Anion-templated self-assembly of tetrahedral cage complexes of cobalt(II) with bridging ligands containing two bidentate pyrazolyl-pyridine binding sites

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The bridging ligands L[1] and L[2] contain two *N,N*-bidentate pyrazolyl-pyridine units linked to a central aromatic spacer unit (1,2-phenyl or 2,3-naphthyl, respectively). Reaction with Ni(II) salts and treatment with the anions tetrafluoroborate or perchlorate result in formation of dinuclear complexes having a 2:3 metal:ligand ratio, with one bridging and two terminal tetradentate ligands. In contrast, reaction of L[1] and L[2] with Co(II) salts, followed by treatment with tetrafluoroborate or perchlorate, results in assembly of cage complexes having a 4:6 metal:ligand ratio; these complexes have a metal ion at each corner of an approximate tetrahedron, and a bis-bidentate bridging ligand spanning each edge. The central cavity is occupied by a tetrahedral counterion that forms multiple hydrogen-bonding interactions with the methylene protons of the bridging ligands. The anionic guest fits tightly into the central cavity of the cage to which it is ideally complementary in terms of shape, size, and charge. Solution NMR experiments show that the central anion acts as a template for cage formation, with a mixture of Co(II) and the appropriate bridging ligand alone giving no assembly into a cage until the tetrahedral anion is added, at which point cage assembly is fast and quantitative. The difference between the structures of the complexes with Ni(II) and Co(II) illustrate how the uncoordinated anions can exert a profound influence on the course of the assembly process.

Scheme 1.

Metal-directed self-assembly has recently become a major tool by which coordination chemists can prepare large and elaborate complexes such as helicates, grids, boxes, rings, and cages from relatively simple components (1–11). Many examples are based on accurate control of metal-ligand coordinate bond formation, with the course of the assembly involving a labile metal ion and a multidentate ligand dictated by the metal/ligand interactions. This behavior is exemplified by the formation of helical complexes with linear oligopyridines, where the partitioning of the ligand into bidentate or terdentate binding domains is dictated by the preference of the metal ion for four-coordinate or six-coordinate geometry (3). Recently, however, it has become apparent that "innocent" anions can dictate the course of the assembly process by acting as a template around which a particular combination of metal ions and ligand can assemble in a way which would not occur in the absence of the anion. For example, Lehn and coworkers (12) showed how a trinuclear M_3L_3 triple helicate converted to a circular M_5L_5 helicate in the presence of chloride ion, which was tightly bound in the center of the resulting cationic cavity. Anions that are chosen for their innocence in terms of coordinating ability can nevertheless direct the course of an assembly process via noncovalent interactions.

Here we describe how the anions perchlorate and tetrafluoroborate act as templates for the formation of edge-bridged tetrahedral $M_4(\mu\text{-}L)_6$ cages from Co(II) and bis-bidentate bridging ligands (Scheme 1). These "adamantoid" cages (Fig. 1) were first described by Saalfrank *et al.* (13–16) and have since been
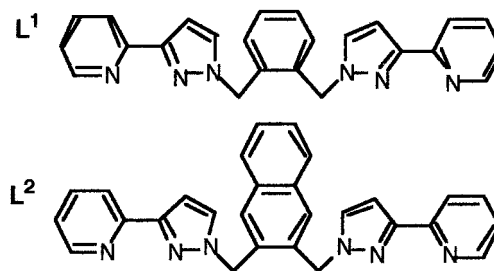
studied by several other groups (17–25). A notable feature of many such complexes is that the central cavity can accommodate guest species, with the nature of the guest depending on the charge carried by the surrounding complex cage. Thus, neutral cages tend to have either no guests (15) or solvent molecules as guests (17) in the cavity, anionic cages are found to contain tetraalkylammonium (19, 21) or ammonium (16) cations as guests, and cationic cages can contain tetrahedral anions such as $[BF_4]^-$ as guests (23, 24). The twin facts that some cages can form without a guest (15, 22) and that some guests can be freely exchanged with other species (19) suggest that in these cases, the assembly of the cage arises from an ideal match between the symmetry properties of the ligands and the coordination preferences of the metal ions, and that no templating effect is necessary. In other cases, however, the guest is trapped, suggesting that the assembly of the cage is caused in these cases by a genuine template effect (16, 21, 23).

Methods

Synthesis of L[2]. A mixture of 2,3-bis(bromomethyl)naphthalene (26) (2.00 g, 6.39 mmol), 3-(2-pyridyl)pyrazole (27) (2.04 g, 14.1 mmol), aqueous NaOH (10 M, 7 cm³), and tetrahydrofuran (THF) (50 cm³) was stirred at reflux for 24 h. After cooling, the organic phase was separated, dried over MgSO₄, filtered, and evaporated to dryness. The crude solid was purified by column chromatography on flash silica with ethylacetate-methanol (99:1); the desired product was the third (major) fraction. Yield: 1.42 g, 50%; electron impact mass spectrum (EIMS): *m/z* 442 (60%, M⁺), 297. ¹H NMR (270 MHz, CDCl₃): δ 8.63 (2 H, d; pyridyl H⁶), 7.96 (2 H, d; pyridyl H³), 7.78 (2 H, m; naphthyl H⁶/H⁷ *or* H⁵/H⁸), 7.70 (2 H, td; pyridyl H⁴), 7.63 (2 H, s; naphthyl H¹/H⁴), 7.49 (2 H, m; naphthyl H⁵/H⁸ *or* H⁶/H⁷), 7.38
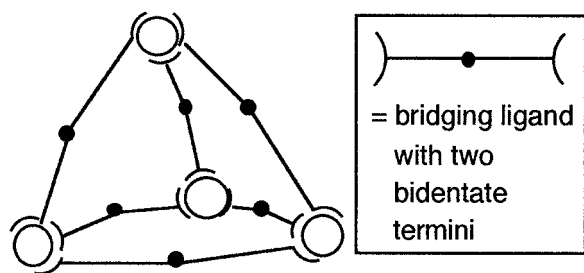
Fig. 1. Diagram of an $M_4(\mu\text{-L})_6$ tetrahedral cage based on a bis-bidentate bridging ligand and 6-coordinate metal centers.

(2 H, d; pyrazolyl H^4 *or* H^5), 7.19 (2 H, ddd; pyridyl H^5), 6.93 (2 H, d; pyrazolyl H^5 *or* H^4), 5.58 (4 H, s; CH_2). Found: C, 76.2; H, 5.3; N, 19.3%. Required for $C_{28}H_{22}N_6$: C, 76.0; H, 5.0; N, 19.0%.

Syntheses of $[Co_4(L^2)_6(ClO_4)][ClO_4]_7$, $[Co_4(L^2)_6(BF_4)][BF_4]_7$ and $[Ni_2(L^2)_3][ClO_4]_4$. A solution of L^2 (0.049 g, 0.11 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a solution the appropriate metal(II) acetate hydrate (0.07 mmol) in MeOH (10 cm^3); the resulting solution was stirred for 1 h at room temperature. Addition of a methanolic solution of $NaBF_4$ or $NaClO_4$ as appropriate resulted in precipitation of a solid, which was filtered off and dried *in vacuo*; yields were typically 30%. Concentrating and cooling the mother liquor could isolate further material. X-ray quality crystals were grown by diffusion of diethyl ether into solutions of the complexes in MeCN at 0°C. Electrospray mass spectroscopic data are as follows. Satisfactory elemental analytical data were obtained: $[Co_4(L^2)_6(ClO_4)][ClO_4]_7$: m/z 1129.0 (calculated 1128.3), $\{Co_4(L^2)_6(ClO_4)_5\}^{3+}$; 822.0 (calculated 821.4), $\{Co_4(L^2)_6(ClO_4)\}^{4+}$; 600.2 (calculated 600.5), $\{Co(L^2)(ClO_4)\}^{+}$. $[Co_4(L^2)_6(BF_4)][BF_4]_7$: m/z 1107.8 (calculated 1107.3), $\{Co_4(L^2)_6(BF_4)_5\}^{3+}$; 809.2 (calculated 808.7), $\{Co_4(L^2)_6(BF_4)\}^{4+}$; 587.9 (calculated 587.8), $\{Co(L^2)(BF_4)\}^{+}$. $[Ni_2(L^2)_3][ClO_4]_4$: m/z 471.1 (calculated 471.3), $\{Ni(L^2)_2\}^{2+}$.

X-Ray Crystallography. Details of the crystal, data collection, and refinement parameters for the new structures are in Table 1. A detailed description of the methods used for unit cell determination and data collection has been published (27). Structure solutions and refinements used SHELXS-97 (28) and SHELXL-97 (29); absorption corrections were applied by using SADABS (30). Full details of the refinements are included in the supporting

text, which is published on the PNAS web site, www.pnas.org, together with selected bond distances and angles.

Results and Discussion

Complexes with L^1: Studying the Template Effect by ^{1}H NMR Spectroscopy. In a recent communication we described briefly the structures of the complexes $[Co_4(L^1)_6(BF_4)][BF_4]_7$ and $[Ni_2(L^1)_3][BF_4]_4$ (24). These are recalled in Figs. 2 and 3, and the contrast between them clearly illustrates how participation of the anion can influence the course of the assembly. In $[Ni_2(L^1)_3][BF_4]_4$, one ligand L^1 is acting as a bridge, but the other two are acting as tetradentate chelates, such that the structure of the cation is $[(L^1)Ni(\mu\text{-}L^1)Ni(L^1)]^{4+}$. This is an unusual arrangement of ligands in M_2L_3 complexes, and is similar to the structure of the Fe(III) complex of the tetradentate siderophore alcilagin (31). In contrast, $[Co_4(L^1)_6(BF_4)]^{7+}$ is a tetrahedral cage, with the $[BF_4]^-$ anion being complementary in both charge and shape to the cavity; with respect to the Co_4 tetrahedron, the $[BF_4]^-$ tetrahedron is inverted such that each F atom is directed to the space at the center of a Co_3 triangular face. The Co–N bond distances lie in the range 2.11–2.21 Å (average 2.151 Å), typical for high-spin Co(II). All four metal ions have the same optical configuration, such that each complex cage has approximate T symmetry (although the crystal is a racemate). The Co⋯Co separations (all different) are between 8.98 and 10.07 Å; the Co⋯B distances are all comparable (5.61–5.98 Å), indicating that the anion is located approximately centrally in the cavity.

Although the $[BF_4]^-$ anion can act as a weak ligand (32), it is clear that the encapsulation cannot be ascribed to Co⋯F interactions in this case, because each fluorine atom of the trapped anion is directed toward the center of a triangular face of the Co_4 tetrahedron, away from the Co apices that are in any case coordinately saturated (Co⋯F distances, 5–6 Å). This behavior contrasts with that found by Huttner and coworkers (23), who found that incorporation of $[BF_4]^-$ into a tetrahedral cage was helped by weak M⋯F interactions, with the F atoms directed exactly toward the metal vertices rather than between them. In $[Co_4(L^1)_6(BF_4)]^{7+}$, however, there are close contacts between the fluorine atoms and the CH_2 spacers of the ligands, with nonbonded C⋯F separations in the range 3.01–3.21 Å (and F⋯H contacts in the range 2.3–2.6 Å), indicative of C–H⋯F hydrogen-bonding interactions (33, 34), which no doubt help to stabilize the assembly. In addition, multiple stacking interactions between overlapping aromatic fragments of adjacent ligands are evident. Variable-temperature ^{11}B and ^{19}F NMR spectra showed that the

Table 1. Crystallographic data for the three new structures

Compound	$[Co_4(L^2)_6(BF_4)][BF_4]_7 \cdot H_2O \cdot 7MeCN$	$[Co_4(L^2)_6(ClO_4)][ClO_4]_7 \cdot 13MeCN$	$[Ni_2(L^2)_3][ClO_4]_4 \cdot 4MeCN \cdot 0.5(^iPr_2O)$
Formula	$C_{182}H_{155}B_8Co_4F_{32}N_{43}O$	$C_{194}H_{171}Cl_8Co_4N_{49}O_{32}$	$C_{95}H_{85}Cl_4N_{22}Ni_2O_{16.5}$
M	3890.7	4220.12	2058.1
Crystal size/mm^3	$0.5 \times 0.5 \times 0.1$	$0.7 \times 0.5 \times 0.2$	$0.4 \times 0.2 \times 0.2$
T/K	123	123	173
System, space group	Hexagonal, $R\bar{3}$	Monoclinic, $P2(1)/n$	Monoclinic, $P2(1)/n$
$a/\text{Å}$	18.540 (4)	27.67 (2)	24.7858 (10)
$b/\text{Å}$	18.540 (4)	18.440 (15)	12.6972 (5)
$c/\text{Å}$	181.09 (5)	40.30 (3)	30.4427 (12)
$\beta/°$	90	109.424 (15)	95.8960 (10)
$U/\text{Å}^3$	53909 (22)	19391 (27)	9529.9 (7)
Z	12	4	4
$\rho_{calc}/\text{g cm}^{-3}$	1.438	1.446	1.434
μ/mm^{-1}	0.463	0.532	0.586
Data/restraints/parameters	15680, 4, 1615	17981, 228, 1339	11264, 88, 1311
Final R_1, wR_2*	0.0721, 0.2142	0.2161, 0.5475	0.0563, 0.1685

Details in common: Siemens SMART diffractometer; Mo-Kα radiation (0.71073 Å°).
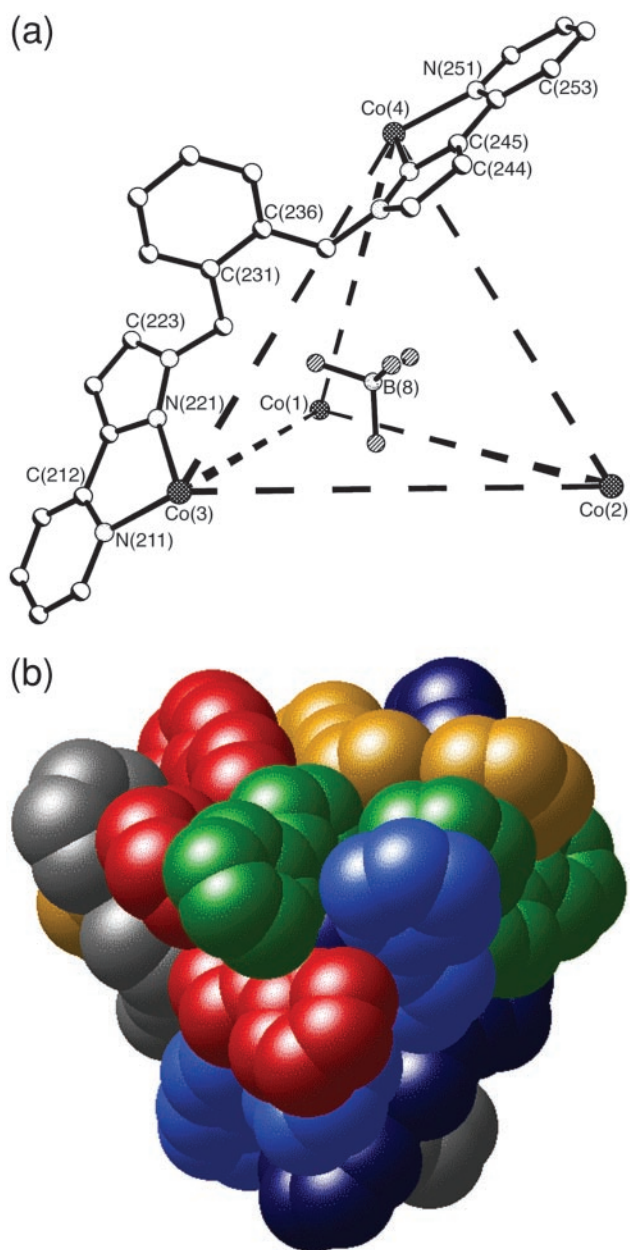*The value of R_1 is for selected data with $F \geq 4\sigma(F)$; the value of wR_2 is for all data.

(a)

(b)

Fig. 2. Crystal structure of the complex cation of $[Co_4(L^1)_6(BF_4)][BF_4]_7$, showing (*a*) one bridging ligand and the encapsulated anion and (*b*) a space-filling view with the ligands colored differently.

Fig. 3. Crystal structure of the complex cation of $[Ni_2(L^1)_3][BF_4]_4$. The terminal and bridging ligands are shaded differently.

signals is not obvious, but on the basis that the degree of shift depends on distance from the paramagnetic centers, we assign the least-shifted peaks I and J to the phenyl spacer.

When Co(II) acetate and L^1 are mixed in a 2:3 molar ratio in CD_3OD/D_2O (necessary to dissolve the metal salt), the ^1H NMR

Fig. 4. ^1H NMR spectra (300 MHz) of (*a*) $[Co_4(L^1)_6(BF_4)][BF_4]_7$ (redissolved crystals) in CD_3OD/CD_3CN; (*b*) a mixture of $Co(MeCO_2)_2 \cdot 2H_2O$ and L^1 in a 4:6 ratio in CD_3OD/D_2O; and (*c*) the solution in *b* after addition of aqueous $NaBF_4$ (similar results were obtained with $NaClO_4$).

trapped $[BF_4]^-$ anion did not exchange with the remaining seven free $[BF_4]^-$ anions on the NMR time scale (24). The reason for the quite different structure of this compared with the complex with Ni(II) is unclear, but may be related to the slightly different ionic radii of Co(II) and Ni(II).

The formation of $[Co_4(L^1)_6(BF_4)][BF_4]_7$ prompted us to carry out solution ^1H NMR studies to see whether a genuine anion-based template effect occurs. The ^1H NMR spectrum of the preformed complex $[Co_4(L^1)_6(BF_4)][BF_4]_7$ in CD_3CN/CD_3OD is in Fig. 4*a*. The paramagnetism of the high-spin Co(II) centers means that the signals from the ligand protons are in the 15–85 ppm range. Assuming that the cage adopts a *T*-symmetric structure in solution we expect 10 resonances—i.e., for each equivalent half of L^1—and this is what occurs (although two of the signals, D and E, are very weak). Assignment of individual
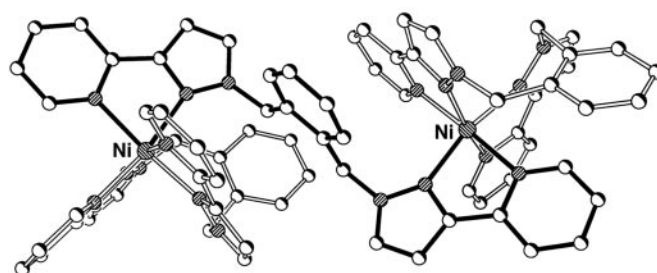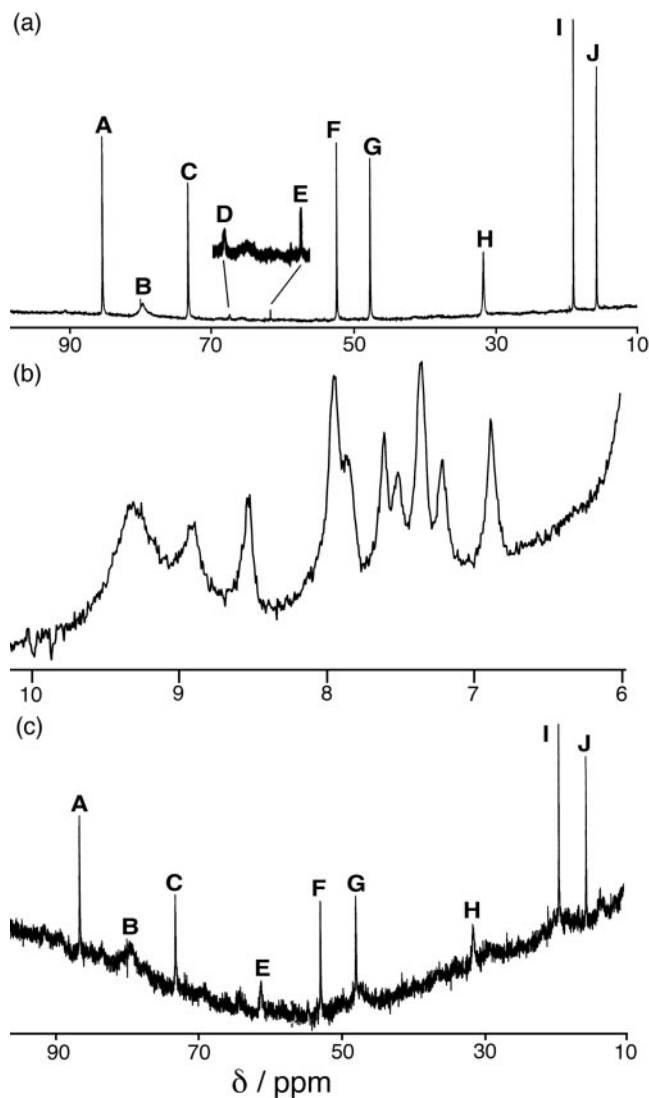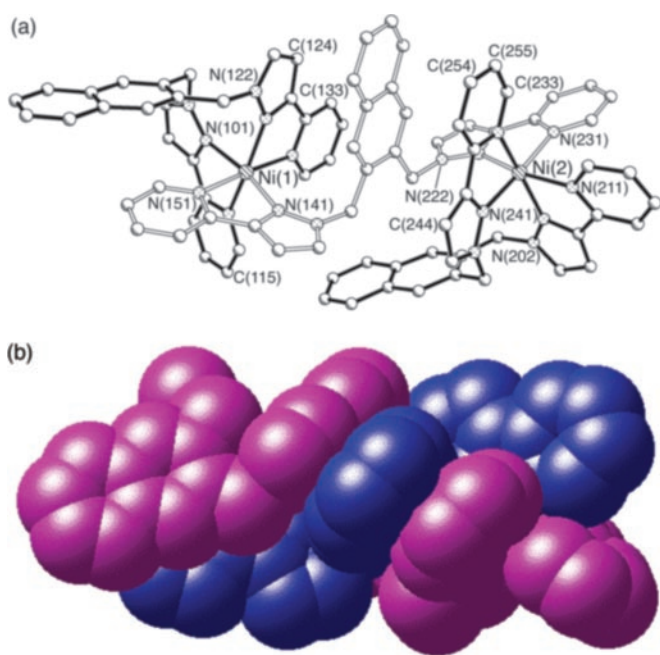
Fig. 5. Crystal structure of the complex cation of [Ni$_2$(L^2)$_3$][ClO$_4$]$_4$ showing (*a*) a conventional view with the terminal and bridging ligands shaded differently and (*b*) a space-filling view emphasizing the aromatic stacking with the bridging ligand in blue and the terminal ligands purple.

spectrum shown in Fig. 4*b* results. It lies in the normal chemical shift range, but is broad and poorly resolved because of some degree of interaction with the paramagnetic metal centers. There are no signals at shifts more positive than 10 ppm, indicating that no significant amount of the cage complex exists under these conditions. On addition of one equivalent of [BF$_4$]$^-$ to the sample, the spectrum changes dramatically (Fig. 4*c*) and becomes essentially identical to that in Fig. 3*a* measured for the preformed complex. This spectrum is rather noisy because of the poor solubility of the cage in this solvent mixture, but all of the principal features of the spectrum of the cage complex in Fig. 4*a* are present at the correct positions, and no other peaks are apparent. Addition of [BF$_4$]$^-$, therefore, results in quantitative assembly of the [Co$_4$(L^1)$_6$(BF$_4$)]$^{7+}$ cage in as much time as it took to make the addition and record a new spectrum (about a minute), and a genuine anion-templated assembly is occurring.

This simple ^{1}H NMR experiment allows us to screen for their templating ability in this system in solution. We found that [PF$_6$]$^-$ does not act as a template, but that [ClO$_4$]$^-$ does, with addition of [ClO$_4$]$^-$ to a mixture of Co(II) and L^1 resulting in a spectrum identical to that obtained by addition of [BF$_4$]$^-$ (Fig. 4*c*). These findings are in agreement with expectations based on the basis of the size and shape of these anions: hexafluorophosphate is clearly too large to fit in the cavity, whereas perchlorate—which is the same size and shape as tetrafluoroborate—is an effective template. We accordingly undertook further syntheses and structural studies with the related ligand L^2 by using both [BF$_4$]$^-$ and [ClO$_4$]$^-$ as anions.

Syntheses of L^2 and Formation of Cage Complexes with Co(II). We prepared L^2 by using the same general method as used for L^1 (24, 35), expecting that it will coordinate in the same manner as L^1 but with additional inter-ligand aromatic stacking interactions in the complexes provided by the naphthyl units. Reaction of Ni(II) acetate with L^2 in a 2:3 molar ratio in CH$_2$Cl$_2$/MeOH afforded a blue solution from which a precipitate appeared on addition of methanolic NaClO$_4$. On the basis of the electrospray mass
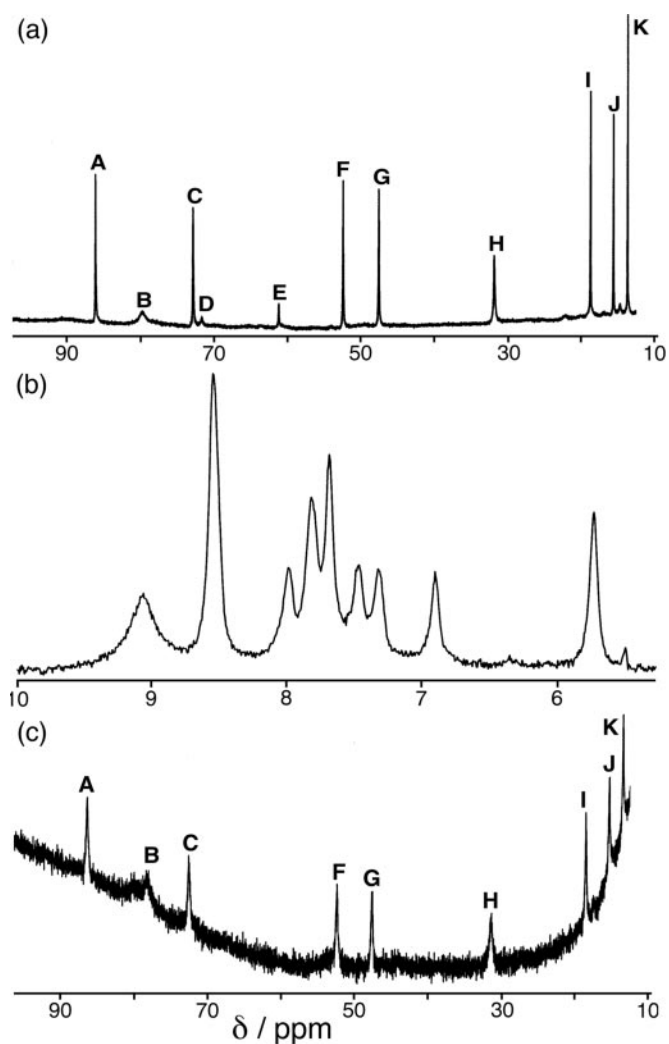

Fig. 6. ^{1}H NMR spectra (300 MHz) of (*a*) [Co$_4$(L^2)$_6$(ClO$_4$)][ClO$_4$]$_7$ (redissolved crystals) in CD$_3$OD/CD$_3$CN; (*b*) a mixture of Co(MeCO$_2$)$_2$·2H$_2$O and L^2 in a 4:6 ratio in CD$_3$OD/D$_2$O; and (*c*) the solution in *b* after addition of aqueous NaClO$_4$ (similar results were obtained with NaBF$_4$).

spectrum [which showed only the fragment {Ni(L^2)$_2$}$^{2+}$] and by analogy with the structure of the Ni(II) complex of L^1, we tentatively identified this complex as [Ni$_2$(L^2)$_3$][ClO$_4$]$_4$; this was confirmed by x-ray crystallography (Fig. 5). The dinuclear complex contains one tetradentate chelating ligand attached to each Ni(II) center, with the third ligand acting as a bis-bidentate bridge spanning the two metals, which are separated by 9.16 Å. The bridging ligand adopts a helical twist that is emphasized in the space-filling view shown in Fig. 5*b*; this view also emphasizes the inter-ligand aromatic stacking. The pseudooctahedral metal ions both have a meridional tris-chelate geometry, with unremarkable bond distances and angles (see supporting text). This structure illustrates the ability of L^2 to act as either a chelating or bridging ligand as circumstances dictate because of the flexibility provided by the methylene units.

Reaction of Co(II) acetate with L^2 in a 2:3 molar ratio in CH$_2$Cl$_2$/MeOH afforded an orange solution from which a precipitate appeared on addition of methanolic NaBF$_4$ or NaClO$_4$. From electrospray mass spectra, and by analogy with the behavior of L^1, we tentatively identified these as the cage complexes [Co$_4$(L^2)$_6$(BF$_4$)][BF$_4$]$_7$ and [Co$_4$(L^2)$_6$(ClO$_4$)][ClO$_4$]$_7$, respectively. In particular, the peak at highest *m/z* value in each

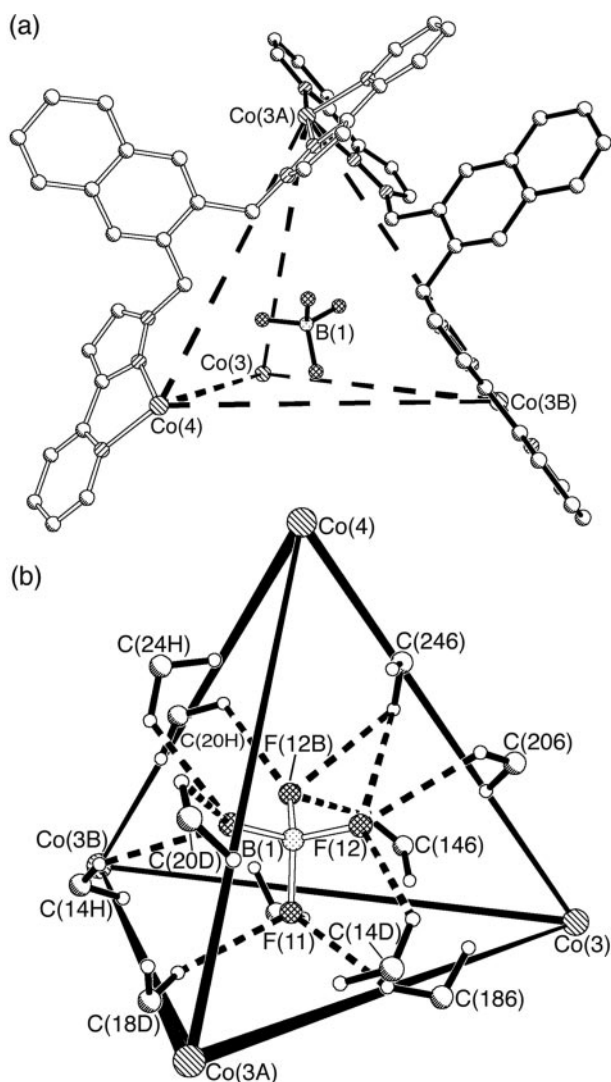**Fig. 7.** Crystal structure of the complex cation of $[Co_4(L^2)_6(BF_4)][BF_4]_7$. (*a*) A view showing two of the bridging ligands and the encapsulated anion. (*b*) The array of CH···F hydrogen-bonding interactions involving the CH₂ units of the ligands and the encapsulated anion.

Fig. 8. Space-filling view of the complex cation of $[Co_4(L^2)_6(BF_4)][BF_4]_7$ with each ligand colored differently. Note that the fluoroborate ion (pale blue) is barely visible through the gap in the center of the face.

case in the mass spectrum corresponds to the species $\{Co_4(L^2)_6(X)_5\}^{3+}$ (X = BF₄ or ClO₄ respectively), confirming the presence of the intact cage.

We followed the anion-templated assembly process in the manner described above (Fig. 6). The ¹H NMR spectrum of the preformed complex gave a characteristic highly shifted pattern of peaks, similar to that seen for the cage complex with L^1 but with three signals (I, J, and K) in the 10–20 ppm region rather than two. We assign these three peaks as arising from the 2,3-disubstituted naphthyl unit (with twofold symmetry), in agreement with their distance from the paramagnetic centers. In all other respects there is a clear correspondence between the signals of the cage complex with L^2 (Fig. 6a) and with L^1 (Fig. 4a). When Co(II) acetate and L^2 were mixed in a 2:3 ratio in MeOD/D₂O in an NMR tube, however, only a broad poorly resolved spectrum was seen in the normal region (5.5–9 ppm) with no sign of the highly shifted pattern of signals from the cage (Fig. 6b). Addition of one equivalent of either [BF₄]⁻ or [ClO₄]⁻ immediately resulted in appearance of the characteristic spectrum of the cage (Fig. 6c). This spectrum is noisy because the cage is poorly soluble, and the two weakest signals (D and E) are
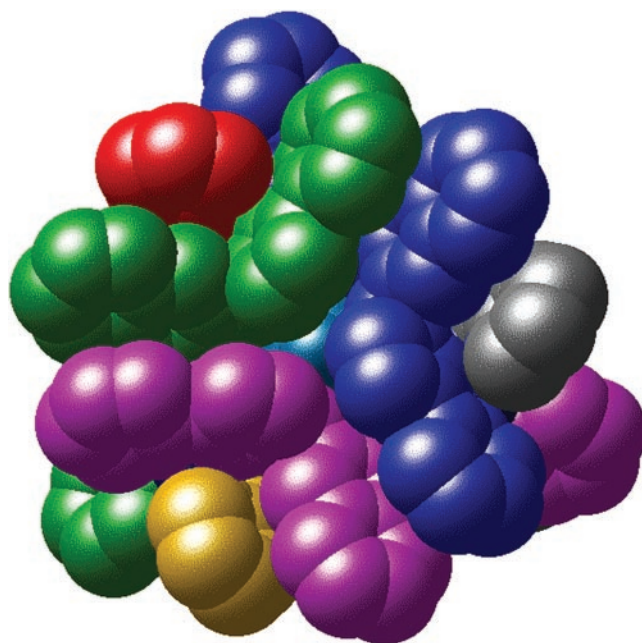
not resolved; but the remaining nine signals correspond exactly with those in Fig. 6a, confirming the templating action of the anions in these complexes also. The absence of any other signals means that assembly of the cage is quantitative in the presence of the template.

$[Co_4(L^2)_6(BF_4)][BF_4]_7$ gave x-ray-quality crystals from MeCN/ether (Figs. 7 and 8). The figures illustrate only one of the crystallographically independent cage cations; the alternate one is similar, and both contain [BF₄]⁻ ions in their central cavity. The Co–N separations are in the range 2.09–2.17 Å, and the coordination environment about each metal center is approximately octahedral with a facial tris-chelate geometry (see supporting text). The gross geometry is similar to that of the complex with L^1 described above: the metal ions form an approximately tetrahedral cage, with the Co···Co separations lying between 9.3 and 10 Å. The cage has approximate *T* symmetry with all four metal centers having the same configuration, such that the racemic crystals contain equal amounts of ΔΔΔΔ and ΛΛΛΛ forms (in solution the symmetry is exactly *T* on the basis of the NMR spectrum). The fluoroborate anion within each cavity is inverted with respect to the Co₄ tetrahedron such that each F atom is directed toward the space at the center of a Co₃ triangular face; the anion is approximately central in the cavity, with all Co···B distances being in the range 5.68–6.16 Å. The F atoms make close contacts with the CH₂ spacer units in some of the ligands, with nonbonded C···F distances lying in the range 3.07–3 38 Å and the associated H···F distances varying from 2.33 to 2.53 Å (Fig. 7b). These distances are characteristic of C–H···F hydrogen bonds (33, 34), and the number of such interactions (three per F atom, or 12 per cage) presumably contributes significantly to stabilization of the cage structure. From the space-filling view in Fig. 8, the intertwining of the six ligands, resulting in substantial aromatic stacking interactions between them, is clear. It is also apparent from this view that the [BF₄]⁻ anion in the cavity is almost completely encapsulated.

$[Co_4(L^2)_6(ClO_4)][ClO_4]_7$ also afforded crystals, which decomposed very fast because of the presence of 13 MeCN molecules per complex. The structural determination is accordingly of

lower precision than that of the $[BF_4]^-$ complex ($R1 = 21.6\%$), and detailed discussion of structural parameters is not warranted. The gross structure is, as expected from the ^{1}H NMR data, essentially identical to that of $[Co_4(L^1)_6(BF_4)][BF_4]_7$, with a perchlorate anion in the central cavity. The Co···Co separations lie in the range 9.2–10.3 Å, and the anion is centrally located with the Co···Cl distances lying between 5.7 and 6.1 Å. The perchlorate oxygen atoms are involved in short contacts with the CH_2 spacers of the ligands L^2 (nonbonded C···O separations in the range 3.0–3.3 Å), corresponding to C–H···O hydrogen-bonding interactions (34).

The behavior of these cage complexes contrasts with some recent examples described by Raymond and coworkers (10, 17), based on bridging ligands whose two binding sites are carefully arranged to optimize cage formation. These ligands cannot act as tetradentate chelates to a single metal, because the binding sites are divergent and give M_4L_6 cages quantitatively without the assistance of a template effect. As described previously, the cavity may contain a counterion or solvent molecules as guest species, but this is not a prerequisite for cage formation and the guests can be freely exchangeable with other species. With L^1 and L^2, however, the flexibility imparted by the methylene spacers means that both tetradentate chelating and bis-bidentate bridging coordination modes are available, giving either M_4L_6 or

M_2L_3 species. The balance between these seems to be in favor of the M_2L_3 complex in the absence of a template effect, with a templating anion altering the balance in favor of cage formation when M = Co(II) but not when M = Ni(II). It follows that larger tetrahedral anions (e.g., pertechnetate, tetrahalometallates) may act as templates for assembly of larger M_4L_6 cage complexes based on longer bridging ligands.

Conclusions

The tetrahedral cage complexes $[Co_4(\mu\text{-}L)_6X][X]_7$, where X = $[BF_4]^-$ or $[ClO_4]^-$ and L = L^1 or L^2, form by an anion-directed templating effect in solution. NMR spectra show that the cages form quantitatively only in the presence of a suitable templating anion (perchlorate or tetrafluoroborate), which is a good fit for the central cavity and which participates in hydrogen-bonding interactions with the ligand CH_2 groups. The anion is completely enclosed, is centrally located in the cavity, and is inverted with respect to the Co_4 tetrahedron. These templating anions seem to be ideally complementary in terms of size, shape, and charge for the cavities in which they are located. In contrast, with Ni(II), open-chain complexes $[Ni_2L_3]X_4$ form in which the same anions do not act as templates for cage assembly.

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