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Supramolecular Cobalt Cages and Coordination Polymers Templated by Anion Guests: Self-Assembly, Structures, and Magnetic Properties

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Abstract: We report the anion-templated syntheses of a variety of supramolecular assemblies of Co^{II}. Remarkably in the presence of a weakly coordinating ion such as BF_4^-, a discrete three-dimensional cage $[BF_4\subset(BF_4)_2Co_2(L^1)_4][BF_4]$ (**2**) is formed with three coordinated BF_4^- ions, a rare example in supramolecular chemistry (L^1 = di(benzimidazole)-1,4-phenylene). Switching to stronger coordinating ions, such as NO_3^- or Cl^-, a one-dimensional coordination polymer $[\{Co(L^1)(NO_3)_2\}_n]$ (**3**) and a metallomacrocycle $[Co_2(L^1)_2(Cl)_4]$ (**5**) were formed, respectively. These results illustrate the powerful effect of the anion-templating chemistry. Finally the magnetic properties of these assemblies **1b**, **2**, **3**, and **5** are presented and discussed.

Keywords: anions · cage compounds · cobalt · host–guest systems · self-assembly · supramolecular chemistry

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, such as helicates,[2] molecular wires,[3] cages,[4] metallocryptands,[5] metallomacrocycles,[6a] and coordination polymers.[6b] This approach becomes particularly powerful when the ease of control offered by the self-assembly of organic components is combined with magnetism,[7] catalysis,[8] and ion sensing[9] of the inorganic components.

In the last decade there has been intensive research in the preparation of inorganic macrocycles, which has shown particular promise in the chemistry of host–guest interactions.[10] 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.[11]

Pursuing our research in this area we reported the self-assembly of the iridocryptates that encapsulate BF_4^- ions through hydrogen bonding.[5a] More recently we described the self-assembly of unusual inorganic cages based on cobalt coordination chemistry and demonstrated their properties as hosts for BF_4^- ions. It is worth mentioning that several examples of supramolecular inorganic anion receptors have been reported by other groups.[12–14] Furthermore polyoxometallate clusters of nanoscale size were able to trap anions within the central cavity.[15]

In this work we describe the role and the nature of the anion guest and how it dictates the final supramolecular structure. Remarkably, structural switching from cages to coordination polymers is driven by the nature of the anion guest in the supramolecular assembly. For instance in case of a weakly coordinating guest anion, such as BF_4^-, cobalt cages were assembled, while in the presence of strongly coordinating guest anions, such as NO_3^-, one-dimensional coordination polymers were obtained, or with Cl^- a metallomacrocycle was constructed (Scheme 1).

On the other hand magnetostructural correlations have been studied extensively in recent years.[16] However, in the host–guest chemistry of metal cages, the magnetic properties

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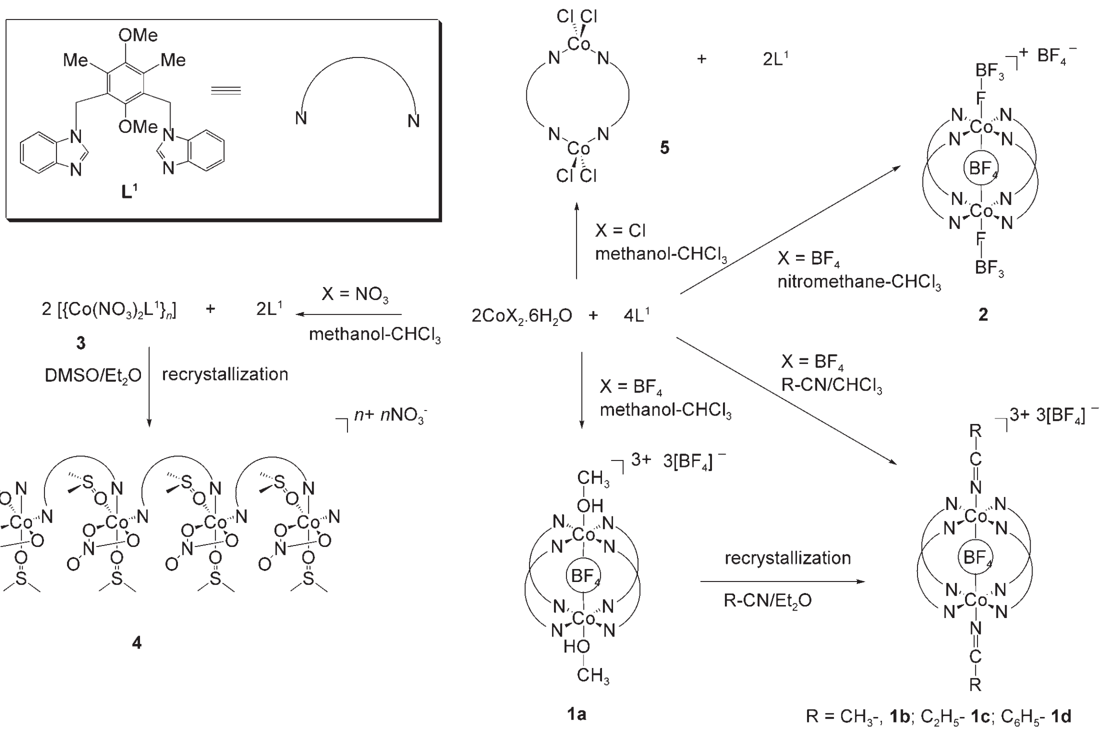

Scheme 1. Schematic drawing of L^1 and the reaction scheme for the related cobalt supramolecular structures **1**–**5**.

of hosts affected by anion guests have rarely been reported, although significant interactions were found to occur through halogen anions.[17] Thus we report the magnetic studies on our cobalt cages, metallomacrocycles, and one-dimensional coordination polymers. Of particular interest, the cobalt cages are rare models in which the magnetic exchange of binuclear Co^{II} is dominated by the weak interactions of the encapsulated anion and the two metal centers.

In a recent paper we have shown that $Co^{II}[BF_4]_2{\cdot}6H_2O$ reacts with two equivalents of L^1 (L^1 = di(benzimidazole)-1,4-phenylene) to give supramolecular host–guest cages of general formula $[BF_4{\subset}(S)_2Co_2(L^1)_4][BF_4]_3$ (**1a–d**) in which S is a coordinating solvent such as a nitrile R-CN (R = Me, Et, Ph) or methanol (Scheme 1). Interestingly two coordinating solvents were found to occupy the axial positions of the dicobalt capsules.[4b] Thus we decided to design new cages, but in the absence of coordinating solvent in which only anions can dictate the final supramolecular structure. Therefore repeating the above experiments, but using nitromethane as a non-coordinating solvent a new deep violet complex was isolated quantitatively and analyzed elementally as $[Co_2(L^1)_4][BF_4]_4$ (**2**). The infra-red of **2** showed the presence of BF_4^- ion. The 400 MHz ^1H NMR spectrum of **2** was recorded in CD_3NO_2 at 292 K and owing to the presence of Co^{II} atoms, the spectrum spanned a broad range from $\delta = -3$ to $+48$ ppm, a range that is consistent with the presence of paramagnetic compounds. Remarkably the ^{11}B NMR spectrum of **2** recorded in CD_3NO_2 showed the presence of a signal at $\delta = 1.92$ ppm and a broad signal at $\delta = -99.23$ ppm attributed to an encapsulated BF_4^- ion. We attribute the large difference in chemical shift values to the paramagnetic nature of the cobalt ions. The (ES) mass spectrum of **2** clearly indicated the formation of a peak at m/z 2083.7, which corresponds to the $[(BF_4)_3Co_2(L^1)_4]^+$ species. To ascertain the structure of **2** an X-ray structural determination was under taken. Crystals of **2** were grown by vapor diffusion of diethyl ether into a solution of the complex in CH_3NO_2.[18] The compound crystallized in the triclinic space group $P\bar{1}$. The structure shows the formation of a novel type of a $Co_2(L^1)_4$ tetragonal cage (Figure 1) in which each cobalt atom adopts a square-pyramidal geometry. Unlike previous cages (**1a–d**) there are two coordinated BF_4^- anions that bind externally (apical positions) to the two cobalt centers instead of a coordinating solvent with $Co(1){-}F(4) = 2.187$ Å. Four benzimidazole arms of the bridging ligands L^1 fill the equatorial positions. Further, a third BF_4^- ion is encapsulated inside the cage cavity with a $Co(1){-}F(1)$ distance of 2.312 Å. This distance is slightly longer than that observed for the externally bonded BF_4 ions, but shorter than that reported for $[BF_4{\subset}(CH_3CN)_2Co_2(L^1)_4][BF_4]_3$ (**1b**) with $Co{-}F = 2.405$ Å in which a single BF_4^- ion was encapsulated inside the cage. In light of this data one might consider that a weak interaction is occurring between the Co^{II} atoms and the apical fluorine centers of the encapsulated BF_4^- ion. The fourth BF_4^- ion is located outside the cavity. The Co–N bond lengths lie in the range of 2.102–2.123 Å, similar to those reported for **1b**.[4b] The Co···Co distance is 6.912 Å and the average distance between two facing phenyl rings is 10.7 Å. Thus the cavity size is slightly smaller than that of **1b**. To our knowledge this is the only example of a cage that exhibits coordination of three fluorinated weakly binding anions, one encapsulated inside the cavity cage and the

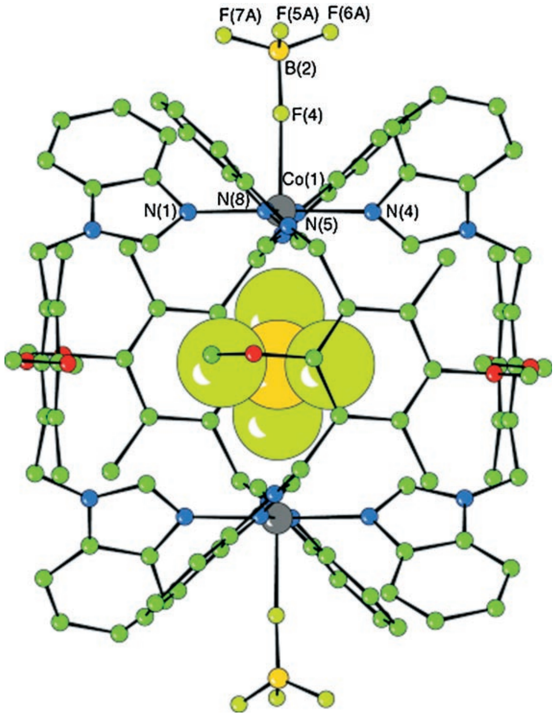

Figure 1. View of the cationic part of **2** "$[BF_4{\subset}(BF_4)_2Co_2(L^1)_4]^+$" (C green, O red, N blue, B yellow, F pale green, Co gray; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Co(1)–N(1) 2.104(3), Co(1)–N(4) 2.123(3), Co(1)–N(5) 2.104(3), Co(1)–N(8) 2.102(3), Co(1)–F(1) 2.312(3), Co(1)–F(4) 2.187(3), N(1)-Co(1)-N(5) 90.54(14), N(5)-Co(1)-N(4) 90.66(14), N(4)-Co(1)-N(8) 89.43(14), N(8)-Co(1)-N(1) 89.31(14).

other two are externally bound through unusual Co–F coordination bonds. This example beautifully illustrates the role of anions in templating supramolecular cages. Further the ES mass spectrum of **2** suggests that the redissolved crystals retain their structure in solution.

Repeating the previous experiments but using $Co^{II}[NO_3]_2{\cdot}6H_2O$ instead of $Co^{II}[BF_4]_2{\cdot}6H_2O$ and two equivalents of L^1 under similar experimental conditions described previously for cages **1b** or **2** a pink precipitate was quantitatively isolated and analyzed elementally as $[Co(L^1)(NO_3)_2]$ (**3**). The electrospray (ES) mass spectrum shows a peak at m/z 973.5 that corresponds to the formation of a $[Co(L^1)_2NO_3]^+$ species in solution. This indicates that the $[Co(L^1)_2NO_3]^+$ subunit is the building block which leads to the formation of the one-dimensional coordination polymer **3**. The infra-red spectrum shows the presence of coordinating nitrate at 1385 cm^{-1}. Complex **3** was insoluble in most polar solvents, such as MeOH, acetone, CH_3CN or nitromethane, hence no NMR spectroscopic studies could be performed; however, after several attempts to crystallize the complex, suitable crystals for an X-ray structural determination were obtained from a solution of **3** in DMSO/Et_2O. The structure shows indeed the formation of one-dimensional coordination polymer $[\{[Co(L^1)(NO_3)(dmso)_2][NO_3]\}_n]$ (**4**) in which the cobalt nodes are linked through the benzimidazole arms of the bridging ligand L^1 (Figure 2). In the cationic part of **4** each cobalt center adopts an octahedral geometry with two nitrogen atoms from different L^1 units occupying one axial site and one equatorial position, the nitrate anion forms a chelate to the Co^{II} ion in the equatorial plane, and finally two DMSO molecules are coordinated to the cobalt center through the oxygen atoms and are located one in the equatorial position and the other at an axial site. The one-dimensional coordination polymer **4** displays a π–π interaction between the central phenyl rings with a plane-to-plane distance of 3.73 Å, $\theta = 21.26°$.[19] This weak π interaction is observed throughout the infinite chain. The Co···Co distance is 10.602 Å. Due to the low solubilities of **3** and **4**, as well as their similar infra-red spectra and ES mass spectra (see Experimental Section), we conclude that **3** is also a one-dimensional coordination polymer similar to **4**.

In an effort to understand the crucial role of the anion in the formation of the cobalt cages **1b–d** and **2** with respect to that of the one-dimensional coordination polymers **3** and **4**, in which the nitrate ion is coordinated to the cobalt center, we added an excess of $[NBu_4]NO_3$ to a stirred solution of **2** in CH_3NO_2 and monitored the reaction. After several minutes a pink precipitate was formed and the reaction was allowed to proceed for 30 min. The product was isolated, characterized by elemental analysis and infrared spectroscopy, and was assigned as the one-dimensional coordination polymer **3**. This result confirms the templating effect of the coordinated NO_3^- ion on the formation of the ultimate supramolecular structure. In this case the anion metathesis leads to a complete rearrangement of the structure from a cobalt cage to a one-dimensional coordination polymer.

We then explored the role of the chloride anion on the formation of the supramolecular structure within our cobalt systems. Thus when $Co^{II}Cl_2{\cdot}6H_2O$ was treated with the bidentate ligand L^1 under similar experimental conditions to those used in the previous reactions, a blue precipitate was immediately formed. The compound was quantitatively isolated and analyzed elementally as a metallomacrocycle $[Co_2(L^1)_2(Cl)_4]$ (**5**; Scheme 1). Unlike the previous supramolecular species **1a–d** and **2–4** the UV/Vis spectrum of **5** recorded in DMF showed an absorption band at 654 nm characteristic of a tetrahedral cobalt(II) complex.[20] The infrared spectrum recorded from KBr discs showed the presence of two bands at 304 and 339 cm^{-1} designated to Co–Cl vibrations. The electrospray mass spectrum of crystals of **5** indicated the formation of $\{Co_2(L^1)_2\}$ species in association with varying numbers of Cl^- ions, indicating that the solution and solid-state structures of the chloride macrocycle **5** are the same. After several attempts of crystallization of **5**, tiny crystals were obtained from DMF/Et_2O mixture. Unfortunately complete structural analysis could not be achieved; however, the electrospray mass spectrum confirmed the formation of a metallomacrocycle $[Co_2(L^1)_2(Cl)_4]$ (**5**; Figure 3) rather than a cobalt cage or a one-dimensional coordination polymer.

As in the previous section we examined the role of the anion to dictate the final supramolecular structure. Thus addition of an excess of $[NBu_4]Cl$ to a stirred solution of **3** in

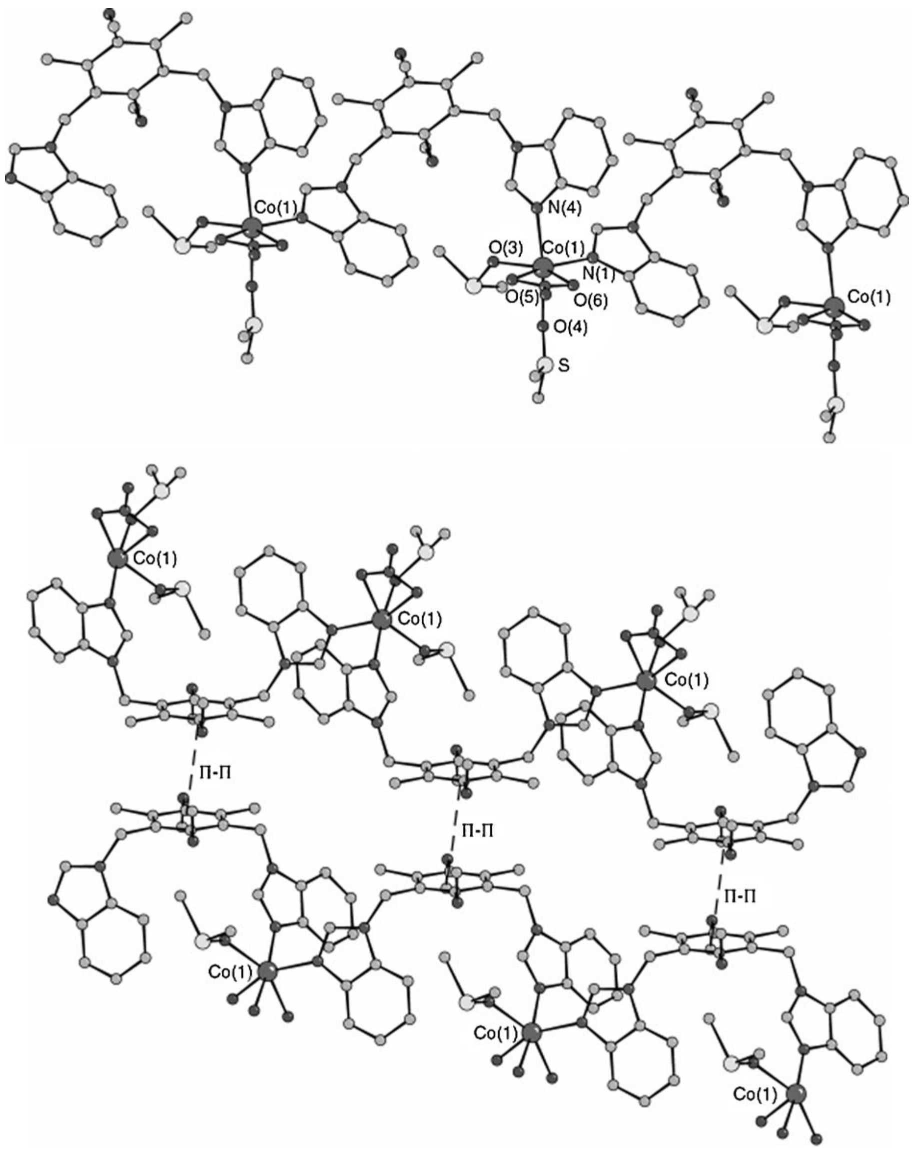

Figure 2. a) View of the cationic part of **4** "$[\{Co(L^1)(NO_3)(dmso)_2\}_n]^{n+}$" showing the chelating NO_3^- ions (H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Co(1)−N(1) 2.067(3), Co(1)−N(4) 2.100(3), Co(1)−O(3) 2.051(2), Co(1)−O(4) 2.119(2) Co(1)−O(5) 2.239(3), Co(1)−O(6) 2.181(3), N(1)-Co(1)-N(4) 91.38(10), O(3)-Co(1)-O(4) 85.74(11), O(5)-Co(1)-O(6) 57.17(12). b) π–π interactions between two adjacent one-dimensional coordination polymers in **4**.

CH_3CN provoked a rapid color change and a blue precipitate was formed. The reaction was allowed to proceed for 30 min. The compound was isolated and characterized by elemental analysis and infrared spectroscopy as a metallomacrocycle **5**. In a similar way addition of $[NBu_4]Cl$ to a solution of the cobalt cages **1a**–**d** or **2** provided in all cases a blue precipitate that was identified as metallomacrocycle $[Co_2(L^1)_2(Cl)_4]$ (**5**).

Spectacularly in this case the Cl^- ion leads to a complete rearrangement of the super structure from a cobalt cages or one-dimensional coordination polymers to a metallomacrocycle. These experiments also imply that in our cobalt supramolecular systems the coordinating effect of these anions decreases in the order $Cl^- > NO_3^- > BF_4^-$.

We then investigated the role of the anions guests on the magnetic properties of these paramagnetic cobalt host cages. The temperature dependence of the magnetic susceptibility of complexes **1b**, **2**, **3**, and **5** was measured with a quantum design MPMS-XL SQUID magnetometer in an applied field of 500 Oe and it is presented in Figure 4 as χT versus T plots. In the cases of compounds **2** and **5**, the data were corrected for a temperature-independent paramagnetic signal (TIP) denoted by the linear and positive variation of $\chi T(T)$ in the high-temperature range (see the Supporting Information Figure S1). The TIP contribution was evaluated to 0.024 and 0.036 emu per mol of Co in **2** and **5**, respectively. Quite high TIP is encountered for Co^{II} complexes due to relatively low excitation energies favoring an admixture of excited levels to the ground state, but the expected values are 5–10 times lower than observed here.[21] Thus, such high values should principally result from small magnetic impurities, the presence of which was denoted by the nonlinear variation of the magnetization versus field at room temperature (Figure S1). Such impurities should be very small, since the chemical and spectroscopic analyses do not indicate their presence. Moreover, the magnetization versus field variation at 1.8 K (Figure S1) for both compounds show the characteristic features for paramagnetic compounds with no hysteresis and the saturation magnetizations, $M_s = 6.2$ and 5 μ_B for **2** and **5**, respectively, agree well with that expected for two isolated Co^{II} ions (4–6 μ_B).[22] It is worth noting that this feature occurs only for the compounds that are blue (tetrahedral sites) and purple (distorted octahedral sites).

The magnetic findings were analyzed after correction of TIP for **2** and **5** as shown in Figure 4. For the four compounds, the susceptibility fits well the Curie-Weiss law in the high temperature region (T > 150 K) and the refined Curie constants are consistent with the presence of Co(II) ions in octahedral (C = 2.8 and 2.6 K.emu/Co mol for **1b** and **3**) and tetrahedral sites (C = 2.5 K.emu/Co mol for **5**). The value obtained for the compound **2** (2.2 K.emu/Co mol) is very similar to that of **5**, suggesting a quenching of the orbital degeneracy leading to S = 3/2 spin state. This can be induced by a site symmetry significantly different from the Oh one,[21,23] in agreement with the fact that **2** is purple colored whereas **1b** and **3** are pink.

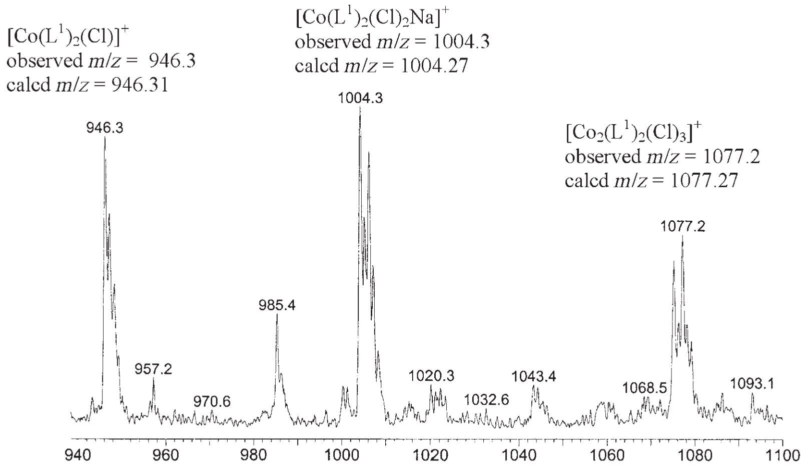

Figure 3. Partial ESI-MS spectrum of $[Co_2(L^1)_2(Cl)_4]$ (**5**), illustrating the sequence of peaks corresponding to the intact metallomacrocycle $[Co_2(L^1)_2(Cl)_3]^+$ associated with different numbers of Cl^- ions . The calculated m/z values are based on the most intense component of the isotope envelope.

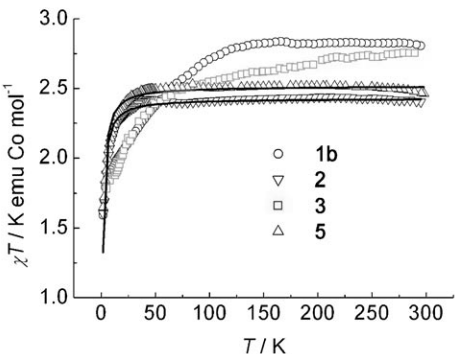

Figure 4. Temperature variation of the χT product for compounds **1b**, **2**, **3**, and **5**. The full lines correspond to the fits by using the $S = 3/2$ dimer model (see text).

The $\chi T(T)$ variation for **3** is typical of quasi isolated Co^{II} ions in octahedral symmetry, the decrease from 2.8 Kemu per mole of Co at 295 K to 1.55 Kemu per mole of Co at 1.8 K being the result of the spin-orbit coupling effect ($S = 3/2$, $L = 1$), which stabilizes the low-lying Kramers doublet $J = \pm 1/2$.[22,24] The one-dimensional compound **3** behaves similarly to the precedent, but with a steeper lowering of the moment that can be assigned to weak antiferromagnetic couplings. In this case there is no theoretical model available for fitting the experimental data for Co^{II} chains taking into account the spin-orbit coupling. In contrast, for compounds **2** and **5** a quenching of the orbital moment can be assumed and then the susceptibility was fit by using a model of $S = 3/2$ spin dimers giving Equation (1),[24] in which $x = J/k_BT$, g is the Landé factor, and J/k is the spin–spin magnetic interaction.

$$\chi T = \frac{(3/8\,g^2(e^x + 5\,e^{3x} + 14\,e^{6x})}{(1 + 3\,e^x + 5\,e^{3x} + 7\,e^{6x})} \qquad (1)$$

As shown in Figure 4, a reasonably good agreement was obtained with the refined values $g = 2.275(3)$, $J/k = -0.69(2)$ K for **2**, and $g = 2.317(3)$, $J/k = -0.74(3)$ K for **5**. The two interactions are antiferromagnetic and very weak compared to those found for other Co^{II} cages.[17] In such cages the Co^{II} atoms were coupled through halogen anions (Cl^- and Br^-) that are expected to be more efficient couplers, due to their polarizing effect, which is higher than for BF_4^- moieties.

In summary we have reported the anion-templated syntheses of a variety of supramolecular assemblies of Co^{II}. Remarkably in the presence of a weakly coordinating anion, such as BF_4^-, a discrete three-dimensional cage (**2**) is formed with three coordinated BF_4^- ions, a rare example in supramolecular chemistry. Switching to stronger coordinating anions, such as NO_3^- or Cl^-, a one-dimensional coordination polymer and a metallomacrocycle were formed, respectively. These results illustrate the powerful effect of the anion-templating chemistry. Finally the magnetic properties of these assemblies **1b**, **2**, **3**, and **5** were presented and discussed. Efforts are now directed to the self-assembly of new cages encapsulating anions with high polarizability.

Experimental Section

All experimental manipulations were carried out under argon by using Schlenk techniques. ^1H and ^{11}B NMR spectra were recorded in CD_3NO_2 by using a Bruker AMX-2 400 NMR spectrometer at 400.13 and 128.38 MHz, respectively, and also a Brucker Avance 400 NMR instrument. Infrared spectra were obtained on a Bio-Rad Win-IR spectrometer version 2.04 A from samples prepared on KBr disks. Elemental analyses were performed by the Microanalytical Laboratory of the Université Pierre et Marie Curie (Paris VI). Positive ESI mass spectra were obtained using a triple quadrupole mass spectrometer (Quattro I Micromass). Automatic data acquisition was processed using the software Masslynx 3.4.

Complex 2: Ligand L^1 (403 mg, 1 mmol) 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_3NO_2 (15 mL). The solution was stirred at room temperature for 4 h, during which time it turned purple. The solvents were then removed. The purple precipitate obtained was washed with CH_2Cl_2 and dried under vacuum (Yield: 81%). This supramolecular cage was recrystallized from CH_3NO_2/Et_2O to afford quantitatively purple crystals and was characterized as $[BF_4\subset(Co_2(L^1)_4(BF_4)_2][BF_4]$. Elemental analysis calcd (%) for $C_{104}H_{104}B_4Co_2F_{16}N_{16}O_8{\cdot}2\,CH_3NO_2$ (2292.73): C 55.52, H 4.83, N 10.99; found: C 54.55, H 4.24, N 10.63; ^1H NMR (400 MHz, CD_3NO_2, 298 K): $\delta = 47.57$ (s, 2H; H_{14}), 41.31 (s, 2H; H_9), 35.31 (s, 2H; H_7), 29.12 (s, 2H; $H_{7'}$), 19.05 (s, 3H; -Me), 12.70 (s, 2H; H_{10}), 11.99 (s, 3H; 1-OMe), 8.03 (s, 2H; H_{11}), 4.33 (m, 2H; H_{12}), −2.81 ppm (s, 3H; 4-OMe); ^{11}B NMR (128 MHz, CD_3NO_2, 298 K): $\delta = 1.92$ (sh, free BF_4^-), −99.23 ppm (brs, encapsulated BF_4^-); IR (KBr disk): $\tilde{\nu} = 1084\ cm^{-1}$ (B−F); ES-MS: m/z calcd: 2083.70 $[BF_4\subset(BF_4)_2Co_2(L^1)_4]^+$, 455.67 $[Co_2(L^1)_4]^{4+}$; found: 2083.5, 456.0; m.p. 250 °C (decomp).

Complex 3: Ligand L^1 (403 mg, 1 mmol,) in CH_2Cl_2 (15 mL) was added to a pink solution of $Co[NO_3]_2{\cdot}6H_2O$ (102 mg, 0.352 mmol) in CH_3OH (15 mL). The solution was stirred at room temperature for 4 h, during which time a pink precipitate formed. The solids were collected by filtration, washed with CH_2Cl_2, and dried under vacuum (Yield: 93%). This one-dimensional polymer was characterized as $[\{Co(L^1)(NO_3)_2\}_n]$. Elemental analysis calcd (%) for $C_{26}H_{26}CoN_6O_8{\cdot}MeOH$ (641.14): C 50.55, H 4.71, N 13.10; found: C 50.51, H 4.43, N 13.32; IR (KBr disk): $\tilde{\nu} = 1385\ cm^{-1}$ (N−O); ES-MS: m/z calcd: 973.96 $[Co(L)_2NO_3]^+$, 455.67 $[Co(L)_2]^{2+}$; found: 973.5, 456.0; m.p. 270 °C (decomp).

Complex 4: This compound was obtained by recrystallization of **3** from DMSO/Et_2O to afford quantitatively pink crystals of $[Co(L^1)(NO_3)(dmso)_2][NO_3]$. IR (KBr disk): $\tilde{\nu} = 1385\ cm^{-1}$ (N−O); ES-MS: m/z calcd: 973.96 $[Co(L)_2NO_3]^+$, 455.67 $[Co(L)_2]^{2+}$; found: 973.6, 456.0.

Complex 5: Ligand L^1 (403 mg, 1 mmol) in CH_2Cl_2 (15 mL) was added to a pink solution of $CoCl_2{\cdot}6H_2O$ (84 mg, 0.352 mmol) in CH_3OH (15 mL). The solution was stirred at room temperature for 4 h, during which time a blue precipitate formed. The solids were collected by filtration, washed with CH_2Cl_2, and dried under vacuum (Yield: 95%). This macrocycle was recrystallized from DMF/Et_2O to quantitatively afford blue crystals and was characterized as $[Co_2(L^1)_2Cl_4]$. Elemental analysis calcd (%) for $C_{52}H_{52}Cl_4Co_2N_8O_4.2\,MeOH$ (1174.21): C 55.11, H 5.14, N 9.52; found: C 55.19, H 5.12, N 9.75; IR (KBr disk): $\tilde{\nu} = 304, 339\ cm^{-1}$ (Co−Cl); ES-MS: m/z calcd: 1077.25 $[Co_2(L^1)_2(Cl)_3]^+$, 1004.27 $[Co(L^1)_2(Cl)_2Na]^+$, 946.31 $[Co(L^1)_2Cl]^+$; found: 1077.2, 1004.3, 946.3; m.p. 330 °C (decomp).

Anion exchange from 2 to 3: A solution of tetrabutylammonium nitrate (21 mg, 0.7 mmol) in CH_3NO_2 (5 mL) was added to a purple solution of **2** (13 mg, 66 μmol) in CH_3NO_2 (5 mL). A pink precipitate immediately appeared. The mixture was stirred at room temperature for a further 30 min. The pink solid was then collected by membrane filtration. Yield: quantitative; analytical data are identical to those obtained for **3** by direct synthesis.

Anion exchange from 2 to 5: A solution of tetrabutylammonium chloride (19 mg, 0.7 mmol) in CH_3NO_2 (5 mL) was added to a purple solution of **2** (13 mg, 66 μmol) in CH_3NO_2 (5 mL). A blue precipitate immediately appeared. The mixture was stirred at room temperature for a further 30 min. The blue solid was then collected by membrane filtration. Yield: quantitative; analytical data are identical to those obtained for **5** by direct synthesis.

Anion exchange from 3 to 5: A solution of tetrabutylammonium chloride (5 mg, 16 μmol) in CH_3CN (5 mL) was added to a pink solution of **3** (10 mg, 1.6 μmol) in CH_3CN (5 mL). A blue precipitate immediately appeared. The mixture was stirred at room temperature for a further 30 min. The blue solid was then collected by membrane filtration. Yield: quantitative; analytical data are identical to those obtained for **5** by direct synthesis.

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[1] a) J.-M. Lehn, *Supramolecular Chemistry, Concept and Perspectives*, VCH, Weinheim, **1995**; b) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, **2000**.

[2] a) A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester **1996**; b) A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, V. Zyk, M. Schroder, *Coord. Chem. Rev.* **2001**, *222*, 155.

[3] a) J. A. Ramsden, W. Weng, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1992**, *114*, 5890; b) W. Weng, J. A. Ramsden, A. M. Arif, *J. Am. Chem. Soc.* **1993**, *115*, 3824; c) T. Bartik, W. Weng, J. A. Ramsden, S. Szafert, S. B. Falloon, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1998**, *120*, 11071; d) R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J. A. Gladysz, *J. Am. Chem. Soc.* **2000**, *122*, 810; e) W. Mohr, J. Stahl, F. Hampel, J. A. Gladysz, *Inorg. Chem.* **2001**, *40*, 3263; f) N. Le Narvor, L. Toupet, C. Lapinte, *J. Am. Chem. Soc.* **1995**, *117*, 7129.

[4] a) L. J. Barbour, G. W. Orr, J. L. Atwood, *Nature* **1998**, *393*, 671; b) H. Amouri, L. Mimassi, M. N. Rager, B. E. Mann, C. Guyard-Duhayon, L. Raehm, *Angew. Chem.* **2005**, *117*, 4619; *Angew. Chem. Int. Ed.* **2005**, *44*, 4543.

[5] a) H. Amouri, M. N. Rager, F. Cagnol, J. Vaissermann, *Angew. Chem.* **2001**, *113*, 3748; *Angew. Chem. Int. Ed.* **2001**, *40*, 3636; b) R. W. Saalfrank, A. Dresel, V. Seitz, S. Trummer, F. Hampel, M. Teichert, D. Stalke, C. Stadler, J. Daub, V. Schunemann, A. X. Trautwein, *Chem. Eur. J.* **1997**, *3*, 2058.

[6] a) L. Mimassi, C. Guyard-Duhayon, L. Raehm, H. Amouri, *Eur. J. Inorg. Chem.* **2002**, 2453; b) L. Raehm, L. Mimassi, C. Guyard-Duhayon, H. Amouri, M. N. Rager, *Inorg. Chem.* **2003**, *42*, 5654; c) C.-Y. Su, Y.-P. Cai, C.-L. Chen, H.-X. Zhang, B.-S. Kang, *J. Chem. Soc. Dalton Trans.* **2001**, 359.

[7] O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647.

[8] M. Fujita, Y. J. Kwon, S. Washizu, K. J. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151.

[9] a) M. Aoyagi, K. Biradha, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 7457; b) A. Tanatani, M. J. Moi, J. S. Moore, *J. Am. Chem. Soc.* **2001**, *123*, 1792; c) K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584; *Angew. Chem. Int. Ed.* **1999**, *38*, 492.

[10] a) P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502; *Angew. Chem. Int. Ed.* **2001**, *40*, 486; b) D. Fiedler, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2004**, *116*, 6916; *Angew. Chem. Int. Ed.* **2004**, *43*, 6748; c) D. Fiedler, D. H. Leung, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2005**, *38*, 349, and references therein.

[11] M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja, R. S. Burkhalter, *J. Am. Chem. Soc.* **1997**, *119*, 6324, and references therein.

[12] a) R. Vilar, *Angew. Chem.* **2003**, *115*, 1498; *Angew. Chem. Int. Ed.* **2003**, *42*, 1460; b) N. Gimeno, R. Vilar, *Coord. Chem. Rev.* **2006**, *250*, 3161, and references therein.

[13] a) J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Angew. Chem.* **1998**, *110*, 1315; *Angew. Chem. Int. Ed.* **1998**, *37*, 1279; b) R. L. Paul, Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4883; c) D. A. McMorran, P. J. Steel, *Angew. Chem.* **1998**, *110*, 3495; *Angew. Chem. Int. Ed.* **1998**, *37*, 3295; d) C. S. Campos-Fernandez, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Basca, J. M. Koomen, D. H. Rusell, K. R. Dunbar, *J. Am. Chem. Soc.* **2005**, *127*, 12909.

[14] S. Manne, G. Huttner, L. Zsolnai, K. Heinze, *Angew. Chem.* **1996**, *108*, 2983; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2808.

[15] a) A. Müller, H. Reuter, S. Dillinger, *Angew. Chem.* **1995**, *107*, 2505; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328; b) A. Müller, L. Toma, H. Boegge, M. Schmidtmann, P. Koegerler, *Chem. Commun.* **2003**, 2000.

[16] a) L. K. Thompson, S. S. Tandon; J. N. Bridson, M. K. Park, *Inorg. Chem.* **1996**, *35*, 3117; b) Y. Suzuki, M. Fujimori, H. Yoshikawa, K. Awaga, *Chem. Eur. J.* **2004**, *10*, 5158.

[17] B. Wu, D. Yuan, B. Lou, L. Han, C. Liu, C. Zhang, M. Hong, *Inorg. Chem.* **2005**, *44*, 9175.

[18] A single crystal of the air/moisture sensitive compounds **2** or **4** was selected rapidly, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected at 250(2) K with a Bruker-Nonius Kappa-CCD with graphite monochromated $Mo_{K\alpha}$ radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs (A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220). Multi-scan absorption correction was applied (R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33). The structures were solved by direct methods using the SHELXS-86 program (G. M. Sheldrick, University of Göttingen, **1986**) and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package (G. M. Sheldrick, University of Göttingen, Germany, **1997**). Hydrogen atoms were simply introduced at idealized positions in the final structure factor calculations with an overall isotropic thermal parameter. The encapsulated BF_4^- ion in cage **2** is disordered on two positions. The atom sites outside the Co(1)···F(1)···F(1)···Co(1) axis, that is, B(1), F(2), and F(3), are half occupied. On the other hand, the outer BF_4^- ions coordinated to the cobalt atoms are disordered around the B(2)–F(4)···Co(1)···Co(1)···F(4)–B(2) axis, leading to two orientations staggered by approximately 45°, the populations of the orientations A and B being 0.5 (F(5), F(6) and F(7)). The free BF_4^- ion in the lattice is located on a centre of symmetry (B(3) atom), and the four F atoms are disordered accordingly with a 0.5 site occupation factor. Crystal data for **2**: purple crystals, $C_{111}H_{117}B_4Co_2F_{16}N_{23}O_{22}$, triclinic, $P\bar{1}$, $a=14.4375(13)$, $b=14.6495(15)$, $c=16.752(2)$ Å, $\alpha=89.086(7)$, $\beta=68.283(7)$, $\gamma=88.777(9)°$, $V=3290.7(6)$ Å^3, $Z=1$, $T=250(2)$ K, $\mu=0.346\ mm^{-1}$, 82446 reflections measured, 19128 independent ($R_{int}=0.0569$), 11245 observed $[I>2\sigma(I)]$, 856 parameters, final R indices $R1[I>2\sigma(I)]=0.0679$ and $wR2$(all data) $=0.1369$, GOF(on F^2) $=1.124$, max/min residual electron density $\rho=1.69/-0.57$ e Å^{-3}. Crystal data for **4**: pink crystals: $C_{32}H_{42}CoN_6O_{11}S_3$, triclinic, $P\bar{1}$, $a=9.8650(10)$, $b=10.6020(10)$, $c=19.950(2)$ Å, $\alpha=102.064(10)$, $\beta=97.223(7)$, $\gamma=101.958(9)$ °, $V=1964.8(4)$ Å^3, $Z=2$, $T=250(2)$ K, $\mu=0.659\ mm^{-1}$, 36298 reflections measured, 11295 independent ($R_{int}=0.0562$), 5857 observed $[I>2\sigma(I)]$, 517 parameters, final R indices $R1[I>2\sigma(I)]=0.0640$ and $wR2$(all data) $=0.1008$, GOF(on F^2) $=1.024$, max/min residual electron density $\rho=1.07/-0.56$ e Å^{-3}. CCDC-611539 (**2**) and CCDC-611540 (**4**) contain 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.

[19] C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, 3885.

[20] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed, Wiley, New York, **1972**, p. 881.

[21] "Theoretical Foundations of Molecular Magnetism":R. Boca, *Curr. Methods Inorg. Chem.* **1999**, *1*, 296.

[22] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**.

[23] A. P. B. Lever, *Inorganic Electronic Spectroscopy*, 2d edition, Elsevier Amsterdam, Oxford, New York, Tokyo, **1984**.

[24] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, Cambridge, **1993**.

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