

5,7,7,12,14,14-Hexamethyl-4,11-diaza-1,8-diazoniacyclotetradecane pentacyanonitrosferrate(II) dihydrate: a supramolecular compound constructed by hydrogen bonds

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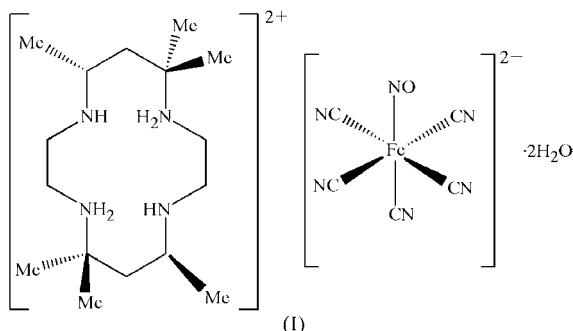
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The title compound, (C₁₆H₃₈N₄)[Fe(CN)₅(NO)]·2H₂O, contains one [Fe(CN)₅(NO)]²⁻ dianion, two half [H₂teta]²⁺ dications (teta is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), each lying about an independent inversion centre, and two solvent water molecules, all of which are held together by hydrogen bonds to form a three-dimensional supramolecular framework.

Comment

There has been much interest in the synthesis of magnetic materials from inorganic coordination complexes (Ökawa *et al.*, 2002; Černák *et al.*, 2002). Among them, cyanide-bridged bimetallic assemblies, derived from [M(CN)₆]ⁿ⁻ (M = Fe, Cr and Mn) building blocks and coordinatively unsaturated transition metal complexes, have been studied structurally and magnetically in order to clarify the magneto-structure correlation of cyano-bridged bimetallic systems (Shen *et al.*, 2001, 2003; Ohba *et al.*, 1998).



Teta (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) is well known as a macrocyclic ligand and can coor-

minate selectively with some transition metal ions, resulting in macrocyclic complexes, such as [Ni(teta)]²⁺ and [Cu(teta)]²⁺. Zou *et al.* (1998) have reported a novel one-dimensional linear chain Fe^{III}-Cu^{II} polymer, [Cu(teta)(H₂O)₂][Cu(teta)Fe(CN)₆]-ClO₄·2H₂O, using [Cu(teta)]²⁺ as a building block. Furthermore, some nitroprusside-bridged polymeric complexes have been prepared and magnetic studies have showed that the nitroprusside anion transmits a very weak antiferromagnetic interaction (Yuan *et al.*, 2003; Shyu *et al.*, 1997). Recently, we attempted to prepare cyano-bridged bimetallic complexes using [Fe(CN)₅(NO)]²⁻ and [Ni(teta)]²⁺ as precursors. Unexpectedly, the compound [H₂teta][Fe(CN)₅(NO)]·2H₂O, (I), was obtained. We report here the synthesis and crystal structure of this complex.

The asymmetric unit of (I) (Fig. 1) consists of one isolated [Fe(CN)₅(NO)]²⁻ anion, two half [H₂teta]²⁺ cations and two solvent water molecules. As usual, the [Fe(CN)₅(NO)]²⁻ fragment exhibits a distorted octahedral structure (Table 1). Both [H₂teta]²⁺ cations are centrosymmetric, and the dihedral angle between the two cations [H₂teta]₁²⁺ (defined by atoms N9, N9A, N10 and N10A) and [H₂teta]₂²⁺ (defined by atoms N7, N7A, N8 and N8A), in which atoms N9, N9A, N7 and N7A act as hydrogen-bond donors, is 50°. The apertures of [H₂teta]₁²⁺ and [H₂teta]₂²⁺ are 6.673 (C15···C15A), 4.641 (C17···C18A), 6.853 (C7···C7A) and 5.233 Å (C9···C10A). The title complex can probably be applied to adsorb and desorb preferentially metal ions through adjusting the pH values of solutions, because the [H₂teta]²⁺ macrocycle has a large aperture and the complex is insoluble in water and many organic solvents. There is, therefore, a great deal of current research interest in this field.

The structural features of complex (I) reported above are different from those of [FeL]₂[Fe(CN)₅(NO)] (Shen *et al.*, 2004; Yuan *et al.*, 2003), derived from cyano-bridged interaction. Details of the intra- and intermolecular hydrogen bonds are given in Table 2. Atoms N9 and N9A in the macrocyclic unit [H₂teta]₁²⁺ act as hydrogen-bond donors, *via* H9A and H9B, respectively, to cyanide atoms N6^{iv} and N2ⁱ in the [Fe(CN)₅(NO)]²⁻ anions (symmetry codes as in Table 2). In addition, atom C18 is hydrogen bonded to atom N2^{vi}, [symmetry code: (vi) *x*, *y*, *z* - 1], forming C18—H19B···N2^{vi} bonds with a C18···N2^{vi} distance of 3.453 (4) Å, which indicates that there is a very weak intermolecular interaction

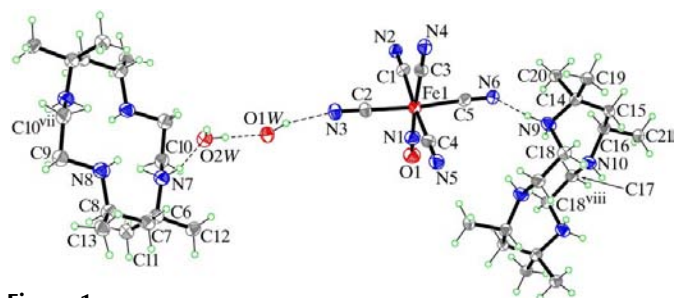


Figure 1

View of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry codes: (vii) $-x, 1 - y, 1 - z$; (viii) $1 - x, 3 - y, 2 - z$.]

between atoms C18 and N2^{vi}. Moreover, atom N9 interacts with atom N10^v [symmetry code: (v) $-x + 1, -y + 1, -z$] to form an intramolecular hydrogen bond with an N9...N10^v distance of 2.899 (4) Å. This kind of hydrogen-bond interaction may help to stabilize the configuration of the macrocyclic dication [H₂teta]²⁺. Atom N7 in the other cation, [H₂teta]₂²⁺, acts as a hydrogen-bond donor to the O2W water molecule.

In addition, the O1W and O2W atoms of the solvent water molecules are hydrogen bonded to the cyanide N atoms (N3, N4 and N5) and atom N7 (N7A) in the cation, with O1W...N3, O1W...N4ⁱ, O2W...N5ⁱⁱ and O2W...N7 distances ranging from 2.846 (4) to 3.164 (4) Å. Simultaneously, two solvent water molecules themselves form an O2W—H2WD...O1W hydrogen bond, with an O2W...O1W distance of 2.628 (3) Å.

The hydrogen bonds lead to the formation of a three-dimensional supramolecular framework, featuring an alternating arrangement of cations and anions.

Experimental

[Ni(teta)](ClO₄)₂ was prepared according to the method described by Curtis (1964). Yellow block-shaped crystals of [H₂teta][Fe(CN)₅(NO)]·2H₂O were obtained by slow diffusion of a yellow dimethylformamide (DMF) solution (15 ml) of [Ni(teta)](ClO₄)₂ (0.15 mmol) and an aqueous solution (15 ml) of Na₂[Fe(CN)₅(NO)]·2H₂O (0.15 mmol) through a U-tube containing agar at room temperature. The resulting crystals were collected, washed with water and DMF sequentially, and dried in air. Analysis calculated for C₂₁H₄₂FeN₁₀O₃: C 46.84, H 7.86, N 26.02%; found: C 46.88, H 7.84, N 26.00%.

Crystal data

(C ₁₆ H ₃₈ N ₄)[Fe(CN) ₅ (NO)]·2H ₂ O	Z = 2
M _r = 538.50	D _x = 1.211 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
a = 8.9527 (12) Å	Cell parameters from 1759 reflections
b = 10.7737 (14) Å	θ = 2.4–21.8°
c = 16.977 (2) Å	μ = 0.55 mm ⁻¹
α = 74.525 (2)°	T = 293 (2) K
β = 78.926 (2)°	Block, yellow
γ = 70.318 (2)°	0.3 × 0.2 × 0.2 mm
V = 1476.5 (3) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	5633 independent reflections
φ and ω scans	3941 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	R _{int} = 0.021
T _{min} = 0.88, T _{max} = 0.90	θ_{max} = 26.0°
7878 measured reflections	h = -11 → 6
	k = -13 → 13
	l = -20 → 20

Refinement

Refinement on F ²	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.4822P]$
R[F ² > 2 σ (F ²)] = 0.058	where $P = (F_o^2 + 2F_c^2)/3$
wR(F ²) = 0.126	(Δ/σ) _{max} < 0.001
S = 1.07	$\Delta\rho_{max}$ = 0.39 e Å ⁻³
5633 reflections	$\Delta\rho_{min}$ = -0.42 e Å ⁻³
322 parameters	Extinction correction: SHELXS97
H-atom parameters constrained	Extinction coefficient: 0.08 (2)

H atoms were visible in difference maps and were subsequently treated as riding atoms, with C—H distances in the range 0.96–0.98 Å,

Table 1

Selected geometric parameters (Å, °).

C1—Fe1	1.931 (3)	C4—Fe1	1.915 (3)
C2—Fe1	1.929 (3)	C5—Fe1	1.945 (3)
C3—Fe1	1.934 (3)		
N2—C1—Fe1	173.8 (3)	N6—C5—Fe1	173.8 (3)
N3—C2—Fe1	178.8 (3)	C4—Fe1—C1	172.34 (14)
N4—C3—Fe1	178.6 (3)	N1—Fe1—C3	176.38 (15)
N5—C4—Fe1	178.4 (3)	C2—Fe1—C5	172.63 (13)

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...N3	0.85	2.05	2.846 (4)	155
O1W—H1WB...N4 ⁱ	0.85	2.31	2.929 (4)	130
O2W—H2WC...N5 ⁱⁱ	0.85	2.58	3.164 (4)	127
O2W—H2WD...O1W	0.85	1.78	2.628 (3)	179
N7—H7B...O2W	0.90	2.01	2.867 (4)	159
N9—H9A...N6	0.90	1.72	2.600 (4)	164
N9—H9B...N2 ⁱⁱⁱ	0.90	2.65	3.303 (4)	130
N10—H10A...N2 ^{iv}	0.90	2.22	3.090 (4)	162

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, 2 - y, 1 - z$; (iii) $1 - x, 2 - y, 2 - z$; (iv) $x, 1 + y, z$.

N—H distances of 0.90 Å and O—H distances of 0.85 Å. U_{iso}(H) values were set equal to 1.2 or 1.5 times U_{eq} of the parent atom.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1254). Services for accessing these data are described at the back of the journal.

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