Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100750. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Anion-Templated Assembly of a Supramolecular Cage Complex[**]

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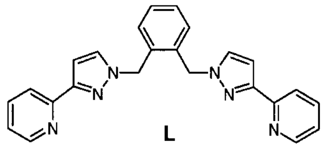
A current goal in supramolecular coordination chemistry is to understand how the self-assembly process between labile metal ions and flexible multidentate ligands is controlled.[1–11] In some cases the course of self-assembly may be controlled by using relatively rigid ligands, in which the symmetry of the arrangement of binding sites dictates only one possible outcome for the self-assembly process with a metal ion of a given stereoelectronic preference; this approach is exemplified by numerous "molecular grids",[2] and by some tetrahedral complexes prepared by Saalfrank et al.[3] and Raymond et al.[4] In other cases two or more different structures can arise from a single metal/ligand combination in which all components have the same stoichiometry (a "virtual combinatorial library" according to Lehn).[5–7] The nature of the product in such cases is thus often impossible to predict and can depend on subtle factors such as interligand stacking interactions[8] and the participation of noncovalently bonded anions[7, 9, 11] or cations[3, 10] in the resultant assembly.

We describe here complexes of the new ligand L, which contains two bidentate pyrazolyl–pyridine binding sites separated by an *o*-xylyl spacer. The complexes are $[Co_4L_6][BF_4]_8$ (**1**) and $[Ni_2L_3][BF_4]_4$ (**2**), which have the same metal-to-ligand stoichiometry but surprisingly different structures given the very similar properties of the metal ions (size, charge, and preference for octahedral coordination).


L

The ligand L was simply prepared from reaction of 3-(2-pyridyl)pyrazole with 1,2-bis(bromomethyl)benzene.[12] Given that it has four donor atoms an M_2L_3 stoichiometry seemed likely to occur with Co^{II} and Ni^{II}. A material analyzing as $[Co_2L_3][BF_4]_4$ was easily prepared,[13] but the FAB mass spectrum (Figure 1) clearly indicated formation of a Co_4L_6 species, associated with varying numbers of $[BF_4]^-$ anions. The

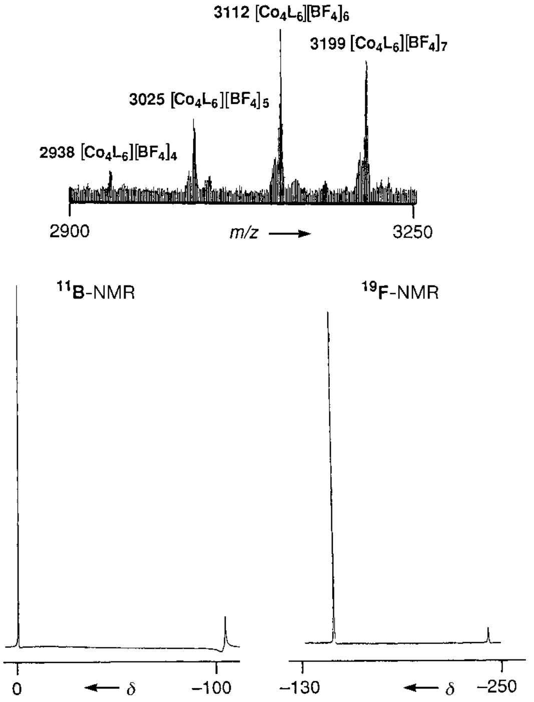


Figure 1. Top: part of the FAB mass spectrum (3-nitrobenzyl alcohol matrix) of **1**. Bottom: ^{11}B and ^{19}F NMR spectra of **1** (MeCN, room temperature): ^{11}B shifts vs. $BF_3(Et_2O)$, ^{19}F shifts vs. $CFCl_3$.

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crystal structure of **1** (Figures 2 and 3) showed it to be a tetrahedral complex in which each metal ion occupies the vertex of a tetrahedron, and each ligand, acting as a bridge between two metal ions, spans one edge of the tetrahedron.[14] Multiple π-stacking interaction between ligands is evident (Figure 2). Each Co^{II} ion is therefore pseudo-octahedrally coordinated by one bidentate arm from each of three separate ligands. The Co–N bond distances lie in the range 2.11–2.21 Å (average 2.151 Å), typical for high-spin Co^{II}. There is no imposed symmetry within each complex unit, and the Co⋯Co separations (all different) are between 8.98 and 10.07 Å. This adamantoid topology is identical to that observed in other complexes where six bridging ligands containing two bidentate compartments span the edges of a tetrahedron of metal ions.[3, 4] Complex **1** has a charge of +8 and has eight $[BF_4]^-$ anions associated with the complex cation, of which one is contained in the tetrahedral cavity. Although the $[BF_4]^-$ anion can act as a weak ligand,[15] the encapsulation cannot be ascribed to weak Co⋯F interactions in this case, because each fluorine atom of the trapped anion is directed towards the center of a triangular face of the Co_4 tetrahedron and away from the Co apices which are in any case coordinatively saturated. There are many examples of the trapping of counterions within the central cavities of discrete polyoxometalate clusters to form supramolecular host–guest species,[16] but in these cases the association is often assisted by coordinative or hydrogen-bonding interactions. No such interactions exist between the $[Co_4L_6]^{8+}$ cation and its trapped $[BF_4]^-$ anion, and in this respect **1** resembles recent examples of two-dimensional molecular rings that bind anions in the central 'circular' cavity,[7, 9] and also a tetrahedral complex reported by Hüttner et al. in which an encapsulated $[BF_4]^-$ anion was also observed.[11] The association in **1** appears to derive from a good size match between the guest and the cavity of the host, and presumably, favorable electrostatic effects will also be associated with encapsulation. We note that crystalline **1** forms in high yield, and all of the crystals have the same habit and appearance; there is no evidence for a mixture of products in the solid state.

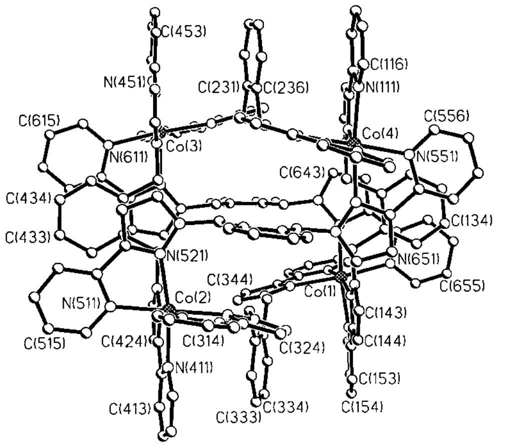

Figure 2. View of the cationic $[Co_4L_6]^{8+}$ unit of $\mathbf{1}\cdot 17.5\,H_2O$ (central $[BF_4]^-$ anion omitted for clarity) showing the labeling.

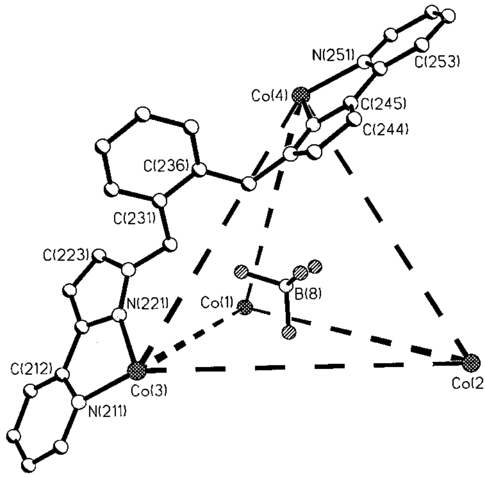

Figure 3. Partial view of **1** from another perspective, emphasizing the tetrahedral array of Co^{II} ions, the edge-bridging mode of the ligands, and the disposition of the central $[BF_4]^-$ anion.

The Ni^{II} complex also analyzed as $[Ni_2L_3][BF_4]_4$.[13] However, its FAB mass spectrum showed no evidence for formation of a tetranuclear Ni_4L_6 complex: the peak with highest mass corresponded only to a dinuclear $\{Ni_2L_3\}$ species. The crystal structure (Figure 4) confirmed the formulation $[Ni_2L_3][BF_4]_4$, in which one ligand linked the two metal ions as a bis-bidentate bridge and the remaining two terminal ligands each coordinate as tetradentate chelates to one (pseudo-octahedral) metal ion.[14] The Ni–N distances lie in the range 2.05–2.13 Å (average 2.096 Å). This structure is an unusual alternative to the triple helical architecture well-known in M_2L_3 complexes and is similar to the structure of the Fe^{III} complex of the tetradentate siderophore alcilagin, which was reported recently.[17]

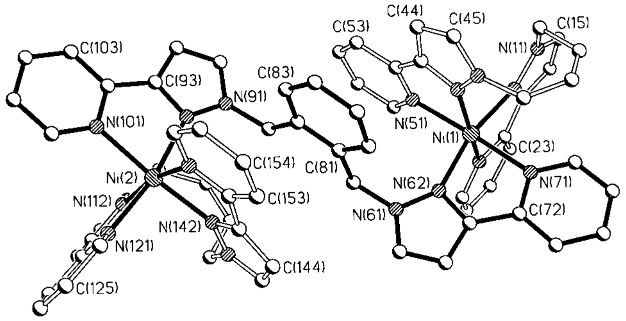

Figure 4. The crystal structure of the $[Ni_2L_3]^{4+}$ unit in $\mathbf{2}\cdot 3\,MeCN\cdot Et_2O\cdot 1.5\,H_2O$. The terminal ligands are shown with hollow bonds, and four of their C atoms [C(3) to C(6) of the central phenyl rings] have been omitted for clarity.

Formation of two such different structures with such similar metal ions would be simple to explain if an equilibrium between the different forms existed in solution, and this equilibrium were pulled to one extreme or the other by crystallization;[5-7] in this case the solution behavior of both complexes would be similar. ^{11}B and ^{19}F NMR spectra of **1** in CD_3CN (Figure 1) both show two peaks: a major one whose position corresponds exactly to free $[BF_4]^-$ ($\delta(^{11}B) = -1$; $\delta(^{19}F) = -150$), and a minor one at much higher field ($\delta(^{11}B) = -105$; $\delta(^{19}F) = -242$).[18] The large negative chemical shifts of the minor peaks do not correspond to any conceivable decomposition product of a $[BF_4]^-$ anion and, significantly, are absent in the spectra of both the batch of $NaBF_4$ used to prepare the complexes and of **2**. Also, they are present reproducibly in the NMR spectra of several different batches of **1**. These peaks therefore correspond to the $[BF_4]^-$ anion encapsulated in the cavity of the paramagnetic tetrahedral complex and exchanging with the free anions slowly on the NMR timescale, if at all (the two distinct signals were retained up to 70°C). The electrospray mass spectra of MeCN solutions of both **1** and **2** show the same general behavior as the FAB spectra. For **1** peaks corresponding to the series $[Co_4L_6(BF_4)_x]^{(8-x)+}$ ($x = 6, 5, 4$) at m/z 1555, 1008, and 734, respectively, are observed: of these the peak at m/z 1008 for $[Co_4L_6(BF_4)_5]^{3+}$ in particular is significant, because no simpler combination of metal, ligand, anion and charge can give the same m/z value. In contrast, for **2** the only significant peak was at m/z 1294, corresponding to $[Ni_2L_3]^+$. The NMR and ES mass spectroscopic data both clearly suggest that the core of **1** is retained to a significant extent in solution (although some dissociation cannot be ruled out), but that no such tetrahedral complex forms in solution when Co^{II} is replaced by Ni^{II}.

There is no simple explanation for the fact that the assemblies of complexes of L with Co^{II} and Ni^{II} proceed along such different lines. However, the observations that a) we could not isolate or detect a $\{M_4L_6\}^{8+}$ core without an encapsulated $[BF_4]^-$ anion and b) any exchange between free and encapsulated $[BF_4]^-$ in **1** is slower than the NMR timescale both suggest that the encapsulated anion is an essential part of the structure. This implies that in **1** the anion may act as a template around which the four metals and six ligands assemble, and that in the absence of this templating effect, simpler dinuclear species such as **2** form.

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[12] A mixture of α,α'-dibromoxylene (5.5 g, 20.9 mmol), 3-(2-pyridyl)-pyrazole[15] (6.4 g, 44.1 mmol), toluene (200 cm^3), $^nBu_4NOH$ (1 cm^3 of a 40% aqueous solution), and aqueous NaOH (14.9 g dissolved in 35 cm^3 water) was heated to 85°C for 24 h whilst stirring vigorously. After cooling the organic phase was separated, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent gave an oil, which afforded a white powder (L) on recrystallization from CH_2Cl_2/Et_2O (Yield: 6.7 g, 82%). EIMS: $m/z = 392$. Satisfactory analytical and NMR spectral data were obtained.

[13] **1** and **2**: Reaction of L (0.24 mmol) with the appropriate metal(II) acetate hydrate (0.16 mmol) in MeOH (5 cm^3) for 1 h resulted in clear orange (Co) or blue (Ni) solutions. Addition of aqueous $NaBF_4$ resulted in precipitation of the complexes, which were filtered off, washed with MeOH, and dried in vacuo to give the complexes in 80–90% yield. Satisfactory analytical data (C, H, N) were obtained for both.

[14] a) Crystal data for $\mathbf{1}\cdot 17.5\,H_2O$: orange block, size $0.25 \times 0.15 \times 0.15$ mm; $C_{144}H_{155}B_8Co_4F_{32}N_{36}O_{17.5}$, triclinic, space group $P\bar{1}$; $a = 16.827(3)$, $b = 18.909(4)$, $c = 25.381(3)$ Å, $\alpha = 87.22(2)$, $\beta = 84.723(14)$, $\gamma = 86.74(2)°$; $V = 8021(3)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.491\ g\,cm^{-3}$; $\mu = 0.518\ mm^{-1}$. A sphere of data collected to $2\theta_{max} = 45°$ gave 20911 unique reflections ($R_{int} = 0.078$). Refinement of 2197 parameters with 12 restraints (applied to the thermal parameters of some of the tetrafluoroborate anions) gave $R1 = 0.0745$, $wR2 = 0.2300$; residual electron density between $+1.06$ and -0.69 e Å^{-3}. Apart from the complex cation and the counterions, each asymmetric unit contains 17.5 molecules of water which form a hydrogen-bonded network also incorporating the $[BF_4]^-$ anions. b) Crystal data for $\mathbf{2}\cdot 3\,MeCN \cdot Et_2O \cdot 1.5\,H_2O$: blue block, size $0.2 \times 0.1 \times 0.1$ mm; $C_{82}H_{82}B_4F_{16}N_{21}Ni_2O_{2.5}$, triclinic, space group $P\bar{1}$; $a = 10.839(2)$, $b = 19.030(5)$, $c = 21.800(8)$ Å, $\alpha = 92.61(2)$, $\beta = 91.61(3)$, $\gamma = 101.83(2)°$; $V = 4393(2)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.411\ g\,cm^{-3}$; $\mu = 0.522\ mm^{-1}$. A sphere of data collected to $2\theta_{max} = 40°$ gave 8192 unique reflections ($R_{int} = 0.139$). Refinement of 1185 parameters with 1764 restraints gave $R1 = 0.0840$, $wR2 = 0.2445$; residual electron density between $+0.55$ and -0.39 e Å^{-3}. This crystal diffracted very weakly. To assist in the refinement, several restraints were applied: 1) all aromatic rings were restrained to be flat; 2) in the tetrafluoroborate anions all B–F bonded and all F⋯F nonbonded distances were restrained to be similar; 3) thermal parameters on adjacent atoms were restrained to be similar. c) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100861. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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[18] The relative integrals of the peaks corresponding to the encapsulated and free $[BF_4]^-$ anions in the ^{11}B and ^{19}F NMR spectra are not exactly in the expected 1:7 ratio due to the slow relaxation of the free $[BF_4]^-$ anions and the paramagnetism of the cavity.