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Construction of 3d–4f heterometallic coordination polymers by simultaneous use of hexacyanometalate building-blocks and exo-bidentate ligands

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The reaction of $Pr(NO_3)_3{\cdot}6H_2O$ with 4,4′-bipyridine *N,N′*-dioxide (L) and $K_3[M(CN)_6]$ [M = Fe^{III}, Co^{III}] gives isomorphous heteropolynuclear complexes with formula $[\{(H_2O)_5LPr{-}NC{-}M(CN)_5\}(\mu\text{-}L)]{\cdot}0.5L{\cdot}4H_2O$, which exhibit a novel supramolecular architecture created by the interplay of coordinative, hydrogen bonding and π–π stacking interactions.

The design of supramolecular polymetallic architectures with novel topologies of the spin carriers is of current interest in the field of molecular magnetism. A successful strategy leading to heteropolymetallic systems with extended structures consists in self-assembly processes involving anionic building-blocks (templates), which contain a paramagnetic ion, and assembling complex cations with potentially free coordination sites. Terminal cyano groups act as efficient bridging ligands, promoting strong ferro- or antiferro-magnetic interactions between adjacent metal ions.[1] The homoleptic cyanometalates, $[M(CN)_6]^{3-}$ (M = Cr^{III}, Fe^{III}),[2] and, recently, $[Mo^{III}(CN)_7]^{4-}$ and $[W(CN)_8]^{3-}$,[3,4] are among the most employed building-blocks and generate an extremely rich coordination chemistry.

In the past decade, a plethora of cyano-bridged bimetallic systems with interesting architectures and spectacular magnetic and photomagnetic properties have been characterized.[1–4] Most of these systems contain either two different 3d metal ions, or a 3d and a 4d/5d transition metal ion. In contrast, the lanthanide cations have been rarely used as nodes for the construction of cyano-bridged heteropolymetallic coordination networks. The following families of cyano-bridged lanthanide–transition metal complexes, exhibiting extended structures, have been obtained by using homoleptic cyanometalates as templates: (a) $LnM^{III}(CN)_6{\cdot}nH_2O$ (M^{III} = Cr^{III}, Fe^{III}, Co^{III}, Ru^{III}, Ir^{III});[5] (b) $KLnM^{II}(CN)_6{\cdot}nH_2O$ (M^{II} = Fe^{II}, Ru^{II});[6] (c) $Ln_2[M^{II}(CN)_4]_3{\cdot}nH_2O{\cdot}m$DMF ($M^{II}$ = Ni^{II}, Pd^{II}, Pt^{II});[7] (d) one-dimensional chain complexes with the general formula $[LnL_2(H_2O)_m\text{-}Fe^{III}(CN)_6]{\cdot}nH_2O$ (Ln = Gd, L = betaine, m = 3, n = 0;[8] Ln = Sm, L = dimethylacetamide, m = 4, n = 5[9]).

Very recently, Champness and coworkers have characterized interesting 2- and 3-D coordination framework polymers of Er^{III} and Sm^{III}, which have been obtained by using 4,4′-bipyridine *N,N′*-dioxide as a bridging ligand.[10] Surprisingly, in comparison with other divergent ligands (*e.g.* 4,4′-bipyridine), the potentialities of 4,4′-bipyridine *N,N′*-dioxide in the construction of coordination networks and crystal engineering have been little exploited.[11,12]

Aiming to combine the bridging ability of the cyano groups with that of 4,4′-bipyridine *N,N′*-dioxide (L), we have obtained two isomorphous heterometallic compounds, $[\{(H_2O)_5Pr{-}NC{-}M(CN)_5\}(\mu\text{-}L)L]{\cdot}0.5L{\cdot}4H_2O$ (M = Fe^{III}, **1**; Co^{III}, **2**), with a novel supramolecular architecture.

The two complexes were obtained by mixing aqueous solutions of $Pr(NO_3)_3$ and $K_3[M(CN)_6]$ (M = Fe, Co) with an ethanolic solution of 4,4′-bipyridine *N,N′*-dioxide.† FTIR spectra show characteristic bands of bridging and terminal cyano groups: 2144, 2065 cm^{-1} (**1**); 2142, 2076 cm^{-1} (**2**).

The crystal structures of **1** and **2** have been solved.‡ Since the cobalt derivative **2**§ is isomorphous with **1**, only the structure of the iron derivative **1** is described here. The supramolecular order at the nanometric scale of $[\{(H_2O)_5LPr{-}NC{-}Fe(CN)_5\}(\mu\text{-}L)]{\cdot}0.5L{\cdot}4H_2O$ is created by an interesting interplay of coordinative, hydrogen bonding and π–π stacking interactions. The structure can be described as being formed by $\{(H_2O)_5LPr{-}NC{-}Fe(CN)_5\}$ neutral binuclear entities, which are bridged by 4,4′-bipyridine *N,N′*-dioxide, resulting in infinite zigzag chains (Fig. 1). Within the binuclear moieties, the $[Fe(CN)_6]^{3-}$ anion acts as a monodentate ligand, that is, with one CN^- group coordinated to the praseodymium atom [Pr–N 2.636(2) Å]. The Fe–CN–Pr linkage is slightly angular [C–N–Pr 162.87(16)°], with a Fe···Pr distance of 5.664 Å. Three 4,4′-bipyridine *N,N′*-dioxide molecules are directly bonded to one Pr^{III} atom. Two form bridges between the praseodymium atoms, while the third acts as a terminal ligand. The Pr^{III} ion exhibits a coordination number of nine: eight oxygen atoms, arising from five aqua and three L ligands, and one nitrogen atom from the cyano bridge. The Pr–O distances vary between 2.406(1) and 2.518(1) Å. The praseodymium atoms are alternately ‘bridged’ through intrachain hydrogen bonds involving uncoordinated 4,4′-bipyridine *N,N′*-dioxide molecules and the aqua ligands (Fig. 1). The distance between the triply ‘bridged’ praseodymium atoms (13.439 Å) is slightly shorter than that between the simply bridged atoms (13.937 Å).

The terminal organic ligands further extend the structure *via* π–π stacking interactions with identical terminal L ligands from adjacent zigzag chains, resulting in brick wall-like sheets (Fig. 2). The distances associated with the ligand-to-ligand π–π interactions are in the range 3.47–3.51 Å. The perfect face-to-face π-stacked alignment of the peripheral pyridyl *N*-oxide moieties of the terminal ligands is clearly favored by dipole–dipole interactions.[13] The uncoordinated 4,4′-bipyridine *N,N′*-dioxide molecules play a special role in increasing the dimensionality of the supramolecular architecture. Each uncoordinated molecule is simultaneously hydrogen bonded to four aqua ligands, two of these being coordinated to two adjacent praseodymium atoms in a chain, while the other two aqua ligands arise from another chain belonging to a neighboring brick wall sheet (Fig. 3).

The cryomagnetic properties of **1** have been investigated between 2 and 300 K. The value of $\chi_M T$ at room temperature (2.15 $cm^3\,mol^{-1}\,K$) roughly corresponds to the expected value for an uncoupled low-spin Fe^{III}(S = ½)–Pr^{III}(J = 4) system.

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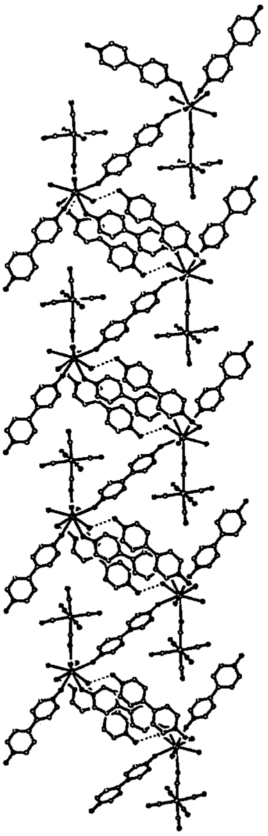

Fig. 1 Perspective view of a zigzag chain, also showing the uncoordinated 4,4′-bipyridine *N,N*′-dioxide molecules, which are hydrogen bonded to the aqua ligands coordinated to two praseodymium atoms. Along a chain, the praseodymium atoms are alternately simply and triply bridged (one genuine bridge and two $OH_2\cdots$4,4′-bipyridine *N,N*′-dioxide$\cdots H_2O$ ‘bridges’).

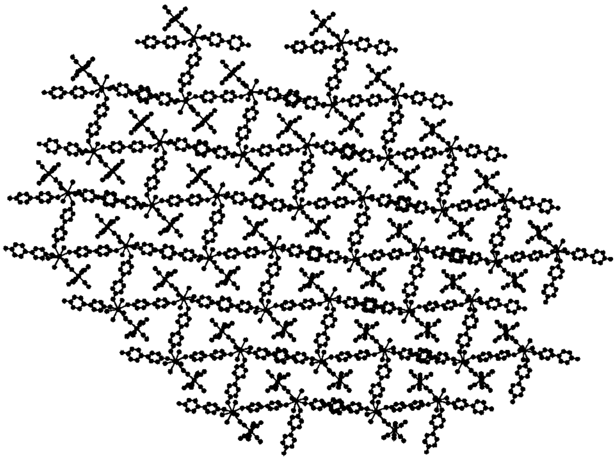

Fig. 2 Packing diagram of compound **1** showing the brick wall-like backbone resulting from π–π stacking interactions between the terminal ligands belonging to different chains. The uncoordinated 4,4′-bipyridine *N,N*′-dioxide molecules, as well as the crystallization water molecules, have been omitted.

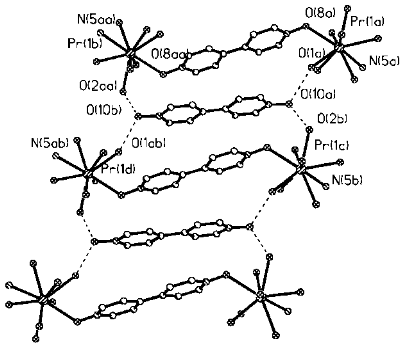

Fig. 3 Hydrogen bond interaction between the uncoordinated 4,4′-bipyridine *N,N*′-dioxide molecule and four aqua ligands arising from two different chains: O(10a)$\cdots$O(1a) 2.832 Å, O(10a)$\cdots$O(2b) 2.739 Å.

The high temperature limit of $\chi_M T$ is calculated using the equation $(\chi_M T)_{HT} = (Ng_{Fe}^2\beta^2/3k)[S_{Fe}(S_{Fe}+1)] + (Ng_{Pr}^2\beta^2/3k)[J_{Pr}(J_{Pr}+1)]$, which gives $(\chi_M T)_{HT} = 1.98$ cm^3 mol^{-1} K. The difference between the experimental and calculated values is due to the intervention of the first-order orbital momentum associated with low-spin Fe^{III}. Upon lowering the temperature, $\chi_M T$ decreases continuously reaching 0.40 cm^3 mol^{-1} K at 2 K.

Since both Pr^{III} and low-spin Fe^{III} ions show a temperature dependence for $\chi_M T$,[14] this system is not appropriate for the accurate investigation of the 3d–4f magnetic interaction. However, these complexes open new perspectives to the magnetochemistry of 3d–4f cyano-bridged systems. Further work on similar compounds, especially on those containing Cr^{III} and Gd^{III} ions, both without orbital contributions to the magnetic susceptibility, is in progress and will be presented in subsequent papers.

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Notes and references

† *Synthesis*: compounds **1** and **2** were obtained following the same general procedure: to an aqueous solution (20 mL) containing 0.4 mmol $K_3[M(CN)_6]$ and 0.4 mmol $Pr(NO_3)_3\cdot 6H_2O$ was added an ethanolic solution (10 mL) of 4,4′-bipyridine *N,N*′-dioxide (1.4 mmol). Slow evaporation of the resulting mixtures led to orange crystals of **1** and yellowish–green crystals of **2**. Correct elemental chemical analysis.

‡ *X-Ray structure determination*: *crystal data* for **1**: $C_{31}H_{38}FeN_{11}O_{14}Pr$, M = 985.48, triclinic, space group $P\bar{1}$, a = 8.3607(2), b = 15.4388(4), c = 15.4924(4) Å, α = 84.780(1), β = 80.671(1), γ = 85.655(1)°; V = 1961.32 Å^3, Z = 2, D_c = 1.669 g cm^{-3}, μ = 1.677 mm^{-1}, $F(000)$ = 996. Crystals of **1** were measured at 183(2) K on a Bruker AXS SMART diffractometer (Mo-Kα radiation monochromator). A total of 28265 of reflections (1.33 < θ < 30.01°) were collected of which 11383 unique reflections (R_{int} = 0.0182) were used. The structure was solved using the program SHELXS-97 and refined using the program SHELXL-93 to $R1$ = 0.0236, $wR2$ = 0.0637 for 10330 reflections with $I > 2\sigma(I)$ and $R1$ = 0.0282, $wR2$ = 0.0727 (all data). CCDC 158134. See http://www.rsc.org/suppdata/cc/b1/b101070k/ for crystallographic data in CIF or other electronic format.

§ *Crystal data* for **2**: a = 8.375, b = 15.410, c = 15.420 Å, α = 84.88, β = 80.66, γ = 85.63°.

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