Formation of a Novel Three-dimensional Network of 48-Membered Rings in the Compound $[Ni(m\text{-}XBP)_3](ClO_4)_2$

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X-Ray diffraction studies on the complex $[Ni(m\text{-}XBP)_3](ClO_4)_2\cdot 3H_2O$ [*m*-XBP = *N,N'*-*m*-phenylenedimethylenebis(pyridin-2-one)] show that it forms a novel three-dimensional network of 48-membered rings arranged about an S_6 axis, creating a series of cross-linked triple helices.

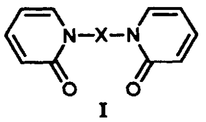
The design and synthesis of new polymeric framework materials containing cavities capable of taking up molecular substrates in a shape- and/or size-selective fashion is a continuing challenge. The selective incorporation of metal ions as integral components of such frameworks offers additional factors, such as electron transfer, that can be exploited in stimulating substrate reactivity. Our studies on the complexes formed by linked pyridone ligands **I** have shown that a variety of unusual polymeric structures containing very large rings can be generated by appropriate choice of the 'spacer' unit X in **I**, the metal ion and/or the counter anion.[1–4] Changes in any one of these three factors often result in quite major differences in the polymeric structure adopted. For example, whereas the use of an *ortho*-phenylenedimethylene bridge **II** results in 11-membered chelate ring formation with lanthanide(III) nitrates,[4] the analogous complexes formed by the *para*-bridged ligand **III** are triple-helically linked dimers.[2] This significant difference prompted us to study the coordination behaviour of the *meta*-bridged ligand (**IV**; *m*-XBP).

Reaction of **IV**† with $[M(H_2O)_6](ClO_4)_2$ (M = Mn^{II}, Co^{II}, Ni^{II}, Zn^{II} and Cd^{II}) in methanol or, for Ni^{II}, a 1 : 1 mixture of methanol and 2,2-dimethoxypropane, resulted in the formation of hydrated complexes of the general type $[M(m\text{-}XBP)_3](ClO_4)_2\cdot xH_2O$, which X-ray powder diffraction studies show form an isostructural series.‡ The yellow-green nickel complex $[Ni(m\text{-}XBP)_3](ClO_4)_2\cdot 3H_2O$, **1**, was obtained as crystals and this member of the series has been fully characterised by single crystal X-ray methods.§

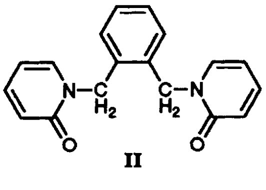
The X-ray study shows the structure to be highly symmetric, having crystallographic S_6 symmetry. Each nickel ion is octahedrally coordinated by six oxygen atoms each of which is provided by a different *m*-XBP ligand. Deviations from O_h geometry at the nickel centre are small, with angles at nickel of 88.6(1) and 91.4(1)°; the Ni–O distances are 2.084(3) Å.

The *m*-XBP ligand has crystallographic C_2 symmetry about an axis lying in the plane of the central *m*-xylyl unit and passing through C(11) and C(12) (Fig. 1); the two pyridone rings are essentially orthogonal (86°) to the *m*-xylyl ring. The *m*-XBP ligands serve to bridge adjacent nickel centres creating a series of linked 48-membered rings, one of which is shown in Fig. 1.

Adjacent nickel atoms on the S_6 axis are linked by three helical strands each comprising three *m*-XBP ligand molecules and two nickel atoms (which also lie on S_6 axes); the Ni-Ni separation along the S_6 axis is 23.95 Å. The three strands are partially unravelled, thus creating a pair of cavities disposed



I



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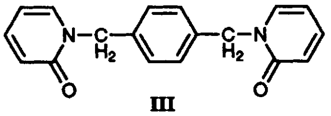
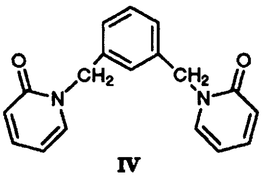


III



IV

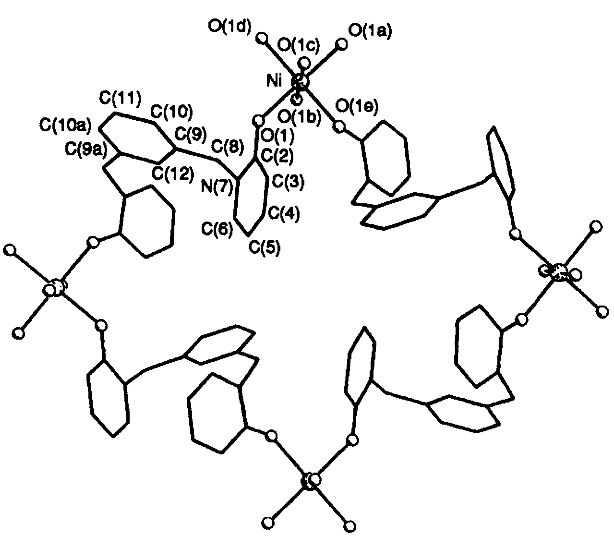


Fig. 1 The 48-membered ring present in the structure of **1** showing the numbering of the atoms in the asymmetric unit (those with a, b, c, d and e suffices are symmetrically equivalent atoms). The minimum transannular Ni···Ni distance is 11.33 Å.

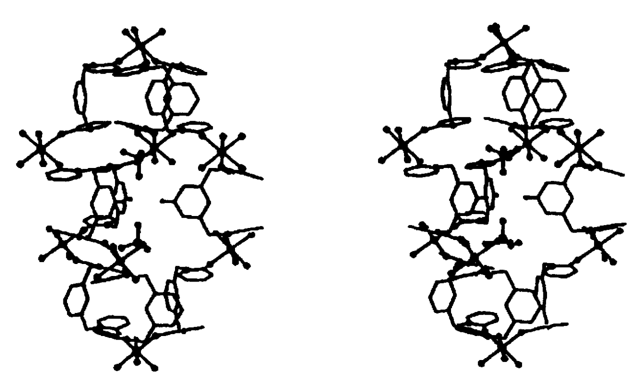


Fig. 2 Stereoscopic view of part of one of the extended triple helical strands viewed normal to the S_6 axis

about the S_6 axis and each containing a perchlorate ion which may be seen in Fig. 2, which shows a stereoscopic representation viewed approximately normal to the S_6 axis. The pathway between the upper and lower cavities is partially blocked by three inwardly-directed C(11) protons of symmetry-related *m*-xylyl rings. The triple helices extend in the crystallographic *c* direction to form an extended rope-like chain. Adjacent 'ropes' are fused in the crystallographic a_1 and a_2 directions, *via* additional Ni–(*m*-XBP)–Ni bridges thus forming an extended three-dimensional network. The water molecules of crystallisation are located between the adjacent helices.¶ The flexing of the helix observed in **1**, permitting inclusion of the anions between the 'opened' strands, contrasts with the 'taut' situation found in the triple helical structure formed by $[M_2(p\text{-XBP})_2(NO_3)_6]$, where M = Pr, Nd, Sm, Er.[2]

This result demonstrates that our approach to the formation of large metallocyclic ring systems can be extended from the sheet-like arrays[1,3] to three-dimensional networks with finite cavity sizes.

We thank the SERC for a Research Studentship (to A. M. S.) and for the diffractometer, and the CEC for a Visiting Fellowship (to S. M.).

Received, 3rd May 1994; Com. 4/02580F

Footnotes

† Obtained by reacting α,α′-dibromo-*m*-xylene and the sodium salt of 2-pyridone in 1:2 mole ratio in butan-1-ol at 100 °C for 5 h, removal of the solvent and recrystallising the resulting oil from hot water to form the crystalline dihydrate; this was further recrystallised from acetone (yield 66%). Satisfactory microanalytical results were obtained.

‡ Subsequent calculation of the powder pattern corresponding to the single crystal structure of **1** showed a perfect match of the calculated pattern with that observed for the series.

§ *Crystal data* for **1**: $C_{54}H_{48}Cl_2N_6NiO_{14}\cdot 3H_2O$, rhombohedral, space group $R\bar{3}c$, $a = b = 13.930(3)$, $c = 47.894(13)$ Å, $U = 8045(4)$ Å^3, $Z = 6$, $M = 1188.6$, $D_c = 1.472$ g cm^{-3}, μ(Cu-Kα) = 21.13 cm^{-1}. Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure was solved by the heavy-atom method and refined anisotropically to give $R = 0.0597$, $R_w = 0.0626$ for 1155 independent observed reflections $[|F_o| > 4\sigma(|F_o|)]$, $2\theta = 3$–$130°$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Although the X-ray study revealed *ca.* three water molecules per nickel, microanalytical data suggested that the occluded water content in samples of this group of compounds is somewhat variable.

References

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