Title	Tetrapotassium [μ_2-N-carboxylato-D-penicillaminato(3-)-5:6κ^2S:S][μ_2-D-penicillaminato(1-)-2:3κ^2S:S]tetrakis[μ_2-D-penicillaminato(2-)]-1:2κ^3N,S:S;1:6κ^3N,S:S;3:4κ^3S:N,S;4:5κ^3N,S:S-2,3,5,6-tetragold(I)-1,4-dinickel(II) ethanol monosolvate decahydrate
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Tetrapotassium [μ_2-*N*-carboxylato-D-penicillaminato(3–)-5:6κ^2*S*:*S*][μ_2-D-penicillaminato(1–)-2:3κ^2*S*:*S*]tetrakis[μ_2-D-penicillaminato(2–)]-1:2κ^3*N*,*S*:*S*;1:6κ^3*N*,*S*:*S*;3:4κ^3*S*:*N*,*S*;4:5κ^3*N*,*S*:*S*-2,3,5,6-tetragold(I)-1,4-dinickel(II) ethanol monosolvate decahydrate

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Tetrapotassium [μ_2-*N*-carboxylato-D-penicillaminato(3–)-5:6κ^2*S*:*S*][μ_2-D-penicillaminato(1–)-2:3κ^2*S*:*S*]-tetrakis[μ_2-D-penicillaminato(2–)]-1:2κ^3*N*,*S*:*S*;1:6κ^3*N*,*S*:*S*;3:4κ^3*S*:*N*,*S*;4:5κ^3*N*,*S*:*S*-2,3,5,6-tetragold(I)-1,4-dinickel(II) ethanol monosolvate decahydrate

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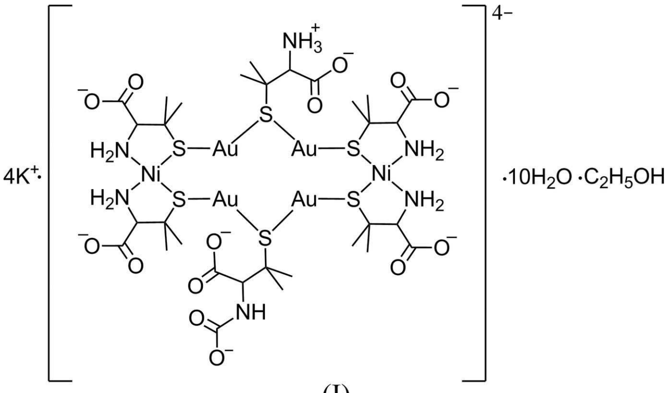
In the crystal structure of the title compound, $K_4[Au_4Ni_2(C_6H_8NO_4S)(C_5H_9NO_2S)_4(C_5H_{10}NO_2S)]\cdot C_2H_6O\cdot 10H_2O$, (I), two planar $[Ni(C_5H_9NO_2S)_2]^{2-}$ units are spanned by $[Au_2(C_5H_{10}NO_2S)]^+$ and $[Au_2(C_6H_8NO_4S)]^-$ linkers through S atoms, forming an *S*:*S*-bridged $Au^{I}_{4}Ni^{II}_{2}$ 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 carbamination 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 deoxyhemoglobin 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 (D-penicillamine or D-H_2pen) 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 $[Au(D\text{-pen})_2]^{3-}$ and Ni^{2+} was allowed to stand in a refrigerator for two months. We report herein the crystal structure of (I) containing a D-carbaminopenicillaminate (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.



(I)

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 Ni1/N1/S1 and Ni1/N2/S2 planes and the Ni2/N3/S3 and Ni2/N4/S4 planes being 10.3 (2) and 6.1 (2)°, respectively. All D-pen *N*,*S*-chelate

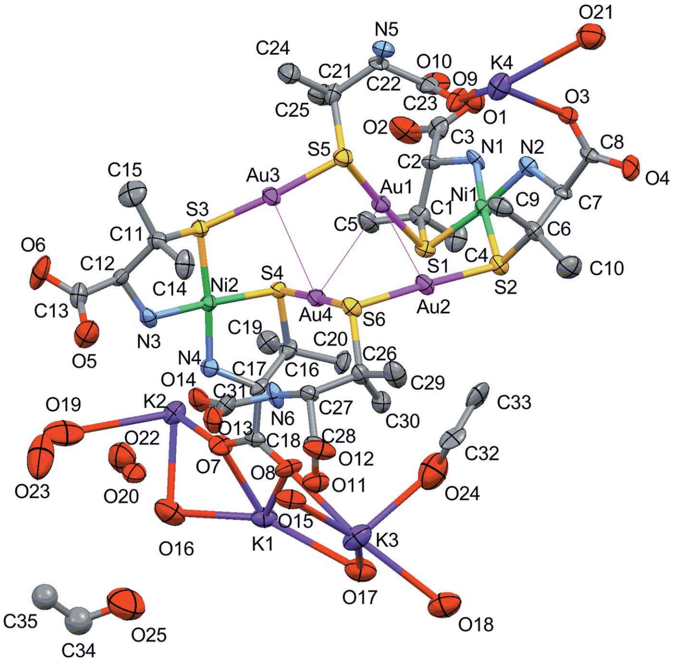


Figure 1
A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level and H atoms have been omitted for clarity. The thin lines indicate Au···Au interactions.

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rings in the Ni^{II} units adopt a δ conformation, as found in bis(D-penicillaminato)nickelate(II) (Baidya *et al.*, 1991). In (I), the two Ni^{II} units are spanned by two digold(I) linkers, *viz.* $[Au_2(\text{D-Hpen})]^+$ and $[Au_2(\text{D-cp})]^-$, forming an *S*:*S*-bridged hexanuclear structure in $\{[Au_2(\text{D-cp})][Au_2(\text{D-Hpen})][Ni(\text{D-pen})_2]_2\}^{4-}$ with a 12-membered $Au^{I}_{4}Ni^{II}_{2}S_6$ metallo-ring. One of the digold(I) linkers contains a D-Hpen ligand that bridges two Au^I atoms through S atoms, while its amino group is in a protonated form (NH_3^+) and is not involved in the coordination. The other digold(I) linker possesses D-cp, in place of D-Hpen, as a bridging ligand, which is considered to be produced by the reaction of D-pen with CO_3^{2-}. A carbamino N atom of the D-cp ligand is in a trigonal planar geometry and the C—N bond [C31—N6 = 1.383 (8) 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)°. This is indicative of the spreading of π-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 carboxylate groups of D-Hpen and the *N*-carboxylate of D-cp form intramolecular hydrogen bonds with amine groups bound to Ni^{II} atoms [N1···O10 = 2.825 (7) Å, N2···O9 = 2.960 (6) Å, N3···O14 = 2.867 (6) Å and N4···O14 = 2.934 (6) Å] (Fig. 2). Furthermore, there is an intramolecular aurophilic interaction (Schmidbaur & Schier, 2008) between Au^I atoms with distances of Au1···Au2 = 3.0635 (5) Å, Au1···Au4 = 3.1730 (6) Å and Au3···Au4 = 3.0542 (5) Å (Fig. 2). These attractive interactions appear to sustain this unique hexanuclear structure in (I).

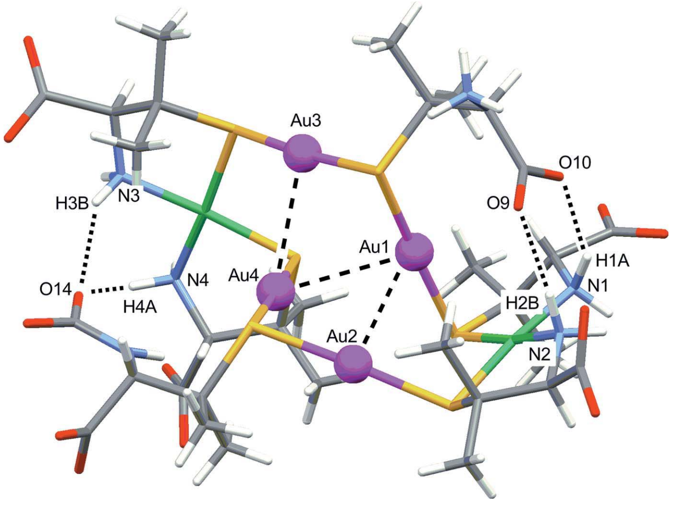

Figure 2
A view of the intramolecular hydrogen bonds and aurophilic interactions in (I). Dotted and dashed lines indicate N—H···O hydrogen bonds and Au···Au interactions, respectively.

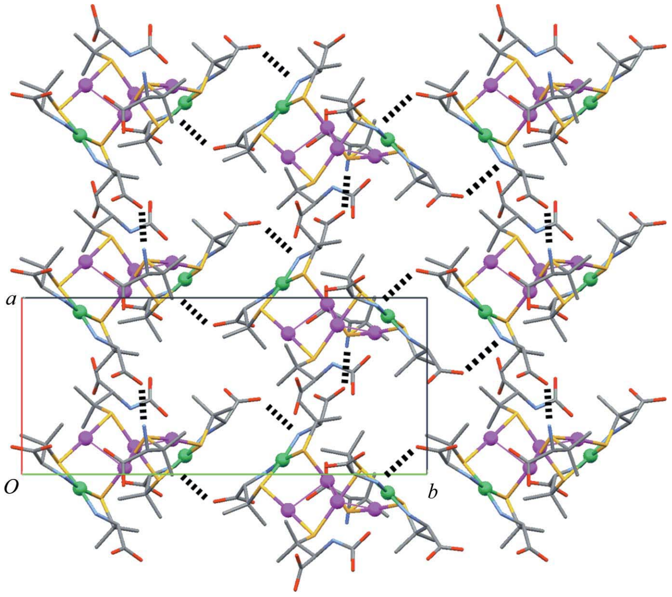

Figure 3
A view of the two-dimensional layer structure of complex anions in (I). Dashed lines indicate N—H···O hydrogen bonds. K^+ ions, solvent molecules and H atoms have been omitted for clarity.

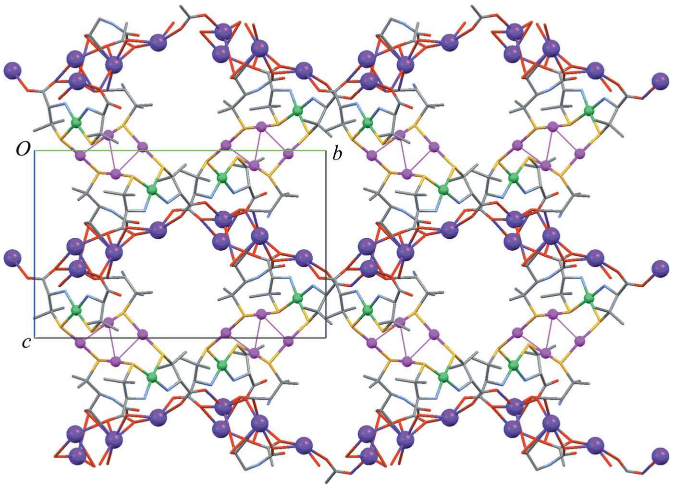

Figure 4
A view of the three-dimensional network structure of complex anions connected by K^+ ions in (I).

In (I), each complex anion is connected to four neighbouring complex anions through N—H···O hydrogen bonds between amine or ammonium groups and carboxylate groups [N1···O6^{i} = 3.013 (6) Å, N4···O4^{iii} = 3.004 (6) Å and N5···O2^{v} = 2.816 (6) 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 $K—O_{carboxylate}$ coordination bonds [2.629 (4)–3.192 (5) Å] to give a three-dimensional network structure (Fig. 4). Besides carboxylate groups, some water and ethanol solvent molecules coordinate to K^+ ions [2.732 (6)–2.918 (7) 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) Å (Table 1).

Experimental

A solution of $Ni(NO_3)_2·6H_2O$ (0.013 g, 0.04 mmol) in ethanol (6 ml) was layered on to a colourless solution of $NH_4[Au(\text{D-Hpen})_2]·3.5H_2O$ (0.050 g, 0.09 mmol) (LeBlanc *et al.*, 1997; Konno *et al.*, 2009) and K_2CO_3 (0.024 g, 0.18 mmol) in water (1 ml) in a test tube (1.5 × 10 cm) and the resulting mixture was left in a refrigerator for two months. Red plate-shaped crystals of (I) formed and were collected by filtration. IR (KBr, cm^{-1}): 1593 (*s*, υ_{as} of OCO^-).

Crystal data

$K_4[Au_4Ni_2(C_6H_8NO_4S)(C_5H_9NO_2S)_4(C_5H_{10}NO_2S)]·C_2H_6O·10H_2O$
$M_r = 2214.06$
Monoclinic, $P2_1$
$a = 9.9638\ (18)$ Å
$b = 22.644\ (4)$ Å
$c = 14.723\ (3)$ Å
$\beta = 97.998\ (7)°$
$V = 3289.5\ (10)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 9.97\ mm^{-1}$
$T = 200$ K
0.15 × 0.15 × 0.04 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.316$, $T_{max} = 0.691$
38154 measured reflections
17713 independent reflections
16029 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.064$
$S = 1.04$
17713 reflections
804 parameters
49 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.14$ e Å^{-3}
$\Delta\rho_{min} = -0.97$ e Å^{-3}
Absolute structure: Flack (1983) 8079 Friedel pairs
Flack parameter: −0.005 (3)

H atoms bound to C and N atoms were placed at calculated positions [C—H = 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (CH) and N—H = 0.91 (NH_3^+), 0.92 (NH_2) or 0.88 Å (NH)] and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$ for CH_2, CH, NH_2 and NH, and $1.5U_{eq}(C,N)$ for CH_3 and NH_3^+. Each of two ethanol solvent molecules shares the same site with a water molecule, and these disordered molecules were refined with occupancies of 0.5. Water and O-bound H atoms of ethanol molecules were placed so as to form reasonable hydrogen bonding, except for two H atoms of disordered water molecules that were not included in the model. All H atoms bound to O atoms were refined with restrained geometric and displacement parameters [O—H = 0.85 (5) Å, H···H = 1.38 (5) Å and $U_{iso}(H) = 1.2U_{eq}(O)$]. In addition, 14 H atoms (H15*A*, H15*B*, H16*B*, H17*A*, H18*A*, H18*B*, H19*A*, H21*A*, H21*B*, H22*B*, H23*A*, H23*B*, H24 and H25) were refined with additional intermolecular H···O distance restraints of 1.90 (5) Å or H···H antibumping restraints of 2.30 (5) Å so as to form reasonable hydrogen bonding.

Data collection and cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3031). Services for accessing these data are described at the back of the journal.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O10	0.92	2.04	2.825 (7)	143
N1—H1*B*···O6^{i}	0.92	2.10	3.013 (6)	172
N2—H2*B*···O9	0.92	2.06	2.960 (6)	167
N3—H3*A*···O18^{ii}	0.92	2.03	2.929 (8)	167
N3—H3*B*···O14	0.92	2.08	2.867 (6)	143
N4—H4*A*···O14	0.92	2.20	2.934 (6)	136
N4—H4*B*···O4^{iii}	0.92	2.13	3.004 (6)	157
N5—H5*A*···O20^{iv}	0.91	1.87	2.768 (7)	169
N5—H5*B*···O15^{iv}	0.91	2.09	2.979 (7)	164
N5—H5*C*···O2^{v}	0.91	1.97	2.816 (6)	154
O15—H15*A*···O8	0.83 (3)	2.05 (3)	2.791 (6)	148 (6)
O15—H15*B*···O11	0.86 (4)	1.95 (3)	2.686 (7)	143 (6)
O16—H16*A*···O20^{vi}	0.86 (4)	1.97 (4)	2.820 (7)	169 (8)
O16—H16*B*···O25	0.89 (4)	2.01 (4)	2.801 (10)	146 (6)
O17—H17*A*···O1^{vii}	1.02 (3)	2.64 (7)	3.187 (7)	113 (5)
O17—H17*B*···O12^{vi}	0.82 (4)	2.06 (5)	2.751 (7)	142 (7)
O18—H18*A*···O22^{viii}	0.86 (3)	1.98 (3)	2.773 (9)	153 (5)
O18—H18*B*···O23^{viii}	0.93 (3)	2.08 (4)	2.958 (10)	156 (7)
O19—H19*A*···O3^{iii}	0.92 (4)	1.90 (4)	2.697 (8)	144 (7)
O19—H19*B*···O21^{ii}	0.95 (4)	1.89 (5)	2.799 (7)	161 (7)
O20—H20*A*···O14	0.80 (4)	1.89 (4)	2.662 (7)	165 (7)
O20—H20*B*···O23	0.85 (4)	1.90 (4)	2.734 (8)	167 (7)
O21—H21*A*···O5^{ix}	0.97 (3)	1.89 (3)	2.791 (8)	154 (6)
O21—H21*B*···O11	0.83 (3)	1.97 (3)	2.763 (7)	160 (7)
O22—H22*A*···O7	0.82 (4)	2.07 (6)	2.817 (7)	151 (9)
O22—H22*B*···O19	0.83 (3)	1.96 (3)	2.766 (8)	163 (7)
O23—H23*A*···O24^{ii}	0.92 (4)	2.00 (4)	2.787 (9)	142 (6)
O23—H23*B*···O21^{x}	0.83 (4)	1.96 (7)	2.754 (9)	158 (8)
O24—H24···O12^{vi}	0.83 (4)	2.00 (4)	2.778 (7)	154 (7)
O25—H25···O2^{vii}	0.90 (4)	1.99 (4)	2.792 (9)	149 (8)

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z$; (ii) $-x, y+\frac{1}{2}, -z+1$; (iii) $-x, y+\frac{1}{2}, -z$; (iv) $x, y, z-1$; (v) $x+1, y, z$; (vi) $x-1, y, z$; (vii) $x, y, z+1$; (viii) $-x, y-\frac{1}{2}, -z+1$; (ix) $-x+1, y-\frac{1}{2}, -z+1$; (x) $-x+1, y+\frac{1}{2}, -z+1$.

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