# metal-organic papers

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#### Key indicators

Single-crystal X-ray study T = 293 K Mean  $\sigma$ (N–C) = 0.009 Å R factor = 0.033 wR factor = 0.095 Data-to-parameter ratio = 20.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e. Pentacyanoferrate(III)-µ-cyano-triaquatetrakis-(dimethylformamide)europium(III) hydrate

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The structure of the title compound,  $[EuFe(CN)_6(DMF)_4$ - $(H_2O)_3]$ · $H_2O$  (DMF is dimethylformamide), is comprised of a neutral bimetallic complex EuFe(CN)<sub>6</sub>(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub> and a solvent water molecule. Approximately octahedral sixfold-coordinated Fe<sup>III</sup> and a slightly distorted square-antiprismatic eightfold-coordinated Eu<sup>III</sup> ions are bridged by a cyanide group to form a dinuclear complex. A three-dimensional framework is formed through  $O-H\cdots N$  and  $O-H\cdots O$  hydrogen-bonding interactions.

# Comment

Kou et al. (1998) first obtained a dinuclear cyano-bridged Ln-Fe complex, [SmFe(CN)<sub>6</sub>(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]·H<sub>2</sub>O (DMF is dimethylformamide), using Sm(NO<sub>3</sub>)<sub>3</sub> as starting material. Later, in 2000, the group of Kautz reported ferricyanide bimetallic complexes of lighter and heavier rare-earth ions  $[LnFe(CN)_6(DMF)_4(H_2O)_3] \cdot H_2O$  (Ln = La, Ce, Er, Yb and Lu; Kautz et al., 2000; Mullica et al., 2000). It is interesting that various amounts of coordinated water molecules have been found in these complexes. When Ln = Sm there are four coordinated water molecules in the complex; however, when Ln = La, Ce, Er, Yb and Lu, three coordinated water molecules are found. In order to further investigate the influence of lanthanide contraction on the composition and structure of such complexes, we synthesized a dinuclear Fe-Eu complex, viz. [EuFe(CN)<sub>6</sub>(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O, (I), the crystal structure of which is reported here.



As shown in Fig. 1, the structure of (I) is composed of neutral bimetallic EuFe(CN)<sub>6</sub>(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub> complex molecules and solvent water molecules. The Fe<sup>III</sup> and Eu<sup>III</sup> ions are bridged by a cyanide group to form a dinuclear complex. The Eu<sup>III</sup> ion is eightfold coordinated by one N atom of the bridging cyanide group [Eu-N = 2.495 (4) Å], four O atoms of DMF molecules [Eu-O<sub>DMF</sub> = 2.353 (3)–2.649 (3) Å, with an average distance of 2.469 (3) Å], and three water molecules, for which the three Eu-O<sub>water</sub> distances are in the range 2.204 (3)–2.589 (3) Å, with an average distance of

 $\odot$  2002 International Union of Crystallography Printed in Great Britain – all rights reserved 2.362 (3) Å. The coordination polyhedron can be described as a slightly distorted square antiprism. A similar situation was found in  $[Ln(Fe(CN)_6(DMF)_4(H_2O)_3] \cdot H_2O$  (Mullica *et al.*, 2000). The Eu1-N1-C1 angle is 165.7 (4)°, deviating slightly from linearity, as was the case in its analog. A three-dimensional framework is formed through O-H···O and O-H···N hydrogen-bonding interactions, with O···O distances of 2.748 (3) Å and average O···N separations of 2.706 (3) Å.

# **Experimental**

The title complex was prepared by mixing a 1:1 molar ratio of EuCl<sub>3</sub>.H<sub>2</sub>O (0.5 mmol) and K<sub>3</sub>[Fe(CN)<sub>6</sub>] (165 mg, 0.5 mmol) in a mixed solution of DMF/H<sub>2</sub>O/EtOH (v:v = 1:2:2). The reaction mixture was filtered and orange single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. Yield = 81%. IR spectra [recorded on an FT–IR 170SX (Nicolet) spectrometer, KBr pellet]: 3614, 3380 (broad band center), 2945, 2125, 1653, 1497, 1381, 1115, 675 cm<sup>-1</sup>.

#### Crystal data

[EuFe(CN) <sub>6</sub> (C <sub>3</sub> H <sub>7</sub> NO) <sub>4</sub> -	$D_x = 1.567 \text{ Mg m}^{-3}$
$(H_2O)_3] \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 728.38$	Cell parameters from 25
Monoclinic, $P2_1/n$	reflections
a = 17.633 (4)  Å	$\theta = 30.1 - 33.9^{\circ}$
b = 8.8791 (18)  Å	$\mu = 2.54 \text{ mm}^{-1}$
c = 19.831 (4)  Å	T = 293 (2)  K
$\beta = 96.12 \ (3)^{\circ}$	Prism, orange
$V = 3087.2 (11) \text{ Å}^3$	$0.80 \times 0.40 \times 0.40$ mm
Z = 4	

#### Data collection

Rigaku AFC-7*R* diffractometer  $2\theta-\omega$  scans Absorption correction:  $\psi$  scan (Molecular Structure Corporation & Rigaku, 2000)  $T_{min} = 0.271, T_{max} = 0.363$ 7448 measured reflections 7067 independent reflections 5832 reflections with  $I > 2\sigma(I)$ 

# Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$	+ 3.1152 <i>P</i> ]
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{\rm max} = 0.003$
7067 reflections	$\Delta \rho_{\rm max} = 1.64 \text{ e} \text{ \AA}^{-3}$
344 parameters	$\Delta \rho_{\rm min} = -1.42 \text{ e } \text{\AA}^{-3}$
H-atom parameters constrained	Extinction correction: SHELXL97
-	Extinction coefficient: 0.00100 (17

 $R_{\rm int} = 0.050$ 

 $\theta_{\rm max} = 31.0^{\circ}$ 

 $h = -7 \rightarrow 25$ 

 $k = -11 \rightarrow 3$ 

 $l = -22 \rightarrow 22$ 

3 standard reflections

every 200 reflections

intensity decay: -1.3%

# Table 1

Selected geometric parameters (Å,  $^{\circ}$ ).

Eu1-O3W	2.204 (3)	Eu1-N1	2.495 (4)
Eu1-O1W	2.293 (3)	Eu1-O2W	2.589 (3)
Eu1-O11	2.353 (3)	Eu1-O21	2.649 (3)
Eu1-O41	2.383 (3)	N1-C1	1.142 (5)
Eu1-O31	2.489 (3)		
C1-N1-Eu1	165.7 (4)	N1-C1-Fe1	176.7 (3)





View of the title compound, shown with 30% probability displacement ellipsoids.

H atoms were located geometrically in calculated positions but were not refined. The maximum and minimum residual electrondensity peaks were 1.97 Å from O1W and 0.85 Å from Eu1, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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