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The Crystal and Molecular Structure of Ferromagnetic Benzylammonium Tetrabromochromate(II)

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Abstract

A single crystal X-ray study of the ferromagnetic salt benzylammonium tetrabromochromate(II) $[NBzH_3]_2[CrBr_4]$ shows that it crystallises in the orthorhombic space group *Pcab*, with $a = 7.909(3)$, $b = 32.06(1)$ and $c = 7.760(1)$ Å. Each square planar $[CrBr_4]^{2-}$ unit is bridged by bromide ions to four like units to form layers so that each chromium ion is six coordinate. The $CrBr_6$ coordination shell is tetragonally-elongated. The Cr–Br distances are 2.548(1) and 3.044(1) Å (both bridging bromide) and 2.552(1) Å. The bridge angle (Cr–Br····Cr) is 164.4°, and the alternation of the distortion axes at 90° in the layers leads to the ferromagnetic interaction. The layers are intercalated by the benzylammonium cations.

Introduction

Ferromagnetic interactions have been found [1] in the monoalkylammonium tetrabromochromates(II) $[NRH_3]_2[CrBr_4]$, R = Me, Et, Pr^n, Bu^n, n-C_5H_{11}, n-C_8H_{17} or n-$C_{12}H_{25}$. Recent extensive magnetic and spectroscopic investigations have shown that the benzylammonium salt $[NBzH_3]_2$-$[CrBr_4]$ behaves similarly. Its Curie temperature is at 52 ± 1 K, some 15 K higher than for the corresponding tetrachlorochromate(II) [2]. With more limited equipment we have confirmed the ferromagnetic behaviour of $[NBzH_3]_2[CrBr_4]$ and some mixed halide salts [3]. From X-ray powder diffraction data $[NBzH_3]_2[CrBr_4]$ has been assigned the layered perovskite structure of analogous tetrachlorochromates(II). Unfortunately, single crystals fell to a powder in the X-ray beam so structure determinations were not possible [2]. We have obtained single crystals of $[NBzH_3]_2[CrBr_4]$ stable to X-rays by a slightly different method and so are able to report the first structure of a ferromagnetic tetrabromochromate(II). The structures of $[C(NH_2)_3]_2[CrBr_4(HO_2CCH_3)_2]$ [4] and $[Hpy]_2$-$[CrBr_4 \cdot 2H_2O]$ [5], which contains *trans*-planar $CrBr_2(OH_2)_2$ units, are known, but these are magnetically-dilute.

Experimental

Synthesis

To prepare $[NBzH_3]_2[CrBr_4]$ a solution of stoichiometric amounts of benzylammonium bromide and anhydrous chromium(II) bromide in hot glacial acetic acid was allowed to cool slowly. The yellow, plate-like crystals were filtered off, washed with glacial acetic acid, and dried at the pump. *Anal.* Calc. for $C_{14}H_{20}N_2CrBr_4$: C, 28.6; H, 3.4; N, 4.8. Found: C, 29.0; H, 3.4; N, 4.9%. The anhydrous chromium(II) bromide was prepared from the hexahydrate by thermal dehydration. Other workers [2] have not isolated the bromide, but obtained it in solution by passing HBr gas through acetic acid under reflux over the metal. All operations were carried out under nitrogen.

X-ray Crystallography

A crystal of approximate dimensions 0.8 × 0.4 × 0.08 mm was sealed in a Lindemann capillary under nitrogen. The X-ray data were collected on an Enraf Nonius CAD4 diffractometer, $\omega/2\theta$ scan mode, with scan speed 3.3° min^{-1}, to a θ limit of 25° ($0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 38$, $0 \leqslant l \leqslant 9$). The unit cell dimensions were determined by least-squares refinement of a set of 22 reflections ($13 \leqslant \theta \leqslant 15$). Out of 3819 unique reflections 2350 had $I \geqslant 3\sigma(I)$. One reflection (4 0 0) monitored hourly showed no significant variation in intensity. The crystal data are given in Table 1.

The structure was solved using Multan [6] and the positions of the Cr and Br atoms were obtained. The other atoms were located on difference Fourier maps. The hydrogen atom positions were calculated. An absorption correction DIFABS [7] was applied with minimum and maximum corrections of 0.589 and 2.213. This was followed by a full matrix anisotropic refinement, first for the heavy atoms and then for all non-hydrogen atoms, which resulted in convergence at $R = 0.055$, $R_w = 0.070$.

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TABLE 1. Crystal data

$C_{14}H_{20}Br_4CrN_2$	
M_r	587.96
Space group	*Pcab*
Crystal system	orthorhombic
a (Å)	7.909(3)
b (Å)	32.06(1)
c (Å)	7.760(1)
U (Å^3)	1967.8
Z	4
D_c (g cm^{-3})	1.984
F(000)	1128
Radiation	graphite-monochromated Mo Kα
λ (Å)	0.71069
μ (cm^{-1})	86.1

TABLE 2. Fractional atomic coordinates[a] and B_{eq} thermal parameters (Å^2)[b]

Atom	x	y	z	B_{eq} (Å^2)
Br(1)	−0.0450(1)	−0.07861(4)	0.0233(1)	3.11(2)
Br(2)	−0.2161(2)	0.01105(4)	0.2392(1)	3.03(2)
Cr	0	0	0	2.47(5)
N(1)	0.534(1)	0.4310(4)	0.529(1)	4.3(3)
C(1)	0.447(2)	0.3957(6)	0.450(1)	4.6(3)
C(11)	0.478(2)	0.3548(5)	0.535(1)	3.9(3)
C(12)	0.618(2)	0.3308(4)	0.500(2)	5.1(4)
C(13)	0.649(2)	0.2949(6)	0.591(3)	6.7(4)
C(14)	0.525(3)	0.2805(7)	0.702(2)	7.7(5)
C(15)	0.397(3)	0.3028(7)	0.750(2)	7.7(6)
C(16)	0.368(2)	0.3401(6)	0.659(2)	6.0(4)

[a] e.s.d.s given in parentheses. [b] The B_{eq} values are calculated according to the equation $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j B_{ij} a_i a_j$.

The final atomic coordinates are listed in Table 2. The atomic numbering scheme and thermal ellipsoids of the non hydrogen atoms are shown in Fig. 1 and the contents of the unit cell in Fig. 2. Bond lengths and angles are in Table 3. Atomic scattering factors and corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography. Refinement was carried out using SDP plus VI.Ia [8].

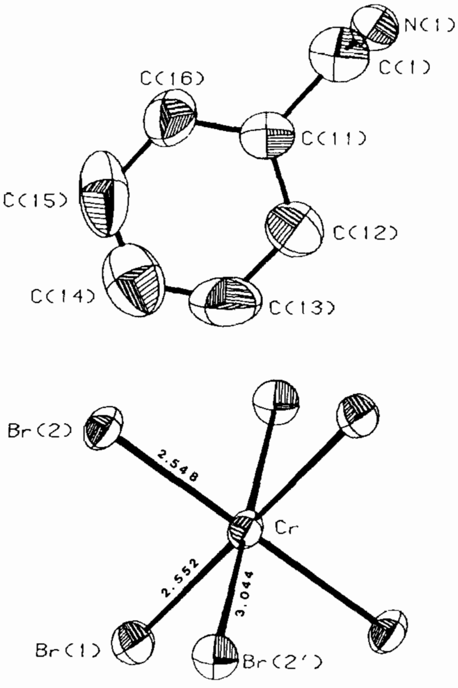

Fig. 1. Atom numbering scheme.

TABLE 3. Bond distances (Å) and bond angles (°) for $[N(CH_2C_6H_5)H_3]_2[CrBr_4]$[a]

Cr–Br(1)	2.552(1)	N(1)–C(1)	1.46(2)	C(12)–C(13)	1.37(3)
Cr–Br(2)	2.548(1)	C(1)–C(11)	1.49(2)	C(13)–C(14)	1.39(3)
Cr–Br(2')[b]	3.044(1)	C(11)–C(12)	1.37(2)	C(14)–C(15)	1.30(3)
Cr–Cr[c]	5.541(1)	C(11)–C(16)	1.38(2)	C(15)–C(16)	1.41(3)
Cr–Br(2)–Cr[c]	164.39(6)			C(1)–C(11)–C(16)	120(1)
Br(1)–Cr–Br(1)[d]	180.00(0)	Br(2)–Cr–Br(2)[d]	180.00(0)	C(12)–C(11)–C(16)	117(1)
Br(1)–Cr–Br(2)	89.56(4)	Br(2)–Cr–Br(2')[b]	91.53(3)	C(11)–C(12)–C(13)	121(2)
Br(1)–Cr–Br(2')[b]	86.61(4)	N(1)–C(1)–C(11)	115(1)	C(12)–C(13)–C(14)	118(2)
		C(1)–C(11)–C(12)	122(1)	C(13)–C(14)–C(15)	123(2)
				C(14)–C(15)–C(16)	117(2)
				C(11)–C(16)–C(15)	122(2)

[a] e.s.d.s given in parentheses. [b] Symmetry code: [b] $\frac{1}{2} + x, \bar{y}, \frac{1}{2} - z$; [c] $-\frac{1}{2} + x, \bar{y}, \frac{1}{2} - z$; [d] $\bar{x}, \bar{y}, \bar{z}$.

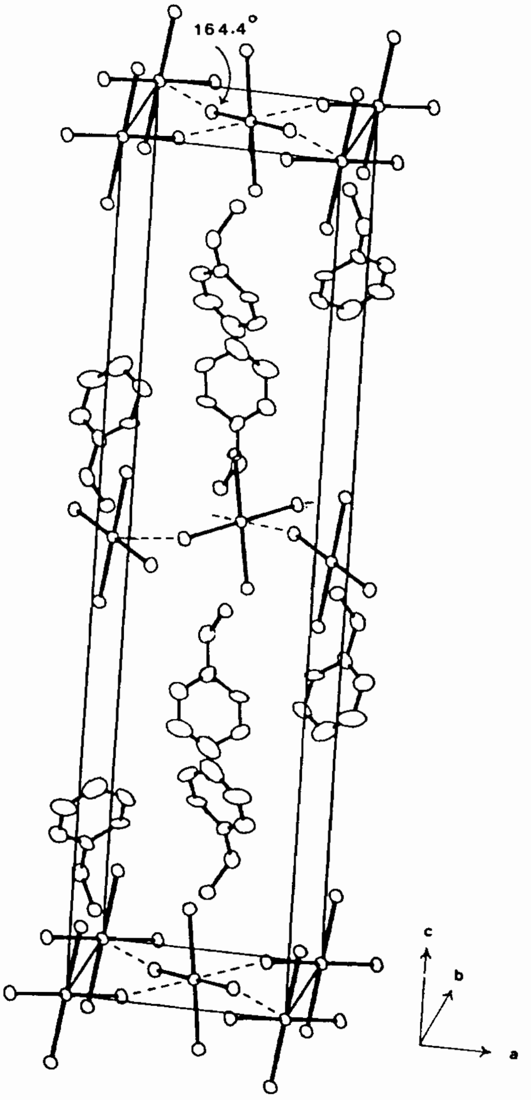

Fig. 2. Unit cell contents.

Results and Discussion

Figures 1 and 2 show that the Cr^{II} atoms are six coordinate. Four Br atoms are disposed in a square planar arrangement with mean Cr–Br distances of 2.55 Å. The $[CrBr_4]^{2-}$ units are held in a two-dimensional network by two long Cr–Br bonds (3.044 Å) to neighbouring anions. The layers so formed are intercalated by the benzylammonium cations. A polymeric structure was expected from the magnetic and spectroscopic properties of the monoalkylammonium bromides generally [1, 2], and their similarities to the tetrachlorochromates(II). The long axes of the $[CrBr_6]$ groups alternate at right angles in the basal plane and this leads to the ferromagnetic interaction [9]. The Cr–Br distances are similar to those in other bromo complexes of chromium(II) (Table 4).

The direct Cr–Cr separation is 5.541 Å, and the bridge angle Cr–Br–Cr is 164.39°. From investigations of the tetrachlorochromates(II) it appears that ferromagnetic interaction, as measured by the exchange integrals J increases the more linear is the bridge [10]. The T_c is 52 K [2], some 15 K higher than for the corresponding tetrachlorochromate(II). Consequently, tetrabromochromate(II) salts with more linear bridges should show higher T_cs.

Supplementary Material

The observed and calculated structure factors and anisotropic thermal factors can be obtained from the authors on request.

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TABLE 4. Compounds of known structure containing Cr–Br bonds

Compound	Coordination sphere (Å)	Reference
$[NBzH_3]_2[CrBr_4]$	Cr–Br, 2 at 2.548 2 at 2.552 2 at 3.044	this work
$CrBr_2$	Cr–Br, 4 at 2.54 2 at 3.00	10
$[C(NH_2)_3]_2[CrBr_4(HO_2CCH_3)_2]$	Cr–Br, 2 at 2.637 2 at 2.839 Cr–O, 2 at 2.06	4
$(Hpy)_2[CrBr_4 \cdot 2H_2O]^a$	Cr–Br, 2 at 2.579 Cr–O, 2 at 2.038	5

[a] This compound contains *trans*-planar $CrBr_2(OH_2)_2$ units and ionic bromide.

References

1 M. A. Babar, L. F. Larkworthy and A. Yavari, *J. Chem. Soc., Dalton Trans.*, (1981) 27; L. F. Larkworthy and A. Yavari, *J. Chem. Soc., Chem. Commun.*, (1977) 172.
2 C. Bellitto, P. Filaci and S. Patrizio, *Inorg. Chem.*, *26* (1987) 191.
3 D. M. Halepoto and L. F. Larkworthy, *Transition Met. Chem.*, *13* (1988) 104.
4 M. A. Babar, M. F. C. Ladd, L. F. Larkworthy, G. A. Leonard and D. C. Povey, *J. Crystallogr. Spectrosc. Res.*, *13* (1983) 325.
5 M. F. C. Ladd, L. F. Larkworthy, G. A. Leonard, D. C. Povey and S. S. Tandon, *J. Chem. Soc., Dalton Trans.*, (1984) 2351.
6 P. Main, S. E. Hill, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, *MULTAN 78*, Universities of York, U.K. and Louvain, Belgium, 1978.
7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, *39* (1983) 158.
8 B. A. Frenz, *Enraf Nonius Structure Determination Package, SDP Users' Guide*, Version 1.1, Enraf Nonius, Delft, The Netherlands, 1983.
9 P. Day, *J. Magn. Magn. Mater.*, *54–57* (1986) 1442.
10 F. Besrest and S. Jaulmes, *Acta Crystallogr., Sect. B*, *29* (1973) 1560.