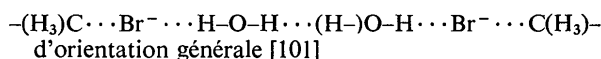
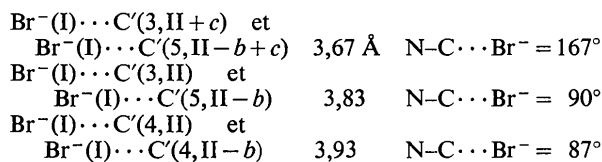


sont alors reliés par l'enchaînement:



— entre deux feuillets existent des interactions méthyle...brome:



D'autre part les proximités méthyle...méthylène et méthyle...méthyle sont toutes supérieures à 3,90 Å.

On relève donc pour chaque anion Br^- une liaison hydrogène très probable avec une molécule d'eau et sept proxi-

mités $-\text{CH}_3\cdots\text{Br}^-$ dont les trois plus courtes sont associées à des angles supérieurs à 155° (Fig. 1): tout se passe comme si une fraction de la charge positive de l'azote se répartissait sur les carbones adjacents; ces derniers deviennent alors capables d'établir des interactions avec des atomes à caractère négatif comme les anions Br^- dans ce cas.

Ce phénomène de délocalisation partielle de charge semble être, d'après nos observations, une caractéristique du groupement triméthylammonium ou même de groupements plus substitués.

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Crystal structure of $\text{Cs}_2\text{NaBiCl}_6$. By LESTER R. MORSS* and WILLIAM R. ROBINSON, *Department of Chemistry, Purdue University, Lafayette, Indiana 47907, U.S.A.*

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$\text{Cs}_2\text{NaBiCl}_6$ crystallizes in a face-centered cubic unit cell with $a_0 = 10.839 \pm 0.001$ Å and $Z = 4$. The most probable space group is $Fm\bar{3}m$. The Bi-Cl distance is 2.66 ± 0.02 Å.

Although many complex compounds of the general formula $A_2BB'X_6$ have been found to be f.c.c. and isomorphous with K_2NaCrF_6 (Knox & Mitchell, 1961) by X-ray powder diffraction (Goodenough & Longo, 1970; Baud, Baraduc, Gaille & Cousseins, 1971), only a few have been studied as single crystals. Several other powder measurements have been interpreted in terms of $B'X_6$ octahedra, or distorted octahedra, rotated slightly from the cubic axes; however, all available single-crystal measurements of these systems have revealed a f.c.c. lattice with $m\bar{3}m$ symmetry at the B' site. We report the first single-crystal determination of the structure of a complex chloride, $\text{Cs}_2\text{NaBiCl}_6$, which crystallizes in the K_2NaCrF_6 structure. This bismuth compound was selected because of its ease of preparation, its convenient morphology, and our concern with possible stereochemically 'active' nonbonded electron pairs of Bi^{3+} .

Crystals of length ~ 0.1 mm, with well-developed (111) faces, were grown by slow cooling of solutions of $\text{C}_2\text{NaBiCl}_6$ in warm 6 M HCl, following the procedure of Morss, Siegal, Stenger & Edelstein (1970).† Rotation photographs (with Ni-filtered Cu $K\alpha$ radiation) and Weissenberg and precession photographs (with Zr-filtered Mo $K\alpha$ radiation) were taken of a nearly octahedral crystal. These photographs, which showed $m\bar{3}m$ diffraction symmetry, revealed absences $[hkl;$

$h+k, k+l, (h+l) = 2n]$ corresponding to the face-centered space groups $F432$, $F\bar{4}3m$, or $Fm\bar{3}m$. In particular, the 320, 510, and 431 reflections, noted by Frondel (1948) for K_2NaAlF_6 , were absent; moreover, several reflections, such as 420, which were too weak for Frondel to have detected in his powder photograph, were observed. Therefore, we confirm that $\text{Cs}_2\text{NaBiCl}_6$ crystallizes in an f.c.c. lattice, in agreement with the results of Knox & Mitchell (1961), Wolberg (1969), and Morss *et al.* (1970).

The unit-cell parameter was determined from Debye-Scherrer photographs taken with a 114.6 mm diameter camera. Pulverized crystals were packed into thin-walled Pyrex capillaries of 0.2 mm diameter. Ni-filtered Cu X-rays ($K\alpha_1 = 1.54051$ Å) revealed an f.c.c. lattice with no unindexable lines. The cubic lattice parameter, a_0 , fitted to the observed reflections by least-squares methods (Williams, 1964, using the Nelson-Riley extrapolation for finite-diameter sample), is 10.839 ± 0.001 Å, in agreement with that of Morss *et al.* (1970).

A second octahedral crystal mounted along a tetragonal [110] axis was used for data collection. 171 reflections with $\sin \theta < 0.33$ were collected from an octant of reciprocal space, using a diffractometer of equi-inclination Weissenberg geometry with Mo $K\alpha$ radiation. Following Lorentz-polarization corrections and correction for absorption in the crystal used (Burnham, 1966), the equivalent reflections were scaled together by the method of Rae (1965), using weights derived from counting statistics. 46 observed independent reflections, with standard deviations determined from the agreement of equivalent reflections, were thus obtained.

The space group $Fm\bar{3}m$ was selected for structure refinement, with the following atomic positions: 4 Bi (*a*) at 0, 0, 0; 4 Na (*b*) at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; 8 Cs (*c*) at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; 24 Cl (*e*) at $x, 0, 0$.

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† Morss *et al.* (1970) originally reported that $\text{Cs}_2\text{NaBiCl}_6$ octahedra crystallized from 2M HCl. However, following their recipe yielded crystals which did not show the $\text{Cs}_2\text{NaBiCl}_6$ powder pattern. Since their solutions were evaporated while hot, it is likely that the HCl concentration substantially exceeded 2M.

This structure is depicted by Knox & Mitchell (1961). The Cl x parameter and isotropic temperature factors were determined by full-matrix least-squares refinement, using scattering factors (with real and imaginary anomalous scattering corrections for Bi and Cs) from *International Tables for X-ray Crystallography* (1962). After the first cycles of refinement, it was apparent that the most intense reflections were systematically weak (most likely because of extinction); accordingly, the 004 and 044 reflections were given zero weight in succeeding refinements. In addition, the 11 weakest reflections were assigned standard deviations which were twice those indicated from the scaling. Refinement of $w(F_o - F_c)^2$ reduced R_1 to 0.077 ($R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$) and R_2 to 0.062 [$R_2 = (\sum w||F_o| - |F_c||^2)^{1/2} / \sum w|F_o|^{1/2}$]. Structure factors are tabulated in Table 1. The final Cl x parameter and the isotropic temperature factors for Cs, Na, Bi, and Cl with their estimated standard deviations were, respectively, 0.246 ± 0.002 , 2.9 ± 0.4 , 5.2 ± 3.0 , 0.1 ± 0.2 , and 3.1 ± 0.5 . The standard deviation of an observation of unit weight was 0.92. Attempts to refine Cl with an anisotropic temperature factor produced no significant improvement in the reliability factor.

Table 1. Calculated and observed values of $F(hkl)$ in electrons

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	19	15	2	2	2	87	87
0	0	4	190	224	2	2	4	121	124
0	0	6	31	17	2	2	6	44	40
0	0	8	139	134	2	2	8	97	86
0	0	10	30	23	2	4	4	22	17
0	2	2	134	144	2	4	6	96	96
0	2	4	22	16	2	4	8	24	21
0	2	6	113	108	2	6	6	22	21
0	2	8	25	20					
0	4	4	164	181	3	3	3	61	52
0	4	6	16	18	3	3	5	52	52
0	4	8	122	118	3	3	7	44	45
0	6	6	87	86	3	3	9	42	45
0	6	8	22	22	3	5	5	50	52
					3	5	7	41	45
1	1	1	77	68					
1	1	3	67	61	4	4	4	145	154
1	1	5	64	60	4	4	6	18	20
1	1	7	51	50	4	4	8	100	106
1	1	9	47	49	4	6	6	77	79
1	3	3	60	56					
1	3	5	56	56	5	5	5	57	51
1	3	7	47	47	5	5	7	40	45
1	3	9	44	47					
1	5	5	54	55					
1	5	7	44	47					
1	7	7	38	42					

The Bi^{3+} ions in $\text{Cs}_2\text{NaBiCl}_6$ are in sites of rigorous octahedral geometry. For this structure, the following metal-chloride distances may be calculated: Bi, 6 Cl at 2.66 ± 0.02 Å; Na, 6 Cl at 2.75 ± 0.02 Å; Cs, 12 Cl at 3.832 ± 0.001 Å. No other single-crystal data are available for BiCl_6^{3-} dimensions in other systems, but Atoji & Watanabe (1952) reported a Bi-Cl distance of 2.52 Å from a powder diffrac-

tion study of $[\text{Co}(\text{NH}_3)_6]\text{BiCl}_6$. There are too few sixfold M^{3+} -Cl distances known to make any generalization other than that the Bi-Cl distances are much shorter than expected from the sum of ionic radii.

Martineau & Milne (1970) ascribe the nonoctahedral chloride environment in some hexachloroantimony(III) compounds to a stereochemical distortion of the nonbonded electron pair of Sb^{3+} , although they find that SbCl_6^{3-} (aq) appears to be octahedral. We find that BiCl_6^{3-} in $\text{Cs}_2\text{NaBiCl}_6$ is octahedral, despite the presence of a $(6s)^2$ nonbonded pair. The comparable fluoroaluminates tabulated by Wells (1962) indicate that cation-packing considerations are principally responsible for the structures of close-packed compounds of this type; Al^{3+} , of course, has no nonbonded lone pairs. Our conclusion, that there is no structurally significant distortion of octahedral symmetry about Bi^{3+} by lone pairs, fits well into the systematization of such species by Urch (1964) and is consistent with similar observations of Lawton & Jacobson (1966), Oertel & Plane (1967), Day (1963), and Birchall, Della Valle, Martineau & Milne (1971).

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