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The Hydrate of Ammonium Ferrocyanide and Possible Ionic Transport Mechanism*

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Abstract. $(NH_4)_4Fe(CN)_6.1{\cdot}5H_2O$, *Ia*3*d*, a = 18·261 (8) Å, Z = 16, D_x = 1·357, D_m = 1·423 (3) g cm^{-3}. The structure (R = 0·068 on 590 Mo $K\alpha$ *hkl* intensities) contains large cavities which possibly could fill with additional H_2O to yield better agreement between the observed and calculated densities. The structural arrangement suggests NH_4^+ and/or H_3O^+ motion rather than H^+ for the ionic conductivity observed using NMR techniques.

Introduction. An NMR study (Whittingham, Connell & Huggins, 1972; hereafter WCH) on the narrowing of the ^{1}H line in $(NH_4)_4Fe(CN)_6.1{\cdot}5H_2O$ (AFC), suggested that this material behaved as a typical solid electrolyte with high ionic conductivity. Unfortunately, the study was not able to differentiate between NH_4^+ or H^+ motion. A structural study was initiated to attempt to understand, on a structural basis, the mechanism for the high ionic conductivity as was done for the H^+ ion conductor, $HUO_2PO_4.4H_2O$ (HUP) (Morosin, 1978, and following paper).

Single crystals suitable for diffraction studies may be obtained by recrystallization of commercially available AFC (Ventron Alfa products) from H_2O. The space group *Ia*3*d* was determined from various photographs taken on the very light-green multifaceted specimen. A light cover of oil tends to reduce the decomposition of the crystals. The observed density (by flotation in halocarbon mixtures) of freshly prepared material [1·423 (3) g cm^{-3}] is somewhat higher than that calculated (1·357 g cm^{-3}) with the formula given above and suggests an additional H_2O content of about $\frac{3}{4}$ molecule; however, no evidence was obtained in the Fourier maps for this additional water. The θ–2θ scan technique on one quadrant to 55° 2θ for Mo $K\alpha$ was used for intensity measurements. Symmetry-equivalent reflections were averaged yielding 590 independent *hkl* intensities; of these, $I < 3\sigma$ for 343 cases and such *hkl*'s were considered as 'less-thans' and included in least-squares refinement whenever $F_o > F_c$. The function $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2$ was minimized. Structure factors were calculated using scattering factors computed from Hartree–Fock wave functions (Cromer & Mann, 1968). Various models were deduced for the placement of the $Fe(CN)_6^{4-}$ ion in the cell from a Patterson Fourier synthesis and resulting Fouriers. Packing requirements together with observed peaks suggested a 48 fold (*g*) site and a 16 fold (*b*) site would account for the N positions of the NH_4^+ ions while the peaks on a 24 fold (*c*) site probably should be associated with the O of H_2O. It should be noted that the space requirements for NH_4^+ and H_2O (as well as NH_3 and H_3O^+ if any proton transfer has occurred) are essentially identical and disorder could be possible. With positional parameters given in Table 1, a final residual index R = 0·068 is obtained.‡ The final difference synthesis contains no unaccounted density around the O or cavity position; the largest peaks in this difference synthesis are 1·0 e Å^{-3} located ~0·7 Å from the Fe position and 0·5 e Å^{-3} located ~0·5 Å from (*b*) N. The thermal parameter for O is about twice those of other light atoms.

Table 1. *Positional parameters for AFC*

	Equi-points	x	y	z
Fe	(*a*)	0	0	0
N(1)	(*h*)	0·0395 (5)	0·4443 (5)	0·1525 (5)
C(2)	(*h*)	0·0255 (5)	0·4646 (5)	0·0946 (4)
N(3)	(*g*)	$\frac{1}{8}$	0·2074 (4)	
N(4)	(*b*)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$
O(5)	(*c*)	0	$\frac{1}{4}$	$\frac{1}{8}$

Discussion. The structure consists of $Fe(CN)_6^{4-}$ ions loosely packed with NH_4^+ and H_2O groups (Fig. 1). The Fe is octahedrally coordinated to the C of the CN^- entity [labeled N(1) and C(2) in Table 1] with an Fe—C bond of 1·902 (8) Å, C—Fe—C angles of 89·8 (4) and 90·2 (4)° and Fe—C—N angles of 179·3 (3)°. The C—N bond distance is 1·15 (1) Å. These values are typical of those observed in such ferrocyanide com-

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‡ A list of the structure factors, a figure showing interatomic distances, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33809 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

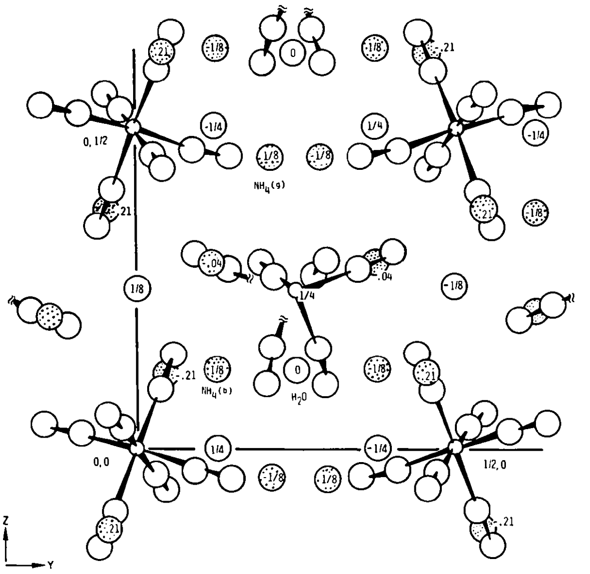

Fig. 1. Structure arrangement found in AFC. Only contents between $\pm\frac{1}{4}$ along x are shown. Stippled circles are NH_4^+ ions while open circles with x values are H_2O. Spiral paths such as that along y involving $O(\frac{1}{8},0,\frac{1}{4})$, $N(\frac{1}{8},\frac{1}{8},\frac{1}{8})$, $O(0,\frac{1}{4},\frac{1}{8})$, $N(-\frac{1}{8},\frac{3}{8},\frac{1}{8})$, $O(-\frac{1}{8},\frac{1}{2},\frac{1}{4})$, $N(-\frac{1}{8},\frac{5}{8},\frac{3}{8})$ *etc.* may be responsible for the molecular ionic transport found in this material. Such paths along the other directions of this cubic material would join at (*b*) symmetry sites, such as at $N(\frac{1}{8},\frac{1}{8},\frac{1}{8})$, which are close to the cavities extending between $O(0,\frac{1}{4},\frac{1}{8})$ and symmetry point $0,\frac{1}{4},0$.

pounds (Buser, Schwarzenbach, Petter & Ludi, 1977). The NH_4^+ ions involve different environments; N(4) has six closest contacts with C(2) at 3·25 Å and three with O(5) at 3·23 Å, separations not favorable for hydrogen bonding. The environment of N(3) is more complex and consists of four contacts with CN^- ions; two of these contacts are with N(1) at 3·12 (1) Å and C(2) at 3·37 Å while the other two are with the N(1) at 2·85 (1) Å. The closest tetrahedral angle formed is 99·3 (3)° between the N atoms at 2·85 Å while the remaining N(1)—N(3)—N(1) angles of 82·8, 91·0, and 162·7° are not typical of those usually found in good hydrogen-bonded systems. Using the C(2) or combinations of C(2) and N(1) positions improves the orientation towards tetrahedral angles only slightly. The closest contact to O(5) is N(4) at 3·23 Å, mentioned above, with N—O—N of 180°. Other contacts involve 3·64 Å or larger separations.* Thus, H_2O cannot be considered as hydrogen bonded in this arrangement. The H_2O sits in a cavity which extends along cell edges normal to the 3·23 Å contacts, *i.e.* for H_2O at $0,\frac{1}{4},\frac{1}{8}$ along positions $0,\frac{1}{4},x$. As x decreases towards 0·0 (corresponding to a 2·28 Å distance), a N(1) contact decreases from 3·65 to 2·19 Å. Intermediate points could serve as saddle points between H_2O positions. Note that a spiral path (Fig. 1) can be selected connecting the loosely held H_2O and (*b*) NH_4^+ sites and that such spirals intersect (*b*) and are almost joined near H_2O sites at a point along the cavity mentioned above. It should be emphasized that no unusually high electron density was observed between such sites in the final difference Fourier map.

One notes from these rather large separations between NH_4^+ and H_2O entities that an H^+ ion transport mechanism (requiring an equilibrium between NH_4^+ and H_2O with NH_3 and H_3O^+) similar to that found in HUP (Morosin, 1978) is not very likely. Ionic conduction observed by WCH (1972) must involve molecular groups rather than H^+ ions. The structure is compatible with such a mechanism along the interconnected spiral paths mentioned above.

NMR measurements in our laboratory have extended those of WCH (1972) to lower temperature (77 K) in an attempt to resolve protons associated with the H_2O and NH_4^+ entities. These observations are consistent with molecular reorientation equivalent to rotation at 77 K and translational motion at room temperature, as required with a molecular transport mechanism suggested by the interconnected spiral paths; however, pulsed techniques need to be used to attempt to distinguish between motion of ammonium and hydrated protons.

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* See previous footnote.

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