990 *Inorg. Chem.* **1982**, *21*, 990–995

no $M(L)_3$ group is present (Table IVa).

The ring and substituent parameters are all normal (Table III) for this type of compound. The average Ru–C(ring) and Ru–C(carbonyl distances of 2.36 (4) and 1.843 (5) Å, respectively, are reasonable [cf. Ru–C(ring) = 2.20 (1) and Ru–C(carbonyl = 1.87 (2) Å in $(C_6H_6)Ru(CO)(GeCl_3)_2$[15]]. The average Ru–Si distance of 2.339 (1) Å is close to the value 2.414 Å found in $Ru(SiMe_3)(CO)_2(C_8H_8(SiMe_3))$.[23] The Ru–C–O angle of 177.1 (5)° is normal. The $SiCl_3$ dimensions are similar to those observed in $(\pi\text{-}C_5H_5)FeH(SiCl_3)_2(CO)$.[24]

Acknowledgment. We wish to thank Drs. R. K. Pomeroy and K. Slessor, of this establishment, for helpful discussion and R.K.P. for the gift of the crystals. We also wish to thank the NSERC for financial support and Dr. E. J. Gabe for the use of his computer programs.

Registry No. $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2\cdot{}^1/_2C_6H_5CH_3$, 79991-87-0.

Supplementary Material Available: Listings of structure factors and final thermal parameters and a table of nonbonded distances (27 pages). Ordering information is given on any current masthead page.

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(22) Masaaki, Y.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 399.

(23) Harris, P. J.; Howard, J. A. K.; Knox, S. A. R.; McKinney, R. J.; Phillips, R. P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1978**, 403.

(24) Manojlović-Muir, L.; Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 447.

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Synthesis and X-ray Structure of the Tetranuclear Heterometallic Anion Bis[μ-[*cis*-bis(D-penicillaminato(2−)-*N*,*S*)nickel(II)]-*S*,*S*′]diaurate(I)(2−) in $Na_2[Au^I_2Ni^{II}_2(SC(CH_3)_2CH(NH_2)COO)_4]\cdot x$ (solvent)

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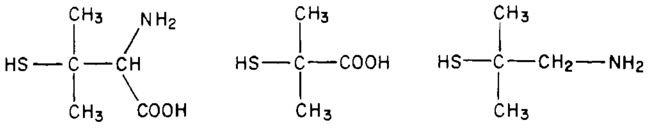
Received July 7, 1981

The synthesis and structural characterization of a new type of polynuclear metal thiolate compound of composition $[Au^I_2M^{II}_2L_4]^{2-}$ is described, where M is Ni or Pd and L is the deprotonated penicillamine ligand $^-SC(CH_3)_2CH(NH_2)COO^-$. The compound $Na_2[Au^I_2Ni^{II}_2L_4]\cdot x$(solvent) crystallizes in the rhombohedral space group *R*3. Described in a hexagonal lattice the unit-cell dimensions are $a = 28.27$ (7) Å and $c = 33.27$ (8) Å. Intensity data were collected on an automatic four-circle diffractometer (Mo Kα radiation; ω–θ scans). The structure was solved by direct methods and full-matrix least squares refined to a final *R* value of 0.079 for 2425 reflections with $I > 2\sigma(I)$. The structure contains two independent complex ions ($Z = 18$). The Au^I atoms are linearly coordinated by two penicillamine S atoms. The Ni^{II} atoms are cis-bidentate coordinated by two chelating penicillamine ligands. Each S atom forms a bridge between an Au^I and a Ni^{II} atom. The Au–Au distances in the two independent complex ions are 2.94 (1), and 2.99 (1) Å, which is only slightly longer than the Au–Au distance in metallic gold (2.884 Å). The formation reaction of this novel compound and the differences with the Cu^I and Ag^I containing penicillamine clusters are discussed.

Introduction

The formation of polynuclear transition-metal compounds is becoming a well-established feature of the coordination chemistry of potentially chelating thiolate ligands such as



H_2Pen H_2MIBA HDMC

D-penicillamine (H_2Pen),[1,2] α-mercaptoisobutyric acid (H_2MIBA),[3] and dimethylcysteamine (HDMC).[4] The common feature of these ligands is their capability of forming five-membered chelate rings and the presence of two alkyl substituents on the carbon atom adjacent to the sulfur atom. Their polynuclear compounds so far characterized have the composition $[M^I_8M^{II}_6L_{12}Cl]^z$, where $M^I = Cu^I$ or Ag^I and $M^{II} = Cu^{II}$, Ni^{II}, or Pd^{II} and L = Pen ($z = -5$), MIBA ($z = -5$), or DMC ($z = +7$).[1-4] In these cluster compounds the M^{II} atoms are cis-bidentate square-planar S_2N_2 or S_2O_2 coordinated by the ligands (see Figure 1). Six of these $M^{II}L_2$ units are located above the six faces of a chloride-centered M^I_8 cube so that the sulfur atoms form bridges between two M^I and one M^{II} atoms. The result is that each M^I atom is planar coordinated by a triangle of S atoms (Figure 1).

In an attempt to obtain analogues of these clusters with Au^I instead of Cu^I and Ag^I, we found much simpler complex ions of composition $[Au^I_2M^{II}_2Pen_4]^{2-}$. The X-ray crystal structure of this novel cluster compound is reported, and the different behavior of Au^I is discussed.

Experimental Section

Materials. D-penicillamine was commercially available (Aldrich, "Gold label"). Bis(thiourea)gold(I) chloride, $Au(tu)_2Cl$ was prepared according to a published method.[5] All other reagents and solvents

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(1) (a) Birker, P. J. M. W. L.; Freeman, H. C. *J. Am. Chem. Soc.* **1977**, *99*, 6890. (b) Birker, P. J. M. W. L. *J. Chem. Soc., Chem. Commun.* **1980**, 946. (c) Birker, P. J. M. W. L.; Reedijk, J.; Verschoor, G. C. *Inorg. Chem.* **1981**, *20*, 2877.

(2) The abbreviations used in this article are as follows: H_2Pen = D-penicillamine, $HSC(CH_3)_2CH(NH_2)COOH$; H_2MIBA = α-mercaptoisobutyric acid, $HSC(CH_3)_2COOH$; HDMC = dimethylcysteamine, $HSC(CH_3)_2CH_2NH_2$. The deprotonated ligands are abbreviated as Pen, MIBA, and DMC, respectively. M = metal, L = ligand, and tu = thiourea.

(3) Birker, P. J. M. W. L. *Inorg. Chem.* **1979**, *18*, 3502.

(4) Schugar, H. J.; Ou, C. C.; Thich, J. A.; Potenza, J. A.; Felthouse, T. R.; Haddad, M. S.; Hendrickson, D. N.; Furey, W.; Lalancette, R. A. *Inorg. Chem.* **1980**, *19*, 543.

(5) Marcotrigiano, G.; Peyronel, G.; Battistuzzi, R. *J. Chromatogr.* **1972**, *425*.

0020-1669/82/1321-0990$01.25/0

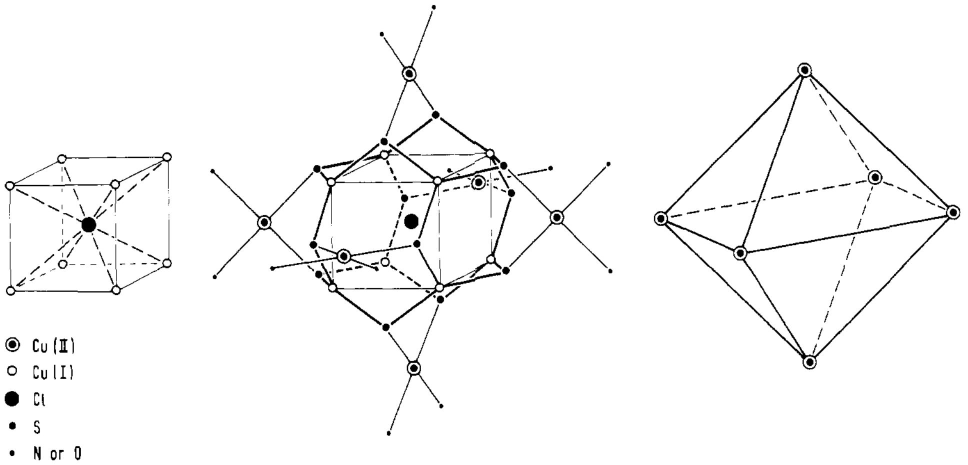

Figure 1. Schematic representation of the $[M^I_8M^{II}_6L_{12}Cl]^{5-}$ ion where M^I = Ag^I or Cu^I, M^{II} = Cu^{II}, Ni^{II}, or Pd^{II} and L = $^-SC(CH_3)_2CH(NH_2)COO^-$. Only the $M^I_8M^{II}_6S_{12}N_{12}Cl$ core of the complex ion is shown. A complete drawing of the complex ion can be found in ref 1a,c.

were of normal reagent grade quality.

Preparation of Crystals of $Na_2[Au^I_2Ni^{II}_2Pen_4]\cdot x$(solvent). To a solution of 300 mg (2 mmol) of D-penicillamine in 80 mL of a 0.2 M aqueous sodium acetate buffer was added a solution of 238 mg (1 mmol) of $NiCl_2\cdot 6H_2O$ in 5 mL of water. The resulting brown solution was subsequently mixed with a solution of 292 mg (0.76 mmol) of $Au(tu)_2Cl$ in 5 mL of water (for explanation of this stoechiometry, see Discussion). The solution turned red within a few minutes and was stirred for 24 h in a stoppered flask. It was then concentrated by repeated treatment with a 1:2 (v/v) alcohol/ether mixture followed by decantation of the colorless upper layer. After about six of those treatments, an almost solid red oil was left which was dissolved in 5 mL of 0.2 M sodium acetate buffer. This red solution was chromatographed over a Sephadex G-25 column (length 45 cm, diameter 2.2 cm, swollen in and eluted with 0.2 M sodium acetate buffer), from which it eluted as a single red band ($R_f \approx 0.5$). The red solution ($\sim$30 mL) was again concentrated as described earlier, and the precipitate was dissolved in 4 mL of a 0.1 M sodium acetate buffer. In a reaction tube a layer of ethanol was carefully introduced above this red solution. After 5 days red needle-shaped crystals had formed on the wall of the test tube which were very soft and deteriorated rapidly when isolated or when suspended in pure ethanol. The compound was characterized by X-ray diffraction (see below).

$[Co(NH_3)_6]_2[Au^I_2Pd^{II}_2Pen_4]_3\cdot 24H_2O$. A mixture of 150 mg (1 mmol) of D-penicillamine, 88 mg (0.5 mmol) of $PdCl_2$, and 75 mg (1 mmol) of KCl was stirred in 25 mL of a 0.2 M sodium acetate buffer for 3 h. The resulting orange solution turned bright yellow when 146 mg (0.38 mmol) of $Au(tu)_2Cl$ in 3 mL of water was added. The solution was stirred for 20 min, and the the compound was precipitated by adding alcohol and ether. A 80-mg sample of the precipitate was dissolved in 3 mL of water, and a solution of 9 mg of $Co(NH_3)_6Cl_3$ in 0.5 mL of water was added. The yellow precipitate was isolated by centrifugation, washed with alcohol and ether, and dried in vacuo. Anal. Calcd for $Co_2Au_6Pd_6C_{60}H_{192}N_{24}S_{12}O_{48}$: Co, 2.7, Au, 27.2; Pd, 14.7; C, 16.60; H, 4.45; N, 7.74; S, 8.86. Found: Co, 2.8; Au, 30.3; Pd, 15.6; C, 17.1; H, 4.61; N, 7.63; S, 8.78.

Titrations. A solution of 94.8 mg (4×10^{-4} mol) of $NiCl_2\cdot 6H_2O$ in 100 mL of a 0.2 M sodium acetate buffer was spectrophotometrically titrated with a 0.16 M solution of D-penicillamine in the same buffer at 450 nm. Equivalence was reached at a Ni:Pen ratio of 1:2 (ϵ/Ni = 115 $dm^3\ mol^{-1}\ cm^{-1}$).

A solution of 23.7 mg (10^{-4} mol) of $NiCl_2.6H_2O$ and 30 mg (2×10^{-4} mol) of D-penicillamine in 100 mL of a 0.2 M sodium acetate buffer was spectrophotometrically titrated at 475 nm with a 1.78×10^{-2} M solution of $Au(tu)_2Cl$ in water. Equivalence was reached at a Au:Ni ratio of 0.76:1.

Physical Measurements. Infrared spectra were measured on a Perkin-Elmer 580 spectrometer and visible spectra on a Beckman DKII-A apparatus. NMR spectra at 100 MHz were recorded on a JEOL PS100 NMR spectrometer. Elemental analyses were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, F.R.G.

X-ray Data Collection and Reduction. An elongated (0.6 mm) triangular prismatic (0.12 × 0.12 × 0.12 mm) crystal of $Na_2[Au_2Ni_2Pen_4]\cdot x$(solvent) was selected for data collection. Together with its surrounding mother liquor, it was carefully transferred from the test tube in which it was grown into a capillary with the use of a Pasteur pipet. In the capillary the crystal was separated from the mother liquor with a glass fiber and the capillary was sealed with solid paraffin. Crystals that were otherwise isolated from the solution deteriorated within seconds, presumably due to loss of cocrystallized solvent molecules. The space group and unit cell dimensions were obtained from diffractometer data. The compound crystallizes in the rhombohedral space group *R*3. The unit cell dimensions appeared to change gradually during the data collection. This is probably caused by loss of solvent molecules from the crystal lattice, although no loss of mother liquor from the capillary was observed. The unit cell dimensions of a = 19.79 (1) Å and α = 91.15 (3)° at the start of the data collection changed to a = 19.68 (1) Å and α = 91.86 (1)° at the end, so that for all further purposes they were taken as a = 19.73 (5) Å and α = 91.5 (4)°. The density of the crystals could not be determined as the crystals rapidly deteriorated in any other liquid but the mother liquor. Profile analysis of a suitable reflection led to the selection of the ω–θ scan mode, an ω scan angle of $(0.80 + \tan \theta)°$, and a horizontal aperture of $(2.20 + 3\tan \theta)$ mm. The crystal-to-counter distance was 173 mm. The vertical aperature was 2 mm. Background correction and calculation of I and $\sigma(I)$ were carried out as described before.[1a] The scan speeds were determined by a required precision of $\sigma(I)/I < 0.02$ with a maximum scan time of 90 s. After every 5400 s of X-ray exposure time, three intensity control reflections were measured. The data were corrected for intensity loss due to decomposition (35%). The orientation of the crystal was checked after every 200 reflections. The intensities of 3508 independent reflections ($\theta < 18°$) were measured on a Nonius CAD4 automatic diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å) and a scintillation counter. A total of 2425 reflections were considered as observed ($I > 2\sigma(I)$). The intensities were corrected for absorption according to the method of de Graaff.[6] The linear absorption coefficient (84.6 cm^{-1}) was calculated from only the composition of the known unit cell contents, viz., $Na_2[Au^I_2Ni^{II}_2Pen_4]$ (see Description of the Structure), with omission of contributions from the unknown number of solvent molecules in the lattice and with an estimated density of 1.8 g cm^{-3}. Errors in this approach were largely compensated by the crystal size optimization procedure inherent in de Graaff's absorption correction method. Lorentz and polarization corrections were applied in the usual way. Scattering factors for neutral atoms were taken from ref 7 and were corrected for anomalous scattering.[7]

Solution and Refinement of the Structure. The structure was solved with the direct-methods program MULTAN.[8] As our verison (MULTAN78) did not accept rhombohedral lattices, the reflection data were reindexed in a hexagonal lattice. The unit cell dimensions became (a = 28.27 (7) and c = 33.27 (8) Å. The structure was refined in the same hexagonal lattice. The MULTAN solution (based on the 500

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(6) Graaff, R. A. G. de *Acta Crystallogr., Sect. A* **1973**, *A29*, 298.

(7) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(8) All programs used in this analysis were locally written except MULTAN (by P. Main, M. M. Woolfson, and G. Germain) and ORTEP (by C. K. Johnson).

Table I. Fractional Positional Parameters[a] for Atoms in $Na_2[Au^I{}_2Ni^{II}{}_2Pen_4]\cdot x$(solvent)[b]

Atom	10^4x	10^4y	10^4z	Atom	10^4x	10^4y	10^4z
Au(1)	1967(1)	564(1)	8678(c)	Au(3)	1021(1)	4899(1)	1484(2)
Au(2)	2166(2)	400(2)	7835(2)	Au(4)	1471(1)	5510(1)	716(2)
Ni(1)	2119(4)	-522(4)	8626(4)	Ni(3)	1396(4)	6241(4)	1387(4)
Ni(2)	2004(4)	1530(5)	8149(4)	Ni(4)	994(4)	4155(4)	579(3)
S(A)	2604(8)	299(8)	8831(8)	S(E)	1386(8)	5692(9)	1856(7)
S(B)	2321(10)	-302(10)	7996(10)	S(F)	2074(9)	6254(8)	1062(9)
S(C)	1371(10)	827(9)	8435(8)	S(G)	613(8)	4084(9)	1153(7)
S(D)	2028(10)	1097(11)	7648(9)	S(H)	824(9)	4772(9)	393(8)

Atom	10^3x	10^3y	10^3z	Atom	10^3x	10^3y	10^3z
N(A)	199(2)	-76(2)	917(2)	N(B)	163(2)	-123(2)	845(2)
C(1A)	197(3)	-34(3)	946(2)	C(1B)	178(5)	-128(5)	799(4)
C(2A)	195(3)	-58(4)	992(3)	C(2B)	154(9)	-159(8)	800(6)
C(3A)	254(3)	17(3)	938(2)	C(3B)	185(4)	-91(4)	769(4)
C(4A)	301(4)	1(4)	947(3)	C(4B)	199(4)	-83(4)	726(4)
C(5A)	258(4)	64(4)	965(3)	C(5B)	131(4)	-90(4)	767(3)
O(1A)	178(4)	-34(3)	1011(3)	O(1B)	127(3)	-215(3)	763(2)
O(2A)	216(2)	-86(2)	995(2)	O(2B)	84(3)	-207(3)	807(2)
N(C)	206(2)	197(2)	857(2)	N(D)	251(3)	225(3)	790(2)
C(1C)	176(3)	164(3)	897(3)	C(1D)	265(4)	216(4)	748(3)
C(2C)	153(6)	197(7)	917(5)	C(2D)	315(6)	253(6)	728(5)
C(3C)	124(3)	114(3)	884(2)	C(3D)	268(4)	155(4)	742(3)
C(4C)	100(4)	79(4)	919(3)	C(4D)	325(3)	171(3)	767(2)
C(5C)	80(3)	131(3)	858(2)	C(5D)	277(4)	152(4)	704(4)
O(1C)	156(3)	193(3)	954(2)	O(1D)	353(3)	286(3)	758(2)
O(2C)	154(3)	238(3)	908(2)	O(2D)	335(3)	271(3)	693(3)
N(E)	81(3)	620(3)	166(2)	N(F)	143(3)	673(3)	99(2)
C(1E)	73(3)	610(3)	209(2)	C(1F)	171(4)	678(4)	61(3)
C(2E)	16(4)	598(4)	228(4)	C(2F)	173(4)	723(5)	46(4)
C(3E)	66(5)	551(5)	211(4)	C(3F)	233(3)	682(3)	77(2)
C(4E)	16(4)	498(4)	206(3)	C(4F)	262(4)	735(4)	104(3)
C(5E)	97(5)	563(5)	256(4)	C(5F)	263(4)	684(4)	45(3)
O(1E)	-14(2)	599(2)	201(2)	O(1F)	177(3)	769(3)	65(2)
O(2E)	23(4)	618(4)	258(3)	O(2F)	200(3)	749(3)	12(2)
N(G)	108(2)	353(2)	75(2)	N(H)	137(2)	423(2)	8(2)
C(1G)	73(4)	336(4)	115(3)	C(1H)	141(4)	472(4)	-13(3)
C(2G)	74(6)	263(6)	111(5)	C(2H)	153(6)	459(6)	-53(5)
C(3G)	80(6)	374(6)	154(4)	C(3H)	95(3)	483(3)	-15(3)
C(4G)	40(3)	337(3)	178(2)	C(4H)	43(4)	436(4)	-40(3)
C(5G)	147(4)	404(4)	163(3)	C(5H)	120(5)	551(5)	-30(4)
O(1G)	140(4)	294(4)	112(3)	O(1H)	139(3)	415(4)	-77(3)
O(2G)	47(4)	236(4)	149(3)	O(2H)	183(3)	494(3)	-84(3)

[a] Estimated standard deviations in parentheses. [b] The atomic labeling is shown in Figure 2. [c] The origin was defined by keeping the z parameter of Au(1) constant.

highest E values) with the highest figure of merit revealed the positions of all independent Au and Ni atoms in the structure. About half of the ligand atoms were found in a series of least-squares refinements and Fourier and difference Fourier maps. Subsequently, the Au, Ni, and S atoms were refined anisotropically and the interatomic distances in the ligand were constrained in a Waser constraints procedure.[9] Inspection of difference Fourier maps followed by constrained least-squares refinements in which all parameter shifts were damped to 0.7 of their calculated values gradually yielded the positions of all ligand atoms, admittedly with great difficulty. Only the metal and ligand atoms of the complex anions could be located. The D-penicillamine ligands appeared to have the correct absolute configuration. In the final refinement cycles all constraints were relaxed and only the damping procedure was applied. The structure was refined until all calculated parameter shifts were less than 50% of their standard deviations. A final difference Fourier map did not reveal any significant features except for some small peaks less than 1.5 Å away from the Au^I atoms which cannot be ascribed to atom positions. The sodium atoms and solvent molecules are apparently disordered as was also observed for counterions and cocrystallized solvent molecules in related structures.[1,3] All refinements were carried out with unit weights and were based on the 2425 observed reflections. A test run using a statistical weighting scheme appeared to be less

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(9) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091.

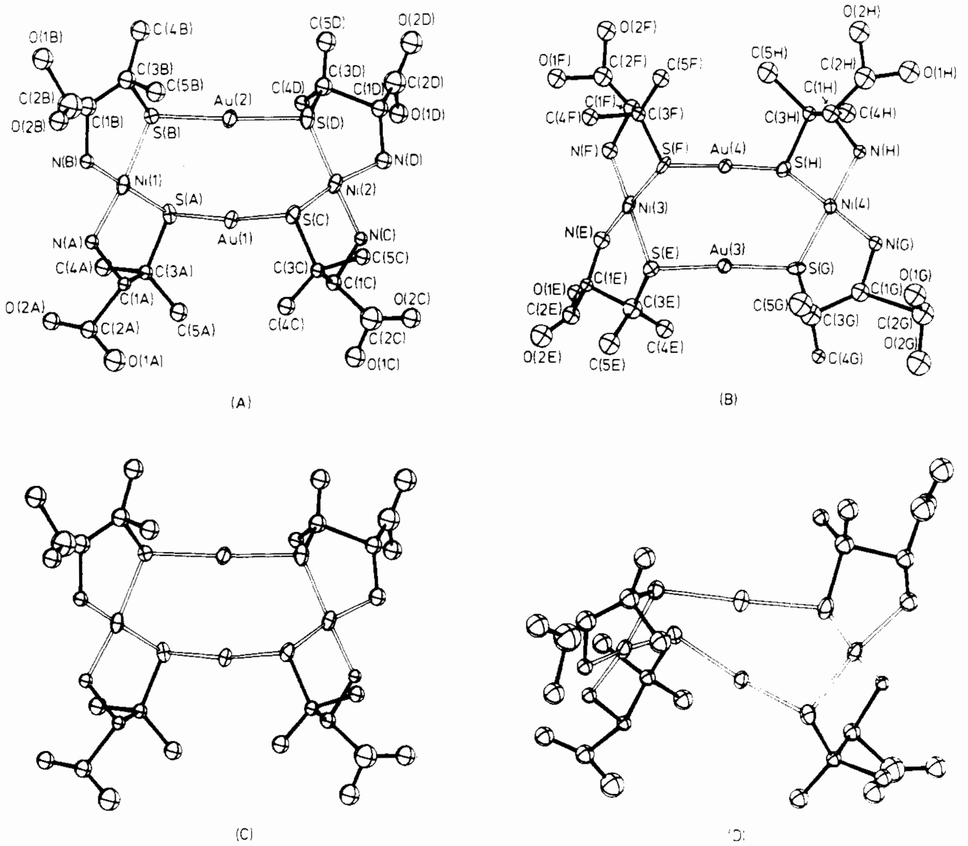

Figure 2. (A and B) ORTEP drawings of the two independent [Au$^{I}_2$Ni$^{II}_2$Pen$_4$]$^{2-}$ ions in Na$_2$[Au$^{I}_2$Ni$^{II}_2$Pen$_4$]·x(solvent) showing the atomic labeling and the vibrational ellipsoids (probability 8%). (C and D) First complex ion in the orientation as in (a) and rotated over 45° about the Ni–Ni vector, showing the bent shape of the complex ion as a result of the tetrahedral interbond angles around the sulfur atoms.

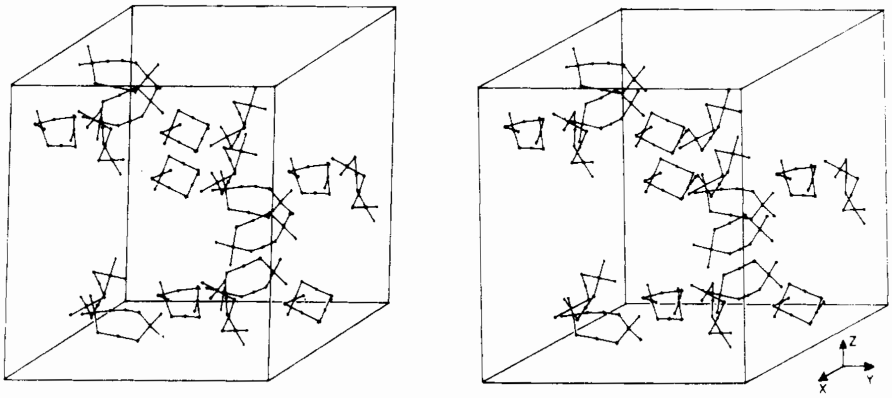

Figure 3. Stereodrawing of the unit cell packing of Na$_2$[Au$^{I}_2$Ni$^{II}_2$Pen$_4$]·x(solvent). For clarity, only the Au$_2$S$_4$Ni$_2$N$_4$ cores of the complex ions are shown.

satisfactory for reasons explained earlier.[1,3] Unit weights appear consistently to be preferable for the refinement of structures which are extensively disordered.

The final residuals are $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.079$ and $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2} = 0.089$.

The atomic parameters are listed in Table I. The thermal parameters, especially those of atoms in the carboxylate groups, are very high. They reflect both the supposedly large thermal motion as well as disorder in the atomic positions in the rather nonrigid highly hydrated crystal lattice caused by the gradual crystal deterioration.

Discussion

Description of the Structure. The structure consists of relatively well-ordered [Au$^{I}_2$Ni$^{II}_2$Pen$_4$]$^{2-}$ ions and disordered Na$^+$ ions and solvent molecules. There are two independent [Au$^{I}_2$Ni$^{II}_2$Pen$_4$]$^{2-}$ ions in the asymmetric unit. The complex ions are shown in Figure 2. Each complex ion contains two Ni^{II} atoms, each planar four-coordinated by two cis-bidentate chelating D-penicillaminato ligands via two N and two S atoms. The two NiPen$_2$ moieties in [Au$^{I}_2$Ni$^{II}_2$Pen$_4$]$^{2-}$ are linked by two bridging Au^{I} atoms. Each Au^{I} atom is linearly coordinated by two penicillamine S atoms. The carboxylate groups of the penicillamine ligands are not involved in metal coordination. They lie at the surface of the complex ion and are involved in hydrogen bonding. The structure is stabilized by hydrogen bonds between the carboxylate oxygen atoms and NH$_2$ groups in adjacent complex ions. A stereodiagram of the unit-cell contents is shown in Figure 3. There are cyclic arrangements of three symmetry-related hydrogen-bonded complex ions around the threefold axes (see lower left corner of Figures 3 and 4).

The stereodiagram of the unit cell (Figure 3) shows the presence of large areas containing unresolved disordered atoms (Na$^+$, water, and perhaps ethanol). The number of counterions and the charge of the complex ion could for this reason not be determined from the X-ray structure. The same problem existed for the related [M$^{I}_8$M$^{II}_6$Pen$_{12}$Cl]$^{5-}$ structures.[1] The

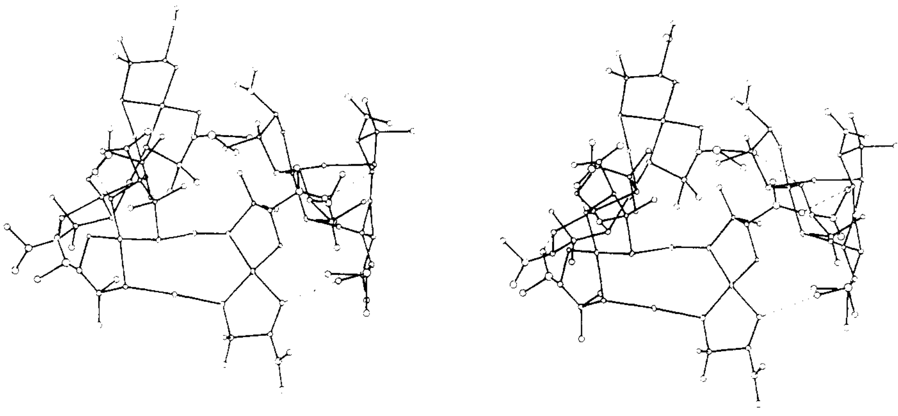

Figure 4. Three complex ions related by a threefold rotation axis as in the lower left corner of Figure 3.

charge of the complex ion is however obvious from the number of $Co(NH_3)_6^{3+}$ counterions in the analogous Pd complex (see Experimental Section). The complete hydrogen-bonding system, most likely involving many disordered solvent molecules as well, will not be described further.

The interatomic distances between ligand and metal atoms are listed in Table II. The individual bond lengths in the penicillamine ligands are not listed because they are only of low precision. Their values lie in the ranges of 1.8 ± 0.2 Å for S–C, 1.5 ± 0.1 Å for C–N, 1.5 ± 0.7 Å for C–C(carboxylate), 1.5 ± 0.4 Å for C–C(other), and 1.4 ± 0.4 Å for C–O.

Comparison with Related Structures. The coordination of the Ni^{II} atoms in the present structure is similar to the coordination of Ni^{II} in $[Ag^I_8Ni^{II}_6Pen_{12}Cl]^{5-}$ (cf. Figure 1 and ref 1c). The difference between the structures of $[Ag^I_8Ni^{II}Pen_{12}Cl]^{5-}$, or in general $[M^I_8M^{II}_6Pen_{12}Cl]^z$ (see Figure 1) and the present structure must entirely be ascribed to the different preferential coordination geometries of Ag^I (or Cu^I) vs. Au^I. Ag^I and Cu^I are known to occur in two-, three-, or four-coordination. The planar S_3 coordination found in the $[M^I_8M^{II}_6L_{12}Cl]^z$ clusters is an acceptable coordination geometry for Cu^I and Ag^I. On the other hand, Au^I has a preference for linear coordination. In bis(ethylenethiourea)gold(I) chloride hydrate,[10] for instance, the Au(I) atom is linearly coordinated by two S atoms at 2.278 (9) and 2.279 (8) Å with an S–Au–S angle of 167.1 (1)°.

Au^I is also linearly coordinated by two S atoms in $Na_3Au(S_2O_3)_2{\cdot}2H_2O$. X-ray structure analysis has shown that the Au–S bond lengths in this compound are 2.280 (3) and 2.272 (3) Å, and that the S–Au–S bond angle is 176.5 (2)°.[11] These values are similar to those in the present compound (see Table I; mean Au–S bond length 2.30 (3) Å; mean S–Au–S angle 175 (3)°). The Au–Au distance in the two independent $[Au^I_2Ni^{II}_2Pen_4]^{2-}$ ions are 2.94 (1) and 2.99 (1) Å. This value is hardly longer than the Au–Au distance of 2.884 Å in metallic gold.[12] suggesting a considerable attractive Au–Au interaction in our compound.

EXAFS studies have indicated linear S–Au–S coordination for (disodium thiomalato-*S*)gold(I) ("Myocrysin") and (thioglucopyranosyl-*S*)gold(I) ("Solganol"), two drugs used for the treatment of rheumatoid arthritis.[13] The Au–S distances derived for these compounds are 2.73 Å, considerably longer than in the present compound.

Table II. Interatomic Distances (Å) and Interbond Angles (Deg) between Metal and Ligand Atoms in $Na_2[Au^I_2Ni^{II}_2Pen_4]{\cdot}x$(solvent)

Atoms	Length	Atoms	Length
Au(1) - Au(2)	2.94(1)	Au(3) - Au(4)	2.99(1)
Au(1) - S(A)	2.33(2)	Au(3) - S(E)	2.30(2)
Au(1) - S(C)	2.30(2)	Au(3) - S(G)	2.28(2)
Au(2) - S(B)	2.29(2)	Au(4) - S(F)	2.25(2)
Au(2) - S(D)	2.28(2)	Au(4) - S(H)	2.24(2)
Ni(1) - S(A)	2.13(2)	Ni(3) - S(E)	2.19(3)
Ni(1) - N(A)	1.90(6)	Ni(3) - N(E)	1.86(7)
Ni(1) - S(B)	2.18(3)	Ni(3) - S(F)	2.18(2)
Ni(1) - N(B)	1.87(6)	Ni(3) - N(F)	1.86(7)
Ni(2) - S(C)	2.12(3)	Ni(4) - S(G)	2.15(2)
Ni(2) - N(C)	1.82(5)	Ni(4) - N(G)	1.98(6)
Ni(2) - S(D)	2.09(3)	Ni(4) - S(H)	2.12(2)
Ni(2) - N(D)	1.99(7)	Ni(4) - N(H)	1.92(6)

Atoms	Angle	Atoms	Angle
S(A) -Au(1)-S(C)	172(1)	S(E) -Au(3)-S(G)	176(1)
S(B) -Au(2)-S(D)	177(1)	S(F) -Au(4)-S(H)	176(1)
S(A) -Ni(1)-N(A)	89(2)	S(E) -Ni(3)-N(E)	85(2)
S(B) -Ni(1)-N(B)	87(2)	S(F) -Ni(3)-N(F)	85(2)
S(A) -Ni(1)-S(B)	94(1)	S(E) -Ni(3)-S(F)	94(1)
N(A) -Ni(1)-N(B)	91(3)	N(E) -Ni(3)-N(F)	96(3)
S(C) -Ni(2)-N(C)	92(2)	S(G) -Ni(4)-N(G)	86(2)
S(D) -Ni(2)-N(D)	93(2)	S(H) -Ni(4)-N(H)	89(2)
S(C) -Ni(2)-S(D)	94(1)	S(G) -Ni(4)-S(H)	92(1)
N(C) -Ni(2)-N(D)	82(3)	N(G) -Ni(4)-N(H)	93(2)
Au(1)-S(A) -Ni(1)	96(1)	Au(3)-S(E) -Ni(3)	98(1)
Au(1)-S(C) -Ni(2)	93(1)	Au(3)-S(G) -Ni(4)	111(1)
Au(2)-S(B) -Ni(1)	109(1)	Au(4)-S(F) -Ni(3)	90(1)
Au(2)-S(D) -Ni(2)	111(1)	Au(4)-S(H) -Ni(4)	102(1)

Formation of the $[Au^I_2Ni^{II}_2Pen_4]^{2-}$ Ion. For the synthesis of this Au^I compound, an Au^I reagent was needed which had to be stable in aqueous solution at pH 6–7 and which would easily exchange its ligands. The Au^I compound $Au(tu)_2Cl$ appeared to be ideally suited for this purpose. The formation of the compound was studied spectrophotometrically (see Experimental Section). The spectrophotometric titration of Ni^{II} with D-penicillamine indicates the formation of a compound in solution of composition $[NiPen_2]_n$ with an absorption maximum at 450 nm. Addition of $Au(tu)_2Cl$ made the maximum at 450 nm disappear and produced a new maximum at 475 nm (good isosbestic points were observed). The band at 475 nm reached its maximum intensity when 0.76 mol Au/mol of Ni had been added. This low value might be

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(10) Jones, P. G.; Guy, J. J.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1976**, *B32*, 3321.

(11) Ruben, H.; Zalkin, A.; Faltens, M. O.; Templeton, D. H. *Inorg. Chem.* **1974**, *13*, 1836.

(12) Batchelder, D. N.; Simmons, R. O. *J. Appl. Phys.* **1965**, *36*, 2864.

(13) Mazid, M. A.; Razi, M. T.; Sadler, P. J.; Greaves, G. N.; Gurman, S. J.; Koch, M. H. J.; Phillips, J. C. *J. Chem. Soc., Chem. Commun.* **1980**, *1261*.

explained by the reaction of released thiourea with Ni^{II}. The red shift of the band from 450 to 475 nm when Au^{I} is bonded to $NiPen_2$ is similar to the red shift observed when Ag^{I} is added to a similar reaction mixture (maximum at 460 nm).[1b,c] These bands must be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition of square-planar coordinated diamagnetic Ni^{II}.

Conclusions. The penicillamine ligand forms stable complexes with d^8, d^9, and d^{10} transition-metal ions, especially when the penicillamine ligand can chelate the d^8 or d^9 ion and the thiolate S atoms can form bridges to one or more d^{10} ions. In $Na_2[Au_2Ni_2Pen_4]\cdot x$(solvent), the Au^{I} atoms act as single atom bridges between two *cis*-$NiPen_2$ moieties. The Au–Au distance is close to the Au–Au distance present in metallic gold.

Acknowledgment. Professor J. Reedijk is gratefully acknowledged for his continuous interest in this work.

Registry No. $Na_2[Au^{I}_2Ni^{II}_2Pen_4]$, 80105-75-5; $[Co(NH_3)_6]_2[Au^{I}_2Pd^{II}_2Pen_4]_3$, 80126-86-9; $Au(tu)_2Cl$, 40764-57-6.

Supplementary Material Available: Tables of the observed and calculated structure factors and positional and thermal parameters (9 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Properties of the Tetranuclear Complexes $[(DENC)CuX]_4$ (DENC = *N*,*N*-Diethylnicotinamide; X = Cl, Br, I) and the Kinetics of Oxidation of the Chloride and Bromide by Dioxygen in Aprotic Solvents[1a]

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Received July 14, 1981

Copper(I) halides dissolve in dioxygen-free aprotic solvents containing *N*,*N*-diethylnicotinamide, DENC, to form the tetranuclear complexes $[(DENC)CuX]_4$. The air-stable iodo complex crystallizes in the space group $P\bar{1}$ with a = 12.0885 (19) Å, b = 15.3834 (24) Å, c = 15.9420 (26) Å, α = 116.84 (1)°, β = 94.10 (1)°, γ = 91.69 (1)°, V = 2632.1 (7) Å^3, and Z = 2. Diffraction data to 2θ = 40° (Mo Kα radiation) were collected on a Syntex $P2_1$ automated four-circle diffractometer, and the structure was refined to R_F = 5.99% and R_{wF} = 4.25% for all 4943 reflections (R_F = 4.15% and R_{wF} = 4.00% for those 4044 reflections with $|F_o| > 3\sigma(|F_o|)$). All 60 nonhydrogen atoms were located, and all hydrogen atoms were included in idealized positions. The Cu_4I_4 core has a distorted "cubane-like" arrangement with Cu–I distances ranging from 2.6299 (17) to 2.7493 (17) Å. The DENC ligands are bound to the copper(I) atoms via Cu–N(ring) bonds of length 2.028 (8)–2.042 (8) Å. Cryoscopic and spectral data are consistent with the same basic core structure for the corresponding chloro and bromo complexes $[(DENC)CuX]_4$. The stoichiometry and kinetics of reactions of excesses of the latter complexes with dioxygen in benzene, methylene chloride, and nitrobenzene have been determined, and analytical, cryoscopic, and spectral properties of the tetranuclear $[(DENC)CuX]_4O_2$ products are reported. The DENC appears to be coordinated only through its pyridine nitrogen atom. The reactions are simple, second-order processes with no detectable intermediates. Their rate constants and activation parameters show little solvent dependence and are inconsistent with electron transfer from copper(I) to dioxygen as the rate-determining step, which is proposed to involve a dioxygen insertion mechanism whose rate decreases in the order Cl > Br >> I. Decreased rates at high added [DENC] or low $[[(DENC)CuX]_4]$ indicate that 1:1 redox complementarity of the reactants is important in determining high rates and a simple bimolecular mechanism. Comparison of the cryoscopic, magnetic, spectral, and chemical properties of $[(DENC)CuX]_4O_2$ with those of other known μ-oxo copper(II) species suggests that their structures are similar to those of $[(DENC)CuX]_4$.

Introduction

The thermal oxidation of slurries of copper(I) halides by dioxygen in pyridine gives polymeric $((py)_mCuO)_n$ species that initiate the oxidative coupling of acetylenes, aromatic amines, and phenols by dioxygen.[2] Such initiator species are stable only in the presence of high concentrations of pyridine, and their spontaneous polymerization gives rise to the development of induction periods in phenolic oxidative coupling reactions and to a decreasing reactivity toward protic substances.[2–4] Efforts have been made to prevent this deactivating polymerization process and isolate solid products by substituting other pyridine derivatives for pyridine in $((py)_mCuO)_n$, but in all cases examined either (1) no detectable substitution took place (presumably because of the necessarily high concentration of pyridine) or (2) oxidation of the ring substituents in the presence of excess dioxygen was observed.[4]

With the objective of isolating intact solid oxo–copper(II) products for structural determinations, we next turned our attention to slurry oxidations in *N*,*N*-dimethylacetamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidinone (nmp).[4,5] Cryoscopic measurements on solutions of the primary product showed them to be $L_3Cu_4X_4O_2$ species, which are relatively poor oxidative coupling initiators and readily disproportionate in the presence of water. The crystal structure of one such disproportionation product, $(nmp)_3Cu_4Cl_6O(OH_2)\cdots nmp$,[6] showed it to be a μ_4-oxo-tetracopper(II) complex with a water molecule attached to one of the four copper(II) centers. To date, we have been unsuccessful in crystallizing these primary $L_3Cu_4Cl_4O_2$ initiator products, which all apparently have the same core structure and contain a terminal oxo group, consistent with their affinity for protic substances and their tendency toward polymerization.[4–6]

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(1) (a) This paper may be considered as part 13 in the series "Molecules with an M_4X_4 Core" by M. R. Churchill et al. For part 12 in this series see: Churchill, M. R.; Missert, J. R. *Inorg. Chem.* **1981**, *20*, 619. (b) State University of New York at Buffalo. (c) Northeastern University.

(2) Bodek, I.; Davies, G. *Inorg. Chem.* **1978**, *17*, 1814.

(3) Bodek, I.; Davies, G. *Inorg. Chim. Acta* **1978**, *27*, 213.

(4) Davies, G.; El-Shazly, M. F.; Kozlowski, D. R.; Kramer, C. E.; Rupich, M. W.; Slaven, R. W. *Adv. Chem. Ser.* **1979**, *No. 173*, 178. Davies, G.; Rupich, M. W. *Strem. Chem.* **1981**, *9*, 15.

(5) Rupich, M. W. Doctoral Dissertation, Northeastern University, 1980.

(6) Davies, G.; El-Shazly, M. F.; Rupich, M. W.; Churchill, M. R.; Rotella, F. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1045; Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1979**, *18*, 853.