Use of Heterometal Combinations to construct Very Large Ring Frameworks; Synthesis and Structural Characterisation of the 36-Membered Ring Compound [{NiNd(4-picolylpyrrolidin-2-one)$_4$(NCS)$_2$(NO$_3$)$_3$}$_n$]

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X-Ray diffraction studies on the complex [{NiNd(PPO)$_4$(NCS)$_2$(NO$_3$)$_3$}$_n$] (PPO = 4-picolylpyrrolidin-2-one) show that the PPO ligands connect the Ni and Nd centres into sheets of 36-membered rings; the structure of [CoCl$_2$(PPO)$_4$] is also described.

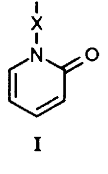
A particularly active field of chemical research in recent years has been the design of extended molecular systems. Advances in this general area have employed a range of synthetic strategies and the products have taken a variety of forms *e.g.* 'star-burst' dendrimers,[1] self-assembly of organic units *via* hydrogen bonding,[2] assemblies of macrocycles for binding sets of metal ions,[3] catenanes, rotaxanes and molecular knots.[4,5] We have recently been developing an approach which exploits the ability of extended reach bis-pyridone **I** and bis-lactam **II** ligands (where X is an organic spacer unit) to bridge sets of metal ions so as to form very large rings in which the metal ions form part of the ring framework rather than being coordinated inside the ring. Appropriate choice of the ring system, the spacer unit X and the metal ion has permitted the formation of, *inter alia*, individual large rings,[6,7] chains of rings,[7,8] sheets of rings[8] and three-dimensional networks.[9]

One of the aims in this work is to achieve control, not only of the sizes of the metallocyclic rings and the geometry of the framework materials that are formed, but also the combinations of metal ions that can be incorporated into such frameworks. The use of ligands of types **I** and **II**, in which both donor atoms are the same, has hitherto resulted in the formation of homometallic products. In this Communication we show that, by appropriate ligand modification, this fruitful general approach can be extended to the formation of heterometallic, large-ring framework materials, thereby significantly expanding and diversifying the range of new materials that may be obtained.

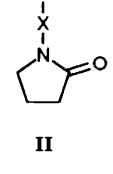
The ligand 4-picolylpyrrolidin-2-one[10] (**III** = PPO) has two donor units with the potential to bind simultaneously to two dissimilar metal ions, and their mutual disposition precludes chelation. As a prelude to investigating mixed metal systems, the binding preference of PPO, *i.e.* O- *versus* N-ligation, towards a first-row transition metal, as a typical target metal, was established by determining the structure[†] of [CoCl$_2$(PPO)$_4$] **1**,[‡] (Fig. 1), which shows the binding to be *via* the nitrogen atoms.

Subsequently, reaction of PPO with a mixture of Ni(NCS)$_2$ and Nd(NO$_3$)$_3$ in MeOH–EtOH gave deep blue crystals of the compound [{NiNd(PPO)$_4$(NCS)$_2$(NO$_3$)$_3$}$_n$] **2**[‡] which has also been characterised by single-crystal X-ray diffraction analysis.[†]

The X-ray analysis of **2** reveals that, as desired, a bimetallic, large-ring framework compound has been formed, in which the PPO ligands bridge the metal centres by binding to the nickel atoms *via* the pyridine ring nitrogen and to neodymium *via* the pyrrolidone oxygen atom (Fig. 2). The coordination geometry about each nickel atom is octahedral with the isothiocyanate ligands occupying *trans*-axial positions. The disposition of the four equatorial PPO ligands is very similar to that observed in **1**. Each neodymium centre is bound to three bidentate nitrates and four oxygen atoms of different PPO ligands in a distorted bicapped square-antiprismatic coordination geometry.



I



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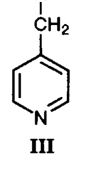

III

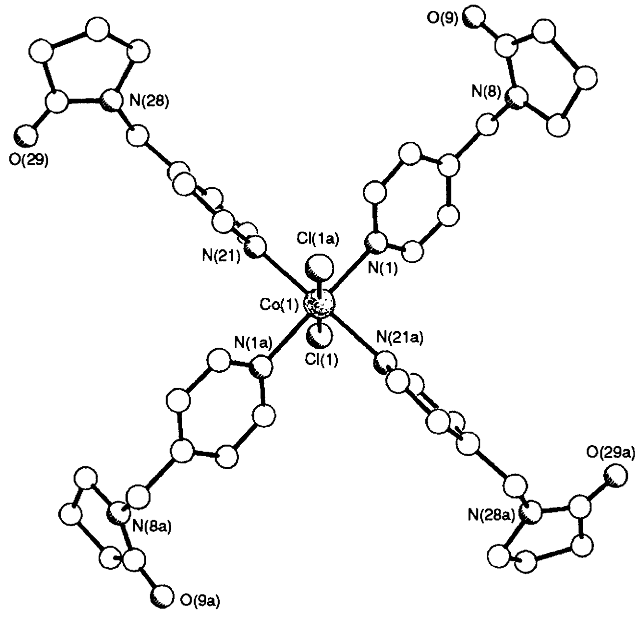

Fig. 1 The molecular structure of **1**. The Co–N distances are Co–N(1) 2.189(4) Å and Co–N(2) 2.228(3) Å and the Co–Cl distance is 2.472(2) Å.

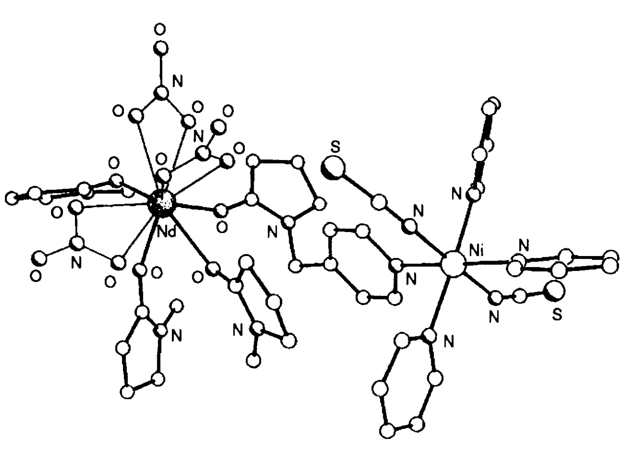

Fig. 2 The asymmetric unit in **2** showing the neodymium and nickel environments and one of the PPO bridges. The Nd–O(nitrate) and Nd–O(PPO) distances are in the ranges 2.529(4)–2.693(5) and 2.397(5)–2.505(4) Å respectively; the Ni–N(pyridine) distances are in the range 2.140(4)–2.187(4) Å and Ni–N(NCS) 2.042(5) and 2.047(5) Å.

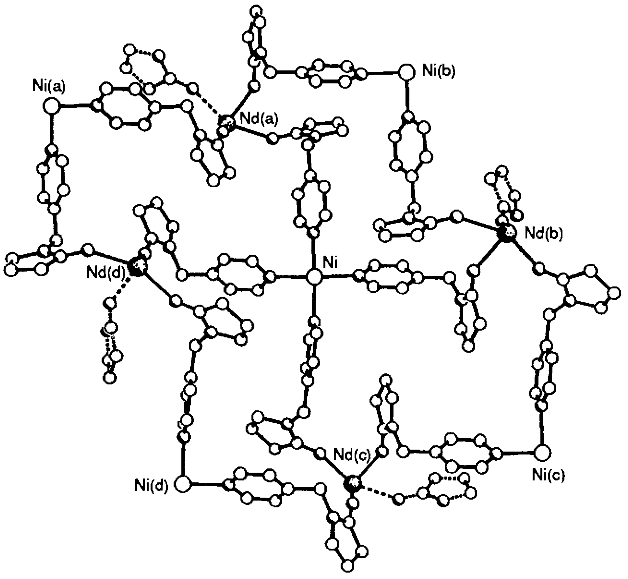

Fig. 3 Part of the extended network present in the crystals of **2** showing the basic repeat motif and the four distinctly different macrocycle conformations. (The coordinated anions have been omitted for clarity). The metal–metal distances (Å) are: Ni···Ni(a) 14.82, Ni···Ni(b) 10.60, Ni···Ni(c) 13.61, Ni···Ni(d) 11.60; Nd(a)···Nd(b) 15.83, Nd(b)···Nd(c) 14.92, Nd(c)···Nd(d) 15.34, Nd(d)···Nd(a) 10.27; Ni···Nd(a) 9.22, Ni···Nd(b) 9.83, Ni···Nd(c) 10.36, Ni···Nd(d) 8.81.

The network comprises sheets of contiguous 36-membered rings each of which contains two Nd and two Ni atoms (Fig. 3). This Figure illustrates the basic repeat motif within each sheet. Each of the four crystallographically independent, centrosymmetric, 36-membered macrocycles has a distinctly different conformation. Accompanying these differences in ring geometry are significant variations in the bridging ligand span (Ni···Nd) and in the transannular metal–metal distances. The distances are in the ranges: Ni···Nd 8.81–10.36 Å, Ni···Ni 10.61–14.82 Å, Nd···Nd 10.27–15.83 Å.

The ability of this relatively simple PPO ligand to facilitate the formation of an extended, large-ring heterometallic network suggests that, by appropriate ligand modification, there is considerable potential for the rational design and synthesis of networks containing specific combinations of metals in predetermined stoichiometric proportions and with a range of metal–metal distances.

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Footnotes

† *Crystal data* for **1**: $C_{40}H_{48}Cl_2CoN_8O_4$, triclinic, space group $P\bar{1}$, $a = 7.842(6)$, $b = 9.049(8)$, $c = 14.829(10)$ Å, $\alpha = 97.21(2)$, $\beta = 97.49(2)$, $\gamma = 101.49(2)°$, $U = 1010$ Å^3, $Z = 1$, $M = 834.7$, $D_c = 1.372$ g cm^{-3}, μ(Mo-Kα) = 0.608 mm^{-1}, $F(000) = 437$.

For **2**: $C_{42}H_{48}N_{13}NdNiO_{13}S_2{\cdot}0.25H_2O$, triclinic, space group $P\bar{1}$, $a = 9.722(3)$, $b = 16.828(6)$, $c = 17.332(7)$ Å, $\alpha = 69.00(2)$, $\beta = 83.05(2)$, $\gamma = 81.00(2)°$, $U = 2608$ Å^3, $Z = 2$, $M = 1214.5$, $D_c = 1.546$ g cm^{-3}, μ(Cu-Kα) = 9.32 mm^{-1}, $F(000) = 1235$.

Data for **1** were collected on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation and ω scans. Data for **2** were collected on a Siemens P4RA diffractometer using graphite-monochromated Cu-Kα radiation and ω scans. Both structures were solved by direct methods and refined anisotropically to give, for **1**, $R = 0.0409$, $R_w = 0.0413$ for 2078 independently observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leqslant 40°]$ and for **2**, $R = 0.0464$, $R_w = 0.0488$ for 7006 independently observed absorption corrected reflections [max, min. transmissiion factors 0.411, 0.168, $|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information Authors, Issue No. 1.

‡ Compound **1** separated as purple crystals on slow evaporation of a solution of hydrated cobalt(II) chloride and PPO in 1 : 4 mole ratio in a 2 : 1 mixture of methanol–2,2-dimethoxypropane; satisfactory microanalyses were obtained.

Compound **2**: $Ni(NCS)_2$ (1 mmol) in ethanol (3 cm^3) was mixed with hydrated neodymium nitrate (0.5 mmol) in hot methanol (10 cm^3). After filtration, this solution was added dropwise to a solution of PPO (3.9 mmol) in hot methanol (10 cm^3). Slow cooling over 1 h gave deep blue crystals of **2**.

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