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

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

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Tetrapotassium [μ_2 -*N*-carboxylato-*D*-penicillaminato(3-)-5:6 κ^2 S:S][μ_2 -*D*-penicillaminato(1-)-2:3 κ^2 S:S]-tetrakis[μ_2 -*D*-penicillaminato(2-)-1:2 κ^3 N,S:S;1:6 κ^3 N,S:S;3:4 κ^3 S:N,S;-4:5 κ^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_4Ni_2 hexanuclear complex anion. One of six organic ligands in the complex anion is a carbamino derivative of *D*-penicillamine (3-mercaptopalane) 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 carbamation 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

$[Au(D\text{-}pen)_2]^{3-}$ and Ni^{2+} was allowed to stand in a refrigerator for two months. We report herein the crystal structure of (I) containing a *D*-carbaminopenicillamate (*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 $Ni1/N1/S1$ and $Ni1/N2/S2$ planes and the $Ni2/N3/S3$ and $Ni2/N4/S4$ planes being $10.3(2)^\circ$ and $6.1(2)^\circ$, 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 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.* $[\text{Au}_2(\text{D-Hpen})]^+$ and $[\text{Au}_2(\text{D-cp})]^-$, forming an *S:S*-bridged hexanuclear structure in $[[\text{Au}_2(\text{D-cp})][\text{Au}_2(\text{D-Hpen})][\text{Ni}(\text{D-pen})_2]_2]^{4-}$ with a 12-membered $\text{Au}_4\text{Ni}_2\text{S}_6$ 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 $\text{N-H}\cdots\text{O}$ hydrogen bonds and $\text{Au}\cdots\text{Au}$ interactions, respectively.

Figure 3
A view of the two-dimensional layer structure of complex anions in (I). Dashed lines indicate $\text{N-H}\cdots\text{O}$ 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 [$\text{C31}-\text{N6} = 1.383(8) \text{ \AA}$] 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 π -conjugation over the carbamino and the *N*-carboxylate groups. A similar structural feature has been observed for previously reported carbamino compounds (*e.g.* Garbaskas *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 [$\text{N1}\cdots\text{O10} = 2.825(7) \text{ \AA}$, $\text{N2}\cdots\text{O9} = 2.960(6) \text{ \AA}$, $\text{N3}\cdots\text{O14} = 2.867(6) \text{ \AA}$ and $\text{N4}\cdots\text{O14} = 2.934(6) \text{ \AA}$] (Fig. 2). Furthermore, there is an intramolecular aurophilic interaction (Schmidbaur & Schier, 2008) between Au^{I} atoms with distances of $\text{Au1}\cdots\text{Au2} = 3.0635(5) \text{ \AA}$, $\text{Au1}\cdots\text{Au4} = 3.1730(6) \text{ \AA}$ and $\text{Au3}\cdots\text{Au4} = 3.0542(5) \text{ \AA}$ (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 $\text{N-H}\cdots\text{O}$ hydrogen bonds between amine or ammonium groups and carboxylate groups [$\text{N1}\cdots\text{O6}^{\text{i}} = 3.013(6) \text{ \AA}$, $\text{N4}\cdots\text{O4}^{\text{iii}} = 3.004(6) \text{ \AA}$ and $\text{N5}\cdots\text{O2}^{\text{v}} = 2.816(6) \text{ \AA}$; 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 $\text{K}-\text{O}_{\text{carboxylate}}$ coordination bonds [$2.629(4)$ – $3.192(5) \text{ \AA}$] to give a three-dimensional network structure (Fig. 4). Besides carboxylate groups, some water and ethanol solvent molecules coordinate to K^+ ions [$2.732(6)$ – $2.918(7) \text{ \AA}$]. All of the water and ethanol molecules participate in the formation of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with carboxylate groups, water molecules, and/or ethanol molecules in the $\text{O}\cdots\text{O}$ distance range of $2.662(7)$ – $3.187(7) \text{ \AA}$ (Table 1).

Experimental

A solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.013 g, 0.04 mmol) in ethanol (6 ml) was layered on to a colourless solution of $\text{NH}_4[\text{Au}(\text{D-Hpen})_2] \cdot 3.5\text{H}_2\text{O}$ (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, ν_{as} of OCO^-).

Crystal data

$\text{K}_4[\text{Au}_4\text{Ni}_2(\text{C}_6\text{H}_8\text{NO}_4\text{S})-(\text{C}_5\text{H}_9\text{NO}_2\text{S})_4(\text{C}_5\text{H}_{10}\text{NO}_2\text{S})] \cdot \text{C}_2\text{H}_6\text{O} \cdot 10\text{H}_2\text{O}$
 $M_r = 2214.06$
 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) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 9.97$ mm⁻¹
 $T = 200$ K
 $0.15 \times 0.15 \times 0.04$ mm

Data collection

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

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
 $\Delta\rho_{\text{max}} = 1.14$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.97$ 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 [$\text{C}-\text{H} = 0.98$ (CH₃), 0.99 (CH₂) or 1.00 Å (CH) and $\text{N}-\text{H} = 0.91$ (NH₃⁺), 0.92 (NH₂) or 0.88 Å (NH)] and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ for CH₂, CH, NH₂ and NH, and $1.5U_{\text{eq}}(\text{C}, \text{N})$ for CH₃ and NH₃⁺. 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 [$\text{O}-\text{H} = 0.85$ (5) Å, $\text{H} \cdots \text{H} = 1.38$ (5) Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$]. 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 $\text{H} \cdots \text{O}$ distance restraints of 1.90 (5) Å or $\text{H} \cdots \text{H}$ 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/MS, 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: *pubCIF* (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, °).

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