

Jacob Overgaard,* Helle Svendsen, Marie A. Chevalier and Bo B. Iversen

Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Correspondence e-mail: jacob@chem.au.dk

Key indicators

Single-crystal X-ray study
 T = 150 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 Disorder in main residue
 R factor = 0.024
 wR factor = 0.068
 Data-to-parameter ratio = 39.8

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

Tetraquatetrakis(dimethylacetamide- κO)-neodymium(III) hexacyanoferrate(III) trihydrate

The crystal structure of the title compound, $[\text{Nd}(\text{C}_4\text{H}_9\text{NO})_4(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, contains two isolated mononuclear ions connected through hydrogen bonding between a water molecule bonded to neodymium(III) and a cyano group bonded to iron(III). The coordination of the six cyano groups around iron(III) is close to ideal octahedral, while the eight ligands around neodymium(III) comprise a slightly distorted square antiprism. Three solvent water molecules are included in the asymmetric unit and hydrogen bonding is abundant, creating an extended network. Three of the four dimethylacetamide (DMA) molecules bonded to Nd have various degrees of common structural disorder.

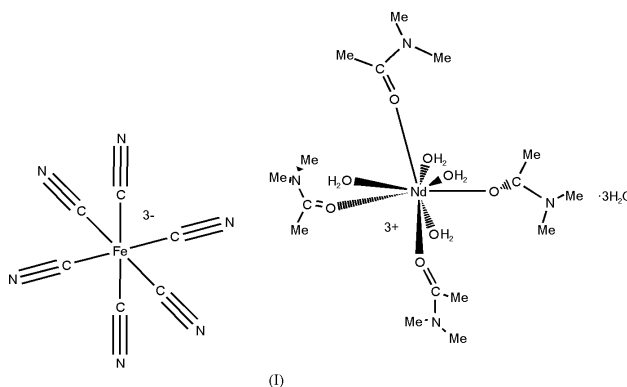
Received 20 December 2004

Accepted 6 January 2005

Online 15 January 2005

Comment

Photoactive magnetic materials possess properties that are amenable to change by light. This type of control can potentially be exploited, e.g. to develop new memory devices (Gutlich *et al.*, 1994) and it is for this reason a rich research field. Hitherto, the development of new magnetic materials with three-dimensional order has concentrated around Prussian blue analogs (Sato *et al.*, 1996). However, more recently a new type of material has emerged, involving cyano-bridged hetero-bimetallic lanthanide-transition metal complexes with



various types of coordinated solvent. In contrast to the Prussian blue type, compounds of this new class are relatively easily crystallized. The entire series including all lanthanides has been synthesized with dimethylformamide (DMF) (Li *et al.*, 2004, and references therein) and found to crystallize only in two slightly different monoclinic space groups – a change proposed to result from the lanthanide contraction. Sun and co-workers showed that a change of solvent to 2-pyrrolidinone resulted in a different crystal packing; however, the molecular framework was maintained (Sun *et al.*, 2002). Also, dimethylacetamide (DMA) has been used as solvent in a reaction with Gd (Yan & Chen, 2000).

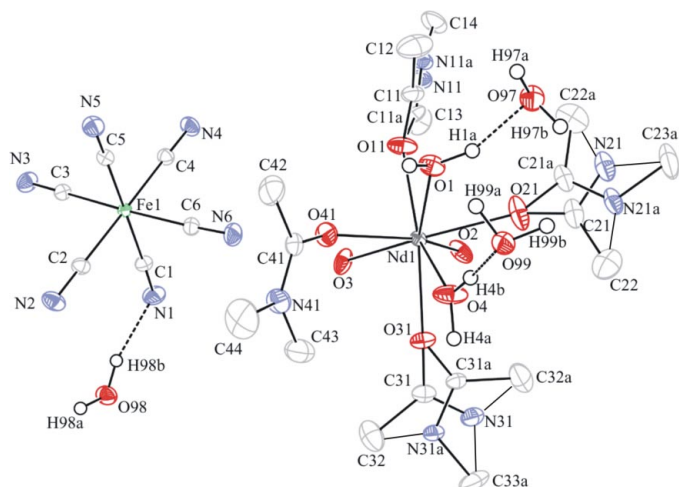


Figure 1

A view of (I), showing the hexacyanoferrate(III) and tetraaquatetra(dimethylacetamide)neodymium(III) ions, with displacement ellipsoids drawn at the 50% probability level. O—H...O hydrogen bonds are indicated by dashed lines. Both components are shown for each disordered ligand. H atoms have been omitted on the DMA ligands.

To investigate further complexes with DMA, we synthesized the analogous Nd complex, (I). As expected from the DMF series, Nd and Gd give different packing schemes. However, as shown in Fig. 1, the Nd complex does not exhibit a cyano bridge and the vacant binding site of Nd is occupied by an extra water molecule, which hydrogen bonds to the cyano group on Fe. In essence, a water molecule has been inserted in the structure. The result is a separation of the bimetallic complex. The Nd...Fe distance, which in the μ -cyano bridged complexes is around 5.4 Å, is now extended to 7.959 (1) Å, an increase of nearly 50%.

The Nd ion is coordinated by O atoms from four nearly equidistant DMA molecules [average Nd—O_{DMA} = 2.371 (7) Å] and four water O atoms [average Nd—O_{water} = 2.50 (2) Å]. Three of the four Nd-coordinating DMA molecules exhibit a special type of structural disorder, which is best described as a rotation around an axis defined by the O atom and the mid-point of the N—C(carbonyl) bond. One N-methyl carbon lies on this rotation axis and is thus not affected by the disorder, while the other N-methyl carbon and the acetate methyl carbon exactly exchange places. The minor components have occupancies in the range from 15.3 to 39.4%. The three solvent water molecules and the four water molecules coordinated to Nd utilize all their hydrogen bond capabilities to form fourteen hydrogen bonds, with O...O distances in the range 2.7135 (13)–2.8802 (13) Å (Table 2).

Experimental

The title compound was prepared on the phase boundary of a purple solution of NdCl₃·6H₂O (1.0 mmol) in DMA (5 ml) on top of a yellow solution of K₃[Fe(CN)₆] (1.0 mmol) in H₂O (10 ml). Upon standing for 5 d, the entire solution had turned a green–yellow color and was poured into a beaker for evaporation. Green–yellow crystals suitable for single-crystal X-ray analysis were formed.

Crystal data

[Nd(C₄H₉NO)₄(H₂O)₄]-
[Fe(CN)₆]-3H₂O
M_r = 830.81
Monoclinic, *P*2₁/*c*
a = 14.3741 (4) Å
b = 14.1573 (4) Å
c = 17.9269 (5) Å
 β = 91.328 (1)°
V = 3647.12 (18) Å³
Z = 4

D_x = 1.513 Mg m⁻³
Mo *K*α radiation
Cell parameters from 9557
reflections
 θ = 2.7–38.5°
 μ = 1.87 mm⁻¹
T = 150 (2) K
Block, green–yellow
0.35 × 0.20 × 0.15 mm

Data collection

Bruker X8 APEX-II diffractometer
 φ and ω scans
Absorption correction: multi-scan
(Blessing, 1995)
*T*_{min} = 0.522, *T*_{max} = 0.756
78 123 measured reflections
20 123 independent reflections

15 868 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.025
 θ _{max} = 38.5°
h = -25 → 25
k = -24 → 13
l = -31 → 30

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.024
wR [*F*²] = 0.068
S = 1.07
20 123 reflections
505 parameters

H atoms treated by a mixture of
independent and constrained
refinement
w = 1/[σ²(*F*_o²) + (0.0364*P*)²]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/σ)_{max} = 0.004
Δρ_{max} = 2.28 e Å⁻³
Δρ_{min} = -0.98 e Å⁻³

Table 1

Selected bond lengths (Å).

Nd1—O11	2.3734 (9)	Nd1—O4	2.4856 (9)
Nd1—O21	2.3624 (9)	Fe1—C1	1.9388 (12)
Nd1—O31	2.3784 (8)	Fe1—C2	1.9451 (10)
Nd1—O41	2.3726 (8)	Fe1—C3	1.9446 (10)
Nd1—O1	2.5293 (9)	Fe1—C4	1.9417 (11)
Nd1—O2	2.5037 (8)	Fe1—C5	1.9433 (10)
Nd1—O3	2.4786 (9)	Fe1—C6	1.9381 (11)

Table 2

Hydrogen-bonding 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—H1A...O97	0.967 (13)	1.787 (7)	2.7135 (13)	159.3 (17)
O1—H1B...O98 ⁱ	0.968 (11)	2.020 (9)	2.8802 (13)	147.1 (13)
O2—H2A...N4 ⁱⁱ	0.966 (11)	1.855 (10)	2.8140 (13)	171.5 (14)
O2—H2B...N5 ⁱⁱⁱ	0.967 (8)	2.040 (7)	2.9529 (13)	156.7 (14)
O3—H3A...N5 ⁱⁱⁱ	0.966 (13)	1.974 (13)	2.9225 (14)	166.4 (17)
O3—H3B...N6	0.967 (13)	1.801 (14)	2.7655 (13)	175.4 (19)
O4—H4A...N2 ^{iv}	0.966 (13)	1.844 (13)	2.8096 (14)	177.1 (16)
O4—H4B...O99	0.964 (3)	1.891 (4)	2.8514 (12)	173.9 (16)
O97—H97A...N1 ⁱ	0.964 (12)	1.989 (12)	2.9459 (15)	171.8 (14)
O97—H97B...N3 ^v	0.966 (13)	1.995 (14)	2.9560 (14)	172.8 (16)
O98—H98A...O99 ^{iv}	0.965 (9)	1.900 (6)	2.8320 (12)	161.6 (14)
O98—H98B...N1	0.965 (12)	1.944 (12)	2.8859 (14)	164.5 (15)
O99—H99A...O98 ⁱ	0.964 (7)	1.826 (4)	2.7773 (13)	168.3 (14)
O99—H99B...N3 ^v	0.964 (13)	1.993 (13)	2.9450 (14)	168.8 (13)

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

The H atoms of the water molecules were located in difference Fourier maps and one common O—H bond length was included in the least-squares refinement [0.97 (1) Å]. The methyl H atoms were refined as riding on the parent C atom. The disorder in three DMA molecules was such that the overlapping atoms were fixed to identical positions and their atomic displacement parameters were kept identical. The sum of the occupancies of the two disordered parts was

fixed to unity [group; occupation factor of major component: O11 84.8 (3)%, O21 65.3 (4)% and O31 60.7 (3)%]. The maximum and minimum residuals were distributed around the metal atoms.

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: *SHELXL97*; software used to prepare material for publication: *enCIFer* (Version 1.1; Allen *et al.*, 2004) and *WinGX* (Farrugia, 1999).

Financial support of this work by the Carlsberg Foundation is gratefully acknowledged.

References

- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruker–Nonius (2004). *APEX2* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gutlich, P., Hauser, A. & Spiering, H. (1994). *Angew. Chem. Int. Ed.* **33**, 2024–2054.
- Li, J.-R., Cai, L.-Z., Guo, G.-C., Bu, X.-H. & Huang, J.-S. (2004). *Acta Cryst.* **E60**, m259–m261.
- Sato, O., Iyoda, T., Fujishima, A. & Hashimoto, K. (1996). *Science*, **272**, 704–705.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Sun, X.-R., Chen, Z.-D., Yan, F., Gao, S., Cheung, K.-K., Che, C.-M. & Zhang, X.-X. (2002). *J. Cluster Sci.* **13**, 103–117.
- Yan, B. & Chen, Z. (2000). *Chem. Lett.* pp. 1244–1245.