metal-organic compounds

Tetrapotassium [μ2-N-carboxylato-D-penicillaminato(3−)-5:6κ2S:S][μ2-D-penicillaminato(1−)-2:3κ2S:S]tetrakis[μ2-D-penicillaminato(2−)]-1:2κ3N,S:S;1:6κ3N,S:S;3:4κ3S:N,S;4:5κ3N,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 $Au_4^INi_2^{II}$ 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 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-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

$[Au(\text{D-pen})_2]^{3-}$ 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.
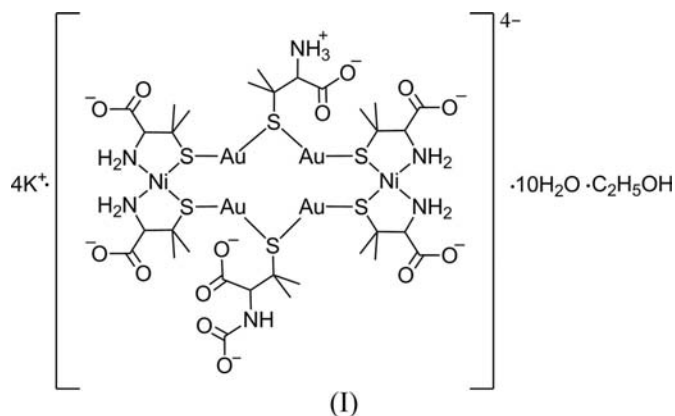

A displacement ellipsoid plot with the atom-numbering scheme of (I) is given in Fig. 1. The hexanuclear complex anion in (I) contains two $[Ni(\text{D-pen})_2]^{2-}$ units, in which each Ni^{II} atom is coordinated by two bidentate D-pen ligands. The two Ni^{II} units have a slightly distorted square-planar 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
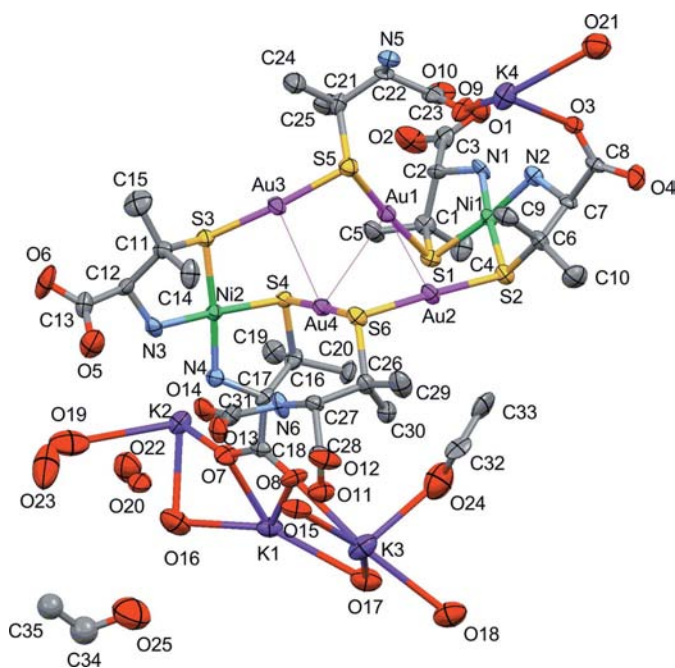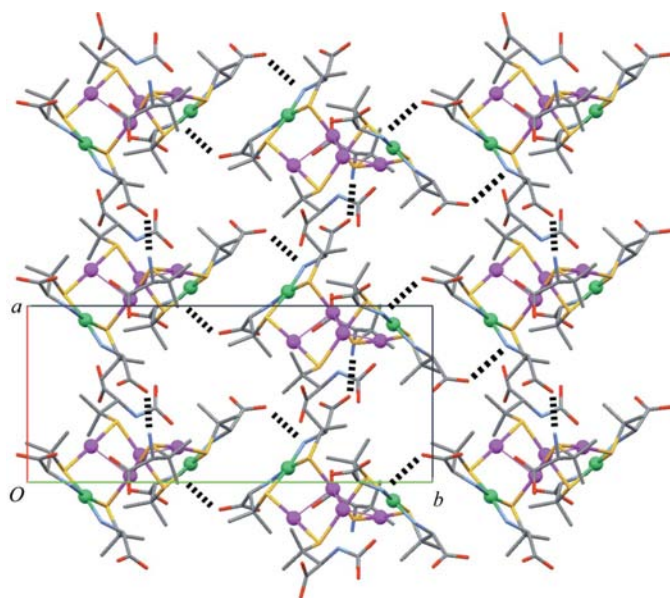

Figure 1
A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level and H atoms have been omitted for clarity. The thin lines indicate Au···Au interactions.

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$_2$(D-Hpen)]$^+$ and [Au$_2$(D-cp)]$^-$, forming an *S*:*S*-bridged hexanuclear structure in {[Au$_2$(D-cp)][Au$_2$(D-Hpen)][Ni(D-pen)$_2$]$_2$}$^{4-}$ with a 12-membered Au$_4^I$Ni$_2^{II}$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
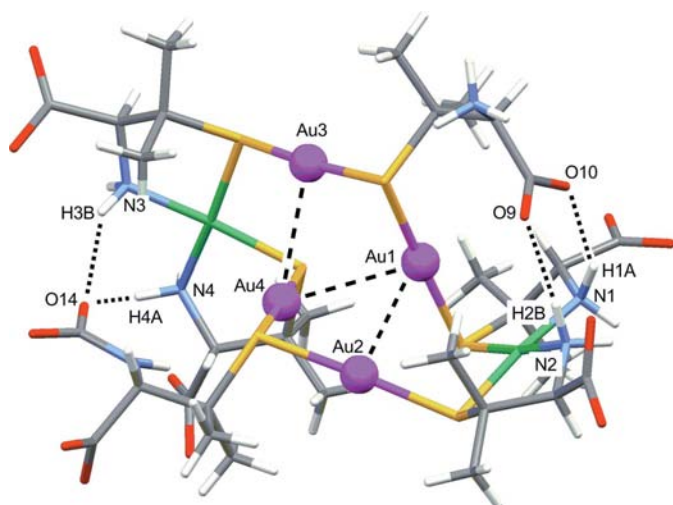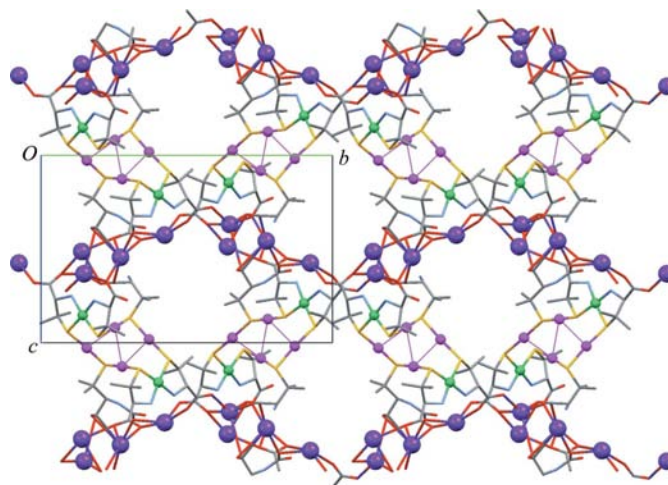

Figure 2
A view of the intramolecular hydrogen bonds and aurophilic interactions in (I). Dotted and dashed lines indicate N—H···O hydrogen bonds and Au···Au interactions, respectively.

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).

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).

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).

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Experimental

A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.013 g, 0.04 mmol) in ethanol (6 ml) was layered on to a colourless solution of $NH_4[Au(D\text{-}Hpen)_2] \cdot 3.5H_2O$ (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

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

Data collection

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.064$	
$S = 1.04$	
17713 reflections	$\Delta\rho_{max} = 1.14$ e Å^{-3}
804 parameters	$\Delta\rho_{min} = -0.97$ e Å^{-3}
49 restraints	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 (H15A, H15B, H16B, H17A, H18A, H18B, H19A, H21A, H21B, H22B, H23A, H23B, 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).

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1A$\cdots$O10	0.92	2.04	2.825 (7)	143
N1—H1B$\cdots$O6^i	0.92	2.10	3.013 (6)	172
N2—H2B$\cdots$O9	0.92	2.06	2.960 (6)	167
N3—H3A$\cdots$O18^{ii}	0.92	2.03	2.929 (8)	167
N3—H3B$\cdots$O14	0.92	2.08	2.867 (6)	143
N4—H4A$\cdots$O14	0.92	2.20	2.934 (6)	136
N4—H4B$\cdots$O4^{iii}	0.92	2.13	3.004 (6)	157
N5—H5A$\cdots$O20^{iv}	0.91	1.87	2.768 (7)	169
N5—H5B$\cdots$O15^{iv}	0.91	2.09	2.979 (7)	164
N5—H5C$\cdots$O2^v	0.91	1.97	2.816 (6)	154
O15—H15A$\cdots$O8	0.83 (3)	2.05 (3)	2.791 (6)	148 (6)
O15—H15B$\cdots$O11	0.86 (4)	1.95 (3)	2.686 (7)	143 (6)
O16—H16A$\cdots$O20^{vi}	0.86 (4)	1.97 (4)	2.820 (7)	169 (8)
O16—H16B$\cdots$O25	0.89 (4)	2.01 (4)	2.801 (10)	146 (6)
O17—H17A$\cdots$O1^{vii}	1.02 (3)	2.64 (7)	3.187 (7)	113 (5)
O17—H17B$\cdots$O12^{vi}	0.82 (5)	2.06 (5)	2.751 (7)	142 (7)
O18—H18A$\cdots$O22^{viii}	0.86 (3)	1.98 (3)	2.773 (9)	153 (5)
O18—H18B$\cdots$O23^{viii}	0.93 (3)	2.08 (4)	2.958 (10)	156 (7)
O19—H19A$\cdots$O3^{iii}	0.92 (4)	1.90 (4)	2.697 (7)	144 (7)
O19—H19B$\cdots$O21^{ii}	0.95 (4)	1.89 (5)	2.799 (7)	161 (7)
O20—H20A$\cdots$O14	0.80 (4)	1.89 (4)	2.662 (7)	165 (7)
O20—H20B$\cdots$O23	0.85 (4)	1.90 (4)	2.734 (8)	167 (7)
O21—H21A$\cdots$O5^{ix}	0.97 (3)	1.89 (3)	2.791 (6)	154 (6)
O21—H21B$\cdots$O11	0.83 (3)	1.97 (3)	2.763 (7)	160 (7)
O22—H22A$\cdots$O7	0.82 (3)	2.07 (6)	2.817 (7)	151 (9)
O22—H22B$\cdots$O19	0.83 (3)	1.96 (3)	2.766 (8)	163 (7)
O23—H23A$\cdots$O24^{ii}	0.92 (4)	2.00 (4)	2.787 (9)	142 (6)
O23—H23B$\cdots$O21^x	0.83 (4)	1.96 (7)	2.754 (9)	158 (8)
O24—H24$\cdots$O12^{vi}	0.83 (4)	2.00 (4)	2.778 (7)	154 (7)
O25—H25$\cdots$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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