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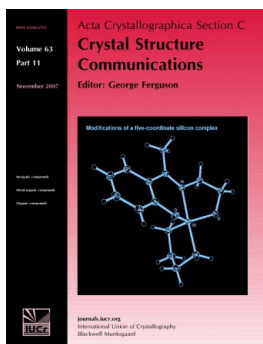
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A cyanide-bridged Fe^{II}–Nd^{III} bimetallic assembly with a one-dimensional ladder-like chain structure

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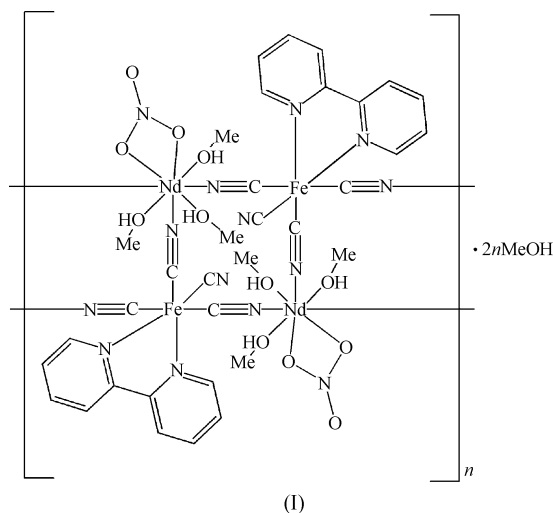
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The title complex, *catena*-poly[[[(2,2'-bipyridine-1*k*²*N,N'*)tris(methanol-2*k**O*)(nitrate-2*k*²*O,O'*)- μ -cyanido-1:2*C:N*:cyanido-1*k**C*-iron(II)neodymium(III)]-di- μ -cyanido-1:2'*C:N*;2:1'*N:C*] methanol solvate], {[Fe^{II}Nd^{III}(CN)₄(NO₃)(C₁₀H₈N₂)(CH₃OH)₃·CH₃OH]_{*n*}, 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.



The asymmetric unit in the structure of (I) comprises one [Fe^{II}(CN)₄(bipy)]²⁻ anion, one [Nd^{III}(NO₃)(CH₃OH)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^{II}(CN)₄(bipy)][Nd^{III}(NO₃)(CH₃OH)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

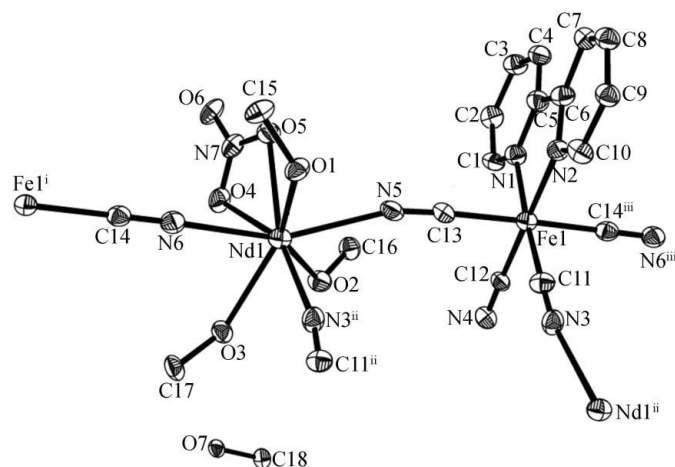


Figure 1

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 $\text{K}_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{bipy})]\cdot 2.5\text{H}_2\text{O}$ [1.987 (4)–2.003 (4) Å; Nieuwenhuyzen *et al.*, 1998] and in the mononuclear $(\text{PPh}_4)[\text{Fe}(\text{CN})_4(\text{bipy})]$ and the trinuclear $[\{\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})\}_2\text{M}^{\text{II}}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ species ($M = \text{Mn}$ or Zn ; Lescouezec *et al.*, 2002). Three of the four cyanide groups of the $[\text{Fe}(\text{CN})_4(\text{bipy})]^{2-}$ 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 $\{[\text{Ru}(\text{CN})_4(\text{phen})]_3[\text{Ln}(\text{terpy})(\text{H}_2\text{O})_3]_2\cdot n\text{H}_2\text{O}\}_\infty$ [2.530 (9)–2.548 (11) Å; Baca *et al.*, 2007]. The nitrate ion acts as a

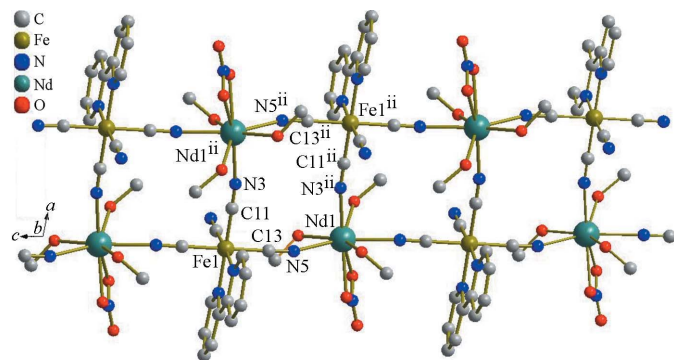


Figure 2
The one-dimensional chain of (I). H atoms have been omitted for clarity. [Symmetry code: (ii) $-x + 1, -y, -z + 1$.]

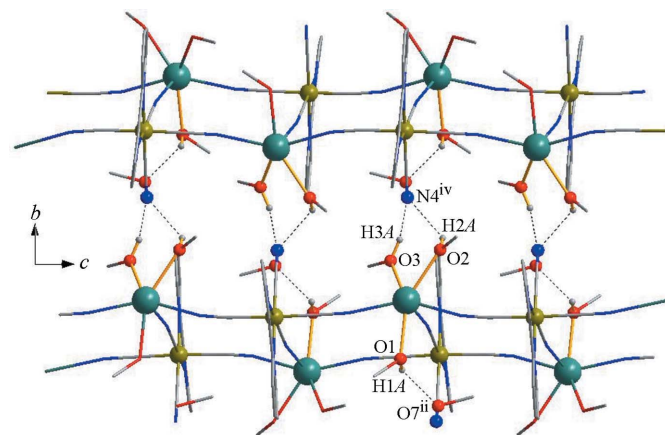


Figure 3
A schematic representation of the two-dimensional structure formed via hydrogen bonds (broken lines) between the bimetallic chains of (I). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii) $-x + 1, -y, -z + 1$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

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 [$\text{Nd1}^{\text{III}}-\text{N3}-\text{C11} = 169.3 (4)^\circ$, $\text{Nd1}-\text{N6}-\text{C14} = 171.1 (4)^\circ$ and $\text{Nd1}-\text{N5}-\text{C13} = 163.2 (4)^\circ$; symmetry code: (ii) $-x + 1, -y, -z + 1$; Fig. 2]. The $\text{Fe}\cdots\text{Nd}$ separations across cyanide bridges are 5.499 (4), 5.518 (5) and 5.452 (4) Å, in good agreement with those in $\{[\text{Ru}(\text{CN})_4(\text{bipy})]_3[\text{Ln}(\text{terpy})(\text{H}_2\text{O})_3]_2\cdot n\text{H}_2\text{O}\}_\infty$ (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 $[\text{Nd}^{\text{III}}(\text{NO}_3)(\text{CH}_3\text{OH})_3]^{2-}$ unit (Table 2).

Adjacent ladder-like chains are also held together by hydrogen bonds between the terminal cyanide ligands of the $[\text{Fe}(\text{CN})_4(\text{bipy})]^{2-}$ units in one chain and the OH donors of CH_3OH ligands from $[\text{Nd}^{\text{III}}(\text{NO}_3)(\text{CH}_3\text{OH})_3]$ units in neighboring chains (Table 2). From this arrangement, a two-dimensional structure is formed (Fig. 3).

Experimental

Red–brown prismatic crystals of (I) were obtained by slow diffusion of a methanolic solution of $\text{K}_2[\text{Fe}(\text{CN})_4(\text{bipy})]\cdot 3\text{H}_2\text{O}$ (0.1 mmol) and an aqueous solution of $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (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

$[\text{FeNd}(\text{CN})_4(\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{CH}_4\text{O})_3]\cdot \text{CH}_4\text{O}$	$\beta = 103.099 (2)^\circ$
$M_r = 650.53$	$V = 2529.3 (6) \text{ \AA}^3$
Monoclinic, $P2_1/c$	$Z = 4$
$a = 12.9908 (17) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 18.311 (3) \text{ \AA}$	$\mu = 2.65 \text{ mm}^{-1}$
$c = 10.9171 (14) \text{ \AA}$	$T = 291 \text{ K}$
	$0.26 \times 0.22 \times 0.20 \text{ mm}$

Data collection

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

Refinement

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

H atoms attached to C atoms of the bipy ligand were placed in calculated positions ($\text{C}-\text{H} = 0.96 \text{ \AA}$) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. 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 $U_{\text{iso}}(\text{H}) =$

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—H1A \cdots O7 ⁱⁱ	0.97	2.11	2.713 (4)	119
O2—H2A \cdots N4 ^{iv}	0.93	2.23	2.773 (5)	117
O3—H3A \cdots N4 ^{iv}	0.93	1.90	2.786 (5)	159

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

1.2 $U_{eq}(O)$ for O1, O2 and O3, and 1.5 $U_{eq}(O)$ 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: *SAINTE* (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*.

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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 *SAINTE*. 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.* **C54**, 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.* **A64**, 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.