Table 2. *Selected bond lengths* (Å) *and angles* (°)

Os(1)—Os(2)	3.088 (1)	Os(1)—Os(3)	2.869 (1)
Os(1)—P	2.386 (4)	Os(1)—C(1)	1.897 (16)
Os(1)—C(2)	1.905 (16)	Os(1)—C(3)	1.890 (15)
Os(1)—H(1)	1.844 (1)	Os(2)—Os(3)	2.797 (1)
Os(2)—C(4)	1.957 (14)	Os(2)—C(5)	1.856 (17)
Os(2)—C(6)	1.867 (16)	Os(2)—C(10)	2.159 (12)
Os(2)—H(1)	1.851 (1)	Os(2)—H(2)	1.854 (1)
Os(3)—C(7)	1.892 (16)	Os(3)—C(8)	1.903 (14)
Os(3)—C(9)	1.908 (15)	Os(3)—C(10)	2.187 (14)
Os(3)—H(2)	1.850 (1)	P—C(111)	1.90 (2)
P—C(121)	1.792 (17)	P—C(131)	1.82 (3)
Os(2)—Os(1)—Os(3)	55.9 (1)	Os(2)—Os(1)—P	118.2 (1)
Os(2)—Os(1)—C(1)	141.2 (5)	Os(2)—Os(1)—C(2)	95.8 (5)
Os(2)—Os(1)—C(3)	80.3 (5)	Os(2)—Os(1)—H(1)	33.4 (1)
Os(3)—Os(1)—P	173.7 (1)	Os(3)—Os(1)—C(1)	86.5 (5)
Os(3)—Os(1)—C(2)	87.0 (5)	Os(3)—Os(1)—C(3)	90.0 (5)
Os(3)—Os(1)—H(1)	88.1 (1)	P—Os(1)—C(1)	99.8 (5)
P—Os(1)—C(2)	91.9 (5)	P—Os(1)—C(3)	90.9 (5)
P—Os(1)—H(1)	85.7 (1)	C(1)—Os(1)—C(2)	90.7 (7)
C(1)—Os(1)—C(3)	91.8 (7)	C(1)—Os(1)—H(1)	174.5 (5)
C(2)—Os(1)—C(3)	175.9 (7)	C(2)—Os(1)—H(1)	89.6 (5)
C(3)—Os(1)—H(1)	87.6 (5)	Os(1)—Os(2)—Os(3)	58.1 (1)
Os(1)—Os(2)—C(4)	93.5 (5)	Os(1)—Os(2)—C(5)	158.7 (5)
Os(1)—Os(2)—C(6)	107.8 (5)	Os(1)—Os(2)—C(10)	78.2 (4)
Os(1)—Os(2)—H(1)	33.2 (1)	Os(1)—Os(2)—H(2)	75.5 (1)
Os(3)—Os(2)—C(4)	119.9 (5)	Os(3)—Os(2)—C(5)	101.9 (5)
Os(3)—Os(2)—C(6)	136.8 (4)	Os(3)—Os(2)—C(10)	50.4 (4)
Os(3)—Os(2)—H(1)	90.1 (1)	Os(3)—Os(2)—H(2)	40.9 (1)
C(4)—Os(2)—C(5)	91.0 (7)	C(4)—Os(2)—C(6)	100.4 (6)
C(4)—Os(2)—C(10)	169.6 (6)	C(4)—Os(2)—H(1)	84.2 (4)
C(4)—Os(2)—H(2)	83.8 (4)	C(5)—Os(2)—C(6)	91.8 (7)
C(5)—Os(2)—C(10)	94.7 (6)	C(5)—Os(2)—H(1)	167.9 (5)
C(5)—Os(2)—H(2)	84.3 (5)	C(6)—Os(2)—C(10)	88.1 (6)
C(6)—Os(2)—H(1)	78.2 (5)	C(6)—Os(2)—H(2)	174.4 (5)
C(10)—Os(2)—H(1)	91.9 (5)	C(10)—Os(2)—H(2)	88.1 (4)
H(1)—Os(2)—H(2)	106.1 (1)	Os(1)—Os(3)—Os(2)	66.0 (1)
Os(1)—Os(3)—C(7)	173.0 (4)	Os(1)—Os(3)—C(8)	91.6 (5)
Os(1)—Os(3)—C(9)	90.2 (4)	Os(1)—Os(3)—C(10)	82.9 (4)
Os(1)—Os(3)—H(2)	81.6 (1)	Os(2)—Os(3)—C(7)	107.0 (4)
Os(2)—Os(3)—C(8)	133.3 (5)	Os(2)—Os(3)—C(9)	120.0 (4)
Os(2)—Os(3)—C(10)	49.5 (3)	Os(2)—Os(3)—H(2)	41.0 (1)
C(7)—Os(3)—C(8)	94.0 (6)	C(7)—Os(3)—C(9)	92.9 (7)
C(7)—Os(3)—C(10)	93.0 (7)	C(7)—Os(3)—H(2)	92.6 (4)
C(8)—Os(3)—C(9)	99.3 (6)	C(8)—Os(3)—C(10)	89.2 (6)
C(8)—Os(3)—H(2)	172.7 (5)	C(9)—Os(3)—C(10)	169.2 (5)
C(9)—Os(3)—H(2)	83.5 (4)	C(10)—Os(3)—H(2)	87.3 (4)

The title complex was obtained in very low yield (0.5%) from the reaction between $Os_3(\mu\text{-}H)_2(CO)_9(P^iPr_3)$ and $Pt(PCy_3)(C_2H_4)_2$, which was used to prepare $Os_3Pt(\mu\text{-}H)_2(CO)_9$(*Pt*-$PCy_3$)(*Os*-$P^iPr_3$) (Farrugia & Rae, 1991). ^1H NMR data (CD_2Cl_2, 218 K), δ: 6.64 [*q*, 1H, $C\underline{H}CH_3$, J(H-H) = 7.3 Hz], 2.45 [*d*, 3H, $CHC\underline{H}_3$, J(H-H) = 7.3 Hz], 2.21 [septet, 3H, $C\underline{H}Me_2$, J(H-H) = 7.1 Hz], 1.10 [*dd*, 18H, $CH(C\underline{H}_3)_2$, J(H-H) = 7.1, J(P-H) = 14.9 Hz], −14.35 [*s*, 1H, Os(μ-H)Os], −20.96 p.p.m. [*d*, 1H, Os(μ-H)Os, J(P-H) = 9.7 Hz]. $^{31}P\{^1H\}$ NMR data (CD_2Cl_2, 190 K), δ: 26.1 p.p.m. (*s*). No signals from an ethyl tautomer (Cree-Uchiyama *et al.*, 1986) were detected either immediately, or on standing for 12 h.

Systematic absences $k = 2n+1$ in $0k0$, $h+l = 2n+1$ in $h0l$ were observed for the data crystal. Data were corrected for decomposition and Lp effects.

The structure was solved by direct methods (*MITHRIL*; Gilmore, 1984), and subsequent full-matrix least-squares refinement included anisotropic thermal parameters for all non-H atoms. Aliphatic H atoms were included at calculated positions (C—H = 1.0 Å) for the methyl and isopropyl groups with fixed contributions to the structure factors. The methine H atom on the ethylidene group was not observed in difference maps and was not included. The metal hydride positions were determined using potential-energy minimization (*HYDEX*; Orpen, 1980) with Os—H = 1.85 Å. Calculations were carried out on a MicroVAX 3600 computer using the Glasgow *GX* suite of programs (Mallinson & Muir, 1985).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71126 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1037]

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Electrooxidation of the Redox Tertiary Phosphine 4-(Diphenylphosphino)-4′,5,5′-trimethyltetrathiafulvalene (P_1) and the Structure of $(P_1O^{\bullet +})_2Mo_6Br_{14}^{2-}$

SILVIA JARCHOW,† MARC FOURMIGUÉ* AND PATRICK BATAIL

Laboratoire de Physique des Solides associé au CNRS, Université Paris-Sud, Bâtiment 510, F-91405 Orsay, France

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Abstract

Electrooxidation of the diphenyl(4′,5,5′-trimethyl-1,1′,3,3′-tetrathia-4-fulvalenyl)phosphine (hereafter P_1) in the presence of $(^nBu_4N^+)_2Mo_6Br_{14}^{2-}$ affords the cation radical salt diphenyl[4-(4′,5,5′-trimethyl-1,1′,3,3′-tetrathia-4-fulvalenyl)]phosphoniumyl oxide–hexamolybdenum tetradecabromide (2/1),

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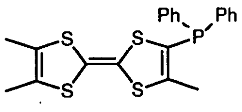
† Erasmus student on leave from the University of Hannover, Germany.

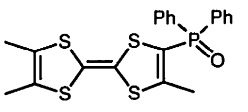
$(P_1O^{+\bullet})_2Mo_6Br_{14}^{2-}$, where P_1O is diphenyl(3′,4,4′-trimethyl-1,1′,3,3′-tetrathia-4-fulvalenyl)phosphine oxide. The $P_1O^{+\bullet}$ cation radicals are located in general positions and the $Mo_6Br_{14}^{2-}$ anions are located on inversion centres. The intramolecular bond distances and angles are as expected for mono-oxidized tetrathiafulvalenes. The P-atom environment is approximately tetrahedral with O—P—C angles of 113.3 (5), 113.6 (5) and 113.9 (5)°. The molybdenum halide cluster core symmetry is O_h, within the estimated standard deviations.

Comment

Tetrathiafulvalene derivatives have been used widely for the elaboration of conducting and superconducting charge-transfer or cation-radical salts. In the search for non-planar redox-active molecules bearing several redox centres, we described recently the synthesis and structure of the tertiary phosphine $P(TTF)_3$ where TTF is tetrathiafulvalene (Fourmigué & Batail, 1991) and extended this work to other tertiary phosphines bearing only one or two TTF moieties (Fourmigué & Batail, 1992). In this paper, we describe the first example of a cation-radical salt of such a phosphine, namely the (diphenylphosphino)trimethyltetrathiafulvalene (P_1). The structure of a salt of the phosphine oxide P_1O with the molybdenum bromide cluster $Mo_6Br_{14}^{2-}$ $[(P_1O^{\bullet +})_2(Mo_6Br_{14}^{2-})]$ is reported, as well as its transport and magnetic properties.



P_1



P_1O

Since the structure determination concludes to the presence of the phosphine oxide cation radical, it is likely that the electrogenerated ${P_1}^{\bullet +}$ becomes oxidized to the phosphine oxide by reaction with traces of water. The TTF moiety of $P_1O^{\bullet +}$ shows some deviation from planarity. The dithiole ring bearing the Ph_2PO substituent is folded by 4 (1)° along the S(3)—S(4) axis, while the other dithiole ring is planar. Intramolecular distances within the mono-oxidized tetrathiafulvalene moiety are in the expected range when compared with those in $TMTFF^{+\bullet}$ in $(TMTTF^{+\bullet})_2Mo_6Cl_{14}^{2-}$ (Ouahab, Batail, Perrin & Garrigou-Lagrange, 1986). The P atom exhibits a distorted tetrahedral environment. The P═O bond [1.509 (9) Å] is noticeably longer than in Ph_3PO [1.46 (1) Å (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970)] or in $(o\text{-tolyl})_3PO$ [1.47 (2) Å (Cameron & Dahlen, 1975)]. This bond weakening may indicate a significant interaction of the P═O π electrons with the π system of the tetrathiafulvalenyl group.

Only a few substituted species with the $[Mo_6Br_8]$ core have been reported so far and structural determinations are scarce (Batail, Livage, Parkin, Coulon, Martin & Canadell, 1991). The cluster anion $Mo_6Br_{14}^{2-}$ is located on an inversion centre and the $[Mo_6Br_8]$ core exhibits O_h symmetry, within the estimated standard deviations. The anion may be described as an octahedron of six Mo atoms with eight face-capping Br atoms. Finally, each of the six Mo atoms binds to an outer Br atom in an apical position. Averaged intramolecular distances in $Mo_6Br_{14}^{2-}$ amount to 2.633 (3) Å for Mo—Mo, 2.598 (4) Å for Mo—Br_{int} and 2.590 (1) Å for Mo—Br_{term} distances. These values are identical to those reported for the same cluster in the ternary compounds $(TTF^{\bullet +})_3(X^-)(Mo_6Br_{14}^{2-})$, $X = Cl$, Br, I (Batail *et al.*, 1991). Note also that the averaged Mo—Mo distance (2.633 Å) is significantly larger than that measured in the isostructural chloride analogue $Mo_6Cl_{14}^{2-}$ [2.606 Å (Ouahab *et al.*, 1986; Batail *et al.*, 1991)]. This may be ascribed to the increased steric hindrance of the larger Br atoms.

In the solid, $P_1O^{\bullet +}$ and $Mo_6Br_{14}^{2-}$ aggregate in a very unusual way (Fig. 1). The organic cation radicals do not stack on top of each other to form dimers or stacks of donor molecules, as observed in the other tetrathiafulvalene salts with such large inorganic cluster anions like $Re_6S_5Cl_9^-$ (Boubekeur, Gabriel & Batail, 1993; Gabriel, Johannsen, Batail & Coulon, 1993), $Mo_6Cl_{14}^{2-}$ (Ouahab *et al.*, 1986) or $Nb_6Cl_{18}^{3-}$ (Pénicaud, Batail, Coulon, Canadell & Perrin, 1990). Instead, discrete single cation radicals are interspersed in the solid, a likely consequence of the steric hindrance of the large Ph_2PO substituent. Each cluster anion, $Mo_6Br_{14}^{2-}$, appears to be sandwiched between two parallel tetrathiafulvalenyl moieties of the $P_1O^{\bullet +}$ molecules, thus forming mixed $[(P_1O^{\bullet +})(Mo_6Br_{14}^{2-})(P_1O^{\bullet +})]$ units.

As expected for discrete cation radicals, the material is insulating. EPR (electron paramagnetic resonance) experiments were conducted on an oriented single crystal from 293 to 294 K. A single Lorentzian line is observed at room temperature. The extremes of the g values and line widths are found when the faces of the crystal are oriented perpendicular to the field. They are respectively 2.0061 [$\Delta H_{pp} = 15.4$ G (1G = 10^{-4} T)] 2.0074 ($\Delta H_{pp} = 7$ G) and 2.0116 ($\Delta H_{pp} = 7.5$ G). The temperature dependance of the EPR line width has been investigated for the orientation where the g_{max} value is observed. It increases smoothly from 7.5 to 10 G upon cooling, suggesting the lack of any sizeable interaction between the organic radical spins, in agreement with the observation of a Curie-type spin susceptibility.

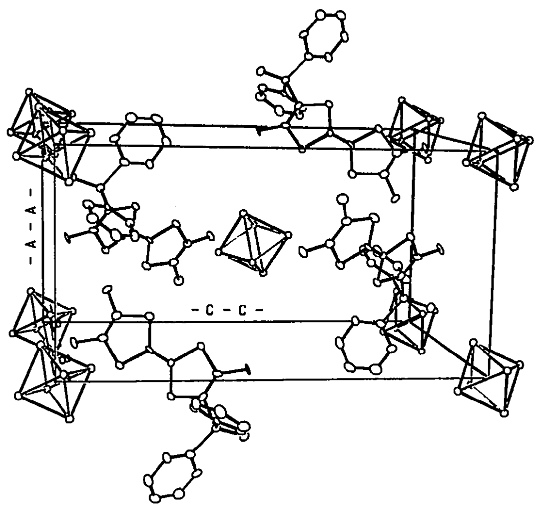


Fig. 1. A view of the unit cell. Br atoms on the $Mo_6Br_{14}^{2-}$ cluster anions have been omitted for clarity.

Experimental

Crystal data

$2[C_{21}H_{19}OPS_4^{+\bullet}][Mo_6Br_{14}^{2-}]$
$M_r = 2587.6$
Monoclinic
$P2_1/n$
$a = 10.941\ (5)$ Å
$b = 14.585\ (4)$ Å
$c = 21.201\ (5)$ Å
$\beta = 90.83\ (3)°$
$V = 3383\ (3)$ Å^3
$Z = 2$
$D_x = 2.54$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–$13.5°$
$\mu = 9.566$ mm^{-1}
$T = 293$ K
Platelet
$0.30 \times 0.21 \times 0.04$ mm
Black

Data collection

Enraf–Nonius CAD-4*F* diffractometer
ω-2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.71$, $T_{max} = 1.34$
7299 measured reflections
5674 independent reflections
2882 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.025$
$\theta_{max} = 26°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -26 \rightarrow 26$
3 standard reflections monitored every 400 reflections
intensity variation: 1.3%

Refinement

Refinement on *F*
Final $R = 0.045$
$wR = 0.051$
$S = 1.63$
2882 reflections
334 parameters
H-atom parameters not refined

$w = 4F_o^2/[\sigma^2(I) + (0.04F_o^2)^2]$
$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}
Mo(1)	0.0666 (1)	0.11563 (7)	0.01506 (6)	2.37 (2)
Mo(2)	−0.0471 (1)	0.03660 (8)	−0.08090 (6)	2.44 (3)
Mo(3)	−0.1491 (1)	0.04016 (8)	0.03091 (6)	2.54 (3)
Br(1)	0.1598 (2)	0.27644 (9)	0.03781 (8)	3.64 (4)
Br(2)	−0.1108 (2)	0.0849 (1)	−0.19420 (8)	4.22 (4)
Br(3)	−0.3552 (2)	0.0963 (1)	0.0741 (1)	5.41 (5)
Br(4)	0.2597 (1)	0.0380 (1)	0.06430 (8)	3.58 (4)
Br(5)	−0.1281 (1)	0.18974 (9)	−0.03438 (8)	3.43 (4)
Br(6)	0.1663 (1)	0.11052 (9)	−0.09562 (7)	3.31 (3)
Br(7)	−0.0359 (2)	0.1172 (1)	0.12489 (8)	3.93 (4)
S(1)	−0.0306 (4)	0.6592 (3)	0.1624 (2)	3.45 (9)
S(2)	0.1861 (4)	0.6208 (3)	0.2359 (2)	4.1 (1)
S(3)	0.0814 (4)	0.7455 (2)	0.3494 (2)	3.21 (9)
S(4)	−0.1377 (4)	0.7808 (3)	0.2755 (2)	3.27 (9)
P	−0.2408 (4)	0.9182 (3)	0.3710 (2)	3.35 (9)
O	−0.283 (1)	0.9013 (7)	0.4374 (5)	4.6 (3)
C(1)	0.000 (1)	0.7277 (8)	0.2795 (6)	2.3 (3)
C(2)	0.046 (1)	0.6748 (9)	0.2324 (7)	2.9 (3)
C(3)	0.079 (1)	0.5912 (8)	0.1269 (7)	3.2 (3)
C(4)	0.178 (1)	0.5717 (9)	0.1612 (8)	3.8 (4)
C(5)	−0.025 (1)	0.8191 (9)	0.3816 (7)	3.0 (3)
C(6)	−0.124 (1)	0.8393 (9)	0.3463 (7)	3.2 (3)
C(7)	0.048 (1)	0.554 (1)	0.0614 (7)	4.2 (4)
C(8)	0.282 (1)	0.513 (1)	0.1408 (8)	5.6 (4)
C(9)	0.004 (2)	0.855 (1)	0.4473 (8)	5.0 (4)
C(10)	−0.171 (1)	1.0279 (9)	0.3600 (6)	2.8 (3)
C(11)	−0.102 (1)	1.049 (1)	0.3080 (8)	4.3 (4)
C(12)	−0.058 (2)	1.137 (1)	0.3022 (8)	5.3 (5)
C(13)	−0.073 (2)	1.200 (1)	0.3495 (9)	6.1 (5)
C(14)	−0.143 (2)	1.180 (1)	0.4020 (8)	5.0 (5)
C(15)	−0.189 (1)	1.093 (1)	0.4072 (8)	4.2 (4)
C(20)	−0.361 (1)	0.9072 (9)	0.3116 (7)	3.4 (4)
C(21)	−0.465 (1)	0.859 (1)	0.3303 (7)	4.0 (4)
C(22)	−0.560 (2)	0.849 (1)	0.2901 (9)	5.7 (5)
C(23)	−0.562 (2)	0.890 (1)	0.2315 (9)	5.8 (5)
C(24)	−0.461 (2)	0.941 (1)	0.2125 (8)	5.1 (4)
C(25)	−0.360 (1)	0.950 (1)	0.2541 (7)	4.1 (4)

Table 2. *Geometric parameters* (Å, °)

S(1)—C(2)	1.71 (1)	P—C(6)	1.81 (1)
S(1)—C(3)	1.74 (3)	P—C(10)	1.79 (1)
S(2)—C(2)	1.72 (1)	P—C(20)	1.81 (1)
S(2)—C(4)	1.74 (1)	C(1)—C(2)	1.37 (1)
S(3)—C(1)	1.74 (1)	C(3)—C(4)	1.33 (2)
S(3)—C(5)	1.73 (1)	C(3)—C(7)	1.52 (2)
S(4)—C(1)	1.69 (1)	C(4)—C(8)	1.49 (2)
S(4)—C(6)	1.73 (1)	C(5)—C(6)	1.34 (2)
P—O	1.509 (9)	C(5)—C(9)	1.52 (2)
C(2)—S(1)—C(3)	96.8 (6)	S(2)—C(2)—C(1)	124.5 (9)
C(2)—S(2)—C(4)	96.7 (6)	S(1)—C(3)—C(4)	117.1 (1)
C(1)—S(3)—C(5)	95.0 (6)	S(1)—C(3)—C(7)	116.9 (6)
C(1)—S(4)—C(6)	96.5 (6)	C(4)—C(3)—C(7)	127 (1)
O—P—C(6)	113.3 (5)	S(2)—C(4)—C(3)	116 (1)
O—P—C(10)	113.9 (5)	S(2)—C(4)—C(8)	118 (1)
O—P—C(20)	113.6 (5)	C(3)—C(4)—C(8)	126 (1)
C(6)—P—C(10)	102.9 (5)	S(3)—C(5)—C(6)	117 (1)
C(6)—P—C(20)	104.6 (6)	S(3)—C(5)—C(9)	116.4 (9)
C(10)—P—C(20)	107.2 (6)	C(6)—C(5)—C(9)	126 (1)
S(3)—C(1)—S(4)	114.8 (6)	P—C(6)—C(5)	123 (1)
S(3)—C(1)—C(2)	121.0 (9)	P—C(10)—C(11)	123 (1)
S(4)—C(1)—C(2)	124.2 (9)	P—C(10)—C(15)	116.5 (9)
S(1)—C(2)—S(2)	113.8 (7)	P—C(20)—C(21)	116 (1)
S(1)—C(2)—C(1)	121.7 (9)	P—C(20)—C(25)	125 (1)

P_1 was prepared as previously described by reacting the trimethyltetrathiafulvalene lithium derivative with Ph_2PCl in

Et_2O at 203 K (Fourmigué, Jarchow & Batail, 1993). Electrochemical oxidation of P_1 (20 mg) was conducted at 293 K in a 2×10^{-3} *M* solution (25 ml) of $(^n\text{Bu}_4\text{N}^+)_2(\text{Mo}_6\text{Br}_{14}{}^{2-})$ (Nanneli & Block, 1970) in a mixture CH_3CN/DMF (95:5) using a constant current density of 5 μA cm^{-2}. Crystals were collected on the platinum electrode after one week and washed with the minimum amount of CH_3CN.

The crystal system and space group were determined from oscillation and Weissenberg photographs. Systematic absences unambiguously led to the space group $P2_1/n$. The selected crystal was mounted along the longest direction. The scan range was $(1 + 0.35\tan\theta)^\circ$. Data were corrected for Lorentz–polarization effects as well as for intensity decay.

Mo atoms were located on a Patterson map and the other atoms were located by successive difference Fourier syntheses. H atoms were introduced at calculated positions. All atoms except H atoms were then refined anisotropically. Calculations were carried out with the *SDP* software (Frenz, 1978).

ESR spectra were recorded on a Varian X-band spectrometer (frequency 9.3 GHz) equipped with an Oxford ER 900 helium cryostat.

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Lists of structure factors, general displacement parameters, H-atom coordinates, bond distances and angles, including H-atom geometry, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71299 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1039]

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Structure of Tetramethylammonium Tetrabromocobaltate at Room Temperature

YASUO NISHIHATA* AND AKIKATSU SAWADA

Faculty of Science, Okayama University, Okayama 700, Japan

HIROFUMI KASATANI AND HIKARU TERAUCHI

School of Science, Kwansei Gakuin University, Nishinomiya 662, Japan

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Abstract

The structure of tetramethylammonium tetrabromocobaltate, $[N(CH_3)_4]_2CoBr_4$, has been determined at room temperature by single-crystal X-ray diffraction. The thermal parameters of the Br and C atoms are unusually large and highly anisotropic. The electron-density contour map and Hamilton significance test indicate that two non-equivalent kinds of $N(CH_3)_4$ molecule and one kind of $CoBr_4$ molecule are all disordered symmetrically with respect to mirror planes. The $CoBr_4$ tetrahedron is almost undistorted, while the distortions of the $N(CH_3)_4$ tetrahedra are large.

Comment

Compounds of the type $[N(CH_3)_4]_2M\text{Br}_4$, with $M =$ Zn, Co, Mn and Cd, undergo a second-order phase transition from *Pmcn* in the normal phase to $P2_1/c$ in the ferroelastic phase. Crystal structures of the compounds where *M* is Zn, Mn and Cd have been reported {$[N(CH_3)_4]_2ZnBr_4$ (Trouelan, Lefebvre & Derollez, 1984, 1985; Asahi, Hasebe & Gesi, 1988), $[N(CH_3)_4]_2MnBr_4$ (Hasebe & Asahi, 1989; Hasebe, Asahi & Gesi, 1990) and $[N(CH_3)_4]_2CdBr_4$ (Asahi, Hasebe & Gesi, 1992)}.

Anomalous temperature dependences of the monoclinic angle β were reported for these compounds. The deviation, $\Delta\beta$, of the monoclinic angle from 90°, increases rapidly to the maximum value below the transition temperature T_c, and gradually decreases with decreasing temperature (Hasebe, Mashiyama, Tanisaki & Gesi, 1984). The behaviour suggests that it does not represent a primary order parameter of the phase transition and that the spontaneous strain consists of sublattice strains with opposite signs and different magnitudes (Sawada, 1991). In this group of compounds, unusually large thermal parameters of the Br and C atoms have been

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