*Host–Guest Chemistry*

# Host–Guest Interactions: Design Strategy and Structure of an Unusual Cobalt Cage That Encapsulates a Tetrafluoroborate Anion**

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The rational design of inorganic artificial receptors for host–guest chemistry is one of the most attractive areas in contemporary supramolecular chemistry.[1] Self-assembly is emerging as an elegant "bottom-up" method for fabricating elaborate architectures[2] such as helicates,[3] cages,[4] metallocryptands,[5] metallomacrocyles,[6] and coordination polymers.[7] This approach is particularly powerful when the ease of control offered by the self-assembly of organic components is combined with electronic, ion-sensing, catalytic, magnetic, or photonic properties of inorganic components.

Over the last decade there has been intensive research into the preparation of inorganic macrocycles, which have shown particular promise in host–guest chemistry.[8]Although the coordination chemistry of cations is well developed, the chemistry of anion encapsulation is still in its infancy despite the fact that anion-coordination chemistry is of interest from environmental, industrial, and health-related perspectives.[9]

We recently reported the self-assembly of iridocryptates that encapsulate $BF_4^-$ anions through hydrogen bonding,[5a] but the present work differs completely to that reported previously in terms of coordination and binding. Herein, we report a rational high-yield strategy (> 90 %) for the preparation of unusual inorganic cages **1a**–**c** (Scheme 1) based on the coordination chemistry of cobalt and demonstrate their properties as hosts for anions. Prior to this work, only a few examples of supramolecular, inorganic-anion receptors had been reported: a metallohelicate that encapsulates a $PF_6^-$ ion[10] and a supramolecular tetrahedral complex that encapsulates a $BF_4^-$ ion[11] are two examples.

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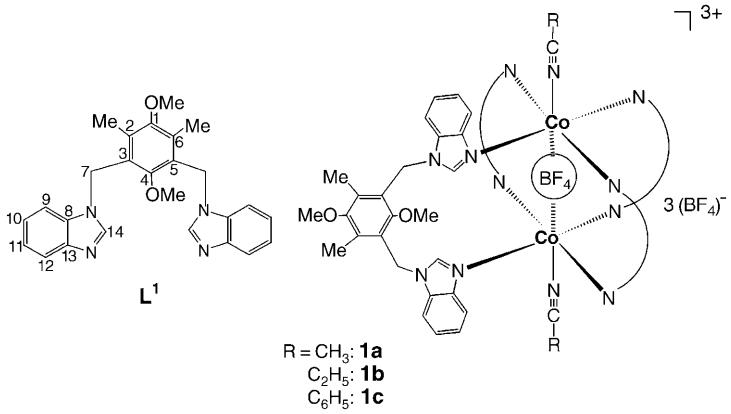


***Scheme 1.*** Schematic drawings of ligand $L^1$ (with atom numbering scheme for $^1$H NMR assignments) and the related $[Co_2(L^1)_4]$ cages **1a–c**.

The novelty of our work is the use of $Co^{II}(BF_4)_2{\cdot}6H_2O$ as a precursor and a coordinatively unsaturated connector to promote a dative interaction between the metal cation and the weakly coordinating anions in the final supramolecular structure. Rational design of these materials is complicated by uncertain factors such as the counteranion, the solvent, and the ligand geometry. Support for this complication is manifested in the only known $Co^{II}$-based cage anion $[Co_4L_6]$ (L = di(pyrazolylpyridine)-1,2-phenylene),[12] in which the geometry about each cobalt center is octahedral with the three bidentate ligands, and the encapsulated $BF_4^-$ anion is bound by Coulombic attraction and a symmetry match between the host and the guest. Here, our system behaves completely different. To the best of our knowledge, we describe the first coordinatively unsaturated cobalt-based $[M_2(L^1)_4]$ cage (see Scheme 1) and demonstrate its encapsulation of $BF_4^-$ anions through direct coordination of the unsaturated metal center and the guest anion.

Treatment of two equivalents of ligand $L^1$ with $Co(BF_4)_2{\cdot}6H_2O$ in a solution of methanol/chloroform for several hours yielded a blue precipitate, which was characterized as $[(CH_3OH)_2Co_2(L^1)_4](BF_4)_4$. The precipitate was recrystallized from $CH_3CN/Et_2O$ to quantitatively afford bright pink crystals, which were characterized as $[(CH_3CN)_2Co_2(L^1)_4](BF_4)_4$ (**1a**). In a similar way, the two other supramolecular cages $[(C_2H_5CN)_2Co_2(L^1)_4](BF_4)_4$ (**1b**) and $[(C_6H_5CN)_2Co_2(L^1)_4](BF_4)_4$ (**1c**) were obtained as light pink and salmon-colored crystals, respectively, through recrystallization from a mixture of the related nitrile solvent RCN ($R = C_2H_5$-; $C_6H_5$-) in $Et_2O$. The NMR spectra ($^1$H,$^{11}$B) of **1a–c** recorded in $CD_3CN$ were all very similar, however, **1b** and **1c** showed displacement of the nitrile solvent RCN ($R = C_2H_5$-; $C_6H_5$-) by the more strongly coordinating NMR solvent $CD_3CN$.

The $^1$H NMR spectrum (400 MHz) of **1a** was recorded in $CD_3CN$ at 292 K, and owing to the presence of $Co^{II}$ atoms the spectrum spanned a broad range from $\delta = 45.70$ to $-6.06$ ppm, a range that is consistent with the presence of paramagnetic compounds. The spectrum of **1a** shows the presence of 10 signals, which were all assigned by means of peak integration ratios, COSY experiments performed at 352.5 K, and $T_1$ measurements at 292 K using the Solomon equation[13] (Figure 1). As $T_1^{-1}$ is proportional to $\Sigma(r_{ij}^{-6})$, where $r_{ij}$ is the distance between the hydrogen atoms and the cobalt

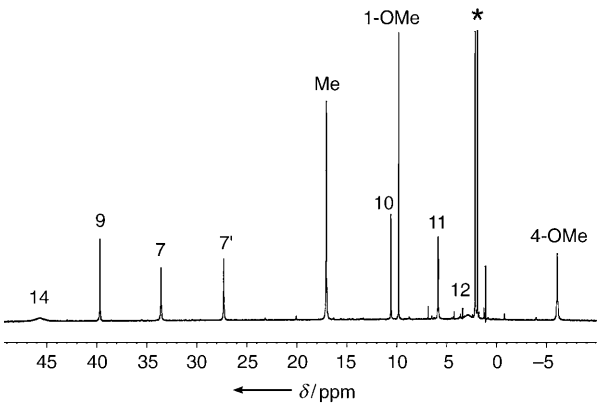


***Figure 1.*** $^1$H NMR spectrum of **1a** recorded in $CD_3CN$ at 292 K. The symbol * denotes the residual solvent peak ($CH_3CN/CD_2HCN$).

ions, the relative values of $T_1$ were estimated and normalized to obtain the best fit with experimental measurements (see Supporting Information). The COSY spectrum showed connectivity between $H^{10}$ and both $H^9$ and $H^{11}$, and between $H^7$ and $H^{7'}$ (see Supporting Information).

Significantly the methylene protons -$CH_2^7$- are inequivalent and show two signals at $\delta = 33.59$ and 27.30 ppm. The inequivalency results from the formation of a rigid cage, with the arene rings lying along the equator of the approximate sphere of the complexed ion. This result suggests that the presence of a guest anion inside the cavity of the cage increases the rigidity. Remarkably the $^{11}$B NMR spectrum of **1a** recorded in $CD_3CN$ showed not only the presence of a sharp singlet at $\delta = -0.82$ ppm that we attribute to the free $BF_4^-$ anion but also another broad signal at $\delta = -105.1$ ppm that was assigned to an encapsulated $BF_4^-$ ion (see Supporting Information). We attribute this large difference in chemical shift values to the paramagnetic nature of the Co ions.

The electrospray mass spectrum of **1a** clearly indicated the formation of the $[Co_2(L^1)_4]$ species in association with varying numbers of $BF_4^-$ anions (see Supporting Information). To ascertain unambiguously the structure of **1a**, an analysis of the crystal structure was undertaken. Crystals of **1a** were grown by vapor diffusion of diethyl ether into a solution of the complex in $CH_3CN/CH_3NO_2$.[14] The compound crystallized in the monoclinic space group $P2_1/n$. The structure shows the formation of a $[Co_2(L^1)_4]$ tetragonal cage (Figure 2), in which each cobalt ion adopts a square-pyramidal geometry. The equatorial positions are filled by four benzimidazole arms of the bridging ligands $L^1$, and the axial position is coordinated by a solvent molecule, $CH_3CN$. The two methoxy groups are arranged in a *trans* fashion with one pointing towards the encapsulated $BF_4^-$ anion while the other is directed in the opposite sense away from the cage cavity. The coordinatively unsaturated cobalt center binds to a $BF_4^-$ anion located inside the cavity through a metal–anion coordination bond with a

  

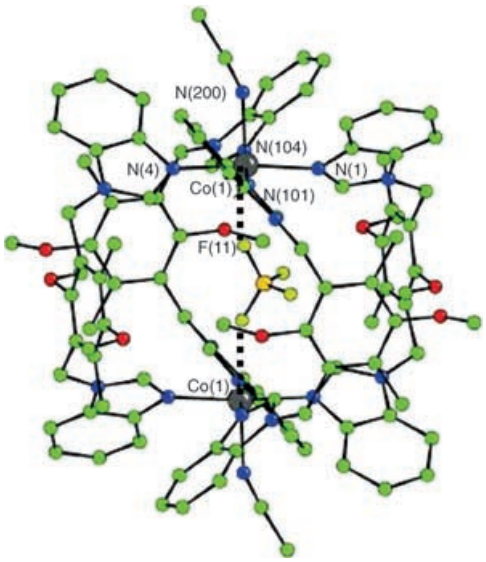


***Figure 2.*** X-ray crystal structure of $[BF_4{\subset}(CH_3CN)_2Co_2(L^1)_4]^{3+}$ (C green, O red, N blue, B yellow, F pale green, Co gray; H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Co(1)–N(1) = 2.082(8), Co(1)–N(101) = 2.094(9), Co(1)–N(4) = 2.088(8) Co(1)–N(104) = 2.110(9), Co(1)–F(11) = 2.405(8); N(1)-Co(1)-N(4) = 175.5(3), N(101)-Co(1)-N(104) = 174.5(3), Co(1)-N(1)-C(1) = 123.6(7).

bond length of 2.405 Å (Co···F). The two nonbridging fluorine atoms (-FB*F*$_2$F-) occupy four sites (each fluorine atom was refined with half-occupancy). The other three $BF_4^-$ anions are located outside the cavity. The Co···N bond lengths lie in the range of 2.08–2.11 Å, typical for complexes of high-spin $Co^{II}$.[12] The Co–Co distance is 7.1 Å, and the average distance between two facing phenyl rings is 11 Å.

The present example describes the first structure of a coordinatively unsaturated cobalt cage, which encapsulates a fluorinated anion through an unusual direct Co···F coordination bond. Anions such as $BF_4^-$ are generally considered to be highly noncoordinating and only weakly interacting. The only previous example of a direct host metal/guest anion interaction was reported for a $PF_6^-$ ion encapsulated through interaction with two Pd centers of a quadruply stranded helicate.[10]

We then examined the behavior of the cage **1a** in solution by recording the $^1$H and $^{11}$B NMR spectra at variable temperatures in the range of 292–352.5 K. The observation of separate signals for the -$CH_2$- protons shows that the structure is rigid. No exchange of the protons H[7] was detected by EXSY (exchange spectroscopy) at the higher temperature which gave a lower limit for the exchange process of $\Delta G^{\neq} = 80\ kJ\,mol^{-1}$. The $^{11}$B NMR spectrum at room temperature showed two signals, as discussed earlier. Neither magnetization-transfer measurements nor EXSY showed any evidence of exchange at 60 °C. This result permits a lower limit of $\Delta G^{\neq} = 75\ kJ\,mol^{-1}$ to be set for the release of the encapsulated $BF_4^-$ ion from the cavity. Therefore, the anion is trapped in the cavity with no or slow exchange with the free anions on the NMR timescale.

Ward and co-workers have prepared several cages of the general formula $\{BF_4{\subset}[Co_4(L^2)_6](BF_4)_7\}$, where $L^2$ is a tetradentate ligand that comprises two pyrazolylpyridine units attached to a 1,2-phenylene or to a 1,2-naphthylene spacer.[15] They found that the ease of exchange of the encapsulated anion depends on the size of the spacer, with facile exchange ($\Delta G^{\neq} = 50\ kJ\,mol^{-1}$) for the complex with a 1,2-naphthylene spacer, while for the rigid bridging 1,2-phenylene spacer the exchange was very slow on the NMR timescale.

In our system the encapsulated $BF_4^-$ anion is an essential part of the structure. In **1a–c** the encapsulated $BF_4^-$ anion plays a pivotal role as a template, around which the two $Co^{II}$ metal ions and the four ligands self-assemble. Furthermore, the rigid nature of the bridging ligand $L^1$ in which a 1,4-phenylene spacer holds two benzimidazole arms to provide a rigid cage (Scheme 1) means that the encapsulated $BF_4^-$ anion is locked in the cavity and is not released. Future objectives are directed towards the preparation of other bidentate ligands that comprise larger spacers so as to develop flexible cages, destined to encapsulate a variety of anions of different sizes and geometries.

## *Experimental Section*

All experimental manipulations were carried out under argon using Schlenk techniques. $^1$H and $^{11}$B NMR spectra were recorded in $CD_3CN$ using a Bruker AMX-2 400 NMR spectrometer at 400.13 and 128.38 MHz, respectively, and also a Bruker Avance 400 NMR instrument. The temperature of the sample was determined by means of a thermocouple and measured using a Comark N9009 thermometer.

**1a**: Ligand $L^1$ (403 mg, 1 mmol; see Scheme 1) in $CHCl_3$ (15 mL) was added to a pink solution of $Co(BF_4)_2{\cdot}6H_2O$ (120 mg, 0.352 mmol) in $CH_3OH$ (15 mL). The solution was stirred at room temperature for 12 h, during which time a deep blue precipitate formed. The solids were collected by filtration, washed with $CHCl_3$, and dried under vacuum. This material was characterized as $[(CH_3OH)_2Co_2(L^1)_4](BF_4)_4$; elemental analysis (%): calcd for $C_{106}H_{112}N_{16}O_{10}Co_2B_4F_{16}$ (2235.24 g mol$^{-1}$): C 56.96, H 5.05, N 10.03; found: C 56.83, H 5.20, N, 10.13.

The precipitate was then dissolved in $CH_3CN$ and recrystallized from $CH_3CN/Et_2O$ to provide bright pink crystals of $\{[BF_4{\subset}(CH_3CN)_2Co_2(L^1)_4](BF_4)_3\}$ (**1a**); elemental analysis (%): calcd for $C_{108}H_{110}N_{18}O_8Co_2B_4F_{16}$ (2253.28 g mol$^{-1}$): C 57.57, H 4.92, N 11.19; found: C 55.49, H 5.05, N 10.09; $^1$H NMR (see Supporting Information); $^{11}$B NMR (128 MHz, $CD_3CN$): $\delta = -0.82$ (sh, free $BF_4$), $-105.1$ ppm (br, encapsulated $BF_4$); IR (KBr disk): $\tilde{\nu}$(B-F) = 1071 cm$^{-1}$; ES-MS (*m*/*z*): calcd for $C_{104}H_{104}O_8N_{16}Co_2B_4F_{16}$ $[M^{4+} + 3BF_4^-]^+$: 2083.5; found: 2084.54; calcd for $[M^{4+} + 2BF_4^-]^{2+}$: 998.35; found: 998.35; calcd for $[M^{4+} + BF_4^-]^{3+}$: 636.63; found: 636.82; calcd for $[M^{4+}]$: 455.77; found: 456.05.

**1b**: This supramolecular cage was prepared in a similar way as described for **1a**, but was recrystallized from $C_2H_5CN/Et_2O$ to afford the title compound quantitatively as light pink crystals of $\{[BF_4{\subset}(C_2H_5CN)_2Co_2(L^1)_4](BF_4)_3\}$ (**1b**); elemental analysis (%): calcd for $C_{110}H_{114}N_{18}O_8Co_2B_4F_{16}$ (2281.31 g mol$^{-1}$): C 57.91, H 5.04, N 11.05; found: C 56.18, H 5.11, N 10.03; the NMR data recorded in $CD_3CN$ were similar to those observed for **1a**, but we note the presence of free displaced $C_2H_5CN$ in the $^1$H NMR spectrum at $\delta$ = 2.38 (q, 4H, $CH_2$) and 1.23 ppm (t, 6H, $CH_3$); $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta = -0.74$ (sh, free $BF_4$), $-105.2$ ppm (br, encapsulated

  

$BF_4$); IR (KBr disk): $\tilde{\nu}$(B-F) = 1083 $cm^{-1}$; ES-MS (*m*/*z*): calcd for $C_{104}H_{104}O_8N_{16}Co_2B_4F_{16}$ $[M^{4+} + 3\,BF_4^-]^+$: 2083.5; found: 2084.91; calcd for $[M^{4+} + 2\,BF_4^-]^{2+}$: 998.35; found: 998.35; calcd for $[M^{4+} + BF_4^-]^{3+}$: 636.63; found: 636.82; calcd for $[M^{4+}]$: 455.77; found: 456.05.

**1c**: This complex was prepared in a similar fashion to **1a**, but was recrystallized from $C_6H_5CN/Et_2O$ to afford the title compound quantitatively as salmon-colored crystals of $\{[BF_4\subset(C_6H_5CN)_2Co_2(L^1)_4](BF_4)_3\}$ (**1c**); elemental analysis (%): calcd for $C_{110}H_{114}N_{18}O_8Co_2B_4F_{16}$ (2377.4 g $mol^{-1}$): C 59.62, H 4.83, N 10.60; found: C 57.41, H 4.82, N 10.48; the NMR data recorded in $CD_3CN$ were analogous to those for **1a**, but we note the presence of free displaced $C_6H_5CN$ in the $^1$H NMR spectrum at $\delta$ = 7.76 (m, $C_6H_5$) and 7.57 ppm (m, $C_6H_5$); $^{11}$B NMR (128 MHz, $CD_3CN$): $\delta$ = −0.98 (sh, free $BF_4$), −108.2 ppm (br, encapsulated $BF_4$); IR (KBr disk): $\tilde{\nu}$(B-F) = 1073 $cm^{-1}$.

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[14] Structural data for **1a**: $C_{112}H_{116}B_4Co_2F_{16}N_{20}O_8$, $M_r$ = 2335.36, pink crystals, crystal dimensions: 0.10 × 0.10 × 0.10 $mm^3$; monoclinic $P2_1/n$, $a$ = 14.418(3) Å, $b$ = 22.387(5) Å, $c$ = 18.844(4) Å, $V$ = 5875.4(21) $Å^3$, $Z$ = 4, $D$ = 1.32 g $cm^{-3}$, $T$ = 180 K, $R$ (*Rw*) 0.0838 (0.0879) for 10923 observed independent reflections, GOF = 1.11; Nonius KAPPA CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71069 Å) collection range $2\theta$ = 2–51°. Empirical DIFABS absorption correction was applied. The structure was determined by direct methods and subsequent difference Fourier syntheses, and refined by full-matrix least-squares on $F$ by using the PC version of the CRYSTALS package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a difference Fourier map, but they were introduced in the refinement in calculated positions and were affected by an overall isotropic thermal parameter. CCDC 265267 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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