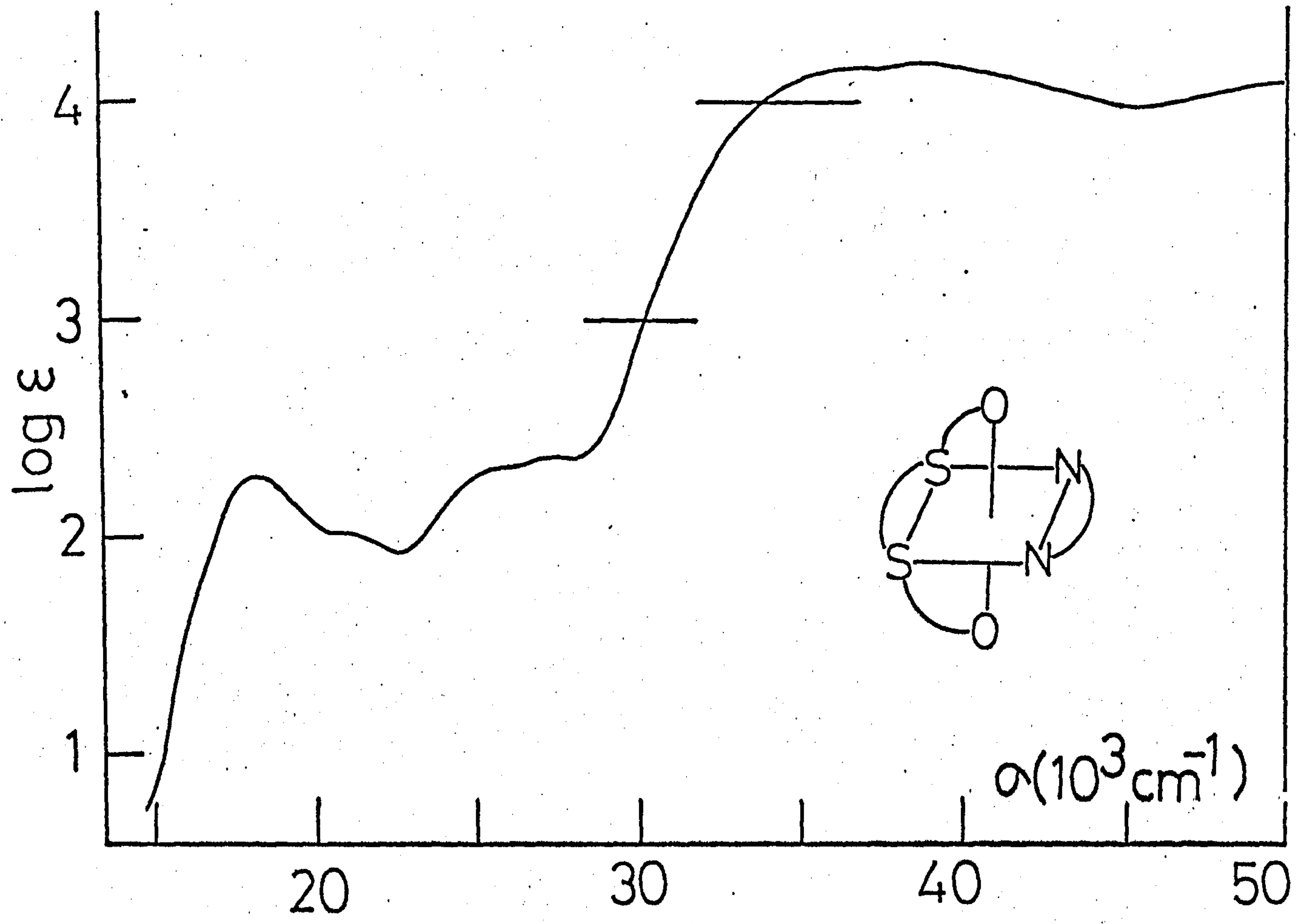


Figure 12. Absorption spectrum of trans(O)-[Co(edth)(en)]Cl.

seems to be observed for both trans(N) and trans(O) isomers but this was only observed for the A-2 isomer. In the $[Co(L\text{-}met)_2]Br$ complex,[29)] both trans(N) and trans(O) isomers showed the marked splitting in the first absorption band region and their splitting patterns differed from each other: that is, trans(O) isomer showed a broad band with a shoulder at higher energy of the major peak, while trans(N) one showed a band with an explicit shoulder at lower energy of the major peak. These results confirm that A-2 isomer is trans(O). Further evidence are given by the corresponding splitting pattern of trans(O)-[Co(edth)(en)]Cl, which shows a band with an explicit shoulder at higher energy side of the major peak as is shown in Figure 12.

Absorption spectra of A-4 and A-5 isomers are similar with each other, though there is a difference with respect to the thioether charge transfer band position. But the assignment of the trans(N) and cisciscis structures for the A-4 and A-5 isomers will be made on the basis of the differences in their NMR spectra described later. The meridional form has not been found so far, which correlates with a molecular model examination in Section I-C.

$[Co(aces)_2]^+$: In the bis(tridentate) cobalt(III) complexes containing a linear tridentate ligand such as A–B–C type, where A–B–C denotes a ligand having three different donor atoms, six geometrical isomers are generally possible. For the present complex of $[Co(aces)_2]^+$, all possible isomers, tr.tr.tr., trans(S), trans(O),

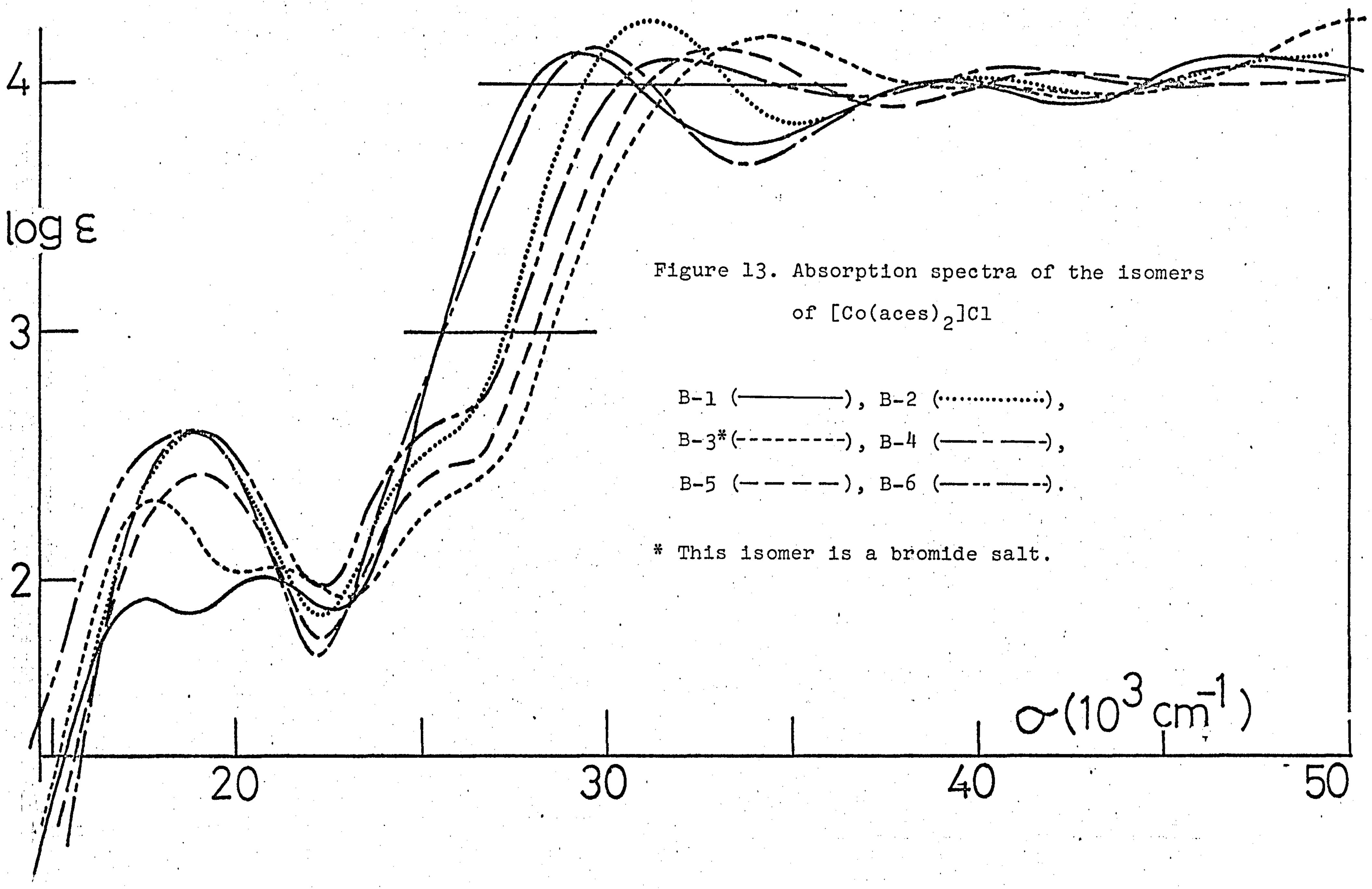


Figure 13. Absorption spectra of the isomers of [Co(aces)$_2$]Cl

* This isomer is a bromide salt.

trans(N), cisciscis and mer-trans(S), were obtained. This is the first example for the isolation of all possible isomers of the $[Co(A\text{-}B\text{-}C)_2]^{n+}$ type complexes.

Absorption spectra for the six isomers are shown in Figure 13 and summarized in Table 5. According to the same discussion described above, B-1 isomer can be assigned to tr.tr.tr., B-2 one to trans(S), B-3 one to trans(O), and B-4 one to trans(S). Of the remaining two isomers, B-5 isomer shows a sharp first absorption band (19000 cm^{-1}, $\log\varepsilon=2.42$), while B-6 one exhibits a vague shoulder at the lower energy side of the major peak (18800 cm^{-1}, $\log\varepsilon=2.60$) in the corresponding region. These spectral behaviors correspond well with the results calculated from the semiempirical theory and therefore confirm that B-5 isomer can be assigned to cisciscis and B-6 one to trans(N). The assignment of the mer-trans(S) and fac-trans(S) structures for B-2 and B-4 isomers will be made later on the basis of the difference of thioether charge transfer band, which locates at higher energy for the former (31200 cm^{-1}, $\log\varepsilon=4.26$) than that for the latter (29700 cm^{-1}, $\log\varepsilon=4.15$).

Thus, the electronic absorption spectra of the corresponding isomers between the $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$ complexes show good correlation with each other but they are found to have some differences in detail. Firstly, most striking difference is that the band intensities of the isomers of $[Co(aces)_2]^+$ are two or three times larger than those of the corresponding isomers of $[Co(acms)_2]^+$. Such kind of intensity difference was observed between trans(N)-RR-$[Co(L\text{-}promp)_2]^-$ and trans(N)-RR-$[Co(L\text{-}proma)_2]^-$ complexes,[86)] where L-promp and L-proma are L-prolinate-N-monopropionate and L-prolinate-N-monoacetate, respectively. This may be mainly due to the increased steric interaction in and between the ligands, because aces ligand which has a five- and a six-membered chelate rings, coordinates to the Co(III) ion in the more crowded manner than acms one which has two five-membered chelate rings. Secondary, in the isomers of the aces complex, the thioether charge transfer band positions are shifted to the lower energy side than those of the corresponding isomers of the acms one and this shift direction is the same as that of the first absorption band positions.

III-C-3. Absorption Spectra of $[Co(L\text{-}met)(N,S,O\text{-}tridentato)]^+$ Type Complexes

$[Co(L\text{-}met)(acms)]^+$: As is shown in Figure 4, six geometrical isomers, tr.tr.tr., trans(S), trans(N), cisciscis-I and cisciscis-II, are possible for the $[Co(L\text{-}met)(N,S,O\text{-}tridentato)]^+$ type complexes. In addition, two isomers due to the absolute configuration of sulfur atom of the coordinated L-methioninate is formally possible for each of the six isomers.

In the present complex, seven isomers were obtained. Their absorption apectra are shown in Figure 14 and Table 6. Of these isomers, thioether charge transfer band for

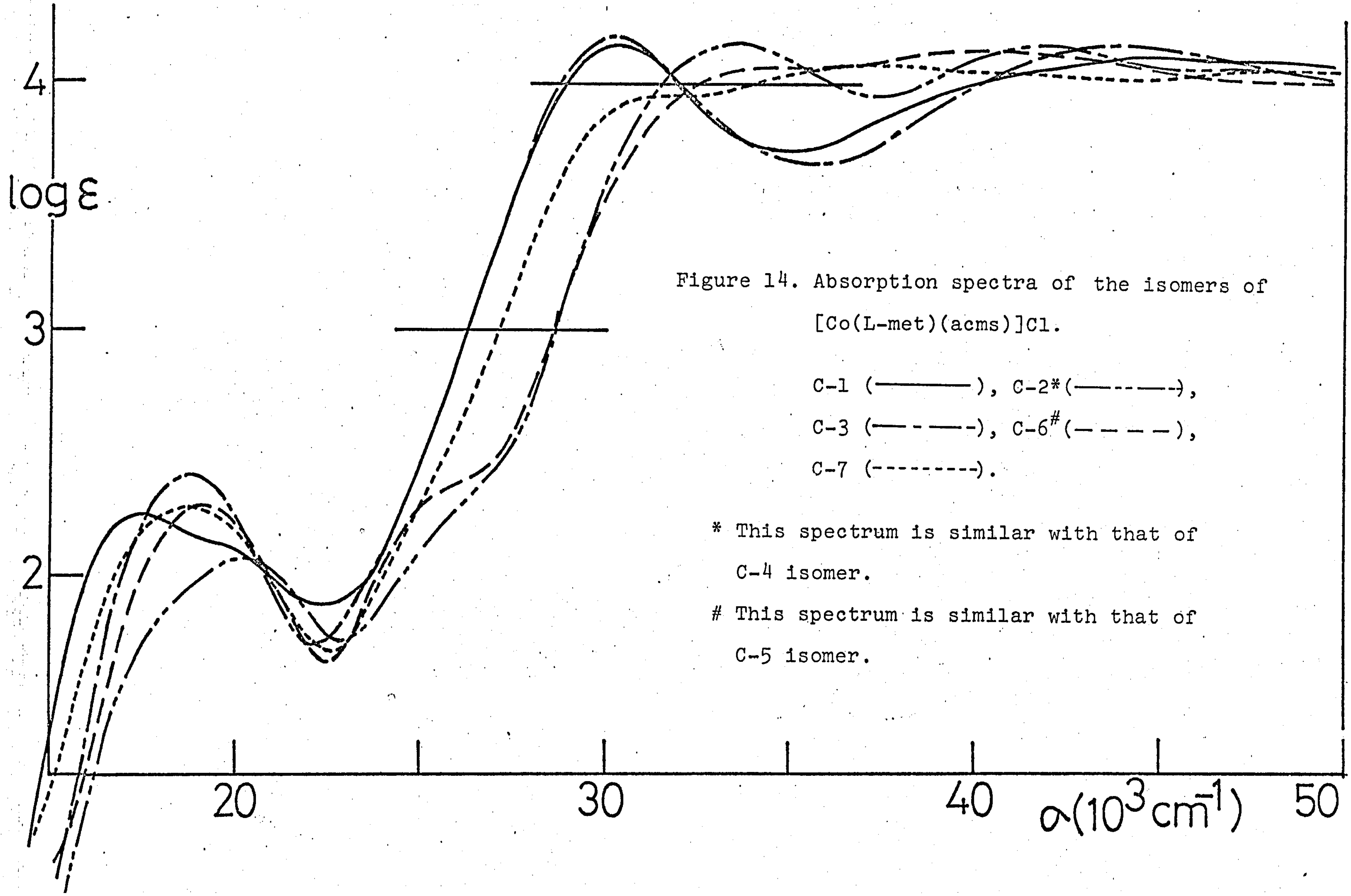


Figure 14. Absorption spectra of the isomers of [Co(L-met)(acms)]Cl.

C-1 (———), C-2*(—-—-—),
C-3 (—-—-—), C-6#(— — — —),
C-7 (---------).

* This spectrum is similar with that of C-4 isomer.

\# This spectrum is similar with that of C-5 isomer.

Table 6

AB Data of Isomers of [Co(acms)(L-met)]Cl and [Co(aces)(L-met)]Cl

[Co(acms)(L-met)]Cl

	σ_{max} (log ε)			
Isomer	I-Band	II-Band	CT-Band	Assignment
C-1	17.5 (2.25)		30.3 (4.16)	tr.tr.tr.
	20 (2.10)*		44.9 (4.11)	
C-2	sh a)	25.5 (2.10)*	33.5 (4.16)	trans(N)
	20.2 (2.07)		41.9 (4.16)	
			47.7 (4.07)	
C-3	18.8 (2.41)		30.3 (4.18)	trans(S)
			44.1 (4.16)	
C-4	sh a)			
	19.9 (2.07)	25.5 (2.20)*	33.0 (4.08)	trans(N)
			42.2 (4.12)	
C-5	19.1 (2.28)	25.5 (2.30)*	34.0 (4.10)	cisciscis
			42.8 (4.10)	
C-6	19.2 (2.29)	25.5 (2.30)*	34.2 (4.06)*	cisciscis
			40.3 (4.14)	
C-7	18.8 (2.28)		31.3 (3.95)*	trans(O)
	sh a)		37.5 (4.08)	
			41.7 (4.05)*	
			48.8 (4.07)	

Table 6 (continued)

[Co(aces)(L-met)]Cl

D-1	19.2 (2.26)		29.0 (4.20)	tr.tr.tr.
			46.7 (4.16)	
D-2	18.6 (2.24)		29.2 (4.02)	trans(S)
			44.3 (4.00)	
D-3	18.4 (1.99)*	25.5 (2.30)*	33.4 (4.20)	trans(N)
	20.4 (2.11)		47.5 (4.08)	
D-4	19.0 (2.39)	25.5 (2.40)*	33.0 (4.13)	cisciscis
			42.4 (4.07)	
D-4a b)	19.1 (2.39)	25.5 (2.40)*	32.8 (4.15)	cisciscis
			42.4 (4.09)	
D-4b b)	19.0 (2.39)	25.5 (2.40)*	32.8 (4.11)	cisciscis
			42.5 (4.06)	
D-5	17.9 (2.37)	sh a)	31.9 (4.04)	trans(O)
	sh a)		34.5 (4.02)*	
			42.4 (4.01)	
D-6	18.8 (2.39)	sh a)	33.3 (4.11)	cisciscis
			46.3 (4.05)	
D-6a b)	18.8 (2.39)	25.5 (2.40)*	33.6 (4.13)	cisciscis
			46.7 (4.07)	
D-6b b)	18.8 (2.39)	sh a)	33.3 (4.11)	cisciscis

* This band is a shoulder.

a) The wave number cannot be decided.

b) The concentration was determined referring that of the mixture (for D-4a and D-4b, D-4; for D-6a and D-6b, D-6).

The wave numbers are given in 10^3 cm^{-1} unit.

C-1 (30300 cm^{-1}, logε=4.16) and C-3 (30300 cm^{-1}, logε=4.18) locate at lower energy side than those for the other five isomers (33500 cm^{-1}, logε=4.16 for C-2; 33000 cm^{-1}, logε=4.08 for C-4; 34000 cm^{-1}, logε=4.10 for C-5; sh.34200 cm^{-1}, logε=4.06 for C-6; sh.31300 cm^{-1}, logε=3.95 for C-7). This indicates that the former two isomers are S-trans form and the latter five S-cis one. With the two S-trans isomers, C-1 shows a broad first absorption band with a shoulder at higher energy of the major peak (17500 cm^{-1}, logε=2.25), while C-3 shows a sharp peak (18800 cm^{-1}, logε=2.24) in the corresponding region. Therefore, C-1 and C-3 can be assigned to tr.tr.tr. and trans(S) structures, respectively. On the other hand, of the five S-cis isomers, C-2 and C-4 isomers show a band with a shoulder at lower energy of the major peak (20200 cm^{-1}, logε=2.07 for C-2; 19900 cm^{-1} logε=2.07 for C-4) and C-7 isomer shows a band with a vague shoulder at higher energy of the major peak (18800 cm^{-1}, logε=2.28), while C-5 and C-6 isomers show apparently a sharp peak (19100 cm^{-1}, logε=2.28 for C-5; 19200 cm^{-1}, logε=2.29 for C-6). These splitting patterns affirm that C-2 and C-4 are trans(N), C-5 and C-6 cisciscis, and C-7 trans(O).

$[Co(L\text{-}met)(aces)]^{+}$: In this complex eight isomers were obtained, and their absorption spectra are shown in Figure 15 and Table 6. These isomers can be assigned according to the same arguments described above; namely, D-1 is tr.tr.tr., D-2 trans(S), D-3 trans(N), D-4a and D-4b cisciscis, D-5 trans(O) and D-6a and D-6b cisciscis.

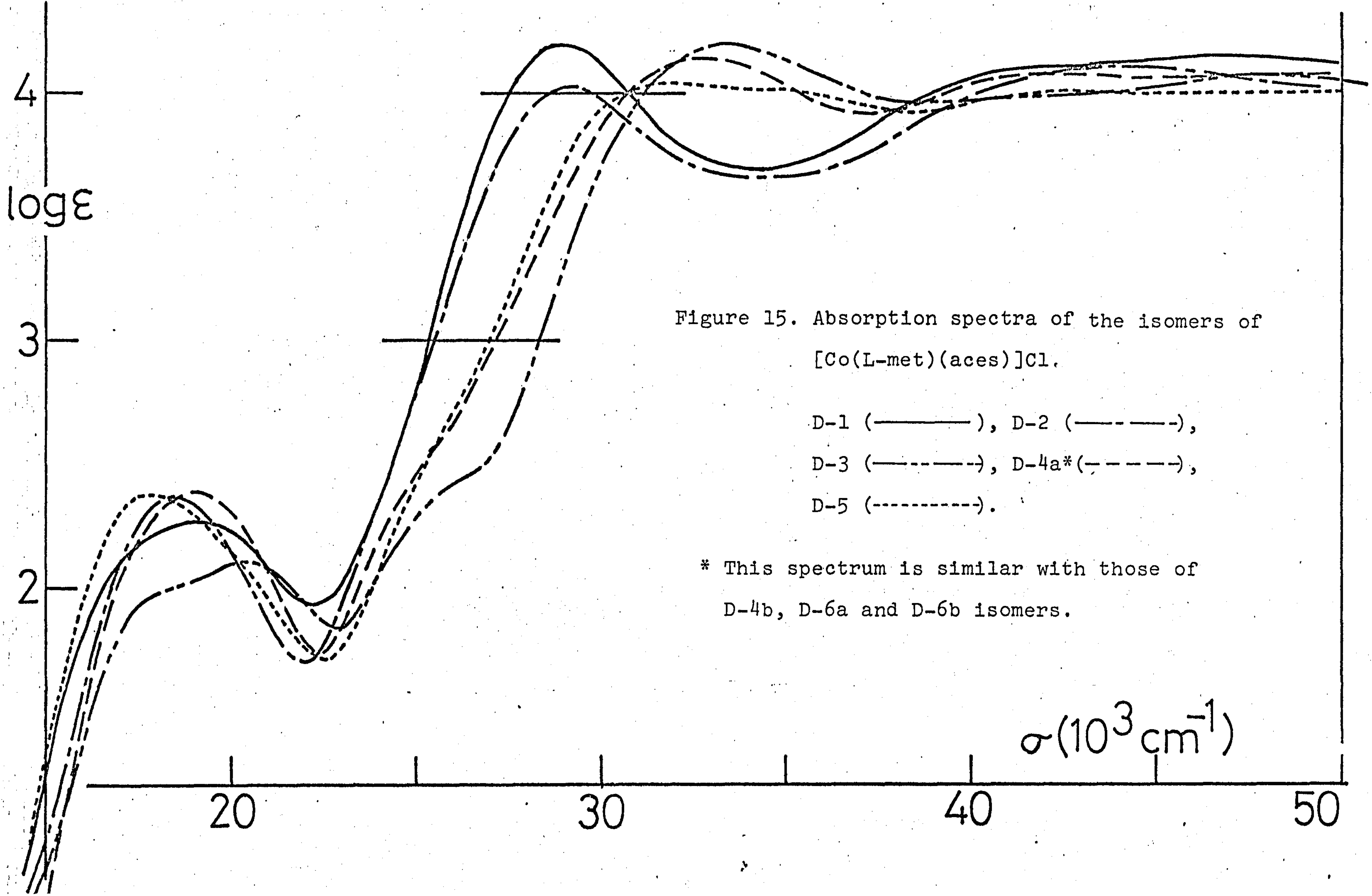


Figure 15. Absorption spectra of the isomers of [Co(L-met)(aces)]Cl.

D-1 (————), D-2 (—·—·——),
D-3 (——·——·—), D-4a*(— — — —),
D-5 (-----------).

* This spectrum is similar with those of D-4b, D-6a and D-6b isomers.

However, the assignment of cisciscis-I and cisciscis-II is impossible from their absorption apectra for both complexes of $[Co(L\text{-}met)(acms)]^+$ and $[Co(L\text{-}met)(aces)]^+$, and will be made later on the basis of the NMR spectra.

III-C-4. Elution Order of Isomers

It has been generally recognized that the elution order of the stereoisomers by means of ion-exchange column chromatography depends on their dipole moments.[87) For example, in the case of bis(glycinato)ethylenediamine-cobalt(III) complex,[83,88) the trans isomer is eluted before the cis one because of its smaller dipole moment.

For the five series of the complexes containing thioether donors, the elution orders are shown in Table 7. The corresponding isomers of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$ have the same elution order except for the B-2-trans(S) isomers; namely, the order is tr.tr.tr., trans(O), trans(S), cisciscis, and trans(N) for both complexes. These facts seem to be very suggestive with respect to the assignment of the mer-trans(S) and fac-trans(S) structures for the B-2 and B-4 isomers (see Section III-C-5).

In the mixed type complexes, the separation was firstly carried out by using a column of Dowex 50Wx8, and then partly re-separated by using a column containing SP-Sephadex C-25 as described in Experimental Section (II-B-14). Nevertheless, the elution order of the isomers with the corresponding geometrical structure seems to be equal; that is, the order is tr.tr.tr., trans(S)≈trans(N)

Table 7. The Elution Order for the Five Series Complexes Containing Thioether Donors

Elution	Complex*				
Order	A	B$^{a)}$	C$^{b)}$	D$^{c)}$	$[Co(L\text{-}met)_2]^+$
F-1	A-1 tr.tr.tr.	B-1 tr.tr.tr.	C-1 tr.tr.tr.	D-1 tr.tr.tr.	trans(S)
F-2	A-2 trans(O)	B-2 trans(S) (mer)	C-2 trans(N)	D-2 trans(S)	trans(N)
F-3	A-3 trans(S)	B-3 trans(O)	C-3 trans(S)	D-3 trans(N)	trans(O)
F-4	A-4 cisciscis	B-4 trans(S)	C-4 trans(N)	D-4(a,b) cisciscis	
F-5	A-5 trans(N)	B-5 cisciscis	C-5 cisciscis	D-5 trans(O)	
F-6		B-6 trans(N)	C-6 cisciscis	D-6(a,b) cisciscis	
F-7			C-7 trans(O)		

* A, B, C and D denote the complexes of $[Co(acms)_2]^+$, $[Co(aces)_2]^+$, $[Co(L\text{-}met)(acms)]^+$ and $[Co(L\text{-}met)(aces)]^+$, respectively.

a) The complete separation of B-3 and B-4 isomers was unsuccessfully attempted.

b),c) These complexes were partly reseparated by the resin of SP-Sephadex C-25.

and cisciscis≈trans(O). It is interesting to note that the tr.tr.tr. isomer is eluted firstly without exception and that the trans(O) one is eluted ealier than the trans(N) one for $[Co(N,S,O\text{-tridentato})_2]^+$ type complexes, while the reverse was found for $[Co(L\text{-met})(N,S,O\text{-tridentato})]^+$ type complexes. The reverse of the elution order between trans(O) and trans(N) isomers seems to correspond well with the progressive substitution effect of L-met, for the series of the complexes, $(N,S,O\text{-tridentate})_2 \longrightarrow (L\text{-met})(N,S,O\text{-tridentate}) \longrightarrow (L\text{-met})_2$, because the trans(N) isomer is eluted ealier than the trans(O) one for $[Co(L\text{-met})_2]^+$.

III-C-5. Assignment of Structures

$[Co(acms)_2]^+$: In the five isomers of the $[Co(acms)_2]^+$ complex, three ealier aluates (A-1, A-2 and A-3) are assigned to tr.tr.tr., trans(O) and trans(S) forms, respectively, from their absorption spectra (see Section III-C-2). However, there are some difficulties with respect to the assignment of A-4 and A-5 isomers. Then, NMR spectra of these isomers were measured (Figure 16). As shown in Figure 16, A-2, A-3 and A-5 isomers show a qualtet due to methylene protons between carboxyl group and sulfur atom,32) whereas A-4 shows two sets of qualtet. Model construction reveals that trans(O), trans(S) and trans(N) structures have C_2 symmetry, while cisciscis one has C_1 symmetry and therefore this isomer should show the most complicated spectral pattern.83) Above results agree

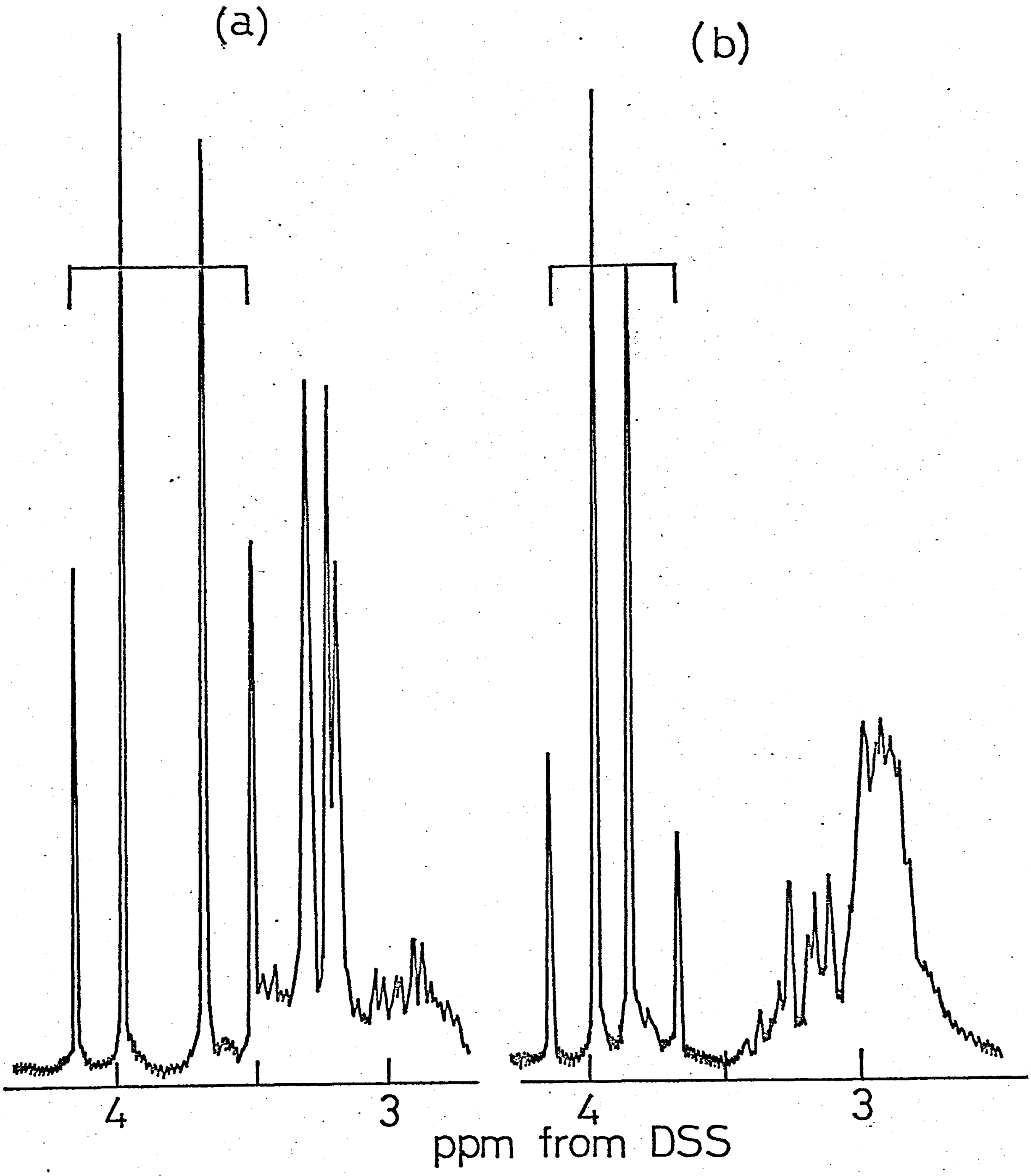


Figure 16. The pmr spectra of the isomers of $[Co(acms)_2]Cl$ in D_2O: (a) A-2, (b) A-3, (c) A-4 and (d) A-5.

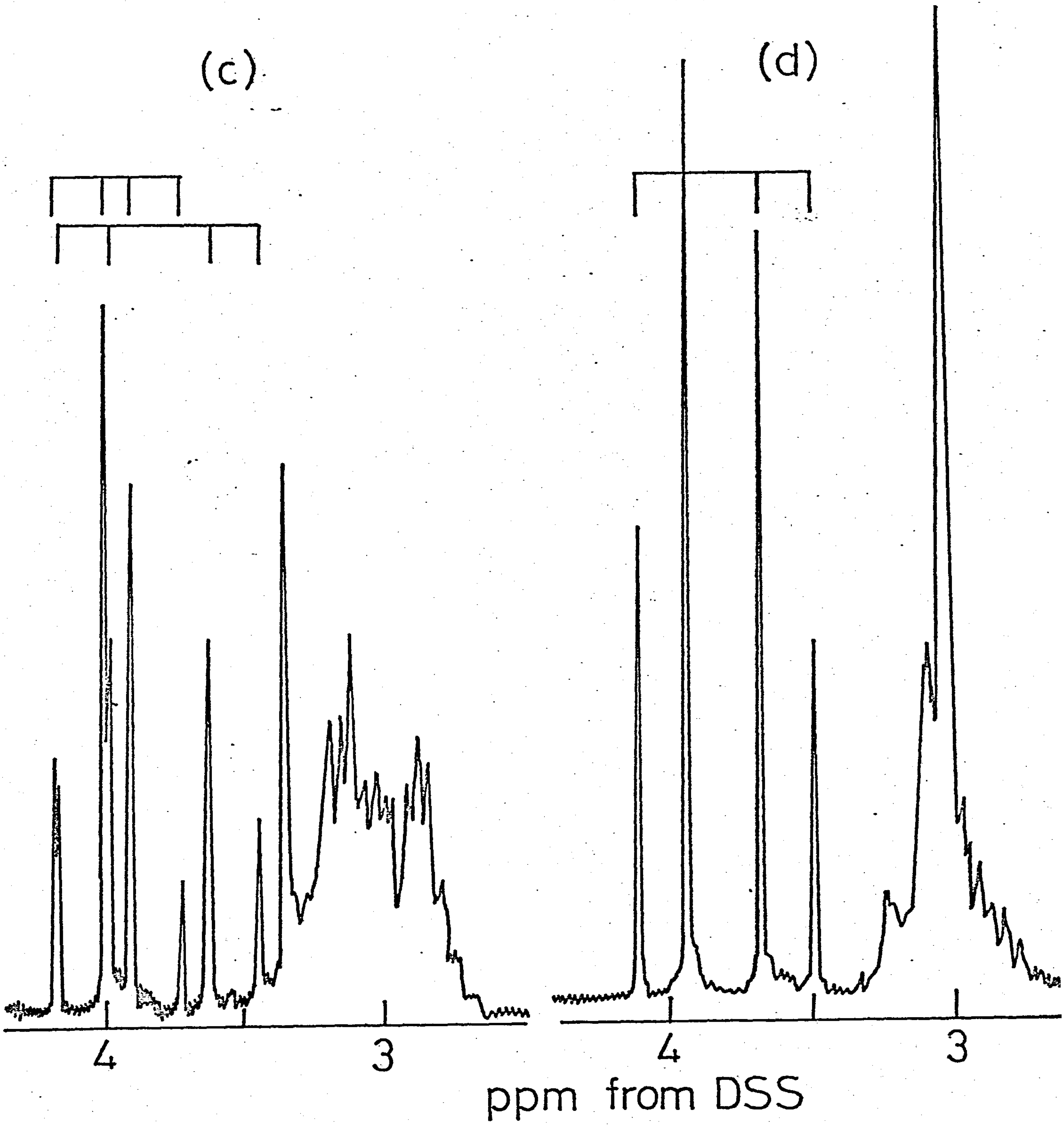


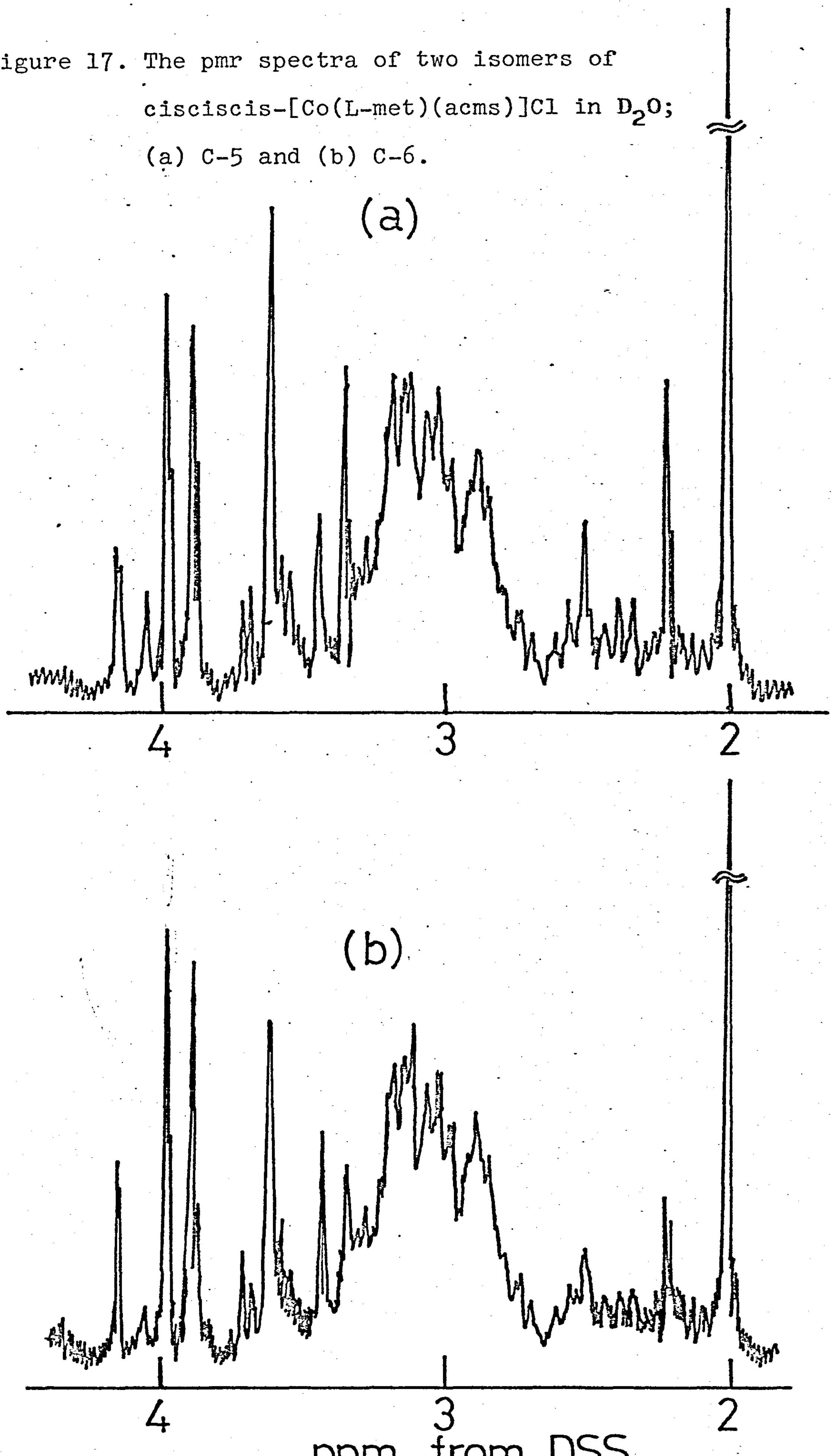
Figure 16. (continue)

well with this argument. Accordingly, A-4 isomer can be assigned to cisciscis and A-5 one to trans(N). Further support is given by the signals in the region of amine protons. That is, the amine signals appear at 6.17 and 6.58 ppm for A-2 isomer, at 4.62 and 4.98 ppm for A-3 one, at 4.49, 4.90 and 6.36 ppm for A-4 one, and at 5.26 and 6.67 ppm for A-5 one. These spectral behaviors are explained qualitatively in terms of the magnetic anisotropy associated with the C-O single bond.89-92) In each of the present isomers, there are two amine groups. Two groups of trans(S) and trans(N) and one group of cisciscis are in the shield position from the C-O bond of the other ligand, whereas the one group of the cisciscis isomer and two groups of the trans(O) isomer are positioned in the deshielded region by the C-O bond of the other ligand. From these reasons it is possible to expect that the cisciscis isomer with C_1 symmetry shows the most complicated signals over the wider region than the other three isomers with C_2 symmetry.

$[Co(aces)_2]^+$: Six isomers, B-1, B-2, B-3, B-4, B-5 and B-6, were assigned to tr.tr.tr., trans(S), trans(O), trans(S), cisciscis and trans(N), respectively, from their absorption spectra (see Section III-C-2). The assignment of the mer-trans(S) and fac-trans(S) structures for the B-2 and B-4 isomers, respectively, can be made on the basis of the preparative result that B-2 has very low yield (see Section II-B-12), and absorption spectral behavior that the thioether charge transfer band of B-2 isomer locate in strikingly exceptional position (see Section III-C-7). Further information on the assignment of B-2 and B-4 isomers was not given, even though there are some differences in the infrared and NMR apectra. The pmr spectral behaviors in the region of amine protons confirm the above assignment that B-2, B-3, B-4 and B-5 isomers are trans(S), trans(O), trans(S) and cisciscis structures, respectively, according to the same argument as that for $[Co(acms)_2]^+$ (4.56 ppm for B-2; 5.84 and 6.54 ppm for B-3; 4.48 and 4.86 ppm for B-4; 4.36 and 6.20 ppm from DSS for B-5: The pmr data of B-1 and B-6 cannot be obtained because of their poor solubility).

$[Co(L\text{-}met)(acms)]^+$: Seven isomers of this complex were assigned from their absorption spectra; namely, C-1 is tr.tr.tr., C-2 trans(N), C-3 trans(S), C-4 trans(N), C-5 and C-6 cisciscis, and C-7 trans(O). As is shown in Figure 4 (Section I-D), there exists only one geometrical isomer for the trans(N) structure. Accordingly, C-2 and C-4 isomers with the trans(N) structure should be diastereomers due to the sulfur atom chirality (R or S) of the coordinated L-methioninate. Two geometrical isomers are expected for the cisciscis form (cisciscis-I and cisciscis-II) but it is impossible to decide the configuration of the C-5 and C-6 isomers from their electronic absorption spectra. In order to achieve these assignments, NMR spectra of C-5 and C-6 isomers were measured in D_2O by adding a small amount of DCl (Figure 17).

Figure 17. The pmr spectra of two isomers of cisciscis-[Co(L-met)(acms)]Cl in D_2O; (a) C-5 and (b) C-6.



These spectra are entirely similar with each other over the all region measured. Furthermore, in the region of amine protons, there are four peaks at 6.35, 5.85, 5.18 and 4.48 ppm from DSS for both isomers. These results indicate that both of the C-5 and C-6 isomers have cisciscis-I or cisciscis-II structure and therefore are diastereomers due to the sulfur atom chirality (R or S) of the coordinated L-methioninate. From the assignment of cisciscis-I and cisciscis-II for $[Co(L\text{-}met)(aces)]^+$ which will be described below, it is expected that both isomers, C-5 and C-6, have the cisciscis-I structure.

$[Co(L\text{-}met)(aces)]^+$: Eight isomers of this complex were assigned from their absorption spectra; namely, D-1 is tr.tr.tr., D-2 trans(S), D-3 trans(N), D-4a and D-4b cisciscis, D-5 trans(O), and D-6a and D-6b cisciscis. It is reasonable to consider that D-4a and D-4b (or D-6a and D-6b) have the same geometrical structure from the similar chromatographic behavior. The assignment of cisciscis-I and cisciscis-II was made on the basis of NMR spectra. D-4 isomer which is a mixture of D-4a and D-4b isomers, showed a methine signal at 3.91 ppm from DSS, and D-6 one which is a mixture of D-6a and D-6b isomers, showed this signal at 3.45 ppm. This very large difference of the chemical shift due to methine proton is explained on the basis of C-O deshielding effect89-92) as follows; in the cisciscis-I structure, methine proton is located just above a line drawn down the C-O bond of the other ligand and will be deshielded by the anisotropy associated with the C-O bond, while in the cisciscis-II form, this effect does not occur. From these reasons, D-4 and D-6 isomers can be assigned to the cisciscis-I and cisciscis-II structures, respectively. In addition, in the region of the amine protons, D-4 isomer showed three peaks at 4.31, 5.03 and 6.19 ppm but D-6 isomer one peak at 5.97 ppm. These results confirm also that D-4 isomer is cisciscis-I and D-6 one cisciscis-II, which correspond well to the results for the C-5 and C-6 isomers of $[Co(L\text{-}met)(acms)]^+$. Thus, D-4a and D-4b (or D-6a and D-6b) are considered to be diastereomers arising from the asymmetric sulfur donor atom of the coordinated L-methioninate.

III-C-6. Comparison of the Absorption Spectra

Since, in the previous Section, twenty-six complexes of the bis(tridentate) and mixed types were assigned on the basis of the absorption spectra, chromatographic behaviors and NMR spectra, it is now possible to compare the absorption spectra among the corresponding isomers.

In the first absorption band region, four tr.tr.tr. isomers (Figure 18) show very broad band with large splitting except that the shoulder at lower energy side is obscured for the $[Co(L\text{-}met)(aces)]^+$ complex. Contrary to this, six trans(S) (Figure 19) and eight cisciscis isomers (Figure 20) exhibit a apparently sharp peak in the corresponding region without exception. In the cases of trans(N) (Figure 21) and trans(O) isomers (Figure 22), their absorption spectra are classified into two groups; namely, two bis(tridentate) type trans(N) isomers of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$ show no splitting and other four trans(N) isomers of $[Co(L\text{-}met)(acms)]^+$, $[Co(L\text{-}met)(aces)]^+$ and $[Co(L\text{-}met)_2]^+$ exhibit a explicit shoulder at lower energy side of the major peak, while two bis(tridentate) type trans(O) isomers show more explicit shoulder at higher energy of the major band rather than the other three trans(O) isomers of $[Co(L\text{-}met)(acms)]^+$, $[Co(L\text{-}met)(aces)]^+$ and $[Co(L\text{-}met)_2]^+$. Thus, the correlation between the two bis(tridentate) type complexes is very good as well as that between the two mixed type complexes. The first spin-allowed d-d absorption bands of $[Co(acms)_2]^+$, $[Co(aces)_2]^+$ and $[Co(L\text{-}met)_2]^+$ are shifted to lower energy

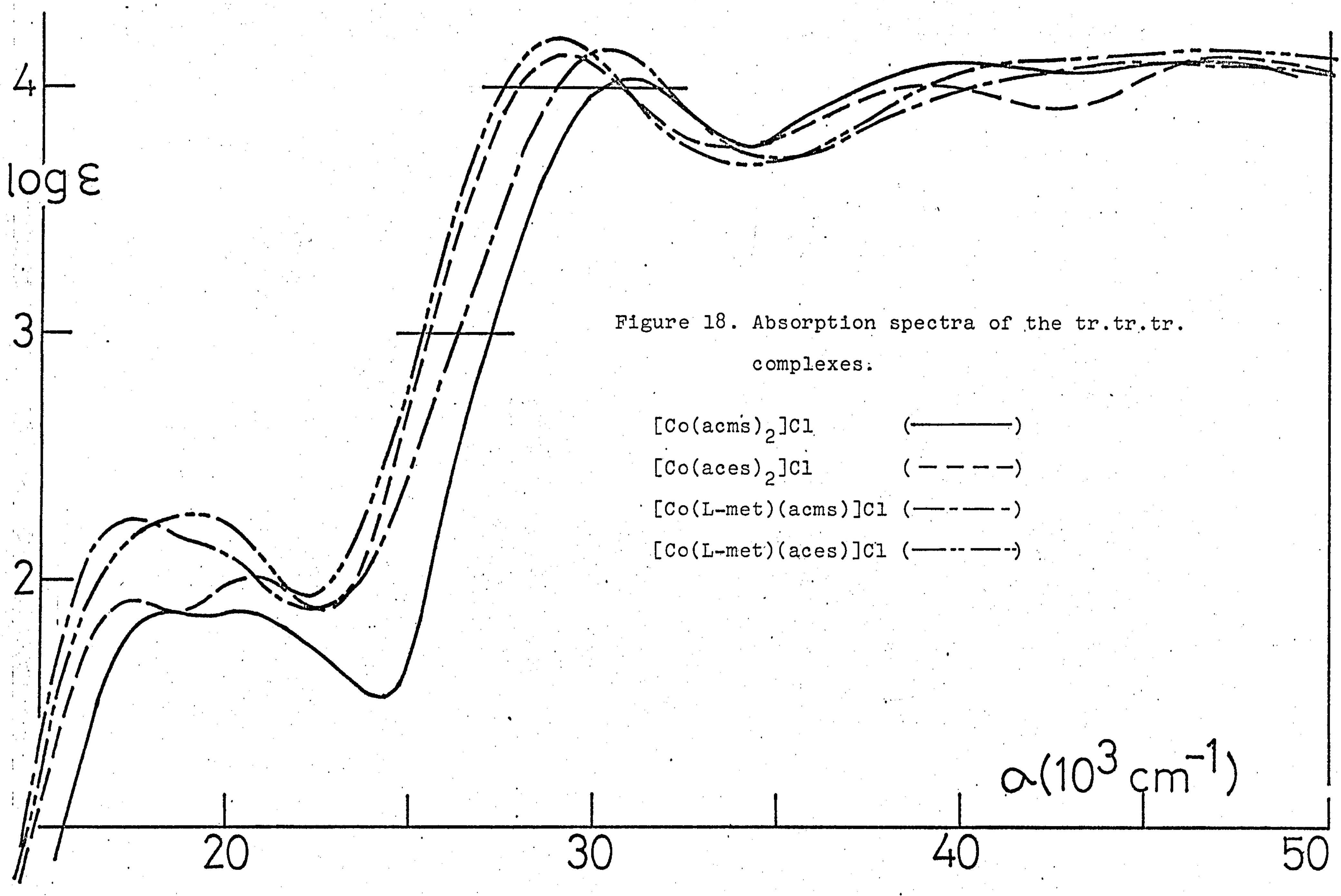


Figure 18. Absorption spectra of the tr.tr.tr. complexes.

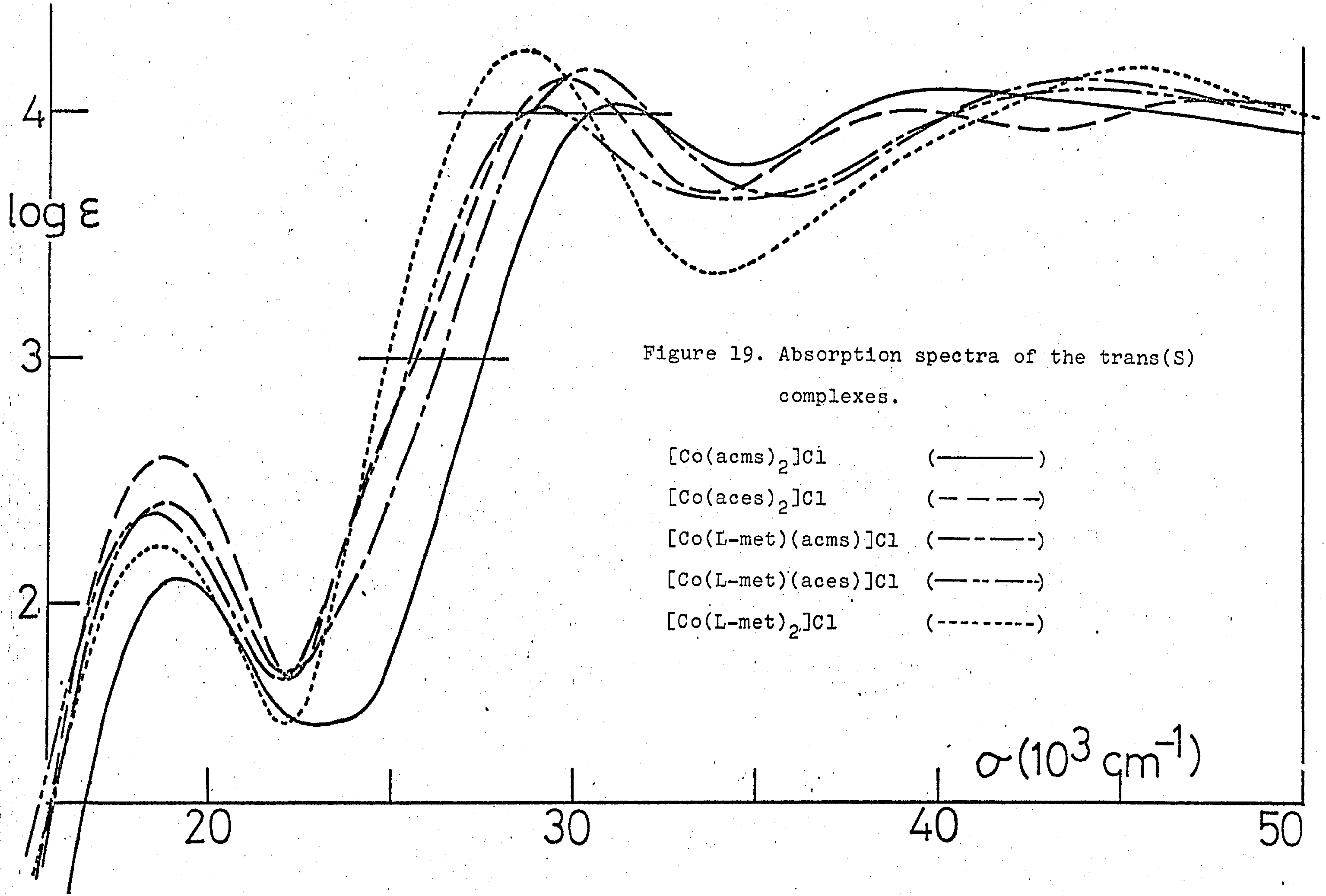


Figure 19. Absorption spectra of the trans(S) complexes.

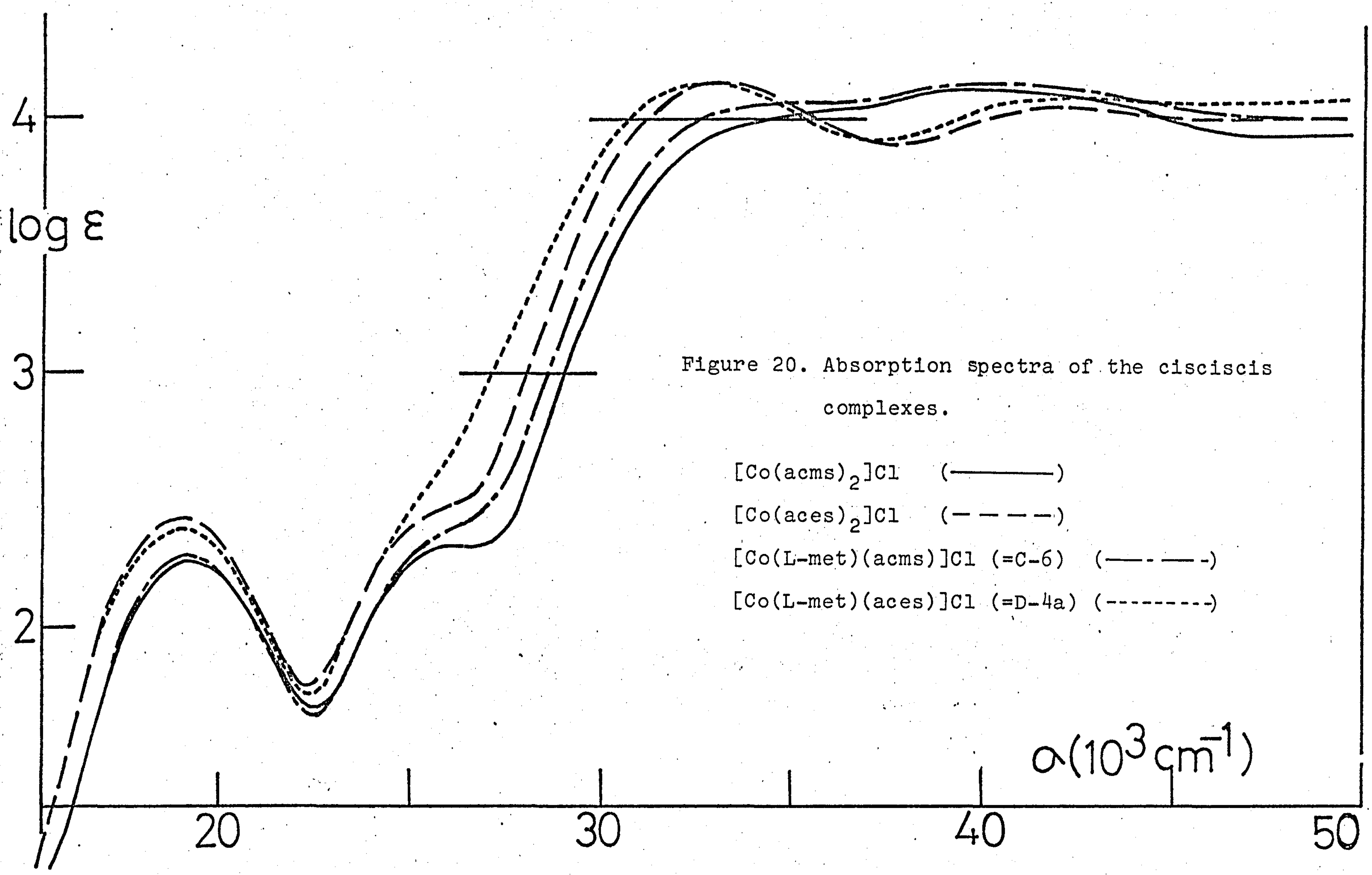


Figure 20. Absorption spectra of the cisciscis complexes.

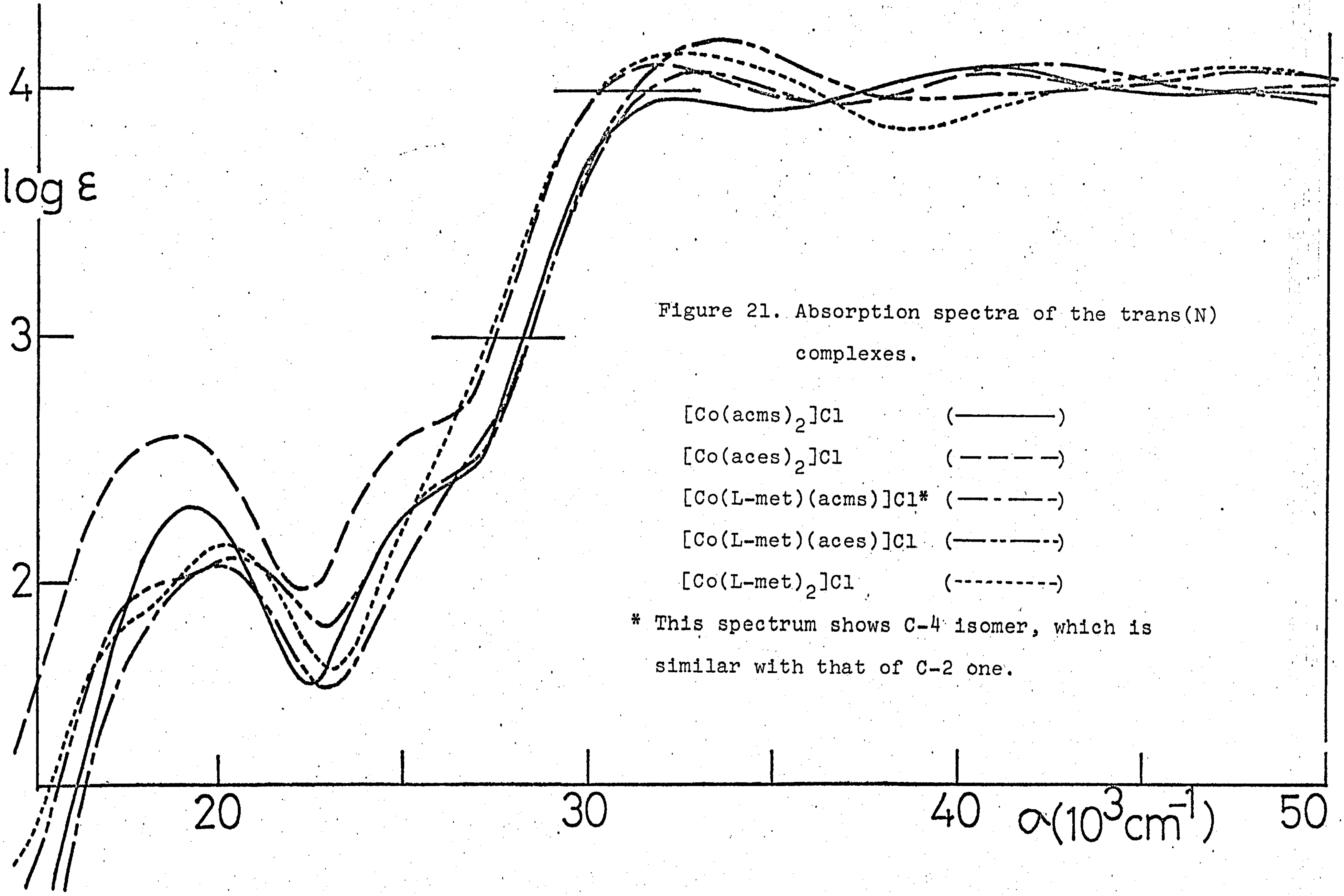


Figure 21. Absorption spectra of the trans(N) complexes.

* This spectrum shows C-4 isomer, which is similar with that of C-2 one.

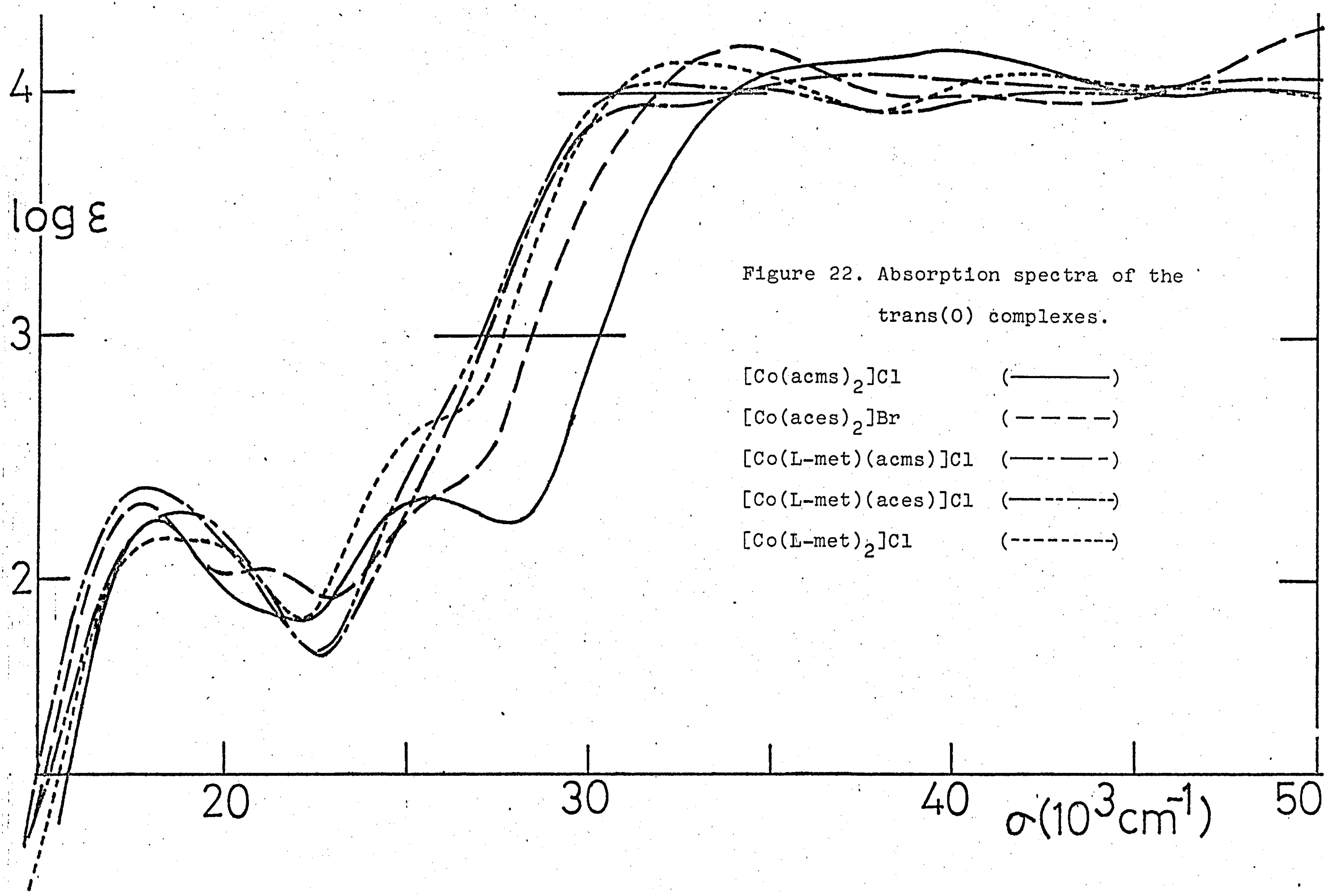


Figure 22. Absorption spectra of the trans(O) complexes.

in the order acms$^-$ > aces$^-$ $\geq$ L-met$^-$, though their band intensities deviate widely. Two mixed complexes, [Co(L-met)(acms)]$^+$ and [Co(L-met)(aces)]$^+$, show an approximate correlation with their parent complexes, [Co(acms)$_2$]$^+$ and [Co(L-met)$_2$]$^+$, and [Co(aces)$_2$]$^+$ and [Co(L-met)$_2$]$^+$, respectively, in the position, though there is no correlation in the intensities. Similar relationship is also substantiated for the other mixed complex, [Co(L-asp)(ida)]$^-$ 93), where L-asp and ida are L-aspartate and iminodiacetate, respectively.

With respect to the second spin-allowed d-d absorption band, tr.tr.tr. and trans(S) isomers do not show even a shoulder because of the overlapping of the thioether charge transfer band located at lower energy, but the other three geometrical isomers, trans(O), trans(N) and cisciscis, exhibit more or less a shoulder in a region of the second absorption band.

The intense band located at 30000-35000 cm^{-1} is the thioether charge transfer band (Tables 1, 3, 5 and 6). The mono-sulfur complexes which are [Co(N)$_4$(S)(O)] type have this absorption bands at a narrow region 34600-35700 cm^{-1} (35700 cm^{-1} for [Co(en)$_2$(mms)]$^{2+}$; 34600 cm^{-1} for [Co(en)$_2$(ems)]$^{2+}$; 35700 cm^{-1} for [Co(tame)(acms)]$^{2+}$; 35000 cm^{-1} for [Co(tame)(aces)]$^{2+}$). This bands of the bis(tridentate) and mixed type complexes which contain two sulfur donors are positioned at the lower energy side than those of the mono-sulfur complexes.

In the case of the trans(N) isomers, the thioether charge transfer band of $[Co(L\text{-}met)_2]^+$ (32600 cm^{-1}) occurs at the higher energy side than those of the two bis(tridentate) type complexes (32400 cm^{-1} for A-5; 31800 cm^{-1} for B-6). Accordingly, the mixed complexes (33500 cm^{-1} for C-2; 33000 cm^{-1} for C-4; 33400 cm^{-1} for D-3) have this band at relatively higher energy compared with the bis(tridentate) type complexes, though the complete additivity between the parent complexes was not recognized.

For the trans(O) isomers, there are apparently large differences in the position of the thioether charge transfer bands between the bis and mixed type complexes (sh.35100 cm^{-1} for A-2; sh.34200 cm^{-1} for B-3; 31300 cm^{-1} for C-7; 31900 cm^{-1} for D-5). However, these results may be interpreted by the consideration that the mixed complexes have two thioether bands, since the trans(O) isomer of $[Co(L\text{-}met)_2]^+$ (at 32700 cm^{-1}) shows this band at the considerably lower energy than those of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$. In fact, C-7 and D-5 isomers show another intense bands at 34500 (sh) and 37500 cm^{-1}, respectively, which correspond roughly to the position of the thioether bands of the bis type complexes.

The cisciscis isomers have a thioether charge transfer band at the same region.

On the other hand, in the case of the tr.tr.tr. or trans(S) isomers, this bands are located at considerably lower energy, compared with the S-cis isomers. Furthermore, the band of the mixed complexes (30300 cm^{-1} for C-1; 29000 cm^{-1} for D-1; 30300 cm^{-1} for C-3; 29200 cm^{-1}

for D-2) are positioned at relatively lower energy than the bis type complexes (30900 cm^{-1} for A-1; 29200 cm^{-1} for B-1; 31200 cm^{-1} for A-3; 29700 cm^{-1} for B-4), because the band of trans(S)-$[Co(L\text{-}met)_2]^+$ occurs at lower energy than the bis type complexes.

Though the positions of the thioether bands deviate to some extent in a series of the corresponding geometrical isomers, some regularities are also found. That is, the shift to higher energy is apparently in the order, tr.tr.tr.≃trans(S)→trans(N)→cisciscis→trans(O) for the bis type complexes, and tr.tr.tr.≃trans(S)→ trans(O)→trans(N)≃cisciscis for the mixed type complexes. Especially, the location of this bands in almost same position for the tr.tr.tr. and trans(S) isomers not only in the bis(tridentate) type complexes but also in the mixed type complexes is important, which was used to the assignment of mer-trans(S) and fac-trans(S).

In the bis(tridentate) type complexes of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$, another intense thioether charge transfer band appears at ca.40000 cm^{-1}. Five isomers of $[Co(acms)_2]^+$ show this band at the same region, while for $[Co(aces)_2]^+$ complex the bands of three S-trans isomers are located at relatively lower energy than those of the other three S-cis isomers though their energy differences are not so large as those for the thioether bands at 30000-35000 cm^{-1}. Thus, this intense band is not very sensitive to the geometric change compared with the lower thioether band, but the similar trend is somewhat observed.

III-C-7. Infrared Spectra

It has been well known that the infrared spectra[94)] sometimes serve as an useful tool to distinguish between the possible structures. Buckingham and Jones [95)] have used this method to distinguish between the s-cis- and u-cis-dianiono(triethylenetetramine)cobalt(III) complexes. It has become, however, apparent that the infrared spectra are not necessarily useful and the observed splitting of the spectra is a strong function of the counter anion.[17)]

In metal-amine compound, the four principal regions of amine absorptions are ~3200, ~1600, ~1300 and ~800 cm^{-1} and have been assigned to N-H stretching, asymmetric deformation, symmetric deformation and rocking modes, respectively. Table 8 shows the frequencies of the five isomers of $[Co(acms)_2]^+$ in the N-H stretching and the NH_2 deformation regions which were assigned with reference to the spectra of related complexes. Each of the isomers exhibits two or three absorptions in the N-H stretching region and a single peak in the NH_2 deformation region, though the cisciscis isomer which has C_1 symmetry should show more complicated absorption than the other four isomers, These results may lead also to the conclusion that the symmetry consideration in the N-H stretching and NH_2 deformation regions is of the limited aplicability.

The infrared spectra of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$ are illustrated in Figures 23 and 24. Each of the five

Table 8. Infrared Absorptions due to the Coordinated NH_2 and COO Groups in the Isomers of $[Co(acms)_2]Cl$ (cm^{-1}).

Isomer	Assignment		
	ν(N-H)	ν_a(COO)	δ(N-H)
tr.tr.tr.	3190 s	1660(sh)	1588 s
	3170(sh)	1631 s	
	(3054 s)		
trans(O)	3270 s	1655(sh)	1583 s
	3210 s	1638 s	1566 m
		1625(sh)	
trans(S)	3260 m	1654 s	
	3200(sh)	1642(sh)	
	3130 s	1606 s	
cisciscis	3200(sh)	1658 s	1585 s
	3100(sh)	1620 s	
trans(N)	3230 s	1657 s	1580(sh)
	3200 s	1640(sh)	
	3090(sh)	1625 s	

Abbreviation; s: strong, m: medium, sh: shoulder.

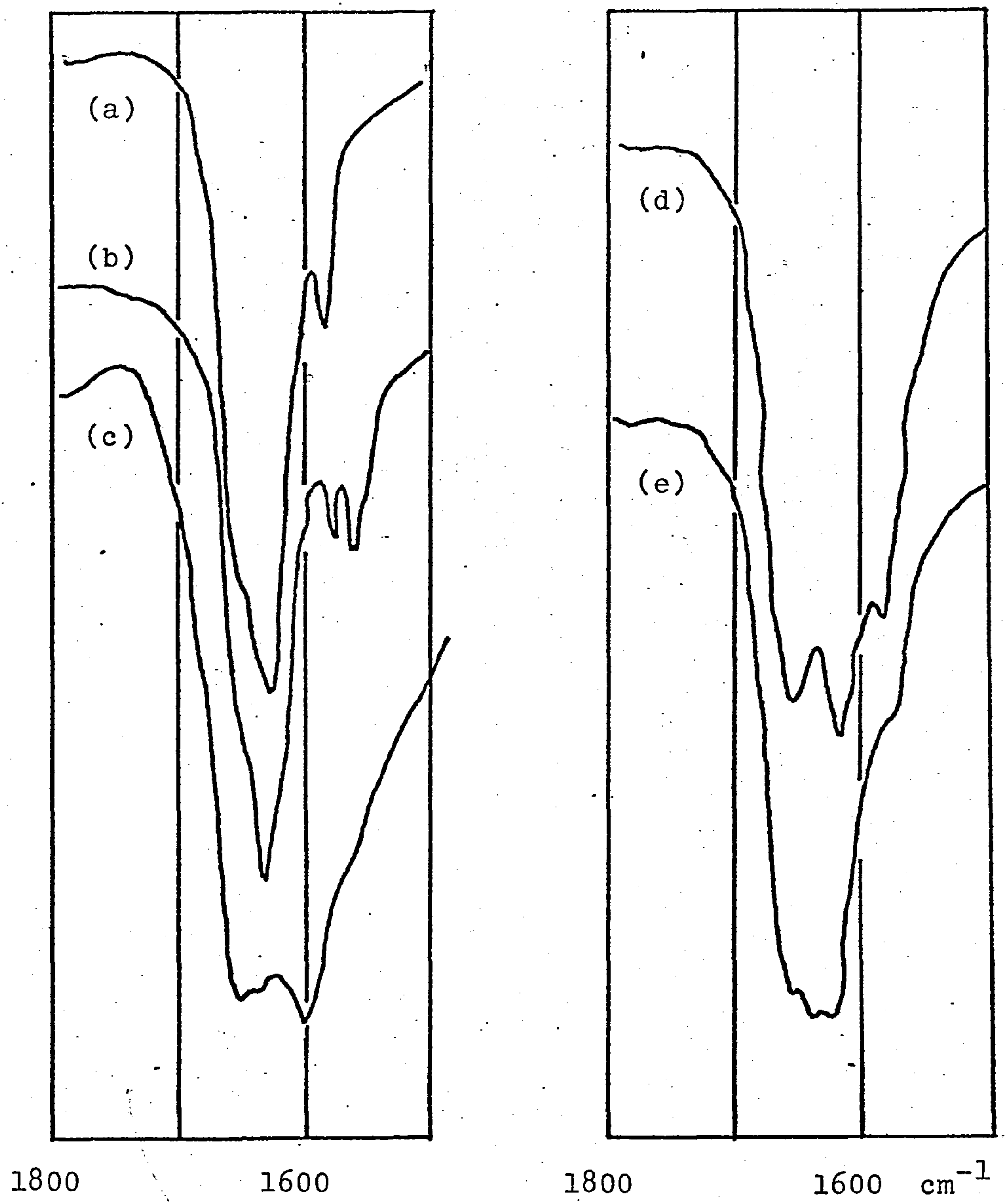


Figure 23. Infrared spectra of the isomers of [Co(acms)$_2$]Cl in the antisymmetric COO stretching band region; (a) tr.tr.tr., (b) trans(O), (c) trans(S), (d) cisciscis and (f) trans(N).

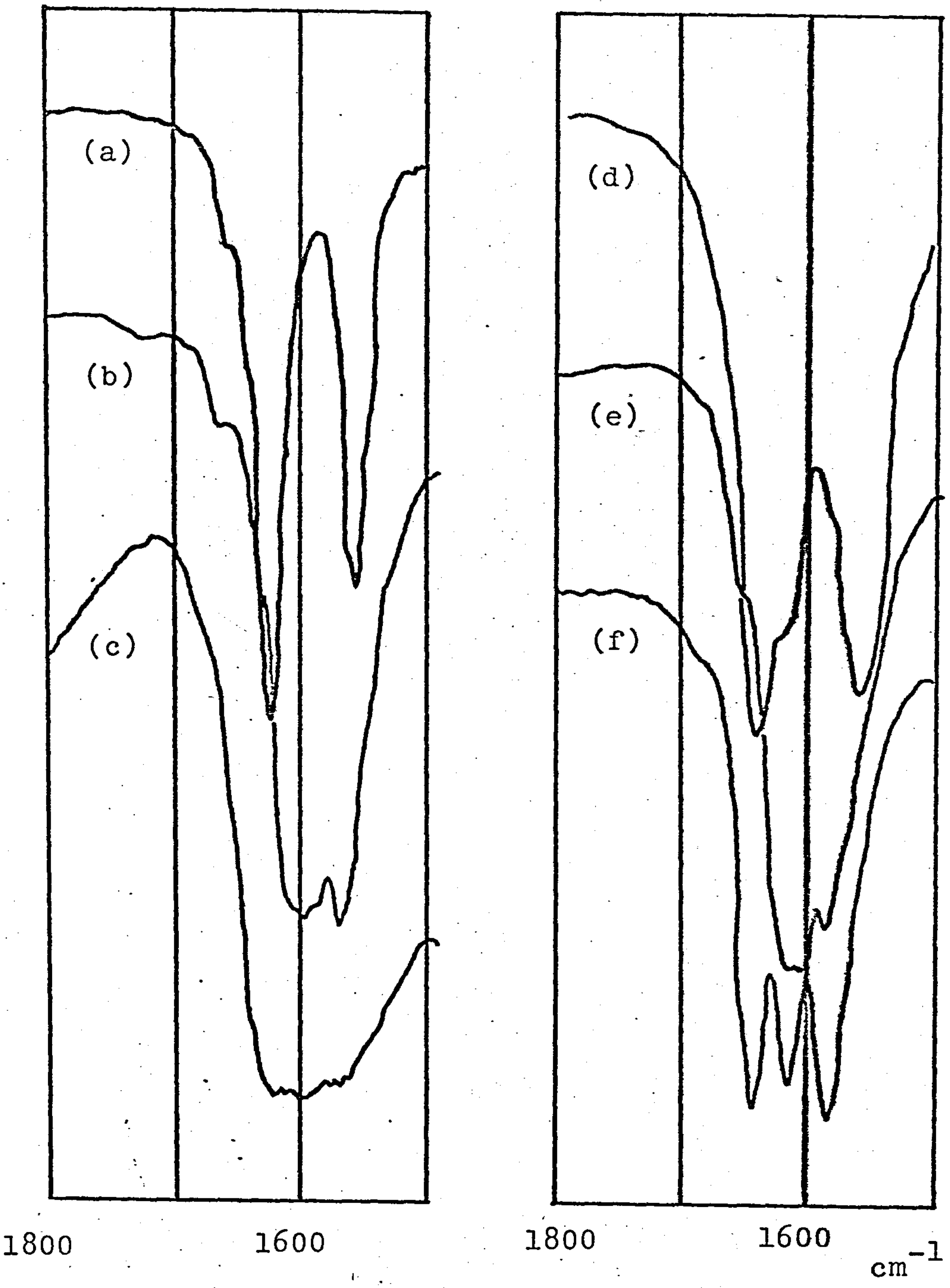


Figure 24. Infrared spectra of the isomers of $[Co(aces)_2]Cl$ {Br salt for (c)} in antisymmetric COO stretching band region; (a) tr.tr.tr., (b) mer-trans(S), (c) trans(O), (d) trans(S), (e) cisciscis and (f) trans(N).

geometrical isomers of $[Co(acms)_2]^+$ has one band at 1620-1630 cm^{-1} and one or two bands at 1640-1660 cm^{-1} (except for trans(S) isomer), which can be assigned to the antisymmetric COO stretching of the coordinated carboxylate groups with the five-membered chelate ring and occur almost at the identical position taken in KBr disk or nujol mull. Thus, none of the five isomers show differences marked enough to distinguish them on the basis of the spectral behavior in this region. The intense band at 1606 cm^{-1} for trans(S) isomer is also assigned to the antisymmetric carboxylate stretching of the five-membered chelate ring.

Each of the six isomers of $[Co(aces)_2]^+$ show one or two bands at 1595-1640 cm^{-1} region, which corresponds to the antisymmetric COO stretching of the six-membered chelate ring. Thus, the frequencies of the antisymmetric COO stretching due to the five-membered chelate ring are higher than those due to the six-membered one in agreement with the earlier studies.53,95)

IV. Circular Dichroism Spectra of $[Co(N,S,O\text{-tridentato})_2]^+$ and $[Co(L\text{-met})(N,S,O\text{-tridentato})]^+$ Type Complexes

IV-A. General Consideration of CD Spectra

As for the present isomers of the $[Co(N,S,O\text{-tridentato})_2]^+$ and $[Co(L\text{-met})(N,S,O\text{-tridentato})]^+$ type complexes, their CD spectra are necessarily complicated by the presence of two types of dissymmetry; namely, that related to the skew pair of chelate rings (=configurational dissymmetry) and that due to the asymmetric centers on the ligand itself (=vicinal dissymmetry).

It has become common to connect the sign of the major CD band of a cobalt(III) complex under its ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition with the absolute configuration. This method depends on a parential argument,76) which note that the exited state wave function of the ${}^1A \rightarrow {}^1A$ transition in a complex of C_2 symmetry has the same orbital form as one of the components of the ${}^1A_1 \rightarrow {}^1E_a$ transition of $[Co(en)_3]^{3+}$ (Figure 25). Therefore, the sign of the ${}^1A_1 \rightarrow {}^1E_a$ transition of $[Co(en)_3]^{3+}$, for which the absolute configuration has been determined by the X-ray diffraction, has been connected with the sign and then the absolute configuration of the C_2 complex; namely, the absolute configuration of the D_3 complex which shows a positive CD band under the ${}^1A_1 \rightarrow {}^1E_a$ transition (or ${}^1A \rightarrow {}^1A$ transition for the C_2 complex) can be assigned as Λ configuration, and the absolute configuration of the D_3 complex which shows a negative one under the corresponding region (or ${}^1A \rightarrow {}^1A$ transition for the C_2 complex) as Δ

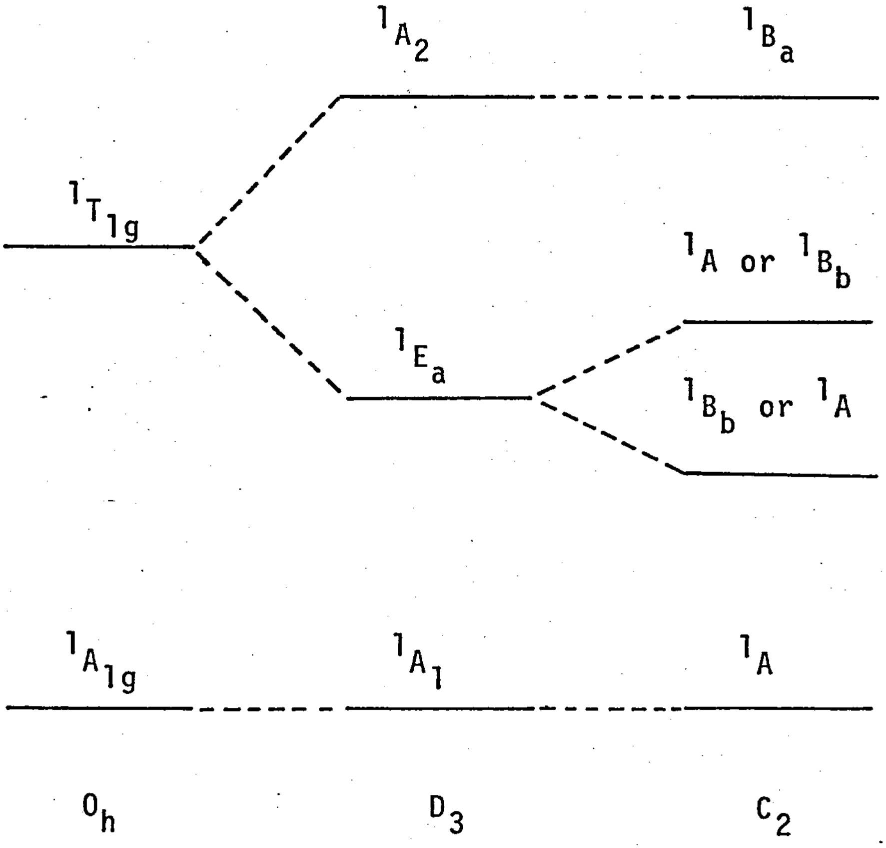


Figure 25. Correlation of energy levels for $^1A_{1g} \rightarrow {}^1T_{1g}$(Oh) transition.

configuration.

However, it is important to ensure that the so-called vicinal dissymmetry do not greatly modify the CD pattern which arise from the configurational dissymmetry. Many studies with respect to the vicinal dissymmetry have been reported for the complexes with the ligands containing the asymmetric carbon atom such as optically active α-amino acids[42-47)] or the asymmetric nitrogen atom such as sarcosinate,[48,49)] N-methyl-L-alaninate,[50,51)] and the other O,N,O-tridentate.[52,53)] These results have indicated that the vicinal dissymmetry has relatively smaller CD contribution than the configurational one.

However, there has been no report concerning the vicinal dissymmetry for the complexes containing the asymmetric sulfur atom, and therefore the CD contribution due to the asymmetric sulfur atom cannot be evaluated. In the present work, the vicinal CD contribution of the asymmetric sulfur donor atom will be discussed together with the configurational CD contribution.

IV-B. Circular Dichroism Spectra of
$[Co(N,S,O\text{-tridentato})_2]^+$ Type Complexes

The CD spectra of the bis(tridentate) type complexes are shown in Figures 26-29 and Table 9. In these complexes, the CD are contributed from the configurational dissymmetry due to the skew pair of chelate rings and vicinal dissymmetry due to the asymmetric sulfur donor atoms, though both contribution could not be separable from each other. The CD spectra of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$ differ significantly among the different geometrical isomers, but are resembled for the isomers with the same geometrical structures. Accordingly, it is reasonable to discuss individually each pair of isomers with the corresponding geometrical configurations.

In the first absorption band region, both $(-)_{589}$-trans(O)-acms and $(-)_{589}$-trans(O)-aces complexes have two CD components, (-) and (+) from lower energy side (Figure 26), though three bands, (+), (-) and (+), are observed for trans(O)-$[Co(L\text{-}met)_2]^+$ 29) and trans(O)-$[Co(L\text{-}smc)_2]^+$ 30) in the corresponding region. In the present trans(O) isomers with C_2 symmetry, there is a weaker field along the unique axis (O-O) than in the other axis perpendicular to it; therefore it is predicted that the $^1A + {}^1B_b(C_2)$ level will be lower in energy than the $^1B_a(C_2)$ level. Consequently, the negative components at about 17800 cm^{-1}($\Delta\varepsilon$=-4.04) for acms complex and 18000 cm^{-1}($\Delta\varepsilon$=-4.51) for aces one are assigned to be $^1A + {}^1B_b$ (C_2), and the positive bands

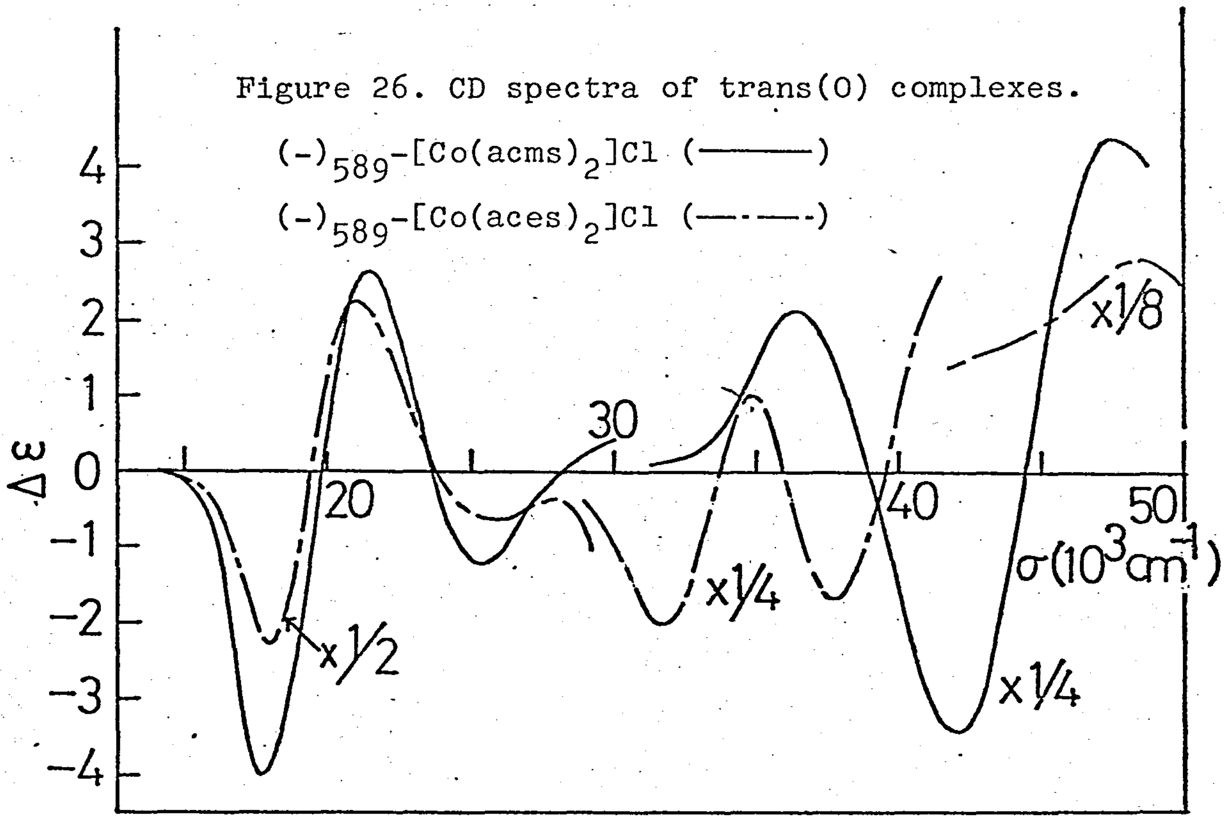


Figure 26. CD spectra of trans(O) complexes.

(−)$_{589}$-[Co(acms)$_2$]Cl (———)

(−)$_{589}$-[Co(aces)$_2$]Cl (—·—)

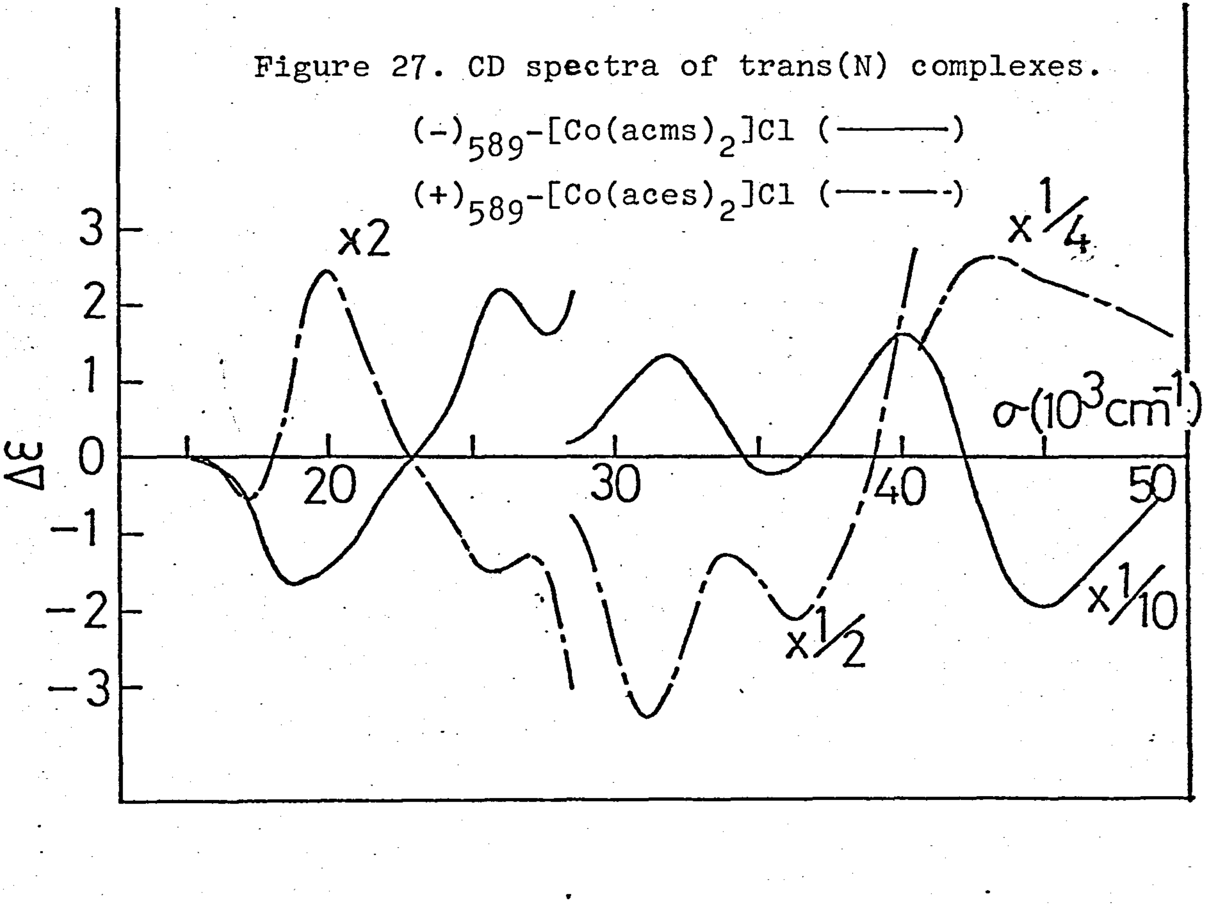


Figure 27. CD spectra of trans(N) complexes.

(−)$_{589}$-[Co(acms)$_2$]Cl (———)

(+)$_{589}$-[Co(aces)$_2$]Cl (—·—)

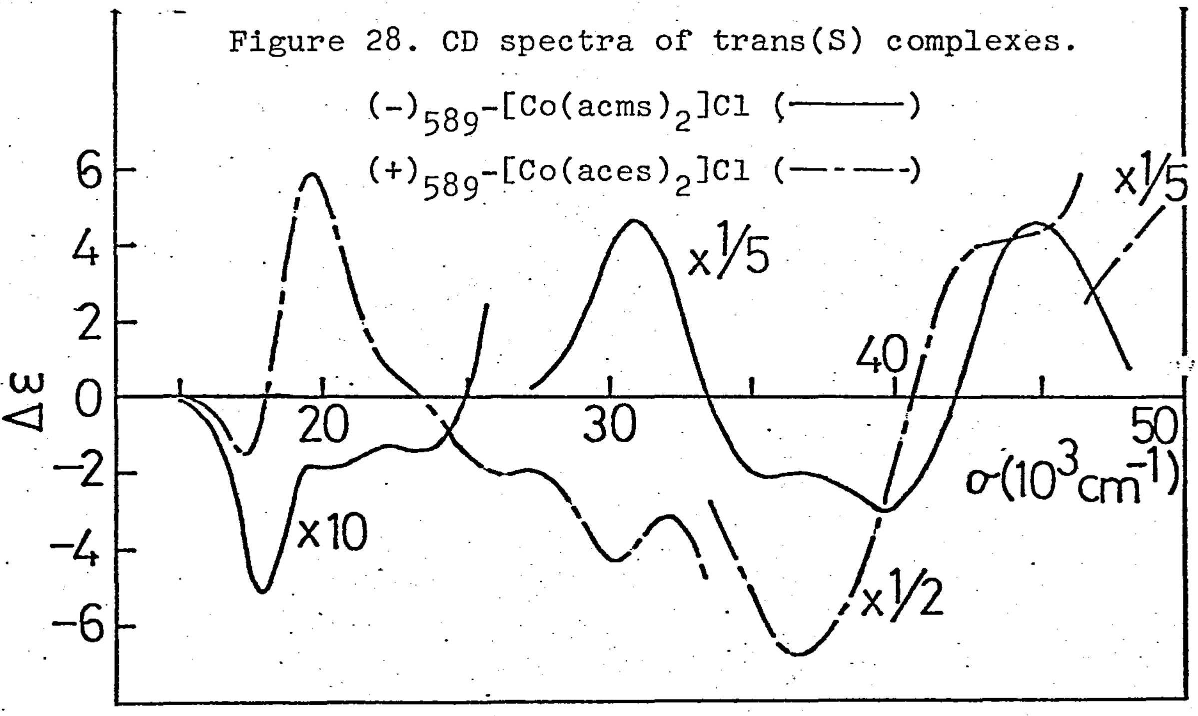


Figure 28. CD spectra of trans(S) complexes.

(-)$_{589}$-[Co(acms)$_2$]Cl (———)

(+)$_{589}$-[Co(aces)$_2$]Cl (—·—·—)

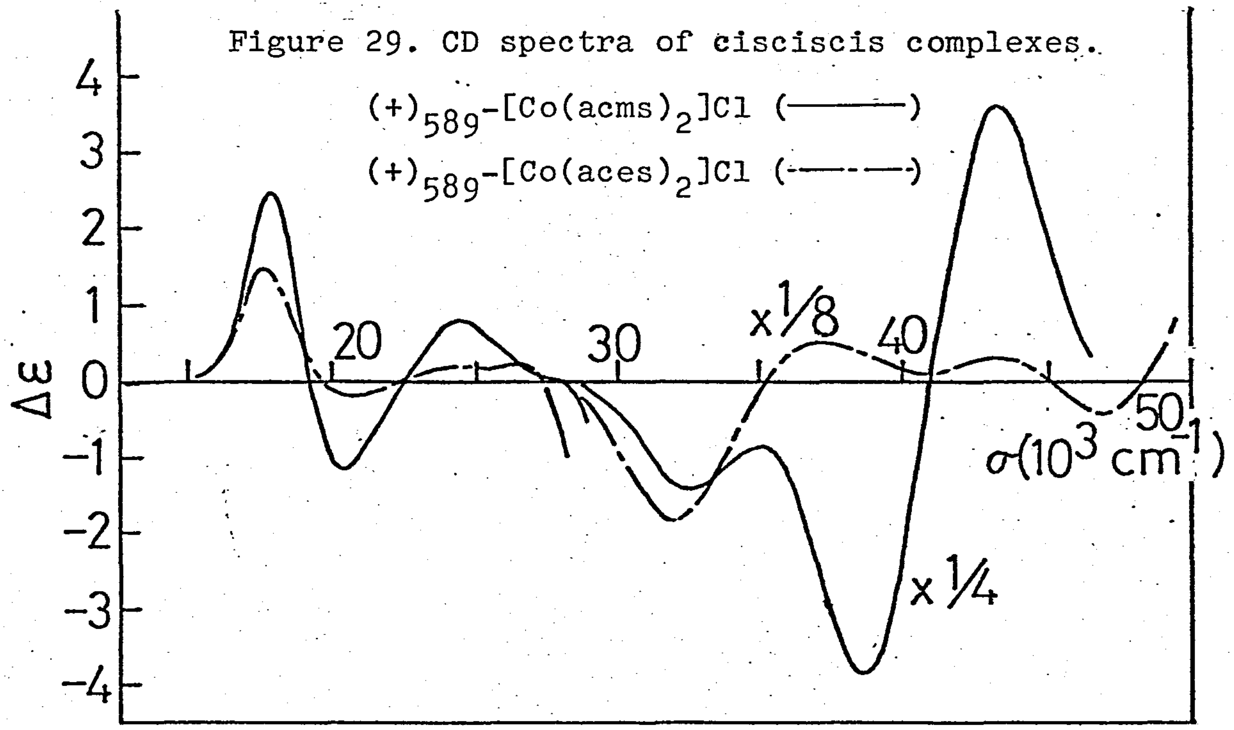


Figure 29. CD spectra of cisciscis complexes.

(+)$_{589}$-[Co(acms)$_2$]Cl (———)

(+)$_{589}$-[Co(aces)$_2$]Cl (—·—·—)

Table 9

CD Data of Isomers of $[Co(acms)_2]Cl$ and $[Co(aces)_2]Cl$

$[Co(acms)_2]Cl$

		Region σ_{ext} ($\Delta\varepsilon$)		
Isomer	Na-D line	I-Band	II-Band	CT-Band
trans(O)	(-)	17.8 (-4.04)	25.4 (-1.23)	36.4 (+10.7)
		21.5 (+2.64)		42.1 (-17.2)
				47.6 (+22.2)
trans(S)	(-)	17.9 (-0.52)	23.7 (-0.15)	30.9 (+23.5)
		20.3 (-0.13)		35.7 (-10.4)
				39.6 (-14.9)
				44.9 (+23.3)
cisciscis	(+)	18.0 (+2.51)	24.6 (+0.82)	32.5 (-5.72)
		20.4 (-1.19)		38.7 (-15.5)
				43.2 (+14.5)
trans(N)a)	(-)	18.7 (-1.63)	26.0 (+2.24)	31.7 (+13.6)
		20.5 (-1.3)*	26	35.5 (-2.09)
				40.3 (+16.5)
				44.8 (-19.5)

$[Co(aces)_2]Cl$

mer-trans(S)a)	(+)	17.3 (+0.37)	25.1 (+0.21)	31.5 (-3.88)
		19.6 (-0.44)		36.1 (+1.17)
				38.6 (-0.43)
				44.4 (+4.22)

Table (continued)

trans(O)	(-)	18.0 (-4.51)	25.8 (-1.25)	31.7 (-8.09)
		21.1 (+4.56)		34.8 (+4.22)
				37.7 (-6.59)
				44.2 (+14.0)*
				48.3 (+21.6)
trans(S)a)	(+)	17.2 (-1.59)	26.2 (-2.47)	30.1 (-4.36)
				36.6 (-13.6)
				43.5 (+8.12)
cisciscisa)	(+)	17.7 (+1.52)	24.2 (+0.19)	31.9 (-14.7)
		20.7 (-0.17)	26.5 (+0.25)	37.2 (+3.97)
				43.3 (+2.59)
				46.8 (-3.16)
trans(N)a)	(+)	17.2 (-0.27)	25.6 (-0.75)	31.1 (-6.85)
		19.8 (+1.25)		36.1 (-4.28)
				42.9 (+10.6)

* This band is a shoulder.

The wave numbers are given in $10^3 cm^{-1}$ unit.

a) CD spectra of these isomers were measured with the eluates.

at 21500 cm^{-1}($\Delta\varepsilon$=+2.46) for acms complex and 21100 cm^{-1} ($\Delta\varepsilon$=+4.56) for aces one are assigned to be $^1B_a(C_2)$. The absolute configurations of $(-)_{589}$-trans(O)-$[Co(acms)_2]^+$ and $(-)_{589}$-trans(O)-$[Co(aces)_2]^+$ are assigned as ΔΛΔ-(RR)= net Δ-(RR) and ΔΛΔ-(SS)=netΔ-(SS) configurations, respectively, according to the sign of the $^1A + {}^1B_b(C_2)$ transition, where (RR) and (SS) represent the chirality due to the asymmetric sulfur atoms (=vicinal dissymmetry) and are reversed between acms and aces complexes with the same absolute configuration. These results agree well with that of $(-)_{589}$-trans(O)-$[Co(NH_2CH_2CH_2NHCH_2CO_2)_2]^+$,97) which exhibits two CD peaks of opposite sign, (+) and (-) from lower energy side, in the first absorption band region and is assigned to have a netΛ absolute configuration on the basis of a dominant CD component.

For the trans(N) isomers (Figure 27), $(-)_{589}$-acms complex exhibit two negative CD bands at 18700 cm^{-1} ($\Delta\varepsilon$=-1.63) and ca.20000 cm^{-1}($\Delta\varepsilon$=-1.48), but $(+)_{589}$-aces one two bands of opposite sign at 17200 cm^{-1}($\Delta\varepsilon$=-0.27) and 19800 cm^{-1} ($\Delta\varepsilon$=+1.25). Using the similar formalism mentioned above, the low-energy band is assigned in each case to the $^1A \rightarrow {}^1B_a(C_2)$ transition and the higher energy component is considered as the transition $^1A \rightarrow {}^1A + {}^1B_b(C_2)$. Worrell and Busch 17) have studied some complexes containing the flexible quadridentate ligand, 1,8-diamino-3,6-dithiaoctane (dadt). Of these complexes, $(+)_{546}$-s-cis-$[Co(dadt)Cl_2]^+$, $(+)_{546}$-s-cis-$[Co(dadt)ClH_2O]^{2+}$ and $(+)_{546}$-s-cis-$[Co(dadt)(H_2O)_2]^{3+}$, which showed a negative and a positive CD components from lower energy side of the first absorption band region, were assigned as Λ absolute configurations, becaise in all three cases, the second CD component is positive and lies closest to the reference ${}^1A_1 \longrightarrow {}^1E_a$ transition positioned at 493 nm for Λ-$[Co(en)_3]^{3+}$, and the sign pattern is in agreement with the sign patterns exhibited by the corresponding ethylenediamine and triethylenediamine complexes. The same arguments are applied to the present system; that is, the absolute configurations of $(-)_{589}$-trans(N)-$[Co(acms)_2]^+$ and $(+)_{589}$-trans(N)-$[Co(aces)_2]^+$ are assigned as $\Delta\Lambda\Delta$-(SS)=netΔ-(SS) and $\Lambda\Delta\Lambda$-(SS)=netΛ-(SS) configurations, respectively, according to the sign of the ${}^1A + {}^1B_b(C_2)$ transition.

In the cisciscis isomers (Figure 28), above parential arguments seem to take limited applicability because of the lowering of the symmetry and the difficulty in the assignment of three components. However, the CD contribution for this geometrical isomers is considered to be mainly due to the configurational dissymmetry, since the absolute configurations of the two asymmetric sulfur atoms become meso-form (R and S). Therefore, it is reasonable to consider that the major CD component in the first absorption band region is related to the molecular framework; namely, both cisciscis isomers of $(+)_{589}$-acms and $(+)_{589}$-aces complexes exhibit a strong positive and a weaker negative bands ($\Delta\varepsilon=+2.51$ at 18000 cm^{-1} and $\Delta\varepsilon=-1.19$ at 20400 cm^{-1} for acms complex;$\Delta\varepsilon=+1.52$

at 17700 cm^{-1} and $\Delta\varepsilon$=-0.17 at 20700 cm^{-1} for aces one) and therefore can be assigned as Λ configuration.

For the trans(S) isomers (Figure 29), $(-)_{589}$-acms complex exhibits two weak CD components in the first absorption band region ($\Delta\varepsilon$=-0.52 at 17900 cm^{-1} and $\Delta\varepsilon$=-0.13 at 20300 cm^{-1}) and a strong CD band in the thioether charge transfer band region ($\Delta\varepsilon$=+23.5 at 30900 cm^{-1}), whereas $(+)_{589}$-aces one shows a strong major CD band in the first absorption band region ($\Delta\varepsilon$=+5.87 at 19600 cm^{-1}) and a relatively weak band in the thioether charge transfer band region ($\Delta\varepsilon$=-4.36 at 30100 cm^{-1}). However, these CD patterns of the first absorption band region cannot be related directly to their absolute configurations in the present system, because it is formally expected that this trans(S) form has not the CD contribution due to the skew pair of chelate rings according to the ring paring method96) but only CD one due to the two asymmetric sulfur donor atoms.

In the thioether charge transfer band region, strong CD bands are generally observed for all isomers. It seems natural to consider that these bands may depend on the absolute configurations of the complex and the asymmetric sulfur atoms. The correlation of the CD spectra between the trans(N) isomers of acms and aces complexes is good in position and sign ($\Delta\varepsilon$=+13.6 at 31700 cm^{-1} for $(-)_{589}$-acms complex; $\Delta\varepsilon$=-6.85 at 31100 cm^{-1} for $(+)_{589}$-aces one). That is, Δ-(SS) configuration for the trans(N) acms complex has (+) band, while Λ-(SS) configuration for the trans(N)-aces one has (-) band. Two trans(O) isomers also have the good correlation between their CD spectra in the thioether charge transfer band region ($\Delta\varepsilon$=+10.7 at 36400 cm^{-1} for $(-)_{589}$-acms complex; $\Delta\varepsilon$=+4.22 at 34800 cm^{-1} for $(-)_{589}$-aces one); Δ-(RR) and Δ-(SS) configurations for the trans(O)-acms and trans(O)-aces complexes, respectively, have (+) band.

IV-C. Circular Dichroism Spectra of [Co(L-met)(N,S,O-tridentato)]$^+$ Type Complexes

CD spectra of fifteen mixed type complexes are shown in Figures 30-34 and Table 10. These structures were assigned in Section III-C-5 except for the absolute configuration of sulfur atom in the L-methioninate ligand. As is shown in Figures 30-34, the CD patterns hardly change with the substitution of the aces ligand for the acms one, especially in the first absorption band region. This suggests that the difference of the chelate ring size in the S-carboxylate moiety has not large effect on the CD spectra as was so for the bis(tridentate) type complexes. In contrast to this result, for the cobalt(III) complexes containing the asymmetric nitrogen donor atom, the drastic change was reported.75)

In the first absorption band region, two tr.tr.tr. isomers show a similar CD pattern (Figure 30); the lower energy CD band have a positive sign and the higher energy one a negative sign ($\Delta\varepsilon$=+3.16 at 16900 cm^{-1} and $\Delta\varepsilon$=-1.28

Figure 30. CD spectra of tr.tr.tr. complexes.

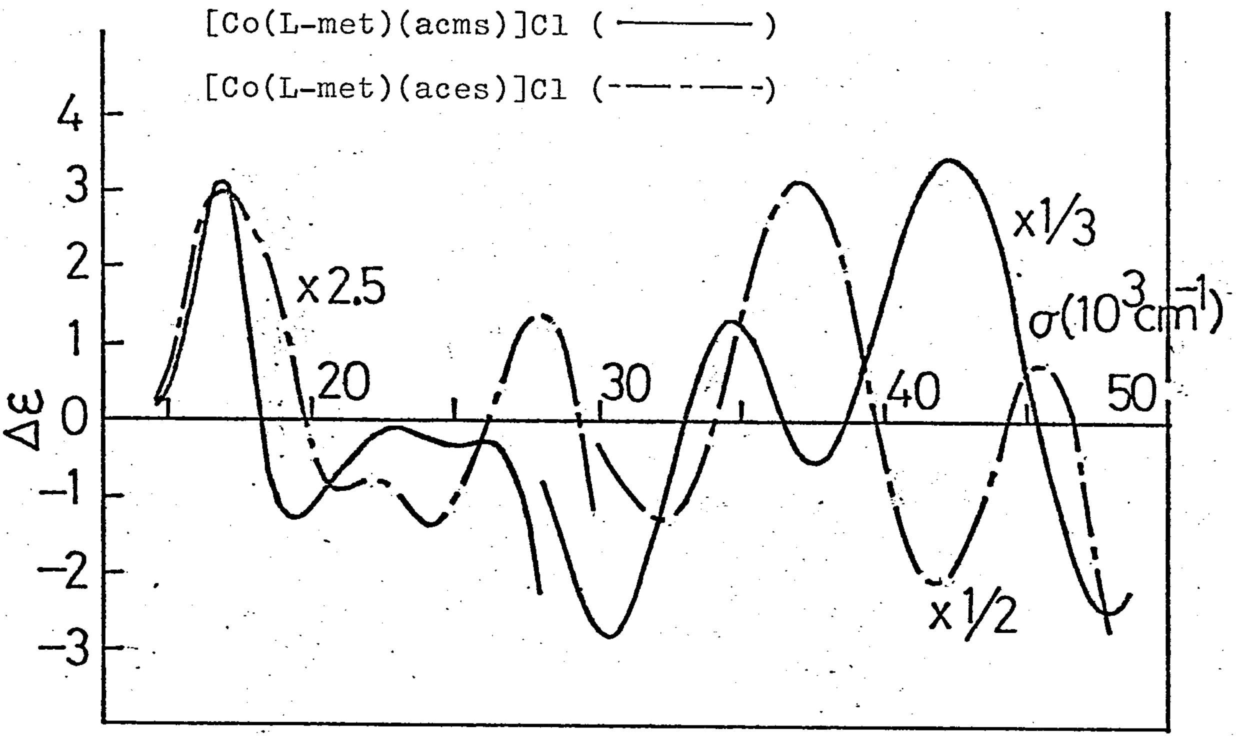


Figure 31. CD spectra of trans(S) complexes.

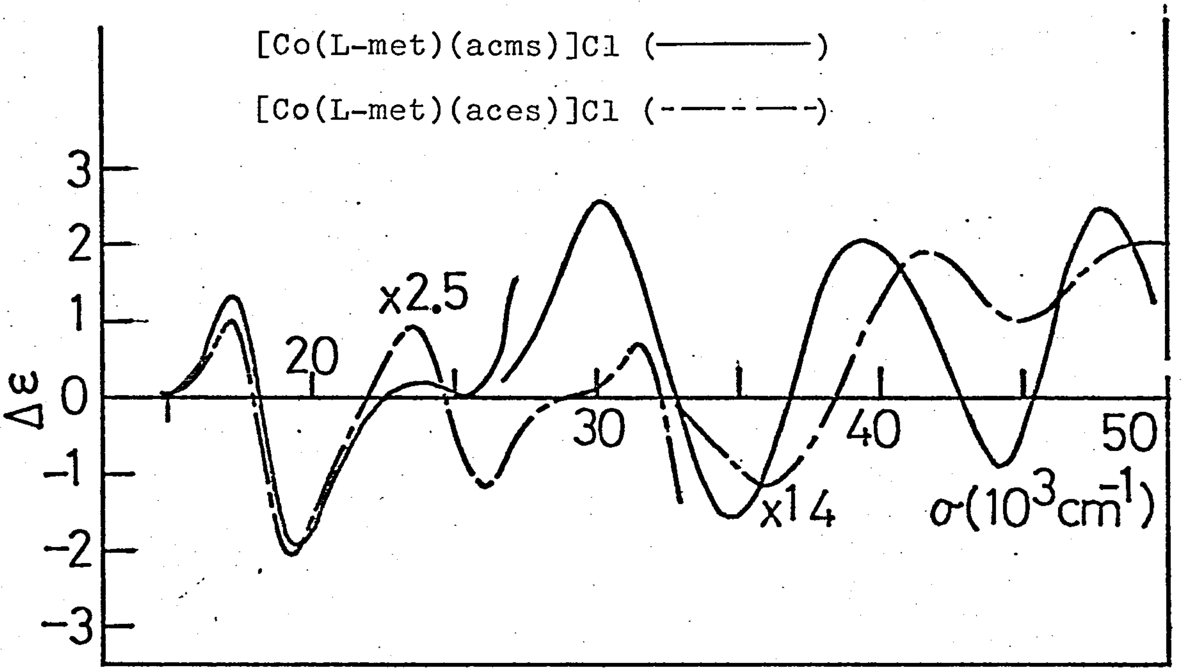


Figure 32. CD spectra of trans(O) complexes.

[Co(L-met)(acms)]Cl (————)

[Co(L-met)(aces)]Cl (— - — - —)

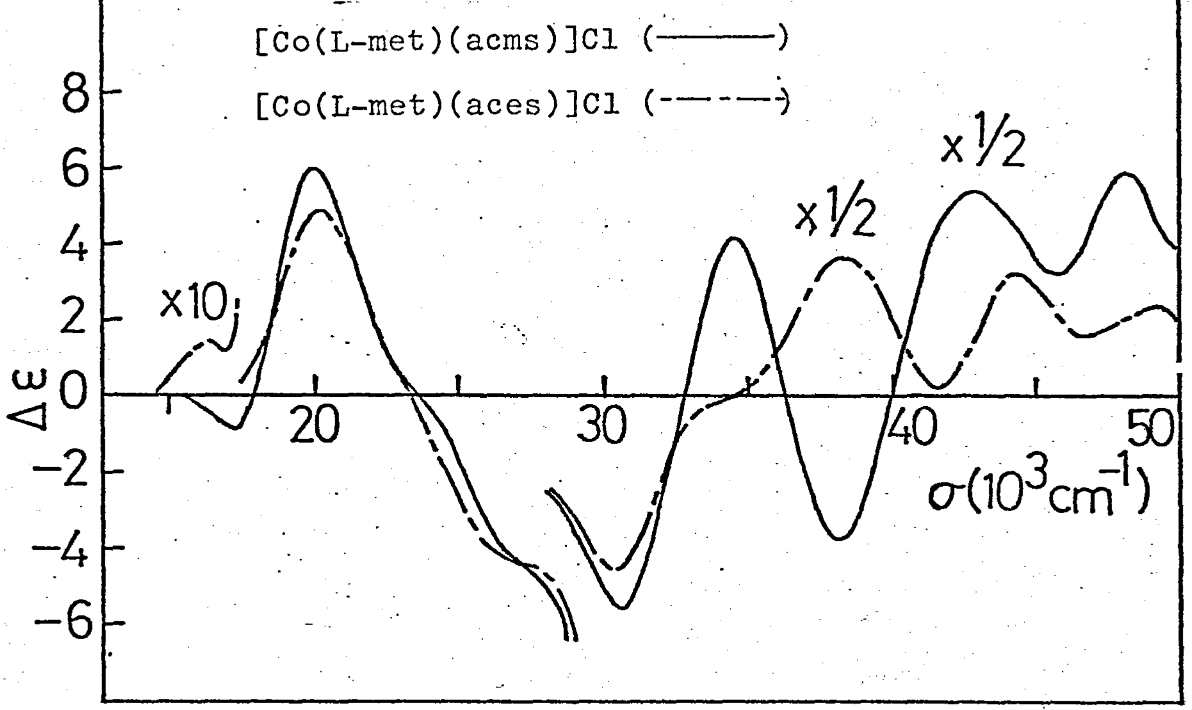
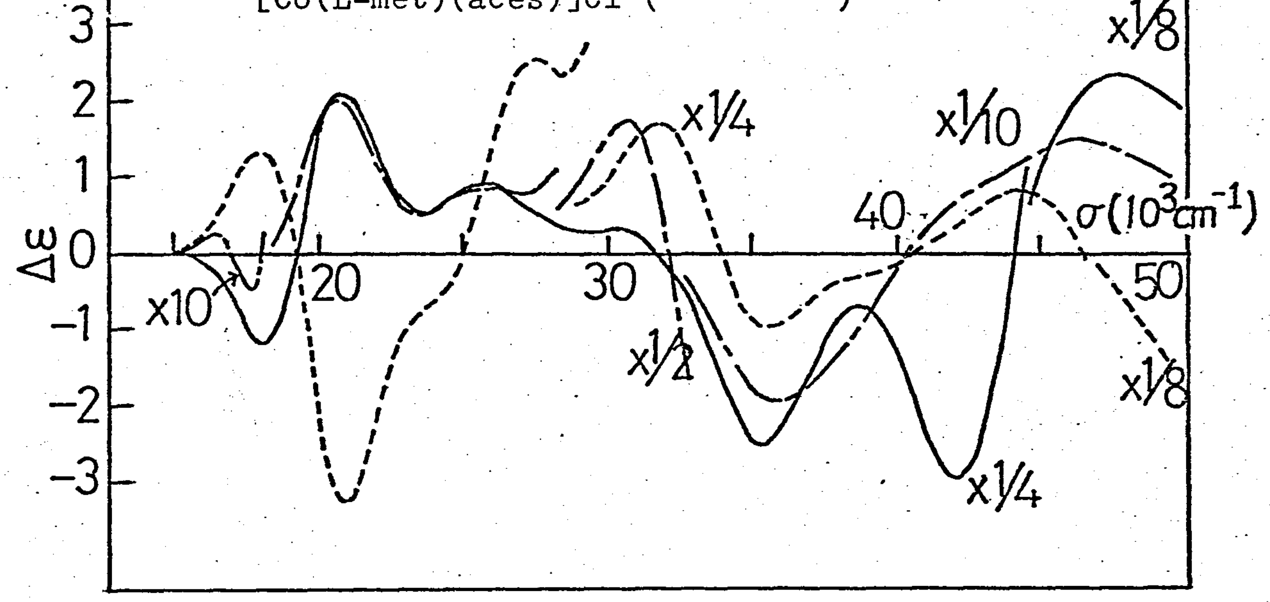


Figure 33. CD spectra of trans(N) complexes.

[Co(L-met)(acms)]Cl (————=C-2), (- - - - - -=C-4)

[Co(L-met)(aces)]Cl (- —— - - ——)



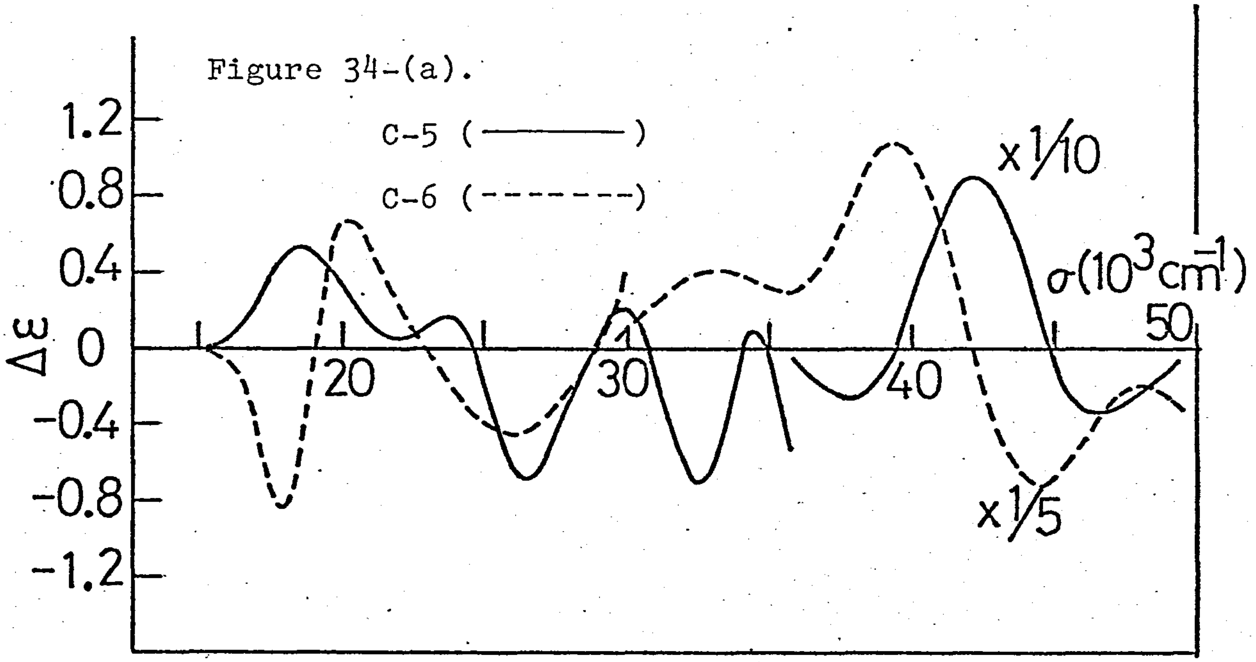


Figure 34. CD spectra of the cisciscis-I complexes.
(a);[Co(L-met)(acms)]Cl (C-5 and C-6 isomers)
(b);[Co(L-met)(aces)]Cl (D-4a and D-4b isomers)

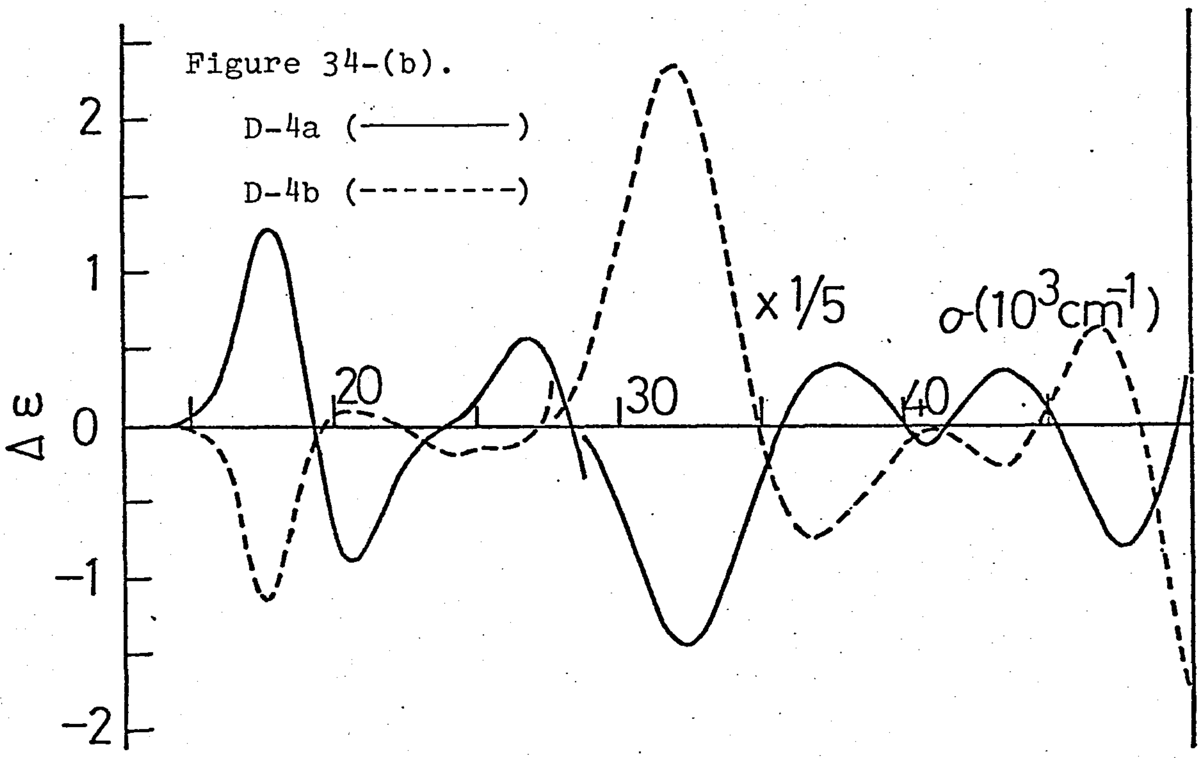


Table 10

CD Data of Isomers of [Co(acms)(L-met)]Cl and [Co(aces)(L-met)]Cl

[Co(acms)(L-met)]Cl

tr.tr.tr.	16.9 (+3.16)	24.9 (-0.33)	30.5 (-8.48)
	19.5 (-1.28)		34.8 (+3.98)
			37.6 (-1.51)
			42.4 (+10.5)
			48.0 (-7.55)
trans(N)	18.0 (-1.19)	25.6 (+0.96)	30.4 (+0.36)
(C-2)	20.7 (+2.14)		35.3 (-9.99)
			42.1 (-11.8)
			47.6 (+19.1)
trans(S)	17.2 (+1.31)	23.7 (+0.20)	30.1 (+10.2)
	19.5 (-1.96)		34.8 (-6.42)
			39.5 (+8.23)
			44.3 (-3.73)
			47.9 (+9.99)
trans(N)	17.9 (+1.31)	27.4 (+2.54)	31.6 (+6.74)
(C-4)	20.7 (-3.29)		35.3 (-4.09)
			44.3 (+3.20)

Table 10 (continued)

cisciscis	18.5 (+0.53)	26.4 (-0.69)	29.9 (+0.22)
(C-5)	23.6 (+0.17)		32.4 (-0.70)
			34.4 (+0.11)
			37.7 (-2.64)
			42.1 (+9.11)
			46.4 (-3.38)
cisciscis	17.8 (-0.84)	26.0 (-0.45)	33.3 (+2.04)
(C-6)	20.1 (+0.69)		39.5 (+5.36)
			44.5 (-3.65)
trans(O)	17.2 (-0.89)		30.6 (-11.2)
	20.0 (+6.01)		34.5 (+8.33)
			38.1 (-7.59)
			42.8 (+10.8)
			48.3 (+11.8)
[Co(aces)(L-met)]Cl			
tr.tr.tr.	16.8 (+1.22)	24.2 (-0.55)	28.2 (+0.58)
	17.3 (+0.97)*		32.3 (-2.56)
	21.1 (-0.35)		37.1 (+6.40)
			41.9 (-4.29)
			45.3 (+1.54)
trans(S)	17.2 (+0.55)	23.6 (+0.22)	31.5 (+4.62)
	20.3 (-0.94)	25.4 (-0.12)	35.9 (-3.98)
			41.8 (+5.19)
			47.3 (+4.51)

Table 10 (continued)

trans(N)	16.5 (+0.03)	25.8 (+0.87)	30.8 (+3.61)
	17.7 (-0.05)		35.9 (-18.9)
	20.6 (+2.05)		46.3 (+15.3)
cisciscis	17.0 (+0.08)		31.5 (+2.30)
(D-4)	18.3 (+0.12)		35.9 (-0.90)
	20.6 (-0.44)		40.3 (-0.42)
			44.8 (+0.32)
cisciscis a)	17.8 (+1.30)	26.9 (+0.59)	32.5 (-7.11)
(D-4a)	20.7 (-0.88)		37.7 (+2.05)
			40.8 (-0.24)
			43.6 (+1.94)
			47.7 (-3.99)
cisciscis a)	17.7 (-1.13)	24.3 (-0.17)	31.9 (+11.9)
(D-4b)	20.5 (+0.11)		36.8 (-3.65)
			43.5 (-1.26)
			46.7 (+3.28)
trans(O)	16.1 (+0.14)	26 (-3.9)*	30.4 (-9.17)
	20.2 (+4.89)		38.3 (+7.37)
			44.4 (+6.60)
			49.3 (+4.86)
cisciscis	17.2 (-0.17)	25.7 (-0.48)	30.9 (-0.48)
(D-6)	19.3 (+0.14)		37.0 (+7.04)
			45.0 (-4.73)

Table 10(continued)

cisciscis[a]	15.6 (+0,04)	25.5 (-0.29)	36.8 (+7.47)
(D-6a)	17.3 (-0.07)		44.4 (-5.63)
	20.5 (-0.21)		
cisciscis[a]	19.5 (+0.64)	26.2 (-0.28)	37.9 (+5.31)
(D-6b)			45.5 (-2.09)

* This band is a shoulder.

a) CD spectra of these isomers were measured with the eluates.

The wave numbers are given in 10^3 cm^{-1} unit.

at 19500 cm^{-1} for acms complex; $\Delta\varepsilon$=+1.22 at 16800 cm^{-1} and $\Delta\varepsilon$=-0.35 at 21100 cm^{-1} for aces one). These results are in good agreement with the fact that both isomers have Λ configuration according to the ring pairing method.96)

On the other hand, two trans(S) isomers (Figure 31) exhibit the same CD pattern as that of the tr.tr.tr. isomers in the first absorption band region ($\Delta\varepsilon$=+1.31 at 17200 cm^{-1} and $\Delta\varepsilon$=-1.96 at 19500 cm^{-1} for acms complex; $\Delta\varepsilon$=+0.55 at 17200 cm^{-1} and $\Delta\varepsilon$=-0.94 at 20300 cm^{-1} for aces one), though they should show the opposite CD pattern compared with the tr.tr.tr. isomers since both trans(S) isomers also have Λ absolute cofiguration and $^1A \rightarrow {}^1A + {}^1B_b(C_2)$ transition is expected to become the higher energy component for the trans(S) isomer. This indicates that the CD spectral pattern cannot be always related to the absolute configuration deduced from the ring pairing method for the complexes containing the ligand such as L-methioninate. The similar result that complexes with the same absolute configuration have approximate mirror image CD spectra has been reported for other system.93,98)

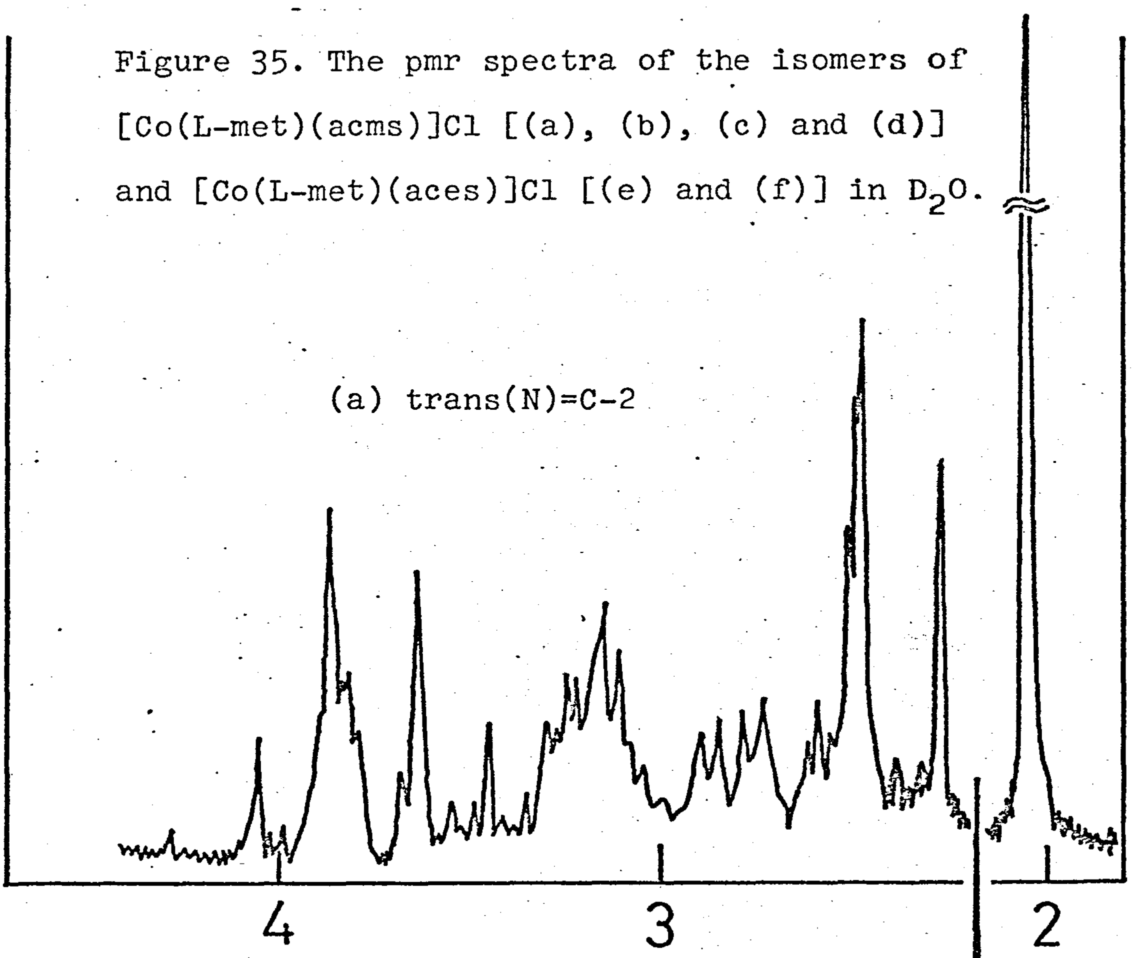
In the first absorption band region of the trans(O) isomers, there occurs a slightly different CD pattern compared with that of the bis(tridentate) type complexes (Figure 32). Both exhibit a major positive CD band at higher energy side ($\Delta\varepsilon$=+6.01 at 20000 cm^{-1} for acms complex; $\Delta\varepsilon$=+4.89 at 20200 cm^{-1} for aces one), though the weak lower energy band has a opposite sign. This suggests that the higher energy positive band may represent a composite transition $^1A \rightarrow {}^1B_a + {}^1B_b$. However, it may be more reasonable to consider that, since these mixed trans(O) isomers have formally no CD contribution due to the configurational effect according to the ring pairing method, the CD contribution due to the asymmetric sulfur donor atom becomes dominant even in the first absorption band region.

For the trans(N) isomers, this viewpoint becomes the most important; that is, two trans(N) isomers of the acms complex, C-2 and C-4, exhibit completely enantiomeric CD patterns in the first absorption band region (Figure33), which can be attributed to the difference of the asymmetric sulfur configuration of the coordinated L-methioninate. In the case of the aces complex, only one isomer was obtained for the trans(N) form and its CD apectral pattern is similar with that of C-2 isomer and therefore its structure is considered to be same as that of C-2.

The C-5 and D-4a cisciscis-I isomers show almost enantiomeric CD spectra to the C-6 and D-4b cisciscis-I isomers (Figure.34). This fact indicates that C-5 and D-4a, or C-6 and D-4b take the same absolute configuration with respect to the asymmetric sulfur donor atom of L-methioninate.

Of the fifteen mixed type complexes, four diastereomeric pairs, C-2 and C-4, C-5 and C-6, D-4a and D-4b, and D-6a and D-6b, have of course a definite

Figure 35. The pmr spectra of the isomers of [Co(L-met)(acms)]Cl [(a), (b), (c) and (d)] and [Co(L-met)(aces)]Cl [(e) and (f)] in D_2O.


(a) trans(N)=C-2

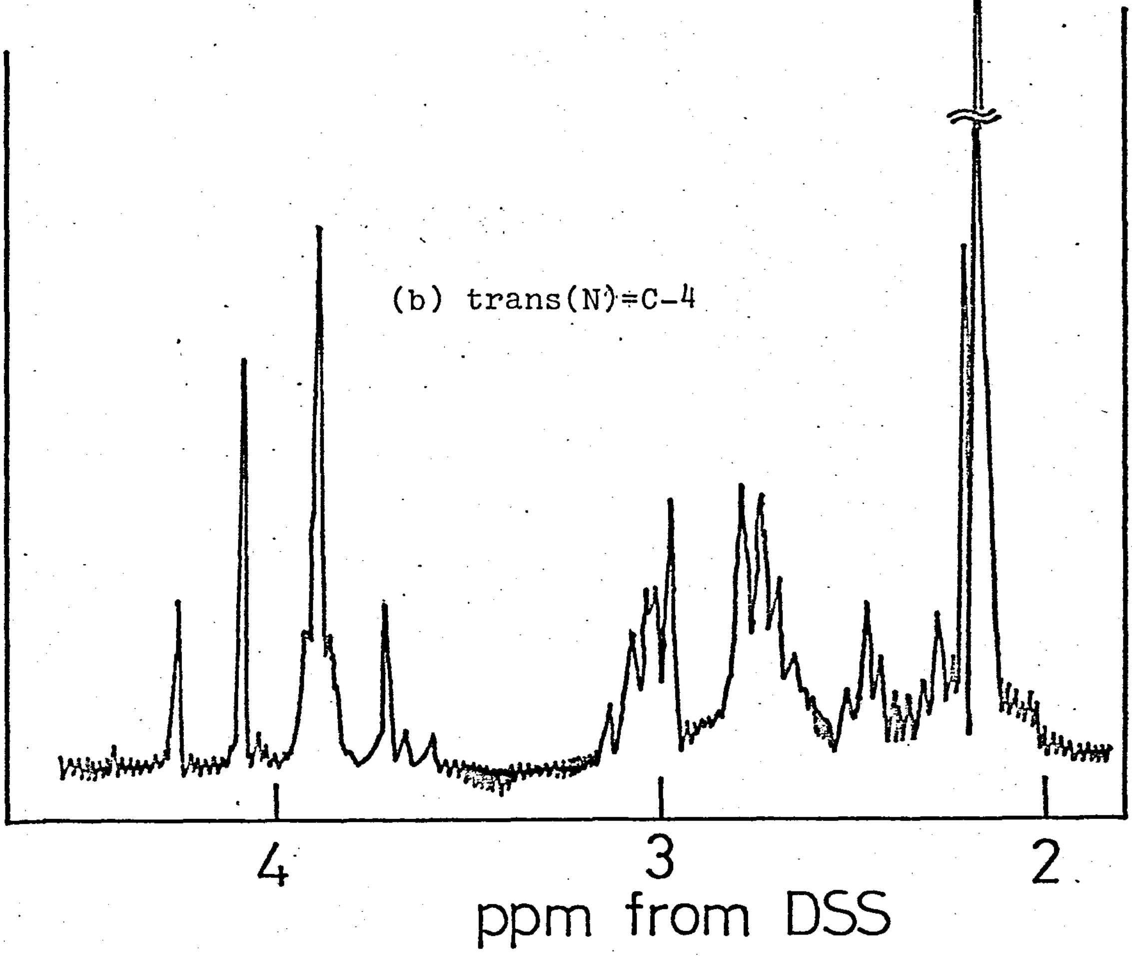
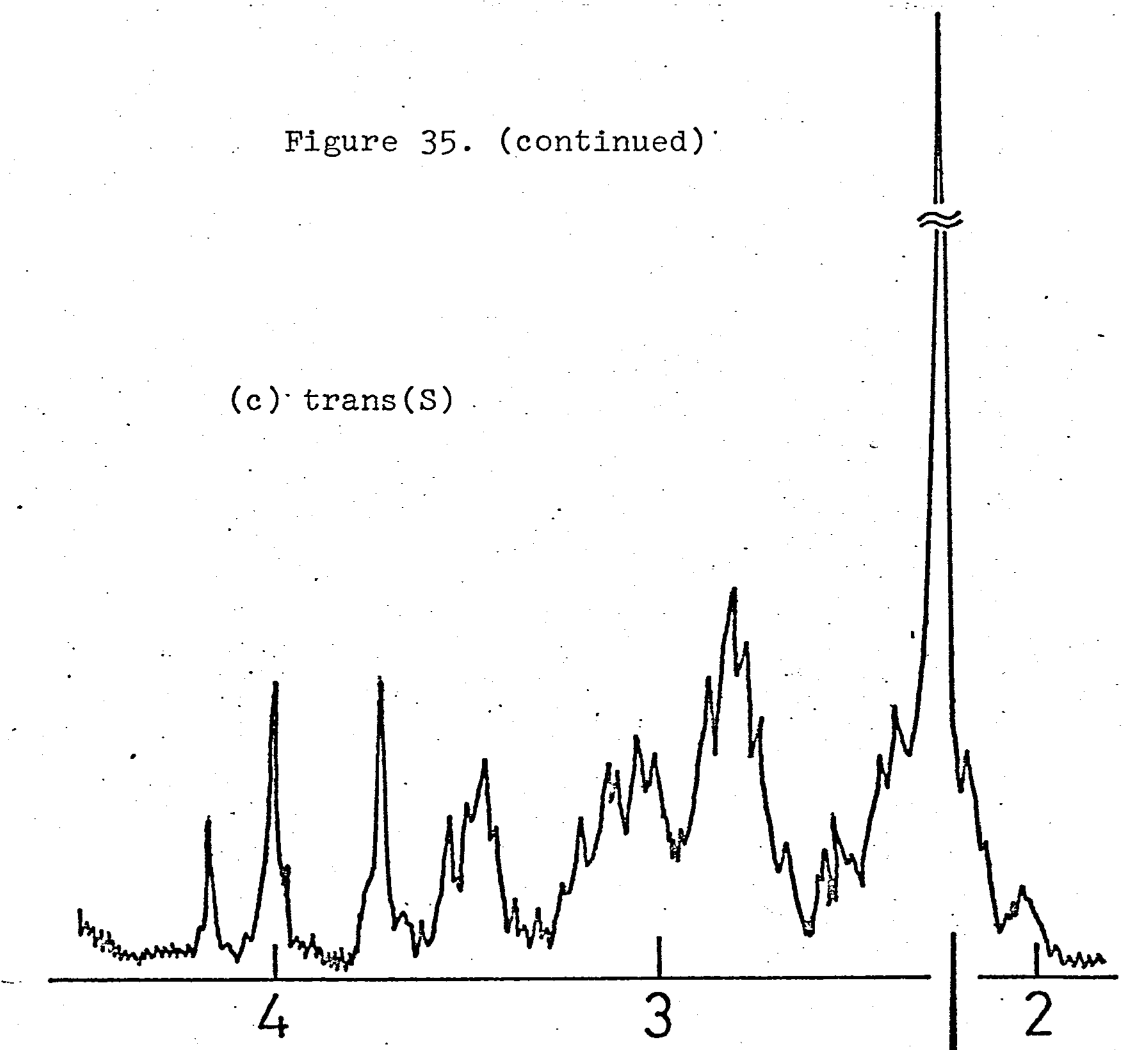

(b) trans(N)=C-4

Figure 35. (continued)

(c) trans(S)



(d) trans(O)

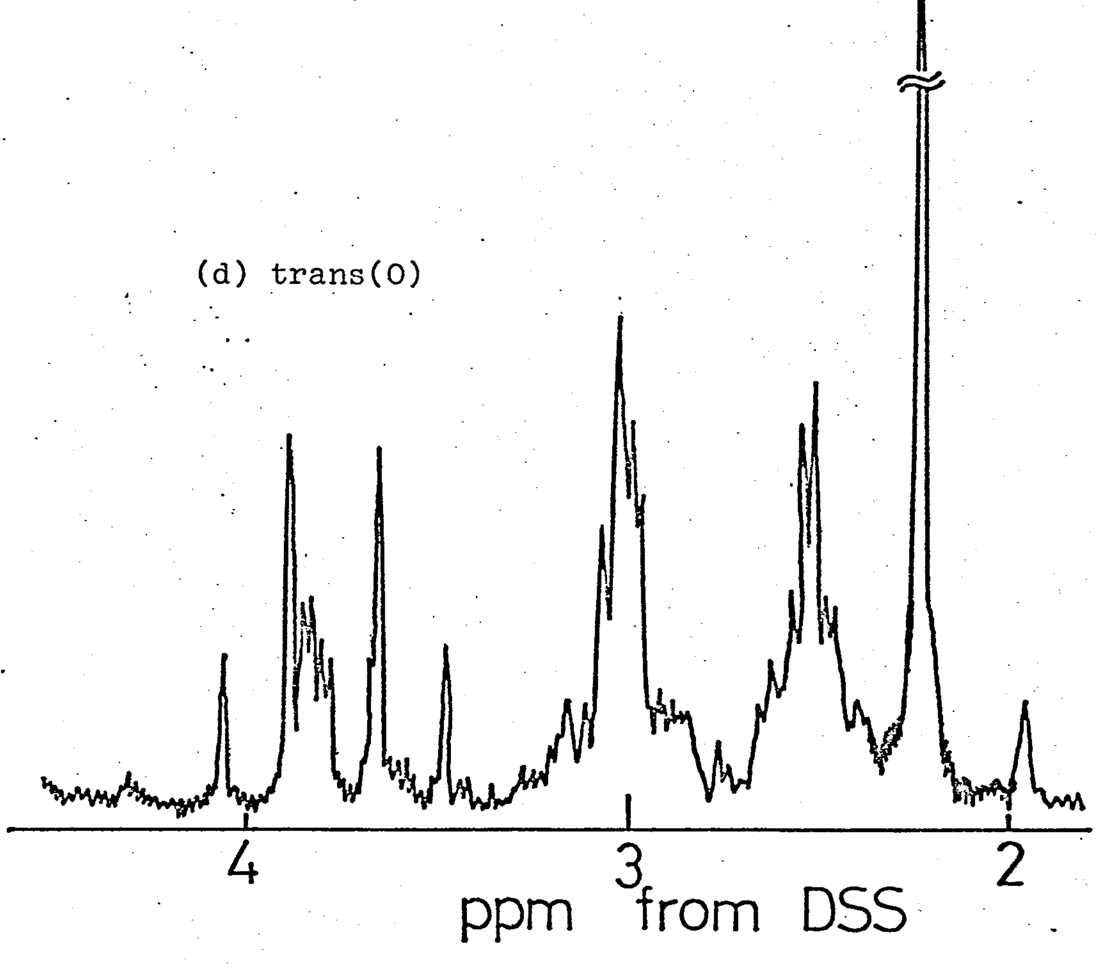
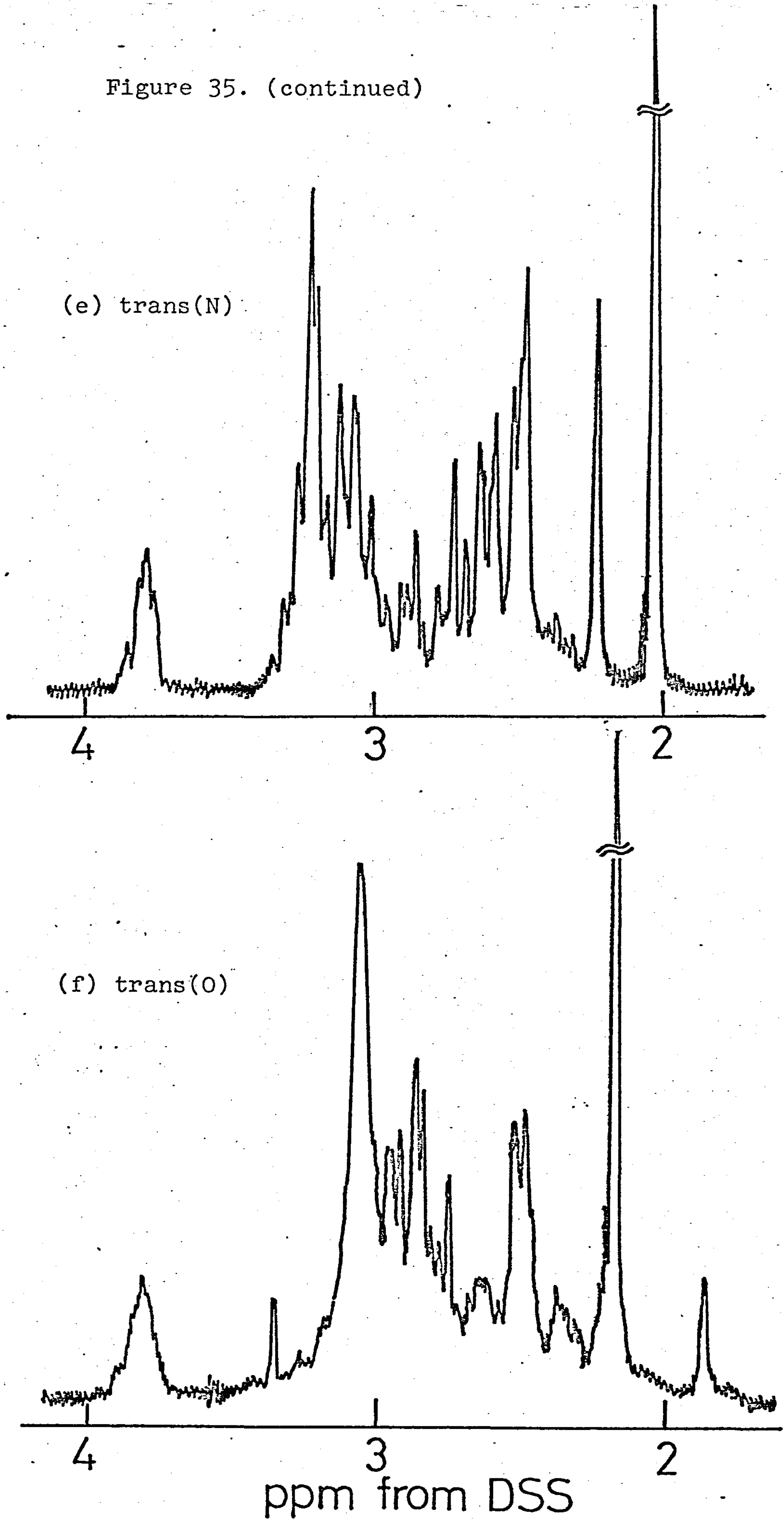


Figure 35. (continued)



configuration, R or S, with respect to the asymmetric sulfur donor atom of L-methioninate. Furthermore, the remaining seven isomers, though these isomers have no corresponding diastereomer, may be considered to take also a definite configuration of the asymmetric sulfur atom of L-methioninate on the basis of the following reasons; firstly, all fractions of these isomers on the chromatographic separation showed the same CD spectra. Secondary, pmr spectra of these isomers showed that there is a single peak in the S-methyl proton region (Figure 35). Thirdly, the corresponding isomers of the two kinds of the mixed complexes show very similar CD spectra and model examination reveals that the isomers except tr.tr.tr. one are expected to prefer S configuration because of the interaction with the chelate ring of the other ligand. The structures of these mixed complexes are summarized in Table 11.

For the present mixed type complexes, there are two kinds of the asymmetric sulfur atoms in the ligands of $acms^-$ (or $aces^-$) and $L\text{-}met^-$. Therefore, the CD band in the thioether charge transfer band region cannot be simply related to the absolute configurations of the sulfur atoms. However, good correlations between the two kinds of the mixed complexes in this region are also found for the trans(S) and trans(N) isomers. Namely, both trans(S) isomers show two CD bands, (+) and (-) from lower energy side ($\Delta\varepsilon$=+10.2 at 30100 cm^{-1} and $\Delta\varepsilon$=-6.42 at 34800 cm^{-1} for acms complex; $\Delta\varepsilon$=+4.62 at 31500 cm^{-1} and $\Delta\varepsilon$=-3.98 at

Table 11. Structures of the Asymmetric Donor Sulfur Atoms in the Mixed Type Complexes .

Complex		Configurations in the Two Kinds of Ligands	
[Co(L-met)(acms)]Cl		L-methioninate	N,S,O-tridentate*
tr.tr.tr.	(C-1)	(R or S)	S
trans(N)	(C-2)	R or S	R
trans(S)	(C-3)	S	R
trans(N)	(C-4)	S or R	R
cisciscis-I	(C-5)	R or S	S
cisciscis-I	(C-6)	S or R	S
trans(O)	(C-7)	S	R
[Co(L-met)(aces)]Cl			
tr.tr.tr.	(D-1)	(R or S)	R
trans(S)	(D-2)	S	S
trans(N)	(D-3)	S	S
cisciscis-I	(D-4a)	R or S	R
cisciscis-I	(D-4b)	S or R	R
trans(O)	(D-5)	S	S
cisciscis-II	(D-6a)	R or S	R
cisciscis-II	(D-6b)	R or S	R

* The sulfur configuration in the ligands of N,S,O-tridentate is reversed between acms and aces complexes with the same absolute configuration.

35900 cm^{-1} for aces one), and both trans(N) isomers also two CD bands of opposite sign ($\Delta\varepsilon$=+0.36 at 30400 cm^{-1} and $\Delta\varepsilon$=-9.99 at 35300 cm^{-1} for acms complex (=C-2);$\Delta\varepsilon$=+3.61 at 30800 cm^{-1} and $\Delta\varepsilon$=-18.9 at 35900 cm^{-1} for aces one).

IV-D. Comparison of Circular Dichroism Spectra between Bis(tridentate) and Mixed Type Complexes

Each series of complexes,

$(L\text{-}met)_2 \longrightarrow (L\text{-}met)(acms) \longrightarrow (acms)_2$ or

$(L\text{-}met)_2 \longrightarrow (L\text{-}met)(aces) \longrightarrow (aces)_2$, offer a means of studying the progressive effect on the circular dichroism spectra[93,98] of substituting $acms^-$ or $aces^-$ for $L\text{-}met^-$ (Figures 36 and 37).

On this substitution, for the both series of trans(O) isomers, the lower energy positive band in the first absorption band region becomes weaker and then negative, while the higher energy CD component is remained to be positive. In the thioether charge transfer band region, there is also a corresponding change from a negative band to a positive one. These rather dramatic change in the CD spectra was reported in the series of $(ida)_2 \longrightarrow (ida)(L\text{-}asp) \longrightarrow (L\text{-}asp)_2$.

Similarly, for the both series of trans(N) or trans(S) isomers, these correlations appear at the higher energy CD component in the first absorption band region, and also at the CD band in the thioether charge transfer band region. That is, in the first absorption band region,

Figure 36. Comparison of CD spectra between bis(tridentate) and mixed type complexes. A, B, and M denote the complexes of $[Co(acms)_2]^+$, $[Co(L\text{-}met)(acms)]^+$ and $[Co(L\text{-}met)_2]^+$, respectively.

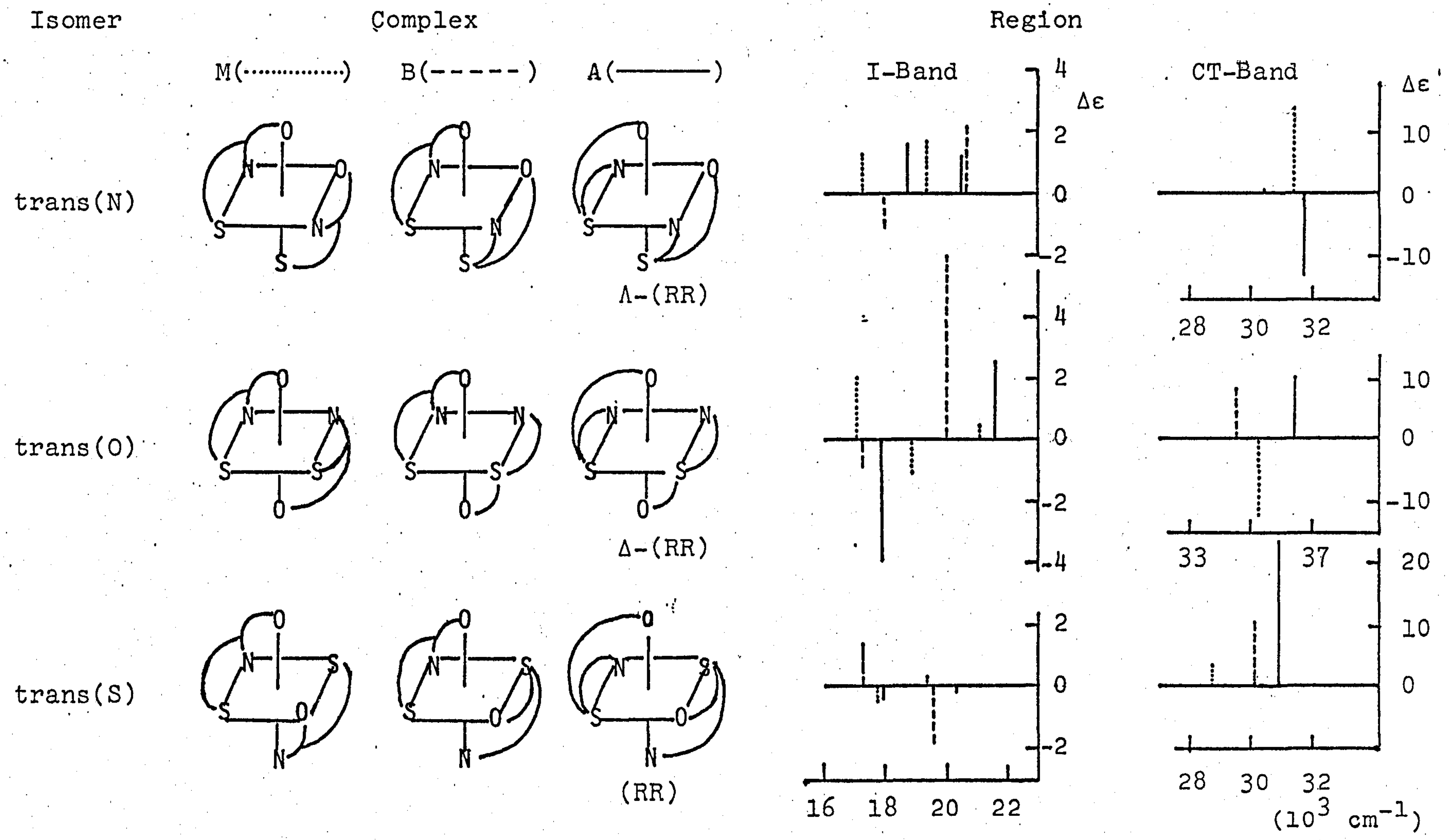
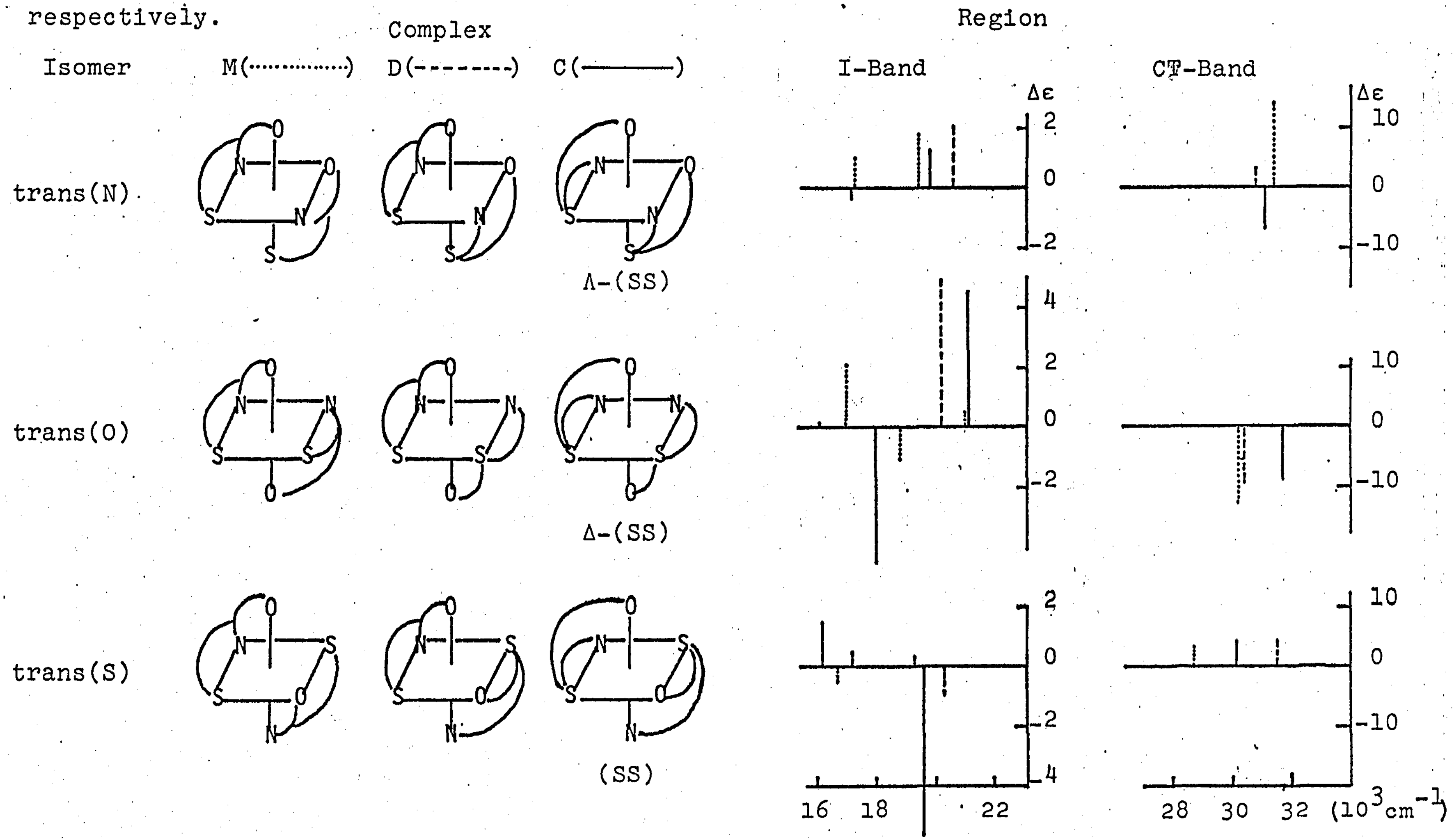


Figure 37. Comparison of CD spectra between bis(tridentate) and mixed type complexes. C, D and M denote the complexes of $[Co(aces)_2]^+$, $[Co(L\text{-}met)(aces)]^+$ and $[Co(L\text{-}met)_2]^+$, respectively.



the higher energy CD component for the both series of trans(N) isomers is remained to be positive, while for the trans(S) series, the sign of the corresponding component is changed from positive to negative. On the other hand, in the thioether charge transfer band region, there is the change from a positive CD band to a negative one for the trans(N) series, while the CD band is remained to be positive for the both series of trans(S) isomers.

These arguments may lead to the assignments of the absolute configurations for the complexes of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$; $(-)_{589}$-trans(O)-$[Co(acms)_2]^+$ and $(-)_{589}$-trans(O)-$[Co(aces)_2]^+$ are assigned as Δ-(RR) and Δ-(SS) configurations, respectively, and $(-)_{589}$-trans(N)-$[Co(acms)_2]^+$ and $(+)_{589}$-trans(N)-$[Co(aces)_2]^+$ as Δ-(SS) and Λ-(SS) configurations, respectively. These results agree well with the assignments of the absolute configurations mentioned in earlier Section (IV-B).

Furthermore, both trans(S) isomers of $(-)_{589}$-$[Co(acms)_2]^+$ and $(+)_{589}$-$[Co(aces)_2]^+$, though their absolute configurations cannot be known so far, are expected to have RR configuration according to the above arguments.

IV-E. CD Contribution due to the Asymmetric Sulfur Donor Atom

In the present mixed complexes, four pairs of diastereomers, C-2 and C-4 of trans(N)-[Co(L-met)(acms)]$^+$, C-5 and C-6 of cisciscis-I-[Co(L-met)(acms)]$^+$, D-4a and D-4b of cisciscis-I-[Co(L-met)(aces)]$^+$, and D-6a and D-6b of cisciscis-II-[Co(L-met)(aces)]$^+$, were obtained. As was mentioned above (Section IV-C), CD spectra of the two isomers in each pair are significantly different and rather enantiomeric to each other. In order to estimate approximately the CD contribution due to the asymmetric sulfur donor atom, additivity rule was applied to these diastereomeric pairs; namely, this contribution can be obtained by subtracting the CD of the one isomer from that of the other isomer of a diastereomeric pair, while the CD contributions due to the remaining factors are calculated by adding the two CD curves. The calculated CD curves are shown in Figures 38-41.

In the case of trans(N)-[Co(L-met)(acms)]$^+$, CD contribution due to the asymmetric sulfur donor atom very large even in the first absorption band region ($\Delta\varepsilon$=-1.24 at 18000 cm^{-1} and $\Delta\varepsilon$=+2.72 at 20700 cm^{-1}).

Similarly, for the isomers of cisciscis-I-[Co(L-met)(acms)]$^+$ and cisciscis-I [Co(L-met)(aces)]$^+$, their vicinal CD curves become dominant in the first absorption band region. It is interesting to note that the CD curve of D-6 isomer which is a mixture of D-6a and D-6b isomers, is similar

Figure 38-(a). CD spectra of the diastereomers of trans(N)-[Co(L-met)(acms)]Cl.

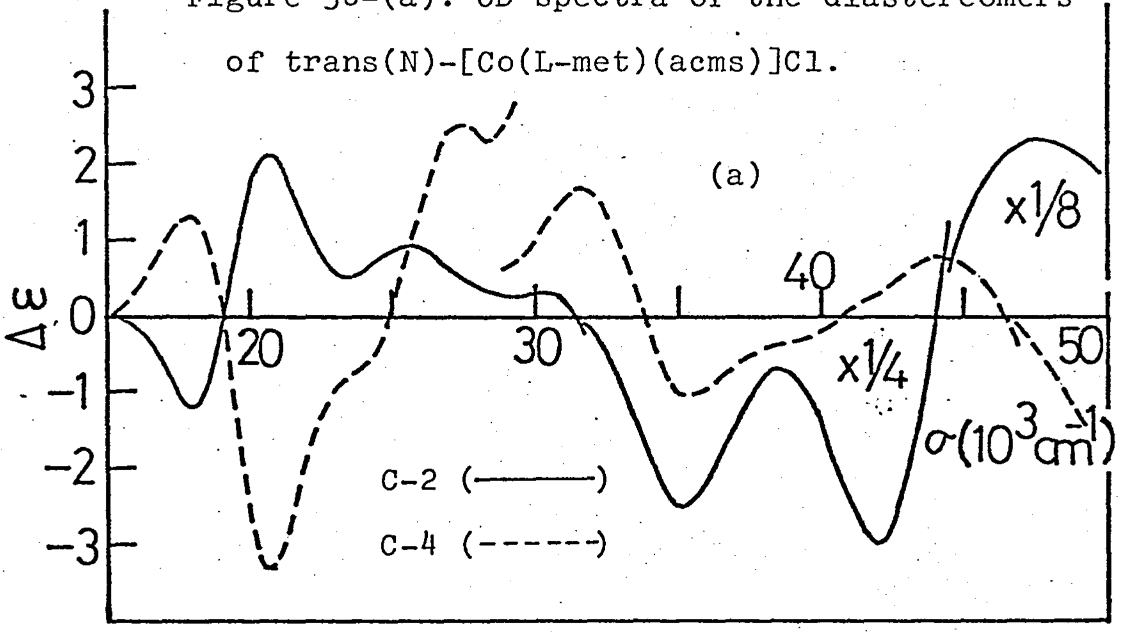


Figure 38. Curve analyses of trans(N)-[Co(L-met)(acms)]Cl complexes.

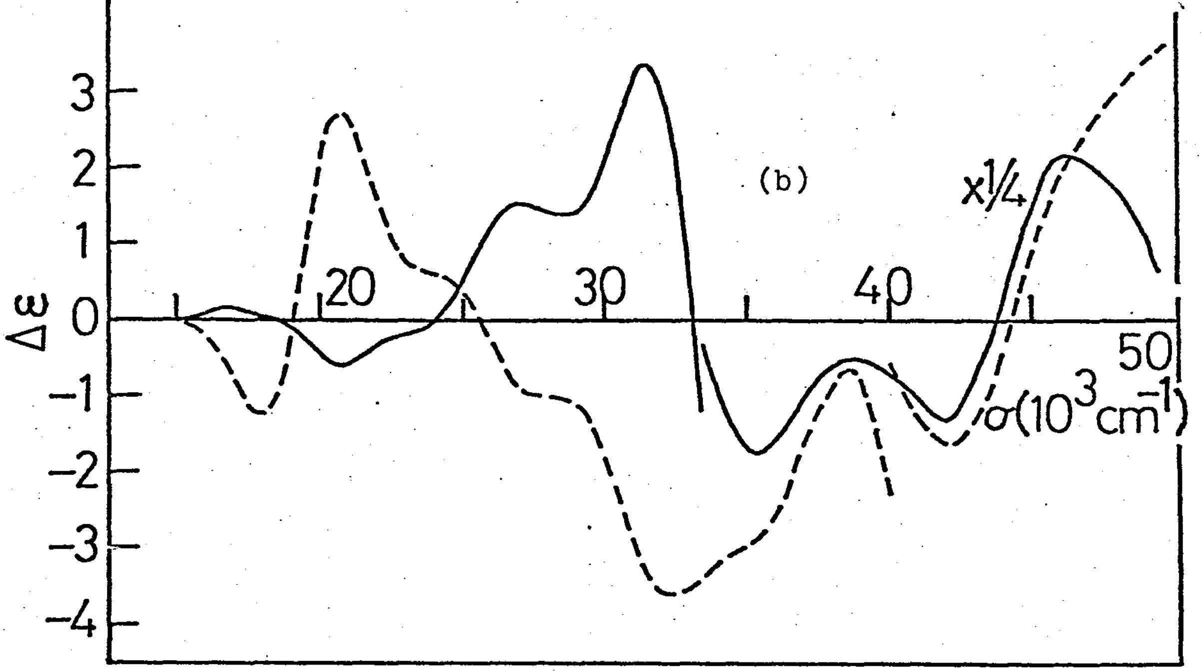


Figure 38-(b).

$1/2 \times \{\Delta\varepsilon(\text{C-2}) + \Delta\varepsilon(\text{C-4})\}$ (————)

$1/2 \times \{\Delta\varepsilon(\text{C-2}) - \Delta\varepsilon(\text{C-4})\}$ (-------)

Figure 39. Curve analyses of cisciscis-I-[Co(L-met)(acms)]Cl complexes (C-5 and C-6).

1/2 × {Δε(C-5) + Δε(C-6)} (————)

1/2 × {Δε(C-5) − Δε(C-6)} (--------)

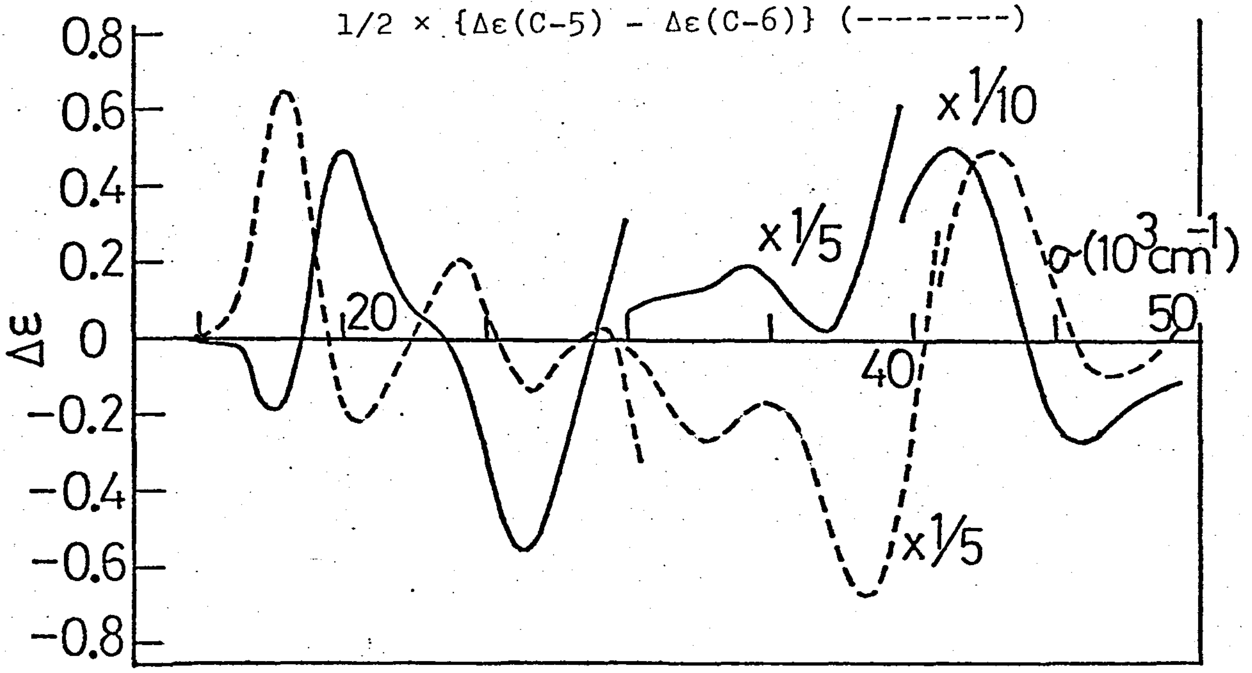
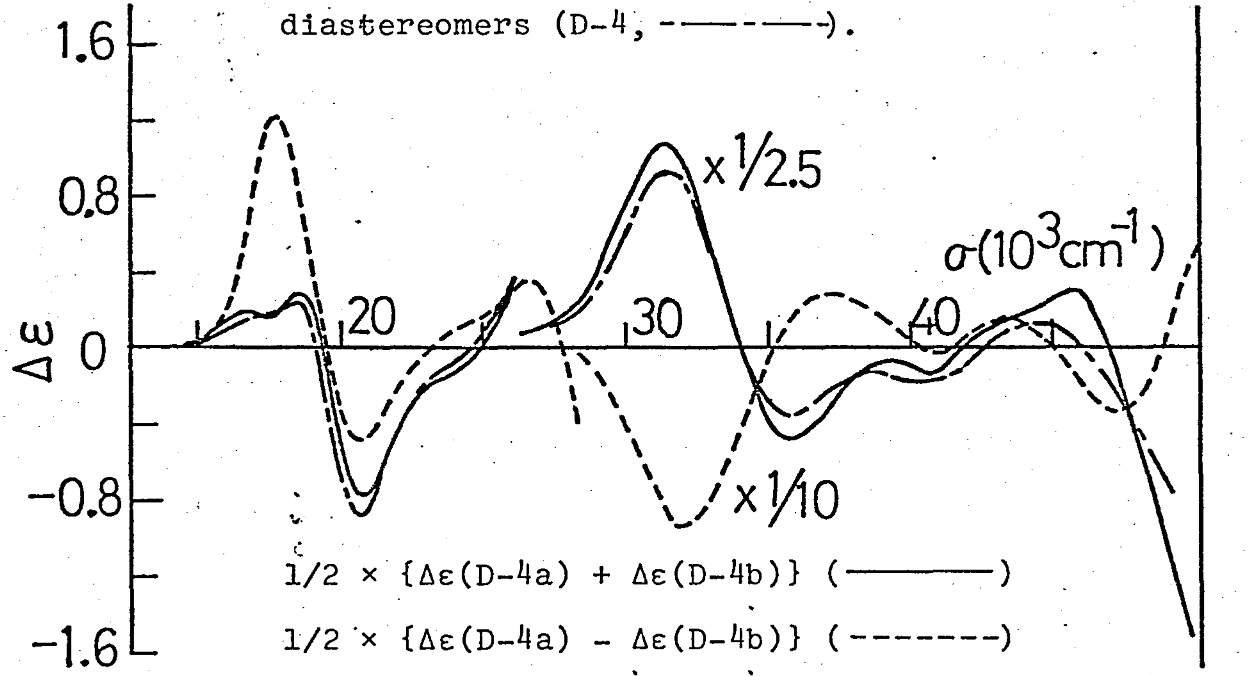


Figure 40. Curve analyses of cisciscis-I-[Co(L-met)(aces)]Cl complexes (D-4a and D-4b), and CD spectrum of a mixture of these two diastereomers (D-4, —— — ——).



1/2 × {Δε(D-4a) + Δε(D-4b)} (————)

1/2 × {Δε(D-4a) − Δε(D-4b)} (-------)

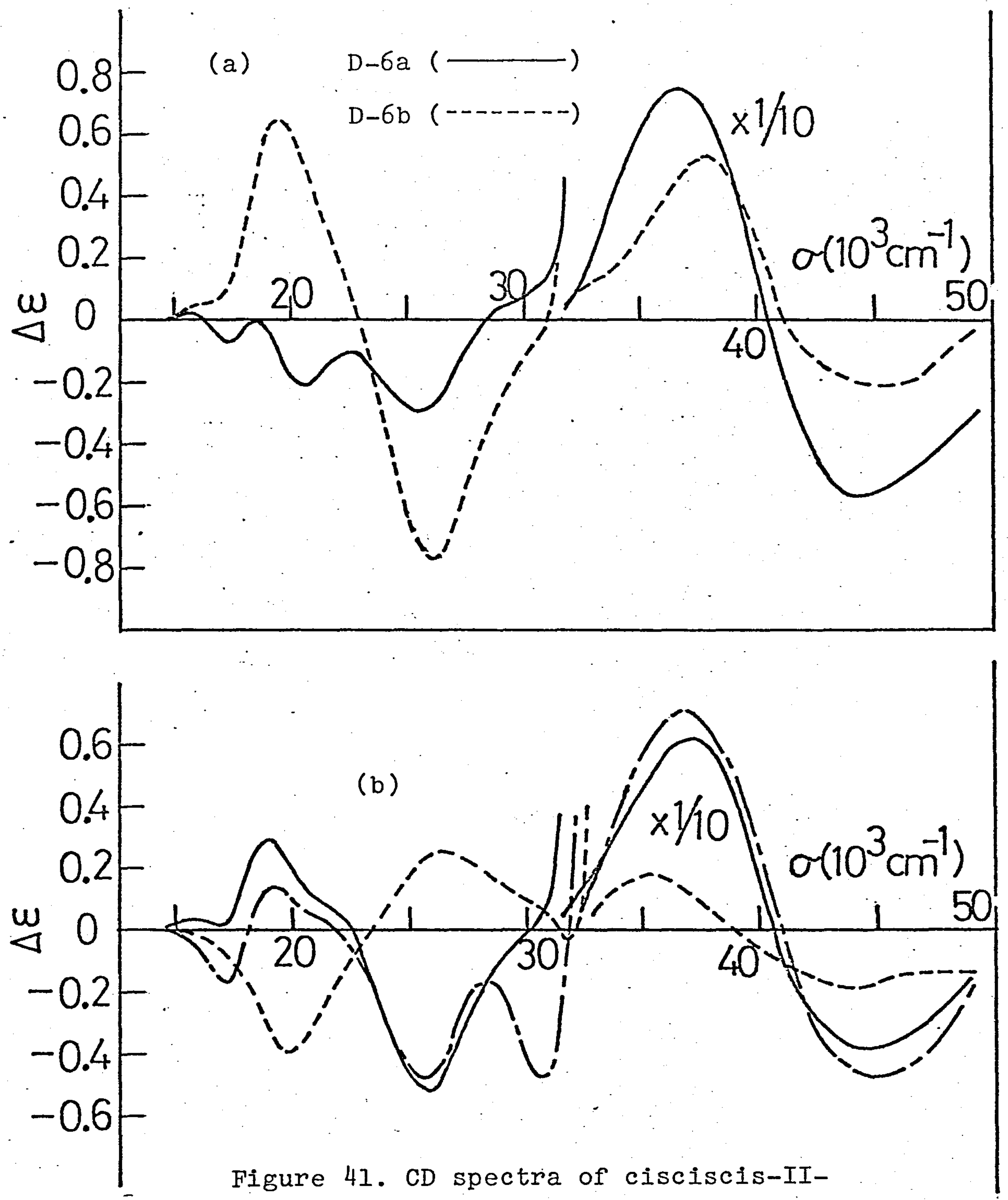


Figure 41. CD spectra of cisciscis-II-[Co(L-met)(aces)]Cl complexes {(a); D-6a and D-6b}, and curve analyses of these complexes [(b); 1/2 × {Δε(D-6a) + Δε(D-6b)} (———), 1/2 × {Δε(D-6a) − Δε(D-6b)} (- - - - - - -), and a mixture of D-6a and D-6b (D-6, —— - ——)].

with the calculated vicinal curve which is mainly contributed by the symmetric sulfur chirality of the aces ligand. This indicates that D-6 isomer is composed of equal amounts of D-6a and D-6b isomers.

Thus, the asymmetric sulfur chirality of the coordinated L-methioninate has the large CD contribution even in the first absorption band region. In this respect,, there seems to be striking difference between the asymmetric sulfur donor atom and the asymmetric carbon[42-47)] or nitrogen[48-53)] donor atoms. Therefore, care must be taken in relating the CD curves to the absolute configurations of the complexes containing L-methioninate ligand.

Summary

1). Five bis(ethylenediamine)cobalt(III) complexes containing N,S- or O,S-bidentate ligands such as mea$^-$, ams, aes, mms$^-$ and ems$^-$ were prepared and optically resolved. From the absorption behaviors, these bidentate ligands in this work can be arranged in a series according to decreasing Dq; ams ~ aes > mms$^-$> ems$^-$> mea$^-$. The absolute configurations were determined from the consideration of their CD spectra. The chromatographic, CD and pmr spectral behaviors suggest that the thioether donor in the bidentate ligands coordinates to a cobalt(III) ion stereospecifically.

2). Three tame complexes containing N,S,O-tridentate ligands such as acms$^-$, aces$^-$ and L-smc$^-$ were prepared and two complexes of acms and aces ligands were optically resolved. From the absorption behaviors, the thioethers of these tridentate ligands are in the higher position of the spectrachemical series than those of the bidentate ligands, and are between H_2O and NH_3. The absolute configurations of acms and aces complexes are determined by connecting with that of the L-smc complex, which show complete stereospecificity because of the optically active ligand.

3). In the bis(tridentate) type complexes, five and six isomers of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$, respectively, were obtained. This is the first example for the isolation of all possible isomers (=six isomers) of the $[Co(A-B-C)_2]^{n+}$ type complexes. They were identified on

the basis of their AB, pmr spectra and chromatographic behaviors. The absorption spectra of the corresponding isomers between the two bis(tridentate) types show a good correlation with each other, though the aces isomers have the band shifted to the slightly lower energy side with the stronger AB intensity in the first absorption band region. For the thioether charge transfer bands, the shift to higher energy is found to be the following order, tr.tr.tr.~trans(S)→trans(N)→cisciscis→trans(O).

Four and five isomers of $[Co(acms)_2]^+$ and $[Co(aces)_2]^+$, respectively, were resolved by the diastereomer formation or the chromatographic technique, and their absolute configurations were connected with their CD spectra and those of the related complexes. A meridional isomer was obtained only for the aces complex and its thioether charge transfer band is located at the higher energy side than that of the corresponding facial trans(S) isomer.

4). In the mixed type complexes, seven and eight isomers of $[Co(L\text{-}met)(acms)]^+$ and $[Co(L\text{-}met)(aces)]^+$, respectively, were separated by the column chromatography and identified based on their AB, pmr spectra, and chromatographic behaviors. The absorption spectra of the corresponding isomers between two mixed type complexes show a good correlation with each other. The thioether charge transfer bands of these complexes are apparently shifted to higher energy side in the following order, tr.tr.tr.~trans(S)→trans(O)→trans(N)~cisciscis-I~cisciscis-II.

The CD spectral patterns are hardly changed with the substitution of the aces ligand for the acms one, especially in the first absorption band region. For these complexes, isomers except for the tr.tr.tr. one are considered to take a definite configuration (R or S) with respect to the asymmetric donor sulfur atom of L-methioninate, based on the CD, pmr spectra, chromatographic behaviors, and model examination. Namely, S-configuration is expected for the complexes of trans(S)-, trans(N)- (=C-2) and trans(O)-$[Co(L\text{-}met)(acms)]^+$, and trans(S)-, trans(N)- and trans(O)-$[Co(L\text{-}met)(aces)]^+$.

5). The sign of the CD band in the thioether charge transfer band region can be related to the absolute configuration of the asymmetric donor atom within each system such as $[Co(en)_2(N,S\text{-bidentate})]^{3+}$, $[Co(en)_2(O,S\text{-bidentate})]^{3+}$, $[Co(tame)(N,S,O\text{-tridentate})]^{2+}$, trans(N)- or trans(O)-$[Co(N,S,O\text{-tridentate})_2]^+$, or trans(S)- or trans(N)-$[Co(L\text{-}met)(N,S,O\text{-tridentate})]^+$.

6). In the present study, four pair of diastereomers due to the sulfur chirality (R or S) of the coordinated L-methioninate were obtained. Applying the additivity rule (of the configurational and vicinal contributions to the CD curves), vicinal CD contributions due to the asymmetric sulfur atom are estimated. These CD spectra show that the asymmetric sulfur donor atom has the strikingly large CD contribution even in the first absorption band region, compared with the configurational one of other complexes.

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