

# Self-Assembly of Anion-Binding Supramolecular Cage Complexes

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**ABSTRACT:** *Three tetradentate ligands, in which two bidentate pyrazolyl-pyridine binding sites are connected by an aromatic spacer unit, have been used to prepare adamantoid tetrahedral cages of the form  $[Co_4L_6(X)][X]_7$  (where X is a uninegative, noncoordinating counterion such as perchlorate, tetrafluoroborate, or hexafluorophosphate). In these complexes an approximately tetrahedral array of metal ions occurs, with a bridging ligand spanning each of the six edges of this tetrahedron; each metal ion is accordingly six coordinate and the cages can have either T or  $C_3$  symmetry, depending on the ligand. The central cavity of each cage is occupied by an anion. In the cases where the anion is a good fit for the central cavity, it is tightly bound (no exchange in solution with external anions) and acts as a template for assembly of the cage, with a mixture of Co(II) and the bridging ligand in the correct proportions not assembling into the  $Co_4L_6$  cage until the templating anion is added. With a longer bridging ligand, the central cavity is too large to encapsulate the anion completely, and accordingly the encapsulated anion can exchange freely with external anions; this behavior can be "frozen out" in the NMR spectra at low temperatures. The host-guest chemistry of the cage complexes is therefore strongly dependent on the size of the central cavity. © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:567–573, 2002; Published online*

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## INTRODUCTION

The self-assembly of architecturally sophisticated complexes from simple metal and ligand components is currently an intensely studied area of research, which is at the interface of coordination and supramolecular chemistry [1–6]. Interest in this area started with the first reports of helicates in the 1980s and the area has grown rapidly to include a wide variety of structural motifs such as grids, cyclic assemblies such as squares, rectangles, and helical "wreaths," and—most recently—an extensive variety of 3-D cage complexes [7–15].

The interest in assembly of cages stems from two sources. Firstly, understanding the geometric principles that underlie their assembly has meant that many remarkably elaborate 3-D assemblies can be prepared from simple (but carefully designed) components. Secondly, cage complexes by definition have central cavities, which can bind guest species, and accordingly there is the scope for studying the host-guest chemistry and molecular recognition properties of the cages and even their use as "microreactors," which have catalytic properties [7–15]. This short review summarizes our recent work in the area, which has focused on the assembly of cage complexes based on the relatively simple bis-bidentate ligands of the type shown in Fig. 1.

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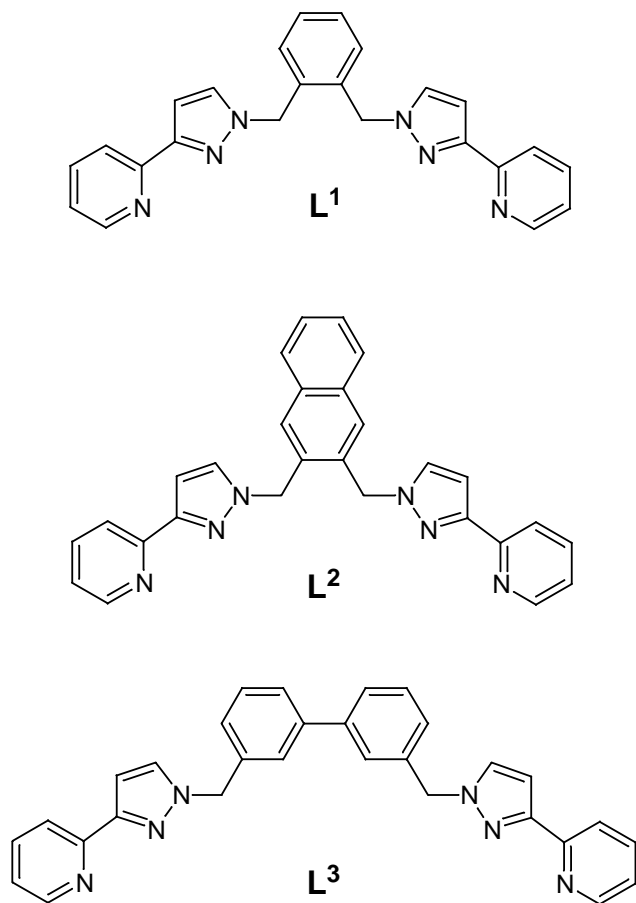


FIGURE 1 The ligands  $L^1$ – $L^3$  used in this work.

### OPEN-CHAIN DINUCLEAR AND TETRAHEDRAL CAGE COMPLEXES WITH $L^1$ AND $L^2$

In the ligands shown in Fig. 1, two bidentate pyrazolyl–pyridine units are linked to a central aromatic spacer by methylene units, which confer conformational flexibility on them. These ligands were all prepared by the same general route, viz. reaction of the known compound 3-(2-pyridyl)-1*H*-pyrazole with the bis(bromomethyl)-aromatic compound in a 2:1 ratio under phase transfer conditions. Thus,  $L^1$  was prepared using 1,2-bis(bromomethyl)benzene [16,17],  $L^2$  using 2,3-bis(bromomethyl)-naphthalene [18], and so on. These ligands are all tetradentate, and accordingly, reaction with metal cations that prefer an octahedral coordination geometry requires 1.5 ligands per metal ion to provide the necessary six donor atoms (assuming that noncoordinating anions are used). The simplest stoichiometry that can occur is therefore  $M_2L_3$ , as commonly found in dinuclear triple helicates based on octahedral metal ions and bis-bidentate bridging ligands [19,20].

Reaction of  $L^1$  or  $L^2$  with nickel(II) acetate in these proportions in MeOH afforded a soluble complex which, was precipitated as its fluoroborate salt by addition of aqueous  $\text{NaBF}_4$ . Analytical data were in accordance with the empirical formula  $[\text{Ni}_2L_3][\text{BF}_4]$ . The crystal structure in each case showed the complexes to be  $[\text{LNi}(\mu-L)\text{NiL}][\text{BF}_4]_4$  ( $L = L^1$  or  $L^2$ ) in which each Ni(II) center has one ligand acting as a terminal tetradentate chelate and the other ligand acts as a bis-bidentate bridge linking the two  $\{\text{NiL}\}^{2+}$  units (Fig. 2) [16,18]. It is evident from these structures that  $L^1$  and  $L^2$  have the capability to act either as tetradentate chelates to a single metal ion or as a bridging ligand linking two metal centers, as circumstances require. This flexibility is also illustrated by comparison of the dinuclear double helicate  $[\text{Cu}_2(L^1)_2][\text{PF}_6]_2$  with Cu(I), in which both ligands are bridging, and the mononuclear Cu(II) complex  $[\text{Cu}(L^1)\text{Cl}][\text{BF}_4]$ , in which  $L^1$  is a tetradentate chelate [17]. The unusual structures of  $[\text{Ni}_2L_3][\text{BF}_4]$  ( $L = L^1$  and  $L^2$ ), in which both coordination modes occur, are a consequence of the flexibility of the ligands and the fact that the two bidentate compartments can converge at a single metal site. With bis-bidentate bridging ligands where this is not possible, triple helical architectures with all three ligands bridging usually occur [19,20].

The Co(II) complexes of  $L^1$  and  $L^2$  were prepared in an exactly similar manner and likewise gave analytical data in agreement with the expected proportions  $[\text{Co}_2L_3][\text{BF}_4]_2$ . However, the electrospray mass spectra indicated the presence of a  $\text{Co}_4L_6$  species—having the same metal-ligand proportions—and the crystal structures revealed the presence of tetrahedral cages  $[\text{Co}_4L_6(\text{BF}_4)][\text{BF}_4]_7$  (Fig. 3) [16,18] of a type studied by Saalfrank [21] and Raymond [22], amongst others. These have a metal ion at each vertex of an approximate tetrahedron with  $\text{Co}\cdots\text{Co}$  separations of ca. 9–10 Å, with a bridging ligand spanning each of the six edges. Each metal ion is

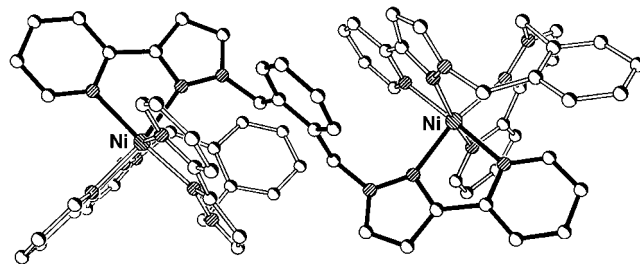
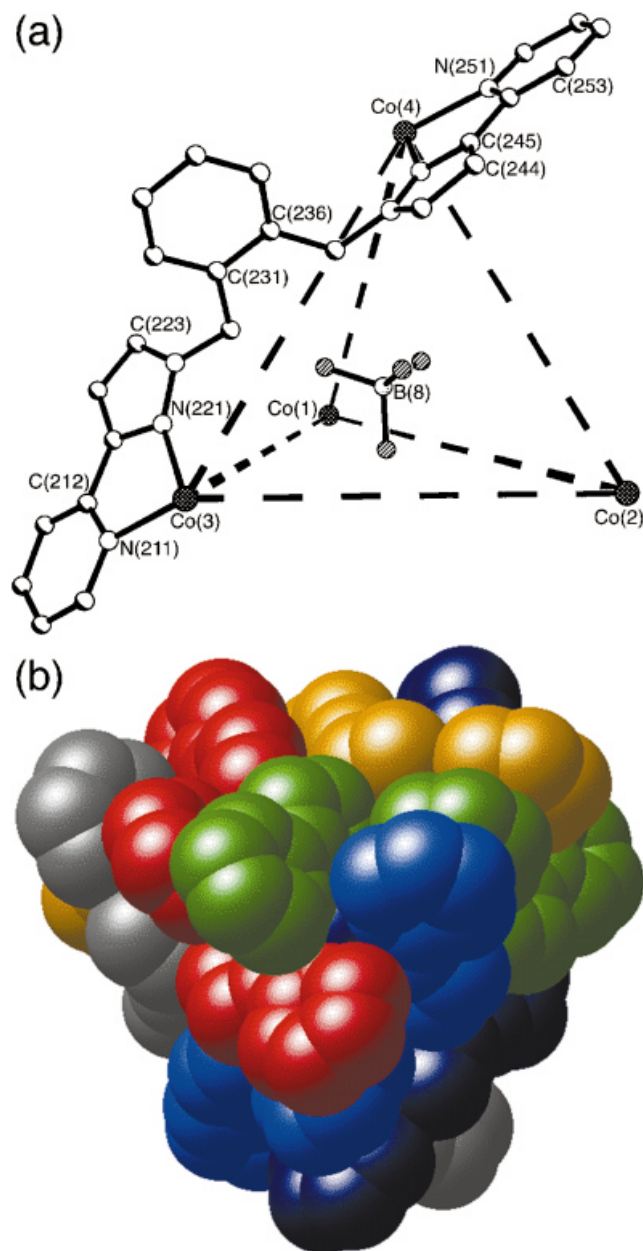


FIGURE 2 Structure of the complex cation  $[\text{Ni}_2(L^1)_3]^{4+}$ ; the complex with  $L^2$  has a similar structure.



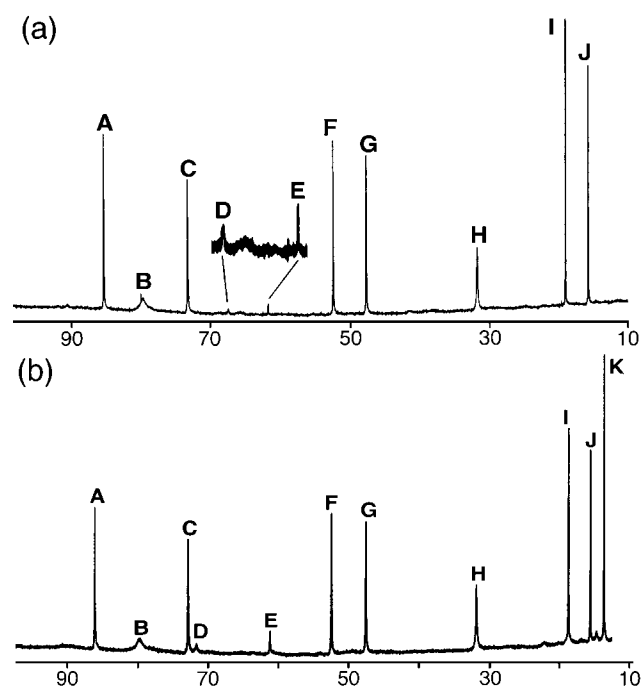
**FIGURE 3** Two views of the structure of  $[\text{Co}_4(\text{L}^1)_6][\text{BF}_4]_8$ : (a) a view emphasizing the  $\text{Co}_4$  tetrahedral array, the bridging coordination mode of  $\text{L}^1$ , and the encapsulated anion; (b) a space-filling picture with each ligand colored separately.

accordingly in an octahedral tris-chelate coordination environment, with a bidentate “arm” provided by each of three different ligands in a *fac* arrangement with the three pyridyl donors on the “external” face of the octahedron and the three pyrazolyl donors on the “internal” face. All four metal centers have the same chirality, such that the complex has overall approximate *T* symmetry; this results in the six ligands being intertwined in such a way that there

is aromatic  $\pi$ -stacking between overlapping sections of adjacent ligands.

Apart from the interesting topology of the cage, the other notable feature of the structure is that the central cavity contains a  $[\text{BF}_4]^-$  anion, which is inverted with respect to the  $\text{Co}_4$  tetrahedron, such that each F atom is directed towards the space at the center of each of the triangular faces of the cage. The good fit of the anion in the cavity is illustrated by the fact that each F atom is involved in close contacts with the methylene spacers of the bridging ligands so that there are 12  $\text{CH}\cdots\text{F}$  contacts whose distances are in the range ca. 3–3.3 Å, characteristic of weak hydrogen-bonding interactions [23] (although it does not follow, of course, that all of these contacts result in stabilizing interactions). All four  $\text{Co}\cdots\text{B}$  separations are similar (ca. 6 Å) indicating that the anion is centrally located. It appears that the anionic guest is perfectly complementary to the host cage in terms of shape, size, and charge [16,18].

NMR spectra ( $^{11}\text{B}$ ,  $^{19}\text{F}$ , and  $^1\text{H}$ ) showed that the integrity of the cage complex is retained in solution, with the  $^1\text{H}$  NMR spectrum of both cages showing the required number of proton environments for *T* symmetry (10 for  $\text{L}^1$  and 11 for  $\text{L}^2$ , see Fig. 4); conveniently, the paramagnetism of the  $\text{Co}(\text{II})$  centers spreads the signals out over the range  $\delta = 10$ –90 ppm such that they are all clearly visible (although



**FIGURE 4**  $^1\text{H}$  NMR spectra of (a)  $[\text{Co}_4(\text{L}^1)_6][\text{BF}_4]_8$  and (b)  $[\text{Co}_4(\text{L}^2)_6][\text{BF}_4]_8$  in  $\text{CD}_3\text{CN}$  solution.

some are of low intensity). The eight most shifted signals in each case (A–H in the figure) are almost superimposable and correspond to the pyridyl, pyrazolyl, and methylene protons. The remaining signals correspond to the expected two (I, J) or three (I, J, K) for the bridging aromatic groups in the  $L^1$  and  $L^2$  complexes, respectively.

The  $^{19}\text{F}$  and  $^{11}\text{B}$  spectra clearly show the two very different environments for free and encapsulated  $[\text{BF}_4]^-$  and do not change up to  $70^\circ\text{C}$ , confirming that the integrity of the cage is maintained and that exchange of free and bound  $[\text{BF}_4]^-$  is slow on the NMR timescale. This is not surprising when one looks at a space-filling picture of the structure; there is essentially no space in the center of each face, such that the anion is completely encapsulated, and exchange with anions outside the cage would require simultaneous cleavage of several metal–ligand bonds.

There is an obvious question to be answered: Is the assembly of these cages the result of an anion-based template effect so that the metals and ligands only assemble around an anion of the correct shape, size and charge, and the cage does not exist without such an anion being present? Or, does the cage form on its own, such that incorporation of the anion is adventitious, with the anion diffusing into the cavity *after* the cage assembles? The presence of a templating effect is suggested—but not proved—by the observations that the central anion is (i) completely encapsulated in the solid state, and (ii) exchanging slowly (if at all) with free anions in solution; it is thus difficult to see how an anion could diffuse into a preformed cage. The occurrence of a genuine template effect in these cages was demonstrated by a simple  $^1\text{H}$  NMR experiment. A mixture of  $\text{Co}(\text{MeCO}_2)_2$  and either  $L^1$  or  $L^2$  in a 2:3 ratio in  $\text{MeOD}/\text{D}_2\text{O}$  gave an NMR spectrum with (broadened) signals for the ligand occurring only in the  $\delta = 6\text{--}10$  ppm region; there were no highly shifted signals above 10 ppm, which are characteristic of the cages. After addition of  $\text{NaBF}_4$  however, the signals between 6 and 10 ppm disappeared and were replaced by the signals in the  $\delta = 10\text{--}90$  ppm region characteristic of the cage complex (Fig. 4). The spectrum so obtained in each case was identical to that of a redissolved sample of the recrystallized cage complex, indicating that assembly of the cage was complete in the time it took to add the fluoroborate salt to the NMR tube and rerecord the spectrum.

This simple experiment allowed us to screen several anions for their templating effect. The hexafluorophosphate ion for example did not cause a mixture of  $\text{Co}(\text{II})$  and either  $L^1$  or  $L^2$  to assemble into the tetrahedral cage, which is not surprising

given that it is too large to fit into the central cavity. However, perchlorate—which is the same size and shape as fluoroborate—acted as a template in exactly the same way to give the cage in solution with both  $L^1$  and  $L^2$ . Accordingly, we prepared and structurally characterized the cage complex  $[\text{Co}_4(\text{L}^2)_6(\text{ClO}_4)][\text{ClO}_4]_7$  (Fig. 5) and its structure is essentially identical to that of  $[\text{Co}_4(\text{L}^2)_6(\text{BF}_4)][\text{BF}_4]_7$  with the O atoms of the central perchlorate ion involved in short  $\text{O}\cdots\text{HC}$  contacts with the methylene spacers of the bridging ligands [18].

The difference between the structures of the open-chain dinuclear complexes with  $\text{Ni}(\text{II})$  and the tetrahedral cage complexes with  $\text{Co}(\text{II})$  is striking, given that the same ligands and the same anions were involved in each case. We found no evidence for formation of a tetrahedral cage with  $\text{Ni}(\text{II})$  and either  $L^1$  or  $L^2$  under conditions that gave quantitative assembly of a tetrahedral cage with  $\text{Co}(\text{II})$ . The problem is compounded by the fact that  $[\text{Zn}_4(\text{L}^2)_6(\text{ClO}_4)][\text{ClO}_4]_7$  is also a tetrahedral cage [24] and so  $\text{Co}(\text{II})$  and  $\text{Zn}(\text{II})$  give one type of structure whereas  $\text{Ni}(\text{II})$  gives a quite different one. The only likely explanation to account for this is that the ionic radius is critical. In octahedral geometry,  $\text{Ni}(\text{II})$  has a smaller ionic radius than either  $\text{Co}(\text{II})$  or  $\text{Zn}(\text{II})$ , as shown by the Irving–Williams series, and it may be that the slight compression of the tetrahedral edifice that would result is sterically unfavorable.

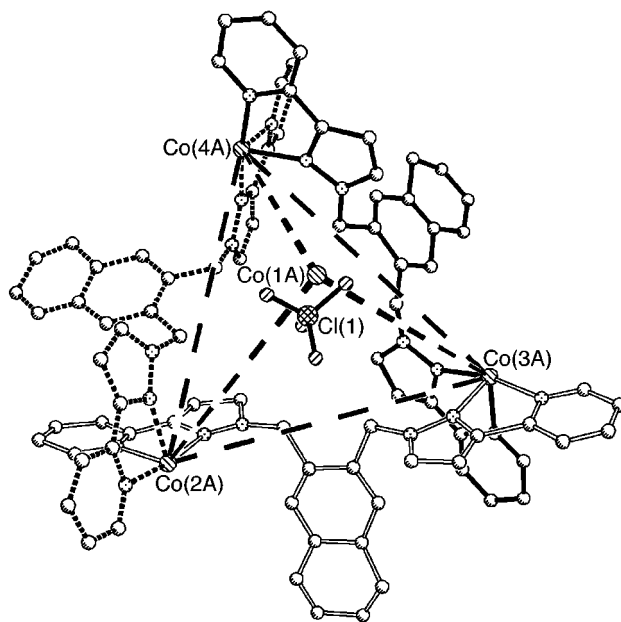


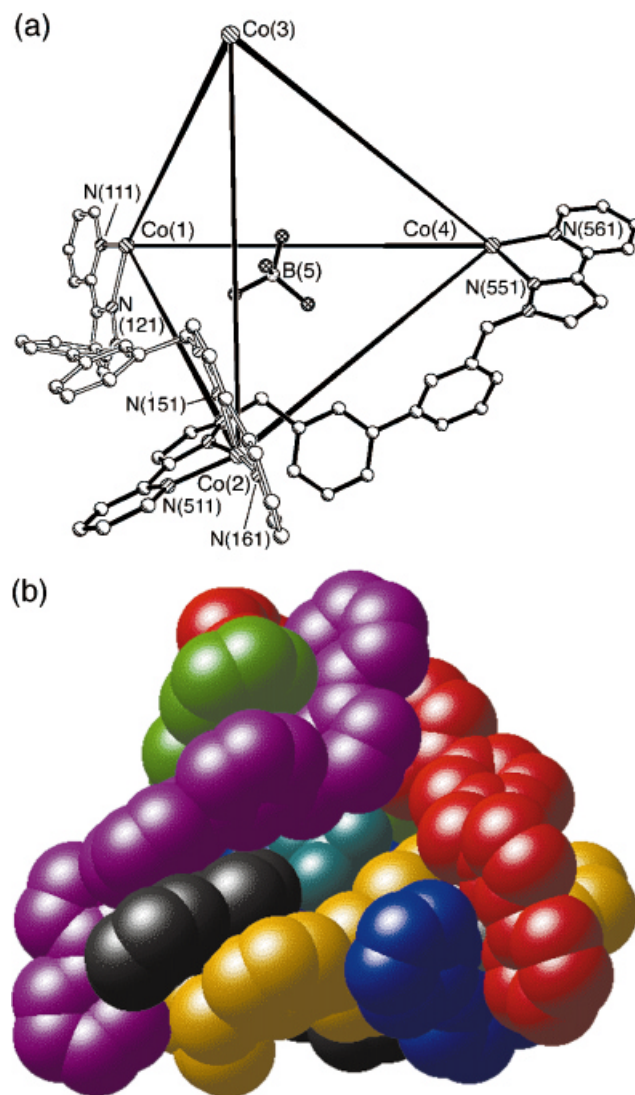
FIGURE 5 A view of the complex cation of  $[\text{Co}_4(\text{L}^2)_6]^{+}[\text{ClO}_4]_8^{-}$ , with three of the bridging ligands shown and shaded differently for clarity.

TETRAHEDRAL CAGE COMPLEXES WITH  $L^3$ 

Following the above results we studied the coordination behavior of ligand  $L^3$ , in which a biphenyl spacer separates the two pyrazolyl–pyridine binding sites [24,25]. The separation between the binding sites is larger than for  $L^1$  and  $L^2$ , which has two important consequences. Firstly, it is not possible for  $L^3$  to act as a tetradentate chelate to a single metal ion; it can only act as a bridging ligand. This would appear to make formation of tetrahedral cages more likely by preventing formation of the alternative  $M_2L_3$  complexes of the form  $(LM)(\mu-L)(ML)$ . Secondly, if  $M_4L_6$  tetrahedral cages do form, they will have a much larger central cavity such that  $[\text{BF}_4]^-$  and  $[\text{ClO}_4]^-$  are no longer an ideal size match and may no longer act as efficient templates; it may be expected that much larger anions will bind in the central cavities instead.

Reaction of  $L^3$  with  $\text{Co}(\text{MeCO}_2)_2$  in MeOH resulted in a clear solution from which a complex precipitated on addition of aqueous  $\text{NaBF}_4$ ,  $\text{NaClO}_4$ , or  $\text{KPF}_6$ . Analytical data for these were in agreement with the proportions  $[\text{Co}_2(L^3)_3]X_4$  ( $X =$  counterion), as expected, and in some cases electrospray mass spectra indicated the presence of  $\text{Co}_4L_6$  cages in solution. All of these have been structurally characterized, and all of the complexes are tetrahedral cages with an encapsulated anion [24–26].

The structure of the complex cation of  $[\text{Co}_4(L^3)_6(\text{BF}_4)][\text{BF}_4]_7$  is shown in Fig. 6; it has the same basic cage structure as the complexes with  $L^1$  and  $L^2$ , but with two important differences. Firstly, the metal vertices do not have the same coordination geometry and the symmetry of the cage is no longer  $T$ . Instead, only one of the metal centers (denoted the “apical” metal) has a *fac* tris-chelate geometry, with the three pyridyl donors on the outward-pointing face of the  $\text{CoN}_6$  octahedron. The remaining three metal centers around the basal plane are also octahedral tris-chelates, but have a meridional (*mer*) configuration. This requires a rather contorted arrangement of the bridging ligands. The result in symmetry terms is that the complex can only have one  $C_3$  axis instead of four, and therefore has at best  $C_3$  symmetry instead of  $T$ . The  $\text{Co}_4$  tetrahedron is accordingly rather irregular, with  $\text{Co}\cdots\text{Co}$  separations spanning the range 10.8–12.7 Å. The low symmetry means that 48 signals would be expected in the  $^1\text{H}$  NMR spectrum, arising from two independent ligand environments in which all protons are inequivalent; the three ligands that span apical and basal Co sites are different from the three around the basal plane, and in each case

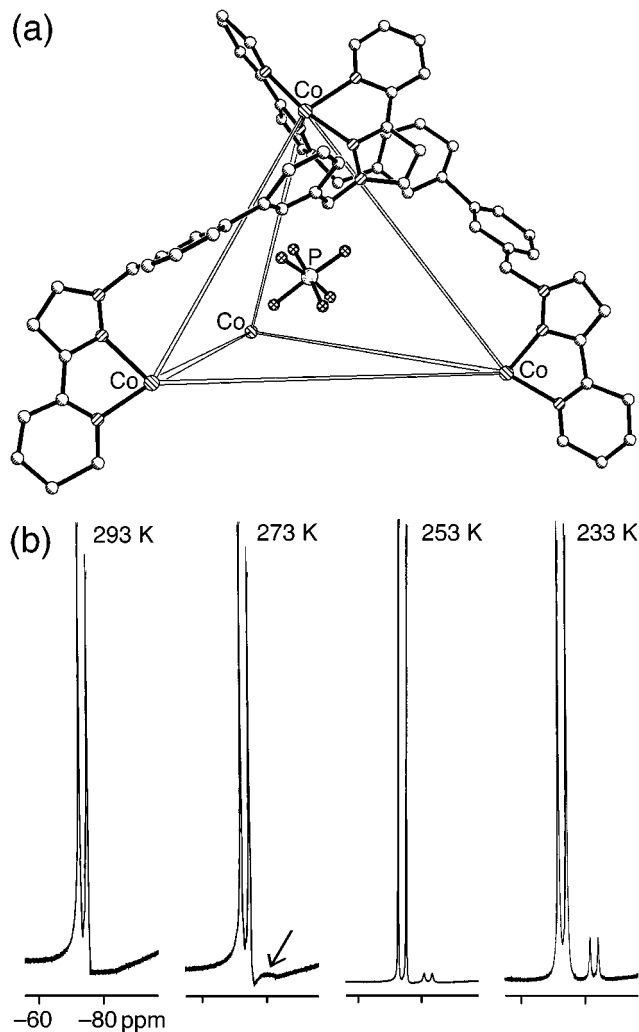


**FIGURE 6** Two views of the structure of  $[\text{Co}_4(L^3)_6][\text{BF}_4]_8$ : (a) a view emphasizing the  $\text{Co}_4$  tetrahedral array, the bridging coordination mode of  $L^3$ , and the encapsulated anion; (b) a space-filling picture with each ligand colored separately (note how the encapsulated anion is clearly visible through the gap in the center of the face).

there is no internal symmetry within the ligand. In fact, the  $^1\text{H}$  NMR spectra of  $[\text{Co}_4(L^3)_6(\text{BF}_4)][\text{BF}_4]_7$  in  $\text{CD}_3\text{CN}$  shows about 40 signals spanning the range  $-20$  to  $+100$  ppm. Because some signals are likely to be hidden under the peak from residual protons in the solvent, and some are likely to be very weak (cf. Fig. 4), this is consistent with the low-symmetry solid-state structure being retained in solution. If the higher  $T$  symmetry occurs (all four metals having a *fac* tris-chelate geometry, as with the complexes of  $L^1$  and  $L^2$ ) only 12 proton signals would occur.

The larger internal volume of the cavity with respect to the cages with  $L^1$  and  $L^2$  means that the encapsulated  $[\text{BF}_4]^-$  anion is now "off-center," being rather nearer to the apical Co(II) center ( $\text{Co}\cdots\text{B}$ , 5.89 Å) than the other three (7.68–7.96 Å). There are still short  $\text{CH}\cdots\text{F}$  interactions whose distance is indicative of weak hydrogen bonds, but not so many because of the poorer size match of the anion for the cavity. This anion is not tightly bound: at room temperature  $^{11}\text{B}$  NMR spectrum shows a single resonance indicating that the encapsulated and free  $[\text{BF}_4]^-$  anions are in fast exchange on the NMR timescale, a process facilitated by the large gaps in the centers of the triangular faces. This behavior can be frozen out at low temperatures, with two  $^{11}\text{B}$  resonances apparent at  $\delta = -5$  and  $-34$  ppm, corresponding to free and encapsulated  $[\text{BF}_4]^-$  respectively when the solution was cooled to  $-40^\circ\text{C}$ . Both the poor fit of the anion for the cavity and the fact that the anion exchanges easily with free external anions suggest that a templating effect involving the anion is less likely, with the cage forming because the separation between the bidentate units precludes formation of simpler complexes based on a tetradentate chelating coordination mode. It is tempting to suggest that the rather contorted geometry of the cage, because of the presence of one *fac* and three *mer* metal centers giving  $C_3$  symmetry, occurs in order to optimize the weak interactions between the host cage and the guest anion; without this folding, the internal volume would be even larger, and the guest anion would be an even poorer fit. However, there is no evidence to support this at present.

The perchlorate and hexafluorophosphate complexes show similar behavior. Given the structural similarity between perchlorate and fluoroborate, it is not surprising that the structure of  $[\text{Co}_4(\text{L}^3)_6(\text{ClO}_4)]_8$  should be essentially identical to that of  $[\text{Co}_4(\text{L}^3)_6(\text{BF}_4)]_8$ ; again, the anion is off-center and involved in  $\text{CH}\cdots\text{O}$  interactions with the methylene spacers of the bridging ligands. The structure of  $[\text{Co}_4(\text{L}^3)_6(\text{PF}_6)]_8$ , however, shows (Fig. 7) how the larger cavity of the cage changes its host-guest chemistry, with it now being possible to accommodate a much larger guest ion than the cages with  $L^1$  and  $L^2$ , which could not accommodate hexafluorophosphate. As with  $[\text{BF}_4]^-$ , this guest ion is exchangeable with external anions in solution at a rate faster than the NMR timescale at room temperature, with the process being frozen out as the temperature is reduced (Fig. 7); the coalescence temperature is about 273 K. We are currently extracting activation parameters for exchange of  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  to see if there is a correlation with the size of the anion.



**FIGURE 7** (a) A view of the complex cation of  $[\text{Co}_4(\text{L}^3)_6][\text{PF}_6]_8$ , showing the anion encapsulated in the central cavity of the cage; (b) variable-temperature  $^{19}\text{F}$  NMR spectra of  $[\text{Co}_4(\text{L}^3)_6][\text{PF}_6]_8$  showing how exchange of free and encapsulated  $[\text{PF}_6]^-$  can be frozen out.

## CONCLUSIONS

These relatively simple bis-bidentate ligands allow formation of two different types of  $\text{M}_4\text{L}_6$  cage complex, having  $T$  symmetry (with  $L^1$  and  $L^2$ ) or  $C_3$  symmetry (with  $L^3$ ). For the  $\text{M}_4\text{L}_6$  cages in the cases where the anion is a good fit for the central cavity (with  $L^1$  and  $L^2$ ), a templating effect is apparent whereby addition of the appropriate anion to the metal-ligand mixture induced assembly of the cage around the anion that becomes trapped in the central cavity. With the larger bridging ligand  $L^3$ ,  $\text{M}_4\text{L}_6$  cages also form, but with a lower symmetry having larger cavities whose guest anions are freely exchangeable with external anions in solution.

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- [26] The initial report of the structure of  $[\text{Co}_4(\text{L}^3)_6(\text{BF}_4)][\text{BF}_4]_7$  (Ref. [25]) states incorrectly that the central cavity of the cage is empty, with all anions outside, in the solid state. This mistake arose from the unusual choice of asymmetric unit when the structure was refined; when the asymmetric unit was viewed, it appeared that all eight anions were outside the cavity. However, one of these anions was located in the cavity of a cage complex in the *next* asymmetric unit; likewise, the anion that was present in the observed cage complex was not shown as it was in a different asymmetric unit. A full packing diagram revealed that the cage cavities are in fact occupied by anions. The conclusions about exchange from the solution NMR studies are not affected by this.