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Hexaaquairon(II) dipicrate dihydrate

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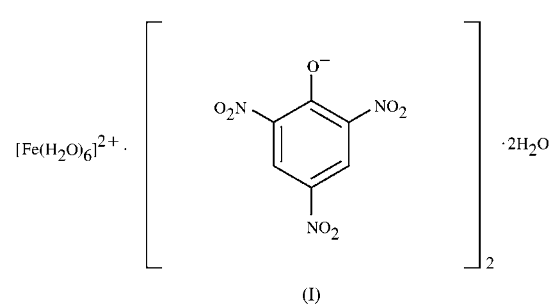
In the crystal structure of the title compound, $[Fe(H_2O)_6](C_6H_2N_3O_7)_2{\cdot}2H_2O$, the centrosymmetric cationic iron complexes and picrate anions form separate stacks extending along the *b* axis. No picrate species ligate to the metal cation. Picrate ions are linked to one another in the stack *via* short intermolecular C···C contacts of 3.083 (4) and 3.055 (4) Å. Variable-temperature X-ray diffraction measurements performed between room temperature and 93 K showed a linear decrease of the lattice parameters, suggesting that there is no phase transition.

Comment

Picric acid (2,4,6-trinitrophenol) was used as a military explosive during the latter part of the nineteenth century and the early part of the twentieth century (Kaye, 1978), and a large number of warheads were abandoned and buried, especially after World War II. It is thought that picric acid reacts with metal ions, such as iron, zinc and copper, from the corroded warheads, resulting in the formation of metal salts, some of which are known to exhibit higher sensitivities to impact than the free acid (Urbański, 1964; Kaye, 1978). Thus, to establish a safe technology with which to treat abandoned warheads, it is both crucial and urgent to investigate the chemical and physical properties of metal picrates. In particular, information about the three-dimensional molecular arrangements is essential if we are to understand other properties. We describe here the crystal structure of the title iron picrate, (I).



(I)

Fig. 1 shows the molecular structures of the hexaaquairon cation and picrate anion, and selected bond lengths and angles are summarized in Table 1. The Fe atom lies on a crystallographic inversion center. Six water molecules are coordinated to the central metal atom and no picrate species ligate to the metal atom. This situation is similar to the crystal structure of hexaaquamagnesium dipicrate trihydrate (Harrowfield *et al.*, 1995), which differs from other metal picrate crystals, in which picrate anions tend to coordinate to metal cations from the main-group, transition, lanthanide and actinide metals (Harrowfield, 1996). The picrate anion adopts a keto form, and the O1—C1 bond distance of 1.256 (2) Å indicates that the O—C bond is a double rather than a single bond. The C1—C2 and C1—C6 bond lengths of 1.448 (3) and 1.452 (3) Å, respectively, are considerably longer than the standard average C—C bond length of 1.395 Å in a phenyl ring. The average values of the corresponding O—C and C—C bond lengths are 1.25 (2) and 1.45 (1) Å, respectively, for 244 picrate anions in 198 non-disordered crystal structures in the Cambridge Structural Database (CSD; Version 5.23; Allen, 2002). This suggests that the picrate anion is likely to prefer the keto form to the enolate form in the crystal structure, which is the case with most metal picrate crystals, regardless of whether the phenolate group ligates directly to the metal cation. The only obvious exception is tris(μ-hydroxo)hexaaquatriberyllium(II) tris(picrate) hexahydrate (Cecconi *et al.*, 1998), in which all of the three independent anions appear to adopt enolate forms (ranges of 1.320–1.334 and 1.389–1.391 Å for the O—C and C—C bonds, respectively). The nitro groups of the anion are twisted slightly out of the molecular plane defined by atoms C1–C6, O1 and N1–N3, with the distances from the plane ranging from 0.215 (2) (for atom O5) to 0.539 (2) Å (for atom O6).

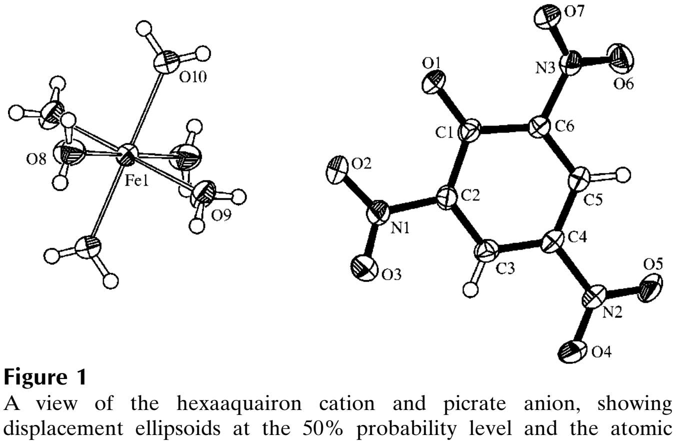


Figure 1
A view of the hexaaquairon cation and picrate anion, showing displacement ellipsoids at the 50% probability level and the atomic labeling scheme.

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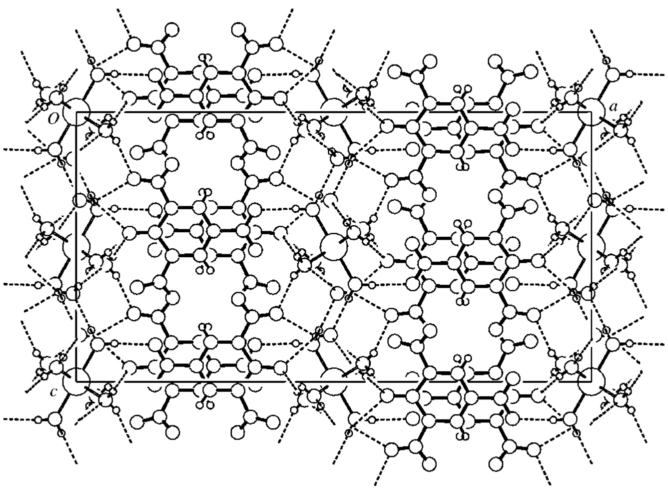

Figure 2
The crystal structure of (I), projected along the *b* axis. Dashed lines indicate intermolecular hydrogen bonds with O···H distances less than 2.4 Å.

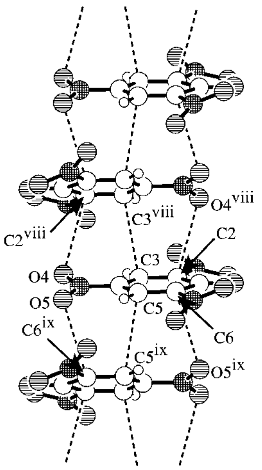

Figure 3
The molecular stacking of the picrate anions, viewed along the *c* axis. The dashed lines indicate short intermolecular contacts with C···C and O···C distances less than 3.2 and 3.0 Å, respectively. [Symmetry codes: (viii) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (ix) $\frac{1}{2} - x, -\frac{1}{2} - y, z$.]

The unit cell contains four iron cations and eight picrate anions (Fig. 2), and the cation complexes and picrate anions form separate stacks extending along the *b* axis. The water molecules of crystallization are linked *via* hydrogen bonds (Table 2) to the surrounding O atoms of the nitro groups of the picrate anions and the aqua ligands of the iron complexes. Fig. 3 illustrates the molecular stacking of the picrate anions, viewed along the *c* axis. Successive anions in the stack are not parallel to one another, the dihedral angle between their phenyl planes being 24.67 (7)°. The anions in the stack are linked *via* short intermolecular C···C and O···C contacts of 3.083 (4), 3.055 (4), 2.994 (2) and 2.962 (3) Å for C3···C3^{viii}, C5···C5^{ix}, O4···C2^{viii} and O5···C6^{ix}, respectively [symmetry codes: (viii) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (ix) $\frac{1}{2} - x, -\frac{1}{2} - y, z$]. These contacts are shorter than those found in 16 non-disordered crystal structures of metal picrates in the CSD, all of which contain stacked picrate anions. The picric acid crystal does not possess such a structure (Duesler *et al.*, 1978).

If the crystal structure exhibits a phase transition, it could potentially affect the explosive sensitivity of the metal picrate. However, variable-temperature X-ray diffraction measurements performed over the temperature range 326–93 K showed a linear decrease of the lattice parameters. The thermal expansion coefficients were 6.85×10^{-5}, 4.78×10^{-5}, 1.44×10^{-5} and 1.30×10^{-4} K^{-1} for *a*, *b*, *c* and *V*, respectively. Diffraction photographs at 93 K did not show any new diffraction spots or any diminution of existing spots compared with the images observed at 299 K. These results imply that the crystal is isomorphous between room temperature and 93 K, and IR spectrometry also indicated that there is no phase transition between 294 and 79 K. The O—H stretching mode peaks in the 3300–3600 cm^{-1} region are shifted to lower frequencies with decreasing temperature, suggesting a monotonous shortening of the hydrogen-bond distances. The rate of the shift for the strongest peak near 3500 cm^{-1} was −0.035 cm^{-1} K^{-1}. The single crystal decomposed and diffraction spots were lost above 326 K; differential scanning calorimetry and thermal gravity analysis confirmed that the solvate water molecules began to be eliminated at approximately this temperature (Matsukawa *et al.*, 2002).

Experimental

The synthesis of (I) has been reported by Matsukawa *et al.* (2002). Single crystals of (I) were prepared by recrystallization from an aqueous solution.

Crystal data

$[Fe(H_2O)_6](C_6H_2N_3O_7)_2 \cdot 2H_2O$
$M_r = 656.16$
Orthorhombic, *Pccn*
$a = 25.248$ (2) Å
$b = 7.1136$ (7) Å
$c = 13.1993$ (9) Å
$V = 2370.7$ (3) Å^3
$Z = 4$
$D_x = 1.838$ Mg m^{-3}
$D_m = 1.839$ (1) Mg m^{-3}
D_m measured by flotation in CH_2Br_2–CH_2Cl_2
Mo *Kα* radiation
Cell parameters from 15 reflections
$\theta = 23.0$–$31.5°$
$\mu = 0.75$ mm^{-1}
$T = 293$ (1) K
Prism, yellow
0.38 × 0.34 × 0.33 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
4140 measured reflections
2722 independent reflections
1899 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.017$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 32$
$k = -3 \rightarrow 9$
$l = -6 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.075$
$S = 1.27$
2722 reflections
228 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Extinction correction: Zachariasen (1967), type 2 Gaussian isotropic
Extinction coefficient: 0.0216 (7)

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Table 1
Selected geometric parameters (Å, °).

Fe1—O8	2.077 (2)	C1—C2	1.448 (3)
Fe1—O9	2.164 (2)	C1—C6	1.452 (3)
Fe1—O10	2.109 (2)	C2—C3	1.380 (3)
O1—C1	1.256 (2)	C3—C4	1.379 (3)
N1—C2	1.457 (2)	C4—C5	1.382 (3)
N2—C4	1.447 (2)	C5—C6	1.372 (3)
N3—C6	1.459 (3)		
O8—Fe1—O9	86.50 (7)	N1—C2—C3	115.3 (2)
O8—Fe1—O9^{i}	93.50 (7)	C1—C2—C3	124.0 (2)
O8—Fe1—O10	91.16 (8)	C2—C3—C4	119.3 (2)
O8—Fe1—O10^{i}	88.84 (8)	N2—C4—C3	119.4 (2)
O9—Fe1—O10	86.55 (7)	N2—C4—C5	119.2 (2)
O9—Fe1—O10^{i}	93.45 (7)	C3—C4—C5	121.4 (2)
O1—C1—C2	124.5 (2)	C4—C5—C6	119.0 (2)
O1—C1—C6	123.8 (2)	N3—C6—C1	119.8 (2)
C2—C1—C6	111.7 (2)	N3—C6—C5	115.6 (2)
N1—C2—C1	120.6 (2)	C1—C6—C5	124.6 (2)

Symmetry code: (i) $1-x, -y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H3···O5^{ii}	0.83 (3)	2.77 (3)	3.156 (2)	110 (2)
O8—H3···O1^{iii}	0.83 (3)	2.10 (3)	2.891 (2)	159 (3)
O8—H3···O7^{iii}	0.83 (3)	2.62 (3)	2.967 (2)	106 (2)
O8—H3···N3^{iii}	0.83 (3)	3.05 (3)	3.531 (2)	118 (2)
O9—H6···O2	0.78 (2)	2.19 (2)	2.931 (2)	160 (2)
O9—H6···O5^{iv}	0.78 (2)	2.75 (2)	3.141 (2)	113 (2)
O9—H5···O1^{v}	0.85 (3)	2.05 (3)	2.889 (2)	174 (2)
O9—H5···O7^{v}	0.85 (3)	2.53 (2)	2.974 (2)	113 (2)
O10—H8···O4^{ii}	0.83 (2)	2.04 (2)	2.871 (2)	174 (2)
O10—H8···O5^{ii}	0.83 (2)	2.89 (2)	3.455 (2)	126 (2)
O10—H8···N2^{ii}	0.83 (2)	2.80 (2)	3.553 (2)	151 (2)
O8—H3···O11^{vi}	0.83 (3)	3.21 (3)	3.546 (2)	107 (2)
O8—H4···O11^{vii}	0.74 (2)	2.06 (2)	2.778 (2)	167 (2)
O10—H7···O11^{i}	0.76 (3)	2.02 (3)	2.777 (2)	176 (3)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $\frac{1}{2}+x, -y, \frac{3}{2}-z$; (iii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $\frac{1}{2}-x, y, z-\frac{1}{2}$; (v) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (vii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

All H atoms were located from difference Fourier maps and were refined isotropically. The O—H and C—H bond lengths are 0.72 (3)–0.85 (3) and 0.86 (2)–0.92 (2) Å, respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku, 2000); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1127). Services for accessing these data are described at the back of the journal.

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