

## Tris-(tetraethylammonium) Hexacyanoferrate (III): Stability of Its Hydrates and X-Ray Structure of the Pentahydrate

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From thermogravimetric analysis performed under controlled water vapor pressures, the domains of stability of  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$  ( $x = 8, 5, 2, 0.2-0.7, 0$ ) have been defined. The thermodynamical values,  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$ , for the dehydration of these hydrated salts have been obtained. At room temperature and atmospheric environment, the pentahydrated salt is stable. Its structure has been determined from single crystal X-ray diffraction. It crystallizes in the monoclinic space group  $P2_1$  (No. 4),  $a = 10.442(4)$ ,  $b = 14.196(5)$ ,  $c = 14.552(5)$  Å,  $\beta = 108.22(4)^\circ$ ,  $V = 2047.7$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calc}} = 1.124$  g cm<sup>-3</sup>,  $R = 0.056$  based on 2481 independent reflections with  $I > 3\sigma(I)$ . Fe-C and N-C averaged bond lengths are 1.953(7) and 1.140(10) Å, respectively. Water molecules and  $\text{Fe}(\text{CN})_6$  units are hydrogen bonded as indicated by N $\cdots$ O contacts (2.85  $\rightarrow$  2.94 Å) and O $\cdots$ O contacts (2.81  $\rightarrow$  2.96 Å). © 1989

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### Introduction

In the field of charge transfer salts based on tetrathiafulvalene (TTF) and its derivatives, the preparation and the X-ray crystal structure of  $(\text{TTF})_{11}\text{Fe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$  have been reported (1). This compound has been obtained by the electrocrystallization technique starting from the tetraethylammonium salt of the hexacyanoferrate anion. Although the experiments were carried out in an anhydrous medium, the TTF salt crystallizes with a high number of water molecules. It can be thought that these water molecules are issued from the starting salt

whose formula would be  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$ . The thermal behavior of this compound under selected water vapor pressures ( $P_{\text{H}_2\text{O}}$ ) and the X-ray crystal structure of the stable hydrate at ambient temperature and pressure were investigated and determined.

### Experimental and Results

#### Thermodynamic Study

The preparation of the title compound and its recrystallization were performed as reported in the literature (2). The experiments were carried out using a Mac-Bain thermobalance. About 12 mg of powdered sample was thoroughly spread out on a

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sample holder ( $\phi = 1$  cm) to avoid mass effect. A constant gaseous water pressure was maintained above the sample by connecting the reaction vessel to another which was kept at a constant temperature and containing either water or sulfuric acid solutions. The values of the water vapor pressure, which depends on the temperature, were calculated from data of Wexler (3). The corresponding values based on sulfuric acid solutions were taken from published tables (4). The experiments were performed with a heating rate of  $6 \text{ K hr}^{-1}$ .

The thermogravimetric (TG) curves obtained for various  $P_{\text{H}_2\text{O}}$  are shown in Fig. 1. As the exact number of water molecules in the sample was not known precisely at the beginning of the TG analysis, the anhydrous compound, obtained at the end of each experiment, was taken as a reference

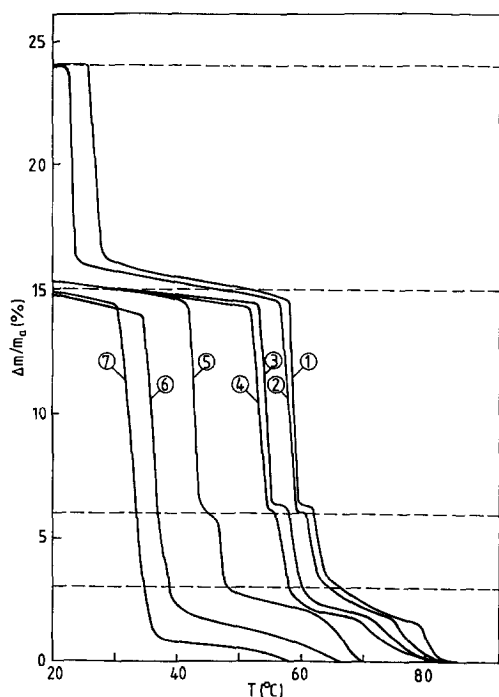
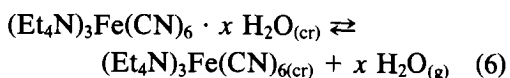
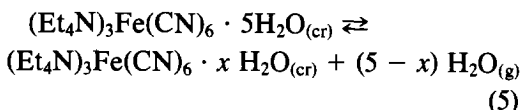
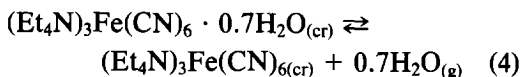
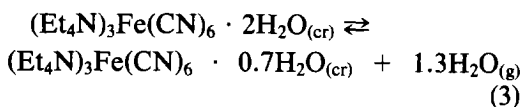
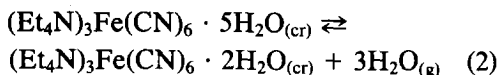
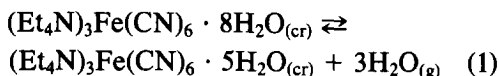


FIG. 1. Variation of  $\Delta m/m_a$  with temperature (heating rate =  $6 \text{ K h}^{-1}$ , sample mass =  $12 \text{ mg}$ ) under fixed water vapor pressure. (1)  $2000 \text{ Pa}$ , (2)  $1595 \text{ Pa}$ , (3)  $1440 \text{ Pa}$ , (4)  $1106 \text{ Pa}$ , (5)  $613 \text{ Pa}$ , (6)  $313 \text{ Pa}$ , (7)  $227 \text{ Pa}$ .

material. The ordinate scale (see Fig. 1) represents  $\Delta m/m_a$ , where  $\Delta m$  is the variation of the mass and  $m_a$  the mass of the anhydrous compound. The horizontal straight dashed lines drawn at the ordinates 3, 6, 15, and 24 correspond to salts with 1, 2, 5, or 8  $\text{H}_2\text{O}$ , respectively.

It can be seen that the octahydrated salt (curves 1 and 2) is obtained at  $20^\circ\text{C}$  for  $P_{\text{H}_2\text{O}} > 1500 \text{ Pa}$ . Complementary experiments have shown that this salt dissolves in its water of crystallization when  $P_{\text{H}_2\text{O}} > 2250 \text{ Pa}$ . For  $P_{\text{H}_2\text{O}}$  ranging between  $227$  and  $1440 \text{ Pa}$  (other curves), the pentahydrated salt is stable at room temperature. However, the actual number of the water molecules ranges between 4.9 and 5.1 depending on  $P_{\text{H}_2\text{O}}$  at room temperature and slowly decreases when the temperature is increased until a very fast dehydration occurs. For instance, this number decreases to 4.7 when  $P_{\text{H}_2\text{O}} = 313 \text{ Pa}$  at the onset of dehydration which occurs near  $34.5^\circ\text{C}$ . The pentahydrate can be also obtained by dehydration of the octahydrate by increasing the temperature. In the case of  $P_{\text{H}_2\text{O}} > 320 \text{ Pa}$ , a further dehydration gives a dihydrated salt in a narrow domain of temperature. At higher temperatures, the TG curves show inflexion points at different values of  $\Delta m/m_a$  depending on  $P_{\text{H}_2\text{O}}$ . These correspond to the formation of hydrates with a number of water molecules less than 1 (mean value: 0.7). For  $P_{\text{H}_2\text{O}} < 320 \text{ Pa}$ , the dehydration of the crystalline (cr) pentahydrate yields compounds with a number of gaseous  $\text{H}_2\text{O}$  (g) molecules, depending on  $P_{\text{H}_2\text{O}}$ , and ranging between 0.2 and 0.5. The last step of these dehydrations corresponds to the formation of the anhydrous compound  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6$ . It has been observed that this behavior is fully reversible, as all these hydrates can be obtained by rehydration of the anhydrous salt when the temperature decreases.

Depending on  $P_{\text{H}_2\text{O}}$  and temperature, the following chemical equilibriums take place:



with  $0.2 < x < 0.5$ .

In consideration to the experimental conditions used, the water vapor pressure in equilibrium with two consecutive hydrates is equal to the one fixed in the vessel reac-

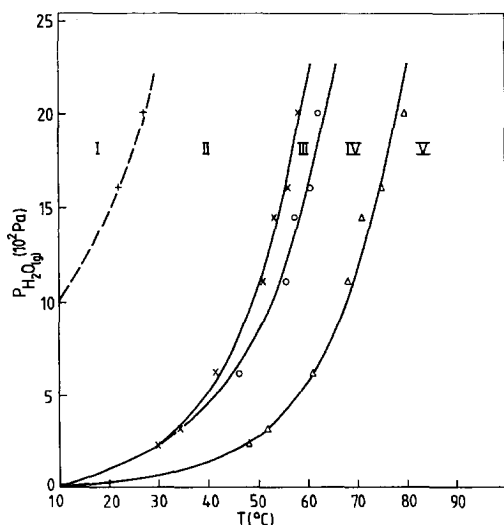


FIG. 2. Pressure temperature diagram. I, II, III, IV and V represent respectively the domains of stability of  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ ,  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ ,  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ ,  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$  ( $0.2 < x < 0.7$ ), and  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6$ .

TABLE I

THERMODYNAMICAL VALUES FOR THE DEHYDRATION REACTIONS

Reaction	1	2	3	4
$\Delta_r H_m^\circ$ (kJ mole <sup>-1</sup> )	99 <sup>a</sup>	193 (2)	74 (1)	47 (1)
$\Delta_r S_m^\circ$ (J mole <sup>-1</sup> K <sup>-1</sup> )	237 <sup>a</sup>	483 (6)	175 (5)	111 (3)

<sup>a</sup> Uncertain values obtained from only two experimental points. The values in parentheses are the standard deviations.

tor at the onset temperature where the dehydration rate of the most hydrated salt increases suddenly. However, the determination of this temperature for the equilibria (4) and (6) is less accurate, especially when the  $P_{\text{H}_2\text{O}}$  is low. The equilibrium curves  $P_{\text{H}_2\text{O}}$  vs  $T$  between two phases are shown in Fig. 2. They define the boundaries of the regions where the five salts are thermodynamically stable. It clearly appears that the domain III of stability of  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  is very narrow. On the other hand, it must be explicit that, particularly inside the domains II and IV, the number of  $\text{H}_2\text{O}$  in the corresponding hydrates varies slightly not only with  $P_{\text{H}_2\text{O}}$  but also with  $T$ .

From these results the values of the standard enthalpy  $\Delta_r H_m^\circ$  and the standard entropy  $\Delta_r S_m^\circ$  have been calculated for dehydration reactions (1-4), see Table I. Indeed,  $\log P_{\text{H}_2\text{O}}$  is related to the inverse of the absolute equilibrium temperature by the equation

$$\ln P_{\text{H}_2\text{O}} = -\frac{\Delta_r H_m^\circ}{nRT} + \frac{\Delta_r S_m^\circ}{nR},$$

where  $n$  is the number of  $\text{H}_2\text{O}_{(\text{g})}$  moles involved in the equilibrium.

From the above thermodynamical study, it appears that the stable salt at room temperature and atmospheric environment is a compound with 5.0 (1) water molecules per formula unit.

## X-ray Structure Determination

A yellow crystal of approximate dimensions of  $0.15 \times 0.10 \times 0.08$  mm was mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-crystal-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda_{\text{mean}} = 0.71023 \text{ \AA}$ ). The unit cell constants were obtained at 293 K from 25 carefully centered reflections in the range  $5 < \theta < 12^\circ$ :  $a =$

TABLE II

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS ( $\text{\AA}^2$ )  $B_{\text{eq}} = \Sigma_j \Sigma_j a_j a_j \beta_{ij}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
Fe	-0.14141(8)	0.333	0.69487(6)	2.92(1)
C1	-0.3030(6)	0.3403(7)	0.5842(4)	3.7(1)
C2	0.0242(6)	0.3269(6)	0.8055(4)	3.5(1)
C3	-0.2457(7)	0.2940(5)	0.7781(5)	3.5(1)
C4	-0.0383(7)	0.3699(5)	0.6086(5)	3.8(2)
C5	-0.1688(8)	0.4643(6)	0.7245(5)	4.3(2)
C6	-0.1147(7)	0.2105(5)	0.6641(5)	3.6(2)
N1	-0.3995(6)	0.3431(7)	0.5178(4)	5.4(2)
N2	0.1189(6)	0.3251(6)	0.8707(4)	5.4(2)
N3	-0.3061(7)	0.2703(6)	0.8270(5)	5.5(2)
N4	0.0235(6)	0.3899(6)	0.5599(5)	5.2(2)
N5	-0.1862(8)	0.5394(5)	0.7435(5)	6.2(2)
N6	-0.0992(7)	0.1246(5)	0.6474(5)	4.9(2)
O1	0.3562(5)	0.3457(6)	0.3586(4)	6.4(2)
O2	0.3021(6)	0.2135(5)	0.2075(4)	6.4(2)
O3	0.3500(6)	0.2521(6)	0.0281(4)	7.8(2)
O4	-0.1568(6)	-0.0641(5)	0.5793(4)	6.4(1)
O5	0.3799(8)	0.7411(9)	-0.0035(6)	14.3(3)
N7	0.3133(6)	0.1060(6)	0.6137(5)	4.9(2)
C7	0.440 (1)	0.152 (1)	0.608 (1)	11.4(4)
C8	0.514 (1)	0.106 (1)	0.5498(9)	12.5(4)
C9	0.204 (2)	0.093 (1)	0.513 (1)	12.1(5)
C10	0.161 (2)	0.177 (1)	0.456 (1)	11.9(5)
C11	0.342 (2)	0.007 (1)	0.653 (1)	14.0(5)
C12	0.243 (1)	-0.047 (1)	0.675 (1)	11.7(4)
C13	0.255 (1)	0.166 (1)	0.6746(9)	9.9(4)
C14	0.332 (2)	0.177 (1)	0.7793(9)	12.1(4)
N8	-0.0214(6)	0.0001(5)	-0.0787(4)	3.9(1)
C15	-0.0123(9)	0.1094(7)	-0.0843(6)	6.1(2)
C16	-0.032 (1)	0.1593(8)	-0.0004(7)	7.9(3)
C17	-0.1529(9)	-0.0324(8)	-0.0693(6)	6.5(3)
C18	-0.279 (1)	0.001 (1)	-0.1516(9)	9.2(4)
C19	0.0858(9)	-0.0387(7)	0.0097(6)	5.8(2)
C20	0.226 (1)	-0.0141(9)	0.0161(8)	7.5(3)
C21	-0.005 (1)	-0.0364(7)	-0.1728(6)	6.0(2)
C22	0.000 (1)	-0.1417(7)	-0.1798(7)	7.4(3)
N9	0.3219(6)	0.5634(5)	0.7473(4)	4.2(1)
C23	0.349 (1)	0.646 (1)	0.6960(8)	8.0(3)
C24	0.245 (1)	0.661 (1)	0.5926(8)	10.1(4)
C25	0.340 (1)	0.474 (1)	0.6951(9)	10.2(4)
C26	0.458 (1)	0.452 (1)	0.683 (1)	12.8(4)
C27	0.418 (1)	0.567 (1)	0.8483(7)	7.5(3)
C28	0.404 (1)	0.478 (1)	0.9066(9)	11.9(4)
C29	0.1771(9)	0.5614(9)	0.7481(7)	6.9(3)
C30	0.134 (1)	0.647 (1)	0.7874(8)	9.7(4)

TABLE III

INTERATOMIC BOND LENGTHS ( $\text{\AA}$ ) FOR  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$

Fe-C1	1.935(5)	C11-C12	1.40 (3)
Fe-C2	1.959(5)	C13-C14	1.49 (2)
Fe-C3	1.946(8)	N8-C15	1.559(12)
Fe-C4	1.965(8)	N8-C17	1.495(12)
Fe-C5	1.955(8)	N8-C19	1.518(9)
Fe-C6	1.959(8)	N8-C21	1.524(11)
C1-N1	1.156(7)	C15-C16	1.482(15)
C2-N2	1.136(7)	C17-C18	1.552(13)
C3-N3	1.141(11)	C19-C20	1.481(14)
C4-N4	1.134(11)	C21-C22	1.501(14)
C5-N5	1.131(11)	N9-C23	1.467(15)
C6-N6	1.140(10)	N9-C25	1.53 (2)
N7-C7	1.501(15)	N9-C27	1.497(10)
N7-C9	1.564(15)	N9-C29	1.515(12)
N7-C11	1.51 (2)	C23-C24	1.569(15)
N7-C13	1.49 (2)	C25-C26	1.33 (2)
C7-C8	1.46 (2)	C27-C28	1.55 (2)
C9-C10	1.44 (2)	C29-C30	1.47 (2)

Note. Numbers in parentheses are estimated standard deviations.

$10.442(4)$ ,  $b = 14.196(5)$ ,  $c = 14.552 \text{ \AA}$ ,  $\beta = 108.32(4)^\circ$ ,  $V = 2047.7 \text{ \AA}^3$ ,  $Z = 2$ . The intensities were collected up to  $2\theta = 50^\circ$  ( $0 < h < 12$ ,  $0 < k < 16$ ,  $-17 < l < 17$ ). 3712 independent reflections were measured, 2481 with  $I > 3\sigma(I)$ . The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Based on the systematic extinctions of  $0k0$ :  $k = 2n + 1$  and the successful refinement of the structure, the space group was determined to be  $P2_1$  (No. 4).

The structure was solved by direct methods (5) and successive Fourier differences. The atomic scattering factors were taken from the "International Tables for X-ray Crystallography" (6). The hydrogen atoms were placed at calculated positions ( $\text{C-H} = 1 \text{ \AA}$  and  $B_{\text{eq}} = 4 \text{ \AA}^2$ ). The coordinates and the anisotropic thermal motion parameters of the all nonhydrogen atoms have been refined by full-matrix least-squares calculations. The weighting scheme,  $\omega = [\sigma^2(\text{Fo}) + (0.07 \text{ Fo})^2]^{-1}$  was used. The final  $R$  and

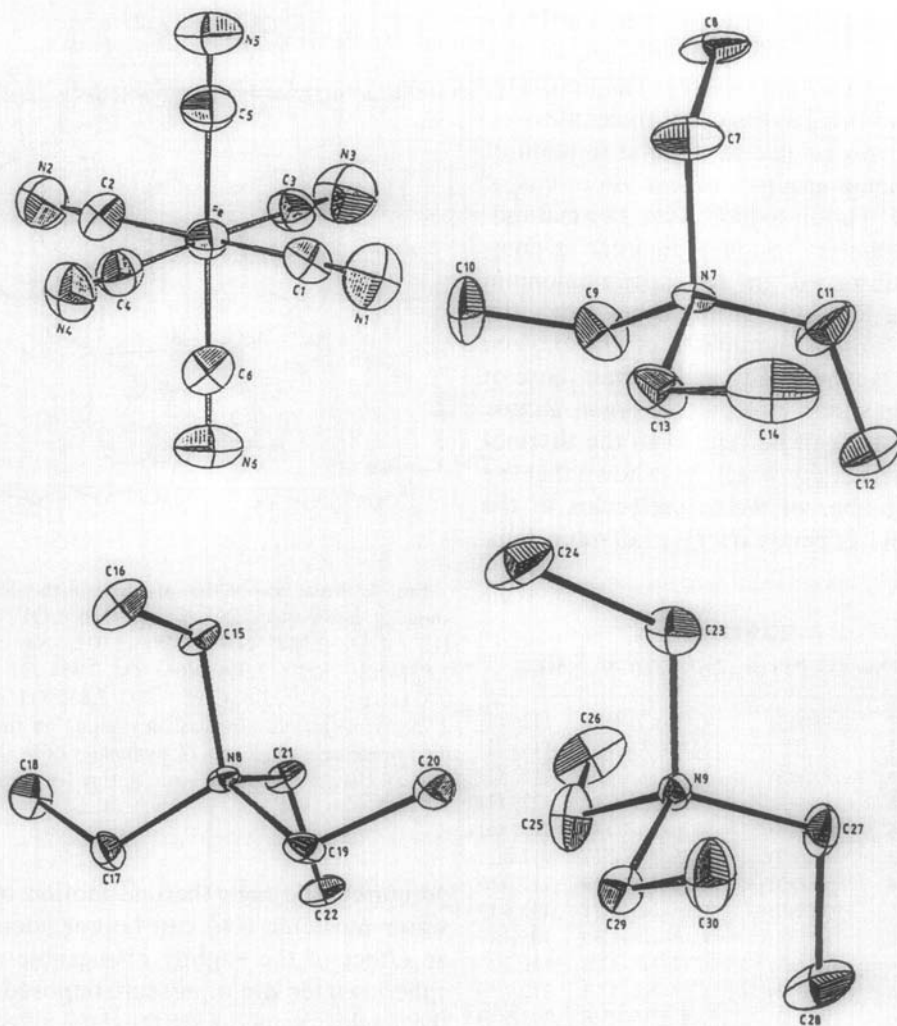


FIG. 3. Atom numbering for the title compound.

$R_w$  values are 0.056 and 0.073, respectively. The goodness of fit is 1.71. The maximum peak observed in the least Fourier difference is  $\sigma_{\max} = 0.41 \text{ e } \text{Å}^3$ . The Enraf-Nonius SDP computing package, described by Frenz (7), was used on a PDP 11/60 computer. Positional parameters and  $B_{\text{eq}}$  are given in Table II. Tables of observed and calculated structure factor amplitudes are available upon request from the authors.

The bond distances and the bond angles are given in Tables III and IV, respectively.

The atomic numbering is shown in Fig. 3. The structural features of the  $\text{Fe}(\text{CN})_6^{3-}$  anion (averaged  $\text{Fe}-\text{C}: 1.953(7)$  and  $\text{C}\equiv\text{N}: 1.140(10) \text{ Å}$ ) are in good agreement with those observed in the literature, e.g.,  $\text{Cs}_2\text{LiFe}(\text{CN})_6$  (8). The crystal structure displayed in Fig. 4 is built from two  $\text{Fe}(\text{CN})_6^{3-}$  and six  $\text{Et}_4\text{N}^+$  units. The latter form layers, parallel the (010) plane, separated by planes containing the  $\text{Fe}(\text{CN})_6^{3-}$  anions and the water molecules. Short  $\text{N}\cdots\text{O}$  and  $\text{O}\cdots\text{O}$  contacts (Fig. 4) are observed indicating

hydrogen bonding between (i) the  $\text{Fe}(\text{CN})_6^{3-}$  anions and the water molecules and (ii) the water molecules themselves. The  $\text{Fe}(\text{CN})_6^{3-}$  anions are bridged by water molecules.

As a consequence of the free rotation of the ethylenic groups, the carbon atoms of the  $\text{Et}_4\text{N}^+$  cation exhibit large thermal motion parameters. Such a disorder is commonly observed in tetraalkylammonium salts, see Ref. (9). On the other hand, the thermal motion parameter of the oxygen atom  $\text{O}_5$  is abnormally higher than those of the other water molecules oxygen atoms. This feature can be related to the thermogravimetric study which has shown that the actual number of water molecules in the compound depends on  $P_{\text{H}_2\text{O}}$  at room tem-

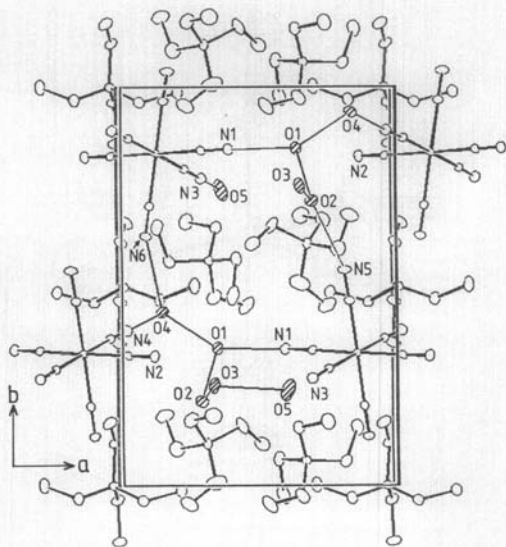


FIG. 4. Projection of the structure in the  $ac$  plane showing intermolecular contacts:  $\text{N1} \cdots \text{O1}^{\text{I}}$ , 2.857;  $\text{N2} \cdots \text{O3}^{\text{II}}$ , 2.944;  $\text{N3} \cdots \text{O5}^{\text{III}}$ , 2.933;  $\text{N4} \cdots \text{O4}^{\text{IV}}$ , 2.871;  $\text{N5} \cdots \text{O2}^{\text{IV}}$ , 2.936;  $\text{N6} \cdots \text{O4}$ , 2.854;  $\text{O1} \cdots \text{O2}$ , 2.811;  $\text{O1} \cdots \text{O4}^{\text{IV}}$ , 2.824;  $\text{O2} \cdots \text{O3}$ , 2.860;  $\text{O3} \cdots \text{O5}^{\text{V}}$ , 2.956 Å; estimated standard deviations on the least digit range between 7 and 12; symmetry code: I(-1 +  $x$ ,  $y$ ,  $z$ ), II( $x$ ,  $y$ , 1 +  $z$ ), III(- $x$ , - $\frac{1}{2}$  +  $y$ , 1 -  $z$ ), IV(- $x$ ,  $\frac{1}{2}$  +  $y$ , 1 -  $z$ ), V(1 -  $x$ , - $\frac{1}{2}$  +  $y$ , - $z$ ).

TABLE IV  
BOND ANGLES (°) FOR  $(\text{Et}_4\text{N})_3\text{Fe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$

C1-Fe-C2	178.8(3)	C11-C7-C13	112. (1)
C1-Fe-C3	91.2(3)	N7-C7-C8	118. (1)
C1-Fe-C4	87.9(3)	N7-C9-C10	116. (1)
C1-Fe-C5	88.9(3)	N7-C11-C12	122. (1)
C1-Fe-C6	90.7(3)	N7-C1-C14	119. (1)
C2-Fe-C3	89.9(3)	C15-N8-C17	112.6(7)
C2-Fe-C4	91.0(3)	C15-N8-C19	111.4(6)
C2-Fe-C5	90.7(3)	C15-N8-C21	105.4(6)
C2-Fe-C6	89.7(3)	C17-N8-C19	105.4(6)
C3-Fe-C4	178.6(3)	C17-N8-C21	110.2(6)
C3-Fe-C5	89.1(3)	C19-N8-C21	112.1(6)
C3-Fe-C6	91.1(3)	N8-C15-C16	113.9(8)
C4-Fe-C5	91.9(3)	N8-C17-C18	114.6(9)
C4-Fe-C6	87.9(3)	N8-C19-C20	114.8(8)
C5-Fe-C6	179.5(3)	N8-C21-C22	114.5(8)
Fe-C1-N1	178.8(9)	C23-N9-C25	110.2(9)
Fe-C2-N2	178.3(7)	C23-N9-C27	107.3(7)
Fe-C3-N3	179.3(7)	C23-N9-C29	111.7(7)
Fe-C4-N4	178.4(6)	C25-N9-C27	111.6(8)
Fe-C5-N5	178.1(8)	C25-N9-C29	105.5(8)
Fe-C6-N6	179.2(7)	C27-N9-C29	110.7(7)
C7-N7-C9	113. (1)	N9-C23-C24	114.3(9)
C7-N7-C11	110.9(9)	N9-C25-C26	121. (1)
C7-N7-C13	108.5(9)	N9-C27-C28	111.2(9)
C9-N7-C11	104. (1)	N9-C29-C30	114.6(9)
C9-N7-C13	108.2(9)		

Note. Numbers in parentheses are estimated standard deviations.

perature. The high thermal motion of this water molecule ( $\text{O}_5$ ) can be considered as an effect of the slightly changeable atmospheric water vapor pressure imposed upon the single crystal during the data collection.

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