

Lanthanide co-ordination frameworks of 4,4'-bipyridine-*N,N'*-dioxide†

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Metal–ligand co-ordination frameworks of 4,4'-bipyridine-*N,N'*-dioxide (L) have been prepared; $\{[\text{Sm}(\text{L})_2(\text{NO}_3)_3] \cdot 0.5\text{H}_2\text{O}\}_\infty$ **1**, $\{[\text{Er}_2(\text{L})_3(\text{NO}_3)_6] \cdot 2\text{CH}_3\text{OH}\}_\infty$ **2**; **1** shows rare two-fold interpenetrating three-dimensional CdSO_4 -like nets, and **2** shows an unprecedented two-dimensional 4.8^2 network.

The construction of inorganic co-ordination networks and crystal engineering have developed rapidly in recent years, the vast majority of reported work being based upon the use of polydentate ligands bound to d-block transition metal ions.¹ Ligands based upon aromatic N-donor ligands, such as 4,4'-bipyridine, have been particularly studied as they can be readily varied, giving a high degree of control over co-ordination framework structure. Aspects of such ligands that can be tuned include: denticity, ligand donor-atom separation, and, consequently, the degree of interpenetration, steric and electronic properties, and even the degree of inter-ligand interaction.

Far less common has been the use of lanthanide ions as nodes in the construction of co-ordination framework polymers.² Such structures can be expected to be more difficult to control than their d-block metal analogues due to the higher co-ordination numbers of lanthanide ions. However, the inherent flexibility of their co-ordination geometry is particularly attractive for the preparation of new network types as this greater structural ambivalence will lead to the synthesis of unprecedented structures. Based on the fact that lanthanide ions have a high affinity for hard oxygen-containing ligands, we have developed a new, widely applicable strategy using, for the first time, 4,4'-bipyridine-*N,N'*-dioxide (L) as a bridging ligand in the construction of fully characterised co-ordination networks. This strategy using poly(*N*-oxide) ligands offers exciting possibilities as the degree of structural manipulation seen in d-block coordination frameworks can now be developed for networks based upon f-block metals.

Although the co-ordination of pyridine-*N*-oxides to lanthanide ions in discrete molecular compounds is reasonably well established,³ we are aware of only one report in the literature of a complex of 4,4'-bipyridine-*N,N'*-dioxide,⁴ with another of a copper(II) co-ordination polymer of the related azobis(pyridine-4,4'-dioxide).⁵ We now report two compounds with very different structures, $\{[\text{Sm}(\text{L})_2(\text{NO}_3)_3] \cdot 0.5\text{H}_2\text{O}\}_\infty$ **1** and $\{[\text{Er}_2(\text{L})_3(\text{NO}_3)_6] \cdot 2\text{CH}_3\text{OH}\}_\infty$ **2** (L = 4,4'-bipyridine-*N,N'*-dioxide).

Yellow crystals of **1**, and pale pink crystals of **2**, were prepared‡ by slow diffusion of $\text{Sm}(\text{NO}_3)_3$ or $\text{Er}(\text{NO}_3)_3$ and 4,4'-bipyridine-*N,N'*-dioxide in a $\text{MeOH}-\text{CH}_2\text{Cl}_2$ solvent mixture, the latter component acting to slow the rate of diffusion and thus the reaction. The crystals of **1** were very stable in air and did not decay upon continuous exposure to moisture, but crystals of **2** lost crystallinity quickly following removal from the mother liquor. Single crystal X-ray analyses§ confirm that these materials have polymeric structures, based on networks of ten-co-ordinate lanthanide centres for **1** and nine-co-ordinate centres for **2**, with L bridging the metal centres. Whereas the $\text{Sm}(\text{III})$ ions in **1** have a regular SmO_{10} co-ordination environ-

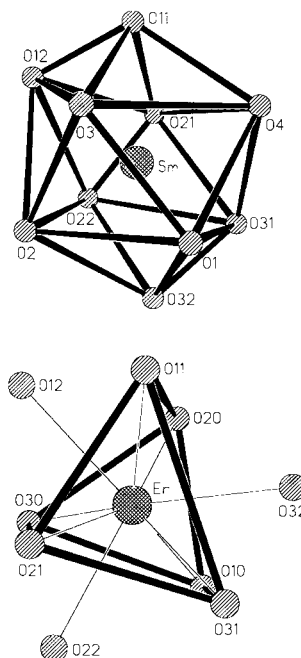
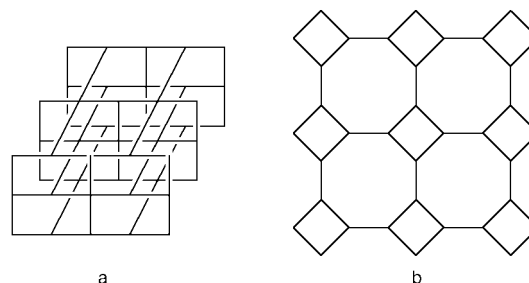


Fig. 1 Metal co-ordination environments in **1** (a) and **2** (b).

ment with the oxygen atoms forming a hexadecahedron (Fig. 1a), the $\text{Er}(\text{III})$ ions in complex **2** have an ErO_9 co-ordination environment, with nine oxygen atoms forming a distorted tricapped trigonal prism (Fig. 1b), reflecting the reduction in the ionic radius from $\text{Sm}(\text{III})$ to $\text{Er}(\text{III})$.

1 adopts a two-fold interpenetrating three-dimensional CdSO_4 -like framework (a in Scheme 1, Fig. 2). The 4,4'-bipyridine-*N,N'*-dioxide ligands sustain a 3-D framework motif through two different linkages. The first propagates along the two diagonal directions of the *ab* face; the ligand is slightly bent, with the two pyridyl rings twisted at an angle of 14.8° and bridging two $\text{Sm}(\text{III})$ centres at a distance of 12.7 \AA . The other linkage exists as a zigzag line propagating along the *c* axis; in this case the ligand is more bent, with the two pyridyl rings twisted at an angle of 29.9° and bridging the two $\text{Sm}(\text{III})$ centres at a much shorter distance of 11.6 \AA . The framework found here



Scheme 1 Schematic representation of (a) a CdSO_4 3D-net and (b) a 2D 4.8^2 net.

† Electronic supplementary information (ESI) available: colour version of Fig. 2 and 3. See <http://www.rsc.org/suppdata/cc/b0/b002363j/>

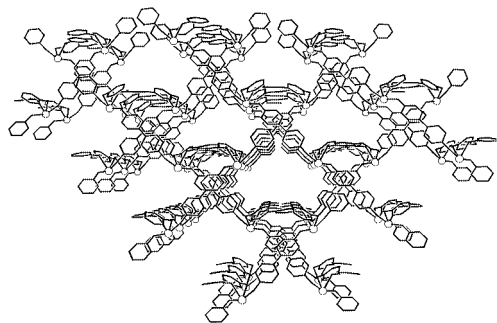


Fig. 2 Packing diagram of compound **1** showing one component of the two interpenetrating frameworks (viewed down the *c* axis). Nitrate groups, solvent molecules and hydrogen atoms are omitted for clarity.

is a severely distorted CdSO_4 -like net,^{6,7} The previous examples of CdSO_4 -type nets, $\{\text{Cu}[1,2\text{-bis}(4\text{-pyridyl})\text{ethane}]_2(\text{NO}_3)_2\}_\infty$ reported by Zaworotko *et al.*⁶ and the related 'dense-net' structure of copper complexed with 1,2-bis(4-pyridyl)ethyne reported by Ciani *et al.*,⁷ are both constructed from *d*-metal junctions. As the conformation of the linking ligands is flexible, the junction at $\text{Sm}(\text{III})$ is distorted from square-planarity causing the connection propagating along the *c* direction to develop into a zigzag line. When viewed along the *c* direction, the structure is seen to contain $12.0 \times 12.0 \text{ \AA}$ channels (Fig. 2). However, these channels are occupied by a second interpenetrating independent framework.

The smaller ionic radius for $\text{Er}(\text{III})$ compared to $\text{Sm}(\text{III})$ results in nine-co-ordinate $\text{Er}(\text{III})$ centres in **2** via six oxygen donors from three nitrates and three from three 4,4'-bipyridine-*N,N'*-dioxide ligands. These latter ligands link the $\text{Er}(\text{III})$ ions to form a 2-D sheet of 4.8^2 topology (b in Scheme 1, Fig. 3). This type of net, predicted by Wells⁸ but not previously observed for co-ordination frameworks, consists of three connected nodes shared by one tetragonal square unit and two octagons. The octagonal unit forms an 88-membered ring, comprising eight metal ions and eight ligands, of *ca.* 2.6 nm diameter. This large cavity is occupied by the four-membered ring motif of an adjacent layer thus inhibiting interpenetration. When viewed along the *c* axis, tetragonal channels with dimensions of $10.0 \times 10.0 \text{ \AA}$ can be seen (Fig. 3), in which methanol solvent molecules are accommodated.

The isolation of complexes **1** and **2** suggests the possibility of constructing designed inorganic networks with lanthanide metal salts and bridging pyridine-*N*-oxide ligands. We have every reason to believe that, in the same way that polypyridines are important for d-block metal ions, poly(pyridine-*N*-oxides) may become equally important for f-block metal ions, thus leading to a new family of inorganic co-ordination networks and framework materials.

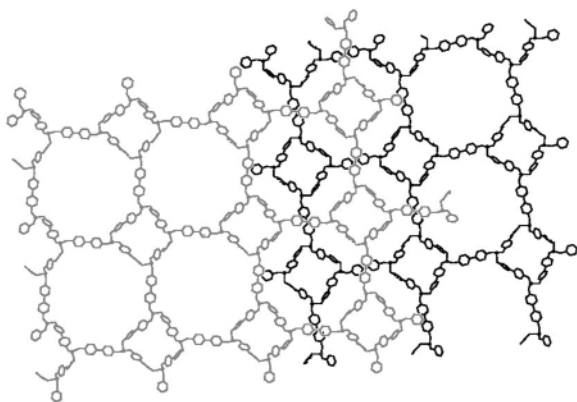


Fig. 3 View of the 4.8^2 nets in compound **2** with two adjacent layers in different colours. Nitrate groups, solvent molecules and hydrogen atoms are omitted for clarity.

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Notes and references

‡ *Experimental procedure:* $\{\text{Sm}(4,4'\text{-bipyridine-}N,N'\text{-dioxide})_2(\text{NO}_3)_3\} \cdot 0.5\text{H}_2\text{O}$ **1**. Solid $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (44 mg, 0.10 mmol) at the bottom of a vial was covered with CH_2Cl_2 (4 cm^3) over which a solution of 4,4'-bipyridine-*N,N'*-dioxide hydrate (44 mg, 0.20 mmol) in MeOH (6 cm^3) was layered. Over a period of 15 days, the solid $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ gradually dissolved with concomitant formation of yellow crystals of the product on the wall of the vial. $\{\text{Er}_2(4,4'\text{-bipyridine-}N,N'\text{-dioxide})_3(\text{NO}_3)_6\} \cdot 2\text{CH}_3\text{OH}$ **2** was prepared by an analogous method, forming pale pink columnar crystals. Satisfactory spectroscopic and analytical data were obtained for both compounds.

§ *X-Ray experimental, general procedures:* data for both compounds were collected on a Stoe Stadi-4 four-circle diffractometer, graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), ω - θ scans. Both structures were solved by direct methods⁹ and refined using full-matrix least squares techniques on F^2 .¹⁰ All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and allowed to ride on their parent atoms.

Crystal data for $[\text{Sm}(4,4'\text{-bipyridine-}N,N'\text{-dioxide})_2(\text{NO}_3)_3] \cdot 0.5\text{H}_2\text{O}$ **1**: $\text{C}_{20}\text{H}_{17}\text{N}_7\text{O}_{13.5}\text{Sm}$, $M = 721.76$, orthorhombic, space group $Pbcn$ (no. 60), $a = 16.529(4)$, $b = 17.616(5)$, $c = 17.244(5) \text{ \AA}$, $U = 5021(2) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 8$, $D_c = 1.907 \text{ Mg m}^{-3}$, $\mu(\text{Mo-}K\alpha) = 2.424 \text{ mm}^{-1}$, 4919 unique reflections [$R_{\text{int}} = 0.0852$] [4144 with $I > 2\sigma(I)$]. Final $R_1 = 0.033$, $wR_2(\text{all data}) = 0.077$.

$\{\text{Er}_2(4,4'\text{-bipyridine-}N,N'\text{-dioxide})_3(\text{NO}_3)_6\} \cdot 2\text{CH}_3\text{OH}$ **2**: $\text{C}_{32}\text{H}_{32}\text{Er}_2\text{N}_{12}\text{O}_{26}$, $M = 1335.22$, tetragonal, space group $P4_2/c$ (no. 114), $a = 26.435(6)$, $c = 7.584(2) \text{ \AA}$, $U = 5300(2) \text{ \AA}^3$, $T = 220(2) \text{ K}$, $Z = 4$, $D_c = 1.673 \text{ Mg m}^{-3}$, $\mu(\text{Mo-}K\alpha) = 3.235 \text{ mm}^{-1}$, 4422 unique reflections, [3542 with $I > 2\sigma(I)$]. Final $R_1 = 0.076$, $wR_2(\text{all data}) = 0.179$.

CCDC 182/1647. See <http://www.rsc.org/suppdata/cc/b0/b002363i/> for crystallographic files in .cif format.

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