A cyanide-bridged Fe^{II}–Nd^{III} bimetallic assembly with a one-dimensional ladder-like chain structure

Yan Xu,[a] Hu Zhou,[b] Ai-Hua Yuan,[b] Xiao-Ping Shen[a]* and Qian Zhang[a]

[a]School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China, and [b]School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, People's Republic of China

Correspondence e-mail: xiaopingshen@163.com

The title complex, *catena*-poly[[[(2,2′-bipyridine-1κ^2N,N')tris-(methanol-2κO)(nitrato-2κ^2O,O')-μ-cyanido-1:2C:N-cyanido-1κC-iron(II)neodymium(III)]-di-μ-cyanido-1:2′C:N;2:1′N:C] methanol solvate], $\{[Fe^{II}Nd^{III}(CN)_4(NO_3)(C_{10}H_8N_2)(CH_3OH)_3]\cdot CH_3OH\}_n$, is made up of ladder-like one-dimensional chains oriented along the *c* axis. Each ladder consists of two strands based on alternating Fe^{II} and Nd^{III} centers connected by cyanide bridges. Furthermore, two such parallel chains are connected by additional cyanide cross-pieces (the 'rungs' of the ladder), which likewise connect Fe^{II} and Nd^{III} centers, such that each $[Fe(CN)_4(bipy)]^{2-}$ unit (bipy is 2,2′-bipyridine) coordinates with three Nd^{III} centers and each Nd^{III} center connects with three different $[Fe(CN)_4(bipy)]^{2-}$ units. In the complex, the iron(II) cation is six-coordinated with a distorted octahedral geometry and the neodymium(III) cation is eight-coordinated with a distorted dodecahedral environment.

Comment

There has been growing interest in the preparation and study of mixed lanthanide–transition metal compounds because lanthanide ions have a rich coordination chemistry with high coordination numbers and significant coordination flexibility, which often leads to unanticipated but remarkable structures (Huang *et al.*, 2008; Zhao *et al.*, 2007; Yeung *et al.*, 2006). A few supramolecular materials have been reported combining hexacyanidometalate ions, $[M(CN)_6]^{3-}$ (M = Fe and Cr), or octacyanidometalate ions, $[M(CN)_8]^{3-/4-}$ (M = Mo, W and Nb), as building blocks with lanthanide ions (Li *et al.*, 2008; Sun *et al.*, 2007; Przychodzen *et al.*, 2007). However, as far as we know, examples of 3*d*–4*f* cyanide-bridged coordination polymers that incorporate diamagnetic $[Fe^{II}(CN)_4(L)]^{2-}$ [L is 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] building blocks (Zhao, Wang & Fang, 2004; Zhao, Wang, Fang & Chen,

2004) are rare. We report here an interesting one-dimensional ladder-like 3*d*–4*f* cyanide-bridged coordination polymer, (I), based on the $[Fe^{II}(CN)_4(bipy)]^{2-}$ building block.

(I)
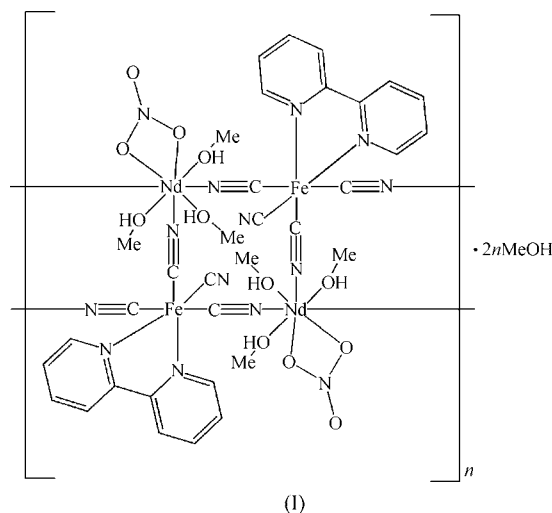
The asymmetric unit in the structure of (I) comprises one $[Fe^{II}(CN)_4(bipy)]^{2-}$ anion, one $[Nd^{III}(NO_3)(CH_3OH)_3]^{2+}$ cation and one methanol solvent molecule (Fig. 1). Selected geometric parameters are given in Table 1. The crystal structure of (I) consists of one-dimensional ladder-like bimetallic neutral chains, $\{[Fe(CN)_4(bipy)][Nd^{III}(NO_3)(CH_3OH)_3]\}_n$, built up from alternating Fe^{II} and Nd^{III} metal centers linked through the cyanide bridges (Fig. 2). The ladder-like bimetallic chains contain centrosymmetric Fe₂Nd₂ rectangular motifs. The $[Fe(CN)_4(bipy)]^{2-}$ fragment exhibits a distorted octahedral structure consisting of two N atoms from a planar bipy ligand and four C atoms from four cyanide groups. The small bite angle subtended by the chelating bipy group [80.19 (16)° for N1—Fe1—N2] is one of the main factors accounting for
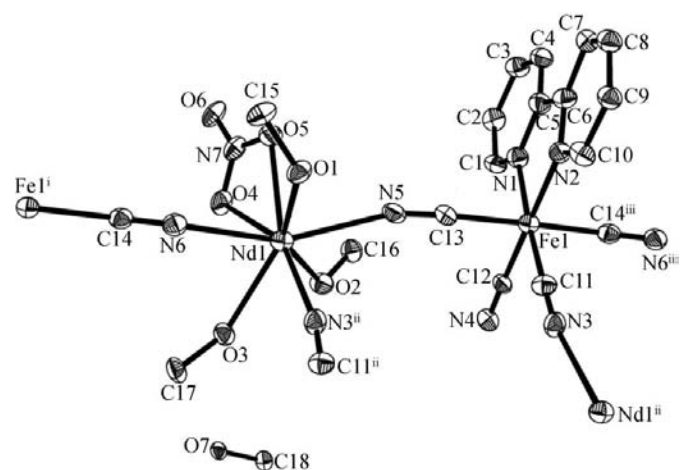

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) −*x* + 1, −*y*, −*z* + 1; (iii) *x*, *y*, *z* + 1.]

this distortion. The bipy Fe—N bond distances [2.003 (4) and 1.995 (4) Å] are practically the same as those observed in the low-spin iron(II) compound $K_2[Fe^{II}(CN)_4(bipy)]\cdot2.5H_2O$ [1.987 (4)–2.003 (4) Å; Nieuwenhuyzen *et al.*, 1998] and in the mononuclear $(PPh_4)[Fe(CN)_4(bipy)]$ and the trinuclear $[\{Fe^{III}(CN)_4(bipy)\}_2M^{II}(H_2O)_4]\cdot4H_2O$ species (M = Mn or Zn; Lescouezec *et al.*, 2002). Three of the four cyanide groups of the $[Fe(CN)_4(bipy)]^{2-}$ unit in (I) are bridging, while the fourth is terminal. The Fe—C—N angles for both terminal [176.6 (4)°] and bridging [175.2 (4), 179.0 (5) and 179.4 (5)°] cyanide groups deviate slightly from strict linearity. Each Nd^{III} cation is eight-coordinated by two O atoms from the NO_3 group, three O atoms from three CH_3OH units and three N atoms from three cyanide ligands, to give a distorted dodecahedral NdN_3O_5 coordination environment (Fig. 1). The Nd—O bond lengths fall within narrow ranges [2.494 (3)– 2.542 (3) Å for nitrate Nd—O and 2.462 (3)–2.499 (3) Å for methanol Nd—O]. The cyanide Nd—N bond distances [2.459 (4)–2.509 (4) Å] are somewhat shorter than those in $\{[Ru(CN)_4(phen)]_3[Ln(terpy)(H_2O)_3]_2\cdot nH_2O\}_\infty$ [2.530 (9)– 2.548 (11) Å; Baca *et al.*, 2007]. The nitrate ion acts as a

bidentate ligand toward Nd^{III} through two of its three O atoms, which is different from previously reported lanthanide– transition metal complexes (Yuan *et al.*, 2004; Liu *et al.*, 2008), in which a nitrate ion coordinated to the lanthanide ion acts as a monodenate ligand.

The angles of the cyanide–Nd^{III} interactions deviate from linear [Nd1^{ii}—N3—C11 = 169.3 (4)°, Nd1—N6—C14 = 171.1 (4)° and Nd1—N5—C13 = 163.2 (4)°; symmetry code: (ii) $-x + 1, -y, -z + 1$; Fig. 2]. The Fe···Nd separations across cyanide bridges are 5.499 (4), 5.518 (5) and 5.452 (4) Å, in good agreement with those in $\{[Ru(CN)_4(bipy)]_3[Ln(terpy)-(H_2O)_3]_2\cdot nH_2O\}_\infty$ (Baca *et al.*, 2007). The uncoordinated methanol solvent molecules are involved in hydrogen-bonding interactions with the one terminal cyanide group and a coordinated methanol molecule from another $[Nd^{III}(NO_3)-(CH_3OH)_3]^{2-}$ unit (Table 2).

Adjacent ladder-like chains are also held together by hydrogen bonds between the terminal cyanide ligands of the $[Fe(CN)_4(bipy)]^{2-}$ units in one chain and the OH donors of CH_3OH ligands from $[Nd^{III}(NO_3)(CH_3OH)_3]$ units in neighboring chains (Table 2). From this arrangement, a two-dimensional structure is formed (Fig. 3).

Figure 2
The one-dimensional chain of (I). H atoms have been omitted for clarity. [Symmetry code: (ii) $-x + 1, -y, -z + 1$.]

Figure 3
A schematic representation of the two-dimensional structure formed *via* hydrogen bonds (broken lines) between the bimetallic chains of (I). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii) $-x + 1, -y, -z + 1$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

Experimental

Red–brown prismatic crystals of (I) were obtained by slow diffusion of a methanolic solution of $K_2[Fe(CN)_4(bipy)]\cdot3H_2O$ (0.1 mmol) and an aqueous solution of $Nd(NO_3)_3\cdot6H_2O$ (0.1 mmol) through a H-tube at room temperature. The resulting crystals were suitable for single-crystal X-ray diffraction analysis. The product was insoluble in water and methanol.

Crystal data

$[FeNd(CN)_4(NO_3)(C_{10}H_8N_2)-$	$\beta = 103.099\ (2)°$
$(CH_4O)_3]\cdot CH_4O$	$V = 2529.3\ (6)$ Å^3
$M_r = 650.53$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.9908\ (17)$ Å	$\mu = 2.65$ mm^{-1}
$b = 18.311\ (3)$ Å	$T = 291$ K
$c = 10.9171\ (14)$ Å	$0.26 \times 0.22 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD diffractometer	19739 measured reflections
Absorption correction: multi-scan ($SADABS$; Bruker, 2002)	4955 independent reflections
	3841 reflections with $I > 2\sigma(I)$
$T_{min} = 0.545$, $T_{max} = 0.619$	$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	311 parameters
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.56$ e Å^{-3}
4955 reflections	$\Delta\rho_{min} = -1.11$ e Å^{-3}

H atoms attached to C atoms of the bipy ligand were placed in calculated positions (C—H = 0.96 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. The hydroxy H atoms of the methanol molecules were located in a difference Fourier map and refined as riding, with O—H restraints (0.97 Å for O1—H, 0.93 Å for O2—H and O3—H, and 0.96 Å for O7—H), and with $U_{iso}(H) =$
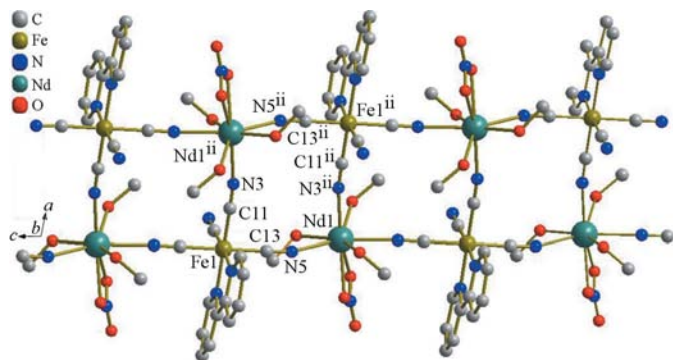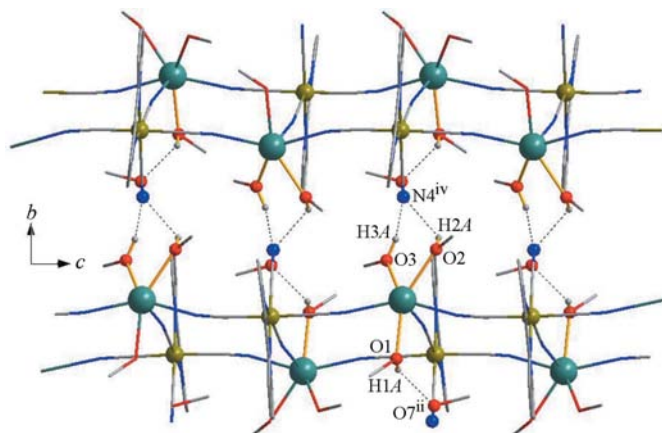
Table 1
Selected bond lengths (Å).

Fe1—C11	1.881 (5)	Nd1—N5	2.509 (4)
Fe1—C12	1.896 (4)	Nd1—N6	2.465 (4)
Fe1—C13	1.922 (5)	Nd1—O1	2.462 (3)
Fe1^i—C14	1.930 (5)	Nd1—O2	2.483 (3)
Fe1—N1	2.003 (4)	Nd1—O3	2.499 (3)
Fe1—N2	1.995 (4)	Nd1—O4	2.542 (3)
Nd1—N3^{ii}	2.459 (4)	Nd1—O5	2.494 (3)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, -y, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$O7^{ii}	0.97	2.11	2.713 (4)	119
O2—H2$A\cdots$N4^{iv}	0.93	2.23	2.773 (5)	117
O3—H3$A\cdots$N4^{iv}	0.93	1.90	2.786 (5)	159

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

$1.2U_{eq}(O)$ for O1, O2 and O3, and $1.5U_{eq}(O)$ for O7. The methyl H atoms of the methanol molecules were placed geometrically (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3099). Services for accessing these data are described at the back of the journal.

References

Baca, S. G., Adams, H., Sykes, D., Faulkner, S. & Ward, M. D. (2007). *Dalton Trans.* pp. 2419–2430.
Bruker (2002). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Huang, Y. F., Wei, H. H. & Katada, M. (2008). *J. Coord. Chem.* **61**, 2683–2689.
Lescouezec, R., Lloret, F., Julve, M., Vaissermann, J. & Verdaguer, M. (2002). *Inorg. Chem.* **41**, 821–826.
Li, J. R., Chen, W. T., Tong, M. L., Guo, G. C., Tao, Y., Yu, Q., Song, W. C. & Bu, X. H. (2008). *Cryst. Growth Des.* **8**, 2780–2792.
Liu, M., Yuan, W. B., Zhang, Q., Yan, L. & Yang, R. D. (2008). *Chin. J. Appl. Chem.* **25**, 1194–1196.
Nieuwenhuyzen, M., Bertram, B., Gallagher, J. F. & Vos, J. G. (1998). *Acta Cryst.* C**54**, 603–606.
Przychodzen, P., Pelka, R., Lewinski, K., Supel, J., Rams, M., Tomala, K. & Sieklucka, B. (2007). *Inorg. Chem.* **46**, 8924–8938.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sun, X. R., Chen, Z. D., Wang, M. W., Wang, B. W., Yan, F. & Cheung, K. K. (2007). *Chin. J. Chem.* **25**, 329–336.
Yeung, W. F., Lau, T. C., Wang, X. Y., Gao, S., Szeto, L. & Wong, W. T. (2006). *Inorg. Chem.* **45**, 6756–6760.
Yuan, W. B., Yan, L. & Yang, R. D. (2004). *Chin. J. Appl. Chem.* **20**, 829–831.
Zhao, H. H., Lopez, N., Prosvirin, A., Chifotides, H. T. & Dunbar, K. R. (2007). *Dalton Trans.* pp. 878–888.
Zhao, Q. H., Wang, Q. H. & Fang, R. B. (2004). *Transition Met. Chem.* **29**, 144–148.
Zhao, Q. H., Wang, Q. H., Fang, R. B. & Chen, Z. D. (2004). *Chin. J. Chem.* **22**, 264–267.