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The Crystal Structure of NH_4MnFeF_6: Re-refinement in a Higher Symmetry Space Group[1]

RICHARD E. MARSH

Chemical Laboratories, California Institute of Technology, Division of Chemistry/Chemical Engineering, Pasadena, California 91125

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The crystal structure of NH_4MnFeF_6, which was originally described in space group *Pb2n*, can be better described in *Pbcn*. Refinement in *Pbcn* has led to an improved *R* of 0.018, smaller standard deviations, and a more regular structure. One of the two structurally independent ammonium groups appears to be ordered, the other disordered.

The crystal structure of NH_4MnFeF_6 has been described as orthorhombic, a = 7.844(4), b = 12.819(8), c = 10.582(6) Å, Z = 8, space group *Pb2n* (*1*). Systematic absences were consistent with the centrosymmetric space group *Pbcn*, but the authors were unable to reduce *R* below 0.21 for their *Pbcn* model; refinement in *Pb2n* then led to an *R* of 0.021 for 755 reflections, and 163 atomic parameters.

I find no difficulty in refining the structure in *Pbcn*. After the *y* coordinates (Table IV, Ref. (*1*)) were decremented by 0.24 and pairs of atoms related by the additional glide plane were averaged, two cycles of full-matrix least-squares refinement led to an *R* of 0.022 for the 755 reflections. A difference map then indicated the arrangement of hydrogen atoms; after they were introduced, refinement converged at a final *R* of 0.018 for 92 atomic parameters. The *Pbcn* parameters are given in Tables I and II.

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While the general features of the revised structure are the same as described earlier for the *Pb2n* model (*1*), some details change. For example, pairs of Fe—F and Mn—F distances which were significantly different in the *Pb2n* description are now identical by the symmetry of *Pbcn* (Table III). Mössbauer measurements were unable to distinguish between the two iron atoms (*1*) which were structurally different in the *Pb2n* description; these atoms are now equivalent. The esd's in the coordinates are smaller by a factor of about 2.

The arrangement of hydrogen atoms as indicated by the difference map is interesting. Those attached to nitrogen atom "AM2,4" appear to be ordered, and refinement of their coordinates led to a moderately satisfactory tetrahedron with distances N—H2,4*a* = 0.87(6) Å and N—H2,4*b* = 0.69(8) Å, and with H—N—H angles ranging from 99(7)° to 128(10)°; the two H2,4a atoms are directed toward fluoride ions F8,9 with $N \cdots F$ = 2.812(6) Å, $H \cdots F$ = 1.96(5) Å and the two H2,4b atoms toward F4,10 ions with $N \cdots F$ =

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TABLE I

COORDINATES (× 10^5) AND EQUIVALENT B's FOR HEAVIER ATOMS, SPACE GROUP *Pbcn*

Atom	Site	*x*	*y*	*z*	B_{eq}
Fe1,2	8d	24958(7)	−13877(4)	7405(5)	0.742(8)
Mn1,2	8d	75067(8)	−14299(4)	7183(5)	0.827(9)
F1,7	8d	21429(24)	−8744(14)	24369(21)	1.50(3)
F2,3	8d	27774(29)	21456(15)	11409(19)	1.29(3)
F4,10	8d	29214(24)	9(20)	51467(24)	1.90(3)
F5,6	8d	1121(30)	−12361(16)	3900(19)	1.71(4)
F8,9	8d	72201(27)	19234(15)	9885(19)	1.25(3)
F11,12	8d	48905(29)	−15206(16)	10625(19)	1.63(4)
AM1,3	4c	0	11046(46)	25000	2.02(8)
AM2,4	4c	0	−42632(43)	25000	1.56(8)

3.123(6) Å, H···F = 2.45(7) Å. However, in the other ammonium group "AM1,3" only one hydrogen atom—H1,3a—is ordered; it lies on a twofold axis with N—H = 0.66(8) Å and is neighbored by two F1,7 ions with N···F = 3.044(6) Å, H···F = 2.52(8) Å. The other three hydrogen atoms appear to be disordered about the twofold axis, and were represented as six half-atoms equally distributed among two sets of tetrahedral positions with N—H assumed to be 0.85 Å. There are four fluoride ions forming an approximate rectangle on this side of the nitrogen atom, two with N···F8,9 distances of 2.901(6) Å and two with N···F2,3 distances of 2.932(6) Å. The difference between the lengths of these two potential hydrogen bonds is apparently too small to provide a clear choice as to the optimum orientation for this ammonium ion.

TABLE II

COORDINATES (× 10^3) AND ISOTROPIC B's FOR THE HYDROGEN ATOMS

Atom	Site	*x*	*y*	*z*	*B*
H1,3a	4c	0	59(6)	250	5.2(2.5)
H1,3b	8d[a]	102	132	250	10.0
H1,3c	8d[a]	−51	132	184	10.0
H1,3d	8d[a]	−51	132	316	10.0
H2,4a	8d	75(7)	−384(4)	284(5)	4.2(1.4)
H2,4b	8d	52(10)	−450(5)	206(7)	7.9(2.6)

[a] These atoms were placed in assumed positions and assigned site population factors of 0.5; see text.

TABLE III

Fe—F AND Mn—F DISTANCES

		Pbcn[a]	*Pb2n*[b]
Fe1,2	−F1,7	1.932	1.922, 1.936
	−F2,3	1.939	1.939, 1.949
	−F4,10	1.915	1.891, 1.937
	−F5,6	1.916	1.916, 1.919
	−F8,9	1.967	1.962, 1.978
	−F11,12	1.917	1.909, 1.927
Mn1,2	−F1,7	2.096	2.095, 2.096
	−F2,3	2.182	2.175, 2.199
	−F4,10	2.077	2.059, 2.099
	−F5,6	2.088	2.084, 2.095
	−F8,9	2.141	2.125, 2.157
	−F11,12	2.087	2.083, 2.094

[a] This investigation. The esd's are 0.002 Å.
[b] Ref. (*1*). The reported esd's are 0.003–0.004 Å.

It is to be presumed that the other compounds of this structural type, NH_4MnCrF_6 and $RbMnFeF_6$ (*1*), can also be described in *Pbcn* rather than *Pb2n*, although the arrangement of hydrogen atoms in the chromium compound may well be somewhat different because of the differences in cell dimensions.

Computational details. The list of 755 independent *F*(obs) values was obtained as NAPS document No. 04026.[2] Refinement was by full-matrix minimization of the quantity $\Sigma w(F_0^2 - F_c^2)^2$; since error estimates were not included in the F table, weights *w* were taken equal to $1/F_0^2$ for $F_0 \geq 10.0$ and equal to $1/10F_0$ otherwise (*2*, *3*).

[2] See NAPS document No. 04026 for 5 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

The maximum shift-to-esd ratio in the final cycle was 0.19, for a hydrogen coordinate. A secondary extinction parameter (*4*) was included; its final value was $g = 0.673(13) \times 10^{-6}$. The final value of the scale factor for F_0 was 0.958(2). A final difference map showed no excursion as great as 0.3 $e.A^{-3}$.

References

1. M. LEBLANC, G. FEREY, Y. CALAGE, AND R. DE PAPE, *J. Solid State Chem.* **47,** 24 (1983).
2. E. W. HUGHES, *J. Amer. Chem. Soc.* **63,** 1737 (1941).
3. R. E. MARSH AND V. SCHOMAKER, *Inorg. Chem.* **18,** 2331 (1979).
4. A. C. LARSON, *Acta Crystallogr.* **23,** 664 (1967).