

A cyclic supramolecular complex containing eight metal ions, twelve bridging ligands, and an anion encapsulated in the central cavity

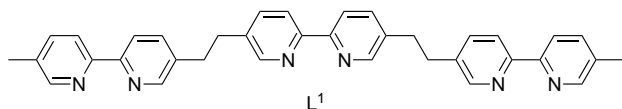
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Reaction of the bis-bidentate ligand bis{3-(2-pyridyl)pyrazol-1-yl}dihydroborate (L^-) with cobalt(II) or nickel(II) salts results in formation of complexes $[M_8L_{12}X]X_3$ ($X = ClO_4, PF_6$), which have a cyclic structure with one anion encapsulated in the central cavity.

The assembly of structurally sophisticated, high-nuclearity coordination complexes from the reactions of relatively simple ligands with suitable metal ions is a burgeoning field. The principles of molecular recognition between components, and how the steric information contained in the number/orientation of ligand binding sites and the stereoelectronic preferences of the metal ion combine to give the final structure, are becoming better understood.¹

In some systems there is only one optimal structure for the supramolecular species defined by a particular metal/ligand combination. Such systems are exemplified by Lehn's molecular grids² and molecular cylinders:³ there is only one way in which the twin conditions (*i*) all of the ligand binding sites being occupied, and (*ii*) all of the metal ions being coordinated in their preferred coordination environment, can be fulfilled. In contrast in other systems a wide variety of stoichiometries and therefore structures are possible, all of which can fulfil the above requirements. These systems are exemplified by Lehn's molecular rings.^{4,5} For example the ligand L^1 has three bidentate chelating binding sites with flexible spacers between them. Coordination to metal ions having a preference for six coordination gave various complexes with a 1:1 metal:ligand stoichiometry but with very different structures: notably the triple helicate $[Ni_3(L^1)_3]^{6+}$ and the molecular ring $[Fe_5(L^1)_5Cl]^{9+}$, which contains a chloride ion tightly bound in the cavity at the centre of the ring.⁵



We describe here the preparation and characterisation of complexes of bis{3-(2-pyridyl)pyrazol-1-yl}dihydroborate (L^-) with Ni^{2+} and Co^{2+} which are octanuclear molecular rings containing encapsulated anions. The ligand L^- was prepared[†] as its potassium salt in high yield by reaction of 3-(2-pyridyl)pyrazole with KBH_4 .⁶ Since it contains two bidentate compartments linked by a flexible spacer, it could act as a tetradentate chelate to one large metal ion, or act as a bridge in oligonuclear species.⁷ With Ni^{II} and Co^{II} , both of which prefer pseudo-octahedral tris-chelate coordination, a 2:3 metal: L^- stoichiometry is likely in the absence of other ligands.

Reaction of KL with $Co(O_2CMe)_2 \cdot 4H_2O$ (1:1 ratio) in MeOH afforded a red-brown solution from which a solid precipitated on addition of KPF_6 . Analytical data suggested the empirical formulation $[Co_2L_3][PF_6]$. A material analysing as $[Ni_2L_3][PF_6]$ was similarly prepared from KL and $Ni(NO_3)_2 \cdot 6H_2O$ in MeOH followed by precipitation with KPF_6 . The yields of these were subsequently optimised (50–60%) by

use of a 2:3 metal:ligand ratio in the preparation. Examination of both complexes by electrospray (ES) mass spectrometry (MeCN; 5 V cone voltage) showed a strong peak at m/z 1410 in each case. These correspond to the species $[Co_8L_{12}(PF_6)]^{3+}$ (calc. for most abundant peak: 1409.7) and $[Ni_8L_{12}(PF_6)]^{3+}$ (calc. for most abundant peak: 1409.0); no other reasonable combination of metal, ligand, counter ion and charge corresponds to these values, and the +3 charge was confirmed by the $\frac{1}{3}$ -integral spacing between isotopic components of the peaks. Numerous fragmentation peaks were also observed. The highest mass peaks indicate in both cases formation of a $\{M_8L_{12}\}$ species which is associated with one anion; no anion-free peaks corresponding to $[M_8L_{12}]^{4+}$ were observed. Exactly similar behaviour was observed for $[Fe_5(L^1)_5Cl]^{9+}$, where loss of chloride was never observed by ESMS.⁵

This result suggested that a $\{M_8L_{12}\}$ molecular ring may have formed, containing one tightly bound anion in the central cavity. Accordingly we attempted to crystallise these complexes, but crystals of the hexafluorophosphate salts could not be obtained. The cobalt(II) complex was therefore re-prepared as the perchlorate salt, $\{[Co_2L_3][ClO_4]\}_n$. After several attempts small crystals were grown from MeCN–diethyl ether which were just suitable for X-ray diffraction, and a partial structural determination showed the complex to be $[Co_8L_{12}(ClO_4)][ClO_4]_3$ in agreement with the ESMS data.[‡] Despite the poor quality of the data the gross structure of the complex cation is quite clear (Fig. 1), consisting of a $\{Co_8L_{12}\}$ ring with a perchlorate ion in the central cavity, and bears obvious similarities to Lehn's $[Fe_5(L^1)_5Cl]^{9+}$ complex. Each ligand L acts as a bridge between two adjacent metal ions, with an alternating pattern of one and then two bridging ligands

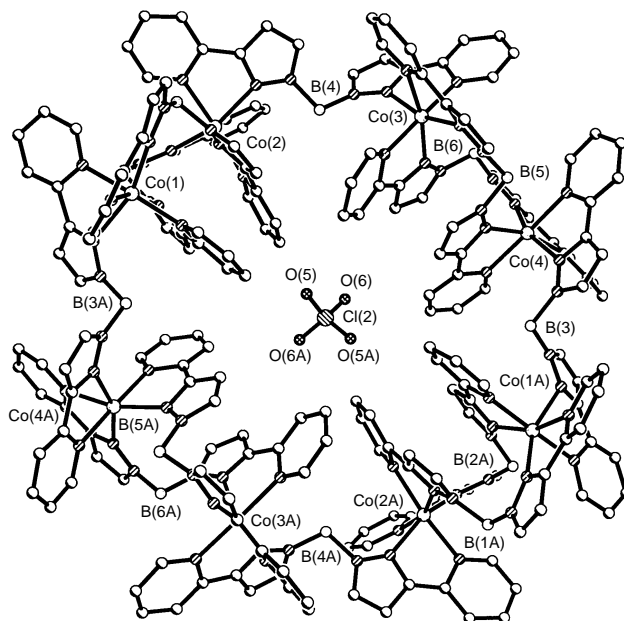


Fig. 1 Crystal structure of the $[Co_8L_{12}(ClO_4)]^{3+}$ cation

between each adjacent pair of metals (see Fig. 2). Each metal is six-coordinated by three bidentate chelating fragments, each from a different ligand, and all ligand binding sites are used. The complex cation lies astride a twofold axis which is perpendicular to the plane of the ring and passes through the Cl atom of the encapsulated perchlorate anion; it is chiral, with all eight metal centres having the same absolute chirality (Δ in the figure) and is therefore a helical ring.

Attempts to examine the solution properties of $[\text{Co}_8\text{L}_{12}(\text{ClO}_4)](\text{ClO}_4)_3$ by NMR spectroscopy were not very successful. Although ^1H NMR spectra of high-spin cobalt(II) complexes can give useful structural information,⁸ the ^1H NMR spectrum of $[\text{Co}_8\text{L}_{12}(\text{ClO}_4)](\text{ClO}_4)_3$ in CD_3CN was broadened to the point where individual signals were not detectable. ^{31}P and ^{19}F NMR spectra of $[\text{Ni}_8\text{L}_{12}][\text{PF}_6]_4$ showed only one signal in each case at the same position observed for NH_4PF_6 . If one anion remained in the ring and did not exchange in the NMR timescale, then two resonances in a 3:1 ratio would be expected; if the ring were intact but exchange of the anion fast, a single shifted signal would be seen. These observations suggest that the kinetic lability of the metal centres results in dissociation of the ring in solution, and that its formation with the encapsulated anion occurs during crystallisation (or at least evaporation of the solvent, as in ESMS).

The formation of this structure raises an important question: does the central anion (perchlorate or hexafluorophosphate) act as a template to control the size of the ring by dictating the assembly pathway, or is the ring a particularly stable structure which forms on its own and then subsequently traps whatever appropriately sized guest can be found in the reaction medium? In the former case the use of a different templating anion could lead to the assembly of a differently sized ring (at least in the solid state); in the latter case, formation of a particular ring size means that a size-specific host is formed which could be of use in, for example, selective extraction or recognition of anions. We note that poly(guanidinium) strands can assemble around templating sulfate anions to give double helicates,⁹ and that other examples of molecular recognition of small guest species by cyclic coordination complexes having large central cavities are known.¹⁰

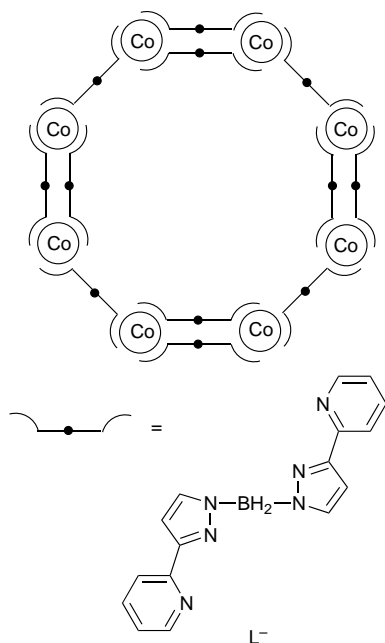


Fig. 2 Schematic drawing of the octanuclear ring showing the alternating disposition of bridging ligands along the edges

We thank the EPSRC and Unilever Research for financial support, and Mr C. Carraz and Dr J. Fleming for the NMR experiments.

Footnotes

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† Potassium bis[3-(2-pyridyl)pyrazolyl]dihydroborate KL. A mixture of 3-(2-pyridyl)pyrazole (3.50 g, 24.1 mmol) and KBH_4 (0.49 g, 9.0 mmol) was ground together finely with a mortar and pestle and then gradually heated to 150°C . Melting occurred at ca. 120°C , at which point evolution of H_2 commenced. The temperature was maintained at 150°C for 30 min, after which time H_2 evolution had ceased. The solid white mixture was cooled and 100 cm^3 of warm toluene was added. The suspension was stirred vigorously overnight to allow the excess unreacted 3-(2-pyridyl)pyrazole to dissolve. The product was filtered off as a white solid, which was washed further with several portions of toluene and then hexane, and dried. Yield of KL: 2.48 g (81%). Negative-ion FAB MS: m/z 301 $[\text{L}^-]$. Satisfactory analytical and ^1H NMR data were obtained.

‡ *Crystallographic details.* $[\text{Co}_8\text{L}_{12}(\text{ClO}_4)](\text{ClO}_4)_3 \cdot n(\text{disordered solvent})$, small orange blocks grown from MeCN–diethyl ether. A crystal of dimensions $0.1 \times 0.1 \times 0.05\text{ mm}$ was mounted on a Siemens SMART diffractometer under a stream of N_2 at -100°C . Orthorhombic, space group *Pbcn*; $a = 31.89(2)$, $b = 18.719(4)$, $c = 41.11(1)\text{ \AA}$; $U = 24\,540(27)\text{ \AA}^3$; $Z = 4$; $\mu = 0.72\text{ mm}^{-1}$. 108 409 reflections were measured with $2\theta_{\text{max}} = 46.5^\circ$; after merging these gave 17 602 unique data with $R(\text{sigma}) = 0.223$. Many factors combined to make this a poor structure. The crystals were small and diffracted weakly; they lost solvent instantly on removal from the mother-liquor and decomposed partially during the transfer to the diffractometer, even when coated with paraffin oil saturated with the recrystallisation solvent mixture; there was substantial disorder in the free counter ions and the large number of lattice solvent molecules; the number of parameters was large (174 non-hydrogen atoms in the asymmetric unit). The lattice solvents were best approximated as four MeCN and two Et_2O molecules per asymmetric unit (*i.e.* eight MeCN and four Et_2O per $\{\text{Co}_8\text{L}_{12}(\text{ClO}_4)\}^{3+}$ unit). The best level of refinement achievable so far was $R_1 = 0.19$, goodness-of-fit 1.233. Consequently the full structural details are not of publishable quality, and it is not possible to extract precise bond lengths and angles. However the complex cation is sufficiently well defined to be quite certain about its gross structure.

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Received in Basel, Switzerland, 19th February 1997; 7/01192J