

Three-dimensional Ln^{III}–W^{IV} complexes with cyanido and carboxylato bridges

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The reaction of Ln(NO₃)₃·6H₂O with 5-methyl-2-pyrazine-carboxylic acid (Hmpca) and K₄[W(CN)₈]·2H₂O has led to the formation of a unique three-dimensional network structure which contains open channels.

Cyanido-bridged heterometallic assemblies based on lanthanides and transition metal ions are attracting increasing interest because of their magnetic and catalytic properties.^{1–4} However, the tendency of the lanthanide ions to adopt high coordination numbers and their ability to easily adapt to a given environment make the design of d–f cyanido-bridged assemblies difficult.^{5–7} Therefore, a better understanding of the property–structure relationship of such materials relies on the synthesis and evaluation of new lanthanide–transition metal complexes. In synthesizing new d–f cyanido-bridged heterometallic species, we have sought to employ (Hmpca) as the primary ligand for coordination to the lanthanide ion. Lanthanide ions have a high affinity for hard donor atoms and ligands containing hybrid oxygen–nitrogen atoms. The variation of binding modes of the carboxylate group may help in the construction of high-dimensionality supramolecular structures. Thus, the simultaneous use of carboxylato and cyanido bridges opens new perspectives in the construction and crystal engineering of multifunctional coordination networks. During such investigations, we have obtained two isostructural d–f cyanido-bridged complexes, *i.e.* [Ln(mpca)₂(H₂O)(CH₃OH)]Ln(H₂O)₆W(CN)₈·nH₂O (Ln = Eu **1**, Nd **2**), containing a unique three-dimensional network structure.

Although d–f cyanido-bridged assemblies with various blocking ligands are reported,⁴ complexes **1** and **2** constitute the first structural examples of d–f cyanido-bridged assemblies with a three-dimensional network. During the preparation of this manuscript, You *et al.* reported a d–f sodalite-like framework, which has been obtained by self-assembly of [Mo^V(CN)₈]^{3–} and Nd³⁺ ions in methanol.⁸

Complexes **1** and **2** were obtained from an aqueous methanol solution containing Ln(NO₃)₃·6H₂O, 5-methyl-2-pyrazinecarboxylic acid (Hmpca) and K₃[W(CN)₈] in the molar ratio 1 : 2 : 1 at room temperature and in the dark.⁹ Using K₄[W^{IV}(CN)₈] instead of K₃[W^V(CN)₈], the complexes **1** and **2** are obtained with yields up to 67% and orange single crystals were obtained in one day.^{10†}

An X-ray single crystal structural analysis reveals that complexes **1** and **2** are isomorphous, crystallizing in the monoclinic

space group *P*2₁/*c*, hence, only the structure of **1** is described in detail.¹¹ The complex **1** has a neutral three-dimensional structure extended through cyanido and carboxylato bridges. Each [W(CN)₈]^{4–} is connected to three [Eu(mpca)₂(H₂O)(CH₃OH)]⁺ units *via* three cyanido bridges to form a two-dimensional network of alternating diamond-like Eu₂W₂(CN)₄ rings and octagon-like Eu₄W₄(CN)₈ rings (Fig. 1). The two-dimensional nets are connected through a second europium(III) center *via* the carboxylato group of one mpca[–] ligand, thus forming a three-dimensional structure with channels having a diameter of *ca.* 15 Å (Fig. 2). The [W^{IV}(CN)₈]^{4–} adopt a distorted square antiprism geometry with the twist angle between the two faces equal to 55.61°. The W–C bond lengths are in the range 2.138(3)–2.184(3) Å, and the C–N bonds in the range 1.147(5)–1.348(5) Å. The three bridging cyanido ligands coordinate to one europium(III) ion, Eu1, in two different ways: two nearly linear (Eu1–N32–C32 = 166.22°, Eu1–N33–C33 = 171.80°) and one bent (Eu1–N31–C31 = 155.85°). The adjacent Eu···W distances fall in the range 5.662–5.743 Å. The Eu1 center has a coordination number of nine due to the N,O-bidentate binding of two anionic mpca[–] ligands, three cyanido ions, one water molecule and one methanol molecule. The Eu1–O bond lengths range from 2.417(2)–2.515(2) Å, while the Eu1–N

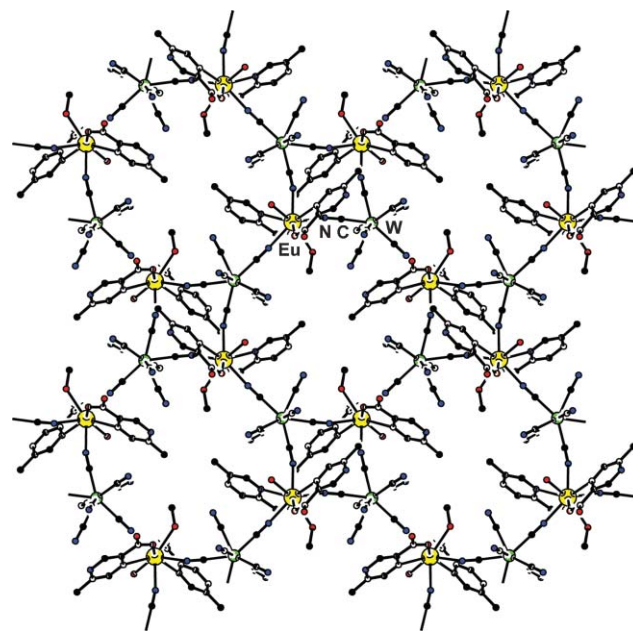


Fig. 1 The two-dimensional connection of Eu1 and W ions in the molecular structure of **1**. Hydrogen atoms and non-coordinated solvent molecules are omitted for clarity. Green, W; yellow, Eu; red, O; blue, N.

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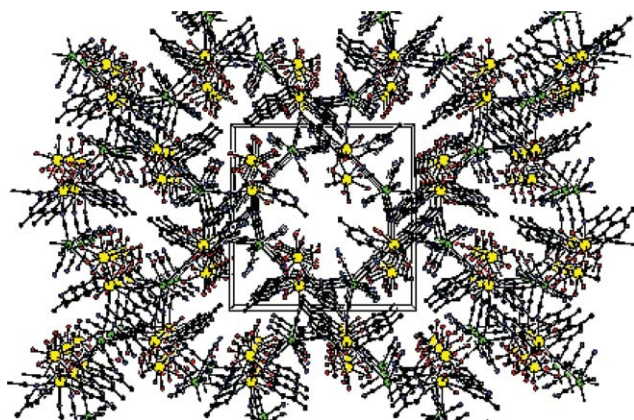


Fig. 2 View of the three-dimensional network structure of **1** along the *a* axis.

bond lengths fall in the range 2.462(3)–2.644(3) Å. The coordination polyhedron of Eu1 is best described as a distorted tricapped trigonal prism; the twist angle between the trigonal planes that define the trigonal prism is 26.68°. The two anionic mpca[−] ligands are bound to Eu1 in a bidentate chelating fashion; the carboxylate group of the second mpca[−] ligand links the two europium(III) ions, Eu1 and Eu2, to form an infinite chain along the *a* axis (Fig. 3); the Eu1⋯Eu2 separation is 6.842 Å. The eight oxygen atoms coordinated to Eu2 come from two carboxylate groups of two different mpca[−] ligands and six water molecules. The Eu2–O bond lengths are in the range 2.344(2)–2.464(3) Å. The coordination geometry around Eu2 can be described as a slightly distorted square antiprism with a twist angle between the two faces of 46.76°.

The three-dimensional structure of **1** is stabilized by multiple hydrogen-bonding interactions involving the cyanido ligands, the carboxylate bridging ligand, both coordinated and non-coordinated water molecules and a non-coordinated methanol molecule. The non-bridging cyanido groups are hydrogen bonded to water molecules; two cyanido groups interact each with water molecules coordinated to the Eu2 center, while the other three cyanido ligands form hydrogen bonds with three non-coordinated water molecules (the donor–acceptor bond distances, O–H⋯N, are in the range 2.808(5)–3.149(5) Å). An intramolecular hydrogen bond is established between the carboxylate oxygen bound to Eu2 and one water molecule coordinated to the same europium(III) center (O53–H5⋯O29 = 2.748(4) Å).

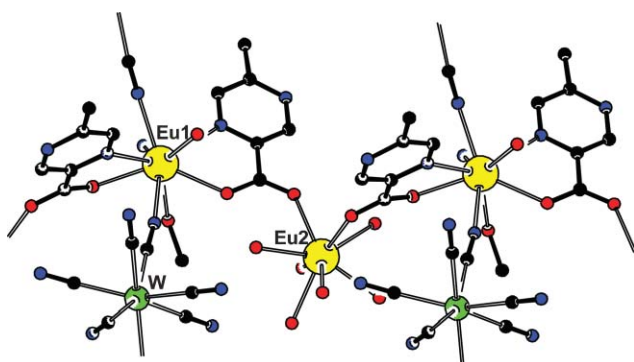


Fig. 3 The coordination environments of Eu1 and Eu2 in the molecular structure of **1**. Hydrogen atoms are omitted for clarity.

The temperature dependent magnetic susceptibility data of the complexes **1** and **2** have been measured for polycrystalline samples in the temperature of range 2–300 K in an external magnetic field of 0.1 T. The plots $\chi_M T$ vs *T* of the two complexes are shown in Fig. 4. The magnetic properties of **1** and **2** are dominated by the thermal depopulation of Stark levels of the lanthanide ions since the [W(CN)₈]^{4−} spacers are diamagnetic. The room temperature $\chi_M T$ value for **1** is 3.28 cm³ K mol^{−1}, which corresponds to the population of an excited state (the theoretical value is 3 cm³ K mol^{−1}) on the basis of two europium(III) ions. By lowering the temperature, the $\chi_M T$ value decreases, owing to the depopulation of the Stark levels with non-zero *J* values for a single europium(III) ion.¹² At 300 K, the product $\chi_M T$ of **2** is equal to 2.87 cm³ K mol^{−1}, a value which is somewhat smaller than the theoretical value expected for two non-interacting Nd(III) ions. This behaviour suggests a partial depopulation of the Stark levels even at room temperature. The free ion value of Nd(III) is 1.64 cm³ K mol^{−1}. The $\chi_M T$ value decreases monotonically with decreasing temperature down to 2 K. Such behaviour is mainly due to the crystal fields effects of Nd(III) ion.¹² The magnetization data reflect the population changes within the ground-state doublet, split by the magnetic field (Fig. 4). The experimental data were fitted by assuming an effective spin equal to 1/2 with an effective angular average of the anisotropic *g*_{eff} factor. A least-squares fit gives *g*_{eff} = 2.53, with a very good agreement between the experimental and calculated data (*R* = 1.2 × 10^{−4}).

In summary, we have successfully synthesized and characterized two unique three-dimensional d–f supramolecular architectures based on octacyanidometallate building-blocks. Our synthetic strategy based on the simultaneous use of carboxylate and cyanido bridges provides new possibilities for the design of stable high-dimensional d–f networks. Further work will be devoted to designing extended species with such linkages that might exhibit magnetic ordering. In the general framework of the study of electron-transfer processes, the complexes reported herein provide the opportunity to study the optical and photoinduced energy

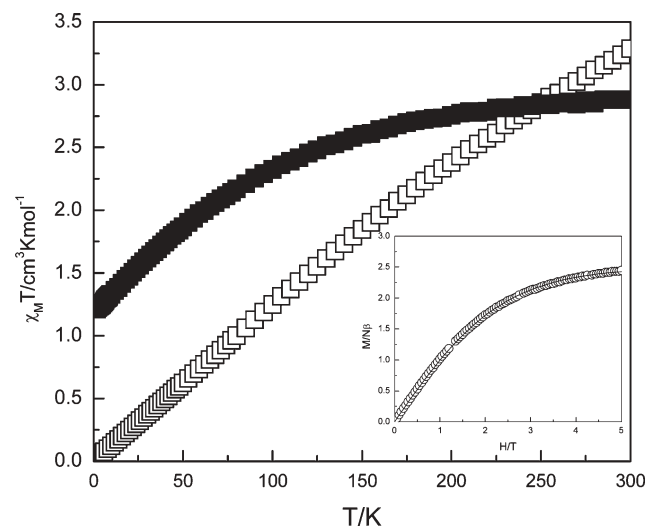


Fig. 4 Temperature dependence of $\chi_M T$ for **1** (□) and **2** (■) measured at 0.1 T. Inset: The field dependence of the magnetization for **2** measured at 2 K (solid lines represent the theoretical curves calculated with the Brillouin function).

transfer in d–f extended systems. Such studies will be the subject of subsequent papers.

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Notes and references

† Complexes **1** and **2** were synthesised by the reaction of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.23 mmol), 5-methyl-2-pyrazinecarboxylic acid (0.46 mmol) and $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ (0.23 mmol) in water–methanol solution at room temperature and in the dark. Uniform, well-shaped orange crystals were obtained by slow diffusion of methanol into the aqueous solution. Both complexes were isolated in high yields (ca. 67%). Elemental analysis for **1**: Calcd for $\text{C}_{22}\text{H}_{40}\text{Eu}_2\text{N}_{12}\text{O}_{18}\text{W}$: C, 21.17; H, 3.23; N, 13.46%; found: C, 21.19; H, 3.41; N, 13.52%. IR ($\nu_{\text{max}}/\text{cm}^{-1}$) for **1**: 3190 br, 2118 s, 2097 m, 1608 m, 1575 s, 1558 m, 1417 s, 1328 m, 1296 w, 1196 w, 1052 m, 1015 w, 806 m, 668 s, 556 m, 489 m. Elemental analysis for **2**: Calcd for $\text{C}_{25}\text{H}_{44}\text{Nd}_2\text{N}_{12}\text{O}_{17}\text{W}$: C, 23.38; H, 3.53; N, 13.37%; found: C, 23.19; H, 3.35; N, 13.72%. IR ($\nu_{\text{max}}/\text{cm}^{-1}$) for **2**: 3183 br, 2119 s, 2095 m, 1608 m, 1577 s, 1558 m, 1417 s, 1329 m, 1292 w, 1199 w, 1052 m, 1015 w, 803 m, 668 s, 553 m, 489 m.

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- 9 In an attempt to avoid the reduction of $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ to $[\text{W}^{\text{IV}}(\text{CN})_8]^{4-}$ that often occurs in alkaline or neutral solution, the Hmpca ligand was used in its neutral form. However, the slow reduction of W^{V} to W^{IV} was observed during the reaction and the yield of products was relatively low (up to 37%).
- 10 The IR spectrum of the complex shows two sharp bands (2157 and 2134 cm^{-1}) in the range 2000–2200 cm^{-1} that are attributed to C=N stretching modes. The splitting of $\nu(\text{C}=\text{N})$ suggests the presence of both bridged and non-bridged CN^- ligands. The bands at about 1600–1500 cm^{-1} correspond to the asymmetric vibration of COO^- groups, while those at about 1450–1350 cm^{-1} are attributable to their symmetric vibrations.
- 11 Crystal data for **1**: $\text{C}_{22}\text{H}_{40}\text{Eu}_2\text{N}_{12}\text{O}_{18}\text{W}$, $M = 1248.43$, monoclinic, space group $P2_1/c$, $a = 10.8755(5)$, $b = 19.129(2)$, $c = 19.3765(18)$ Å, $V = 3984.2(6)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.114$ g cm^{-3} , $R1 = 0.0197$, $wR2 = 0.0448$, $\mu = 6.076$ mm⁻¹, $S = 1.14$. Crystal data for **2**: $\text{C}_{25}\text{H}_{44}\text{Nd}_2\text{N}_{12}\text{O}_{17}\text{W}$, $M = 1257.05$, monoclinic, space group $P2_1/c$, $a = 10.9221(5)$, $b = 19.266(2)$, $c = 19.4537(9)$ Å, $V = 4049.8(5)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.029$ g cm^{-3} , $R1 = 0.0269$, $wR2 = 0.0656$, $\mu = 5.441$ mm⁻¹, $S = 1.13$. Intensity data for single crystals of **1** and **2** were collected using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer. The intensity data were corrected for Lorentz and polarization effects and for absorption (SADABS multiscan correction). The structures were solved by Patterson methods. The programs EvalCCD, DIRDIF96 and SHELXL-97 were used for data reduction, structure solution and structure refinement, respectively. Refinement of $F2$ was done against all reflections. The weighted R factor, wR , and goodness of fit S are based on $F2$. Conventional R factors are based on F , with F set to zero for negative $F2$. All non-hydrogen atoms were refined with anisotropic temperature factors. Where possible, hydrogen atoms were placed at calculated positions. If not, hydrogen positions (as many as possible) were found from a difference Fourier map. All hydrogen atoms were refined isotropically in riding mode. CCDC reference numbers 606487 and 606488. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614215j.
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