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Rubidium Tetrabromomanganate(II)

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Abstract. $Rb_2[MnBr_4]$, tetragonal, $I4/mmm$, $a = 5.37$ (2), $c = 17.32$ (5) Å, $D_o = 3.60$, $D_x = 3.63$ Mg m^{-3} , $Z = 2$. The final R was 0.090 for 123 visually estimated data. $MnBr_6$ octahedra share equatorial vertices to form layers of linked octahedra perpendicular to [001], there being two such layers in the unit cell. The Rb ions lie in the same z planes as the Br ions at the unshared vertices. The structure is isomorphous with that of $K_2[NiF_4]$.

Introduction. This work forms part of an investigation of the structures of compounds in the systems $RbCl/MnCl_2$ and $RbBr/MnBr_2$. The structure of $Rb_2[MnCl_4]$ (Goodyear, Ali & Steigmann, 1977) was found to be isomorphous with that of $K_2[NiF_4]$ and the cell parameters and observed density of $Rb_2[MnBr_4]$ suggest that the latter also has the same structure.

Pink crystals of the material were prepared by heating stoichiometric amounts of $RbBr$ and $MnBr_2$ in an evacuated silica tube until molten and then cooling the sample to room temperature at a rate of about 5 K h^{-1} . The crystal selected for X-ray study was mounted in a sealed Lindemann-glass tube because of the hygroscopic nature of the material.

Cell dimensions were determined from $\alpha_1 - \alpha_2$ doublet separations on a zero-layer Weissenberg photograph taken with $Cu K\alpha$ radiation ($\lambda_{\alpha_1} = 1.54051$ Å).

Intensities were collected from equi-inclination Weissenberg photographs taken about a with $Mo K\alpha$ radiation. The intensities of 123 symmetrically independent reflexions were measured visually from layers 0–4 from accurately timed film exposures. The only systematically absent reflexions were of the type $h + k + l = 2n + 1$, consistent with the space group ($I4/mmm$) of $K_2[NiF_4]$. The observed data were

corrected for the Lorentz–polarization factor and for absorption by assuming the crystal to be cylindrical with a mean $\mu r = 0.96$.

Positional parameters and individual isotropic temperature factors suggested by the $Rb_2[MnCl_4]$ structure were assumed and after least-squares refinement $R = \sum |F_o| - |F_c| / \sum |F_o|$ attained a minimum value of 0.090 at which stage the shift in each atomic parameter was $< 0.1\sigma$. The calculated values of the structure factors of the 100 unobserved reflexions were all less than the minimum observable value. Scattering factors for Rb^+ , Mn^{2+} and Br^- were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. Final atomic parameters (origin at centre $4/mmm$)

	Equipoint	x	y	z	B (Å ²)
Mn	2(a)	0	0	0	1.65 (71)
Rb	4(e)	0	0	0.3505 (11)	1.56 (28)
Br(1)	4(e)	0	0	0.1495 (11)	1.72 (29)
Br(2)	4(c)	0	$\frac{1}{2}$	0	1.55 (22)

Table 2. Selected interatomic distances (Å)

		Multiplicity	Location of atoms		
Mn–Br octahedron					
Mn–Br(1 ^l)	2.589 (20)	2	Mn	0	0 0
Mn–Br(2 ^l)	2.685 (10)	4	Rb	$\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$ $-z$
Br(1 ^l)–Br(2 ^l)	3.730 (16)	8	Br(1 ^l)	0	0 z
Br(2 ^l)–Br(2 ^{ll})	3.797 (14)	4	Br(1 ^{ll})	$\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$ $-z$
			Br(2 ^l)	0	$\frac{1}{2}$ 0
Rb–Br distances					
Rb–Br(1 ^l)	3.797 (14)	4	Br(2 ^{ll})	$\frac{1}{2}$	0 0
Rb–Br(1 ^{ll})	3.481 (28)	1			
Rb–Br(2 ^l)	3.730 (16)	4			

The final atomic parameters and selected inter-atomic distances are given in Tables 1 and 2 respectively.*

Discussion. The structure is related to that of perovskite in a simple way. A single slice of perovskite-type structure, one unit cell thick, has the composition $\text{Rb}_2[\text{MnBr}_4]$ and the tetrabromomanganate structure can be regarded as consisting of such slices stacked perpendicular to c , alternate slices being displaced $a/\sqrt{2}$ in the $[110]$ direction. Mn and Br(2) ions lie in the middle of these slices, whilst Rb and Br(1) ions are situated on their surfaces and within the accuracy of the analysis lie on the same z planes.

The MnBr_6 octahedra within a perovskite-type slice share equatorial, Br(2), vertices to form a layer of com-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34093 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

position MnBr_4 . Because of the mutual repulsion of the Mn^{2+} ions in such a layer, Mn—Br(2) is significantly longer than Mn—Br(1). The mean Mn—Br and Br—Br distances are 2.65 and 3.75 Å, respectively, somewhat shorter than the corresponding values (2.68 and 3.79 Å) found in the MnBr_6 octahedron in $\text{Cs}[\text{MnBr}_3]$ (Goodyear & Kennedy, 1972). Each Br—Mn—Br angle is exactly 90° .

Each Rb ion is coordinated by four Br(2) and five Br(1) ions and the very short Rb—Br(1^{II}) bond can be explained by the unsymmetrical nature of this coordination group.

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The Structure of Triindenylcerium Pyridinate

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Abstract. $\text{Ce}(\text{C}_9\text{H}_7)_3 \cdot \text{C}_5\text{H}_5\text{N}$, $\text{C}_{32}\text{H}_{26}\text{CeN}$, orthorhombic, $Pbca$, $a = 13.106$ (3), $b = 26.364$ (7), $c = 13.832$ (2) Å, $Z = 8$; $D_x = 1.57$ Mg m^{-3} ; $\mu(\text{Mo } K\alpha) = 2.10$ mm^{-1} . Final $R = 0.028$. The π -bonded five-membered portions of the three indenyl groups and the σ -bonded N atom of the pyridine ring are arranged tetrahedrally around the metal Ce atom.

Introduction. The title compound was obtained by reaction of $\text{Ce}(\text{OPr}^i)_4 \cdot \text{Py}$ with AlEt_3 in indene at 323 K. Yellow, air-sensitive crystals were obtained by cooling the red-orange reaction solution to 273 K.

In view of the considerable interest now being shown in the organometallic chemistry and stereochemistry of lanthanides (Baker, Halstead & Raymond, 1976), the crystal structure determination of the title compound was undertaken. Preliminary Weissenberg photographs established the space group $Pbca$ (systematic extinctions: $hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$).

4673 independent intensities (maximum $\sin \theta/\lambda = 0.62$ Å⁻¹) were collected from a crystal of about $0.3 \times 0.3 \times 0.5$ mm, mounted with the c axis parallel to the spindle axis of an on-line Siemens AED diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), the θ – 2θ scan mode, and 'five-points' technique (Hoppe, 1969). 3222 intensities with $I > 3\sigma(I)$ were classed as observed and used in the structure determination. Absorption correction was ignored because of the irregular shape of the crystal used.

The structure was solved by conventional heavy-atom techniques and refined by a block-diagonal least-squares procedure. The function minimized was $\sum w(F_o - F_c)^2$, using Cruickshank's (1965) weighting scheme. Atomic scattering factors were those of Cromer & Mann (1968) for non-hydrogen atoms, and of Stewart, Davidson & Simpson (1965) for the H atoms. The anomalous-dispersion correction for Ce was taken into account in the structure factor calculations ($f' = -0.42$, $f'' = 3.04$) (Cromer, 1965). The computer