

at refining a non-centrosymmetric structure by ordering our final structure as an initial model made the value of  $R(F)$  worse by about 1%. Restraints on the geometry of the NH<sub>3-x</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3-x</sub> [enH;  $x = 0.348(2)$ ] molecule were needed to assist refinement using the program *RAELS96* (Rae, 1996). The C atoms make no close contacts and two mirror-related molecules were included in the asymmetric unit. In this fourfold disorder model, the terminal N atoms of the two molecules in an asymmetric unit were conditionally restrained to stay within 0.2 Å (*i.e.* the restraint to be 0.2 Å apart is only included if the distance is greater). The reference molecule was constrained to have a twofold rotation axis, the bonds were restrained to approach 1.54 Å and the N—C—C—N torsion angle constrained to approach -60° (implying the other molecule has a torsion angle approaching 60°). The final occupancy ratio was 0.62(4):0.38(4). The framework atoms were refined as independent anisotropic atoms, but the thermal motion of the enH molecule was refined as having TLX thermal motion with a single re-orientable relocatable libration axis (11 parameters) (Rae, 1975). The occupancy of each of the amine protons were constrained to maintain overall lattice charge neutrality. H atoms were relocated in implied positions after each refinement cycle and given the same displacement parameters as the atoms to which they were attached. An uncorrelated 3% error in  $F$  was included in the estimation of errors for evaluating the weighting scheme. The observation to parameter ratio was influenced by the necessity for a disorder model to fit the data. Constraints were used to reduce the number of variables to an acceptable number. By excluding reflections with  $I_{\text{obs}} < \sigma(I_{\text{obs}})$ , convergence was rapidly obtained with  $\Delta/\sigma < 0.1$  in the final cycle.

Data collection: *XSCANS* (Fait, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *RAELS96*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIFTAB* in *SHELXL93* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1204). Services for accessing these data are described at the back of the journal.

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## A Linear-Chain Copper(I) Coordination Polymer with Hexakis(methylthio)benzene

YUSAKU SUENAGA,<sup>a</sup> TAKAYOSHI KURODA-SOWA,<sup>a</sup> MEGUMU MUNAKATA,<sup>a</sup> MASAHIKO MAEKAWA<sup>b</sup> AND HIROSHI MORIMOTO<sup>a</sup>

<sup>a</sup>Department of Chemistry, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577, Japan, and <sup>b</sup>Research Institute for Science and Technology, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577, Japan. E-mail: suenagay@chem.kindai.ac.jp

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## Abstract

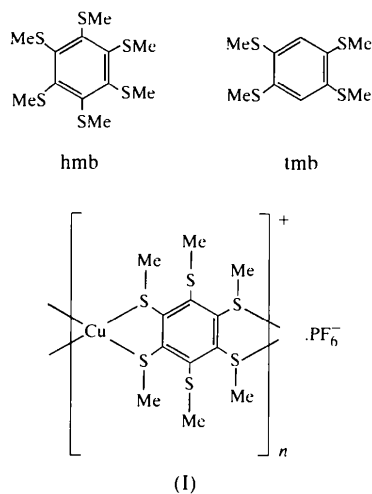
In the structure of *catena*-poly[copper(I)- $\mu$ -[hexakis(methylthio)benzene- $S^1, S^2: S^4, S^5$ ]] hexafluorophosphate,  $\{[\text{Cu}(\text{C}_{12}\text{H}_{18}\text{S}_6)]\text{PF}_6\}_n$ , each Cu atom is coordinated to four S atoms of two hexakis(methylthio)benzene ligands in a tetrahedral arrangement to give a cationic linear-chain polymer. The electrical resistivity of compacted pellets was measured by the conventional two-probe technique. Iodine-doped black products in powder form behave as a semiconductor with a conductivity of  $1.5 \times 10^{-6} \text{ S cm}^{-1}$ .

## Comment

The use of sulfur-containing molecules as precursors for the synthesis of conductive or superconductive materials is of continuing interest. Many metal–dithiolenes complexes have been synthesized and studied (McCleverty, 1968; Eisenberg, 1970; Rivera & Engler, 1979). Cu<sup>I</sup>–halide complexes of tetrakis(methylthio)-tetrathiafulvalene contain organic molecules arranged between copper halide polymeric chains and sheets, with S··S contacts of about 3.6 Å (Munakata *et al.*,

1995). Dirk *et al.* (1986) reported complexes of  $\text{Fe}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  with 1,2,4,5-tetrathio benzene, which have high conductivity and magnetic properties, but the crystal structures were unknown. We subsequently synthesized  $\text{Cu}^{\text{I}}$  complexes of the methyl derivative 1,2,4,5-tetrakis(methylthio)benzene, tmb (Ohru *et al.*, 1996); in  $[(\text{Cu}X)_2(\text{tmb})]$ , there are zigzag chains ( $X = \text{I}$ ) and sheets ( $X = \text{Br}$ ).

We report here the polymeric structure of  $[\text{Cu}(\text{hmb})]\text{PF}_6$ , (I), in which hexakis(methylthio)benzene, hmb, was used in place of tmb, as part of our interest in two- and three-dimensional polymers of metal ions interconnected by aromatic ligands with novel stereochemistry and special physical properties.



Each Cu atom is coordinated by four S atoms from two different hmb ligands in a distorted tetrahedral geometry. All four Cu—S bonds are of equal length, 2.2897 (7) Å, which is shorter than those in the tmb complexes of copper(I) halides ( $X = \text{Br}$ , Cu—S = 2.337 Å;  $X = \text{I}$ , Cu—S = 2.363 Å). The six methyl groups of the ligand are directed out of the benzene plane, three above and three below, alternating. This conformation is different from that of free hmb, which

has the six methyl groups in the benzene plane. Four S atoms of each ligand coordinate to copper, while two mutually *para* S atoms remain uncoordinated. The ligand acts as a bridge between pairs of Cu atoms to give a linear-chain polymer (Fig. 1). This result is different from the two-dimensional sheet and one-dimensional zigzag chain structures of the copper(I)-halide-tmb complexes.

In the crystal structure of  $[\text{Cu}(\text{hmb})]\text{PF}_6$ , the cationic polymer chains are separated by  $\text{PF}_6^-$  anions. Inter-chain distances are large, with no specific stacking interactions; the shortest S...S distance between chains is 4.195 (2) Å, similar to those of the tmb complexes (Table 2), and is larger than twice the van der Waals radius of sulfur (3.6 Å). These complexes thus do not have significant S...S interactions such as are found in  $\text{Cu}^{\text{I}}$  complexes of tetrakis(methylthio)tetrathiafulvalene (Table 2).

The electrical resistivity of compacted pellets of the complex 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  $1.5 \times 10^{-6} \text{ S cm}^{-1}$ . A similar phenomenon has been reported for the corresponding  $\text{Cu}^{\text{I}}$  complexes (Munakata *et al.*, 1996). This is very different from the iodine-doped copper(I) complexes with tmb, which are insulators. One of the common features of conducting complexes is that the constituent molecules are in a mixed-valence state (Torrance, 1979; Inoue *et al.*, 1986). Interestingly, an ESR (electron spin resonance) signal attributable to  $\text{Cu}^{\text{II}}$  ions was detected in the black complex, indicating partial formation of a mixed-valence state.

## Experimental

In a three-necked flask equipped with a magnetic stirring bar, septum cap and argon gas inlet tube was placed sodium methylthiol (2.0 g, 28.5 mmol) and dry 1,3-dimethyl-2-imidazolidinone (16 ml) (Dirk *et al.*, 1985). To this suspension

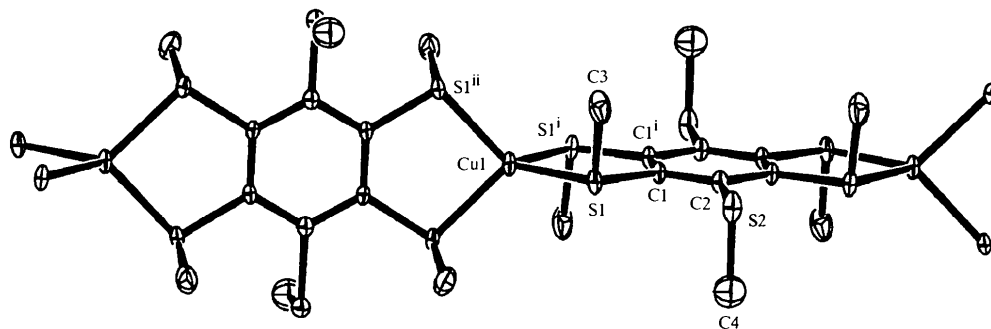


Fig. 1. The structure of  $[\text{Cu}(\text{hmb})]\text{PF}_6$  showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

was added, with stirring, hexafluorobenzene (0.81 g, 0.5 ml, 4.4 mmol) *via* syringe through the septum cap. The addition was at a relatively fast rate, resulting in a mildly exothermic reaction. After 3 d at room temperature, TLC (silica gel, 3:1 hexane/ether) showed only one spot. At this point, the reaction mixture was added to water (50 ml) and the white precipitate was filtered and washed copiously with water and sparingly with cold methanol to yield 1.5 g (98%) of white powder. Recrystallization from chloroform/pentane yielded colourless needles of hmb (1.1 g, 71%; m.p. 361–362 K). IR data [ $\nu$  (cm<sup>-1</sup>)] on KBr discs: 2912 (C—H), 849 (S—CH<sub>3</sub>); <sup>1</sup>H NMR data (CDCl<sub>3</sub>/TMS, 270 MHz):  $\delta$  = 2.52 (s, CH<sub>3</sub>S); MS: *m/z* = 354 (100% *M*). Tetrakis(acetonitrile)copper(I) hexafluorophosphate was prepared according to literature procedures (Kubas *et al.*, 1979). Crystals of [Cu(hmb)]PF<sub>6</sub> were obtained by reaction of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (30 mM) and hmb (20 mM) in acetone under an argon atmosphere. The metal and hmb solutions were poured into a glass tube without mixing. After standing for 1 week at room temperature, light-yellow prismatic crystals were obtained. IR data [ $\nu$  (cm<sup>-1</sup>)] on KBr discs: 2930 (C—H), 839 (PF<sub>6</sub>).

### Crystal data

[Cu(C<sub>12</sub>H<sub>18</sub>S<sub>6</sub>)]PF<sub>6</sub>  
*M<sub>r</sub>* = 563.1  
 Tetragonal  
*I*4/*m*  
*a* = 10.901 (2) Å  
*c* = 17.403 (2) Å  
*V* = 2068.1 (7) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.809 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.7107 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 13.6–16.0°  
 $\mu$  = 1.787 mm<sup>-1</sup>  
*T* = 296.2 K  
 Prismatic  
 0.20 × 0.10 × 0.10 mm  
 Yellow

### Data collection

Rigaku AFC-7R diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: none  
 1357 measured reflections  
 1232 independent reflections  
 908 reflections with *I* > 3 $\sigma$ (*I*)

*R*<sub>int</sub> = 0.018  
 $\theta$ <sub>max</sub> = 27.5°  
*h* = 0 → 14  
*k* = 0 → 14  
*l* = 0 → 22  
 3 standard reflections every 150 reflections  
 intensity decay: 0.7%

### Refinement

Refinement on *F*<sup>2</sup>  
*R* = 0.031  
*wR* = 0.040  
*S* = 1.310  
 908 reflections  
 66 parameters  
 H atoms riding  
*w* = 1/[ $\sigma^2(F_o)$  + 0.00022|*F<sub>o</sub>*|<sup>2</sup>]

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho$ <sub>max</sub> = 0.41 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = -0.40 e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

Cu1—S1	2.2897 (7)	S2—C4	1.796 (7)
S1—C1	1.794 (3)	C1—C1'	1.398 (5)
S1—C3	1.814 (4)	C1—C2	1.407 (3)
S2—C2	1.777 (4)		
S1—Cu1—S1 <sup>ii</sup>	119.26 (2)	S1—C1—C1'	121.52 (9)
S1—Cu1—S1 <sup>i</sup>	91.29 (3)	S1—C1—C2	118.7 (2)

Cu1—S1—C1	102.82 (9)	C1'—C1—C2	119.8 (2)
Cu1—S1—C3	101.0 (1)	S2—C2—C1	119.8 (2)
C1—S1—C3	100.0 (1)	C1—C2—C1 <sup>iii</sup>	120.4 (4)
C2—S2—C4	98.9 (3)		

Symmetry codes: (i) 1 - *x*, -*y*, *z*; (ii)  $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$ ; (iii) *x*, *y*, -*z*.

Table 2. Electroconductive properties and bonding properties of copper(I) complexes with sulfur-rich ligands

	Dim <sup>†</sup>	$\sigma_{298\text{K}}^{\ddagger}$ (S cm <sup>-1</sup> )	S...S (Å)	Cu—S (Å)	S—Cu—S (°)
[Cu(hmb)]PF <sub>6</sub> <sup>a</sup>	1	1.5 × 10 <sup>-6</sup>	4.195 (2)	2.2897 (7)	91.29 (3)– 119.26 (2)
[(CuI) <sub>2</sub> (tmb)] <sup>b</sup>	1	Insulator	3.93	2.363 (5)	85.57 (6)
[(CuBr) <sub>2</sub> (tmb)] <sup>c</sup>	2	Insulator	4.4	2.337 (1)	105.31 (4)
[(CuBr) <sub>2</sub> -(TMT-TTF)] <sup>d</sup> §	2	1.3 × 10 <sup>-2</sup>	3.68	2.419 (2)	87.13 (6)
[Cu(TTC <sub>2</sub> -TTF)]-ClO <sub>4</sub> <sup>e</sup> ¶	1	6.0 × 10 <sup>-1</sup>	4.0	2.311 (2)	93.1 (1)– 122.2 (1)

† Dim = dimension. ‡ After iodine doping. § TMT-TTF = tetrakis-(methylthio)tetrathiafulvalene. ¶ TTC<sub>2</sub>-TTF = tetrakis(ethylthio)-tetrathiafulvalene.

References: (a) this work; (b) Ohru *et al.* (1996); (c) Suenaga *et al.* (1997); (d) Munakata *et al.* (1996); (e) Gan *et al.* (1995).

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1991). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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### *cis-syn-cis*-Dicyclohexano-18-crown-6 Sodium Perrhenate†

JEFFREY C. BRYAN

*Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, USA.  
E-mail: bryanjc@ornl.gov*

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#### Abstract

The effect of the anion in a crown ether–cation structure is examined by comparing the structure of [ $\{\text{Na}(\text{C}_{20}\text{H}_{36}\text{O}_6)\}(\text{ReO}_4)$ ] with one containing the same crown ether and cation, but a different anion. The title compound shows that the crown ether does not form an ideal cavity for sodium, as the Na–O bond lengths vary from 2.470 (4) (O3) to 2.863 (4) Å (O1).

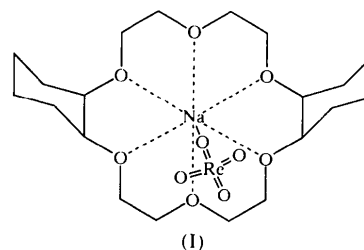
#### Comment

As part of our current research investigating the role played by the anion in cation-separation processes (Moyer & Bonnesen, 1997), we are interested in examining perturbations of the cation–crown structure when the anion is varied.

Only one structure of the  $\text{Na}^+$  ion with *cis-syn-cis*-dicyclohexano-18-crown-6 ether (csc-DC18C6) has been reported. The anion is phenolate, and it forms a 1:2 host–guest complex, with the crown ether adopting a ‘highly irregular conformation’. The irregularity is a result of the displacement of two cyclohexano ether O atoms by 1.9 and 2.6 Å out of the plane defined by the four other donors. The phenolate anion is bound to sodium on the crown ether face opposite that of the two bulky cyclohexano groups, and is a bridging group to an uncomplexed ion pair (Fraser *et al.*, 1986).

The structure of the title compound, (I) (Fig. 1), is quite different from the phenolate complex described above. A 1:1 host–guest stoichiometry and a confor-

† Alternative name: (2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0<sup>9,14</sup>]hexacosane-2κ<sup>6</sup>O)-μ-oxo-1:2κ<sup>2</sup>O-trioxo-1κ<sup>3</sup>O-rheniumsodium.



mation more typical of crown ethers are observed. The  $\text{Na}^+$  ion is seven-coordinate, with the donor atoms arranged in a capped trigonal prism geometry. The four cyclohexano O-donor atoms (O1, O2, O4 and O5) and sodium are coplanar, with a maximum deviation from this plane of 0.023 (4) Å (O2 and O4). The other two ether O atoms deviate from this plane by 0.929 (5) (O6) and 1.532 (5) Å (O3).  $\text{Na}^+$  sits in the plane defined by O1, O2, O4 and O5 [deviation 0.012 (3) Å], yet is displaced by 0.111 (3) Å from the calculated centroid of these four O atoms. The Na–O bond distances (Table 1) vary considerably in this structure. A similar variability has been observed previously in sodium–DC18C6 complexes (Fraser *et al.*, 1986; Mercer & Truter, 1973). This consistent variability may be one factor in understanding why the  $\text{Na}^+$  ion is not extracted as well as the slightly larger  $\text{K}^+$  ion by DC18C6 (Pedersen & Frensdorff, 1972; Fraser *et al.*, 1986; Hay & Rustad, 1994).

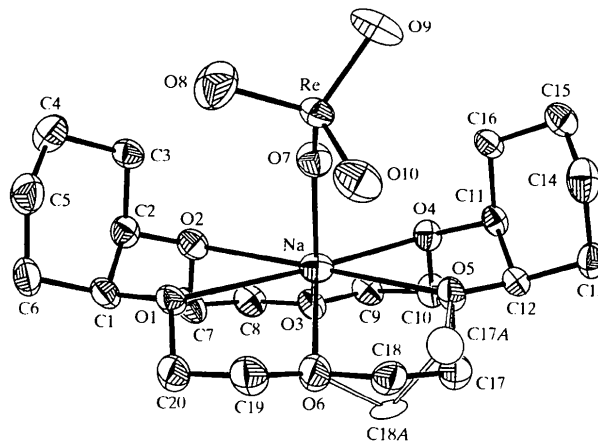


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. The minor components of disorder are drawn only with a boundary ellipse. H atoms have been omitted for clarity.

The perrhenate anion is bound to sodium through one O atom and is on the same side of the crown ether as the two cyclohexyl groups. The Na–O7 bond distance [2.286 (5) Å] is significantly shorter than the distance of 2.378 (8) Å reported for (15-crown-5)NaReO<sub>4</sub> (Weller *et al.*, 1989), the only other structurally characterized