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## X-ray Crystal and Molecular Structure of Tetra-*n*-butylammonium Bis(toluene-3,4-dithiolato)aurate(III). Reversible Association with SO<sub>2</sub> in Solution

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The green title complex has been prepared and crystallized. X-ray analysis shows that it contains a square-planar AuS<sub>4</sub> unit. Both toluene groups are tilted with respect to this, on the same side (10 and 17°). A weak, reversible association of the complex with SO<sub>2</sub> in solution was detected by <sup>1</sup>H and <sup>13</sup>C NMR and Raman spectroscopy; the CH<sub>3</sub> and C(6)H <sup>1</sup>H NMR resonances exhibit marked exchange broadening. It is suggested that SO<sub>2</sub> binding occurs either at coordinated S or to the toluene ring, rather than directly to Au.

### Introduction

Our interest in gold thiolate complexes arises from the clinical use of gold(I) thiolates such as "Myocrisin" (thiomalate) and "Solganol" (thioglucose) as antiarthritic drugs.<sup>1,2</sup> Although thiols would be expected to reduce Au(III) to Au(I), we show here that a stable, green Au(III) complex with toluene-3,4-dithiol is readily formed. The ligand can accommodate the square-planar geometry demanded by Au(III), forming five-membered chelate rings. Other examples previously reported include dithiocarbamate<sup>3</sup> and ethylenedithiolato<sup>4,5</sup> complexes of Au(III). We also report a curious association of the complex with SO<sub>2</sub>. It appears to bind to coordinated sulfur or the toluene ring rather than directly to Au. This seems to be the first report of such an interaction for a gold complex, although those of the former type are known for Cu(I) and Ag(I) complexes.<sup>6</sup>

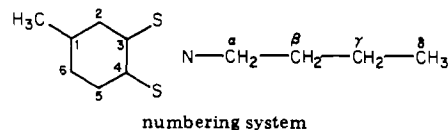
### Experimental Section

**Materials and Methods.** NaAuCl<sub>4</sub>·2H<sub>2</sub>O was obtained on loan from Johnson Matthey Ltd. All other chemicals were reagent grade. <sup>1</sup>H NMR spectra were recorded on Varian XL 200 or JEOL MH 100 spectrometers and <sup>13</sup>C spectra on a JEOL FX 60 (15 MHz). Infrared spectra were obtained on a Perkin-Elmer 597 instrument using KBr disks and electronic absorption spectra on a Perkin-Elmer 402 machine with 1-cm cells. Laser Raman spectra of spinning KBr disks or solutions in chloroform or acetone were recorded by Dr. P. Beardwood of the University of London Intercollegiate Research Service at Imperial College. The sample was irradiated with the 530.9-nm laser line. Molar conductivities were measured at 25 °C with use of a Griffin conductivity bridge.

**Preparation of [n-Bu<sub>4</sub>N][Au(S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>].** To a solution of 0.625 g (4 mmol) of 3,4-dithioltoluene in 20 mL of MeOH was added a solution of 0.432 g (8 mmol) of NaOMe in 10 mL of MeOH. To this was added 0.796 g of NaAuCl<sub>4</sub>·2H<sub>2</sub>O (2 mmol) dissolved in 20 mL of MeOH. A green solution with some dark brown precipitate was obtained. After filtration, the green solution was poured into a continuously stirred solution of 0.649 g (2 mmol) of *n*-Bu<sub>4</sub>NBr in 10 mL of MeOH. The resultant microcrystalline solid was filtered off and dried. The complex melted at 144–146 °C; yield 0.598 g (40%). Anal. Calcd for C<sub>30</sub>H<sub>48</sub>NS<sub>4</sub>Au: C, 48.19; H, 6.24; N, 1.87; S, 17.13. Found: C, 48.20; H, 6.49; N, 2.05; S, 16.86.

Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in MeOH. Recrystallization can also be carried out, with difficulty, from acetone. The complex is soluble in acetone (and stable for >6 months), chloroform, and methanol and in acetone solutions containing up to 30% v/v H<sub>2</sub>O (in which it is very stable

Table I. <sup>1</sup>H NMR Data for [Bu<sub>4</sub>N][Au(S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Me)<sub>2</sub>]



nucleus	ligand	chemical shift, <sup>a</sup> δ			
		complex		complex + SO <sub>2</sub>	
		295 K	188 K	295 K	188 K
C(1)–CH <sub>3</sub>	2.232	2.181 <sup>d</sup>	2.203	2.247 <sup>i</sup>	2.281
C(2)H	7.257 <sup>b</sup>	6.902 <sup>e</sup>	6.944	6.955 <sup>e</sup>	6.996
C(5)H	7.303 <sup>c</sup>	6.956 <sup>f</sup>	7.016	7.008 <sup>h</sup>	7.065
C(6)H	6.913	6.606	6.711	6.739 <sup>i</sup>	6.858
C(α)H <sub>2</sub>		3.362	3.356 <sup>i</sup>	3.307	3.285 <sup>i</sup>
C(β)H <sub>2</sub>		1.741	1.706 <sup>i</sup>	1.733	1.680 <sup>i</sup>
C(γ)H <sub>2</sub>		1.376	1.325 <sup>i</sup>	1.397	1.341 <sup>i</sup>
C(δ)H <sub>3</sub>		0.930	0.909 <sup>i</sup>	0.957	0.957 <sup>i</sup>

<sup>a</sup> Relative to Me<sub>4</sub>Si, (solvent acetone-*d*<sub>6</sub>). <sup>b</sup> <sup>4</sup>J(2,6) = 1.8 Hz. <sup>c</sup> <sup>3</sup>J(5,6) = 7.9 Hz. <sup>d</sup> <sup>4</sup>J(CH<sub>3</sub>,6) = ca. 0.4 Hz; <sup>4</sup>J(CH<sub>3</sub>,2) = ca. 0.4 Hz. <sup>e</sup> <sup>4</sup>J(2,6) = 1.8 Hz. <sup>f</sup> <sup>3</sup>J(5,6) = 8.2 Hz. <sup>g</sup> <sup>4</sup>J(2,6) = 1.8 Hz. <sup>h</sup> <sup>3</sup>J(5,6) = 8.2 Hz. <sup>i</sup> Broadened peaks.

Table II. <sup>13</sup>C NMR Data<sup>a</sup> for [Bu<sub>4</sub>N][Au(S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Me)<sub>2</sub>]

	δ		
	ligand	complex	complex + SO <sub>2</sub>
C(1)–CH <sub>3</sub>	20.72	20.16	20.27 <sup>b</sup>
C(1)	127.54	132.61	134.24
C(3)	132.48	140.15	138.65
C(4)	137.42	143.46	142.29
C(2)	131.70	128.13	128.84
C(5)	131.89	128.90	129.49
C(6)	128.06	124.42	125.85
C(α)		59.39	59.25
C(β)		24.43	24.03
C(γ)		20.27	20.27 <sup>b</sup>
C(δ)		13.71	13.77

<sup>a</sup> Solvent acetone-*d*<sub>6</sub>; temperature 301 K; shifts relative to Me<sub>4</sub>Si; for numbering system see Table I. <sup>b</sup> Resonance appears to be broadened and split, complicated by overlap with C(γ).

as judged by the electronic absorption spectrum).

The conductivity of a 1 mM solution in acetone at 25 °C was 104 cm<sup>2</sup> mol<sup>-1</sup> Ω<sup>-1</sup>.

The electronic absorption spectrum of a solution of the complex in MeOH gave broad peaks at 237, 293, 428, and 646 nm with extinction coefficients of 4.65 × 10<sup>4</sup>, 1.94 × 10<sup>4</sup>, 168, and 74 M<sup>-1</sup> cm<sup>-1</sup>, respectively. An acetone solution has a very similar spectrum in the visible region. The ligand alone, 3,4-dithioltoluene, gave only the short-wavelength bands at 224 and 298 nm with extinction coefficients of 2.42 × 10<sup>4</sup> and 1.19 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively.

**Other Cations.** The analogous green complexes containing [Et<sub>4</sub>N]<sup>+</sup> and [Me<sub>4</sub>N]<sup>+</sup> as counterions were similarly prepared and had

- (1) Sadler, P. J. *Structure Bonding (Berlin)* 1976, 171; *Gold Bull.* 1976, 5, 110.
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- (3) Noordik, J. H.; Beurskens, P. T. J. *Cryst. Mol. Struct.* 1971, 1, 339.
- (4) Enemark, J. H.; Ibers, J. A. *Inorg. Chem.* 1968, 7, 2636.
- (5) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* 1963, 2, 1227.
- (6) Eller, P. G.; Kubas, G. J. *J. Am. Chem. Soc.* 1977, 99, 4346.

Table III. Crystal Data, Details of Data Collection, and Structure Analysis

formula	[C <sub>14</sub> H <sub>12</sub> AuS <sub>4</sub> ][C <sub>16</sub> H <sub>36</sub> N]
mol wt	747.0
systematic absence	0 <i>k</i> 0 ( <i>k</i> odd), <i>h</i> 0 <i>l</i> ( <i>h</i> odd)
crystal system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>a</i> (No. 14)
<i>a</i> , Å	18.823 (4)
<i>b</i> , Å	19.126 (5)
<i>c</i> , Å	9.336 (5)
β, deg	96.72 (3)
<i>V</i> , Å <sup>3</sup>	3337.9
<i>Z</i>	4
<i>D</i> <sub>m</sub> , g cm <sup>-3</sup>	1.49
<i>D</i> <sub>c</sub> , g cm <sup>-3</sup>	1.48
<i>F</i> (000)	1512
λ(Cu Kα), Å <sup>o</sup>	1.5418
μ(Cu Kα), cm <sup>-1</sup>	107.6
crystal size, mm	0.37 × 0.30 × 0.08
crystal faces	{001}, {010}, {100}
scan mode	ω/2θ
ω-scan parameters: <i>A</i> , <i>B</i> , deg	0.80, 0.15
in scan width = <i>A</i> + <i>B</i> tan θ	
horizontal aperture parameters:	4.0, 0.0
<i>A</i> , <i>B</i> , mm in apt = <i>A</i> + <i>B</i> tan θ	
reflectns measd	±( <i>hkl</i> )
θ <sub>min</sub> , θ <sub>max</sub> , deg	3, 65
no. of reflectns recorded	5821
no. of unique reflectns	5131
no. of reflectns used in refinement with <i>I</i> <sub>0</sub> > 2.5σ( <i>I</i> <sub>0</sub> )	3104
no. of parameters refined	329
weighting scheme coefficient <i>g</i> , in <i>w</i> = 1/[σ( <i>F</i> <sub>0</sub> ) + <i>g</i> ( <i>F</i> <sub>0</sub> ) <sup>2</sup> ]	0.0015
final <i>R</i> = Σ Δ <i>F</i>  /Σ  <i>F</i> <sub>0</sub>	0.066
<i>R</i> ' = [Σ <i>w</i> (Δ <i>F</i> ) <sup>2</sup> /Σ <i>wF</i> <sub>0</sub> ] <sup>1/2</sup>	0.088
where Δ <i>F</i> = <i>F</i> <sub>0</sub> -   <i>F</i> <sub>0</sub>	
diffractometer	Enraf-Nonius CAD-4

satisfactory microanalyses. The [Et<sub>4</sub>N]<sup>+</sup> derivative was not suitable for crystallography, but good crystals of the [Me<sub>4</sub>N]<sup>+</sup> complex were formed by slow evaporation from MeOH.

**NMR Spectroscopy.** <sup>1</sup>H NMR resonances were unambiguously assignable on the basis of chemical shifts, coupling patterns, and selective decoupling (Table I).

In order to assign <sup>13</sup>C NMR peaks, we have assumed that the three resonances from the nonprotonated carbons C(1), C(3), and C(4) will have lower intensities than C(2), C(5), and C(6) since they are expected to have longer relaxation times and to lack full NOE's. For the ligand alone, this assignment was confirmed by off-resonance decoupling. It is probably also reasonable to assume that the resonances for C(1) and C(6) are shifted to low frequency, that C(2) and C(5) have similar chemical shifts, and that C(3) and C(4) have the largest coordination shifts. Thus, although some peak positions are bracketed in Table II, the most likely assignments are as shown.

**Infrared and Raman Spectroscopy.** In the range 200–1300 cm<sup>-1</sup>, the Raman spectrum gave the following bands for a CHCl<sub>3</sub> solution of the [*n*-Bu<sub>4</sub>N]<sup>+</sup> complex: 304 (m), 336 (m, sh), 447 (m), 525 (w), 608 (w), 638 (vw), 653 (s), 687 (sh), 868 (m, b), 880 (w), 1040 (m), 1116 (s), 1278 (s) cm<sup>-1</sup>.

Between 300 and 3000 cm<sup>-1</sup>, the infrared spectrum (KBr disk) has the following bands: 360 (m), 390 (w), 435 (w), 542 (w), 633 (w), 684 (m), 700 (vw), 735 (w), 798 (m), 805 (m), 860 (w), 880 (w), 1020 (vw), 1035 (w), 1112 (s), 1130 (vw), 1142 (w), 1205 (vw), 1248 (m), 1275 (m), 1365 (sh), 1375 (m), 1446 (sh), 1458 (vs), 1480 (s), 1535 (w), 1550 (vw), 1580 (w), 2870 (m), 2938 (w), and 2960 (s) cm<sup>-1</sup>.

The bands at 304, 336, 360, and 390 cm<sup>-1</sup> are likely to arise from Au–S stretching modes. They are not present in spectra of the cation or ligand alone. There are few reports of ν(Au–S). Those associated with AuX(SMe<sub>2</sub>)<sub>2</sub> and [AuMe<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>]<sup>+</sup> appear to lie in the ranges 270–293 and 330–345 cm<sup>-1</sup> and for Au<sub>3</sub>(S<sub>2</sub>CNBu<sub>2</sub>)<sub>2</sub>, between 328 and 375 cm<sup>-1</sup>.<sup>7</sup> Gold(I) thiomalate has a band at 340 cm<sup>-1</sup>.<sup>8</sup>

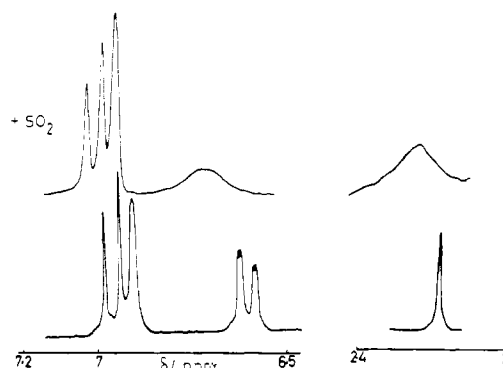


Figure 1. 200-MHz <sup>1</sup>H NMR spectra at 295 K of 25 mM solution of [*n*-Bu<sub>4</sub>N][Au(S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Me)<sub>2</sub>] in acetone-*d*<sub>6</sub> showing the CH<sub>3</sub> signal (δ 2.18), C(6)H (δ 6.61), C(2)H (δ 6.90), and C(5)H (δ 6.96). The top spectrum was obtained from the same solution after saturation with SO<sub>2</sub>. At 188 K the peaks for the anion shift further and sharpen up again.

**X-ray Crystallography.** The crystal system and initial parameters were determined from oscillation and Weissenberg photographs. Accurate cell constants and orientation matrices used for data collection were determined by least-squares refinement of the setting angles of 25 reflections automatically centered on the diffractometer. Details of the crystal, data collection, and structure refinement are given in Table III.

For each measurement the ω scan width (deg) was determined by the equation *s* = *A* + *B* tan θ; horizontal aperture settings were determined with use of a similar relationship. Each reflection was given a fast prescan (20° min<sup>-1</sup>), and only those considered significant were rescanned slowly such that the final net intensities satisfied the preset condition, *I*<sub>0</sub> > 33σ(*I*<sub>0</sub>), subject to a maximum measuring time of 60 s unless the desired accuracy had been achieved during the prescan. The crystal remained stable during data collection, as judged by two standard reflections monitored about every 1 h. The first and last 16 steps of each 96-step scan constituted the left (*B*<sub>L</sub>) and right (*B*<sub>R</sub>) backgrounds and the remaining 64 the net count *C*. The final structure factor amplitudes, *F*<sub>0</sub>, and standard deviations, σ(*F*<sub>0</sub>), were calculated from eq 1 and 2, where *K* is a scale factor incorporating

$$F_0 = [[C - 2(B_L + B_R)]K]^{1/2} \quad (1)$$

$$\sigma(F_0) = [[C + 4(B_L + B_R)]^{1/2}K]/2F_0 \quad (2)$$

the variable measuring times and the Lorentz and polarization factors. The data were also corrected for absorption effects.

The position of the Au atom was determined from a three-dimensional Patterson map. The remaining nonhydrogen atoms were located from successive difference electron density syntheses interspersed with cycles of full-matrix least-squares refinement. Isotropic refinement of all nonhydrogen atoms gave an *R* value of 0.21. The data were corrected for absorption effects at this stage, and the refinement continued to an *R* value of 0.12. Further refinement with anisotropic temperature factors reduced *R* to 0.069. All H atoms in the cation and rings of the anion were inserted in geometric positions and their contributions included in the structure factor calculations. One common *U*<sub>iso</sub> for the H atoms was refined and had a final value of 0.142 (9) Å<sup>2</sup>. The methyl hydrogens on C(7) and C(14) were ignored. The final *R* value was 0.066, with a corresponding *R*' of 0.088. The weighting scheme applied was *w* = 1/[σ(*F*<sub>0</sub>) + 0.0015*F*<sub>0</sub><sup>2</sup>]. This gave nearly flat analyses of variance with sin θ and (*F*<sub>0</sub>/*F*<sub>max</sub>)<sup>1/2</sup>. A final difference showed two small peaks (2 e Å<sup>-3</sup>) in the vicinity of the Au atom.

Fractional atom coordinates and anisotropic temperature factors are given in Tables IV and V. Calculations were performed on the Queen Mary College ICL 2980 and the University of London CDC 7600 computers with use of the programs SHELX-76,<sup>9</sup> XANADU,<sup>10</sup> and PLUTO.<sup>11</sup> The scattering factors for neutral atoms were taken from

(7) Puddephat, R. J. "The Chemistry of Gold"; Elsevier: Amsterdam, 1978.

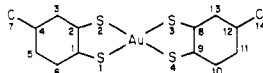
(8) Isab, A. A. Thesis, University of London, 1978.

(9) SHELX-76, crystallographic calculation program: G. M. Sheldrick, University of Cambridge.

(10) XANADU program for least-squares planes and dihedral angles of calculations: P. Roberto and G. M. Sheldrick, University of Cambridge.

**Table IV.** Final Positional Parameters (Au,  $\times 10^5$ ; Others,  $\times 10^4$ ) for the Nonhydrogen Atoms with Esd's in Parentheses<sup>a</sup>

atom	x	y	z
Au	32507 (3)	60221 (3)	66590 (7)
S(1)	4203 (2)	5892 (2)	8431 (5)
S(2)	3371 (2)	7217 (2)	6826 (5)
S(3)	2291 (2)	6163 (2)	4889 (5)
S(4)	3084 (2)	4822 (2)	6498 (4)
C(1)	4394 (8)	6757 (8)	8949 (19)
C(2)	4042 (7)	7315 (8)	8298 (16)
C(3)	4173 (8)	7996 (9)	8785 (21)
C(4)	4682 (10)	8135 (11)	9998 (27)
C(5)	5054 (11)	7569 (15)	10649 (24)
C(6)	4916 (9)	6880 (11)	10126 (25)
C(7)	4831 (14)	8830 (13)	10840 (28)
C(8)	1895 (8)	5334 (7)	4805 (15)
C(9)	2224 (8)	4751 (7)	5540 (16)
C(10)	1866 (11)	4129 (8)	5395 (19)
C(11)	1191 (12)	4063 (9)	4630 (23)
C(12)	837 (9)	4623 (9)	3936 (20)
C(13)	1196 (8)	5267 (8)	4080 (16)
C(14)	143 (10)	4573 (10)	3182 (21)
N	3133 (5)	4173 (6)	1453 (12)
C(15)	2440 (7)	4619 (7)	1407 (17)
C(16)	2350 (8)	5137 (8)	174 (17)
C(17)	1706 (8)	5573 (9)	232 (20)
C(18)	1599 (9)	6107 (9)	-1020 (20)
C(19)	3124 (7)	3742 (7)	81 (16)
C(20)	2475 (8)	3255 (8)	-238 (17)
C(21)	2577 (9)	2745 (8)	-1456 (17)
C(22)	1943 (10)	2306 (12)	-1892 (24)
C(23)	3133 (7)	3699 (7)	2760 (15)
C(24)	3766 (9)	3197 (7)	3002 (18)
C(25)	3729 (9)	2800 (8)	4315 (21)
C(26)	4400 (10)	2229 (9)	4432 (24)
C(27)	3802 (8)	4645 (6)	1542 (16)
C(28)	3892 (8)	5125 (8)	2815 (17)
C(29)	4524 (11)	5535 (9)	2763 (20)
C(30)	4684 (11)	6063 (9)	3965 (25)

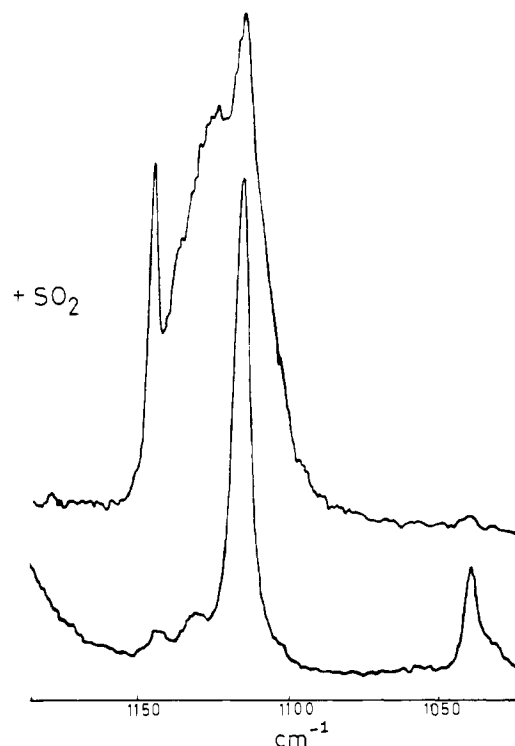
<sup>a</sup> Numbering system for X-ray crystallography

ref 12 (H), 13 (S, N, C), and 14 (Au), with those for the heavier elements modified for anomalous dispersion by using  $\Delta f'$  and  $\Delta f''$  values taken from ref 15.

**Reaction of  $[n\text{-Bu}_4\text{N}][\text{Au}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2]$  with Sulfur Dioxide.** When a solution of the complex in acetone- $d_6$  was saturated with  $\text{SO}_2$ , the color changed from green to brownish yellow. The tube was sealed and  $^1\text{H}$  NMR spectrum recorded. A pronounced broadening of the  $\text{CH}_3$  and H(6) resonances was observed (see Figure 1). At 100 MHz their line widths ( $\Delta\nu_{1/2}$ ) were ca. 14 Hz and at 200 MHz about double this, ca. 25 Hz. Homonuclear decoupling experiments showed that there were small couplings between H(6) and  $\text{CH}_3$ , H(2) and  $\text{CH}_3$ , and between H(6) and H(2) which all are four bonds apart. The effects of  $\text{SO}_2$  on the spectrum were fully reversible when the solvent was removed in vacuo and the (green) complex redissolved in acetone.

Attempts were made to isolate the  $\text{SO}_2$  complex by crystallization from liquid  $\text{SO}_2$  and precipitation from an MeOH solution with  $n\text{-Bu}_4\text{NBr}$  while continuously passing  $\text{SO}_2$ ; all failed. Each time the original green complex was obtained.

$^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts and coupling constants are listed in Tables I and II. There was no evidence for cis-trans isomerism from a study of the temperature dependence of the  $^1\text{H}$  NMR spectrum.



**Figure 2.** Part of the Raman spectrum of a solution of  $[n\text{-Bu}_4\text{N}][\text{Au}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2]$  in  $\text{CHCl}_3$ . The top spectrum was obtained after saturation of the solution with  $\text{SO}_2$ . The new sharp peak at  $1146\text{ cm}^{-1}$  is from  $\nu_4(\text{SO}_2)$  of free  $\text{SO}_2$ , and the new broad peak is probably from bound  $\text{SO}_2$ .

The two methyl groups are either exclusively cis as in the crystal or isomerization (presumably via a tetrahedral intermediate) is very rapid on the NMR time scale, even at 188 K. The broadening of the cation peaks at low temperature in the order  $\alpha\text{-CH}_2 > \beta\text{-CH}_2 > \gamma\text{-CH}_2 > \delta\text{-CH}_2$  suggests that ion pairing occurs. Only small chemical shift changes are induced by  $\text{SO}_2$  binding. At 295 K the largest  $^1\text{H}$  NMR shift is for H(6) ( $\delta$  0.13). Those for  $^{13}\text{C}$  resonances are larger:  $\text{CH}_3$ , ca.  $\delta$  1.0 (overlap with cation peak); C(1), +1.63; C(2), +0.71; C(3), -1.50; C(4), -1.14; C(5), +0.59; C(6), +1.43 on the basis of the assignments given in the table. It is evident that the resonances from the carbon atoms attached directly to the S (thiolate) shift in the opposite direction to those from the rest of the ring carbon atoms. At 188 K the  $^1\text{H}$  NMR peaks for  $\text{CH}_3$  and C(6)H become sharp again, indicating that the broadening at 295 K is probably caused by exchange between complex and  $\text{SO}_2$ -bound complex. The shifts induced by  $\text{SO}_2$  binding at 188 K are as follows:  $\text{CH}_3$ , 0.078; C(2)H, 0.052; C(5)H, 0.049; C(6)H, 0.147 ppm. Since only one set of resonances are seen at this temperature, it appears that the  $\text{SO}_2$  complex is fully formed and that  $\text{SO}_2$  binding maintains the equivalence of the two dithiolate ligands.

The effect of  $\text{SO}_2$  on the Raman spectrum of the complex was examined in  $\text{CHCl}_3$  solution. The  $\nu_4(\text{S-O})$  region of the spectrum is shown in Figure 2. Peaks attributable to bound  $\text{SO}_2$  at  $1126\text{ cm}^{-1}$  (broad) and free  $\text{SO}_2$  at  $1146\text{ cm}^{-1}$  are seen. There appeared to be some intensity changes in other regions of the spectrum, but these were complicated by the presence of intense solvent absorptions.

$\text{SO}_2$  had little effect on the two bands in the visible region of the electronic absorption spectrum.  $\text{SO}_2$  itself has strong absorptions in the ultraviolet region.

## Results and Discussion

**Description of the Structure.** A projection of the crystal structure down the  $b$  axis is shown in Figure 3.  $[\text{Au}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2]^-$  and  $[n\text{-Bu}_4\text{N}]^+$  ions are held together by van der Waals forces. The shortest interionic contact between two nonhydrogen atoms is  $3.564\text{ \AA}$ , which indicates light packing. The bond distances and interbond angles are given in Table VI.

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Table V. Anisotropic Temperature Factors ( $\times 10^3$ ) of the Nonhydrogen Atoms with Esd's in Parentheses<sup>a</sup>

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Au	88.7	74.1 (4)	94.9 (5)	-2.6 (3)	29.9 (3)	4.0 (3)
S(1)	96 (2)	105 (3)	106 (3)	5 (2)	16 (2)	6 (2)
S(2)	99 (3)	79 (2)	137 (4)	-8 (2)	16 (3)	-5 (2)
S(3)	110 (3)	70 (2)	118 (3)	10 (2)	8 (2)	3 (2)
S(4)	121 (3)	76 (2)	99 (3)	2 (2)	20 (2)	13 (20)
C(1)	79 (9)	112 (12)	115 (13)	15 (10)	44 (9)	5 (9)
C(2)	84 (9)	106 (10)	100 (11)	-5 (9)	47 (8)	-6 (8)
C(3)	83 (10)	124 (14)	143 (16)	-22 (11)	33 (10)	-19 (10)
C(4)	90 (12)	122 (14)	189 (22)	-6 (15)	57 (13)	8 (11)
C(5)	101 (13)	192 (23)	147 (19)	-42 (17)	50 (13)	-61 (15)
C(6)	80 (10)	153 (18)	161 (18)	21 (4)	47 (11)	-13 (11)
C(7)	216 (27)	168 (21)	167 (22)	-35 (16)	-13 (19)	-50 (18)
C(8)	102 (10)	69 (8)	87 (10)	-15 (7)	27 (8)	6 (7)
C(9)	114 (11)	71 (8)	104 (11)	-2 (7)	47 (9)	8 (8)
C(10)	148 (16)	73 (10)	125 (14)	-6 (8)	43 (12)	-7 (10)
C(11)	138 (16)	98 (12)	151 (18)	-12 (11)	60 (14)	-25 (12)
C(12)	92 (10)	93 (11)	145 (16)	-10 (10)	36 (11)	0 (9)
C(13)	107 (11)	93 (10)	98 (11)	6 (8)	37 (9)	3 (9)
C(14)	122 (14)	142 (15)	136 (16)	-27 (12)	27 (12)	-25 (12)
N	71 (6)	77 (6)	104 (9)	2 (6)	24 (6)	5 (5)
C(15)	70 (7)	87 (9)	108 (11)	-9 (8)	22 (8)	17 (7)
C(16)	91 (10)	103 (10)	122 (13)	18 (9)	27 (9)	27 (8)
C(17)	95 (10)	112 (12)	161 (17)	29 (11)	53 (11)	37 (9)
C(18)	111 (11)	125 (14)	107 (12)	7 (10)	15 (10)	37 (9)
C(19)	86 (9)	83 (8)	93 (11)	-8 (7)	21 (8)	10 (7)
C(20)	87 (9)	114 (11)	105 (12)	-17 (9)	26 (8)	7 (8)
C(21)	126 (13)	99 (10)	106 (12)	-24 (9)	29 (10)	-1 (9)
C(22)	112 (13)	185 (20)	181 (20)	-94 (16)	30 (13)	-13 (13)
C(23)	98 (10)	69 (7)	86 (10)	6 (7)	14 (8)	1 (7)
C(24)	128 (13)	74 (9)	119 (13)	9 (8)	-4 (10)	13 (9)
C(25)	114 (12)	75 (9)	165 (17)	22 (10)	4 (12)	-3 (9)
C(26)	176 (18)	137 (14)	220 (20)	19 (13)	-7 (16)	0 (13)
C(27)	68 (7)	77 (8)	113 (12)	4 (8)	20 (7)	-1 (6)
C(28)	94 (10)	90 (10)	116 (12)	-17 (9)	25 (9)	-13 (8)
C(29)	191 (19)	90 (11)	123 (15)	-15 (10)	29 (14)	-37 (12)
C(30)	134 (16)	110 (14)	171 (20)	-3 (12)	21 (14)	-13 (11)

<sup>a</sup> The temperature factor is of the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31} + 2hka^*b^*U_{12})]$ .

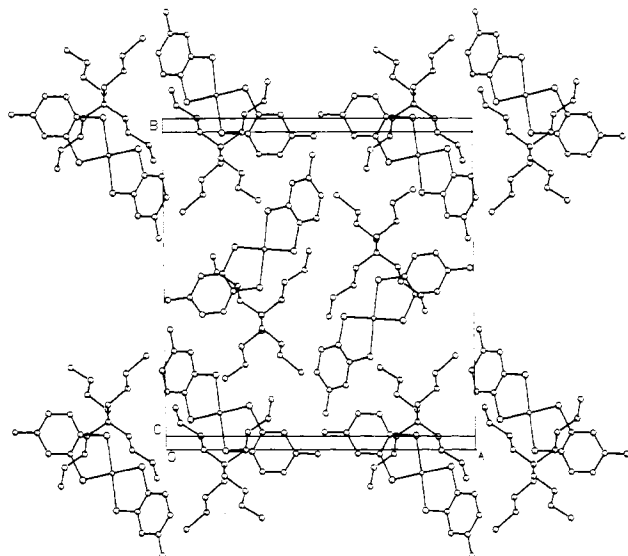


Figure 3. Projection of the structure down the *c* axis showing the packing of molecules in the unit cell.

The structure of the  $[\text{Au}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2]^-$  anion is shown in Figure 4. The numbering scheme is indicated in Table IV. The Au atom has an approximate square-planar configuration with all four Au-S distances (2.299–2.319 Å) equal within experimental error. The mean Au-S distance, 2.310 Å, is comparable with those observed in other (1,2-dithiolato)-gold(III) complexes: 2.288 Å for R=CF<sub>3</sub> in  $[\text{Au}(\text{S}_2\text{C}_2\text{R}_2)_2]^-$  and 2.309 Å for R=CN. In 1,1-dithiolato complexes this

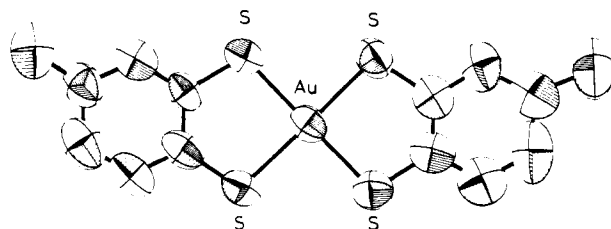


Figure 4. Structure of the  $[\text{Au}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2]^-$  anion showing the tilting of the two toluene rings on the same side of the AuS<sub>4</sub> plane.

distance is slightly longer: 2.335 Å in bis(di-*n*-butyldithiocarbamato)aurate(III). The S-Au-S angle is constrained by the restricted bite of CS<sub>2</sub> to 75° in the latter complex, whereas in 1,2-dithiolato complexes it is close to 90° (88.9–91.6° in the present case).

The anion has an approximate mirror plane of symmetry passing through the Au atom and relating to two S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Me ligands. Calculated least-squares planes through selected atoms in the anion (Table VII) show that the AuS<sub>4</sub> core is coplanar to within 0.018 Å, but the anion as a whole is significantly nonplanar. Both toluene groups are tilted on the same side of the AuS<sub>4</sub> plane (Figure 4). Planes through the phenyl ring atoms C(1)–C(6) and C(8)–C(13) make dihedral angles of 9.9 and 16.9°, respectively, with the AuS<sub>4</sub> plane. The nonplanarity of the anion may be caused by overall packing requirements. Although the two methyl groups approach to within 4 Å (C(18) and C(30)), no significant distortion of the square-planar coordination geometry of Au results.

The S-C distances are all equal and comparable with those in other complexes (ca. 1.75 Å). They are slightly shorter than

Table VI

(a) Bond Lengths (Å) for the Nonhydrogen Atoms with Esd's in Parentheses			
Au-S(1)	2.306 (4)	Au-S(3)	2.317 (4)
Au-S(2)	2.299 (4)	Au-S(4)	2.319 (4)
S(1)-C(1)	1.75 (2)	S(3)-C(8)	1.75 (1)
S(2)-C(2)	1.76 (2)	S(4)-C(9)	1.76 (2)
C(1)-C(2)	1.36 (2)	C(8)-C(9)	1.41 (2)
C(2)-C(3)	1.39 (2)	C(9)-C(10)	1.37 (2)
C(3)-C(4)	1.42 (3)	C(10)-C(11)	1.39 (3)
C(4)-C(5)	1.39 (3)	C(11)-C(12)	1.38 (2)
C(4)-C(7)	1.55 (3)	C(12)-C(13)	1.40 (2)
C(5)-C(6)	1.42 (3)	C(12)-C(14)	1.41 (2)
C(6)-C(1)	1.41 (2)	C(13)-C(8)	1.41 (2)
N-C(15)	1.55 (2)	N-C(23)	1.52 (2)
N-C(19)	1.52 (2)	N-C(27)	1.54 (2)
C(15)-C(16)	1.51 (2)	C(23)-C(24)	1.53 (2)
C(16)-C(17)	1.48 (2)	C(24)-C(25)	1.45 (2)
C(17)-C(18)	1.55 (2)	C(25)-C(26)	1.66 (2)
C(19)-C(20)	1.54 (2)	C(27)-C(28)	1.50 (2)
C(20)-C(21)	1.53 (2)	C(28)-C(29)	1.43 (2)
C(21)-C(22)	1.48 (2)	C(29)-C(30)	1.51 (2)

(b) Bond Angles (Deg) for the Nonhydrogen Atoms with Esd's in Parentheses			
S(1)-Au-S(2)	89.8 (1)	S(2)-Au-S(3)	89.7 (1)
S(1)-Au-S(3)	179.4 (1)	S(2)-Au-S(4)	177.9 (1)
S(1)-Au-S(4)	91.6 (1)	S(3)-Au-S(4)	88.9 (1)
Au-S(1)-C(1)	102.3 (6)	Au-S(3)-C(8)	102.6 (5)
Au-S(2)-C(2)	102.4 (6)	Au-S(4)-C(9)	102.6 (4)
S(1)-C(1)-C(2)	123 (2)	S(3)-C(8)-C(9)	122 (1)
S(1)-C(1)-C(6)	118 (1)	S(3)-C(8)-C(13)	118 (1)
S(2)-C(2)-C(1)	122 (1)	S(4)-C(9)-C(8)	121 (1)
S(2)-C(2)-C(3)	116 (1)	S(4)-C(9)-C(10)	122 (1)
C(1)-C(2)-C(3)	122 (2)	C(8)-C(9)-C(10)	117 (2)
C(2)-C(3)-C(4)	121 (2)	C(9)-C(10)-C(11)	123 (2)
C(3)-C(4)-C(5)	117 (2)	C(10)-C(11)-C(12)	122 (2)
C(3)-C(4)-C(7)	129 (2)	C(11)-C(12)-C(13)	116 (2)
C(5)-C(4)-C(7)	113 (2)	C(11)-C(12)-C(14)	123 (2)
C(4)-C(5)-C(6)	121 (2)	C(13)-C(12)-C(14)	121 (2)
C(5)-C(6)-C(1)	121 (2)	C(12)-C(13)-C(8)	122 (1)
C(6)-C(1)-C(2)	119 (2)	C(13)-C(8)-C(9)	120 (1)
C(15)-N-C(19)	110 (1)	C(19)-N-C(23)	111 (1)
C(15)-N-C(23)	106 (1)	C(19)-N-C(27)	107 (1)
C(15)-N-C(27)	111 (1)	C(23)-N-C(27)	112 (1)
N-C(15)-C(16)	114 (1)	N-C(23)-C(24)	115 (1)
C(15)-C(16)-C(17)	111 (1)	C(23)-C(24)-C(25)	101 (1)
C(16)-C(17)-C(18)	112 (1)	C(24)-C(25)-C(26)	107 (2)
N-C(19)-C(20)	115 (1)	N-C(27)-C(28)	115 (1)
C(19)-C(20)-C(21)	112 (1)	C(27)-C(28)-C(29)	109 (1)
C(20)-C(21)-C(22)	114 (1)	C(28)-C(29)-C(30)	116 (2)

Table VII

Distances (Å) of Relevant Atoms from the  
Least-Squares Planes for the  $[\text{Au}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2]^-$  Anion<sup>a</sup>

Plane i: Au, S(1), S(2), S(3), S(4)					
$-13.401x + 0.610y + 7.282z = 0.875$					
Au -0.016, S(1) -0.009, S(2) 0.018, S(3) -0.010, S(4) 0.017					
Plane ii: C(1), C(2), C(3), C(4), C(5), C(6)					
$14.728x + 1.921y - 6.553z = 1.917$					
C(1) -0.012, C(2) 0.003, C(3) 0.008, C(4) -0.011, C(5) 0.002, C(6) 0.009, C(7) -0.209					
Plane iii: C(8), C(9), C(10), C(11), C(12), C(13)					
$-9.731x + 4.047y + 8.255z = 4.312$					
C(8) -0.031, C(9) 0.020, C(10) -0.003, C(11) -0.004, C(12) -0.006, C(13) 0.024, C(14) 0.026					
Dihedral Angles (Deg)					
i-ii	9.9	i-iii	16.9	ii-iii	26.8

<sup>a</sup> Planes are in the form  $Ax + By + Cz = D$ , where  $x$ ,  $y$ , and  $z$  are fractional coordinates.

the sums of the single-bond radii of S and  $sp^2$  C (1.81 Å), indicative of a small contribution from multiple bonding. The geometries of the toluene rings are normal: mean C-C(ring)

1.396 Å and mean C9(ring)-Me 1.480 Å.

The N atom of the  $[\eta\text{-Bu}_4\text{N}]^+$  cation has tetrahedral geometry with C(N)C angles varying from 106 to 112 (1)°. The N-C distances (1.52-1.55 (2) Å) are longer than the sum of the N and C atomic radii (1.47 Å) and reflect steric crowding around the N atom. The C-C distances range from 1.43 to 1.66 Å (mean 1.51 Å).

**General Properties.** The stability of gold(III) dithiolate complexes is perhaps surprising in view of the strong reducing power of the ligands and  $\text{SO}_2$ . The present complex is even stable in aqueous media. It does not have strong electron-withdrawing groups on the ligands as have the previously reported, related complexes<sup>3,4</sup>  $[\text{Au}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$  and  $[\text{Au}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]^-$ . In a separate study we shall show that Au(I) and Au(III) complexes can be isolated with 1,2-dithiolates such as dimercaptosuccinic acid. This may be relevant to the biological chemistry of Au.

The weak electronic absorption bands at 428 ( $\epsilon$  168) and 646 nm ( $\epsilon$  74) are either d-d or  $\text{S} \rightarrow \text{Au}$  charge-transfer transitions. Very few clear assignments of d-d bands in Au(III) complexes have been reported.<sup>7</sup>  $[\text{Au}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$  has a band at 465 nm ( $\epsilon$  100),<sup>16</sup> and  $[\text{Au}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]^-$  is also a green ion.<sup>4</sup>

In the crystal the two methyl groups are in the cis configuration. Only one  $^1\text{H}$  and  $^{13}\text{C}$  resonance is observed in solution, suggesting that the conformation is the same or that a rapid exchange is occurring between cis and trans, possibly via a tetrahedral intermediate.

**Association with  $\text{SO}_2$ .** This appears to be the first report of a reversible association of  $\text{SO}_2$  with a gold complex. However,  $\text{SO}_2$  is a common reagent in gold chemistry: a standard method for the production of (so-called)  $[\text{Au}^+\text{Cl}_2]^-$  involves reduction of  $\text{AuCl}_4^-$  with  $\text{SO}_2$  in a concentrated NaCl solution.  $\text{SO}_2$  complexes are known for the other group 1B elements Cu and Ag. The best characterized example is  $\text{Cu}^+(\text{PPh}_2\text{Me})_3(\text{SPh})(\text{SO}_2)$ , in which  $\text{SO}_2$  acts as a Lewis acid and binds to S of the coordinated thiolate.<sup>6</sup> The S- $\text{SO}_2$  bond is long (2.530 Å) and  $\text{SO}_2$  readily dissociates. The S- $\text{SO}_2$  geometry is pyramidal.

In all, five categories of  $\text{SO}_2$  complexes of metals have been established by X-ray crystallography:<sup>17</sup> (i) pyramidal Z- $\text{SO}_2$  where Z = metal ion or ligand ( $\text{I}^-$ ,  $\text{RS}^-$ ), (ii) coplanar M- $\text{SO}_2$  ( $\text{SO}_2$  as a Lewis base), (iii) bridging M- $\text{SO}_2$ -M, (iv) S,O bonded, and (v) O bonded. Usually, only in class i is  $\text{SO}_2$  reversibly bound, and M- $\text{SO}_2$  can often be distinguished from ML- $\text{SO}_2$  (L = ligand) by  $\nu_3(\text{S-O})$ : 990-1065  $\text{cm}^{-1}$  for the former and 1051-1135  $\text{cm}^{-1}$  for the latter. We observe  $\nu_3(\text{S-O})$  at 1126  $\text{cm}^{-1}$  suggesting that  $\text{SO}_2$  is ligand bound rather than Au bound. Since no perturbation of the electronic absorption bands in the visible region occurs and these are expected to be d-d or charge transfer ( $\text{S} \rightarrow \text{Au}$ ), it is possible that  $\text{SO}_2$  binds to the toluene ring. This might account for the NMR shifts at the ring periphery. It is notable that although the C(6)H  $^1\text{H}$  NMR signal loses all fine structure when  $\text{SO}_2$  binds to the complex, its coupling to C(5)H is still well resolved on the C(5)H resonance. The field and temperature dependences of line widths confirm that the broadening is due to a chemical-exchange process and that the conformation of the ring, as indicated by the  $^1\text{H}$ - $^1\text{H}$  coupling constant, is unchanged. It is possible that  $\text{SO}_2$  causes a large change in the tilt of the toluene rings with respect to the  $\text{AuS}_4$  plane. Since the two dithiolate ligands remain equivalent in the  $\text{SO}_2$  complex, it seems likely that it is a 2:1 complex with one  $\text{SO}_2$  molecule bound to each ligand. It would be interesting to isolate such a novel species, but, so far, our attempts to do this have been unsuccessful.

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**Registry No.** [*n*-Bu<sub>4</sub>N][Au(S<sub>2</sub>C<sub>7</sub>H<sub>6</sub>)<sub>2</sub>], 77880-82-1; [Et<sub>4</sub>N][Au(S<sub>2</sub>C<sub>7</sub>H<sub>6</sub>)<sub>2</sub>], 77880-83-2; [Me<sub>4</sub>N][Au(S<sub>2</sub>C<sub>7</sub>H<sub>6</sub>)<sub>2</sub>], 77880-84-3; SO<sub>2</sub>, 7446-09-5; NaAuCl<sub>4</sub>, 15189-51-2.

**Supplementary Material Available:** A listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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## Synthesis, Structure, and Properties of Cluster Compounds with D-Penicillamine Containing Cu<sup>I</sup>, Cu<sup>II</sup>, Ag<sup>I</sup>, Ni<sup>II</sup>, and Pd<sup>II</sup>. X-ray Structure of Pentakis(hexaamminecobalt(III))

### Tris[μ<sub>3</sub>-chloro-octahedro-hexakis[μ<sub>4</sub>-[cis-bis(D-pencillaminato(2-))-N,S]nickel(II)]-S,S']-cubo-octaargentate(I)]-*n*-Water, [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>5</sub>[Ag<sub>8</sub>Ni<sub>6</sub>(SC(CH<sub>3</sub>)<sub>2</sub>CH(NH<sub>2</sub>)COO)<sub>12</sub>Cl]<sub>3</sub>·~197H<sub>2</sub>O

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Metal thiolate cluster compounds of composition [M<sup>I</sup><sub>8</sub>M<sup>II</sup><sub>6</sub>L<sub>12</sub>Cl]<sup>5-</sup> have been prepared with M<sup>I</sup> = Cu<sup>I</sup> or Ag<sup>I</sup>, M<sup>II</sup> = Cu<sup>II</sup>, Ni<sup>II</sup>, or Pd<sup>II</sup>, and L = the deprotonated penicillamine ligand (SC(CH<sub>3</sub>)<sub>2</sub>CH(NH<sub>2</sub>)COO)<sup>2-</sup>. The X-ray crystal structure of [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>5</sub>[Ag<sub>8</sub>Ni<sub>6</sub>L<sub>12</sub>Cl]<sub>3</sub>·~197H<sub>2</sub>O has been solved. The compound crystallizes in the cubic space group *F*432 with *a* = 51.774 (7) Å and with 32 cluster anions per unit cell. The intensities of 2927 reflections with *I* > 2σ(*I*) were measured on an automatic diffractometer using Mo Kα radiation. The structure was solved by heavy-atom methods and refined with unit weights by using block-diagonal least-squares methods and a Waser constraints procedure. The final residual *R* is 0.058. Each [Ag<sub>8</sub>Ni<sub>6</sub>L<sub>12</sub>Cl]<sup>5-</sup> ion lies on a threefold axis. It contains several regular atomic polyhedra. A Cl<sup>-</sup>-centered Ag<sub>8</sub> cube is inscribed into an icosahedron of S atoms. Each S atom functions as a bridging ligand between two Ag<sup>I</sup> atoms and a Ni<sup>II</sup> atom. The Ag atoms are planar coordinated by three S atoms with the common central Cl<sup>-</sup> as a weak fourth ligand at ~3.0 Å. The six Ni<sup>II</sup> atoms lie at the apices of an octahedron (edge ~ 7.0 Å). Each Ni<sup>II</sup> atom is square-planar cis-bidentate coordinated by two S and two N atoms. The crystal structure is stabilized by hydrogen bonds between adjacent cluster anions, water molecules, and Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ions. Only the Cu<sup>II</sup>-containing compounds of this composition are paramagnetic. The ESR and NMR parameters of the complexes are presented. The ESR spectra of Cu<sup>II</sup>-doped diamagnetic clusters show that the unpaired electron is localized on the Cu<sup>II</sup> atom.

## Introduction

The complex formation of thiolate ligands with Cu<sup>II</sup> is often complicated by simultaneous redox reactions. With thiolate ligands capable of forming five-membered chelate rings, intensely colored mixed-valence Cu<sup>I</sup>-Cu<sup>II</sup> complexes can be formed.<sup>1</sup> Such compounds are rather unstable unless there are two alkyl substituents on the carbon atom adjacent to sulfur. Examples of such ligands are penicillamine (H<sub>2</sub>Pen, HSC(CH<sub>3</sub>)<sub>2</sub>CH(NH<sub>2</sub>)COOH), α-mercaptoisobutyric acid (H<sub>2</sub>MIBA, HSC(CH<sub>3</sub>)<sub>2</sub>COOH), and β,β-dimethylcysteamine (HDMC, HSC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>).<sup>2</sup> X-ray structure determinations have shown that complex ions of composition [Cu<sup>I</sup><sub>8</sub>Cu<sup>II</sup><sub>6</sub>L<sub>12</sub>Cl]<sup>z-</sup> are formed, where L is the deprotonated thiolate ligand Pen (*z* = 5-),<sup>3</sup> MIBA (*z* = 5-),<sup>4</sup> or DMC (*z*

= 7+).<sup>5</sup> The structure of these compounds is schematically depicted in Figure 1. Each of the Cu(I) atoms in the structure is bound by three sulfur atoms in a trigonal coordination geometry. The central chloride ion in the structure is a weak ligand bridging between the eight Cu<sup>I</sup> atoms (Cu<sup>I</sup>-Cl ≈ 2.8 Å). The Cu<sup>II</sup> atoms are four-coordinated by two sulfur and two nitrogen atoms in a cis-bidentate coordination geometry.

We now show that the formation of such cluster compounds is not restricted to copper. Other metals accepting similar coordination geometries stabilize similar cluster structures. With D-penicillamine as a ligand, clusters were obtained not only with Cu<sup>I</sup> and Cu<sup>II</sup> but also with Ag<sup>I</sup>, Ni<sup>II</sup>, and Pd<sup>II</sup>. Compounds containing the metal combinations shown in Table I have been prepared. Only the Cu<sup>II</sup>-containing complexes are paramagnetic. A ferromagnetic exchange interaction couples the unpaired spins on the six Cu<sup>II</sup> sites in the structure, resulting in an *S* = 3 ground state.<sup>5,6</sup> All other compounds

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(2) Abbreviations used in this article: H<sub>2</sub>Pen = D-penicillamine, HSC(CH<sub>3</sub>)<sub>2</sub>CH(COO<sup>-</sup>)NH<sub>3</sub><sup>+</sup>; H<sub>2</sub>MIBA = α-mercaptoisobutyric acid, HSC(CH<sub>3</sub>)<sub>2</sub>COOH; HDMC = β,β-dimethylcysteamine, HSC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>; PenSSPen = penicillamine sulfide. The deprotonated ligands are abbreviated as Pen, MIBA, and DMC, respectively. M = metal, L = ligand.

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