refined, the latter two being fixed by instrumental characteristics. In addition to these parameters, a zero-point error, cell parameters and atomic and anisotropic thermal parameters for all atoms were refined, giving a total of 39 variables during the final cycles. The program *VDELSQ*, incorporating subroutines from the Cambridge Crystallographic Subroutines Library package (Brown & Matthewman, 1987), and *GENIE* spectrum manipulation software (David *et al.*, 1986) were used for all data analysis. Atomic coordinates for the isomorphous La_2NiRuO_6 (Battle & Jones, 1987) were used as a starting model for the refinement, in space group *Pbnm;* the systematic absences of this space group were consistent with those observed in our data. A smooth refinement was achieved, with convergence at the final agreement factors $R_I = 8{\cdot}4\%$, $R_p = 3{\cdot}0\%$, $R_{wp} = 3{\cdot}2\%$. The statistically expected R factor, $R_{\rm exp}$, was 2·5%, leading to a goodness-of-fit index χ^2 $(=[R_{wp}/R_{\rm exp}]^2)$ of 2·47. All the R factors are defined in the original paper of Rietveld (1969). The most obvious discrepancy between the observed and calculated diffraction profiles occurs at $d \sim 2{\cdot}6$ Å; we have no convincing explanation for this anomaly.

Discussion. Final atomic coordinates and anisotropic temperature factors are given in Table 1, and selected bond distances and angles in Table 2. The phase adopts an orthorhombic, $GdFeO_3$-like perovskite structure with final, refined cell parameters $a = 5{\cdot}5670\ (1)$, $b = 5{\cdot}5304\ (1)$ and $c = 7{\cdot}8446\ (2)$ Å. A plot of the final observed, calculated and difference profiles for the Rietveld refinement is shown in Fig. 1,* and a polyhedral representation (Fischer, 1985) of the distorted perovskite structure in Fig. 2. All bond lengths lie within chemically sensible limits, the Ru—O bond lengths being comparable to those in other Ru^{IV} oxides, for example RuO_2 [2 × 1·942 Å and 4 × 1·984 Å (Boman, 1970)].

We are grateful to the SERC for financial support.

---

* A list of numerical data corresponding to Fig. 1 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51563 (84 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Battle, P. D. & Jones, C. W. (1987). *Mater. Res. Bull.* **22**, 1623–1627.

Boman, C. E. (1970). *Acta Chem. Scand.* **24**, 116–122.

Bouchard, R. J. & Gillson, J. L. (1972). *Mater. Res. Bull.* **7**, 873–878.

Brown, P. J. & Matthewman, J. C. (1987). Rutherford–Appleton Laboratory Report RAL-87-010.

Callaghan, A., Moeller, C. W. & Ward, R. (1966). *Inorg. Chem.* **5**, 1572–1576.

David, W. I. F., Johnson, M. W., Knowles, K. J., Moreton-Smith, C. M., Crosbie, G. D., Campbell, E. P., Graham, S. P. & Lyall, J. S. (1986). Rutherford–Appleton Laboratory Report RAL-86-102.

Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

Geller, S. (1956). *J. Chem. Phys.* **24**, 1236–1239.

Randall, J. J. & Ward, R. (1959). *J. Am. Chem. Soc.* **81**, 2629–2631.

Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

Acta Cryst. (1989). C**45**, 367–371

The Structure of Ferric Oxonium Bis(hydrogenphosphate), $Fe^{3+}.(H_3O)^+.2(PO_4H)^{2-}$

By Ivo Vencato

Departamento de Física, Universidade Federal de Santa Catarina, 88049 *Florianópolis, SC, Brazil*

Enrico Mattievich and Lígia de F. Moreira

Instituto de Física, Universidade Federal do Rio de Janeiro, 21941 *Rio de Janeiro, RJ, Brazil*

and Yvonne P. Mascarenhas

Instituto de Física e Química de São Carlos, Universidade de São Paulo, 13560 *São Carlos, SP, Brazil*

(*Received* 3 *March* 1988; *accepted* 14 *October* 1988)

Abstract. The new synthetic compound with $M_r = 266{\cdot}8$ is monoclinic, $P2_1/c$, $a = 5{\cdot}191\ (2)$, $b = 8{\cdot}748\ (2)$, $c = 14{\cdot}448\ (2)$ Å, $\beta = 94{\cdot}81\ (2)°$, $V = 653\ (1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}69$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 26{\cdot}6$ cm^{-1}, $F(000) = 520$, room temperature, final $R = 0{\cdot}058$ for 976 observed reflections. The structure consists of Fe^{3+} ions coordinated by $(PO_4H)^{2-}$ ligands forming interconnected octahedra

through the vertices of phosphate groups. The species shows the coexistence of acid $(PO_4H)^{2-}$ and oxonium $(H_3O)^+$ groups. The isolated oxonium ion is a disordered hydrogen donor to seven O atoms. The presence of the $(H_3O)^+$ ion was verified by infrared spectroscopy as a stretching vibration ν of 3392 cm^{-1} and by thermogravimetric analysis.

Introduction. In a series of hydrothermal syntheses of iron phosphates under acid conditions, pink needle crystals of ferric phosphate were obtained. Synthetic phosphoferrite, $3Fe^{2+}.2PO_4^{3-}.3H_2O$, was placed in a teflon cartridge with a perforated bottom. This cartridge was fitted in the top of a quartz tube half-filled with ferric phosphate. The ferric phosphate was previously obtained by reacting Fe_2O_3 with concentrated boiling phosphoric acid. The hydrothermal synthesis lasted a week and was done with relative volume (water/vessel net volume) of about 90%, at a temperature of 500 K and pH $\sim$ 2. The pink needle crystals grew in the bottom part of the cartridge.

The room-temperature Mössbauer spectrum (Fig. 1) shows that only the Fe^{3+} ion is present. The spectral fitting shows the following values: IS (isomer shift) $= 0{\cdot}446$ mm s^{-1} (relative to metallic iron), QS (quadrupole splitting) $= 0{\cdot}279$ mm s^{-1} and line width $\Gamma = 0{\cdot}275$ mm s^{-1}.

The thermogravimetric analysis (Fig. 2) in an inert atmosphere shows water loss in two steps, with the following transformations: the first at 670 K, when the acid orthophosphate groups transform into acid pyrophosphate

$$2\{Fe^{3+}.(H_3O)^+.(PO_4H)_2^{2-}\} \xrightarrow{670\,K} 2\{Fe^{3+}.(OH)^-.(P_2O_7H_2)^{2-}\} + 2H_2O\uparrow.$$

The second transformation occurs between 670 and 870 K. In the latter process part of the pyrophosphate is transformed into metaphosphate

$$2\{Fe^{3+}.(OH)^-.(P_2O_7H_2)^{2-}\} \xrightarrow[870\,K]{670\,K} Fe_2^{2+}.(P_2O_7)^{4-} + (PO_3)_2^{2-} + H_2O\uparrow + 2H_2O\uparrow.$$

Table 1 gives the pyrolytic results in an inert atmosphere, as compared with calculated values assuming the title stoichiometric composition.

Experimental. A clear pink needle-shaped crystal of size $0{\cdot}35 \times 0{\cdot}08 \times 0{\cdot}06$ mm was mounted on a CAD-4 Enraf–Nonius automatic diffractometer with Mo $K\alpha$ radiation filtered with a graphite monochromator. The unit-cell parameters were derived from 19 reflections with $8{\cdot}2 \leq 2\theta \leq 24{\cdot}3°$ with variable scan rate (7–20° min^{-1}) and two standard reflections ($0\bar{2}5$ and $0\bar{3}3$) measured every 30 min without significant change of intensities; systematic absences ($l \neq 2n + 1$ for $h0l$, $k \neq 2n + 1$ for $0k0$) consistent with space group $P2_1/c$. The intensities were measured by the θ–2θ scan technique with width $(0{\cdot}60 + 0{\cdot}35\tan\theta)°$ and collected with $\theta < 25°$ corresponding to $-6 \leq h \leq 6$, $0 \leq k \leq 10$, $0 \leq l \leq 17$; $R_{int} = 4{\cdot}1\%$. Of the 1680 measured reflections, 1140 were unique, and 976 were observed with $I \geq 3\sigma(I)$. The data were corrected for Lp effects but not for absorption because of the lack of definite zone faces at the surface of the needle-shaped single crystal used. Inspection of F_c and F_o values indicated that a secondary-extinction correction was required: $F_{corr} = F_c/(1-10^{-4}xF_c^2/\sin\theta)$, where x refined to $0{\cdot}01526$ in the final run. The atomic scattering factors and the dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by direct methods using *MULTAN*80 (Main *et al.*, 1980). Anisotropic full-matrix refinement using *SHELX*76 (Sheldrick, 1976) was successful for all non-H atoms except for O(3) where non-positive-definite values were obtained,

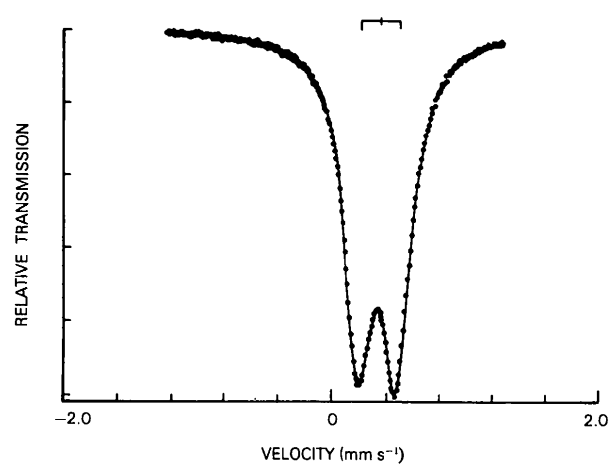

Fig. 1. Mössbauer spectrum of the powder sample at room temperature (velocity relative to metallic iron).

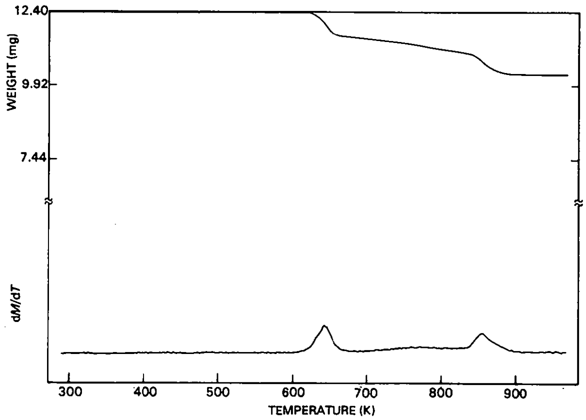

Fig. 2. Thermogravimetric analysis of the sample. dM/dT = mass variation/temperature variation.

Table 1. *Comparison of the experimental data from thermogravimetric analysis and the calculated data from the proposed pyrolytic reactions*

	Experimental (mg)	Calculated (mg)	Calculated mol. of of water loss
Starting mass	12·40		
First mass loss	0·85	0·84	2 H_2O
Second mass loss	1·24	1·25	3 H_2O
Total	2·09	2·09	5 H_2O

probably owing to the lack of absorption correction. With minimization of $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0{\cdot}05475F^2]^{-1}$ and $\sigma(F_o)$ is the e.s.d. for the observed amplitudes based on counting statistics. Only two H atoms, H(1) and H(2), were found by difference Fourier techniques. The other H atoms expected from the electrostatic balance of charges were not found owing to their low discrimination against the background and because they are disordered. The refinement converged to $R = 0{\cdot}058$ and $wR = 0{\cdot}069$ for 976 observed reflections, $R = 0{\cdot}081$ for all reflections. 105 parameters were refined, with a ratio of max. least-squares shift to e.s.d. in the final refinement cycle of less than 0·1 and the final difference map had maximum peaks of 0·39 and −0·34 e Å^{-3}. The calculations were performed on a VAX computer with the *SHELX76* program. The projection given in Fig. 3 was calculated with the program *ORTEP* (Johnson, 1965).

The atomic coordinates and equivalent isotropic temperature factors are given in Table 2. The interatomic distances and angles are given in Table 3.*

Discussion. The structure of this phosphate consists of oxygen octahedra coordinating the Fe^{3+} ions and tetrahedral phosphate groups $(PO_4H)^{2-}$. The octahedra are linked through their vertices to tetrahedra of the acid phosphates. The latter are connected to different octahedra of Fe^{3+} through three of their vertices (Fig. 3).

The observed values of the mean distance Fe—O = 1·999 Å and the mean distance P—O = 1·541 Å of the two crystallographically independent phosphates are in agreement with the values observed in other iron phosphates (Moore & Araki, 1976; Moore, Kampf & Irving, 1974; Vencato, Mascarenhas & Mattievich, 1986).

Table 2. *Atomic coordinates and equivalent isotropic temperature factors*

	x	y	z	B_{eq}*(Å^2)
Fe = Fe^{3+}	0·2416 (2)	0·4634 (1)	0·3498 (1)	0·64 (4)
P(1)	0·2237 (4)	0·1554 (2)	0·0595 (1)	0·61 (6)
P(2)	0·7204 (4)	0·2422 (2)	0·3088 (1)	0·58 (6)
O(1)	−0·056 (1)	0·1169 (6)	0·0780 (3)	1·0 (2)
O(2)	0·417 (1)	0·0415 (6)	0·1011 (4)	1·1 (2)
O(3)	0·246 (1)	0·1833 (6)	−0·0437 (3)	0·73 (9)
O(4) = $(OH)^-$	0·289 (1)	0·3192 (6)	0·1054 (4)	1·2 (2)
O(5)	0·924 (1)	0·3637 (6)	0·2912 (4)	1·3 (2)
O(6)	0·448 (1)	0·3013 (6)	0·2820 (4)	1·1 (2)
O(7)	0·769 (1)	0·0915 (6)	0·2617 (4)	1·1 (2)
O(8) = $(OH)^-$	0·737 (1)	0·1991 (6)	0·4160 (3)	0·9 (2)
O(9) = $(H_3O)^+$	0·229 (2)	0·0042 (9)	0·3900 (6)	3·2 (3)
H(1)	0·3009	0·3632	0·1752	3·9
H(2)	0·8420	0·2599	0·4608	3·9

* $B_{eq} = \frac{4}{3}\sum_i\sum_j T_{ij}B_{ij}$ and $\sigma(B_{eq}) = T_{ij}\,\sigma(B_{ij})$.

Table 3. *Interatomic distances* (Å) *and angles* (°)

Estimated standard deviations for interatomic distances are 0·006 Å and for angles 0·3°.

Fe—O(1$^{\rm i}$)	1·997
—O(2$^{\rm ii}$)	1·975
—O(3$^{\rm iii}$)	2·002
—O(5$^{\rm iv}$)	1·990
—O(6)	2·073
—O(7$^{\rm ii}$)	1·959
Average	1·999

	O—O′	O—Fe—O′
O(1$^{\rm i}$)—O(2$^{\rm ii}$)	2·861	92·2
—O(3$^{\rm iii}$)	2·834	90·3
—O(5$^{\rm iv}$)	2·955	95·6
—O(7$^{\rm ii}$)	2·885	93·6
O(2$^{\rm ii}$)—O(3$^{\rm iii}$)	2·803	89·6
—O(7$^{\rm ii}$)	2·864	93·4
O(5$^{\rm iv}$)—O(3$^{\rm iii}$)	2·826	90·1
—O(7$^{\rm ii}$)	2·702	86·3
O(6)—O(2$^{\rm ii}$)	2·750	85·6
—O(3$^{\rm iii}$)	2·811	87·2
—O(5$^{\rm iv}$)	2·788	86·7
—O(7$^{\rm ii}$)	2·827	89·0
Average	2·826	90·0

P(1) tetrahedron		P(2) tetrahedron	
P(1)—O(1)	1·534	P(2)—O(5)	1·536
—O(2)	1·503	—O(6)	1·525
—O(3)	1·525	—O(7)	1·514
—O(4)	1·603	—O(8)	1·590
Average	1·541	Average	1·541

	O—O′	O—P—O′		O—O′	O—P—O′
O(1)—O(2)	2·535	113·1	O(5)—O(6)	2·524	111·1
—O(3)	2·521	110·9	—O(7)	2·539	112·7
—O(4)	2·524	107·1	—O(8)	2·562	110·1
O(2)—O(3)	2·528	113·2	O(6)—O(7)	2·511	111·5
—O(4)	2·521	108·5	—O(8)	2·512	107·5
O(3)—O(4)	2·454	103·3	O(7)—O(8)	2·439	103·6
Average	2·513	109·4	Average	2·514	109·4

Symmetry code: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $-1+x, y, z$.

The presence of the free group H_3O^+ was verified with an infrared absorption spectrum (Fig. 4) obtained with a Perkin Elmer 1320 spectrometer using KBr pellets. The stretching vibration ν occurs at 3392 cm^{-1} and is consistent with H_2O as well as $(OH)^-$. This value is a little high for strongly bonded H_3O^+ but owing to the weak interaction between H_3O^+ and its environment this frequency is acceptable.

The region occupied by the atoms O(4$^{\rm ii}$), O(4$^{\rm iii}$), O(8) and O(8$^{\rm iv}$) (symmetry operations given in Fig. 3) around the symmetry center at $\frac{1}{2}$, 0, $\frac{1}{2}$ (and also at 0, $\frac{1}{2}$, 0) is similar to that observed in the synthetic phosphate structure $Fe^{2+}.2Fe^{3+}.4(PO_3OH)^{2-}.4H_2O$ (Vencato *et al.*, 1986). In this case, however, the center of the region is occupied by the oxonium ion while in the other case it was vacant.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51495 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The electrostatic balance of cations relative to anions, calculated according to the Brown & Shannon (1973) universal curve and with the use of R_1 and N parameters given by Brown & Wu (1976), gives 3·16 v.u. (valence units) for the Fe^{3+} ion, showing small distortions of the respective octahedron. The approach of Brown & Shannon gives a better analysis since it takes into account the observed bond lengths. Such an analysis is shown in Table 4 calculated using the parameters of Brown & Altermatt (1985). Sums around O atoms using the Fe—O and P—O bonds show that only O(4), O(8) and O(9) can possibly act as donors. Since O(4) and O(8) are potential donors of hydrogen bonds because they are not coordinating the Fe^{3+} ion and have lengthened P—O distances of 1·603 and 1·590 Å, respectively, O(9) must bond to the remaining three H atoms making it an H_3O^+ ion.

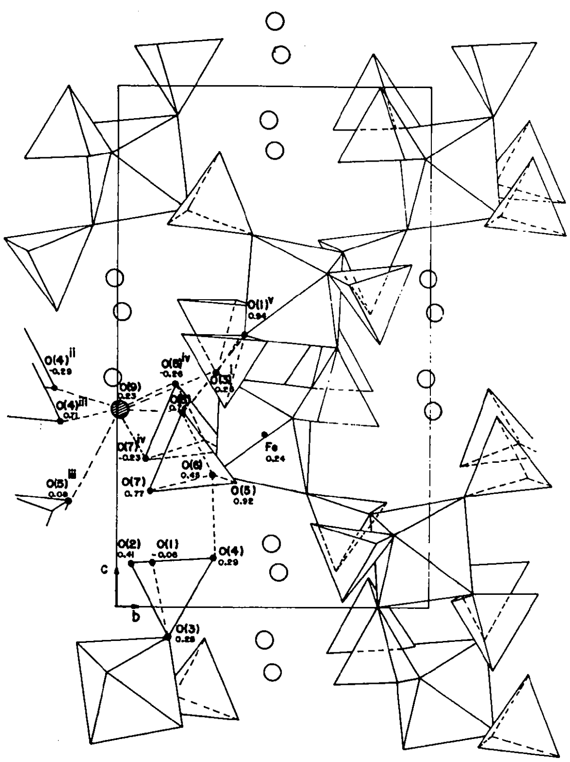

Fig. 3. Polyhedral projection of the $Fe^{3+}.(H_3O)^+.2(PO_4H)^{2-}$ structure along the *a* axis, with proposed hydrogen bonds indicated by dotted lines. The heights are given as fractional coordinates in *x*. The atom labels refer to Table 2. The symmetry operations are: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-1+x, y, z$; (v) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$.

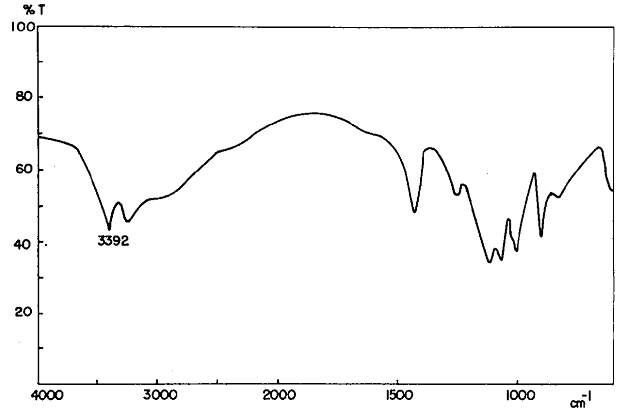

Fig. 4. Infrared absorption spectrum in KBr pellets. The stretching vibration ν occurs at 3392 cm^{-1}.

Table 4. *Bond valences in* $Fe^{3+}.(H_3O)^+.2(PO_4H)^{2-}$

	Fe	P(1)	P(2)	Sum (no H)	H(1)	H(2)	Sum including H(1), H(2)	H bonds from O(9) Distances	H bonds from O(9) Valences	Sum all bonds
O(1)	0·53	1·25		1·78		0·12	1·90			1·90
O(2)	0·56	1·36		1·92			1·92			1·92
O(3)	0·52	1·28		1·80			1·80	2·90	0·15	1·95
O(4)		1·04		1·04	0·79		1·83	2·98 3·14	0·14	1·97
O(5)	0·54		1·24	1·78			1·78	2·94	0·13	1·91
O(6)	0·43		1·28	1·71	0·21		1·92			1·92
O(7)	0·58		1·32	1·90			1·90	3·00	0·10	2·00
O(8)			1·08	1·08		0·88	1·96	3·12 3·14	0·06	2·02
O(9)									2·42*	2·42
										mean
	3·16	4·93	4·92	13·01	1·00	1·00			3·00	2·00

* Sum for all three H atoms.

A strong hydrogen bond occurs between O(4) as a donor and O(6) as an acceptor with an O(4)—H(1)···O(6) angle of 134·6 (3)° and O—H, H···O and O···O distances of 1·007, 1·749 (6) and 2·620 (6) Å. A weak hydrogen bond, O(8)—H(2)···O(1) $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$, has an O—H···O angle of 159·5 (3)° and O—H, H···O and O···O distances of 0·969, 2·039 (6) and 2·967 (6) Å. With these values and with the help of Fig. 1 of Brown & Altermatt (1985), the sum including H(1) and H(2) is given in Table 4.

The oxonium ion $O(9) = H_3O^+$ is 2·90–3·14 Å from seven other O atoms; all distances are much larger than the three 2·65 Å O···O distances that could be expected for an ordered oxonium ion. However if the oxonium ion were rotating or disordered (*cf.* the different modes of bonding adopted by the ammonium ion, *i.e.* 4 coordination and 8 coordination), then the O···O distances of about 2·90 Å are not unexpected. It is notable that the shortest O(9)···O distances are those to O atoms that have the smallest sums (1·78–1·83 v.u.) after the phosphate H bonds have been taken into account. The valences for the acceptor parts of the H bonds can be estimated from Fig. 2 of Brown & Altermatt. The valence of the donor part is chosen so that the sum around O(9) is 3·0 v.u. The seven distances around the O atom account for 0·58 v.u. of the expected charge of 1·00 v.u. around the H_3O^+ ion, an acceptable agreement in a situation of this kind.

The infrared spectrum was obtained at the Departamento de Química e Física Molecular (IFQSC/USP) by courtesy of Dr Antonio Aprigio da Silva Curvelo.

The thermogravimetric analysis was performed at CEPEL (Rio de Janeiro) by courtesy of Mr Alexandre Gomes da Cunha.

This work has received the support of FINEP, FAPESP, CNPq, and PADCT, which are hereby gratefully acknowledged.

The manuscript benefitted greatly from the comments of Dr I. D. Brown.

References

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* B**32**, 1957–1959.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Moore, P. B. & Araki, T. (1976). *Inorg. Chem.* **15**, 316–321.

Moore, P. B., Kampf, A. R. & Irving, A. J. (1974). *Am. Mineral.* **59**, 900–905.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Vencato, I., Mascarenhas, Y. P. & Mattievich, E. (1986). *Am. Mineral.* **71**, 222–226.

Acta Cryst. (1989). C**45**, 371–374

Structure of Undeca(tetrathiafulvalene)* Tris(hexacyanoferrate) Pentahydrate

By Soraya Bouherour and Lahcène Ouahab†

Laboratoire de Chimie des Matériaux Moléculaires et de Cristallochimie, Institut de Chimie, Université de Constantine, Algeria

and Octavio Peña, Jean Padiou and Daniel Grandjean

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UA CNRS 254, *Université de Rennes* I, 35042 *Rennes, France*

(*Received* 29 *June* 1988; *accepted* 7 *October* 1988)

Abstract. $11\text{C}_6\text{H}_4\text{S}_4.3[\text{Fe(CN)}_6].5\text{H}_2\text{O}$, $M_r = 2973\cdot84$, triclinic, $P\bar{1}$, $a = 10\cdot795$ (5), $b = 10\cdot889$ (6), $c = 25\cdot212$ (2) Å, $\alpha = 85\cdot21$ (4), $\beta = 89\cdot59$ (3), $\gamma = 80\cdot54$ (4)°, $V = 2913\cdot2$ Å^3, $Z = 1$, $D_x = 1\cdot695$ g cm^{-3}, λ(Mo $K\alpha$) $= 0\cdot71073$ Å, $\mu = 11\cdot83$ cm^{-1}, $F(000) = 1506$, $T = 293$ K, $R = 0\cdot035$ for 4554 observed reflections. Eight fully oxidized tetrathiafulvalene (TTF) molecules form dimerized stacks, parallel to the [011] direction with the three other molecules perpendicular to this. Four types of overlap are observed in the stack [shortest inter-TTF S$\cdots$S contact 3·270 (3) Å]. Strong interactions between $[\text{Fe(CN)}_6]^{3}$ anions and the TTF stack are also observed: N$\cdots$S = 3·099 (7). $[\text{Fe(CN)}_6]^{3-}$ units and water molecules are associated *via* hydrogen bonding [N$\cdots$O = 2·76 (1) Å]. The compound is a semiconductor ($\sigma_{300\,\text{K}} = 8\cdot5 \times 10^{-4}\,\Omega^{-1}\text{cm}^{-1}$).

Introduction. In the course of our investigation of organo-mineral materials (Ouahab, 1985; Ouahab, Batail, Perrin & Garrigou-Lagrange, 1986), we have prepared new compounds made of organic donors [such as tetrathia(selena)fulvalene and its derivatives] and octahedral hexacyanometalates {$[M(\text{CN})_6]$; M = Fe, Co, Cr, Mn}. Some of the anions are magnetic {$[\text{Fe(CN)}_6]^{3-}$: $S = 3/2$; $[\text{Mn(CN)}_6]^{3-}$: $S = 5/2$} and offer the possibility of access to compounds where electron delocalization on the organic systems coexists with paramagnetic centers localized on the inorganic anion. Similar materials have been reported (Lacroix, Kahn, Gleizes, Valade & Cassoux, 1984; Batail, Ouahab, Torrance, Pylman & Parkin, 1985). We report here the preparation and the structure of the 3:11 $[\text{Fe(CN)}_6]$: TTF.$5\text{H}_2\text{O}$.

Experimental. Black crystals of the title compound were prepared by electrocrystallization from the neutral donor (5 m*M*) in rigorously dried acetonitrile, using the tetraethylammonium salts of the anion (15 m*M*). The latter was prepared according to the literature (Masharak, 1986). The electrocrystallization was carried out under constant low current (0·95 μA) in a 50 ml cell. The working electrode was a platinum wire. Crystal 0·15 × 0·2 × 0·2 mm. Enraf–Nonius CAD-4

---

* Alternative nomenclature. Tetrathiafulvalene ≡ 2,2′-bi-1,3-dithiolylidene.

† To whom all correspondence should be addressed.

0108-2701/89/030371-04$03.00