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 $(^n\mathrm{Bu_4N^+})_2(\mathrm{Mo_6Br_{14}}^{2-})$ (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]

References

Bandoli, G., Bortolozzo, G., Clemente, D. A., Croatto, U. & Panattoni, C. (1970). *J. Chem. Soc.* pp. 2778–2780.

Batail, P., Livage, C., Parkin, S. S. P., Coulon, C., Martin, J. D. & Canadell, E. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 1498–1500.

Boubekeur, K., Gabriel, J.-C. & Batail, P. (1993). *Inorg. Chem.* **32**, 2894–2900.

Cameron, T. S. & Dahlen, B. (1975). *J. Chem. Soc. Perkin Trans.* pp. 1737–1751.

Fourmigué, M. & Batail, P. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1370–1372.

Fourmigué, M. & Batail, P. (1992). *Bull. Soc. Chim. Fr.* **129**, 29–36.

Fourmigué, M., Jarchow, S. & Batail, P. (1993). *Phosphorus Sulfur*, **75**, 175–178.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Gabriel, J.-C., Johannsen, I., Batail, P. & Coulon, C. (1993). *Acta Cryst.* C**49**, 1052–1056.

Nanneli, P. & Block, B. P. (1970). *Inorg. Synth.* **12**, 170–178.

Ouahab, L., Batail, P., Perrin, C. & Garrigou-Lagrange, C. (1986). *Mater. Res. Bull.* **21**, 1223–1230.

Pénicaud, A., Batail, P., Coulon, C., Canadell, E. & Perrin, C. (1990). *Chem. Mater.* **2**, 123–132.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1993). C**49**, 1939–1941

Structure of Tetramethylammonium Tetrabromocobaltate at Room Temperature

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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 $[N(CH_3)_4]_2MBr_4$, 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 reported, together with highly anisotropic thermal motion, suggesting disordering of the tetrahedral molecules with regard to mirror planes. Recently, Asahi *et al.* (1992) showed electron-density contour maps with double peaks around C atoms with respect to the mirror planes. The crystal structure of $[N(CH_3)_4]_2CoBr_4$ has not been studied previously. The structure analysis of the title compound was undertaken in the normal phase in order to clarify the microscopic origin of the sublattice strains.

Single crystals of $[N(CH_3)_4]_2CoBr_4$ were grown by slow evaporation from an aqueous solution which contained $N(CH_3)_4Br$ and $CoBr_2$ in stoichiometric molar ratio. The crystal structure was studied at 300 K, above the transition temperature T_c of 287 K. Systematic absences of the observed reflections were checked. The space group and the setting of crystal axes were assigned according to Hasebe *et al.* (1984). At the initial stage of the analysis we tried an ordered model in which each atom was assumed to have mirror symmetry. Positional parameters of $[N(CH_3)_4]_2ZnBr_4$ by Trouelan *et al.* (1984) were used as the starting parameters of the non-H atoms. The least-squares calculations, with 72 parameters refined, converged at the discrepancy factors $R = 0.0672$ and $wR = 0.0512$ for 727 independent reflections. It was found that the thermal parameters of the Br and C atoms were unusually large and the thermal motion of the atoms was highly anisotropic, as already reported for the other compounds in this group. A difference Fourier synthesis produces the electron-density contour map of the C(2) atom near the mirror plane (Fig. 1). Two maxima, which are separated by 0.63 Å within the resolution estimated as 0.6 $\lambda/2\sin\theta_{\max} \simeq 0.5$ Å, represent the disorder of the C(2) atom around the mirror plane. Similar electron-density maps were obtained around all the other C atoms, implying that both of the non-equivalent $N(CH_3)_4$ molecules are in a disordered state at room temperature. On the other hand, two maxima were not found around the Br atoms.

At the second stage of the analysis, we examined a partly disordered model in which the $CoBr_4$ molecules are still in the ordered state, while two non-equivalent $N(CH_3)_4$ molecules are disordered with respect to the mirror plane. That is, the C atoms were split into two symmetric positions with respect to the mirror plane at $x = 0.25$ with equal probability (split-atom method). The least-squares calculations, with 111 parameters refined, converged at $R = 0.0635$ and $wR = 0.0482$.

Finally, we refined the structure with a fully disordered model in which the $CoBr_4$ tetrahedron is in a disordered state with respect to the mirror plane, as well as the $N(CH_3)_4$ tetrahedra. Here we assumed that the Co, N(1) and N(2) atoms were on the mirror plane ($x = 0.25$) at all times since the electron-density distribution for these atoms was almost isotropic and the centre of the distribution was located on the mirror plane. Thus, the split-atom method was applied to the Br and the C atoms. From the significance test proposed by Hamilton (1965), the second model was rejected in comparison with the fully disordered model at the significance level 0.005; $R = 0.0482/0.0465 = 1.037$ (3) $> R_{15,601,0.005} = 1.0274$. We can conclude that all the tetrahedra are disordered symmetrically with respect to the mirror planes at room temperature.

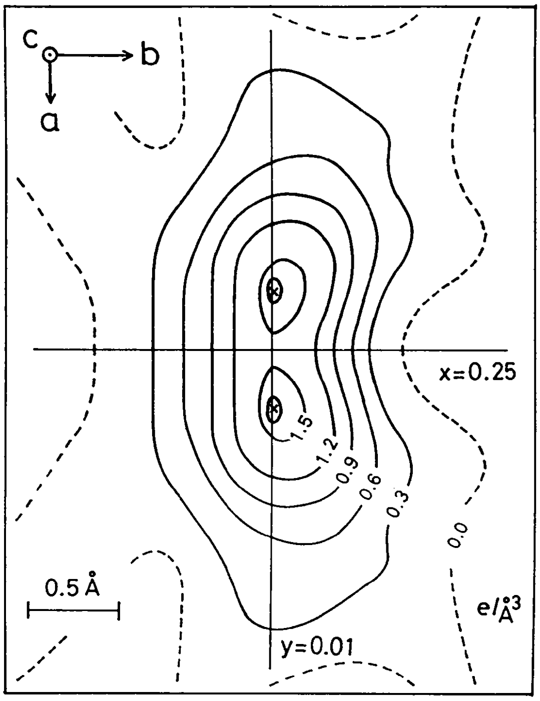

Fig. 1. Electron-density contour map of the C(2) atom near the mirror plane: a cross section at $z = 0.11$ obtained by difference Fourier synthesis. The positions of the C(2) atoms, finally determined by least-squares calculations, are marked with a ×.

The tetrahedral molecules take two configurations with respect to the mirror planes; only one of them is shown in Fig. 2 for clarity. The bond lengths are not corrected for thermal motion. The distortion of the $CoBr_4$ tetrahedron is relatively small, while that of the $N(CH_3)_4$ tetrahedron is large. N—C bond lengths range from 1.43 to 1.53 Å with standard deviations of approximately 0.04 Å, and C—N—C angles range from 100 to 122° with standard deviations of approximately 2°. No H atoms were located because the compound contains heavy atoms such as Co and Br and there are large thermal vibrations of the C atoms of the $N(CH_3)_4$ molecules. A structural study of the low-temperature phase is now in progress so as to reveal the relationship between the disordered array of tetrahedral molecules and the anomalous temperature dependence of the deviation angle $\Delta\beta$.

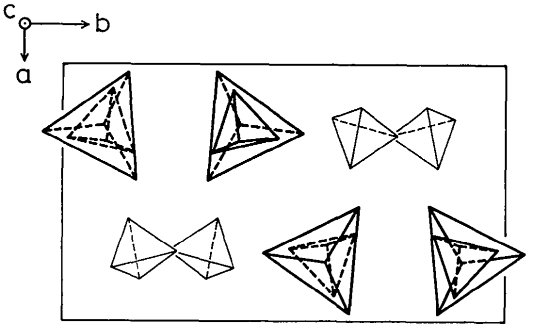

Fig. 2. Projection of the structure of $[N(CH_3)_4]_2CoBr_4$ in the unit cell along the *c* axis. The $CoBr_4$ and $N(1)(CH_3)_4$ molecules are represented by large and small bold tetrahedra and the $N(2)(CH_3)_4$ molecule by small non-bold tetrahedra. The apices correspond to the positions of Br and C atoms.

Experimental

Crystal data

$[(CH_3)_4N]_2[CoBr_4]$
$M_r = 526.90$
Orthorhombic
Pmcn
$a = 9.247$ (2) Å
$b = 16.052$ (6) Å
$c = 12.683$ (3) Å
$V = 1882$ (1) Å^3
$Z = 4$
$D_x = 1.859$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7\text{-}13°$
$\mu = 9.304$ mm^{-1}
$T = 300$ (2) K
Sphere
0.233 (6) mm (diameter)
Clear blue

Data collection

Rigaku AFC off-centre diffractometer
θ-2θ scans
Absorption correction: by integration from crystal shape (spherical)
$T_{min} = 0.222$, $T_{max} = 0.243$
1152 measured reflections
1152 independent reflections

727 observed reflections $[F > 3\sigma(F)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 100 reflections
intensity variation: 1%

Refinement

Refinement on *F*
Final $R = 0.0605$
$wR = 0.0465$
$S = 1.323$
727 reflections
126 parameters
$w = 1/\sigma^2$

$(\Delta/\sigma)_{max} = 0.067$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ 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)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co	0.25	0.4079 (2)	0.2488 (2)	0.054 (1)
Br(1)	0.2299 (6)	0.4030 (2)	0.0605 (2)	0.084 (1)
Br(2)	0.2638 (10)	0.5474 (2)	0.3143 (2)	0.114 (1)
Br(3)	0.0268 (4)	0.3489 (2)	0.3110 (3)	0.098 (1)
Br(4)	0.4500 (4)	0.3286 (2)	0.3141 (3)	0.102 (1)
N(1)	0.25	0.097 (1)	0.151 (1)	0.074 (6)
C(1)	0.299 (4)	0.100 (2)	0.265 (2)	0.129 (19)
C(2)	0.284 (7)	0.011 (2)	0.107 (2)	0.17 (2)
C(3)	0.342 (4)	0.161 (2)	0.105 (3)	0.136 (17)
C(4)	0.095 (4)	0.114 (4)	0.119 (4)	0.28 (3)
N(2)	0.25	0.829 (1)	0.486 (1)	0.068 (6)
C(5)	0.273 (5)	0.741 (1)	0.447 (2)	0.139 (12)
C(6)	0.205 (6)	0.889 (2)	0.407 (2)	0.19 (2)
C(7)	0.401 (3)	0.851 (2)	0.526 (2)	0.090 (12)
C(8)	0.167 (3)	0.825 (2)	0.581 (3)	0.135 (16)

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

Co—Br(1)	2.397 (4)	N(1)—C(3)	1.45 (3)
Co—Br(2)	2.392 (4)	N(1)—C(4)	1.52 (4)
Co—Br(3)	2.404 (4)	N(2)—C(5)	1.50 (3)
Co—Br(4)	2.393 (4)	N(2)—C(6)	1.44 (3)
N(1)—C(1)	1.52 (3)	N(2)—C(7)	1.53 (3)
N(1)—C(2)	1.52 (3)	N(2)—C(8)	1.43 (3)
Br(1)—Co—Br(2)	112.4 (1)	C(2)—N(1)—C(3)	112 (2)
Br(1)—Co—Br(3)	104.4 (2)	C(2)—N(1)—C(4)	105 (3)
Br(1)—Co—Br(4)	112.8 (1)	C(3)—N(1)—C(4)	109 (1)
Br(2)—Co—Br(3)	107.5 (2)	C(5)—N(2)—C(6)	116 (1)
Br(2)—Co—Br(4)	109.7 (2)	C(5)—N(2)—C(7)	101 (2)
Br(3)—Co—Br(4)	109.9 (1)	C(5)—N(2)—C(8)	108 (1)
C(1)—N(1)—C(2)	108 (1)	C(6)—N(2)—C(7)	110 (2)
C(1)—N(1)—C(3)	100 (1)	C(6)—N(2)—C(8)	117 (2)
C(1)—N(1)—C(4)	122 (2)	C(7)—N(2)—C(8)	103 (1)

The integrated intensities were measured using a diffractometer with a large χ-cradle installed at Kwansei Gakuin University. Lorentz, polarization and absorption corrections were applied. The structure was refined by block-diagonal-matrix least squares using the *AXS89* program system which was rewritten from *UNICS* by Mashiyama (1991). An NEC PC-9801RX personal computer with a co-processor was used for the calculations.

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Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71339 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1026]

References

Asahi, T., Hasebe, K. & Gesi, K. (1988). *J. Phys. Soc. Jpn*, **57**, 4219–4224.
Asahi, T., Hasebe, K. & Gesi, K. (1992). *J. Phys. Soc. Jpn*, **61**, 1590–1597.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
Hasebe, K. & Asahi, T. (1989). *Acta Cryst.* **C45**, 841–843.
Hasebe, K., Asahi, T. & Gesi, K. (1990). *Acta Cryst.* **C46**, 759–762.
Hasebe, K., Mashiyama, H., Tanisaki, S. & Gesi, K. (1984). *J. Phys. Soc. Jpn*, **53**, 1866–1868.
Mashiyama, H. (1991). *J. Phys. Soc. Jpn*, **60**, 180–187.
Sawada, A. (1991). *J. Phys. Soc. Jpn*, **60**, 3593–3595.
Trouelan, P., Lefebvre, J. & Derollez, P. (1984). *Acta Cryst.* **C40**, 386–389.
Trouelan, P., Lefebvre, J. & Derollez, P. (1985). *Acta Cryst.* **C41**, 846–850.