Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C(1)	0.5055 (5)	−0.1874 (4)	0.5434 (5)	0.0430 (9)
C(2)	0.5637 (5)	0.1010 (5)	0.4162 (6)	0.049 (1)
C(3)	0.5120 (4)	0.2659 (4)	0.5111 (5)	0.0369 (9)
C(4)	0.5334 (4)	0.2296 (4)	0.7263 (5)	0.0354 (8)
C(5)	0.4639 (5)	0.0429 (4)	0.7628 (5)	0.041 (1)
C(6)	0.5400 (4)	0.4475 (4)	0.9887 (5)	0.0328 (8)
C(7)	0.4580 (5)	0.6074 (5)	1.0513 (5)	0.046 (1)
O(1)	0.5605 (3)	−0.1081 (3)	0.7333 (4)	0.0441 (7)
O(2)	0.4524 (4)	−0.0522 (3)	0.3946 (4)	0.0442 (7)
O(3)	0.3491 (3)	0.3201 (3)	0.4036 (4)	0.0448 (7)
O(4)	0.6662	0.3782 (3)	1.1011	0.0442 (6)
N(1)	0.4670 (4)	0.3834 (3)	0.8054 (4)	0.0366 (7)

Table 2. *Geometric parameters* (Å, °)

C(1)—O(1)	1.411 (4)	C(2)—C(3)	1.508 (5)
C(1)—O(2)	1.401 (4)	C(3)—O(3)	1.424 (4)
C(4)—C(5)	1.523 (5)	C(2)—O(2)	1.435 (5)
C(5)—O(1)	1.430 (5)	C(6)—C(7)	1.498 (5)
C(3)—C(4)	1.530 (5)	C(6)—O(4)	1.228 (3)
C(4)—N(1)	1.448 (5)	C(6)—N(1)	1.342 (4)
O(1)—C(1)—O(2)	112.9 (3)	C(3)—C(2)—O(2)	109.9 (3)
C(4)—C(5)—O(1)	109.7 (3)	O(4)—C(6)—N(1)	122.3 (3)
C(5)—C(4)—N(1)	110.5 (3)	C(7)—C(6)—N(1)	116.4 (3)
C(5)—C(4)—C(3)	114.2 (3)	C(7)—C(6)—O(4)	121.3 (3)
C(3)—C(4)—N(1)	110.7 (3)	C(1)—O(1)—C(5)	115.3 (3)
C(4)—C(3)—O(3)	110.6 (3)	C(1)—O(2)—C(2)	113.9 (3)
C(4)—C(3)—C(2)	112.7 (3)	C(4)—N(1)—C(6)	122.1 (3)
C(2)—C(3)—O(3)	111.3 (3)		

Table 3. *Hydrogen-bond geometry* (Å, °)

D—H···*A*	*D*···*A*	*D*—H	*D*—H···*A*	Symmetry code for *A*
O3—H(O3)···O2	2.808 (3)	0.82 (4)	109 (4)	*x,y,z*
H1—H(N1)···O3	2.774 (4)	0.83 (3)	103 (2)	*x,y,z*
O3—H(O3)···O1	2.836 (3)	0.82 (4)	150 (4)	$-0.5+x, -y, -0.5+z$
N1—H(N1)···O4	3.054 (3)	0.83 (3)	166 (3)	$-0.5+x, 1-y, -0.5+z$

STRUFA (*ZOAK7*; Vicković, 1975). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PLUTON* (Spek, 1982).

The ω-scan width was 1.20° with an ω-scan rate of 2.4° min^{-1}. To define the origin of the space group the x and z coordinates of O(4) were fixed. Refinement was performed by the full-matrix least-squares method.

This work was supported by the Croatian National Science Foundation.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55051 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1006]

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Structure of Bis(dipicolinato)ferrate(III) Dihydrate

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Abstract

The Fe atom is octahedrally surrounded by two tridentate dipicolinate anions. These two ligands are orthogonal to each other. The two water molecules are linked through the proton required for electricial neutrality and form an H_5O_2 cation. The protons of these two water molecules are bonded to the O atoms of the carboxylate groups which are not coordinated to the Fe atom. Metal–nitrogen and metal–oxygen distances are comparable to those of other transition-metal dipicolinate complexes.

Comment

The complexation of metal ions by 2,6-pyridinedicarboxylic acid (H_2dpa) has been extensively studied. Part of the interest results from the unique ability of the ligand to form stable chelates, as indicated by the slow exchange rates (Erikson, Grenthe & Puigdomenech, 1987; Ducommun, Helm, Laurenczy & Merbach, 1989) and thermodynamic

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parameters (Martell & Smith, 1974), and part arises from its biological relevance in stabilizing bacterial spores by increasing its resistivity to heat (Bailey, Karp & Sacks, 1965; Murrell & Warth, 1965). The latter effect was attributed to the formation of polymeric Cadpa.xH_2O chelates which cover the cortex of the spores and extend to the remainder through a hydrogen-bonded system (Strahs & Dickerson, 1968).

In the search for the factors that may affect bonding of this anion to different cations, we have initiated a systematic structural investigation of its complexes and also those of the corresponding picolinates. The structures of two uranyl complexes, $H_2[UO_2(dpa)_2].C_6H_5NO_2.6H_2O$ (I) and $H_2[(UO_2)_3(dpa)_4].2H_2O$ (II) (Cousson, Proust & Rizkalla, 1991; Cousson, Nectoux, Pagès & Rizkalla, 1992), have been discussed. In the first, the U ion has a hexagonal bipyramidal environment with the uranyl O atoms occupying the axial positions, whereas with the trimer complex (II), two of the uranyl groups have a pentagonal bipyramidal coordination polyhedron and the third one has an environment similar to that in compound (I). The U—N bond lengths were found to be 2.64 and 2.53 Å for hexacoordinated and pentacoordinated species, respectively. The shortening in the U—N bond length was attributed to the relief of van der Waals strain associated with O···O contact distances in the hexacoordinate anion. The type of bonding in these complexes is non-directional and is dominated by the interplay between steric and electrostatic forces. The present report deals with an extension of these measurements to the structure of $H[Fe(dpa)_2].2H_2O$.

The unit cell consists of two iron(III) anionic complexes. Both are very similar (Figs. 1 and 2) and each exhibit an octahedral coordination about the Fe centre with two tridentate dipicolinate ligands coordinated *via* their carboxylate and nitrilo donors. The planes defining the rings are orthogonal to each other. Thus the structure has a similar geometry to $[Cu(dpa)(H_2dpa)].xH_2O$ (Sarchet & Loiseleur, 1973), $[Ni(Hdpa)_2].3H_2O$ (Quaglieri, Loiseleur & Thomas, 1972) and $Na[Cr(dpa)_2].2H_2O$ (Furst, 1977). The Fe centre has symmetric coordination to each dipicolinate anion; however, the Fe—N and Fe—O bond lengths in the two ligands are different, *i.e.* Fe—O(1) ≠ Fe—O(3); Fe—N(1) ≠ Fe—N(2) and Fe—O(5) ≠ Fe—O(7); Fe—N(3) ≠ Fe—N(4); the differences, though small, are statistically significant. There is, however, a larger difference between the orientation of the two perpendicular [N(2) and N(3) containing] ligands in the unit cell as can be seen from the difference in the angles. Presumably this provides the driving force for the extra lengthening of the Fe(2)—N(3) bond. The ligand would possibly take this orientation as a result of the difference in the

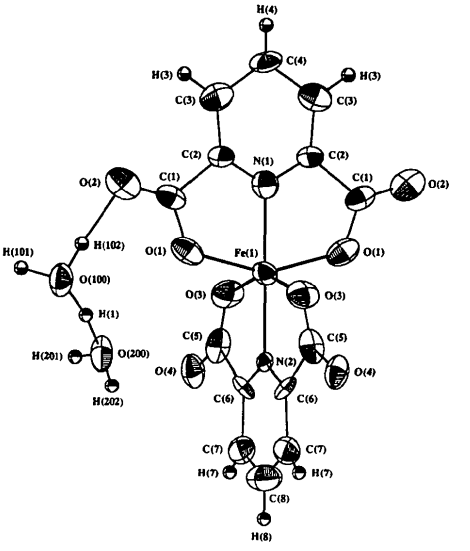

Fig. 1. *ORTEP* (Johnson, 1965) plot of the title compound. H-atom thermal ellipsoids are drawn as small circles of arbitrary radius.

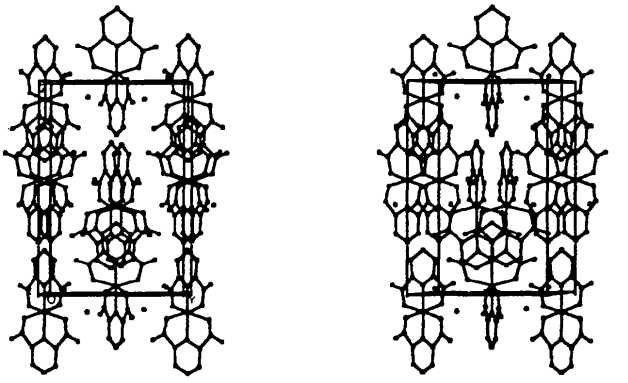

Fig. 2. *ORTEP* stereoview of the title compound.

contact distances between O(6)···H(202) (1.77 Å) and O(4)···H(201) (1.62 Å) and O(6)···O(200) (2.73 Å) and O(4)···O(200) (2.55 Å), which lead to a larger repulsion in the latter case and hence a larger cavity for the N(3) molecule.

One carboxylate group in each dipicolinate anion has approximately equal C—O bond lengths (*ca* 1.24 and 1.25 Å or 1.25 and 1.28 Å) suggesting resonance stabilization with 50% double-bond character and equal distribution of charge on both O atoms. The other carboxylate has significantly different C—O bond lengths (1.19 and 1.31 Å or 1.22 and 1.30 Å) almost identical with those observed for uncoordinated dipicolinic acid (Takusagawa, Hirotsu & Shimada, 1973). This would suggest the presence of carbonyl (C=O) and C—O^- types of bonds. These conclusions are supported by the expansion of the O—C—O angle where symmetric charge distribution is observed.

The two water molecules are placed in interstitial positions. One of them is hydrogen bonded to the uncoordinated O(2) and O(8) of the two complex anions. In addition, it is hydrogen bonded through the counter proton to the second water molecule.

Comparison of the metal–nitrogen and metal–oxygen bond lengths of Fe with those of other related systems (Table 3) indicates that the former are significantly longer than expected from differences of ionic radii. It also suggests that the Fe dipicolinate anion is probably of high spin.

Experimental

Crystal data

$H[Fe(C_7H_3NO_4)_2].2H_2O$
M_r = 423.093
Orthorhombic
*Pnn*2
a = 8.860 (8) Å
b = 11.007 (2) Å
c = 16.316 (4) Å
Cell parameters from 25 reflections
θ = 17.5–18°
V = 1591 (1) Å^3
Z = 4
D_x = 1.766 Mg m^{-3}
Mo $K\alpha$
λ = 0.71069 Å
μ = 10.05 mm^{-1}
T = 293 K
Rectangular prism
0.40 × 0.20 × 0.15 mm
Green

Data collection

Enraf–Nonius diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.766, T_{max} = 1.293
2218 measured reflections
2218 independent reflections
1566 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.0
θ_{max} = 28.00°
h = 0 → 13
k = 0 → 17
l = 0 → 25
2 standard reflections
frequency: 60 min
intensity variation: 1.7%

Refinement

Refinement on F
Final R = 0.041
wR = 0.040
S = 2.15
1566 reflections
251 parameters
Only H-atom U's refined
w = 1.0
$(\Delta/\sigma)_{max}$ = 0.746
$\Delta\rho_{max}$ = 0.2 e Å^{-3}
$\Delta\rho_{min}$ = −0.5 e Å^{-3}
Extinction correction: according to Larson (1969)
Extinction coefficient: 52 (4)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Fe(1)	0.0000	0.0000	0.5385 (2)	0.0314
Fe(2)	0.0000	0.5000	0.4158 (2)	0.0319
C(1)	−0.149 (1)	−0.176 (1)	0.6450 (6)	0.0332
C(2)	−0.068 (1)	−0.0853 (9)	0.7033 (6)	0.0337
C(3)	−0.073 (1)	−0.0960 (9)	0.7882 (8)	0.0445
C(4)	0.0000	0.0000	0.8373 (6)	0.0407
C(5)	−0.766 (1)	−0.0982 (9)	0.4355 (8)	0.0308
C(6)	−0.885 (1)	−0.0555 (8)	0.3761 (5)	0.0216
C(7)	−0.881 (1)	−0.054 (1)	0.2886 (7)	0.0414
C(8)	−1.0000	0.0000	0.251 (1)	0.0559
C(9)	−0.141 (1)	−0.3303 (9)	0.3107 (8)	0.0352
C(10)	−0.077 (1)	−0.4101 (8)	0.2486 (6)	0.0260
C(11)	−0.078 (1)	−0.415 (1)	0.1646 (7)	0.0376
C(12)	0.0000	−0.5000	0.1306 (7)	0.0429
C(13)	−0.775 (1)	−0.3990 (9)	0.5241 (6)	0.0319
C(14)	−0.8899 (9)	−0.4494 (9)	0.5821 (6)	0.0280
C(15)	−0.889 (1)	−0.4389 (9)	0.6632 (7)	0.0308
C(16)	−1.0000	−0.5000	0.7093 (9)	0.0357
N(1)	0.0000	0.0000	0.6642 (8)	0.0388
N(2)	−1.000	0.0000	0.4136 (7)	0.0166
N(3)	0.0000	−0.5000	0.2880 (7)	0.0211
N(4)	−1.000	−0.5000	0.5399 (9)	0.0320
O(1)	−0.1193 (9)	−0.1477 (7)	0.5688 (4)	0.0424
O(2)	−0.229 (1)	−0.2579 (6)	0.6640 (6)	0.0430
O(3)	−0.8046 (9)	−0.0866 (8)	0.5084 (5)	0.0451
O(4)	−0.6515 (8)	−0.1371 (6)	0.3995 (4)	0.0417
O(5)	−0.1088 (9)	−0.3464 (6)	0.3845 (4)	0.0389
O(6)	−0.229 (1)	−0.2476 (6)	0.2832 (6)	0.0530
O(7)	−0.8074 (8)	−0.4090 (6)	0.4464 (5)	0.0347
O(8)	−0.6507 (9)	−0.3590 (8)	0.5430 (6)	0.0479
O(100)	−0.3597 (8)	−0.3332 (8)	0.5274 (6)	0.0462
O(200)	−0.3702 (8)	−0.1719 (7)	0.4228 (6)	0.0450

Table 2. *Geometric parameters* (Å, °)

Fe(1)—N(1)	2.05 (1)	Fe(1)—N(2)	2.04 (1)
Fe(1)—O(1)	2.001 (7)	Fe(1)—O(3)	2.036 (9)
Fe(2)—N(3)	2.08 (1)	Fe(2)—N(4)	2.03 (1)
Fe(2)—O(5)	2.012 (7)	Fe(2)—O(7)	2.040 (7)
C(1)—C(2)	1.55 (1)	C(1)—O(1)	1.31 (1)
C(1)—O(2)	1.19 (1)	C(2)—C(3)	1.39 (2)
C(2)—N(1)	1.29 (1)	C(3)—C(4)	1.48 (1)
C(5)—C(6)	1.51 (1)	C(5)—O(3)	1.25 (1)
C(5)—O(4)	1.24 (1)	C(6)—C(7)	1.43 (1)
C(6)—N(2)	1.337 (9)	C(7)—C(8)	1.36 (1)
C(9)—C(10)	1.46 (1)	C(9)—O(5)	1.25 (1)
C(9)—O(6)	1.28 (1)	C(10)—C(11)	1.37 (2)
C(10)—N(3)	1.362 (9)	C(11)—C(12)	1.29 (1)
C(13)—C(14)	1.50 (1)	C(13)—O(7)	1.30 (1)
C(13)—O(8)	1.22 (1)	C(14)—C(15)	1.33 (2)
C(14)—N(4)	1.32 (1)	C(15)—C(16)	1.41 (1)

N(2)—Fe(1)—N(1)	180	O(1)—Fe(1)—N(1)	75.7 (2)
O(1)—Fe(1)—N(2)	104.3 (2)	O(1)—Fe(1)—O(1)	151.4 (4)
O(3)—Fe(1)—N(1)	103.9 (3)	O(3)—Fe(1)—N(2)	76.1 (3)
O(3)—Fe(1)—O(1)	97.4 (4)	O(3)—Fe(1)—O(1)	89.5 (3)
O(3)—Fe(1)—O(3)	152.2 (5)	N(4)—Fe(2)—N(3)	180
O(5)—Fe(2)—N(3)	75.3 (2)	O(5)—Fe(2)—N(4)	104.7 (2)
O(5)—Fe(2)—O(5)	150.6 (4)	O(7)—Fe(2)—N(3)	104.2 (2)
O(7)—Fe(2)—N(4)	75.8 (2)	O(7)—Fe(2)—O(5)	92.9 (3)
O(7)—Fe(2)—O(5)	94.2 (3)	O(7)—Fe(2)—O(7)	151.6 (5)
O(1)—C(1)—C(2)	109.8 (8)	O(2)—C(1)—C(2)	127.0 (10)
O(2)—C(1)—O(1)	123.2 (11)	C(3)—C(2)—C(1)	122.7 (10)
N(1)—C(2)—C(1)	112.3 (9)	N(1)—C(2)—C(3)	125.0 (11)
C(4)—C(3)—C(2)	117.6 (10)	C(3)—C(4)—C(3)	114.4 (12)
O(3)—C(5)—C(6)	112.8 (9)	O(4)—C(5)—C(6)	111.9 (10)
O(4)—C(5)—O(3)	135.3 (9)	C(7)—C(6)—C(5)	128.8 (9)
N(2)—C(6)—C(5)	112.6 (9)	N(2)—C(6)—C(7)	118.2 (9)
C(8)—C(7)—C(6)	116.0 (11)	C(7)—C(8)—C(7)	125.9 (16)
O(5)—C(9)—C(10)	119.6 (9)	O(6)—C(9)—C(10)	115.0 (11)
O(6)—C(9)—O(5)	125.3 (11)	C(11)—C(10)—C(9)	135.8 (9)
N(3)—C(10)—C(9)	107.8 (9)	N(3)—C(10)—C(11)	116.5 (10)
C(12)—C(11)—C(10)	117.2 (11)	C(11)—C(12)—C(11)	128.9 (14)
O(7)—C(13)—C(14)	115.6 (8)	O(8)—C(13)—C(14)	125.8 (10)
O(8)—C(13)—O(7)	118.4 (10)	C(15)—C(14)—C(13)	126.3 (9)
N(4)—C(14)—C(13)	109.3 (10)	N(4)—C(14)—C(15)	124.3 (9)
C(16)—C(15)—C(14)	118.9 (9)	C(15)—C(16)—C(15)	115.6 (13)
C(2)—N(1)—Fe(1)	119.8 (7)	C(2)—N(1)—C(2)	120.4 (14)
C(6)—N(2)—Fe(1)	117.2 (6)	C(6)—N(2)—C(6)	125.7 (12)
C(10)—N(3)—Fe(2)	118.2 (6)	C(10)—N(3)—C(10)	123.7 (13)
C(14)—N(4)—Fe(2)	121.5 (7)	C(14)—N(4)—C(14)	117.0 (14)
C(1)—O(1)—Fe(1)	122.2 (7)	C(5)—O(3)—Fe(1)	120.9 (7)
C(9)—O(5)—Fe(2)	118.2 (7)	C(13)—O(7)—Fe(2)	117.7 (6)

Table 3. *M*—N *and* *M*—O *average bond distances* (Å) *and ionic radii* (Å) (*Shannon*, 1976) *for the iron*(III), *chromium*(III), *nickel*(II) *and copper*(II) *dipicolinate complexes*

M	*M*—N	*M*—O	Ionic radii	
Fe^{III}	2.05	2.02	0.645	High spin
			0.550	Low spin
Cr^{III}	1.97	2.00	0.615	
Ni^{II}	1.97	2.10	0.692	
Cu^{II}	1.90	2.04	0.730	

The title compound was prepared under hydrothermal conditions. Stoichiometric amounts of ferric hydroxide and dipicolinic acid were intimately mixed and suspended in water in a sealed Pyrex tube and allowed to react at 423 K for 24 *h*. The resultant green crystals were stable to air exposure. The structure was solved by the Patterson method and successive Fourier maps. H atoms were found from difference Fourier syntheses. All calculations were performed using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) on a VAX 6310 computer.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles involving H atoms, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54982 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1001]

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Structure of a New Natural Tungstate Arsenate, $[Ca_2Y(AsO_4)(WO_4)_2]$,† Structurally Related to Scheelite

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Abstract

The structure of the new natural tungstate arsenate $[Ca_2Y(AsO_4)(WO_4)_2]$ found in the Alpine fissures of the Pizzo Cervandone Area (Ossola Valley, Italy) is reported. It conforms to the scheelite-type structure and consists of layers with composition $YAsO_4$ and $CaWO_4$ stacked in an orderly manner along [001] in the molar ratio 1:2.

Comment

The region of Pizzo Cervandone in the Central Alps (Italy/Switzerland) is particularly interesting because of its Alpine fissure minerals. This area is characterized by a striking positive arsenic anomaly (Graeser, 1965) which gives rise to a number of unique or unusual arsenic minerals in the gneiss fissures. A single specimen of the new mineral investigated here was found in 1990 by the mineral collector Fausto Parani, in the Italian side of this region (Alpe Devero – Ossola Valley). It occurs as small creamy yellow crystals (up to 3 mm), with elongated bipyramidal habit, closely resembling scheelite ($CaWO_4$). A quantitative wavelength-dispersion microprobe analysis on the sample revealed the presence of W, Ca, As and Y as major constituents, together with minor quantities of heavy lanthanides (Er and Yb) and traces of Nb and U. The unit-cell parameters and the symmetry of the

† Mineral submitted to IMA (International Mineralogical Association) for approval 'as Paranite-(Y)'.