

References

- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
- Farrugia, L. J. (1997). *ORTEP-3 for Windows*. University of Glasgow, Scotland.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Rigaku Corporation (1990). *RASAIL. X-ray Data Collection Package*. Rigaku Corporation, Tokyo, Japan.
- Taka, J., Ogino, S. & Kashino, S. (1998). *Acta Cryst.* **C54**, 384–386.

Acta Cryst. (1999). **C55**, 1623–1625

A linear-chain silver(I) coordination polymer with tetrakis(isopropylthio)-*p*-benzoquinone

YUSAKU SUENAGA,^a TAKAYOSHI KURODA-SOWA,^a
MASAHIKO MAEKAWA^b AND MEGUMU MUNAKATA^a

^aDepartment of Chemistry, Kinki University 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan, and ^bResearch Institute for Science and Technology, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan. E-mail: suenagay@chem.kindai.ac.jp

(Received 18 February 1999; accepted 20 April 1999)

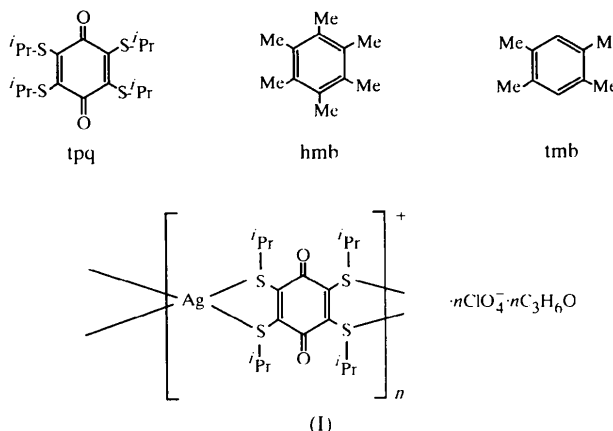
Abstract

The silver(I) complex of tetrakis(isopropylthio)-*p*-benzoquinone (tpq), *catena*-poly[silver(I)- μ -[2,3,5,6-tetrakis(isopropylthio)-*p*-benzoquinone- $S^2, S^3:S^5, S^6$]] perchlorate acetone solvate, $\{[Ag(C_{18}H_{28}S_4O_2)]ClO_4 \cdot nC_3H_6O\}_n$, has been prepared and the molecular structure determined. The silver ion prefers a tetrahedral coordination geometry comprising four S atoms from two different tpq molecules, giving a linear-chain structure of alternating metal cations and organic ligands. Also, the four isopropyl groups of the tpq molecule lie in the perpendicular direction of the plane of the benzoquinone ring.

Comment

Many metal–dithiolene complexes have been synthesized and studied (McCleverty, 1968; Eisenberg, 1970; Rivera & Engler, 1979; Munakata *et al.*, 1995). We synthesized aromatic multi-alkyl thioether ligands and have recently reported the formation of a metal–complex polymer with aromatic multi-alkyl thioether ligands. We have been able to use the metal–complex polymer to construct linear chain $[Cu(hmb)]PF_6$ [hmb is hexakis(methylthio)benzene; Suenaga *et al.*, 1998], zigzag

chain $[(CuI)_2(tmb)]$ [tmb is 1,2,4,5-tetrakis(methylthio)benzene; Ohruai *et al.*, 1996], two-dimensional $[(CuBr)_2(tmb)]$ sheets (Suenaga *et al.*, 1997) and a two-dimensional $[Ag(hmb)]PF_6$ network with inter-chain $S \cdots S$ contacts (Suenaga *et al.*, 1999). We prepared tetrakis(isopropylthio)-*p*-benzoquinone (tpq) for use in place of hmb as an acceptor organic compound. We report here the polymeric structure of $[Ag(tpq)](ClO_4)$ -acetone, (I), as part of our studies on two and three-dimensional polymers of metal ions interconnected by aromatic ligands with novel stereochemistry and special physical properties.



The Ag^I atom lies on the twofold axis along **a**. The C11, O3, and O4 atoms of the perchlorate ion, the O1, C2, O2 and C4 atoms of tpq, and the O6 and C11 atoms of acetone lie on mirror planes perpendicular to **c**. Each Ag^I atom is coordinated by four S atoms from two tpq ligands in a distorted tetrahedral geometry, with bond angles around silver ranging from 81.25 (7) to 151.5 (1)°. The $Ag-S$ distances of 2.521 (2) and 2.601 (2) Å are comparable to those in the complexes of hmb with silver(I) hexafluorophosphate [2.565 (2) Å]. Four isopropyl groups are perpendicular to the benzoquinone ring plane. Interestingly, all the isopropyl groups are directed to the same side of the $S-Ag^I-S$ plane. The suggested classification for the description of possible ‘leg’ orientations in spider host molecules comprises 14 types (MacNicol *et al.*, 1985); descriptors *a* and *b* denote side-chain hydrocarbon moieties projecting, respectively, above and below the mean plane of the benzene core, *e.g.* the conformation of hexakis(phenyloxy)benzene and hexakis(phenylthio)benzene, with regular alternation of pairs of legs, is *ababab*. In contrast, complex (I) exhibits the previously unknown type *aaaa* conformation. In this complex, the O atom of the acetone solvent molecule is positioned on the same side of the four isopropyl groups. This stereospecific orientation may occur because of dipole–dipole interactions. Thus, one tpq bridges two Ag atoms

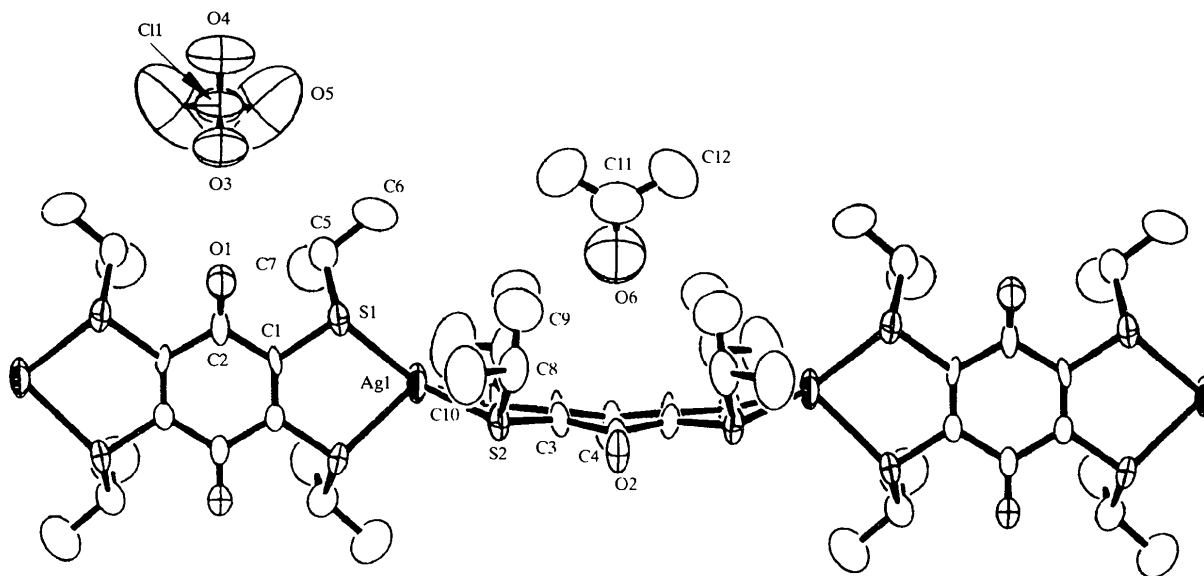


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

to give a linear-chain polymer along the *c* axis, as shown in Fig. 1. In (I), polymeric chains are separated from each other by perchlorate ions and acetone molecules.

The electrical resistivity of compacted pellets was measured by the conventional two-probe technique. Although the complex is an insulator at room temperature [$\sigma(298\text{ K}) < 10^{-12}\text{ S cm}^{-1}$], its iodine-doped black products in powder form behave as a semiconductor with a conductivity of $1.5 \times 10^{-3}\text{ S cm}^{-1}$. A similar phenomenon has been reported in the corresponding Cu^I complexes (Munakata *et al.*, 1996). This is very different from the iodine-doped silver(I) complexes with hmb, which have conductivities of $7.2 \times 10^{-7}\text{ S cm}^{-1}$. One of the common features of a conducting complex is that the constituent molecules are in a mixed-valence state (Torrance, 1979; Inoue *et al.*, 1986).

Experimental

To a 1,3-dimethyl-2-imidazolidinone solution (20 ml) (Dirk *et al.*, 1985) of sodium isopropylmercaptide (3.42 g, 28.5 mmol) was added 1,2,4,5-tetrafluoro-*p*-benzoquinone (1.0 g, 0.5 ml, 4.4 mmol) with stirring under argon. After 2 d at room temperature, the reaction mixture was added to water (100 ml) and the black microcrystals which precipitated were filtered off. Recrystallization from chloroform/pentane yielded black prisms of tpq (150 mg, 7%, m.p. 375 K). IR (KBr discs, cm^{-1}): 2866–2964 (C—H), 1651 (C=O), 721–780 (S—CH₃); ¹H NMR (CD₃CN/TMS, 270 MHz): δ 1.26 (*d*, CH₃), 3.92 p.p.m. (hep, CH); EI-MS: *m/z* 404 (100% *M*). Acetone solutions of AgClO₄ (15 mM) and tpq (15 mM) were poured into a glass tube without mixing under argon and sealed. Red prisms of (I) were obtained from the solution after standing for

2 d. IR (KBr discs, cm^{-1}): 2864–2963 (C—H), 1657 (C=O), 1041–1095 (ClO₄), 721–783 (S—CH₃). Analysis calculated for C₂₁H₃₄AgClO₇S₄: C 37.6, H 5.1, Ag 16.1%; found: C 36.7, H 5.2, Ag 17.7%.

Crystal data

[Ag(C₁₈H₂₈O₂S₄)]ClO₄·
C₃H₆O

M_r = 670.06

Orthorhombic

Pbcm

a = 8.668 (4) Å

b = 18.944 (2) Å

c = 18.196 (1) Å

V = 2987 (1) Å³

Z = 4

D_x = 1.489 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25
reflections

θ = 12.0–14.2°

μ = 1.076 mm⁻¹

T = 296.2 K

Prismatic

0.2 × 0.2 × 0.1 mm

Red

Data collection

Rigaku AFC-7R diffractometer

ω –2 θ scans

Absorption correction:

ψ scan (North *et al.*,
1968)

T_{min} = 0.594, *T_{max}* = 0.898

3463 measured reflections

3463 independent reflections

1344 reflections with

I > 2 σ (*I*)

θ_{max} = 27.5°

h = 0 → 11

k = 0 → 24

l = –21 → 0

3 standard reflections

every 150 reflections

intensity decay: 2.53%

Refinement

Refinement on *F*

R = 0.070

wR = 0.190

S = 1.020

(Δ/σ)_{max} < 0.001

$\Delta\rho_{\text{max}}$ = 1.08 e Å⁻³

$\Delta\rho_{\text{min}}$ = –1.10 e Å⁻³

Extinction correction: none

3157 reflections
169 parameters
H atoms constrained
 $w = 1/[\sigma^2(F_o)$
 $+ 0.00022|F_o|^2]$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Suenaga, Y., Maekawa, M., Kuroda-Sowa, T., Munakata, M., Morimoto, H., Hiyama, N. & Kitagawa, S. (1997). *Anal. Sci.* **13**, 1047–1049.
Torrance, J. B. (1979). *Acc. Chem. Res.* **12**, 79–86.

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Ag1—S1	2.521 (2)	O1—C2	1.21 (1)
Ag1—S2	2.601 (2)	O2—C4	1.20 (1)
S1—C1	1.769 (7)	O6—C11	1.23 (2)
S1—C5	1.83 (1)	C1—C2	1.512 (9)
S2—C3	1.750 (7)	C1—C3'	1.347 (10)
S2—C8	1.854 (10)	C3—C4	1.494 (9)
S1—Ag1—S1'	151.5 (1)	Ag1—S1—C1	103.1 (3)
S1—Ag1—S2	118.22 (8)	Ag1—S1—C5	114.1 (3)
S1—Ag1—S2'	81.25 (7)	Ag1—S2—C3	102.2 (2)
S2—Ag1—S2'	98.8 (1)	Ag1—S2—C8	110.0 (3)

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

Data collection: *Rigaku/AFC Diffractometer Control* (Rigaku Corporation, 1991). Cell refinement: *Rigaku/AFC Diffractometer Control*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We thank Ms Mikiko Nakamura and Mr Tomohiro Ohno for their assistance with the X-ray measurements.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1009). Services for accessing these data are described at the back of the journal.

References

- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
Dirk, C. W., Cox, S. D., Wellman, D. E. & Wudl, F. (1985). *J. Org. Chem.* **50**, 2395–2397.
Eisenberg, R. (1970). *Prog. Inorg. Chem.* **12**, 295–369.
Inoue, M. B., Inoue, M., Fernand, Q. & Nebesny, K. W. (1986). *Inorg. Chem.* **25**, 3976–3980.
MacNicol, D. D., Mallinson, P. R. & Robertson, C. D. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1649–1651.
McCleverty, J. A. (1968). *Prog. Inorg. Chem.* **10**, 49–221.
Molecular Structure Corporation (1985, 1992). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Munakata, M., Kuroda-Sowa, T., Maekawa, M., Hirota, A. & Kitagawa, S. (1995). *Inorg. Chem.* **34**, 2705–2710.
Munakata, M., Wu, L. P., Gan, X., Kuroda-Sowa, T. & Suenaga, Y. (1996). *Mol. Cryst. Liq. Cryst.* **284**, 319–327.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst. A* **24**, 351–359.
Ohru, T., Kondo, M., Matsuzaka, H. & Kitagawa, S. (1996). Personal communication.
Rigaku Corporation (1991). *Rigaku/AFC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.
Rivera, N. M. & Engler, E. M. (1979). *J. Chem. Soc. Chem. Commun.* pp. 184–185.
Suenaga, Y., Kuroda-Sowa, T., Munakata, M., Maekawa, M. & Morimoto, M. (1998). *Acta Cryst. C* **54**, 1566–1569.
Suenaga, Y., Kuroda-Sowa, T., Munakata, M., Maekawa, M. & Morimoto, M. (1999). *Polyhedron*, **18**, 429–436.

Acta Cryst. (1999). **C55**, 1625–1627

Bis(imidazolidine-2-thione)gold(I) diiodaurate(I)

STEFFI FRIEDRICH AND PETER G. JONES*

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

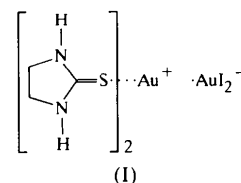
(Received 24 May 1999; accepted 15 June 1999)

Abstract

The title compound, $[\text{Au}(\text{C}_3\text{H}_6\text{N}_2\text{S}_2)_2][\text{AuI}_2]$, is ionic rather than molecular. The Au atoms of both ions lie on inversion centres. The ions are linked to form linear chains by $\text{Au} \cdots \text{Au}$ contacts. Two weak $\text{N} \cdots \text{I}$ hydrogen bonds are observed: one is formed within the chain and one links adjacent chains.

Comment

Imidazoline-2-thione (ethylenethiourea, etu) has been known as a ligand in gold(I) complexes since the work of Morgan & Burstall (1928). Amongst other compounds, they reported $[(\text{etu})_2\text{Au}]\text{Cl} \cdot \text{H}_2\text{O}$, the structure of which was determined, and then recently redetermined with higher precision by us (Jones *et al.*, 1976; Jones & Friedrichs, 1999a); $'[(\text{etu})\text{Au}]_2\text{O}'$, which we have recently shown to be a tetramer of gold(I) with deprotonated etu (Jones & Friedrichs, 1999b); and $(\text{etu})\text{AuI}$, (I), the structure of which we report here.



The asymmetric unit of the title compound is shown in Fig. 1. It is in fact ionic, having the form $[(\text{etu})_2\text{Au}]^+[\text{AuI}_2]^-$, rather than being the molecular $(\text{etu})\text{AuI}$. Both Au atoms lie on inversion centres and thus exhibit ideal linear coordination geometry, with