

A closed molecular cube and an open book: two different products from assembly of the same metal salt and bridging ligand

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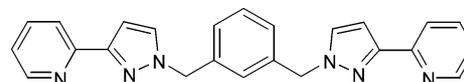
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Reaction of the bis-bidentate bridging ligand L^1 with $\text{Co}(\text{ClO}_4)_2$ or $\text{Zn}(\text{BF}_4)_2$ affords a mixture of complexes $[\text{M}_8(\text{L}^1)_{12}]\text{X}_{16}$ and $[\text{M}_6(\text{L}^1)_9]\text{X}_{12}$ having the same metal : ligand ratio: the former is a molecular cube with a metal ion at each vertex and a bridging ligand spanning each edge, whereas the latter has a metal framework like that of an 'open book' containing cross-linked double helical metal–ligand subunits.

In the general area of metallocsupramolecular chemistry, three-dimensional coordination cages have achieved particular prominence recently due to (i) their elegant and appealing polyhedral structures, (ii) the insights they provide into how careful control of ligand structure and metal type can be used as a powerful synthetic tool to give elaborate structures from simple components structures, and (iii) for the host–guest chemistry associated with their central cavities.^{1,2} In many cases the cages appear to be robust structures which form as the unique product from a particular combination of metal and ligand. In other cases, however, two or more different structural forms based on the same components can arise having the same metal : ligand ratio; these may be in equilibrium (a 'dynamic combinatorial library'), or can be interconverted by guest-induced interactions which favour one form of the assembly over another.^{3–7} Thus, Lehn and co-workers demonstrated how a linear trinuclear triple helicate M_3L_3 could be converted to a cyclic pentanuclear helicate M_5L_5 in the presence of a templating chloride ion.³ In the field of three-dimensional cages, Raymond *et al.* and Albrecht *et al.* have demonstrated how tetrahedral cage complexes can form in the presence of a suitable guest which matched the tetrahedral cavity; in the absence of the template, other simpler species were formed.⁴ In each of these examples the metal : ligand ratio is necessarily the same between the different self-assembled forms. In other cases, different sizes of cage complexes,⁵ and cyclic helicates,⁶ and molecular grids⁷ are in dynamic equilibrium with one another in solution.

We describe here how a simple bis-bidentate bridging ligand L^1 , containing two pyrazolyl-pyridine termini, reacts with $\text{Co}(\text{II})$ or $\text{Zn}(\text{II})$ to form a mixture of two types of polynuclear complex with the same metal : ligand ratio: an $[\text{M}_8(\text{L}^1)_{12}]^{16+}$ cage with a cubic topology, and an $[\text{M}_6(\text{L}^1)_9]^{12+}$ open-framework structure. The structures are unusual in their own right, but the appearance of both types in the same reaction illustrates how the same 'instructions' provided by the ligands and metal ions can be interpreted in two quite different ways. We have shown recently

that ligands of this type, with four donors, react with six-coordinate M^{2+} ions to afford a range of structures based on a $2\text{M} : 3\text{L}$ ratio,^{8–11} with cages varying in size from an M_4L_6 tetrahedron⁸ to an $\text{M}_{16}\text{L}_{24}$ tetra-capped truncated tetrahedron.⁹ The $2\text{M} : 3\text{L}$ ratio is necessary to match the number of donors provided by the ligands with the number of coordination sites available at the metal ions, and all members of this series described so far are based on a metal polyhedron in which there is a vertex : edge ratio of 2 : 3, such that a metal ion occupies each vertex and a bridging ligand spans each edge.



L^1 (above) was prepared by reaction of 3-(2-pyridyl)pyrazole with 1,3-bis(bromomethyl)benzene according to a standard procedure.^{8–12} Reaction of L^1 with $\text{Co}(\text{ClO}_4)_2$ in MeNO_2 afforded a pink solution, whose ES mass spectrum showed peaks at m/z 1555.1, 1226.9, 1144.6, 1007.8, 898.2, 734.0 and 617.7. These do not fit to a single product, but can be separated into two distinct sequences. Peaks at m/z 1555.1, 1226.9, 1007.8 and 734.0 can be assigned to $[\text{Co}_8(\text{L}^1)_{12}(\text{ClO}_4)_{16-x}]^{x+}$ ($x = 4, 5, 6, 8$), all arising from the same octanuclear complex core but with different numbers of counter-ions. Peaks at 1555.1, 1144.6, 898.2, 734.0 and 617.7 in contrast can be assigned to $[\text{Co}_6(\text{L}^1)_9(\text{ClO}_4)_{12-x}]^{x+}$ ($x = 3, 4, 5, 6, 7$), arising from a hexanuclear complex but with the same $\text{Co} : \text{L}^1$ ratio. Clearly, there are some peaks in common between the two species: m/z 1555.1 could arise from either $[\text{Co}_8(\text{L}^1)_{12}(\text{ClO}_4)_{12}]^{4+}$ or $[\text{Co}_6(\text{L}^1)_9(\text{ClO}_4)_9]^{3+}$ (or both), and m/z 734.0 could arise from either $[\text{Co}_8(\text{L}^1)_{12}(\text{ClO}_4)_8]^{8+}$ or $[\text{Co}_6(\text{L}^1)_9(\text{ClO}_4)_6]^{6+}$ (or both). However the remaining members of each series are unambiguous and confirm formation of two distinct polynuclear assemblies. Exactly comparable results were obtained from reaction of L^1 with $\text{Zn}(\text{BF}_4)_2$ in a 3 : 2 ratio in MeCN ; ESMS of the resulting solution showed sequences of peaks arising from both $[\text{Zn}_8(\text{L}^1)_{12}(\text{BF}_4)_{16-x}]^{x+}$ ($x = 4, 5, 6, 8$) and $[\text{Zn}_6(\text{L}^1)_9(\text{BF}_4)_{12-x}]^{x+}$ ($x = 3, 4, 5, 6, 7$).

Slow diffusion of diethyl ether vapour into the product solutions afforded a mixture of small crystals in each case; fortuitously, it turned out that the best crystal from each batch corresponded to a different component of the mixture (see Fig. 1 and 2). \ddagger $[\text{Zn}_8(\text{L}^1)_{12}][\text{BF}_4]_{16} \cdot 20\text{MeCN} \cdot \text{Et}_2\text{O}$ (Fig. 1) is an approximate cube with a metal ion at each vertex and a bridging ligand along each edge, affording the necessary metal : ligand ratio of 2 : 3. The $\text{Zn} \cdots \text{Zn}$ distances are in the range 9.72 to 10.27 Å, averaging 9.96 Å; the cube is slightly slanted, with angles at the corners in the range 76.2–103.7°. $\text{Zn}(1)–\text{Zn}(4)$ all have the same optical configuration, with their symmetry-equivalent partners generated by an inversion centre; the cube is accordingly achiral. Also $\text{Zn}(2)$, $\text{Zn}(3)$, $\text{Zn}(4)$ have a *mer* tris-chelate geometry whereas $\text{Zn}(1)$ has a

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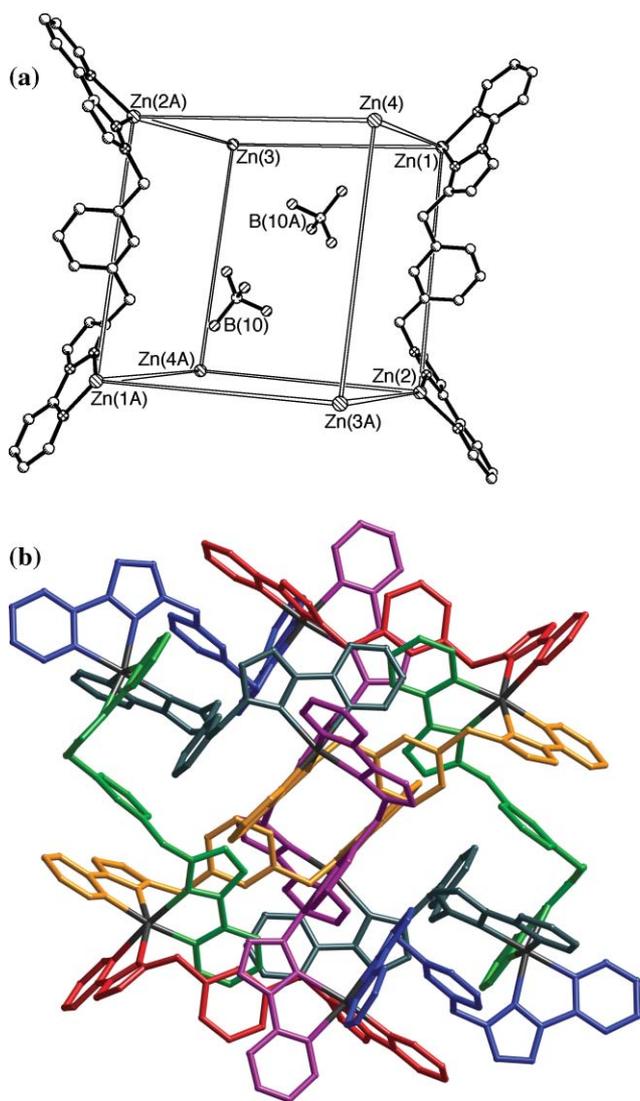


Fig. 1 Two views of the structure of the metal complex framework of $[\text{Zn}_8(\text{L}^1)_{12}][\text{BF}_4]_{16} \cdot 20\text{MeCN} \cdot \text{Et}_2\text{O}$. Top: the near-cubic array of metal ions, two of the edge-bridging ligands, and the two anions in the central cavity. Bottom: the whole metal–ligand assembly, with symmetry-equivalent ligands coloured the same.

fac geometry. This results in a (non-crystallographic) S_6 axis along the long diagonal of the cube, joining Zn(1) and Zn(1A). The central cavity contains two (symmetry-related) $[\text{BF}_4]^-$ anions. Extensive aromatic π -stacking between parallel, overlapping sections of ligands around the periphery of the complex is clear. There are a few other examples of molecular cubes in the literature, prepared using a range of different design principles;^{11,13} this one is similar to an example we described recently based on a related bridging ligand.¹¹ The relatively low symmetry of the cube (two independent ligand environments) means that ^1H spectra were uninformative due to numerous overlapping signals in the aromatic region. ^{11}B NMR spectra gave only one signal for the $[\text{BF}_4]^-$ anions, indicative of either fast exchange of internal/external anions through the cube faces, or interconversion of the closed cube with more open structures in solution.

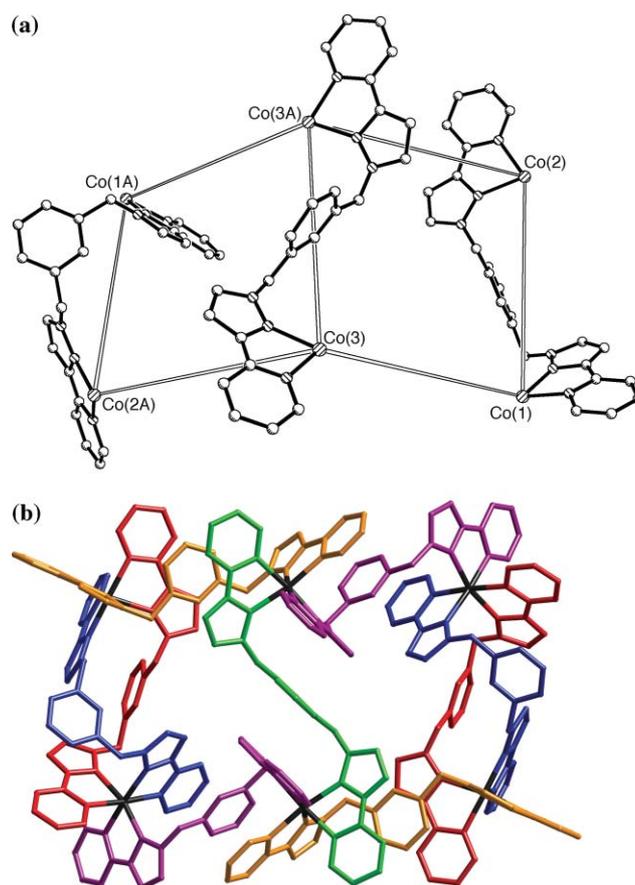


Fig. 2 Two views of the structure of the metal complex framework of $[\text{Co}_6(\text{L}^1)_9][\text{ClO}_4]_{12} \cdot (\text{CH}_3\text{NO}_2)_{9.5}$ (only one independent complex is shown). Top: the 'open-book' array of metal ions, and three of the edge-bridging ligands. Bottom: the whole metal–ligand assembly, with symmetry-equivalent ligands coloured the same.

In contrast, $[\text{Co}_6(\text{L}^1)_9][\text{ClO}_4]_{12} \cdot (\text{CH}_3\text{NO}_2)_{9.5}$ has an unusual open framework structure based on an array of Co(II) centres (Fig. 2) consisting of two squares that share an edge.

The array is folded about the central two Co(II) ions, like a book that is not completely open, with a Co(II) ion at each corner and two at either end of the central spine. The 2 : 3 metal : ligand ratio requires nine ligands; there are two spanning each of the terminal pairs of Co(II) ions (the opposed open edges of the book—red and blue ligands in the figure) in a double helical arrangement, with all remaining Co–Co vectors (from each corner of the book to the spine, and along the spine) having one bridging ligand. The two double helical sections are homochiral as they are related by a C_2 rotation through the centre of the complex. The Co...Co separations lie in the range 9.66–9.97 Å (average 9.79 Å), with the Co–Co–Co angle at the spine (*i.e.* the extent of folding) being 119° . Co(2) and Co(3) have the same optical configuration as each other, and a *fac* tris-chelate geometry, with Co(1) having the opposite optical configuration and a *mer* tris-chelate geometry. There are numerous regions of aromatic π -stacking between near-parallel, overlapping sections of different ligands (*e.g.* red/orange/green, purple/green/purple and blue/purple/yellow triple stacks, and red/blue and blue/purple stacks between pairs of ligand sections,

using the colour scheme in Fig. 2). This type of open-framework structure is unprecedented in our investigations with this series of ligands.

This pair of complexes represents an unusual example of how a single combination of a metal salt and a ligand can follow two quite different self-assembly pathways to give a mixture of different products which nevertheless obey the same basic stoichiometric principle of having a 2M : 3L ratio. Whether they are in dynamic equilibrium in solution is not clear as we have not yet been able to isolate enough of one type of crystal completely pure to see if it establishes an equilibrium with the other form in solution; the two crystal types are intimately mixed following crystallisation. This suggests in itself, however, that the closed cage and open framework species are very similar in energy.

Acknowledgements

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Notes and references

† A mixture of 1,3-bis(bromomethyl)benzene (1.20 g, 4.55 mmol), 3-(2-pyridyl)pyrazole (1.35 g, 9.32 mmol), aqueous NaOH (10 M, 20 cm³), toluene (50 cm³) and Bu₄NOH (40% aqueous solution, 3 drops) was stirred vigorously at room temperature for 40 min. The mixture was diluted with H₂O (100 cm³) and the organic layer separated, dried over MgSO₄ and concentrated before purification using an alumina column (5% THF/dichloromethane) to give L¹ as a yellow oil (Yield: 1.48 g, 83%). ¹H-NMR (270 MHz, CDCl₃): δ 8.61 (2H, ddd, *J* 4.8, 1.8, 0.9; pyridyl H⁶), 7.90 (2H, d, *J* 7.9; pyridyl H⁵), 7.68 (2H, td, *J* 7.6, 1.8; pyridyl H⁴), 7.39 (2H, d, *J* 2.4; pyrazolyl H⁵), 7.21–6.98 (6H, m, 5:1, 4; pyridyl H³ and 4 × phenyl), 6.89 (2H, d, *J* 2.4; pyrazolyl H⁴), 5.35 (4H, s, CH₂). EIMS *m/z* 392 (*M*⁺). Found: C, 73.0; H, 5.1; N, 20.9%. Required for C₂₄H₂₀N₆: C, 73.4; H, 5.1; N, 21.4%.

‡ Elemental analyses were performed on samples of the crystalline materials that were dried *in vacuo* to remove lattice solvent. The results indicated some uptake of atmospheric water after drying. For [Zn₈(L¹)₁₂][BF₄]₁₆·5H₂O: found C, 51.5; H, 3.8; N, 14.5. Required for C₃₈₈H₂₄₀B₁₆F₆₄N₇₂Zn₈·5H₂O: C, 51.4; H, 3.8; N, 15.0%. For [Co₆(L¹)₉][ClO₄]₁₂·3H₂O: found C, 50.2; H, 3.5; N, 15.0. Required for C₂₁₆H₁₈₀Cl₁₂Co₆N₅₄O₄₈·3H₂O: C, 50.5; H, 3.7; N, 14.7%.

§ Crystallography. A crystal of [Zn₈(L¹)₁₂][BF₄]₁₆·20MeCN·Et₂O (0.33 × 0.20 × 0.15 mm) was mounted on a Bruker-AXS SMART-1000 diffractometer at 150 K. Formula: C₃₃₁H₃₀₂B₁₆F₆₄N₉₂O₂Zn₈; formula weight 7512.6; triclinic, *P*-1; *a* = 19.440(3), *b* = 21.855(4), *c* = 23.828(4) Å; *a* = 106.286(3), *β* = 105.450(3), *γ* = 107.424(3)°; *V* = 8566(3) Å³; *Z* = 1; *ρ* = 1.456 g cm⁻³; *μ*(Mo-Kα) = 0.655 mm⁻¹; *λ* = 0.71073 Å. 30121 unique data were collected; refinement of 1538 parameters with 34 restraints converged at *R*₁ = 0.0896 [selected data with *I* > 2σ(*I*)], *wR*₂ = 0.2651 (all data). The asymmetric unit contains one half of the complex molecule adjacent to an inversion centre. A crystal of [Co₆(L¹)₉][ClO₄]₁₂·(CH₃NO₂)_{9.5} (0.50 × 0.25 × 0.18 mm) was mounted on a Bruker-AXS SMART-1000 diffractometer at 100 K. Formula: C₄₅₁H₄₁₇Cl₁₂Co₆N₁₂₇O₁₂₂; formula weight 11019.7; monoclinic, *P*2₁/*n*; *a* = 29.108(5), *b* = 26.238(4), *c* = 37.671(6) Å; *β* = 91.369(4)°; *V* = 28762(8) Å³; *Z* = 2; *ρ* = 1.272 g cm⁻³; *μ*(Mo-Kα) = 0.516 mm⁻¹; *λ* = 0.71073 Å. 65214 unique data were collected; refinement of 1052 parameters with 1549 restraints converged at *R*₁ = 0.1519 [selected data with *I* > 2σ(*I*)], *wR*₂ = 0.2682 (all data). The asymmetric unit contains two independent half-molecules astride *C*₂ axes. Both sets of crystals diffracted very poorly due to a combination of immediate solvent loss on removal from the mother liquor and extensive disorder of counter-ions and lattice solvent molecules. Extensive use of restraints was necessary to keep the geometries of anions and lattice solvent molecules reasonable. For [Co₆(L¹)₉][ClO₄]₁₂·(CH₃NO₂)_{9.5} a 'SQUEEZE'

function was applied to remove areas of diffuse electron density which could not be modelled. Consequently only 21 of the expected 24 counterions could be located, which is reflected in the molecular formula and formula mass given above. Only the metal atoms could be refined anisotropically. In both cases however the structure of the metal/ligand assembly is clearly defined, although detailed analysis of metal–ligand bond distances *etc.* is not appropriate. CCDC reference numbers 287971 and 287972. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515296h.

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