

Diversity of linking modes by *N,N'*-*p*-phenylenedimethylenebis(pyridin-4-one) [*p*-XBP4] in the novel 'linked lantern' framework complex $\{[\text{Nd}_2(\textit{p}\text{-XBP4})_6(\text{H}_2\text{O})_4](\textit{p}\text{-XBP4})(\text{H}_2\text{O})_3(\text{ClO}_4)_6\}_n$

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The title compound has a complex framework structure in which pairs of Nd atoms are linked by four *p*-XBP4 ligands to form 'lanterns' which are further connected by interwoven Nd-(*p*-XBP4)-Nd bridges, and yet again by non-coordinated *p*-XBP4 molecules hydrogen bonded to aqua ligands on the Nd centres.

The field of supramolecular chemistry has undergone a veritable explosion of activity opening up a wide diversity of themes and applications.¹ A particularly interesting topic within this field is the use of the 'self-assembly' process for the formation of, for example, macrocycles, catenanes and cages and the range of approaches for achieving these objectives has very recently been reviewed.² We have shown that a particularly versatile ligand for forming such materials is *N,N'*-*p*-phenylenedimethylenebis(pyridin-4-one) (**I**, *p*-XBP4). It has the ability to form interwoven metallomacrocyclic networks^{3,4} and also to bring pairs of metal ions into close proximity within these arrays by forming μ -O atom bridges.³ Further studies with **I** have produced an extensive range of lanthanide (Ln) compounds with unusual stoichiometries;⁵ examples include $\text{Ln}_4(\textit{p}\text{-XBP4})_7(\text{NO}_3)_{12}\cdot 4\text{H}_2\text{O}$ (Ln = La–Eu), $\text{Ln}_2(\textit{p}\text{-XBP4})_3(\text{NO}_3)_6\cdot 2\text{H}_2\text{O}$ (Ln = Gd–Yb) and $\text{Ln}_2(\textit{p}\text{-XBP4})_7(\text{ClO}_4)_6\cdot 7\text{H}_2\text{O}$ (Ln = La, Nd, Sm, Gd). In view of our previous observations of the propensity for **I** to generate novel structures with transition-metal ions, the non-integral stoichiometries of the lanthanide compounds pointed to the formation of yet further types of framework arrays. Full X-ray characterisation of most of these compounds has been hindered by their formation only as poorly crystalline powders. However X-ray quality crystals have been obtained for $\text{Nd}_2(\textit{p}\text{-XBP4})_7(\text{ClO}_4)_6\cdot 7\text{H}_2\text{O}$ **I**,[†] and the structural study[‡] of this reveals not only a particularly novel framework array but also a new type of networking role for **I**.

This analysis reveals that each neodymium atom is eight coordinate (Fig. 1) being bound to one oxygen atom from each of six different *p*-XBP4 ligands [Nd–O in the range 2.373(4)–2.433(4) Å] and to two aqua ligands with Nd–O(aqua) distances of 2.551(4) and 2.639(4) Å. The coordination geometry around each neodymium atom is essentially bicapped trigonal prismatic with O(21) and O(91) as the capping atoms. There are four different *p*-XBP4 ligand geometries (A, B, C and D)[§] in the structure, and, although all the *p*-XBP4 ligands act as bridges, they do so in three quite different ways.

Pairs of adjacent neodymium centres are directly bridged by four *p*-XBP4 ligands, two each of types A and B (shown in red in Fig. 2), forming a 'pumpkin'- or 'lantern'-like oblate spheroidal 'box', with a Nd...Nd separation of 11.9 Å and with distances between the centroids of the opposite pairs of *p*-C₆H₄ rings of ca. 14 Å, thereby producing an effective cage volume

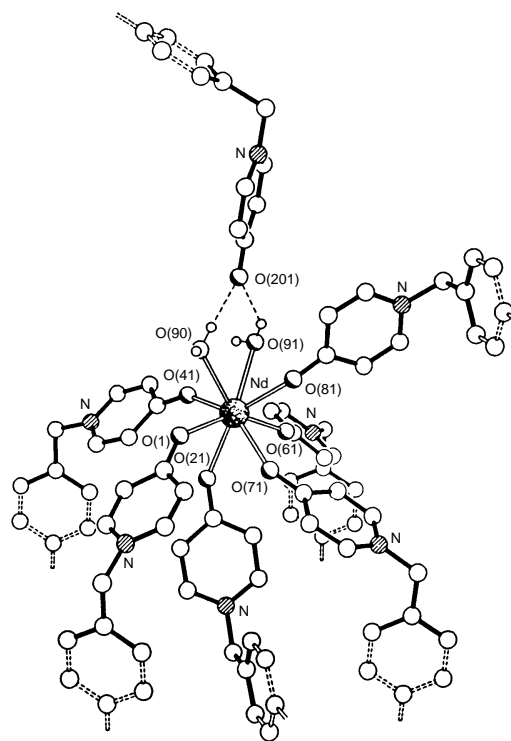
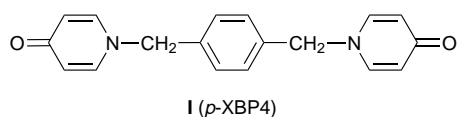


Fig. 1 The neodymium coordination environment in **1** showing also the hydrogen bonding of part of a D-type *p*-XBP4 molecule to the aqua ligands

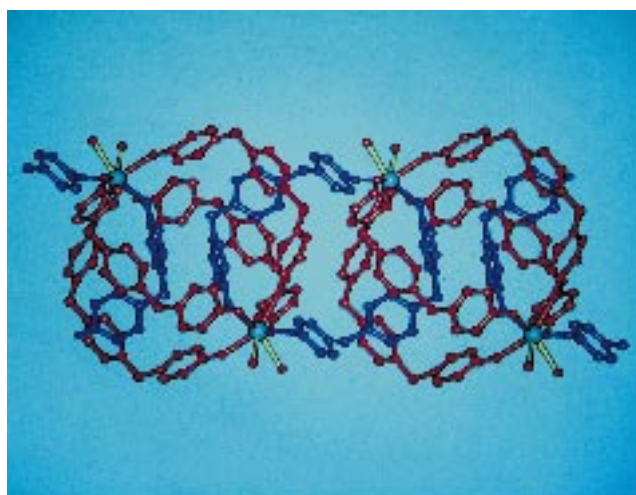


Fig. 2 Part of one of the covalently linked chains of 'lanterns' formed by **1** in the solid state. Ligands of types A and B are shown in red and the interpenetrating C-type linkages are shown in blue.

of ca. 1260 Å³. The 'surfaces' of these globular lanterns comprise sets of 34-membered metalocycles which are sufficiently large to permit the interweaving capability of **1** to operate. Pairs of type C ligands (shown in blue in Fig. 2) are initially directed into the central cavity but then fold and pass through the centres of the rings that form the opposite lantern faces and, by interpenetrating adjacent lanterns, form a further set of 34-membered macrocycles and link them into chains.

Pyridinone rings from the type C ligands form π - π stacked pairs within the central cavity of each lantern (Fig. 2) (mean interplanar separation of 3.37 Å and centroid-centroid distance of 3.66 Å). There is a further strong π - π interaction between pairs of pyridinone rings of type B ligands of adjacent lanterns (mean interplanar separation of 3.34 Å and centroid-centroid distance of 3.73 Å).

The solid-state structure of **1** also reveals a further type of bridging role for the *p*-XBP4 molecule not seen hitherto. The chains of lanterns are connected into sheets by cross-struts comprising non-coordinated *p*-XBP4 molecules of type D *via* strong hydrogen bonds between each of the carbonyl oxygen atoms and the pairs of aqua ligands bonded to each neodymium centre (Fig. 3).¶ The resulting voids within each sheet, *i.e.* between the D-type molecules, are occupied by the perchlorate ions, water molecules of solvation and the lantern-like spheruloids of offset adjacent sheets.

The 'superstructure' described above demonstrates the ability of the *p*-XBP4 molecule to act, not only as a unit for the

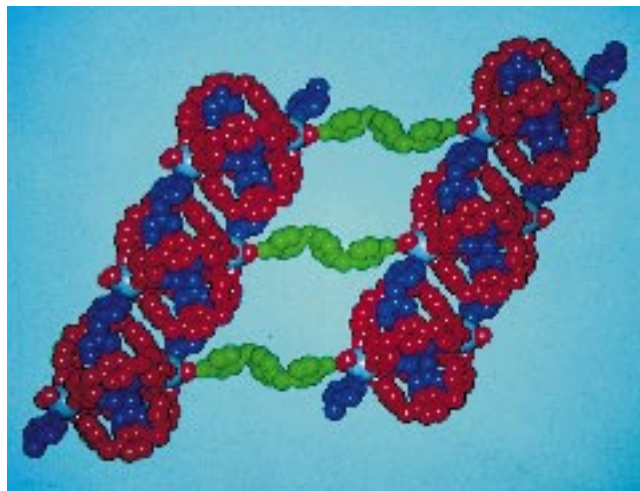


Fig. 3 The linking of adjacent chains *via* hydrogen bonds from the aqua ligands to D-type *p*-XBP4 molecules (shown in green)

self-assembly of complex networks by virtue of its versatile ligand coordination behaviour, but also as an efficient hydrogen-bonding acceptor, thereby extending its crystal engineering potential.

We thank the EPSRC for a Research Studentship (to A. M. S.), the BBSRC for a postdoctoral fellowship (to S. M.) and the Wolfson Foundation for equipment.

Footnotes

† Pale mauve crystals of **1** were obtained in 43% yield by slow (2 weeks) evaporation of a solution of Nd(ClO₄)₃·6H₂O (0.04 mmol) and **1**·4H₂O (0.2 mmol) in a mixture of methanol (6 cm³), acetonitrile (4 cm³) and water (1 cm³). Satisfactory analyses were obtained.

‡ *Crystal data*: C₆₃H₆₃Cl₃N₇NdO_{22.5} **1**, crystal dimensions 0.10 × 0.16 × 0.17 mm, triclinic, space group *P* $\bar{1}$, *a* = 14.083(2), *b* = 15.754(2), *c* = 17.519(2) Å, α = 67.01(1), β = 73.51(1), γ = 69.08(1)°, *U* = 3294.8(6) Å³, *Z* = 2, *M* = 1528.8, *D_c* = 1.541 g cm⁻³, λ = 0.71073 Å, μ (Mo-K α) = 0.993 mm⁻¹, *T* = 293 K, Siemens P4/PC diffractometer, graphite-monochromated Mo-K α radiation, ω scans. The structure was solved by the heavy-atom method and was refined anisotropically, on *F*² data, using the SHELXTL program package (version 5.03)⁶ to *R*₁ = 0.0454, *wR*₂ = 0.1168 for 7016 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], 2θ = 3.5–45.0°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/351.

§ In type A ligands, the pyridinone rings have a skewed open-book conformation with respect to the central *p*-C₆H₄ rings, whereas in type B the geometry is closer to orthogonal. The type C ligands have their pyridinone rings oriented so that one is essentially orthogonal to the central *p*-C₆H₄ ring whilst the other is in an open-book conformation. Type D molecules have their pyridinone rings in an *anti* open-book arrangement.

¶ The O(aqua)⋯O(*p*-XBP4) distances are 2.65 and 2.70 Å and the O⋯O(*p*-XBP4)⋯O angle [O(90)⋯O(201)⋯O(91)] is 67.6°, with associated H⋯O and O-H⋯O distances and angles of 1.76 Å, 174° and 1.92 Å, 144° respectively.

References

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Received, 15th November 1996; Com. 6/07764A