

Triaquatetrakis(dimethylacetamide- κ O)-gadolinium(III) hexacyanoferrate(III) dihydrate

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Key indicators

Single-crystal X-ray study

$T = 100$ K

Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å

Disorder in main residue

R factor = 0.028

wR factor = 0.070

Data-to-parameter ratio = 35.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Gd}(\text{C}_4\text{H}_9\text{NO})_4(\text{H}_2\text{O})_3][\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, is a bimetallic complex containing two isolated metal complexes. The Fe atom is bonded to six cyano ligands forming an almost ideal octahedron. One of the cyano groups is also connected through a hydrogen bond to a water molecule bonded to the Ga atom. Aside from three water molecules, gadolinium is also coordinated by four dimethylacetamide molecules, two of which show various degrees of structural disorder. The asymmetric unit also includes two solvent water molecules, which take part in hydrogen bonding, forming an extended network.

Comment

Photoinduced magnetization is an interesting property in materials, with a special focus on the development of new memory devices (Gutlich *et al.*, 1994). Earlier focus has been on Prussian blue analogues (Sato *et al.*, 1996). In 2003 it was found that a cyano-bridged hetero-bimetallic neodymium–iron complex showed an increase in magnetization upon UV irradiation at low temperatures (Li *et al.*, 2003). Magnetic materials of this new type are, unlike Prussian blue analogues, relatively easily crystallized, hence possibly enabling a characterization of the structural changes associated with the magnetic transitions. The entire series of lanthanide elements together with $[\text{Fe}(\text{CN})_6]^{3-}$ have been synthesized using dimethylformamide (DMF) as solvent, and it was found that they crystallize in two slightly different monoclinic space groups (Li *et al.*, 2004, and references therein).

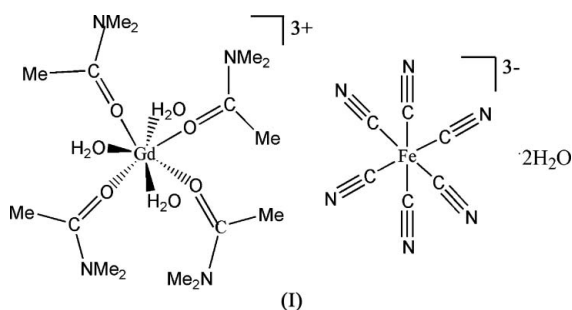
As an alternative solvent to dimethylformamide (DMF), dimethylacetamide (DMA) has been used in reactions with neodymium (Overgaard *et al.*, 2005) and ytterbium (Svendsen *et al.*, 2006). Using this solvent, the Nd complex does not exhibit a cyano bridge linking the metal centers that are connected only through hydrogen bonds. For the Yb–DMA complex, the surprising outcome is a tetrametallic complex, which crystallizes in the orthorhombic space group, $Pna2_1$, with two iron and two ytterbium metal centers connected through three cyano bridges.

Recently, the crystal structure of a compound with gadolinium and DMA has been published (Yan & Chen, 2000), which showed a completely different packing scheme and stoichiometry compared with the above-mentioned Nd and Yb complexes. The Gd compound is trimetallic – one iron and two gadolinium centers – and crystallizes in the orthorhombic space group $P2_12_12$. The Fe atom is linked to both Ga atoms by two cyano bridges. However, we have not been able to repeat this synthesis. Instead, we find a crystal structure strongly resembling the Nd–DMA complex (Overgaard *et al.*, 2005). Fig. 1 shows the structure of this complex, (I). There is

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no linkage between the metal centers except for a hydrogen bond between a water molecule on gadolinium and a cyano group on iron. The Gd...Fe distance, which in the μ -cyano-bridged complex using DMF as solvent is around 5.5 Å, is here extended to 7.294 (2) Å. This is an increase of nearly 35%. The coordination number of gadolinium in the DMF complex is eight, but in this complex using DMA as solvent gadolinium is only coordinated by only seven ligands – four nearly equidistant DMA solvent molecules [average Gd–O_{DMA} = 2.273 (3) Å] and three water molecules [average Gd–O_{water} = 2.406 (2) Å]. The Fe atom sits in an octahedral coordination environment comprising six cyano ligands with bond lengths in the range 1.9342 (16)–1.9652 (16) Å. The bond lengths are listed in Table 1.



Three of the four Gd-coordinated DMA molecules exhibit disorder as two different structural arrangements seem possible. This disorder can be described as a rotation around an axis going through the O and the mid-point of the N–C_{carbonyl} bond. In groups 20 and 40, 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. In group 30 all atoms except oxygen are affected by the disorder – here no atoms are positioned on the rotation axis. The minor occupancies range from 0.137 (5) to

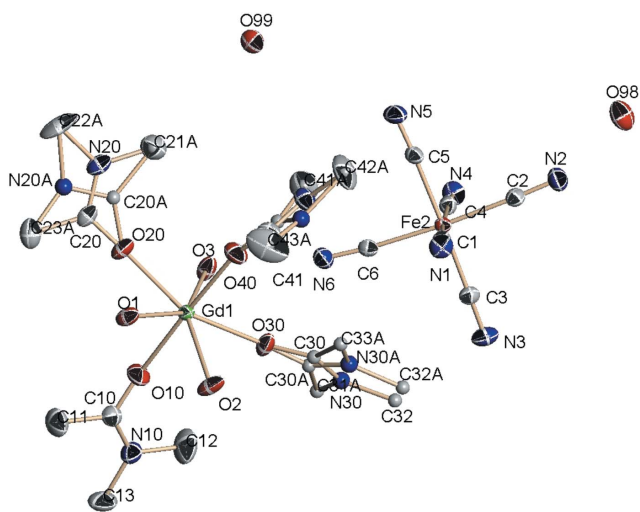


Figure 1
A view of the structure of (I), with displacement ellipsoids shown at the 50% probability level. Both components are shown for the disorder in the DMA ligands. H atoms have been omitted for clarity.

0.384 (5). The two solvent water molecules and the three water molecules coordinated to Gd form ten hydrogen bonds with D...A distances in the range 2.705 (2)–3.148 (2) Å (Table 2).

Experimental

The title compound was synthesized by mixing K₃[Fe(CN)₆] (1 mmol) with water (10 ml). Gd(NO₃)₃ (1 mmol) dissolved in DMA (5 ml) was then added very slowly down the side of the glass. Green–yellow crystals precipitated and after evaporation the crystals were suitable for single-crystal X-ray analysis.

Crystal data

[Gd(C ₄ H ₉ NO) ₄ (H ₂ O) ₃]- [Fe(CN) ₆]-2H ₂ O	Z = 8
<i>M_r</i> = 807.77	<i>D_x</i> = 1.556 Mg m ⁻³
Orthorhombic, <i>Pbca</i>	Mo K α radiation
<i>a</i> = 16.0883 (3) Å	μ = 2.38 mm ⁻¹
<i>b</i> = 19.2620 (4) Å	<i>T</i> = 100 (2) K
<i>c</i> = 22.2566 (4) Å	Block, green–yellow
<i>V</i> = 6897.2 (2) Å ³	0.25 × 0.15 × 0.10 mm

Data collection

Bruker X8 APEX-II diffractometer	147578 measured reflections
φ and ω scans	14850 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	11939 reflections with <i>I</i> > 2 σ (<i>I</i>)
<i>T_{min}</i> = 0.61, <i>T_{max}</i> = 0.79	<i>R_{int}</i> = 0.030
	θ_{max} = 35.4°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 1.8917P]$
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] = 0.028	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>wR</i> (<i>F</i> ²) = 0.070	($\Delta\sigma$) _{max} = 0.003
<i>S</i> = 1.28	$\Delta\rho_{max}$ = 2.21 e Å ⁻³
14850 reflections	$\Delta\rho_{min}$ = -0.93 e Å ⁻³
423 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected bond lengths (Å).

Fe2–C5	1.9342 (16)	Gd1–O40	2.2639 (13)
Fe2–C4	1.9369 (16)	Gd1–O20	2.2730 (12)
Fe2–C2	1.9499 (17)	Gd1–O30	2.2942 (12)
Fe2–C3	1.9506 (17)	Gd1–O2	2.3945 (13)
Fe2–C1	1.9514 (16)	Gd1–O1	2.4065 (12)
Fe2–C6	1.9652 (16)	Gd1–O3	2.4180 (12)
Gd1–O10	2.2606 (13)		

Table 2

Hydrogen-bond geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
O1–H1B...O99	0.969 (13)	1.809 (13)	2.7682 (19)	169.9 (17)
O1–H1A...N4 ⁱ	0.971 (13)	1.779 (13)	2.743 (2)	171 (2)
O2–H2A...N5 ⁱⁱ	0.969 (13)	1.742 (13)	2.705 (2)	172 (2)
O2–H2B...O99	0.969 (13)	1.848 (13)	2.7878 (18)	162.4 (17)
O3–H3A...N6	0.968 (13)	2.118 (13)	3.061 (2)	164.6 (18)
O3–H3B...N1 ⁱⁱⁱ	0.969 (13)	1.855 (14)	2.823 (2)	176.5 (18)
O98–H98B...N2	0.968 (13)	1.954 (11)	2.913 (2)	171 (2)
O98–H98A...N2 ^{iv}	0.968 (13)	2.212 (15)	3.148 (2)	162.4 (19)
O99–H99B...O98 ^v	0.967 (13)	1.812 (14)	2.770 (2)	170.8 (16)
O99–H99A...N3 ^{vi}	0.968 (13)	1.899 (14)	2.863 (2)	173.6 (18)

Symmetry codes: (i) *x*, -*y* + ½, *z* - ½; (ii) -*x* + ½, *y* - ½, *z*; (iii) *x* + ½, *y*, -*z* + ½; (iv) -*x*, -*y* + 1, -*z* + 1; (v) -*x*, *y* - ½, -*z* + ½; (vi) -*x* + ½, -*y*, *z* - ½.

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···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 three DMA molecules was such that the overlapping atoms were constrained to identical positions. Group 30 was refined isotropically and the displacement parameters of the overlapping atoms were kept identical. In groups 20 and 40, the disordered part with the highest occupancy was refined with anisotropic displacement parameters. The other part was refined isotropically with the corresponding U_{eq} from the anisotropic part as displacement parameters. The sum of the occupancies of the two disordered parts was fixed to unity. Seven peaks were greater than $1 \text{ e } \text{Å}^{-3}$ in the electron-density difference map density, the highest peak is located about 0.49 Å from atom N30.

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: *XSELL* (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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