Table 2. *Selected geometric parameters (Å, °)*

Au—S	2.2900 (13)	C3—N31	1.491 (7)
S—C2	1.841 (5)	C3—C4	1.522 (8)
C2—C21	1.502 (8)	C4—O41	1.225 (10)
C2—C1	1.515 (8)	C4—O42	1.257 (10)
C2—C3	1.554 (6)		
S—Au—S^{i}	178.47 (7)	C3—C2—S	109.5 (3)
C2—S—Au	107.6 (2)	N31—C3—C4	109.4 (5)
C21—C2—C1	111.3 (5)	N31—C3—C2	111.1 (4)
C21—C2—C3	107.6 (5)	C4—C3—C2	112.9 (5)
C1—C2—C3	112.6 (5)	O41—C4—O42	127.3 (7)
C21—C2—S	110.3 (4)	O41—C4—C3	117.0 (7)
C1—C2—S	105.6 (4)	O42—C4—C3	115.6 (8)

Symmetry code: (i) $\frac{1}{3}+x-y, \frac{2}{3}-y, \frac{5}{3}-z$.

Attempts to model O2 as a disordered atom off the special position did not give an improved solution. For the disordered water molecules (O3 and O4) along the 0,0,*z* threefold axis, the isotropic displacement parameters were constrained to be equivalent and the occupancies were allowed to vary, with the constraint that their sum must be no greater than 1. The site occupancies were then fixed and the displacement parameters were allowed to vary. In the final stages, all non-H atoms were refined anisotropically. H atoms were added at calculated positions and allowed to ride on the atoms to which they were attached. Their isotropic displacement parameters (U's) were set to $1.5U_{\rm eq}$ of the atom to which they were attached. H atoms were not added to the ammonium counter-cations or the water molecules of hydration.

Data collection: *P3 Software* (Siemens, 1989). Cell refinement: *P3 Software*. Data reduction: *P3 Software*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1038). Services for accessing these data are described at the back of the journal.

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cyclo-Hexakis[(2,4,6-triisopropylthiophenolato-*S*:*S*)gold(I)] Diethyl Ether Solvate

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Abstract

In the title compound, $[\mathrm{Au_6S_6(C_{15}H_{23})_6}].\mathrm{C_4H_{10}O}$, the gold–thiolate molecule, a centrosymmetric cyclic hexamer with a cyclohexane chair-like structure, lies about an inversion centre. The Au atoms are coordinated in a near-linear fashion to bridging S atoms [Au—S 2.281 (2)–2.288 (3) Å and S—Au—S 173.68 (9)–175.82 (9)°]. Bond lengths and angles are normal.

Comment

The structure of the hexakis[2,4,6-tri(isopropyl)thiophenolatogold(I)] complex has been reported previously as a tetrahydrofuran solvate (Schröter & Strähle, 1991). In an effort to follow up on gold–thiolate mass spectrometry experiments (Howard-Lock, LeBlanc, Lock, Smith & Wang, 1996), it was decided to prepare a sample of Schröter & Strähle's complex and try to obtain a mass spectrum by electrochemical ionization. A slightly different preparation method and a different gold starting material were used as compared to Schröter & Strähle's procedure, but the conditions of crystal growth were similar. An X-ray powder diffraction pattern of the isolated product suggested that the unit cell was different from that observed by Schröter & Strähle (1991) and this was confirmed by determination of the unit cell from a single crystal. It was assumed that a different oligomer had been produced, such as a closed ring tetramer, two of which have recently been reported

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† Deceased.

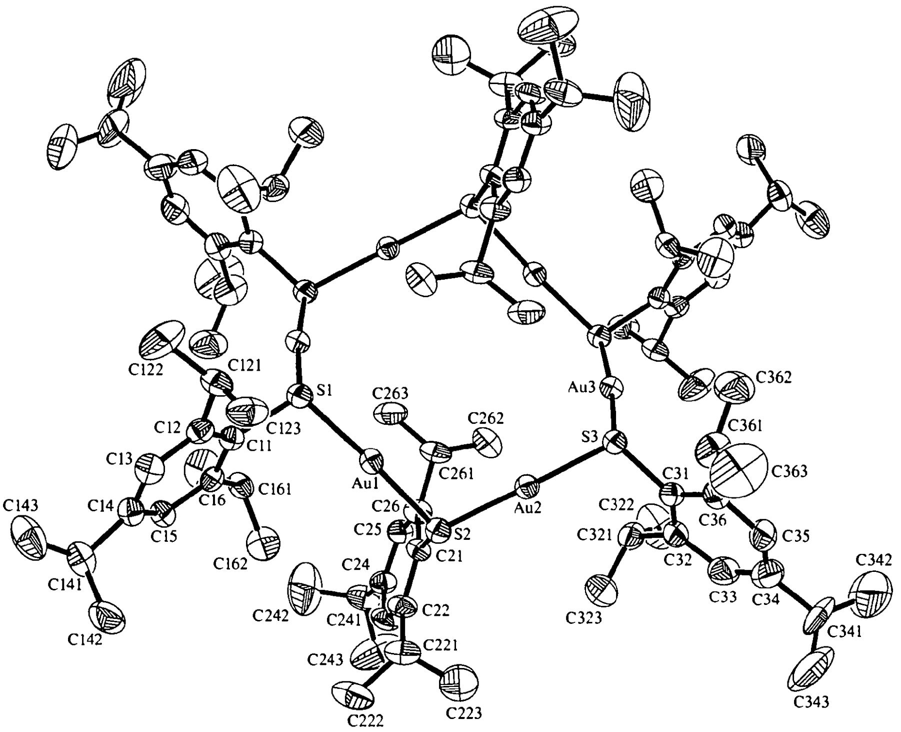
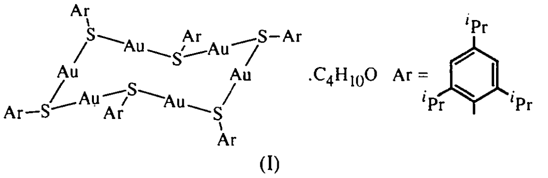


Fig. 1. The title molecule drawn with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

(Bonasi, Gindelberger & Arnold, 1993; Wojnowski *et al.*, 1994). Therefore, the structure of the obtained complex, (I), was determined and is presented here.



(I)

This structural investigation confirmed that the tri(isopropyl)thiophenolatogold(I) complex has a hexameric structure, essentially the same as reported by Schröter & Strähle (1991). It appears that the product isolated in this work differs from that of Schröter & Strähle in crystal packing and the solvent of crystallization. Despite the fact that a 50:50 mixture of diethyl ether–THF was used in both cases, the complex reported here has diethyl ether of crystallization whereas that of Schröter & Strähle had tetrahydrofuran of crystallization.

The Au_6S_6 ring has a chair conformation, of the type predicted by Isab & Sadler (1981) for the gold-based antirheumatoid arthritis drug myochrysine (gold sodium thiomalate). Like the Schröter & Strähle's complex, the title hexamer, (I), has two axial and four equatorial substituents and lies about an inversion centre. To date, this complex is the only example of a 12-membered ring structure for any thiolate of gold, silver or copper.

The Au—Au distances are too long [Au1···Au2 3.661 (1), Au2···Au3 3.507 (1) and Au3···Au1^{i} 3.529 (1) Å; symmetry code: (i) $-x$, $2-y$, $2-z$] for the weak 'aurophilic' attractive interactions, often observed for gold complex structures (Schmidbaur, Graf & Müller, 1988; Schmidbaur, Dziwok, Grohmann & Müller, 1989), to be a factor in this complex. The deviations of the S—Au—S angles from linearity are not excessive and are consistent with the Au—S—Au angles being larger than the value of ~95° predicted for complexes of this type (Elder & Eidsness, 1987; Elder, Ludwig, Cooper & Eidsness, 1985). All other bond lengths and angles are normal.

Experimental

The 2,4,6-triisopropylthiophenol ligand was prepared according to the method of Blower, Dilworth, Hutchinson & Zubieta (1985). Chloro(tetrahydrothiophene)gold(I) (395 mg, 1.23 mmol) was added to a stirred solution of 350 mg (1.5 mmol) of 2,4,6-triisopropylthiophenol in anhydrous diethyl ether (50 ml). A cloudy suspension resulted and, after it was stirred for 10 min, more ligand was added dropwise until after ~1 g (4 mmol) of extra ligand was added, the cloudy solution became clear. The clear solution was stirred for 1 h and then gravity filtered in order to remove a small amount of suspended material. Extra ether was used for rinsing, to a total volume of 75 ml. Tetrahydrofuran (75 ml) was then added and the flask was put aside in a fume hood and covered with a box in order to exclude light and keep foreign material from falling into the solution. After four days, a colourless crystalline product appeared. The product was collected by filtration and washed with ice-cold 50:50 ether–THF (2 × 20 ml); yield: 300 mg (50%).

Crystal data

$[\mathrm{Au_6S_6(C_{15}H_{23})_6}].\mathrm{C_4H_{10}O}$
$M_r = 2668.28$
Monoclinic
$P2_1/n$
$a = 14.2087\ (1)$ Å
$b = 20.3168\ (3)$ Å
$c = 19.8322\ (2)$ Å
$\beta = 110.0850\ (1)^\circ$
$V = 5376.89\ (9)$ Å^3
$Z = 2$
$D_x = 1.648$ Mg m^{-3}
$D_m = 1.68\ (3)$ Mg m^{-3}
D_m measured by suspension in $\mathrm{CCl_4/CH_2I_2}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1.48$–26.37°
$\mu = 8.310$ mm^{-1}
$T = 300\ (2)$ K
Parallelepiped
0.20 × 0.10 × 0.06 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
0.3° rotations on φ or ω scans
Absorption correction: empirical from redundant measurements (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.520$, $T_{\max} = 0.607$
42 693 measured reflections

10 760 independent reflections
6000 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.094$
$\theta_{\max} = 26.43^\circ$
$h = -17 \rightarrow 12$
$k = -25 \rightarrow 25$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R = 0.053$
$wR(F^2) = 0.105$
$S = 1.006$
10 760 reflections
460 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.737$ e Å^{-3}
$\Delta\rho_{\min} = -0.630$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Au1—S1	2.287 (3)	C14—C15	1.361 (12)
Au1—S2	2.288 (3)	C15—C16	1.401 (12)
Au2—S2	2.281 (2)	C12—C121	1.535 (13)
Au2—S3	2.283 (2)	C14—C141	1.520 (13)
Au3—S3	2.288 (3)	C16—C161	1.533 (13)
S1—C11	1.820 (9)	C121—C122	1.52 (2)
S2—C21	1.800 (9)	C121—C123	1.491 (14)
S3—C31	1.791 (11)	C141—C142	1.49 (2)
C11—C12	1.394 (12)	C141—C143	1.50 (2)
C11—C16	1.403 (12)	C161—C162	1.494 (15)
C12—C13	1.393 (13)	C161—C163	1.502 (14)
C13—C14	1.380 (13)		
S1—Au1—S2	175.82 (9)	C11—S1—Au1	106.5 (3)
S2—Au2—S3	173.68 (9)	C11—S1—Au3^{i}	111.4 (3)
S1^{i}—Au3—S3	174.30 (9)	C21—S2—Au1	104.9 (3)
Au3^{i}—S1—Au1	101.03 (9)	C21—S2—Au2	112.1 (3)
Au2—S2—Au1	106.51 (10)	C31—S3—Au2	110.5 (3)
Au2—S3—Au3	100.22 (10)	C31—S3—Au3	110.1 (3)

Symmetry code: (i) $-x, 2-y, 2-z$.

During data collection, no specific reflections were chosen as standards for repeat measurements in order to monitor the stability of the crystal. However, because of the design of the area detector data collection procedure, many reflections were repeatedly measured and these allowed for corrections for both crystal decay and absorption (*SADABS*; Sheldrick, 1996). Analysis of the data revealed that crystal decay was negligible during the data collection. It became apparent from examination of $\Delta\rho$ maps that there were disordered solvent molecules in the crystal lattice. The presence of diethyl ether was confirmed by NMR spectroscopy and by recrystallization of the bulk product from pure diethyl ether, followed by unit-cell determination of an isolated crystal. However, it proved impossible to adequately model the solvent disorder. Therefore, the contribution of the density of the disordered solvent molecules was subtracted from the measured structure factors with use of the *SQUEEZE* option (Spek, 1994) in *PLATON*97 (Spek, 1997). This indicated that there was approximately half a solvent molecule per asymmetric unit, one per hexamer molecule. Subsequent refinement then converged with *R* factors and parameter errors significantly better than for all attempts to model the solvent disorder. The displacement parameters for one of the terminal isopropyl groups (C341–C343), which borders the solvent region of the crystal, also suggested disorder. However, attempts to model the isopropyl disorder did not result in an improved solution. The parameter errors for that isopropyl group are relatively large. All non-H atoms were refined anisotropically. H atoms were added at calculated positions and allowed to ride on the atoms to which they were attached. Their isotropic displacement parameters (*U*'s) were set to $1.2U_{\mathrm{eq}}$ ($1.5U_{\mathrm{eq}}$ for methyl H atoms) of the atom to which they were attached.

Data collection: *SMART* (Siemens, 1996*b*). Cell refinement: *SAINT* (Siemens, 1996*a*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1278). Services for accessing these data are described at the back of the journal.

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A New Perylene Salt: Diperylenium(1+) Bis[quinoxaline-2,3-dithiolato(2–)-*S*,*S*′]-cuprate(III)

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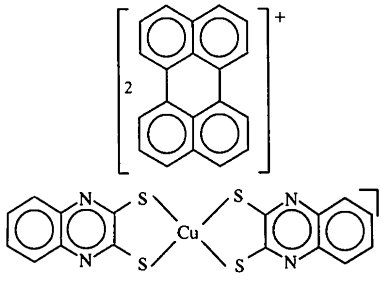
Abstract

A new perylene salt, $(C_{20}H_{12})_2[Cu(C_8H_4N_2S_2)_2]$, $(per)_2[Cu(qdt)_2]$, has been prepared by electrocrystallization and characterized by single-crystal X-ray diffraction. The crystal structure consists of tetramerized stacks of perylene species along the *c* axis, with three crystallographically independent interplanar distances, 3.50 (1), 3.42 (1) and 3.55 (1) Å. These tetramers are flanked by a centrosymmetrically related pair of $[Cu(qdt)_2]^-$ anions.

Comment

Perylene is an electron-donor molecule which has been widely used in the preparation of several molecular compounds exhibiting high electrical conductivity and even metallic properties. Different acceptor counterions have been employed to produce these materials, from I_3^- to several metal–dithiolate complexes (Almeida & Henriques, 1997). Our group has investigated extensively the (per)[M(mnt)$_2$] (mnt is maleonitriledithiolate or *cis*-2,3-dimercapto-2-butenedinitrile) family of molecular conductors (Gama *et al.*, 1993). The specific redox properties of [M(mnt)$_2$] anions make them particularly good acceptor counterions and the possible use of different metals allows manipulation of the physical properties of those materials. As part of an effort to obtain new molecular conductors based on perylene, we modified the (per)$_2$[M(mnt)$_2$] materials by substitution of the acceptor anion with other planar metallic complexes.

Complexes of quinoxaline-2,3-dithiolate (qdt) are analogous to metal–bis(dithiolenes) and include pyrazine rings which can also undergo redox reactions and provide advantageous interactions with an electron donor. They therefore appear to be good candidates for combination with perylene.



$(per)_2[Cu(qdt)_2]$

The crystal structure of $(per)_2[Cu(qdt)_2]$ (Fig. 1) consist of tetramerized stacks of perylene units along the *c* axis, separated by centrosymmetrically-related pairs of $[Cu(qdt)_2]^-$ anions (Fig. 2). The unit cell contains two independent perylene species [per(A) and per(B)] and one independent $[Cu(qdt)_2]^-$ anion, which are at general positions. The two perylene units are planar and have, within experimental uncertainty, the same bond distances and angles. The charge of the $[Cu(qdt)_2]^-$ anion can be assigned by comparison of the Cu—S bond distances (2.18 Å average) with those in $(PPh_4)_2[Cu^{II}(qdt)_2]$ and $(PPh_4)_2[Cu^{III}(qdt)_2]$ (Boyde, Garner & Clegg, 1987). Consequently, the charge balance indicates one positive charge for every two $C_{20}H_{12}$ units in the stacks. The perylene stacks, consisting of the repeat B—A—A^{i}—B^{i} [symmetry code: (i) $1-x$, $1-y$, $1-z$], are well separated in the *ab* plane by anions and no interstack contacts exist in the **a** direction. The two perylene units are planar and almost parallel [their normal makes an angle of 2.44 (6)°] and

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