<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Tetrapotassium (\mu_2\text{-N-carboxylato-D-penicillaminato}(3^-)\text{-5:6}\kappa^2\text{S:S})(\mu_2\text{-D-penicillaminato}(1^-)\text{-2:3}\kappa^2\text{S:S})tetraakis(\mu_2\text{-D-penicillaminato}(2^-))(1:2\kappa^3\text{N,S:S;1:6}\kappa^3\text{N,S:S;3:4}\kappa^3\text{N,S;4:5}\kappa^3\text{N,S:S-2,3,5,6-tetragold(I)-1,4-dinickel(II) ethanol monosolvate decahydrate}}</th>
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<tr>
<td><strong>Author(s)</strong></td>
<td>Hashimoto, Yuji; Taguchi, Mai; Yoshinari, Nobuto et al.</td>
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<td><strong>Note</strong></td>
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Osaka University Knowledge Archive: OUKA

https://ir.library.osaka-u.ac.jp/

Osaka University
Tetrapotassium
\[
[\mu_2-N\text{-carboxylato-}\text{D-penicillaminato}(3\text{--})-5:6\kappa^2S:S][\mu_2-D-penicillaminato(1\text{--})-2:3\kappa^2S:S]\text{tetrakis}[\mu_2-D\text{-penicillaminato}(2\text{--})]-1:2\kappa^3N,S:S;1:6\kappa^3N,S:S;3:4\kappa^3S:N,S;4:5\kappa^3N,S:S-2,3,5,6-tetragold(I)-1,4-dinickel(II) ethanol monosolvate decahydrate}
\]

Yuji Hashimoto, Mai Taguchi, Nobuto Yoshinari and Takumi Konno

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Tetrapotassium \([\mu_2-N\text{-carboxylato-D-penicillaminato(3–)-5:6}\kappa^2S:S][\mu_2-D\text{-penicillaminato(1–)-2:3}\kappa^2S:S]\text{-tetrakis[\mu_2-D\text{-penicillaminato(2–)-1:2}\kappa^3N,S:S;1:6}\kappa^3N,S:S;3:4}\kappa^3S:N,S;4:5\kappa^3N,S:S;2,3,5,6\text{-tetragold(I)-1,4-dinickel(II) ethanol monosolvate decahydrate}}

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In the crystal structure of the title compound, \(K_4[Au_4Ni_2-(C_6H_8NO_4S)(C_5H_9NO_2S)_4(C_5H_{10}NO_2S)]\cdot C_2H_6O\cdot 10H_2O\), (I), two planar \([Ni(C_5H_9NO_2S)_2]^{2–}\) units are spanned by \([Au_2(C_6H_8NO_4S)]^{+}\) and \([Au_2(C_6H_8NO_4S)]^{-}\) linkers through S atoms, forming an S:S-bridged \(Au^{I}\) \(4Ni^{II}\) hexanuclear complex anion. One of six organic ligands in the complex anion is a carbamino derivative of \(d\)-penicillamine (3-mercaptovaline) and the others are deprotonated \(d\)-penicillamines. Each complex anion binds to nine \(K^+\) ions through six carboxylate and one carbamino groups to construct a three-dimensional structure.

Comment

Carbamino derivatives of amino acids, which are formed by the reaction of an amino group with \(CO_2\), are important species in biological systems because the carboxamination of an N-terminal valine residue of hemoglobin is related to its \(CO_2\) delivery and oxygen affinity (Jensen, 2004). While the carbamino derivative of deoxycyemoglobin has been determined crystallographically by Fantl et al. (1987), the structural determination of carbaminated amino acids has been carried out only for an achiral carbaminoglycinate salt (Kovbasyuk et al., 1997).

While studying the reactivity of the 3-mercapto derivative of valine (3-mercaptovaline or \(d\)-H2pen) bound to a gold(I) centre towards various metal ions (Toyota et al., 2005; Taguchi et al., 2007), we found that red crystals containing \(Au^I\) and \(Ni^{II}\) atoms in a 2:1 ratio are formed when a solution containing \([Au(d\text{-pen})_2]^{1–}\) and \(Ni^{2+}\) was allowed to stand in a refrigerator for two months. We report herein the crystal structure of (I) containing a \(d\)-carbaminopenicilliminate (\(d\)-cp) ligand that bridges two \(Au^I\) atoms through a thiolate group. To our knowledge, this is the first example of a structurally characterized chiral carbamino amino acid bound to metal centres.

A displacement ellipsoid plot with the atom-numbering scheme of (I) is given in Fig. 1. The hexanuclear complex anion in (I) contains two \([Ni(d\text{-pen})_2]^{2–}\) units, in which each \(Ni^{II}\) atom is coordinated by two bidentate \(d\)-pen ligands. The two \(Ni^{II}\) units have a slightly distorted square-planar geometry, with the dihedral angles between the \(Ni_1/N_1/S_1\) and \(Ni_1/N_2/S_2\) planes and the \(Ni_2/N_3/S_3\) and \(Ni_2/N_4/S_4\) planes being 10.3 (2) and 6.1 (2)°, respectively. All \(d\)-pen \(N,S\)-chelate

Figure 1
A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level and H atoms have been omitted for clarity. The thin lines indicate \(Au\cdots Au\) interactions.
rings in the NiII units adopt a \( ^\delta \) conformation, as found in bis
(\( \alpha \)-penicillaminato)nickelate(II) (Baidya et al., 1991). In
(I), the two NiII units are spanned by two digold(I) linkers, viz.
[\( \text{Au}_2(\text{d-Hpen}) \)]\(^+\) and [\( \text{Au}_2(\text{d-cp}) \)]\(^+\), forming an \( SS \)-bridged
hexanuclear structure in \( [[\text{Au}_2(\text{d-cp})][\text{Au}_2(\text{d-Hpen})][\text{Ni}(\text{d-pen})_2]] \)\(^+\) with a 12-membered
\( \text{Ni}_2\text{S}_6 \) metallo-ring. One of
the digold(I) linkers contains a \( \text{d-Hpen} \) ligand that bridges two
AuI atoms through S atoms, while its amino group is in a
protonated form (\( \text{NH}_3^+ \)) and is not involved in the coordi-
nation. The other digold(I) linker possesses \( \text{d-cp} \), in place of
\( \text{d-Hpen} \), as a bridging ligand, which is considered to be
produced by the reaction of \( \text{d-pen} \) with \( \text{CO}_3^{2-} \). A carbamino N
atom of the \( \text{d-cp} \) ligand is in a trigonal planar geometry and
the C—N bond \( [\text{C}31—\text{N}6 = 1.383 (8) \text{ Å}] \) is obviously shorter
than normal C—N single bonds. In addition, the carbamino
and N-carboxylate groups lie roughly on the same plane; the
dihedral angle between the N6/C27/H6 and C31/O13/O14
planes is 9.0 (8)\(^\circ\). This is indicative of the spreading of \( \pi \)-conjugation over the carbamino and the N-carboxylate
groups. A similar structural feature has been observed for
previously reported carbamino compounds (e.g. Garbauskas
et al., 1983; Schmitt et al., 2002; Shi et al., 2006). It is noted that
the carbamino groups of \( \text{d-Hpen} \) and the N-carboxylate of
\( \text{d-cp} \) form intramolecular hydrogen bonds with amine groups
bound to NiII atoms \( [\text{N}1—\text{O}6 \text{i} = 3.013 (6) \text{ Å}, \text{N}4—\text{O}4 \text{ii} = 3.004 (6) \text{ Å} \text{ and } \text{N}5—\text{O}2 \text{ii} = 2.816 (6) \text{ Å}] \). Furthermore, there is an intramolecular
aurophilic interaction (Schmidbaur & Schier, 2008) between
AuI atoms with distances of \( \text{Au}_1—\text{Au}_2 = 3.0635 (5) \text{ Å}, \text{Au}_1—\text{Au}_4 = 3.1730 (6) \text{ Å} \text{ and } \text{Au}_3—\text{Au}_4 = 3.0542 (5) \text{ Å} \)
(Fig. 2). These attractive interactions appear to sustain this
unique hexanuclear structure in (I).

In (I), each complex anion is connected to four neigh-
bouring complex anions through N—H···O hydrogen bonds
between amine or ammonium groups and carboxylate groups
\( [\text{N}1—\text{O}6 \text{i} = 3.013 (6) \text{ Å}, \text{N}4—\text{O}4 \text{ii} = 3.004 (6) \text{ Å} \text{ and } \text{N}5—\text{O}2 \text{ii} = 2.816 (6) \text{ Å}] \). symmetry
codes and geometric parameters are given in Table 1], forming a two-dimensional
layer structure in the \( ab \) plane (Fig. 3). In addition, the layers
are connected with each other through K—O carboxylate coor-
dination bonds \( [2.629 (4)—3.192 (5) \text{ Å}] \) to give a three-dimen-
sional network structure (Fig. 4). Besides carboxylate groups,
some water and ethanol solvent molecules coordinate to K+
ions \( [2.732 (6)—2.918 (7) \text{ Å}] \). All of the water and ethanol
molecules participate in the formation of O—H···O hydrogen
bonds with carboxylate groups, water molecules, and/or
ethanol molecules in the O···O distance range of 2.662 (7)—
3.187 (7) \text{ Å} (Table 1).

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metal-organic compounds

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Figure 2
A view of the intramolecular hydrogen bonds and aurophilic interactions
in (I). Dotted and dashed lines indicate N—H···O hydrogen bonds and
Au···Au interactions, respectively.

Figure 3
A view of the two-dimensional layer structure of complex anions
connected by K+ ions in (I). Dashed lines indicate N—H···O hydrogen bonds.
K+ ions, solvent molecules and H atoms have been omitted for clarity.

Figure 4
A view of the three-dimensional network structure of complex anions
connected by K+ ions in (I).
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