

Hexaaqua-1 κ^3 O,3 κ^3 O-tri- μ -cyano-1:2 κ^2 N:C;2:3 κ^2 C:N;3:4 κ^2 N:C-nona-cyano-2 κ^4 C,4 κ^5 C-pentakis(*N,N*-dimethylacetamide)-1 κ^3 O,3 κ^2 O-diiron(III)-diytterbium(III) dihydrate**Helle Svendsen, Jacob Overgaard,* Marie A. Chevalier and Bo B. Iversen**

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Key indicatorsSingle-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
Disorder in main residue
 R factor = 0.027
 wR factor = 0.054
Data-to-parameter ratio = 62.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Fe}_2\text{Yb}_2(\text{CN})_{12}(\text{C}_4\text{H}_9\text{NO})_5(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$, is a tetranuclear complex, where the four metal centres are connected through three cyano bridges, the iron centres making one and two bridges, respectively. Each Fe atom is surrounded by six cyano ligands, forming almost ideal octahedra. The two Yb atoms have different ligand environments; both are coordinated by seven ligands, consisting of water molecules, dimethylacetamide (DMA) solvent and cyano groups, but not in the same ratio. Four of the five DMA molecules show various degrees of common structural disorder. The asymmetric unit also includes two solvent water molecules, which take part in hydrogen bonding, forming an extended network of tetramers.

Comment

Photoinduced magnetization is an interesting property in materials, with a special focus on the development of new memory devices (Gutlich *et al.*, 1994). Previously, much attention has been paid to the Prussian blue analogues (Sato *et al.*, 1996). However, it was recently found that a cyano-bridged hetero-bimetallic Nd–Fe complex with coordinated solvent showed an increase in magnetization upon UV irradiation (Li *et al.*, 2003). This new type of magnetic materials is, unlike the Prussian blue analogues, relatively easy to crystallize. The entire series with lanthanide elements have been synthesized using dimethylformamide (DMF) as solvent, and it was found that they crystallized in two different monoclinic space groups (Li *et al.*, 2004, and references therein). Another solvent, dimethylacetamide (DMA), has been used in a reaction with gadolinium (Yan & Chen, 2000) and neodymium (Overgaard *et al.*, 2005). The Nd complex with DMA as solvent does not exhibit a cyano bridge and the two metal centres are not connected through covalently bonded bridges. In a further attempt to investigate the DMA-type complexes, we carried out a synthesis with DMA and the lanthanide element ytterbium. This gives rise to a new coordination compound, (I), which crystallizes in the orthorhombic space group $Pna2_1$.

As shown in Fig. 1, compound (I) contains four metal centres connected through three cyano bridges, whereas only two centres are present in the other complexes mentioned above. Each of the two Fe atoms sits in an octahedral coordination environment formed by six cyano ligands, with bond lengths in the range 1.919 (1)–1.950 (2) Å (Table 1). The Yb atoms have a coordination number of 7: one cyano ligand, two DMA molecules and three water molecules are present for

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each. Atom Yb2 has one extra DMA ligand, whereas atom Yb1 has one extra bridging cyano ligand, thereby linking to both Fe centres.

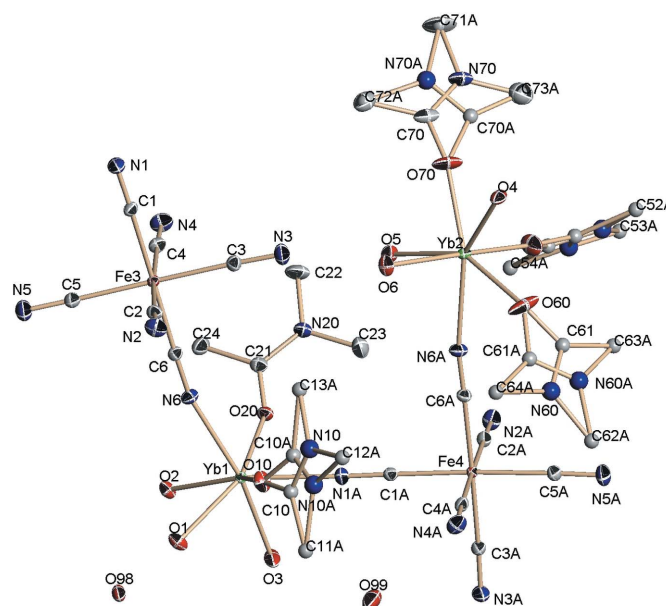
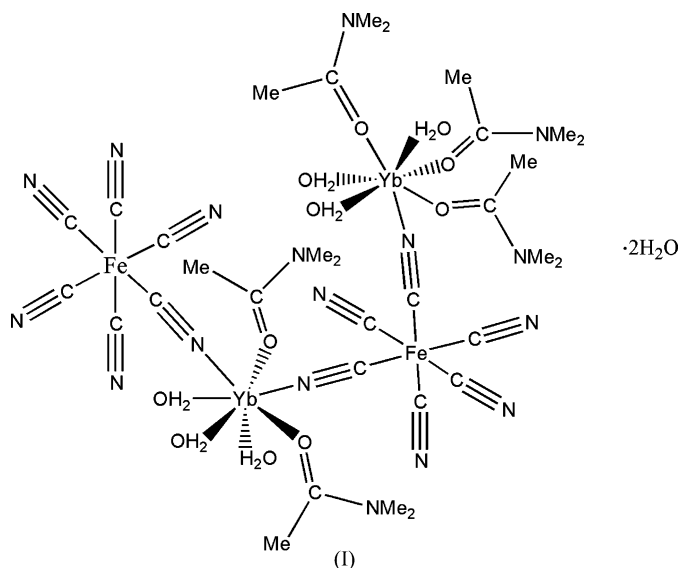


Figure 1
A view of the molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Both components are shown for the disorder in the DMA ligands. H atoms have been omitted for clarity.

Four of the five Yb-coordinated DMA molecules exhibit disorder as two different structural arrangements seem possible. It can be described as a rotation around an axis passing through the O atom and the mid-point of the N—C_{carbonyl} bond. One of the N-methyl C atoms is unaffected by the rotation as it is positioned on the rotation axis, whereas the other changes place with the acetate methyl C atom. The minor occupancies range from 6.3 to 44.6%.

Experimental

The title compound was synthesized by mixing K₃[Fe(CN)₆] (1 mmol) with H₂O (10 ml). YbCl₃ (1 mmol) dissolved in DMA (5 ml) was then added very slowly down the side of the glass vessel. Yellow–greenish crystals precipitated and, after evaporation of the solvent, the crystals were suitable for single-crystal X-ray analysis.

Crystal data

[Fe ₂ Yb ₂ (CN) ₁₂ (C ₄ H ₉ NO) ₅ ·(H ₂ O) ₆]·2H ₂ O	<i>D_x</i> = 1.725 Mg m ⁻³
<i>M_r</i> = 1349.76	Mo K α radiation
Orthorhombic, <i>Pna</i> 2 ₁	Cell parameters from 9695 reflections
<i>a</i> = 25.2387 (9) Å	θ = 5.7–85.4°
<i>b</i> = 14.4943 (6) Å	μ = 4.18 mm ⁻¹
<i>c</i> = 14.2058 (5) Å	<i>T</i> = 100 (2) K
<i>V</i> = 5196.7 (3) Å ³	Block, yellow
<i>Z</i> = 4	0.20 × 0.15 × 0.10 mm

Data collection

Bruker X8 APEXII diffractometer	32727 reflections with <i>I</i> > 2 σ (<i>I</i>)
φ and ω scans	<i>R</i> _{int} = 0.033
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	θ _{max} = 43.3°
<i>T</i> _{min} = 0.45, <i>T</i> _{max} = 0.66	<i>h</i> = -37 → 48
271064 measured reflections	<i>k</i> = -27 → 27
37796 independent reflections	<i>l</i> = -27 → 27

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 1.3004P]$
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] = 0.027	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.054	(Δ/σ) _{max} = 0.011
<i>S</i> = 1.17	$\Delta\rho$ _{max} = 2.36 e Å ⁻³
37796 reflections	$\Delta\rho$ _{min} = -1.51 e Å ⁻³
607 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	with 17930 Friedel pairs
	Flack parameter: -0.007 (3)

Table 1

Selected bond lengths (Å).

Fe3—C1	1.9187 (13)	Yb1—O10	2.2293 (15)
Fe3—C6	1.9296 (12)	Yb1—O1	2.2836 (13)
Fe3—C2	1.941 (2)	Yb1—O3	2.2866 (11)
Fe3—C3	1.9430 (15)	Yb1—O2	2.3143 (14)
Fe3—C4	1.944 (2)	Yb1—N1A	2.3535 (13)
Fe3—C5	1.9494 (17)	Yb1—N6	2.3578 (11)
Fe4—C1A	1.9265 (15)	Yb2—O50	2.1779 (18)
Fe4—C3A	1.9326 (16)	Yb2—O70	2.1947 (14)
Fe4—C5A	1.9329 (18)	Yb2—O60	2.2106 (18)
Fe4—C4A	1.9370 (18)	Yb2—O6	2.2567 (13)
Fe4—C2A	1.9418 (17)	Yb2—O4	2.3504 (13)
Fe4—C6A	1.9440 (14)	Yb2—O5	2.3549 (14)
Yb1—O20	2.2154 (14)	Yb2—N6A	2.4026 (13)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1B...O98	0.969 (18)	1.708 (16)	2.6604 (19)	166.7 (19)
O1—H1A...N2A ⁱ	0.966 (3)	1.777 (6)	2.728 (2)	168 (2)
O2—H2B...O98	0.970 (18)	1.755 (18)	2.7154 (19)	170.0 (19)
O2—H2A...N4A ⁱⁱ	0.970 (14)	1.812 (12)	2.721 (2)	155 (2)
O3—H3A...O99	0.968 (18)	1.911 (19)	2.714 (2)	139 (2)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3–H3B \cdots N1 ⁱⁱⁱ	0.970 (15)	1.858 (11)	2.7821 (18)	158 (2)
O4–H4A \cdots N5 ^{iv}	0.968 (7)	1.958 (6)	2.914 (2)	169.0 (19)
O4–H4B \cdots N3A ^v	0.967 (9)	1.905 (7)	2.8567 (19)	167 (2)
O5–H5B \cdots N2 ^{vi}	0.971 (9)	1.816 (13)	2.775 (2)	169 (2)
O5–H5A \cdots N3	0.971 (14)	1.963 (10)	2.889 (2)	159 (2)
O6–H6B \cdots N3	0.971 (16)	1.957 (11)	2.855 (2)	153 (2)
O6–H6A \cdots N4 ^{vii}	0.972 (3)	1.736 (4)	2.708 (2)	180 (2)
O98–H98B \cdots N5A ^{viii}	0.966 (7)	1.741 (6)	2.695 (2)	169 (2)
O98–H98A \cdots N1 ⁱⁱⁱ	0.969 (14)	1.836 (8)	2.7718 (19)	162 (2)
O99–H99A \cdots N3A	0.965 (16)	2.005 (15)	2.961 (2)	170 (2)
O99–H99B \cdots N5 ⁱⁱⁱ	0.969 (17)	2.231 (12)	3.094 (2)	147.8 (17)

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

The H atoms of the water molecules were located in a difference Fourier analysis and one common O–H bond length was included in the least-squares refinement [0.97 (1) Å]. In order to control the angle between the H atoms in the water molecules, the H \cdots H distance was also restrained [1.58 (1) Å]; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Methyl H atoms were refined as riding on the parent C atom, with C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The disorder in four DMA molecules was such that the overlapping atoms were constrained to identical positions. Groups 10, 50 and 60 were refined isotropically, and the displacement parameters of the overlapping atoms were kept identical. In the last group (group 70), the disordered part with the highest occupancy was refined with anisotropic displacement parameters. The sum of the occupancies of the two disordered parts was fixed to unity. 28 peaks of greater than $1 e \text{ \AA}^{-3}$ were found in the electron-density difference map. About 40% of these were located near the DMA molecules because of the inadequate description of the disorder. The remaining peaks were distributed around the metal atoms. The deepest hole in the final difference map was located 0.58 Å from atom Yb1.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT-Plus* (Bruker–Nonius, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSHELL* (Bruker, 2000); software used to prepare material for publication: *enCIFer* (Version 1.1; Allen *et al.*, 2004) and *WinGX* (Farrugia, 1999).

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