

Pentacyanoferrate(III)- μ -cyano-[triqua-tetrakis(dimethylformamide)gadolinium(III)] monohydrate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

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

R factor = 0.034

w R factor = 0.078

Data-to-parameter ratio = 14.4

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

The crystal structure of the title complex, $[\text{Gd}(\text{C}_3\text{H}_6\text{NO})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\{\text{Fe}(\text{CN})_5\}]\cdot\text{H}_2\text{O}$, is built of neutral bimetallic Gd–Fe complexes and solvent water molecules. The Gd^{III} atom, with the coordination of a distorted square antiprism, and the octahedral six-coordinated Fe^{III} atom are bridged by an almost linear cyanide link [$\text{Fe}-\text{C} = 1.934(2)\text{ \AA}$, $\text{C}-\text{N} = 1.149(2)\text{ \AA}$, $\text{N}-\text{Gd} = 2.449(2)\text{ \AA}$, $\text{Fe}-\text{C}-\text{N} = 177.2(2)^\circ$, $\text{C}-\text{N}-\text{Gd} = 162.6(1)^\circ$ and $\text{Fe}\cdots\text{Gd} = 5.457(3)\text{ \AA}$]. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into a three-dimensional framework.

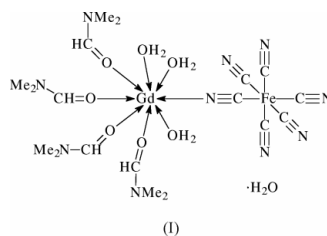
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Comment

There has been continued interest in cyanide-bridged lanthanide–transition metal complexes because of their potential as precursors in the preparation of rare earth orthoferrites, fluorescent and magnetic materials (Dunbar & Heintz, 1997). Based on the Prussian Blue–lanthanide complexes, diverse structures have been obtained by using different ligands to fill the coordination sites of lanthanide ions (Yi *et al.*, 1998; Yang *et al.*, 2001). For the series of dinuclear complexes of $[\text{Ln}(\text{DMF})_4(\text{H}_2\text{O})_m(\mu\text{-CN})\text{Fe}(\text{CN})_5]\cdot n\text{H}_2\text{O}$ composition ($m = 3$ or 4 , $n = 1$ or 1.25 ; DMF is dimethylformamide), the crystal structures of the La, Ce (Kautz *et al.*, 2000), Pr, Tm (Figuerola *et al.*, 2003), Nd (Li, Guo *et al.*, 2003), Sm (Kou *et al.*, 1998), Eu (Li *et al.*, 2002), Dy (Li, Cai *et al.*, 2003), Er, Yb and Lu (Mullica *et al.*, 2000) complexes have been reported. Recently, in a further systematic investigation of the magnetic behaviour of this series of complexes, the Pr and Tm complexes have been structurally characterized by X-ray diffraction; the Gd complex was also synthesized (Figuerola *et al.*, 2003), but no crystal structure of the latter was reported. In the present paper, we report the crystal structure of $[\text{Gd}(\text{DMF})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{Fe}(\text{CN})_5]\cdot\text{H}_2\text{O}$, (I).



It is interesting to note that the above-mentioned previously published 11 structures of rare-earth metal complexes of this composition fall into two structural types. Complexes of the beginning of the lanthanide series La–Eu (with the exception of Pm whose structure is unknown) belong to type A (space group $P2_1/n$ and cell dimensions of 17.5, 8.9, 19.9 \AA and $\beta = 95.7^\circ$), whereas the complexes of the second half of the series

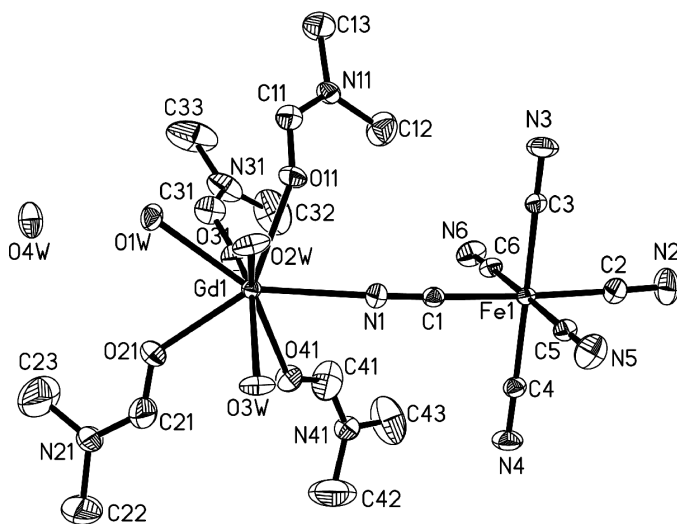


Figure 1
View of the title compound, with 30% probability ellipsoids. H atoms have been omitted.

Dy–Lu (Ho structure is unknown) belong to the alternative structural type *B* (space group $P2_1/c$ and cell dimensions 13.9, 8.9, 24.8 Å and $\beta = 96.4^\circ$; in spite of the identical unique *b*-axis dimension, unit cells of the *A* and *B* types represent different lattices and cannot be transformed into each other). In this sense, the structure of the title compound is of special interest, as it represents the first occurrence of the type *B* structure, in moving along the rare-earth metal series, with Gd immediately following Eu, whose complex still belongs to type *A*. These considerations allow us to make a prediction that the yet unknown Tb complex should also belong to structural type *B*.

As shown in Fig. 1, the crystal structure of (I) is built from dinuclear $[\text{Gd}(\text{DMF})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{Fe}(\text{CN})_5]$ molecules and uncoordinated water molecules. In the dinuclear unit, Gd^{III} and Fe^{III} atoms are bridged together by the almost linear cyanide ligand [$\text{Fe1}-\text{C1} = 1.934(2)$ Å, $\text{C1}-\text{N1} = 1.149(2)$ Å, $\text{N1}-\text{Gd1} = 2.449(2)$ Å, $\text{Fe1}-\text{C1}-\text{N1} = 177.2(2)^\circ$, $\text{C1}-\text{N1}-\text{Gd} = 162.6(1)^\circ$ and $\text{Fe1}\cdots\text{Gd1} = 5.457(3)$ Å]. Atom Gd1 has a distorted square antiprismatic coordination, formed by an N atom of the bridging cyanide group and seven O atoms of four DMF and three water molecules. The average Gd–O(DMF) bond length is 2.364(2) Å; all six Fe–C bonds are nearly equivalent, spanning the narrow range 1.934(2)–1.952(2) Å.

Intermolecular O–H \cdots O and O–H \cdots N hydrogen bonds link the molecules into a three-dimensional framework (see Table 2).

Experimental

The title complex was prepared by mixing $\text{GdCl}_3 \cdot n\text{H}_2\text{O}$ (1.0 mmol) and $\text{K}_3[\text{Fe}(\text{CN})_6]$ (1.0 mmol) in a solution of DMF/ H_2O /EtOH (1:2:2 by volume). The reaction mixture was filtered and orange single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent (yield 82%). IR spectra were recorded on an FT-IR 170SX (Nicolet) spectrometer (KBr pellet): 675 (*s*), 1114 (*m*), 1386 (*s*), 1657 (*vs*), 2121 (*vs*), 2142 (*s*), 2951 (*m*), 3382 (*s*) cm^{-1} .

Crystal data

$[\text{GdFe}(\text{CN})_6(\text{C}_3\text{H}_6\text{NO})_4(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$
 $M_r = 733.67$
 Monoclinic, $P2_1/c$
 $a = 13.9921(1)$ Å
 $b = 8.9030(1)$ Å
 $c = 24.9658(3)$ Å
 $\beta = 96.259(1)^\circ$
 $V = 3091.49(6)$ Å³
 $Z = 4$

$D_x = 1.576$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 951 reflections
 $\theta = 2.8\text{--}26.9^\circ$
 $\mu = 2.65$ mm⁻¹
 $T = 293(2)$ K
 Prism, orange
 0.30 × 0.28 × 0.26 mm

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.463$, $T_{\text{max}} = 0.502$
 9861 measured reflections

5403 independent reflections
 4563 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -16 \rightarrow 16$
 $k = -10 \rightarrow 8$
 $l = -24 \rightarrow 29$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.078$
 $S = 1.08$
 5403 reflections
 376 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 5.8035P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 1.07$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.99$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00129(4)

Table 1

Selected geometric parameters (Å, °).

Gd1–O11	2.348 (1)	Gd1–O2W	2.404 (1)
Gd1–O21	2.360 (1)	Gd1–O3W	2.387 (1)
Gd1–O31	2.382 (1)	Gd1–N1	2.449 (2)
Gd1–O41	2.367 (1)	Fe1–C1	1.934 (2)
Gd1–O1W	2.382 (1)	N1–C1	1.149 (2)
C1–N1–Gd1	162.6 (1)	N1–C1–Fe1	177.2 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
O4W–H4WB \cdots N5 ⁱ	1.00 (3)	1.84 (2)	2.842 (3)	176 (3)
O1W–H1WA \cdots N3 ⁱⁱ	0.85 (2)	2.03 (2)	2.870 (3)	169 (2)
O1W–H1WB \cdots O4W	0.93 (2)	1.70 (2)	2.623 (2)	170 (2)
O2W–H2WA \cdots N6 ⁱⁱⁱ	0.85 (2)	1.98 (2)	2.832 (3)	170 (2)
O2W–H2WB \cdots N3 ⁱⁱ	0.82 (3)	2.10 (3)	2.842 (3)	152 (3)
O3W–H3WA \cdots N4 ^{iv}	0.87 (2)	1.86 (2)	2.723 (3)	172 (2)
O4W–H4WA \cdots N2 ^v	0.93 (2)	1.90 (2)	2.829 (3)	170 (2)
O3W–H3WB \cdots N6 ⁱⁱⁱ	0.75 (2)	2.29 (2)	3.015 (3)	163 (2)

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

The H atoms of the water molecules were located in Fourier difference maps and refined isotropically. H atoms attached to C atoms were included in calculated positions and treated as riding atoms, with C–H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The maximum and minimum peaks in the final difference map are in the vicinity of the Gd atom. Atoms of one of the DMF molecules have unusually large displacement parameters; however, our attempts to introduce disorder into the model were unsuccessful, and did not produce any improvement of the structure.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART* and *SAINTE* (Siemens, 1994); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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