

Ligand-induced Formation of a Triple Helical Bridge involving O-Donor Ligands in Dimeric Lanthanide Complexes

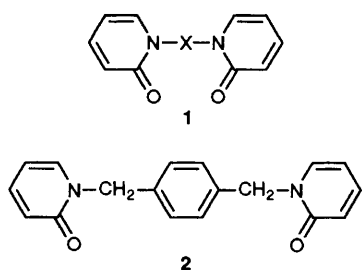
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The complexes $[M_2(p\text{-XBP})_3(\text{NO}_3)_6]$ [$M = \text{Pr, Nd, Sm, Er}$; $p\text{-XBP} = N,N'$ -xylene-1,4-diylbis(pyridin-2-one)] are shown by X-ray diffraction methods to contain the first example of an O-bonded triple helical bridge.

The interest in helical chain polymers originally sparked by the structure of DNA, has recently taken a new twist by the recognition that self-assembling helices can be generated by an appropriate choice of metal ions and polydentate ligands. There are two prime requirements in the design of helical structures: (i) the template influence of a rigid threefold directing centre as in, *e.g.*, an octahedrally coordinated metal ion; (ii) the conformational preferences of the bridging ligands. Hitherto, attention has been focused on the use of polydentate nitrogen donor ligands, *e.g.* polypyridyls,¹ polybipyridyls² or polyphenanthrolines.³ Double-helical structures formed by metal complexes with ligands of these types are now well established but, to our knowledge, there are only two structurally characterised examples of a triple-helical complex formed by using an organic ligand.^{4,5}

During our studies of the ability of bridged 2-pyridone ligands (**1**, where X is a range of organic linking units) to generate polymers with unusual structures,⁶ we have found that **2** ($p\text{-XBP}$)[†] produces the first example of an O-bonded triple-helical bridge, in the complexes $[M_2(p\text{-XBP})_3(\text{NO}_3)_6]$ ($M = \text{Pr, Nd, Sm, Er}$).[‡] X-Ray powder diffraction studies



[†] Obtained by heating a mixture of the sodium salt of 2-pyridone (5.85 g) and α,α' -dibromo-*p*-xylene (6.25 g) at 155–170 °C for 7 h and extracting the product with boiling toluene.

[‡] Compound **3** separated as lilac-purple clumps of platelets by slow evaporation (several days in a desiccator over conc. sulfuric acid) of a solution obtained by adding hydrated neodymium nitrate (0.1 mmol) in MeCN (3 cm³) to **2** (0.2 mmol) dissolved in a mixture of MeCN (3 cm³) and MeOH (2 cm³). The praseodymium (pale-green), samarium (white), and erbium (pink) analogues were obtained in the same way. The compounds gave satisfactory elemental analyses.

show that these four complexes are isostructural. Good quality crystals of the neodymium complex **3** were readily formed from the reaction mixture as an MeCN solvate and these were therefore chosen for a single crystal structural analysis.[§]

The X-ray study of $3 \cdot 1\frac{1}{2}\text{MeCN}$ reveals a dimeric structure (Fig. 1) in which each neodymium centre is nine-coordinate and is bound to three bidentate nitrates and to one oxygen atom of each of three $p\text{-XBP}$ ligands.[¶] (The Nd–O distances are in the ranges: 2.349(7)–2.358(8) Å to oxygen atoms of **2**, and 2.532(8)–2.605(7) Å to nitrate oxygen atoms.) The $p\text{-XBP}$ ligands in turn serve to bridge the adjacent metal centres forming a triple helically-bridged structure. The pitch of the helix is *ca.* one-third of a turn between the two metal centres. (As the space group is centrosymmetric, there are equal numbers of right- and left-handed helices in the crystal.)

The complex has approximate molecular D_3 symmetry about the Nd–Nd direction (Fig. 2) and crystallographic C_2 symmetry perpendicular to this axis and passing through the centre of one of the $p\text{-xylyl}$ rings. As may be seen from the sectioned space-filling representation shown in Fig. 3, the central cage formed by the three $p\text{-XBP}$ ligands is self-filling.

[§] Crystal data for $3 \cdot 1.5\text{MeCN}$: $\text{C}_{54}\text{H}_{48}\text{N}_{12}\text{O}_{24}\text{Nd}_2 \cdot 1.5\text{MeCN}$, monoclinic, space group $C2/c$, $a = 17.493(10)$, $b = 17.354(9)$, $c = 23.115(15)$ Å, $\beta = 107.63(2)^\circ$, $U = 6688(6)$ Å³, $Z = 4$, $M = 1600.6$ $\mu(\text{Mo-K}\alpha) = 16$ cm⁻¹, $D_c = 1.59$ g cm⁻³. Siemens P4/PC diffractometer, ω -scan, graphite monochromated Mo-K α radiation. The structure was solved by the heavy atom method and refined anisotropically to give $R = 0.0532$, $R_w = 0.0499$, for 3539 independent observed reflections [$4 \leq 2\theta \leq 50^\circ$, $|F_0| > 4\sigma(|F_0|)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[¶] The geometry about each neodymium centre is distorted tricapped trigonal prismatic. It alternatively may be visualised as distorted 'octahedral' if one set of three bidentate nitrate groups is considered to represent one face of the 'octahedron' and the three $p\text{-XBP}$ oxygen atoms the opposite face. [The three O–Nd–O angles subtended to $p\text{-XBP}$ oxygen atoms are in the range 83.5(2)–84.8(2)°.] The three nitrate nitrogen atoms are in a staggered relationship to the oxygen atoms of the organic ligand.

A feature of a triple-helical type linkage, which can be visualised as a three-stranded rope-like molecule, is its ability to 'breathe', *i.e.* the three strands may tighten as the two metal centres are moved apart, or may unravel, creating a central cavity, as the metal centres approach each other. In **3**, however, with the three *para*-methylene-linked aromatic strands, very little change in the volume of the central cavity appears to be possible.

The bimetallic triple-helically linked arrangement in **3** is reminiscent of that found^{4a,b} in the cobalt(II) dimer **4** formed by bis[1-methyl-2-(6'-methyl-2'-pyridyl)benzimidazol-5-yl]-

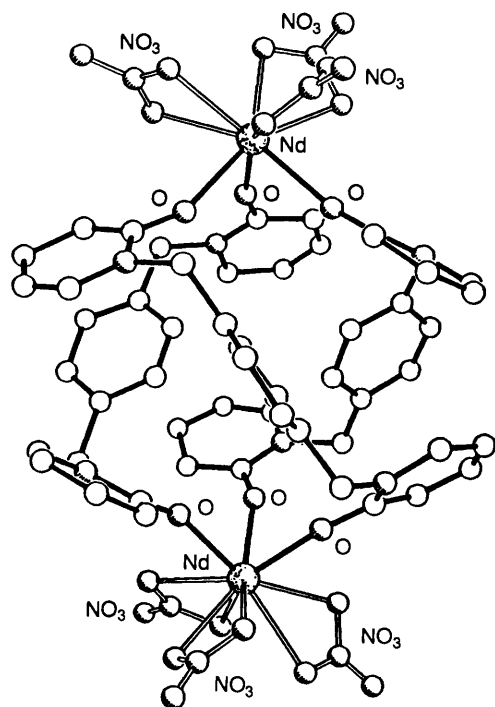


Fig. 1 Triple helical structure adopted by **3**

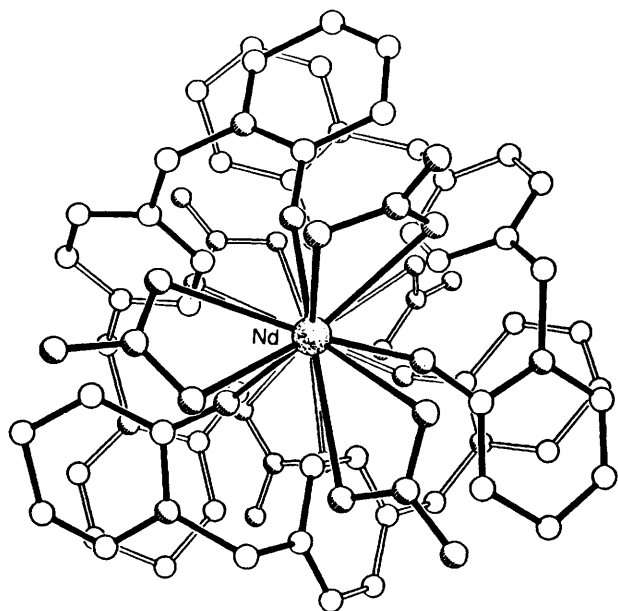


Fig. 2 View down the molecular D_3 (Nd-Nd) axis in the solid-state structure of **3**

|| In **3** the intradimer Nd-Nd separation is 9.95 Å.

methane. In **4** the linkage is facilitated by the binding, *via* nitrogen, of the ligand in an octahedral coordination geometry about the cobalt(II) ions. Here, in **3**, a very similar geometrical bridging arrangement is achieved by the two nine-coordinate lanthanide centres binding to the oxygen atoms of the organic ligands **2**. In contrast to the helical structure found^{4c} in the dimeric europium complex which utilises three bis[1-methyl-2-{6'-[1''-(3,5-dimethoxybenzyl)benzimidazol-2''-yl]-2'-pyridyl} benzimidazol-5-yl]methane ligands, each of which contains a single methylene bridge, in **3** the same motif is achieved *via* three aryl units and two methylene bridges. This latter arrangement exploits the preference for a non-orthogonal relationship that exists within a methylene-bridged diaryl unit coupled with an approximately parallel stacking of the aryl rings of adjacent strands within the helix.** This demonstrates that a bidentate directing ligand attached to an octahedral centre is not a prerequisite for the formation of a helical structure.

The intermolecular packing arrangement is dominated by aromatic-aromatic π -stacking and nitrate-nitrate electrostatic interactions, the solvent MeCN molecules occupying the interstices. Under 379 nm excitation the samarium complex shows phosphorescent emission at 563.5 nm ($^4G_{5/2} \rightarrow ^6H_{5/2}$), 598.5 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), and 642 nm ($^4G_{5/2} \rightarrow ^6H_{9/2}$).

To our knowledge, the complex described here is the first to involve a triple helical bridge by utilising an oxygen-donor ligand, in contrast to the nitrogen-donor ligands previously employed. Moreover the helicity is achieved *via* the conformational preferences of the triaryl, bis-methylene unit without resorting to the directing influence of a bidentate ligand attached to an octahedral metal centre.

These observations suggest an alternative approach to the creation, *via* self-assembly processes, of extended linear metal-linked rope-like molecules of the type indicated in Scheme 1, incorporating a wide range of metal species. However a potential disadvantage of this approach is that in multimetallic, polymeric structures reversal of the helicity could occur at any of the metal centres. In **3** and its analogues

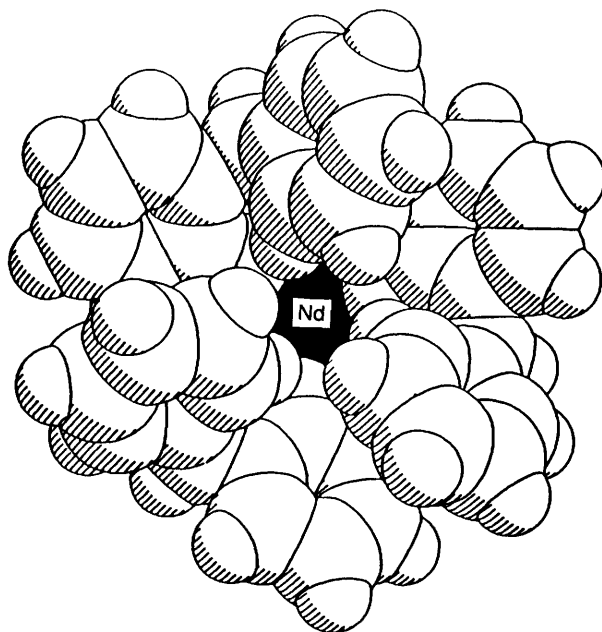
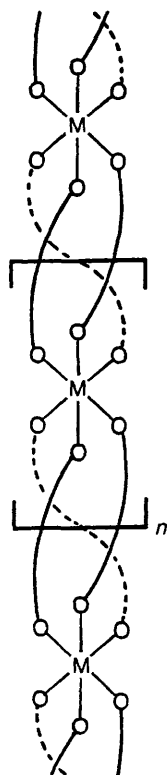


Fig. 3 Space-filling representation of the central region of the helix in **3**, viewed down the Nd-Nd direction

** The centroid-centroid separations of the stacked aryl rings in adjacent strands are in the range 4.1–4.4 Å. The pairs of centroid-centroid vectors between adjacent rings within each three aryl ring stack each subtend an angle of 152° at the central ring.



Scheme 1 Schematic representation of an extended 'rope-like' metal complex formed by triple helical bridges. (The octahedral metal coordination depicted here can be replaced by *e.g.* tricapped trigonal prismatic geometry to achieve a similar helical chain propagation.)

long chain growth appears to have been stopped by the 'capping' action of the three nitrate groups binding to each lanthanide ion because of the good affinity of the lanthanide ions for nitrate oxygen atoms. We are currently attempting to

circumvent this problem by both anion and metal variation and have indeed observed some important differences in complex formation when nitrate ions are replaced by more poorly coordinating ions. For example, reaction of *e.g.* hydrated yttrium or dysprosium perchlorate with *p*-XPB, using the same experimental conditions employed for **3**, resulted in the immediate precipitation of complexes of stoichiometry $M(p\text{-XPB})_3(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ($M = \text{Y}$ or Dy). Although we have not yet been able to obtain crystals of these compounds for X-ray characterisation, the combination of their much lower solubility, compared with **3** and its analogues, and the difference in the stoichiometry suggests the formation of an infinite polymeric structure. In the light of the results for **3**, a structure such as that in Scheme 1, with the addition of three aqua ligands to bring the coordination to nine, seems quite likely, but other polymeric geometries are, of course, possible.

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