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Sodium Bis(dipicolinato)ferrate(III) Dihydrate

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Abstract

The Fe centre in Na[Fe(C₇H₃NO₄)₂].2H₂O is surrounded by an approximately octahedral arrangement of two pyridine N and four carboxylate O atoms from the two dipicolinate ligands (dipicolinic acid is 2,6-pyridine-dicarboxylic acid). The mean Fe—N and Fe—O bond distances are 2.05 and 2.02 Å, respectively. The complex units are bridged by Na⁺ ions which are coordinated to four carboxylate O atoms (of which three are not used for Fe chelation) and to two water molecules. The six donor O atoms form a distorted octahedron around the Na⁺ ion with the water molecules *trans* to each other.

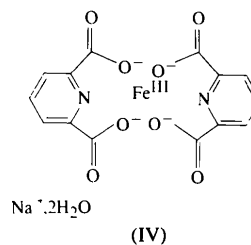
Comment

In other papers (Cousson, Proust & Rizkalla, 1991; Cousson, Nectoux, Pagés & Rizkalla, 1995) we have reported structural studies on uranyl dipicolinates and have found different coordination modes for the metal ion. As a result of the dipicolinate/(UO₂)²⁺ ratio, either H₂[UO₂(dipic)₂(pic)].6H₂O (I) or H₂[(UO₂)₃(dipic)₄].2H₂O (II) can be formed (dipic = dipicolinate, pic = picolinate). The former has a flattened hexagonal bipyramidal environment around the metal centre and the latter has a composite uranium coordination polyhedron. The U—N and U—O distances vary significantly from one structure to the other.

† Deceased.

For covalently bonded compounds, however, the metal-coordination polyhedron is not expected to alter with the different packing conditions which arise when the type and valence of the counter ion(s) are changed. Thus, the iron(III) analogue of compound (I), H[Fe(dipic)₂].2H₂O (III) (Cousson, Nectoux & Rizkalla, 1992), was shown to have octahedral coordination at the metal ion with the two dipic planes orthogonal to each other. Octahedral coordination is retained in H₂[Ni^{II}(dipic)₂].3H₂O (Quagliari, Loiseleur & Thomas, 1972) and H₂[Cu^{II}(dipic)₂].*n*H₂O (Sarchet & Loiseleur, 1973). These structures differ in the mode of coordination of the counter protons. In the Fe^{III} complex the proton is remote from the metal-coordination sphere, being hydrogen bonded to the two water molecules in an interstitial position, whereas in the Ni^{II} and Cu^{II} chelates the counter protons are bound to the non-coordinating O atoms of the carboxylate groups, symmetrically in the Ni^{II} complex but unsymmetrically in the Cu^{II} complex.

This paper describes the crystal and molecular structure of monoclinic Na[Fe(dipic)₂].2H₂O, (IV), which is derived from (III) through replacement of the counter proton by an Na⁺ ion.



The structure of the iron complex is shown in Fig. 1 (Pearce & Watkin, 1994). The metal ion is hexacoordinated by two *trans* pyridine N atoms and by four O atoms [O(1), O(4), O(5) and O(7)] provided by the carboxylate groups of the nearly orthogonal ligands. Thus, the structure of (IV) shows a basic similarity to the geometry of H[Fe(dipic)₂], (III). The only significant difference between (III) and (IV) concerns the N(1)—Fe—N(2) angle, which decreases from 180° in (III) to 168.3(1)° in (IV).

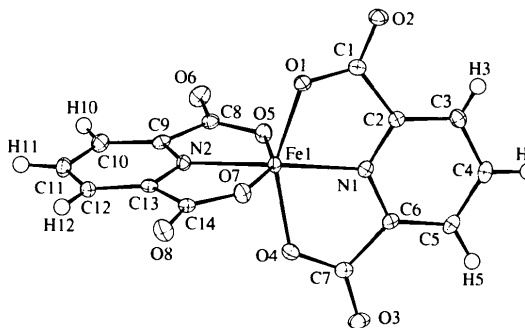


Fig. 1. CAMERON (Pearce & Watkin, 1994) plot of the [Fe(dipic)₂]⁻ anion showing 50% probability ellipsoids.

While all carboxylate groups in (IV) retain a similar degree of ionicity [mean O—C—O bond angle of 125.6(6)° and mean C—O bond lengths of 1.221(8) and 1.283(8) Å], those in (III) display wider ranges of O—C—O angles and C—O bond distances (119–135° and 1.19–1.31 Å) reflecting the involvement of the COO groups in the hydrogen-bonding network.

The linearity of the N(1)—Fe—N(2) group in the protonated complexes seems to indicate a significant strain in the bond angles and bond lengths of the pyridine groups as compared with those in dipicolinic acid itself (Takusagawa, Hirotsu & Shimada, 1973). This strain is relieved in (IV) through N—Fe—N angle contraction; the pyridine rings retain their approximate C_{2v} symmetry to within experimental error.

The unit cell contains four Na[Fe(dipic)₂] units with the Na⁺ ions located in interstitial positions. Each Na⁺ ion is surrounded by six O atoms in a pseudo-octahedral orientation. Three of these O atoms [O(2), O(6) and O(8)] are provided by non-coordinating carboxylate O atoms, with an average Na···O distance of 2.453(6) Å. The fourth atom, O(5), shares coordination with Fe^{III} and is 2.683(3) Å from Na⁺. The coordination sphere is completed by two water O atoms with an average Na···O distance of 2.347(5) Å.

The [Fe(dipic)₂][−] polyhedra are interconnected both by O(2), O(5), O(6) and O(8) bridging through Na⁺ ions and by a set of hydrogen bonds. The strongest, perhaps, is that of O(3ⁱ)··H(92)—O(9) as judged by the O(3ⁱ)··O(9ⁱⁱ) distance [2.939(4) Å] and near linear angle O(3ⁱ)··H(92)—O(9) [169(4)°] [symmetry codes: (i) $x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - x, z - \frac{1}{2}$]. Other probable hydrogen bonds are O(4)··O(10ⁱⁱ) 3.116(5) Å, O(4ⁱ)··H(101)—O(10) 166(5)°, O(8)··O(9ⁱⁱⁱ) 2.990(4) Å, O(8^{iv})··H(91)—O(9) 167(5)° and O(2)··O(10) 2.842(4) Å, O(2)··H(102)—O(10) 160(6)° [symmetry codes: (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$; (iv) $\frac{1}{2} + x, y - \frac{1}{2}, z$].

The shortest contact distances between non-H atoms of different anions are 2.939(4) and 2.991(4) Å for O(3)··O(9^v) and O(8)··O(9^{vi}), respectively [symmetry codes: (v) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $x - \frac{1}{2}, \frac{1}{2} + y, z$]. All other contact distances are greater than 3.00 Å.

Experimental

The title compound was prepared under hydrothermal conditions. Stoichiometric amounts of ferric hydroxide, sodium 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 resulting pale green crystals were stable on exposure to air.

Crystal data

Na[Fe(C₇H₃NO₄)₂].2H₂O
 $M_r = 445.07$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å

Monoclinic
 Cc
 $a = 14.904(4)$ Å
 $b = 12.434(2)$ Å
 $c = 8.645(3)$ Å
 $\beta = 93.12(2)^\circ$
 $V = 1599.69$ Å³
 $Z = 4$
 $D_x = 1.85$ Mg m^{−3}

Cell parameters from 25 reflections
 $\theta = 15\text{--}16.8^\circ$
 $\mu = 1.028$ mm^{−1}
 $T = 293$ K
Prism
 $0.25 \times 0.25 \times 0.15$ mm
Pale green

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
2151 measured reflections
1934 independent reflections

1783 observed reflections [$I \geq 3\sigma(I)$]
 $R_{int} = 0.03$
 $\theta_{max} = 28^\circ$
 $h = -19 \rightarrow 19$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 11$
2 standard reflections
frequency: 60 min
intensity decay: <0.7%

Refinement

Refinement on F
 $R = 0.0306$
 $wR = 0.0343$
 $S = 1.08$
1783 reflections
289 parameters
One U_{eq} value for all H atoms
Chebyshev weighting scheme with parameters 6.25, −2.15, 4.60
 $(\Delta/\sigma)_{max} = 0.1$

$\Delta\rho_{max} = 0.08$ e Å^{−3}
 $\Delta\rho_{min} = -0.3$ e Å^{−3}
Extinction correction: Larson (1970)
Extinction coefficient: 621.1 (248)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

Origin defined by constraints on the sum of the x and z coordinates.
 $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$

	x	y	z	U_{eq}
Fe(1)	−0.00007(6)	0.24700(3)	−0.0001(1)	0.0184
Na(1)	0.2406(1)	0.1333(1)	0.7506(2)	0.0277
C(1)	0.0864(2)	0.0712(2)	0.1637(3)	0.0178
C(2)	0.0189(2)	0.0165(2)	0.0525(3)	0.0158
C(3)	0.0048(2)	−0.0933(2)	0.0322(3)	0.0223
C(4)	−0.0636(2)	−0.1252(2)	−0.0731(4)	0.0239
C(5)	−0.1153(2)	−0.0491(2)	−0.1560(3)	0.0231
C(6)	−0.0964(2)	0.0588(2)	−0.1295(3)	0.0169
C(7)	−0.1399(2)	0.1565(2)	−0.2065(3)	0.0198
C(8)	0.1438(2)	0.3284(2)	−0.1796(3)	0.0203
C(9)	0.1063(2)	0.4284(2)	−0.1078(3)	0.0192
C(10)	0.1313(2)	0.5343(2)	−0.1295(4)	0.0242
C(11)	0.0834(2)	0.6141(2)	−0.0575(4)	0.0252
C(12)	0.0130(2)	0.5874(2)	0.0342(3)	0.0225
C(13)	−0.0070(2)	0.4791(2)	0.0520(3)	0.0185
C(14)	−0.0787(2)	0.4288(2)	0.1465(3)	0.0188
N(1)	−0.0308(2)	0.0874(2)	−0.0266(3)	0.0180
N(2)	0.0393(2)	0.4045(2)	−0.0189(3)	0.0181
O(1)	0.0789(1)	0.1742(2)	0.1644(2)	0.0231
O(2)	0.1396(2)	0.0180(2)	0.2452(3)	0.0267
O(3)	−0.2032(2)	0.1459(2)	−0.3016(3)	0.0285
O(4)	−0.1039(2)	0.2453(2)	−0.1621(3)	0.0269
O(5)	0.0986(2)	0.2424(2)	−0.1534(3)	0.0242
O(6)	0.2101(2)	0.3309(2)	−0.2552(3)	0.0292
O(7)	−0.0773(2)	0.3258(2)	0.1465(3)	0.0242

O(8)	-0.1308 (2)	0.4851 (2)	0.2140 (3)	0.0293
O(9)	0.2876 (2)	0.1573 (3)	0.0099 (3)	0.0360
O(10)	0.2309 (3)	0.1449 (4)	0.4774 (3)	0.0416

structure: *CRYSTALS*. Molecular graphics: *CRYSTALS*. Software used to prepare material for publication: *CRYSTALS*.

Table 2. Selected geometric parameters (Å, °)

Fe(1)—N(1)	2.047 (2)	C(6)—N(1)	1.333 (4)
Fe(1)—N(2)	2.053 (2)	C(7)—O(3)	1.225 (4)
Fe(1)—O(1)	2.012 (2)	C(7)—O(4)	1.277 (4)
Fe(1)—O(4)	2.030 (2)	C(8)—C(9)	1.510 (4)
Fe(1)—O(5)	2.034 (2)	C(8)—O(5)	1.290 (4)
Fe(1)—O(7)	2.013 (2)	C(8)—O(6)	1.214 (4)
C(1)—C(2)	1.515 (4)	C(9)—C(10)	1.384 (4)
C(1)—O(1)	1.285 (4)	C(9)—N(2)	1.327 (4)
C(1)—O(2)	1.225 (4)	C(10)—C(11)	1.389 (5)
C(2)—C(3)	1.392 (4)	C(11)—C(12)	1.390 (5)
C(2)—N(1)	1.318 (4)	C(12)—C(13)	1.389 (4)
C(3)—C(4)	1.386 (4)	C(13)—C(14)	1.516 (4)
C(4)—C(5)	1.394 (5)	C(13)—N(2)	1.327 (4)
C(5)—C(6)	1.387 (4)	C(14)—O(7)	1.281 (4)
C(6)—C(7)	1.514 (4)	C(14)—O(8)	1.218 (4)
Na(1)···O(2 ⁱ)	2.409 (3)	Na(1)···O(8 ⁱⁱⁱ)	2.450 (3)
Na(1)···O(5 ⁱⁱ)	2.683 (3)	Na(1)···O(9 ⁱⁱ)	2.331 (3)
Na(1)···O(6 ⁱⁱ)	2.500 (3)	Na(1)···O(10)	2.363 (3)
N(1)—Fe(1)—N(2)	168.26 (9)	C(6)—C(7)—O(4)	113.5 (2)
N(1)—Fe(1)—O(1)	76.20 (9)	O(3)—C(7)—O(4)	126.2 (3)
N(2)—Fe(1)—O(1)	109.04 (9)	C(9)—C(8)—O(5)	113.7 (2)
N(1)—Fe(1)—O(4)	75.82 (9)	C(9)—C(8)—O(6)	122.0 (3)
N(2)—Fe(1)—O(4)	99.57 (9)	O(5)—C(8)—O(6)	124.3 (3)
O(1)—Fe(1)—O(4)	151.39 (9)	C(8)—C(9)—C(10)	128.3 (3)
N(1)—Fe(1)—O(5)	93.74 (9)	C(8)—C(9)—N(2)	111.1 (2)
N(2)—Fe(1)—O(5)	75.82 (9)	C(10)—C(9)—N(2)	120.5 (3)
O(1)—Fe(1)—O(5)	91.83 (9)	C(9)—C(10)—C(11)	118.1 (3)
O(4)—Fe(1)—O(5)	95.8 (1)	C(10)—C(11)—C(12)	120.5 (3)
N(1)—Fe(1)—O(7)	114.22 (9)	C(11)—C(12)—C(13)	117.9 (3)
N(2)—Fe(1)—O(7)	76.20 (9)	C(12)—C(13)—C(14)	128.4 (3)
O(1)—Fe(1)—O(7)	96.13 (9)	C(12)—C(13)—N(2)	120.5 (3)
O(4)—Fe(1)—O(7)	89.9 (1)	C(14)—C(13)—N(2)	111.1 (2)
O(5)—Fe(1)—O(7)	152.00 (8)	C(13)—C(14)—O(7)	113.6 (2)
C(2)—C(1)—O(1)	113.3 (2)	C(13)—C(14)—O(8)	120.5 (3)
C(2)—C(1)—O(2)	120.6 (2)	O(7)—C(14)—O(8)	125.9 (3)
O(1)—C(1)—O(2)	126.1 (3)	Fe(1)—N(1)—C(2)	118.3 (2)
C(1)—C(2)—C(3)	127.7 (2)	Fe(1)—N(1)—C(6)	119.0 (2)
C(1)—C(2)—N(1)	111.4 (2)	C(2)—N(1)—C(6)	122.6 (3)
C(3)—C(2)—N(1)	120.9 (3)	Fe(1)—N(2)—C(9)	119.1 (2)
C(2)—C(3)—C(4)	117.7 (3)	Fe(1)—N(2)—C(13)	118.2 (2)
C(3)—C(4)—C(5)	120.6 (3)	C(9)—N(2)—C(13)	122.5 (2)
C(4)—C(5)—C(6)	118.0 (3)	Fe(1)—O(1)—C(1)	119.5 (2)
C(5)—C(6)—C(7)	128.7 (3)	Fe(1)—O(4)—C(7)	120.6 (2)
C(5)—C(6)—N(1)	120.2 (3)	Fe(1)—O(5)—C(8)	119.6 (2)
C(7)—C(6)—N(1)	111.1 (2)	Fe(1)—O(7)—C(14)	119.8 (2)
C(6)—C(7)—O(3)	120.4 (3)		
O(2 ⁱ)···Na(1)···O(5 ⁱⁱ)	84.14 (8)	O(6 ⁱⁱ)···Na(1)···O(9 ⁱⁱ)	86.5 (1)
O(2 ⁱ)···Na(1)···O(6 ⁱⁱ)	130.9 (1)	O(8 ⁱⁱⁱ)···Na(1)···O(9 ⁱⁱ)	90.3 (1)
O(5 ⁱⁱ)···Na(1)···O(6 ⁱⁱ)	50.43 (7)	O(2 ⁱ)···Na(1)···O(10)	91.4 (1)
O(2 ⁱ)···Na(1)···O(8 ⁱⁱⁱ)	91.20 (9)	O(5 ⁱⁱ)···Na(1)···O(10)	105.7 (1)
O(5 ⁱⁱ)···Na(1)···O(8 ⁱⁱⁱ)	168.3 (1)	O(6 ⁱⁱ)···Na(1)···O(10)	85.3 (1)
O(6 ⁱⁱ)···Na(1)···O(8 ⁱⁱⁱ)	136.99 (9)	O(8 ⁱⁱⁱ)···Na(1)···O(10)	85.0 (1)
O(2 ⁱ)···Na(1)···O(9 ⁱⁱ)	105.9 (1)	O(9 ⁱⁱ)···Na(1)···O(10)	162.2 (1)
O(5 ⁱⁱ)···Na(1)···O(9 ⁱⁱ)	80.7 (1)		

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

The structure was solved by the Patterson method and successive Fourier maps. H atoms were found from difference Fourier syntheses and their positions were subsequently refined. Anomalous dispersion was taken into account. The absolute configuration was confirmed; the Flack enantiopole parameter χ was refined [$\chi = 0.06$ (2)] using the expression $F_c = [(1-\chi)F(h)^2 + \chi F(-h)^2]^{1/2}$. All calculations were performed using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) on a VAX 6310 and a PC computer.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: *CRYSTALS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{*exo*-2,7,11- μ_3 -[(μ -H)₂Cu(PPh₃)]-2-(PPh₃)-*closo*-2,1-CuTeB₁₀H₈}.CH₂Cl₂

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Abstract

The title compound, 2-triphenylphosphine-2,7,11- μ_3 -[dihydro(triphenylphosphine)copper-2Cu,7H,11H]-octahydro-2-cupra-1-tellura-*closo*-dodecaborane (C₃₆H₄₀B₁₀Cu₂P₂Te.CH₂Cl₂), has a triangulated icosahedral