

(Johnson, 1970) and by the large difference between $X-H$ stretching and bending vibrational frequencies. A spherical temperature factor corresponds to too large a thermal motion along the bond direction, thereby partly compensating for the deficiency of the spherical atom wave function. The X-ray data do not allow the determination of anisotropic thermal parameters for the hydrogen atoms, but the use of complementary spectroscopic information should lead to a sharper minimum in R as a function of the mixing coefficient μ .

Second, without the introduction of complementary information on the dynamics of the hydrogen atom little can be learned about the details of the hydrogen atom density. Therefore, it is doubtful that calculations with other reasonable nonspherical hydrogen atom formalisms would lead to results differing considerably from those described here.

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The crystal structure of CsMnBr_3 . By J. GOODYEAR and D. J. KENNEDY, *Department of Physics, University of Hull, England*

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The crystal structure of CsMnBr_3 , determined from Weissenberg data, is hexagonal with $a=7.609$ (15), $c=6.52$ (5) Å and $Z=2$. Cs, Mn and Br atoms are located at the special positions $2(d)$, $2(a)$ and $6(h)$, respectively, of the space group $P6_3/mmc$, the structure being isomorphous with that of CsNiCl_3 .

Introduction

Many structures of CsMCl_3 compounds, where M denotes a metal ion in the first transition series, have been found to be isomorphous with CsNiCl_3 (Tishchenko, 1955), which is hexagonal (space group, $P6_3/mmc$) with $a \approx 7.2$ Å and $c/a \approx 0.82$. Single-crystal studies of RbNiCl_3 and RbNiBr_3 (Asmussen, Larsen & Soling, 1969) and of CsMgCl_3 (McPherson, Kistenmacher & Stucky, 1970) have shown that these compounds also have this structure.

The unit-cell dimensions of the material examined in this work suggested that its structure might be of the CsNiCl_3 type; this was assumed at the beginning and the subsequent refinement of the structure proved it to be so.

Experimental

The material was prepared by heating a stoichiometric mixture of CsBr and MnBr_2 to a temperature above the melting point in a sealed evacuated silica tube, and then cooling the specimen at about 10°C per hr to room temperature. The resulting red crystalline mass was unstable in the presence of water vapour, and single crystals, suitable for X-ray Weissenberg study, were selected in a stream of dry nitrogen and then sealed in Lindemann glass tubes containing P_2O_5 .

The unit-cell dimensions were determined from rotation and Weissenberg photographs taken about the c -axis with $\text{Cu } K\alpha$ radiation ($\lambda = 1.5418$ Å). Agreement between the observed and X-ray densities was obtained by assigning two formula units of CsMnBr_3 per unit cell. The appropriate crystal data are presented in Table 1.

Table 1. *Crystal data*

Formula, CsMnCl_3 ;	F. W. 427.60
Hexagonal;	$a = 7.609$ (15), $c = 6.52$ (5) Å
	$Z = 2$; $D_o = 4.30$, $D_x = 4.34$ g.cm $^{-3}$
Mean r (cm)	0.0032
μ (cm $^{-1}$)	269 ($\lambda = 0.7107$ Å)

Intensity data were collected from equi-inclination multiple-film Weissenberg photographs taken about the c axis with $\text{Mo } K\alpha$ radiation using a crystal of cross-section 0.04×0.08 mm. Reflexions with indices hkl , $l = 2n + 1$, were systematically absent, in keeping with space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. The intensities of about 380 reflexions from layer lines 0 to 5 were measured using a Joyce-Loebl flying-spot microdensitometer; of these about 95 were symmetrically independent. These data were corrected for the Lorentz-polarization factor and for absorption using the correction factors given by Bond (1959) for a cylindrical crystal.

Structure determination

Since CsMnBr_3 was expected to be isostructural with CsNiCl_3 the atoms were assigned to the following positions in the space group $P6_3/mmc$: Cs at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, Mn at $(0,0,0)$ and Br at $(x, 2x, \frac{1}{2})$. A two-dimensional least-squares refinement of the $hk0$ data was carried out using an initial positional parameter for the bromine atom the same as that of the chlorine atom in the CsNiCl_3 structure and the isotropic temperature factors found for Cs_2MnBr_4 by Goodyear, Steigmann & Kennedy (1972). After 10 cycles the reliability

factor $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ decreased to 0.065. After a further 10 cycles of refinement of the full three-dimensional data R took a minimum value of 0.071, at which stage the shifts in the atomic parameters were all less than $\frac{1}{50}$ of the estimated standard deviations. In these calculations the atomic scattering factors given in *International Tables for X-ray Crystallography* (1962) for Cs^+ , Br^- and Mn^{2+} were used and inter-layer scaling was achieved by scaling the observed to the calculated structure factors.

The calculated structure factors of 55 symmetrically independent unobserved reflexions were all less than the minimum observable value. The final atomic parameters are given in Table 2 and the observed and calculated structure factors compared in Table 3.

Table 2. Final atomic parameters

Standard deviations are given in parentheses.

Equipoint	x	y	z	$B(\text{\AA}^2)$
Mn $2a$	0	0	0	1.78 (32)
Cs $2d$	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{3}{4}$	2.34 (17)
Br $6h$	0.1617 (10)	0.3234 (10)	$\frac{1}{4}$	1.72 (11)

Table 3. Observed and calculated structure factors

H	K	F_o	F_c	H	K	F_o	F_c	H	K	F_o	F_c	H	K	F_o	F_c	H	K	F_o	F_c	
L=0																				
2 0	96	-92	6 2	29	-30	3 1	17	-24	2 2	151	-154	4 1	13	-11	6 1	16	15			
3 0	69	-60	8 2	2	50	56	4 4	1	17	13	13	3 2	2	19	16	2	2	173	158	
4 0	70	-64	3 3	3	39	38	3 2	32	25	4 2	86	82	4 2	108	100	3 2	2	26	23	
6 0	132	134	6 3	3	18	17	4 5	2	19	-19	7 2	2	27	24	5 2	2	35	-36	16	
7 0	27	26	4 4	4	109	106	6 6	2	82	73	8 8	2	41	-38	6 6	6	6	22	20	
8 0	28	-24	5 4	4	17	21	6 4	4	55	-48	4 3	35	34	4 4	24	-23	3 3	20	-23	
1 1	81	75	6 6	6	22	-19	6 4	4	30	26	6 4	4	35	34	2 2	2	2	39	43	
2 1	7	10	L=1	0	168	162	2 0	0	145	147	L=2	0	175	170	3 0	50	-50	4 4	83	80
3 1	26	22	2 0	0	106	106	2 2	0	175	170	L=3	0	175	170	4 0	37	-37	4 4	114	-118
4 1	48	43	3 0	0	18	-18	3 0	0	17	14	4 0	0	13	97	99	0	0	94	93	
6 1	1	19	4 0	0	145	153	4 0	0	129	-93	5 0	0	129	-93	6 0	0	0	37	-39	
7 1	1	19	5 0	0	39	-39	5 0	0	39	-42	6 0	0	45	51	7 0	0	0	80	74	
2 2	202	231	7 0	0	23	15	7 0	0	23	-28	8 0	0	23	-28	8 0	0	0	50	-48	
3 2	32	31	8 0	0	50	-59	8 0	0	50	53	10 0	0	23	-28	9 0	0	0	46	46	
4 2	53	49	9 0	0	32	31	9 0	0	32	31	10 0	0	11	-14	3 1	20	15	29	32	
5 2	30	26	10 0	0	1	17	10 0	0	1	17	19	11 0	0	1	14	11 0	0	1	14	19

Discussion

Cs and Br atoms form an approximate hexagonal close-packed array such that each Cs atom has 12 nearest Br neighbours. The Mn atoms occupy those octahedral sites which are bounded exclusively by Br atoms.

The Mn-Br octahedra share opposite faces to form chains, of composition $(\text{MnBr}_3)_n^{2-}$, parallel to the c axis. The trigonal distortion of the octahedra is presumably due to the repulsion of successive Mn^{2+} ions in the chains so

that the Br atoms in the shared faces are brought closer together, thereby making the Br(1)-Mn-Br(1) and Br(2)-Mn-Br(2) angles less than 90° and the Br(1)-Mn-Br(2) angle correspondingly greater. Bond lengths and angles are given in Table 4.

Table 4. Bond lengths and angles

Standard deviations are given in parentheses.

	Multiplicity	
Mn-Br octahedron:		
Mn-Br(1,2)	6	2.683 (6) Å
Br(1)-Br(1)	3 } 3 }	3.691 (12)
Br(2)-Br(2)	3 }	
Br(1)-Br(2)	6	3.893 (5)
Angles		
Br(1)-Mn-Br(1)	3 } 3 }	86.9 (0.2)°
Br(2)-Mn-Br(2)	3 }	
Br(1)-Mn-Br(2)	6	93.1 (0.2)
Cs-Br distances:		
Cs-Br(2)	6	3.805 (8) Å
Cs-Br(1)	3 } 3 }	3.967 (4)
Cs-Br(3)	3 }	
Location of atoms:		
Mn at (000)		
Cs at ($\frac{1}{2}$, $\frac{3}{4}$, $\frac{3}{4}$)		
Br(1), Br(2), Br(3) at $z = -\frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}$ respectively.		

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The crystal structure of the nitroxide free radical 2,2,5,5-tetramethyl-3-carbamidopyrroline-1-oxyl. By JUNE W. TURLEY and F. PETER BOER, *The Dow Chemical Company, Midland, Michigan 48640, U.S.A.*

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The crystal and molecular structure of 2,2,5,5-tetramethyl-3-carbamidopyrroline-1-oxyl, $\text{C}_9\text{H}_{15}\text{N}_2\text{O}_2$, has been determined by a three-dimensional X-ray diffraction study. The crystals are in the monoclinic space group $P2_1/c$, with four molecules in a unit cell of dimensions: $a = 8.039$ (2), $b = 11.324$ (2), $c = 11.537$ (2) Å, and $\beta = 91.75$ (1)° measured at 24°C ; $D_x = 1.160$ g.cm $^{-3}$. Intensity data were measured on a four-circle diffractometer using Cu $K\alpha$ radiation (1.5418 Å), and the structure was solved by statistical methods. Full-matrix least-squares refinement converged at $R = 5.2\%$ for 1474 reflections above background, with anisotropic thermal parameters assumed for C, N, and O and isotropic thermal parameters for H. The ring system and the nitroxide function were found to be planar.

The current interest in nitroxide free radicals stems largely from their utility in electron spin resonance spectroscopy as spin labels in normally diamagnetic systems (Griffith &

Waggoner, 1969; Snipes & Keith, 1970). The sensitivity of these labels to the local environment of the diamagnetic molecule is related to the geometry of the label itself. The