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Structure of Bis(benzene-1,2-dithiolato)gold(IV)

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Abstract. $[\text{Au}(\text{C}_6\text{H}_4\text{S}_2)_2]$, $M_r = 477.44$, monoclinic, $P2_1/n$, $a = 12.435$ (2), $b = 3.750$ (1), $c = 14.495$ (1) Å, $\beta = 111.88$ (1)°, $V = 627.2$ (2) Å³, $Z = 2$, $D_x = 2.52$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 123.0$ cm⁻¹, $F(000) = 446$, $T = 298$ K. Final $R = 0.024$ for 1167 observed reflections. Au has square-planar coordination to four S atoms forming planar units which are regularly stacked along the b axis, which makes an angle of 18.5 (1)° with the normal of the complex. The average Au—S distance is 2.300 (1) Å. A weak superstructure is observed but has been ignored in the present analysis.

Introduction. The recent discoveries of superconductivity in $(\text{TTF})[\text{Ni}(\text{dmit})_2]_2$ (TTF = tetra-thiafulvalene, dmit = 4,5-dimercapto-1,3-dithiole-2-dithione) (Brossard, Ribault, Bousseau, Valade & Cassoux, 1986) and $[(\text{CH}_3)_4\text{N}][\text{Ni}(\text{dmit})_2]$ (Kobayashi, Kim, Sasaki, Kato, Kobayashi, Moriyama, Nishio, Kajita & Sasaki, 1987) have stimulated renewed interest in the structure and properties of related compounds containing a central metal atom (Ni, Pt, Pd or Au) bonded to four S atoms in a nearly square-planar coordination. Such compounds have previously been intensively studied because of their magnetic properties involving a spin-Peierls transition (see, for example, Bray, Interrante, Jacobs & Bonner, 1983). The planar metal complexes, which

are often stacked in the crystal structure, may be charged or uncharged corresponding to different formal oxidation states of the metal atom. The present study deals with the neutral gold(IV) complex $[\text{Au}(\text{bdt})_2]^0$ (bdt = benzene-1,2-dithiolato) which may be reduced to the anion $[\text{Au}(\text{bdt})_2]^-$ corresponding to the well known oxidation state of +3 for Au. A similar compound formally containing gold(IV), bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)-gold(IV) was reported earlier (Schultz, Wang, Soderholm, Sifter, Williams, Bechgaard & Whangbo, 1987). This material exhibits a pronounced dimerization of the radicaloid gold(IV) species. Such dimerization is not found in the title compound, which contains uniform stacks of formally neutral gold(IV) radicals.

Experimental. Crystals of $[\text{Au}(\text{bdt})_2]^0$ were obtained by electrochemical oxidation (3 μA) in a standard H cell of the $(\text{C}_4\text{H}_9)_4\text{N}^+$. $[\text{Au}(\text{bdt})_2]^-$ salt. A platinum wire, which could be adjusted to keep only the tip in the electrolyte, was used as the anode. The crystals of best quality were obtained when grown from the tip of the electrode only throughout the entire electrolysis. A crystal of dimensions 0.30 × 0.08 × 0.03 mm was selected for study on an Enraf-Nonius CAD-4 diffractometer. The unit cell was derived from 25 reflections ($12.5 < \theta < 17.5^\circ$). X-ray intensity data

were collected with ω scans [$\Delta\omega = (1.20 + 0.35 \tan\theta)^\circ$] in the range $2 < \theta < 28^\circ$, $-16 < h < 16$, $-9 < k < 9$, $0 \leq l < 19$ with 5992 reflections measured in a supercell (a , $2b$, c) and merged to 3017 unique reflections, $R_{\text{int}} = 0.026$. The data set was later reduced to 1496 unique reflections in the subcell with $b = 3.750 \text{ \AA}$ when the superstructure reflections were deemed too broad for accurate measurement. No decay was found for the intensity control reflections. The intensities were corrected for Lorentz, polarization and absorption effects (transmission factors in the range 0.38–0.73). The structure was solved by Patterson and direct methods using *SHELXS86* (Sheldrick, 1986). 79 parameters were refined by minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0004|F_o|^2]$ using *SHELX76* (Sheldrick, 1976). Anisotropic temperature factors were used, no H atoms were included. Complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final residuals were $R = 0.024$, $wR = 0.0336$ and $S = 1.37$ for 1167 reflections with $I > 3\sigma(I)$. Max. and min. difference electron density was 0.66 and -1.06 e \AA^{-3} . $\Delta/\sigma < 0.003$ in final cycle. The resultant positional and thermal parameters are given in Table 1.*

Discussion. The atomic numbering of the unique half of $[\text{Au}(\text{bdt})_2]^0$ is shown in Fig. 1. Bond lengths and angles are listed in Table 2.

The coordination of Au is planar by symmetry and the ligand S atoms form an almost perfect square. Au—S distances are very similar to those observed in three related compounds: tetra-*n*-butylammonium bis(toluene-3,4-dithiolato)aurate(III) (Mazid, Razi & Sadler, 1981), bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)gold(IV) (Schultz, Wang, Soderholm, Sifter, Williams, Bechgaard & Whangbo, 1987) and tetrathiafulvalenium bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)aurate(III) (Geiser, Schultz, Wang, Beno & Williams, 1988). The average Au—S distance is $2.300(1) \text{ \AA}$ in the present structure and $2.310(2)$, $2.30(2)$ and $2.306(9) \text{ \AA}$ in the three related structures mentioned. Apparently, the geometry of the ligand is hardly sensitive to the overall charge of the complex, but more accurate studies may reveal some systematic effects, e.g. a lengthening of the Au—S bond with increasing negative charge as noted for some Ni complexes (Eisenberg, 1970).

The complex is almost planar with a dihedral angle of 3.0° between the plane defined by Au, S1 and S2 and the plane of the benzene ring. The ideal

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52820 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
Au	0	0	0	37 (1)
S(1)	-1302 (1)	-696 (4)	-1602 (1)	41 (1)
S(2)	1394 (1)	1728 (5)	-596 (1)	48 (1)
C(1)	-496 (5)	511 (12)	-2311 (4)	36 (2)
C(2)	-1031 (5)	362 (13)	-3348 (5)	43 (2)
C(3)	-444 (5)	1450 (19)	-3943 (5)	52 (2)
C(4)	713 (5)	2649 (17)	-3503 (4)	50 (2)
C(5)	1238 (4)	2763 (16)	-2485 (5)	46 (2)
C(6)	662 (4)	1643 (15)	-1869 (4)	40 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Au—S(1)	2.298 (1)	C(2)—C(3)	1.384 (9)
Au—S(2)	2.302 (2)	C(3)—C(4)	1.415 (8)
S(1)—C(1)	1.743 (6)	C(4)—C(5)	1.374 (8)
S(2)—C(6)	1.727 (5)	C(5)—C(6)	1.402 (8)
C(1)—C(2)	1.400 (8)		
S(1)—Au—S(2)	89.9 (1)	C(2)—C(3)—C(4)	119.9 (6)
Au—S(1)—C(1)	102.8 (2)	C(3)—C(4)—C(5)	119.4 (6)
Au—S(2)—C(6)	103.0 (2)	C(4)—C(5)—C(6)	121.6 (5)
S(1)—C(1)—C(2)	118.4 (4)	C(5)—C(6)—C(1)	118.8 (5)
S(1)—C(1)—C(6)	121.9 (4)	C(5)—C(6)—S(2)	118.9 (4)
C(2)—C(1)—C(6)	119.8 (5)	C(1)—C(6)—S(2)	122.3 (5)
C(1)—C(2)—C(3)	120.5 (5)		

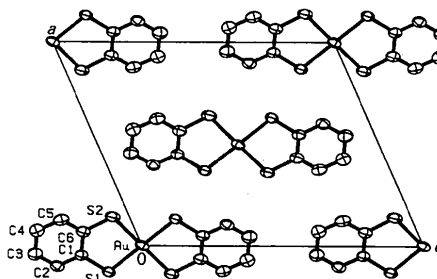


Fig. 1. Thermal ellipsoid plot (Johnson, 1976) showing atomic numbering and view along the b axis.

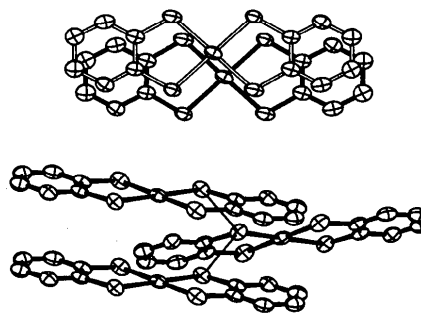


Fig. 2. Thermal ellipsoid plots (Johnson, 1976) showing (upper): molecular overlap viewed along normal to molecular plane, (lower): side view of two molecules in one stack as well as one molecule in an adjacent stack with short S1...S1 contacts marked as a thin line.

molecular symmetry of *mmm* is thus almost retained in the crystal structure. The complexes are parallel and equally spaced by symmetry in stacks along the *b* axis (Figs. 1 and 2). The normal to the molecular plane (all atoms) makes an angle of 18.5 (1)° with the *b* axis. The molecules in a stack are thus 'slipped' with respect to each other. The S...S contact distance within a stack is equal to the *b* axial translation of 3.75 Å. Between the stacks there is one shorter S1...S1 distance of 3.66 Å (marked on Fig. 2), indicating some transverse interaction. The van der Waals contact distance S...S is 3.60 Å (Bondi, 1964).

As mentioned above, a weak superstructure (*a*, *2b*, *c*) was observed and most clearly on long exposure rotation films. This additional scattering is rather diffuse with very extended Bragg spots. It was realized that these intensities were not correctly measured during data collection, and we chose to solve the structure in the subcell with *b* = 3.750 Å. The resulting low residuals of the present analysis strongly suggest that the superstructure modulation is very small. The nature of this distortion is not yet known, but a weak Peierls or spin-Peierls distortion may be a possibility. The details of the magnetic and electrical properties of this interesting molecular solid are presently being investigated and will appear in a separate paper.

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Structure of a Dicopper(II) Complex of the Flexible, Dinucleating Ligand, *N,N,N',N'*-Tetrakis(3-aminopropyl)-1,5-diamino-3-oxapentane

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Abstract. Tetrachloro- μ -[*N,N'*-di(3-aminopropyl)-4,10-diaza-7-oxatridecanediamine-*N,N',N'',N''',N''''*]-*N''''''*]-dicopper(II) hydrate, $[\text{Cu}_2\text{Cl}_4\{\text{[NH}_2\text{-(CH}_2\text{)}_3\text{]}_2\text{N(CH}_2\text{)}_2\}_2\text{O}\cdot\text{H}_2\text{O}] \cdot \text{C}_{16}\text{H}_{42}\text{Cl}_4\text{Cu}_2\text{N}_6\text{O}_2$, $M_r = 619.44$, monoclinic, $P2_1/c$ (C_{2h}^2 , No. 14), $a = 13.989$ (24), $b = 10.568$ (22), $c = 16.783$ (34) Å, $\beta = 90.65$ (15)°, $V = 2481$ (8) Å³, $Z = 4$, $D_x = 1.658$ g cm⁻³, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo } K\alpha) = 21.80$ cm⁻¹, $F(000) = 1287.70$. 3097 independent reflections at 298 K gave $R = 0.0599$. The copper(II) atoms are coordinated at either end of the ligand to a triamine

fragment and to two chlorine atoms, leading to coordination geometries intermediate between trigonal bipyramidal and square-based pyramidal. The intermetallic separation is 8.875 Å.

Introduction. Since the disclosure that the dioxygen binding site in deoxyhaemocyanin does not contain an endogenous protein bridge (Gaykema, Volbeda & Hol, 1986) efforts have been made to seek compatible model complexes which are capable of sustaining two copper atoms 3.6 Å apart as in the biological system (Sorrell, 1989; Tyeklar & Karlin, 1989). Copper(II) chloride complexes of the flexible, dinucleating ligand *N,N,N',N'*-tetrakis(3-amino-

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