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The Structure of Bis(methylammonium) Tetrabromoferrate(III) Bromide, (H$_3$CNH$_3$)$_2$[FeBr$_4$]Br

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The crystal and molecular structure of bis(methylammonium) tetrabromoferrate(III) bromide, (CH$_3$NH$_3$)$_2$[FeBr$_4$]Br, has been determined from three-dimensional X-ray data gathered by a counter scan technique. Least-squares refinement on F has provided a final $R = 0.115$ and $R_w = 0.067$ for the structure. The compound crystallizes as red needles in the orthorhombic space group, $Pna2_1$, with eight formula weights in a unit cell of dimensions $a = 14.989$ (6), $b = 6.463$ (3), and $c = 28.130$ (11) Å. The tetrahedral tetrabromoferrate(III) ions occur as two independent forms, with an average Fe–Br interatomic distance of 2.32 ± 0.1 Å. Methylammonium cations are apparently hydrogen bonded through the nitrogen–hydrogen atoms to both the ligand and nonligand bromide ions. Each unit cell has two independent sets of atoms that are related to one another by a pseudoinversion center at $^1/_8$, $^1/_4$, $\sim$0. The possibility exists that this compound will exhibit the ferroelectric effect.

The number and arrangement of halide ligands coordinated to a transition metal in a complex anion is often surprisingly dependent on the nature of cationic counterions present. With Ni(II) and medium-sized cations such as K$^+$,[1] Rb$^+$,[2] and (CH$_3$)$_4$N$^+$,[3] it has been found that chains of face-shared halide octahedra are formed in the solid state. On the other hand, tetrahedra are stabilized by large cations such as [(C$_6$H$_5$)$_3$(CH$_3$)As]$^+$[4] and (C$_2$H$_5$)$_4$N$^+$.[5] The five-coordinate bridged anion Ni$_2$Cl$_8^{4-}$ is isolated with the large hydrogen-bonding cation HN(C$_2$H$_4$)$_3$NCH$_3^+$.[6]

Similar results have been found for Fe(III). Thus, the medium-sized cation Cs$^+$ gives the μ-trichloro-bridged anion Fe$_2$Cl$_9^{3-}$.[7] Tetrahedral tetrachloroferrate(III) is obtained with a large cation, such as AsCl$_4^+$[8] and PCl$_4^+$.[9] Clausen and Good[10] reported stabilization of the octahedral hexachloroferrate(III) ion by the medium-sized univalent CH$_3$NH$_3^+$ cation. Crystallization of the FeCl$_6^{3-}$ species with the methylammonium cation was unique in that this occurred with a counterion that is univalent, significantly smaller than the anionic species and capable of hydrogen bonding. Others[11] have reported crystals in which the counterion was of equal but opposite charge and of similar size. The larger bromide ion would make octahedral FeBr$_6^{3-}$ considerably less stable than FeCl$_6^{3-}$ and should result in coordination numbers of 5 or 4 for the Fe(III) atom. Spectroscopic data[12-14] have been interpreted in terms of the FeBr$_4^-$ anion, although no crystallographic structural investigations have been carried out for crystals containing the FeBr$_4^-$ species. The study of FeBr$_3$[15] is the only structural study of iron(III) in which the bromide ion is the only ligand; the iron was found to be octahedrally coordinated by powder diffraction techniques. In view of the results obtained for the [CH$_3$NH$_3$]$_3$FeCl$_6$ system, there seemed a good possibility that the methylammonium cation could provide an interesting counterion in the iron(III)–bromide system. Although previously unreported, the iron(III) compound was readily prepared as long red-black needles. Chemical analysis indicated the product could be either (CH$_3$NH$_3$)$_2$FeBr$_5$ or (CH$_3$NH$_3$)$_3$Fe$_2$Br$_9$. Because either stoichiometry would be interesting, a crystallographic investigation of the material was undertaken.

Experimental Section

(CH$_3$NH$_3$)$_2$[FeBr$_4$]Br was made by cooling 5 g (64 mmol) of 40% aqueous methylamine and adding 40% aqueous HBr until the solution became acidic. To this was added 6 g (20 mmol) of FeBr$_3$ dissolved in aqueous HBr. The mixture was concentrated on a steam bath and slowly cooled. On the surface of the solution, large dark needles resulted which appeared red-black to transmitted light. The crystals are hygroscopic. Density was determined in bromoform and carbon tetrachloride by flotation to be 2.48 ± 0.06 g/cm^3. Because it was not possible to purify the crystals by recrystallization, approximate atomic composition was determined from an unpurified powder containing large crystals. *Anal.* Calcd for (CH$_3$NH$_3$)$_2$FeBr$_5$: H, 2.3; C, 4.6; Fe, 10.8; Br, 77.1. Found: H, 1.9; C, 3.9; Fe, 12.9; Br, 78.9.

Using Mo Kα and Cu Kα radiation, zero and first level precession and Weissenberg photographs were made of two different crystals of (CH$_3$NH$_3$)$_2$FeBr$_5$ rotating around two different axes. Systematic absences of $k + l \neq 2n$ for $0kl$ and $h \neq 2n$ for $h0l$ ($Pna2_1$) indicated that the space group is either $Pnma$ or $Pna2_1$.

The 1:1 methylammonium bromide–ferric bromide compound ([CH$_3$NH$_3$]$^+$[FeBr$_4$]$^-$) can also be readily made. FeBr$_3$ (1.81 g, 6.1 mmol) and CH$_3$NH$_3$Br (1.36 g, 12.1 mmol) were dissolved in 20% aqueous HBr and evaporated on a steam bath. Slow cooling produced dark needles that appeared green-black to reflected light and dark red to transmitted light. Density was determined pycnometrically to be 2.72 ± 0.03 g/cm^3. Precession photographs of several crystals mounted along the needle axis indicate the space group is $Pnma$ or $Pna2_1$, with cell constants $a = 8.33$ (2),[16] $b = 13.11$ (3), and $c = 9.61$ (2) Å (in $Pnma$). The molecular weight calculated on this basis is 430 amu for $Z = 4$, which compares favorably with 407.6 calculated for the 1:1 salt. *Anal.* Calcd for (CH$_3$NH$_3$)[FeBr$_4$]: H, 1.5; C, 3.0; Fe, 13.7; Br, 78.4. Found: H, 1.6; C, 3.4; Fe, 13.3; Br, 77.7.

Because the majority of space groups of simple ionic crystals

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are centric,[17] indexing for $(CH_3NH_3)_2[FeBr_4]Br$ was initially based on *Pnma* symmetry. However, assuming an ordered structure, $Pna2_1$ proved to be the proper space group. In the conventional coordinate system of $Pna2_1$, the needle axes of the crystals are parallel to [010].

For intensity measurement, a cleaved rectangular block of approximate dimensions 0.19 × 0.21 × 0.28 mm was mounted along the growth axis in a glass capillary. Collimators of 0.50-mm bore were chosen and the radiation analyzer was set at about 95% of the maximum intensity for a relatively intense reflection. Mo Kα radiation (λ 0.71069 Å) was monochromated by a graphite crystal. A takeoff angle of 1.35° was chosen, which gave 72% of the maximum intensity as a function of the takeoff angle for a typical reflection. Using a PDP8/I computer to control a Picker four-circle diffractometer, twelve reflections were centered automatically, and the lattice constants were cetermined to be a = 14.989 (6), b = 6.463 (3), and c = 28.130 (11) Å (23°, $Pna2_1$). The density calculated for $(CH_3NH_3)_2FeBr_5$ with eight formula units per unit cell is 2.53 g/cm³. This compares acceptably well with the measured value of 2.48 (6) g/cm³. An ω scan with a half-width at half-height of 0.2° was obtained for the crystal used for intensity measurements.

The orientation matrix for data collection was calculated on the basis of three automatically centered reflections. A 1°/min 2θ scan rate was used for data collection. The 2θ scan width was 1.40° plus a correction for the increased resolution between the Kα_1 and Kα_2 components of the diffracted beam with increasing 2θ. Data were collected to 50° in 2θ, using MoKα radiation. After scanning each peak, 10-sec stationary background counts were taken on each side of the peak; in data reduction, true background was assumed to be a linear function between these counts. Two standard reflections were monitored every 40 reflections.

Toward the end of data collection, the standard reflections had decreased approximately 10% from their initial intensity. The orientation matrix was recalculated and agreed with that originally used. The peaks had broadened slightly, so that a 1.7° 2θ scan was used for the remainder of data collection. This necessitated the use of two different scale factors during refinement. The standards continued to lose intensity as data collection continued, indicating decomposition, with a total decrease in intensity of about 15%. At the end of data collection, it was found that the corner of the crystal that had been most directly exposed to the incident X-ray beam was noticeably discolored.

The 1817 measured reflections were corrected for background and Lorentz–polarization effects[18] and crystal decomposition (see below). Standard deviations $\sigma(F_o)$ were assigned on the basis of modified counting statistics.[19] There were 1135 reflections, designated observed, for which $F_o \geq 3\sigma(F_o)$. An effort was made to correct the data for the loss in intensity due to decomposition of the crystal by fitting a monotonic analytical function to the average of the two decay curves. The maximum error introduced into F_o by using this averaged decomposition correction was estimated to be 2.5%. An absorption correction was made using a linear absorption coefficient of 166 cm^{-1}; resulting transmission coefficients ranged from 0.06 to 0.12.

The atomic scattering factor tables used in refinement were those of Cromer and Waber[20] for neutral atoms and the anomalous dispersion corrections for iron and bromine atoms were those of Cromer.[21]

Structural Solution and Refinement

Broad unresolved peaks were obtained on a normal Patterson map[22] and it was necessary to calculate a sharpened Patterson map. This was done using E's from FAME,[22] which produced a significantly better resolved map. In addition to the E's FAME provides a tabulation for comparison of certain E functions with values expected for centric and acentric structures of the same composition. The fractions of E's greater than 1, 2, and 3 indicated that the structure was hypersymmetric. On the other hand, the average magnitude of E's tended to support an acentric structure. The average value of $E^2 - 1$ gave an uncertain indication. In the early stages of solution, these indications seemed ambiguous and contradictory and were ignored.

The sharpened Patterson functions and, subsequently, direct-method techniques were first used to attempt to solve the structure in *Pnma;* neither produced conventional residuals $R_1 = \Sigma|\Delta F|/\Sigma|F_o|$ [23] lower than 0.40. The possibility remained that $Pna2_1$ was the proper space group. The low-angle data were transformed into the conventional noncentrosymmetric coordinate system ($Pna2_1$), and three bromide ions were positioned from Patterson parameters. The calculated Fourier map showed peaks for all other bromide ions. Two additional Fourier maps were used to position the remaining heavy atoms, and three cycles of isotropic refinement gave R_1 = 0.14. A difference Fourier indicated the positions of the methylammonium cations; inclusion of carbon and nitrogen atoms as carbon atoms gave R_1 = 0.09.

The absorption-corrected observed reflections were used with the modified counting statistics weighting scheme in final stages of refinement, and the function $\Sigma w(\Delta F)^2$ was minimized. Methylammonium ions were refined as rigid groups with an interatomic distance of 1.47 Å. Nitrogen atoms were chosen on the basis of chemical intuition and proven by interchange; when the scattering factors of the carbon and nitrogen atoms of a methylammonium cation were exchanged, the temperature factor of the nitrogen atom decreased to a negative value.

TABLE I

CORRELATION COEFFICIENTS OF ATOMS IN $(CH_3NH_3)_2[FeBr_4]Br$ RELATED BY PSEUDOINVERSION, $100\rho_{ij}$

Atoms	*xx*	*yy*	*zz*	Atoms	*xx*	*yy*	*zz*
Fe(1)–Fe(2)	52	54	82	Br(3)–Br(7)	77	18	87
Br(1)–Br(5)	76	41	88	Br(4)–Br(8)	60	38	83
Br(2)–Br(6)	83	−25	86	Br(9)–Br(10)	83	19	. . .

With refinement, the bond distances between iron ions and their tetrahedral bromide ions became widely different (ranging from 2.18 to 2.50 Å). Full-matrix least-squares produced very large correlations between the x parameters and z parameters of certain pairs of atoms (values ranged between 0.6 and 0.9) (Table I). The correlation found here apparently arises from a pseudoinversion center[24] at $^1/_8$, $^1/_4$, z (for the coordinates reported here, z is nearly zero). In consequence, the least-squares values of the x and z coordinates are nearly linear combinations of the true values, and the iron–bromine interatomic distances were widely different (2.30 ± 0.24 Å). In order to produce chemically reasonable interatomic distances, the coordinates of the two crystallographically independent $FeBr_4^-$ tetrahedra were rechosen. The two tetrahedra were approximately superimposed by inverting the coordinates of one tetrahedron through the pseudoinversion center onto the other tetrahedron. Four bro-

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(17) The ratio of the number of structures from space groups $Pna2_1$ to the number from both $Pna2_1$ and *Pnma* is less than 5% in "Crystal Data Determination Tables," 2nd ed, J. D. H. Donnay and G. Donnay, Ed., American Crystallographic Association Monograph No. 5, Polycrystal Book Service, Pittsburgh, Pa., 1963.

(18) The factor used for Lorentz–polarization with a monochromator was $\sin 2\theta(1 + \cos 2\theta_m)/(\cos^2 2\theta + \cos^2 2\theta_m)$, 2θ being the Bragg angle of the reflection and $2\theta_m$ being that for the monochromator crystal, here 11.73°.

(19) Standard deviation of an observed structure factor F_o for a reflection of observed intensity I_{tot} corrected for backgrounds B_1 and B_2 to I is $\sigma(F_o) = F_o/2I(I_{tot} + (t_s/t_b)^2(B_1 + B_2) + p^2I^2)^{1/2}$ where t_s and t_b are the scan background times and the undetermined p factor was taken as 0.05. See P. W. R. Corfield, R. J. Doedens, and I. A. Ibers, *Inorg. Chem.*, **6,** 197 (1967).

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(22) Fourier and Patterson maps were computed using the program of J. Gvildys, "A Two- and Three-Dimensional Fourier Summation Program." The least-squares program was a local version of W. R. Busing, K. O. Martin, and H. A. Levy's ORFLS. The set of direct-methods programs, including FAME for the production of E's, was that of R. B. K. Dewar and A. L. Stone. Absorption corrections were made with a local version of D. J. Wehe, W. R. Busing, and H. A. Levy's ORABS. Standard deviations of variables were determined using ORFFE, the program of W. R. Busing, K. O. Martin, and H. A. Levy. Molecular views were plotted using ORTEP, written by C. K. Johnson.

(23) Here and elsewhere F_o is the observed structure factor, F_c is the calculated structure factor, s_q is the qth scale factor, $\Delta F = F_o - s_qF_c$, and $w = 1/\sigma^2(F_o)$ (where w is the weighting factor for the reflection of standard deviation $\sigma(F_o)$).

(24) Pseudoinversion centers are known to create large off-diagonal elements in the variance–covariance matrix. See E. C. Lingafelter, P. L. Orioli, and B. J. B. Schein, *Acta Crystallogr.*, **20**, 451 (1966); B. J. B. Schein, J. M. Stewart, and E. C. Lingafelter, Abstracts, 7th International Congress and Symposium of the I.U.C., Moscow, 1966; *Acta Crystallogr., Sect. A*, **21**, 68 (1966).

TABLE II

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR $(CH_3NH_3)_2[FeBr_4]Br$

Atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.0634 (13)	0.1541 (27)	0.8516 (10)	0.0093 (18)	0.0169 (68)	0.0004 (4)	0.0016 (29)	0.0001 (7)	0.0001 (17)
Br(1)	0.2041 (13)	0.2836 (22)	0.8660 (10)	0.0097 (16)	0.0331 (70)	0.0012 (4)	0.0042 (26)	−0.0005 (6)	0.0014 (15)
Br(2)	−0.0304 (14)	0.2484 (24)	0.9083 (11)	0.0076 (15)	0.0642 (116)	0.0024 (5)	0.0067 (25)	0.0000 (8)	0.0021 (15)
Br(3)	0.0044 (12)	0.2738 (19)	0.7788 (10)	0.0058 (12)	0.0328 (70)	0.0015 (4)	−0.0026 (19)	−0.0001 (6)	0.0019 (13)
Br(4)	0.0749 (11)	−0.2067 (20)	0.8508 (9)	0.0101 (15)	0.0165 (58)	0.0023 (4)	0.0008 (22)	−0.0008 (6)	0.0004 (14)
Fe(2)	0.1869 (11)	0.8372 (25)	0.1556 (11)	0.0044 (13)	0.0205 (59)	0.0010 (4)	0.0012 (24)	−0.0003 (7)	0.0005 (19)
Br(5)	0.0427 (11)	0.7094 (19)	0.1424 (10)	0.0028 (10)	0.0345 (60)	0.0020 (5)	−0.0012 (19)	−0.0006 (6)	−0.0009 (14)
Br(6)	0.2828 (14)	0.7474 (21)	0.0926 (9)	0.0091 (16)	0.0346 (85)	0.0013 (4)	0.0072 (23)	0.0027 (7)	0.0017 (11)
Br(7)	0.2508 (15)	0.7136 (22)	0.2258 (9)	0.0125 (17)	0.0372 (68)	0.0008 (3)	0.0088 (27)	−0.0019 (6)	−0.0019 (13)
Br(8)	0.1761 (11)	1.1956 (18)	0.1636 (9)	0.0087 (14)	0.0205 (48)	0.0018 (4)	−0.0002 (21)	0.0003 (6)	−0.0011 (15)
Br(9)	0.4549 (13)	0.2702 (20)	0.0547^b	0.0080 (16)	0.0286 (69)	0.0013 (4)	0.0031 (20)	0.0006 (7)	0.0012 (11)
Br(10)	0.2921 (12)	0.7645 (17)	0.9487 (5)	0.0044 (12)	0.0107 (54)	0.0015 (4)	0.0022 (18)	−0.0006 (6)	0.0014 (11)

Group	x^c	y	z	χ^d	θ	ρ	B_C	B_N
1	0.4246	0.3830	0.1670	3.368	0.592	0.0	4.19	2.51
2	0.1536	0.3702	0.3409	3.339	5.323	0.0	1.04	2.15
3	0.5224	0.2141	0.5253	1.395	5.575	0.0	2.83	2.52
4	0.2097	0.7831	0.4889	4.640	0.402	0.0	5.03	0.42

[a] B is the isotropic temperature factor, while the fomula for the anisotropic temperature factor is $\exp[-(-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] The z parameter of Br(9) was held constant. [c] The nitrogen atom is taken as the origin of the rigid group. [d] For definition of the angles, see C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

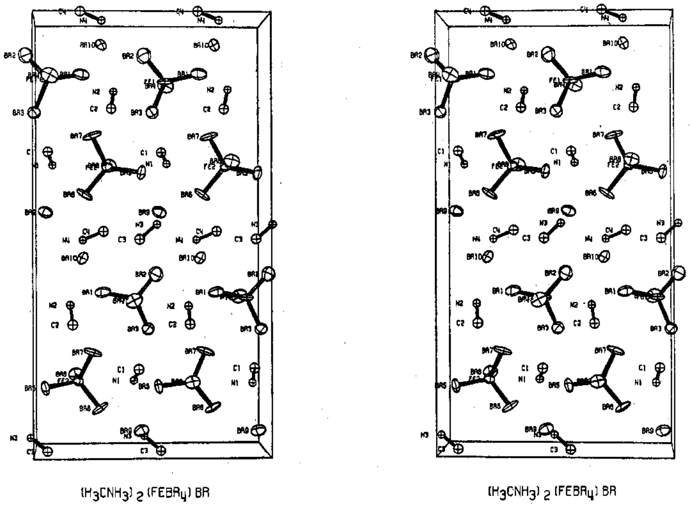

Figure 1.—Stereoscopic view of packing in one unit cell of $(CH_3NH_3)_2[FeBr_4]Br$.

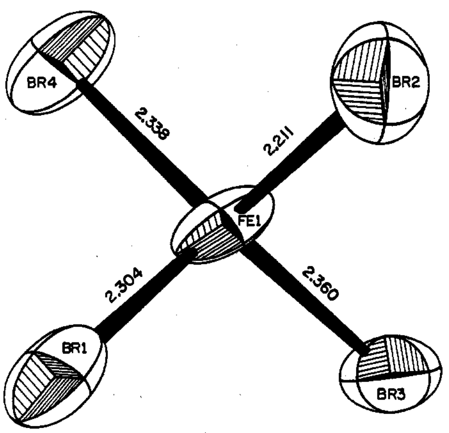

Figure 2.—Tetrahedral $FeBr_4^-$ complex for Fe(1) in $((CH_3)NH_3)_2[FeBr_4]Br$.

mine atoms were chosen for each of the two iron atoms such that the iron–bromine interatomic distances were similar (2.33 ± 0.05 Å). One of the sets of $FeBr_4^-$ coordinates was reinverted through the pseudoinversion center. Subsequent refinement produced significantly more consistent interatomic distances.

Despite high correlation in isotropic thermal parameters for the bromide ions (0.5–0.8), it was decided to attempt anisotropic refinement. For refinement with all but the rigid groups, the weighted residual $R_2 = \Sigma w(F_o - s_qF_c)^2/\Sigma wF_o^2$ dropped from 0.119 with isotropic temperature factors to 0.092 with anisotropic heavy atoms. Heavy-atom anisotropy is significant to the 0.005 level by Hamilton's $\mathcal{R}$ ratio test;[25] systematic errors implied by correlation may, however, be great enough to affect the significance of this drop in R_2. Full-matrix least-squares dropped R_2 to 0.085.

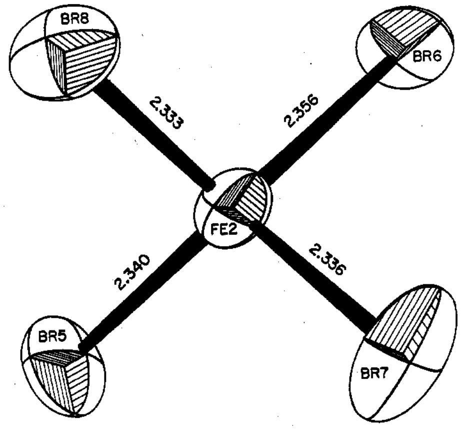

Figure 3.—Tetrahedral $FeBr_4^-$ complex for Fe(2) in $((CH_3)NH_3)_2[FeBr_4]Br$.

In the polar space group $Pna2_1$, the atomic z coordinates are not defined by symmetry. This not only allows free choice of one atomic position in the z direction but also produces an ambiguity in the chirality of that direction. The two sets z, $\bar{z}$ (or the equivalent hkl, $\overline{hkl}$) would be indistinguishable were it not for anomalous scattering. By employing Mo radiation with this compound, however, the proper polarity can be determined. Thus, when the reflection indexes were transformed from hkl to $\overline{hkl}$, R_2 dropped from 0.085 to 0.074 in one cycle. The final residuals were $R_1 = 0.115$ and $R_2 = 0.067$, the largest shift to standard deviation ratio was 0.6, and the final error in an observation of unit weight was $S = 3.8$.[26] Although an analysis of the weighting scheme revealed a definite inverse relationship of variation of the function $\overline{w\Delta F^2}$ with $(\sin\theta)/\lambda$, this is thought to arise in part from not including hydrogen atoms in the refinement. A final difference Fourier was calculated using the positional and thermal coordinates given in Table II and revealed no peaks greater than ±2.1 e/Å^3.

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[25] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[26] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1647. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Results and Discussion

The crystal structure of $(CH_3NH_3)_2FeBr_5$ consists of two independent tetrahedral $FeBr_4^-$ anions, two independent bromide ions, and four methylammonium cations in the asymmetric unit. The packing is shown in Figure 1 and the two tetrahedra are shown in Figures 2 and 3. Both ionic and hydrogen bonding are apparently important in stabilizing this compound. Each nitrogen atom has from three to five nearest neighbor bromine atoms, with nitrogen to nearest bromine atom distances ranging from 3.1 (1) to 3.7 (1) Å. The phase IV structure of ND_4Br[27] shows nitrogen atoms surrounded by a cube of bromine atoms at 3.47 Å. Iron–bromide distances average 2.32 Å, ranging from 2.30 to 2.36 Å except for one anomalously low value of 2.21 Å. Bromide–iron–bromide angles in the $FeBr_4^-$ moiety vary up to 4° from true tetrahedral (see Table III for bond distances and angles).

TABLE III

BOND DISTANCES (Å) AND ANGLES (DEG) FOR $(CH_3NH_3)_2[FeBr_4]Br$

Significant Interatomic Distances			
Fe(1)–Br(1)	2.30 (3)[a]	Fe(2)–Br(5)	2.34 (2)
Fe(1)–Br(2)	2.21 (3)	Fe(2)–Br(6)	2.36 (3)
Fe(1)–Br(3)	2.36 (3)	Fe(2)–Br(7)	2.34 (3)
Fe(1)–Br(4)	2.34 (2)	Fe(2)–Br(8)	2.33 (2)
Significant Interatomic Angles			
Br(2)–Fe(1)–Br(1)	110.8 (1.3)	Br(8)–Fe(2)–Br(7)	106.6 (1.2)
Br(2)–Fe(1)–Br(4)	109.2 (1.1)	Br(8)–Fe(2)–Br(5)	107.6 (0.9)
Br(2)–Fe(1)–Br(3)	107.2 (1.0)	Br(8)–Fe(2)–Br(6)	111.0 (1.1)
Br(1)–Fe(1)–Br(4)	107.3 (1.0)	Br(7)–Fe(2)–Br(5)	113.1 (1.2)
Br(1)–Fe(1)–Br(3)	112.1 (1.2)	Br(7)–Fe(2)–Br(6)	107.4 (0.9)
Br(4)–Fe(1)–Br(3)	110.2 (1.2)	Br(5)–Fe(2)–Br(6)	110.9 (1.2)

[a] Numbers in parentheses here and elsewhere are estimates of error in the least significant digits.

In attempting to interpret optical absorption bands for the tetrahedral $FeBr_4^-$ anion, Ginsberg and Robin[14] as well as Breman and Balt[13] assigned a large degree of covalency to the iron–bromine bond. The iron–bromine bond distances found in $(CH_3NH_3)_2[FeBr_4]Br$ are about 0.2 Å shorter than would be estimated by summing octahedral ionic radii. In the crystal structure of $[(C_6H_5)_4As][FeCl_4]$, Zaslow and Rundle[8] similarly found an iron–chlorine bond length that was considerably shorter than would be predicted by summing octahedral ionic or covalent radii. In order to explain the short interatomic distance, these authors invoked a π-type interaction of metallic antibonding electrons with chloride orbitals. This back-bonding scheme could be used to rationalize the short Fe–Br distances in the $FeBr_4^-$ anion. However, the octahedral ionic radius used does not take into account the decrease in the repulsive coefficient in going to a tetrahedral anion.[28] With this very important correction, one obtains the value of 2.36 Å for the predicted interatomic ferric–bromide ionic bond distance.

This structure has the interesting possibility of being a ferroelectric material. The requirements for ferroelectric behavior[29] are (1) a dipole moment often created by a deformation from strictly symmetrical ions such as SO_4^{2-} or PO_4^{3-} and (2) that the dipoles are aligned spontaneously by hydrogen bonds. In $(CH_3NH_3)_2[FeBr_4]Br$, the presence of a pseudoinversion center[23] indicates that the $FeBr_4^-$ tetrahedra may be easily deformed into inversion images of each other. The methylammonium cation provides the necessary linking mechanism.

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