Inorganic Chemistry

Article

Anion-Templated Synthesis of Metallacages as a Means for the Colorimetric Detection of Chlorides

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In the presence of chloride or bromide in the appropriate mixture of solvents, 6 equiv of nickel(II) and 8 equiv of Hatu [Hatu = $H_2NC(=NH)NHC(=S)NH_2$] assemble to yield the metallacages [$Ni_6(atu)_8X$][ClO_4]$_3$ (atu = deprotonated form of Hatu; X = Cl, **5**; Br, **6**) where four "units" of the square-planar complex $Ni(atu)_2$ are coordinated to two further nickel centers, forming an octahedral cage around an encapsulated chloride or bromide anion. Synthesis of the cages is highly dependent on the nature of the anions and the solvents used. In methanol, the cage only forms if chloride is present; in a mixture of acetone/methanol, the cage forms in the presence of either chloride or bromide. An interesting feature of the templation process is that there is a dramatic color change associated with assembly of the building blocks in the presence of the appropriate anion to yield the cages. This color change has been used as the basis for the colorimetric detection of chloride anions in methanol. The reaction of 4 equiv of nickel(II), 8 equiv of Hatu, and 2 equiv of platinum(II) has also been carried out, yielding the mixed-metal cage [$Pt_2Ni_4(atu)_8$-Cl][ClO_4]$_3$ (**7a**); the X-ray crystal structure of this compound is reported herein.

Introduction

Metal-containing cages and macrocycles are receiving increasing attention since they can combine the properties of metal centers (e.g., optical, magnetic, or structural) with the recognition abilities of organic ligands to yield assemblies with potential applications in catalysis[1] and in the development of chemical sensors.[2] To realize these applications, efficient synthetic methods for the preparation of metalla-assemblies are required. Self-assembly of small building blocks—especially when directed by a templating agent—

has been shown to be a very successful route to metalla-assemblies in high yields.[3] Templating agents usually make use of noncovalent interactions such as electrostatic forces, H-bonding, $\pi\cdots\pi$ interactions, and hydrophobic effects to prearrange a group of building blocks in a suitable geometry for the targeted assembly to be formed.[4] While cationic and neutral species have been widely used as templates for many years, anions have been comparatively neglected until relatively recently.[5] The limited literature has been attributed to the more diffuse nature (small charge-to-radius ratio), pH sensitivity, and the relatively high solvation free energy of

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Scheme 1
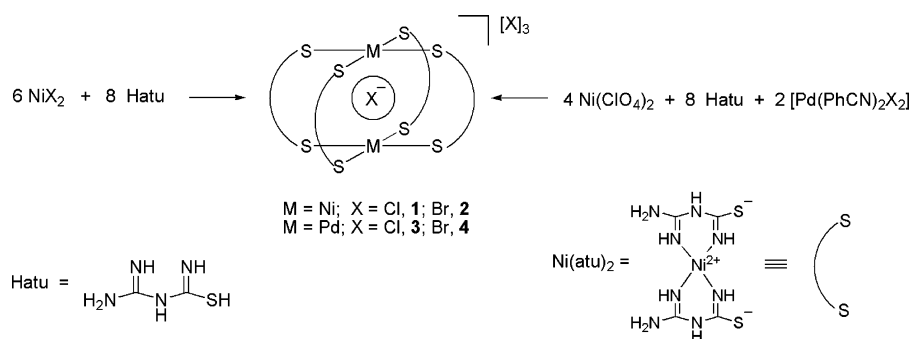
anions.[6] Despite these reservations, several recent reports have demonstrated that anions can be successfully employed as templates for the formation of a wide range of organic[7,8] and metal–organic[9,10] assemblies.

The species generated in a templated process should, in principle, be good receptors for the specific species that acts as a template. Consequently a potentially useful strategy to design anion receptors would be to use the anion of interest as a template for the formation of the molecular receptor and then remove it from the system to yield an "empty" host (in case the host produced is stable enough without the templating anionic guest). Furthermore, if such receptors are designed so that a signaling component is incorporated (e.g., chromophore, luminophore, or electrochemically active species), the basis for a chemical sensor emerges.

We previously reported as a preliminary communication the halide-templated syntheses of the metallacages $[M_2Ni_4(atu)_8X][X]_3$ (Hatu = amidinothiourea; atu = deprotonated form of Hatu; M = Ni, X = Cl, **1**; Br, **2**; M = Pd, X = Cl, **3**; Br, **4**) where four "units" of the square-planar complex $Ni(atu)_2$ are coordinated to two square-planar metal centers forming an octahedral cage around the central halide (see Scheme 1).[11,12]

An interesting feature of the templating process to form **1** and **2** is a dramatic color change from orange to dark green when the cage forms.[11] In this paper we report a detailed study in solution of the anion-templated synthesis of the above-mentioned metallacages and the use of this very distinct color change as the basis for a colorimetric chloride sensor. The synthesis and X-ray crystal structure of the new nickel–platinum cage $[Pt_2Ni_4(atu)_8Cl][Cl]_3$ (**7b**) is also presented.

Experimental Section

Materials. $Ni(ClO_4)_2 \cdot 6H_2O$, amidinothiourea (Hatu), and all the ammonium salts of the anions were purchased from Aldrich and used without further purification. Organic solvents with analytical purity were supplied by commercial sources and used as received. CAUTION! Perchlorates are potentially explosive and have to be handled with care and in small quantities.

Synthesis of $[Ni_6(atu)_8Cl][ClO_4]_3$ (5). $Ni(ClO_4)_2 \cdot 6H_2O$ (137.2 mg, 0.37 mmol) was added to a solution of Hatu (58.9 mg, 0.50 mmol) in a 3:1 methanol:acetone mixture (ca. 10 mL) and stirred for 15 min. One equivalent of $[NBu_4][Cl]$ (19.3 mg, 0.07 mmol) was then added as a solid, and an almost immediate color change from orange to dark green was observed. The reaction was stirred overnight and then concentrated under reduced pressure to one-half its volume. Upon addition of diethyl ether a dark green crystalline material precipitated. The solid was isolated by filtration and dried under reduced pressure for 24 h under vacuum at ca. 80 °C. Yield: 45% (46.8 mg, 0.028 mmol). Anal. Calcd for $C_{16}H_{40}N_{32}S_8Cl_4O_{12}Ni_6 \cdot 3H_2O$ (FW = 1674.22 g/mol): C, 11.5; H, 2.8; N, 26.7. Found: C, 11.4; H, 2.6; N, 26.8. MS (FAB$^+$ m/z

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Table 1. Crystallographic Data for Compound **7b**[a]

data	7b
chemical formula	$[C_{16}H_{40}N_{32}S_8Ni_4Pt_2 \cdot Cl](Cl)_3$
solvent	8EtOH
fw	2072.64
T (°C)	−100
space group	$I2/a$ (No. 15)
a (Å)	21.308(5)
b (Å)	17.396(3)
c (Å)	23.274(11)
β (deg)	97.47(2)
V (Å^3)	8554(5)
Z	4[b]
ρ_{calcd} (g cm^{-3})	1.609
λ (Å)	0.710 73
μ (mm^{-1})	4.497
R_1[c]	0.064
wR_2[d]	0.147

[a] Siemens P4 diffractometer, graphite-monochromated Mo Kα radiation, refinement based on F^2. [b] The molecule has crystallographic C_2 symmetry. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$.

(relative intensity)): 1521 (55) [M − ClO$_4$]$^+$, 1422 (30) [M − 2ClO$_4$]$^+$. IR (ν cm^{-1}, KBr): 3368.2, 3319.5 (N−H), 1657.8, 1599.2 (C=N), 1087.7 (ClO$_4{}^-$).

Synthesis of [Ni$_6$(atu)$_8$Br][ClO$_4$]$_3$ (6). Ni(ClO$_4$)$_2$·6H$_2$O (0.23 mmol, 82.5 mg) was added to a solution of Hatu (0.30 mmol, 35.7 mg) in a 1:3 methanol:acetone mixture (ca.. 4 mL) and stirred for 15 min. One equivalent of [NBu$_4$][Br] (13.0 mg, 0.04 mmol) was then added to the reaction mixture. The reaction was stirred for 1 h, during which time a change in color from orange to dark green was observed. The mixture was left stirring overnight. Upon addition of an excess of diethyl ether to the reaction mixture a dark green solid precipitated. The solid was isolated by filtration, washed twice with diethyl ether, and dried under reduced pressure at ca. 80 °C. Yield: 52% (33.0 mg, 0.02 mmol). Anal. Calcd for C$_{16}$H$_{40}$N$_{32}$BrS$_8$Ni$_6$Cl$_3$O$_{12}$ (FW = 1666.54 g/mol): C, 11.5; H, 2.4; N, 26.9. Found: C, 11.4; H, 2.6; N, 26.8. IR (ν cm^{-1}, KBr): 3368.2, 3319.5 (N−H), 1676.1 (C=N), 1578.4 (C=S), 1089.5 (ClO$_4$).

Synthesis of [Pt$_2$Ni$_4$(atu)$_8$Cl][ClO$_4$]$_3$ (7a). Ni(ClO$_4$)$_2$·6H$_2$O (183.0 mg, 0.50 mmol) was added to a solution of amidinothiourea (117.9 mg, 1.00 mmol) in ca. 25 mL of methanol, and the mixture was stirred for 15 min. A suspension of [Pt(MeCN)$_2$Cl$_2$] (86.8 mg, 0.25 mmol) in a 1:1 mixture of methanol:dichloromethane (ca. 25 mL volume) was then added to the reaction mixture, which was stirred for 1 h at room temperature. During this time an orange-yellow solid precipitated. The solid was separated by filtration and dried under vacuum. Yield: 14% (33.0 mg, 0.017 mmol). Anal. Calcd for C$_{16}$H$_{40}$N$_{32}$S$_8$Ni$_4$Pt$_2$Cl$_4$O$_{12}$ (FW = 1894.92 g/mol): C, 10.13; H, 2.11; N, 23.64. Found: C, 9.90; H, 2.15: N, 23.31. MS (FAB$^+$ m/z (relative intensity)): 1795 (98) [M − ClO$_4$]$^+$, 1696 (82) [M − 2ClO$_4$]$^+$. IR (ν cm^{-1}, KBr): 3299.6 (N−H), 1661.7 (C=N), 1592.7 (C=S), 1176.9 (ClO$_4$).

X-ray Crystallography. Table 1 provides a summary of the crystallographic data for compound **7b**. CCDC 235817.

Spectrophotometric Measurements. Electronic absorption spectra were recorded using a double-beam Shimadzu 1601 UV−vis recording spectrophotometer. All experiments were carried out at room temperature (ca. 21 °C). The solutions used to produce the photograph in Figure 1 were prepared in volumetric flasks using 6 equiv of Ni(ClO$_4$)$_2$ and 8 equiv of Hatu (the concentration of Hatu was 0.02 mol dm^{-3}. The solutions used for the UV−vis experiments were prepared in volumetric flasks using a concentration of Hatu of 0.01 mol dm^{-3}. Volume corrections were taken into account in all calculations. The absorbance reported in the plots was
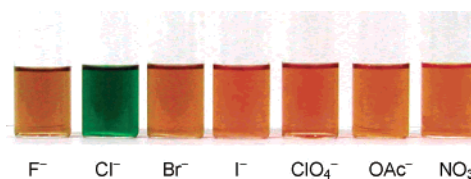

Figure 1. Colorimetric sensing of anions performed by adding 1 equiv of the selected anion as its ammonium salt (NR$_4$X, R = Me, Bu; X = F$^-$, Cl$^-$, Br$^-$, I$^-$, ClO$_4{}^-$, OAc$^-$, and NO$_3{}^-$) to 5 mL of a methanolic solution containing 6 equiv of Ni(ClO$_4$)$_2$ and 8 equiv of Hatu (the concentration of Hatu being 0.02 mol dm^{-3}).
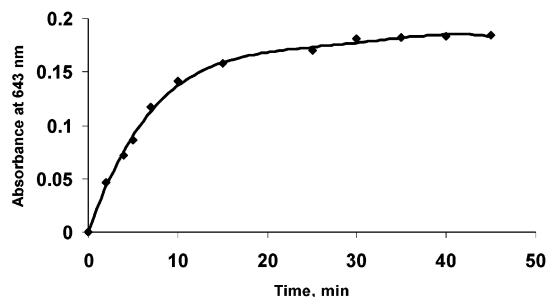

Figure 2. Graphical representation of the formation of [Ni$_6$(atu)$_8$Cl][ClO$_4$]$_3$ in MeOH as a function of time. The experiment was performed by monitoring the absorbance (λ_{max} = 643 nm) at different times (from 0.17 to 45 min, assuming A = 0 for t = 0 min) after adding 1 equiv of chloride (3.75 μL from a 0.1 mol dm^{-3} stock solution of [NMe$_4$][Cl] in MeOH) to a methanolic solution (ca. 3 mL, 3 × 10^{-6} mol of Hatu) containing 6 equiv of Ni(ClO$_4$)$_2$ and 8 equiv of Hatu.

considered as $\Delta A = A_i - A_o$, where A_o is the absorbance of the 6Ni(ClO$_4$)$_2$/8Hatu solutions in the region under study.

Solution Studies of the Formation of 5 over Time. Measurements to determine the formation of **5** as a function of time were carried out in the UV−vis cell (3 mL) containing a stock solution of 6Ni(ClO$_4$)$_2$/8Hatu (see above). After recording the spectrum of the initial solution (i.e., without chloride), 1 equiv of chloride was added from a previously prepared 0.5 M solution of [NBu$_4$][Cl] in methanol (7.5 μL). The formation of the cage was monitored by recording the UV−vis spectra at different times (see Figure 2).

Solution Studies of the Formation of 5 upon Addition of Increasing Amounts of Chloride. The formation of the cage as a function of the amount of chloride added (see Figure 3) was monitored by adding increasing amounts of the halide to a UV−vis cell (3 mL) containing a methanolic stock solution of 6Ni(ClO$_4$)$_2$/8Hatu (see above). Before recording the spectra, the reaction mixtures were left to equilibrate after each anion addition (equilibration was generally found to occur after ca. 30 min, vide infra). The different amounts of chloride were added using previously prepared methalonic solutions of [NBu$_4$][Cl] of different concentrations.

Anion Exchange Studies. Three milliliters of equilibrated solutions of [Ni$_6$(atu)$_8$Br][ClO$_4$]$_3$ in methanol/acetone (1:1, v/v) was titrated with increasing amounts of a stock 0.5 M solution of [NBu$_4$][Cl] in acetone. A minimum time of 1 h was left between each anion addition to ensure equilibration of the systems. UV−vis spectra, recorded after each anion addition, showed a shift of the original absorption (655 nm) attributed to the bromide-containing cages to the characteristic value assigned to the product templated by chloride (643 nm).

Results and Discussion

Synthesis of [Ni$_6$(atu)$_8$Cl][ClO$_4$]$_3$ (5). We previously reported that the reaction between 6 equiv of NiCl$_2$ and 8
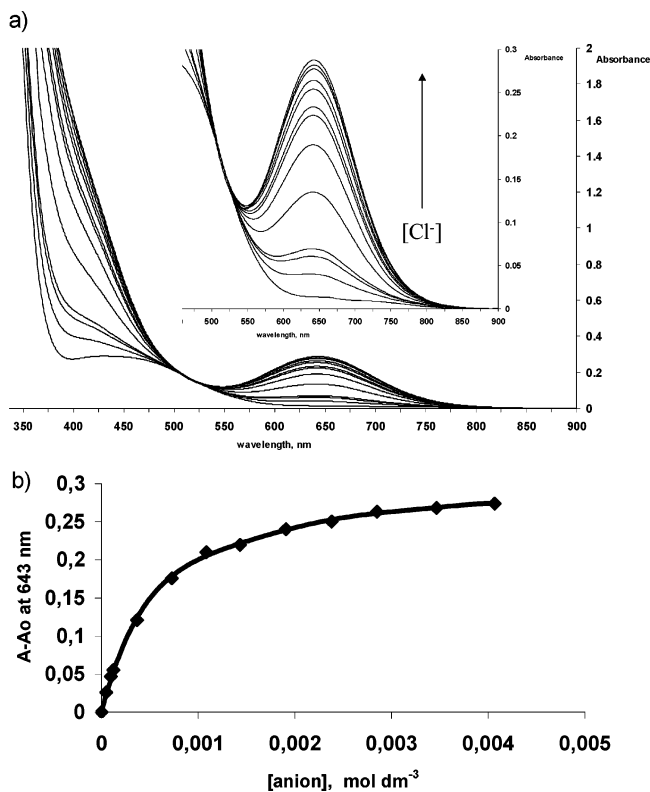
a)

b)

Figure 3. Titration with chlorides of a methanolic solution containing 6 equiv of $Ni(ClO_4)_2$ and 8 equiv of Hatu. (a) Variation of the absorbance of the cage **5** ($\lambda_{max} = 643$ nm) upon addition of increasing amounts of $[NBu_4]$-[Cl] (from 0 to 3.5 equiv of anion). After the addition of each amount of anion, the solution was allowed to equilibrate for 1 h. (b) Plot of the absorbance at 643 nm vs the concentration of chloride added.

equiv of amidinothiourea (Hatu) in methanol yields the hexanickel cage $[Ni_6(atu)_8Cl][Cl]_3$ (**1**).[11] By contrast, when the same reaction is repeated using other nickel sources such as NiX_2 (where $X = Br^-$, I^-, AcO^-, NO_3^-, ClO_4^-), formation of the cages is not observed and instead the simple square-planar orange compound $Ni(atu)_2$ (**6**) is formed (see Scheme 1).[12] If a chloride salt is added to any of these mixtures a change in color from orange to dark green is observed, indicating formation of the chloride-templated hexanickel cage. This clear color change associated with the formation of the metallacage (with a characteristic band at $\lambda = 643$ nm when the spectrum is measured in methanol) is very useful for monitoring the course of the reaction and studying the templating ability of the different anions. Consequently, we engaged in a detailed investigation of the assembly process that leads to the formation of these cages in solution.

To confirm that the addition of 1 equiv of chloride to mixtures of NiX_2/Hatu (with X being anions different to chloride, e.g., AcO^-, NO_3^-, ClO_4^-) leads to the formation of the hexanickel cage, isolation of the compound giving rise to the dark green color from the solution was required. The nickel(II) source chosen to carry out this study was Ni-$(ClO_4)_2$ due to the higher solubility properties of the compounds formed. It should be mentioned that one of the problems previously encountered when studying hexanickel cages **1** and **2** (with the corresponding halides both at the

center of the cage *and* as "exterior" counterions) was their insolubility once crystallized, which prevented their study in solution.

When 6 equiv of $Ni(ClO_4)_2$ was mixed with 8 equiv of Hatu in methanol, a dark orange solution was obtained. After 5 min, 1 equiv of $[NMe_4][Cl]$ was added and an immediate color change to dark green took place. The solution was analyzed by UV−vis spectroscopy, which, as expected, indicated the formation of the cage, showing its characteristic band at $\lambda = 643$ nm. Diethyl ether was added to the solution to precipitate a dark green compound. On the basis of spectroscopic and analytical data, this solid was characterized as the cage $[Ni_6(atu)_8Cl][ClO_4]_3$ (**5**) where the "exterior" counterions are ClO_4^- instead of the chlorides present in the original cage **1**. This clearly demonstrates the templating role of the anion as the cage has been formed directly following introduction of chloride to the $Ni(ClO_4)_2$/Hatu mixture.

The observed dark green color of **5** might be associated with the interaction of the "NiS_4" units with the encapsulated chloride anion. As can be seen from the previously reported crystal structures of **1** and **2**, the Ni^{II} centers of these units do interact strongly with the encapsulated halides.[11] It is well established that the electronic spectra of nickel(II) d^8 complexes are very sensitive to changes in the axial ligand position, and hence,[13] it is not surprising that association of the four orange $Ni(atu)_2$ units around two nickel(II) centers to form the hexanickel cage yields an important change in color.

To evaluate the templating ability of other anionic species, solutions containing $Ni(ClO_4)_2$ and Hatu in a 6:8 ratio were prepared and 1 equiv of the corresponding anion (namely F^-, Br^-, I^-, NO_3^-, and AcO^-) was added to each one. As can be seen in Figure 1, only the addition of chloride generated a color change from orange to dark green, which is associated with formation of the hexanickel cage. Addition of further equivalents of the different anions to the corresponding orange solutions did not lead to any significant change in their color or spectroscopic properties.

Colorimetric Sensor for Detection of Chlorides in Solution. The studies described in the previous section indicated the very selective templating role played by the chloride anion in the assembly of nickel(II) and Hatu in methanol. In addition, the color change associated with cage formation means this system can be considered a colorimetric sensor for the detection of chlorides. However, to realize this potential application, the system needed to be studied in more detail.

We first investigated the time it takes the system to reach equilibrium. For this, a mixture of 6 equiv of $Ni(ClO_4)_2$, 8 equiv of Hatu, and 1 equiv of $[NMe_4][Cl]$ dissolved in methanol was monitored over a period of 1 h by UV−vis spectroscopy. The results obtained indicate that although a very clear color change can be detected immediately after addition of chloride to the $Ni(ClO_4)_2$/Hatu mixture, the reaction takes approximately 30 min to reach equilibrium (see Figure 2).

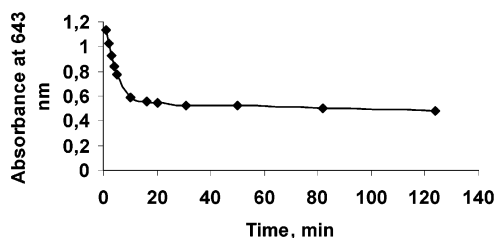(13) Green, M.; Tasker, P. A. *J. Chem. Soc. (A)* **1970**, 2531.

Figure 4. Plot of absorbance vs time indicating the decomposition of [Ni$_6$(atu)$_8$Cl][ClO$_4$]$_3$ when redissolved in MeOH. The absorbance associated with **5** (λ_{max} = 643 nm) decreases with time until it reaches equilibrium.

Once the time to reach equilibrium was established, a titration of the Ni(ClO$_4$)$_2$/Hatu mixture with increasing amounts of chloride was performed. After addition of each amount of chloride, the reaction mixture was left to equilibrate for 60 min before recording the UV−vis spectrum. The recorded spectra show that the intensity of the band at 643 nm (associated to **5**) increases upon addition of chloride while the band at ca. 426 nm (corresponding to the Ni(atu)$_2$ complex in the starting solution) disappears under a stronger intensity band from the cage (see Figure 3). It is not surprising that this absorption is retained in **5** (although shifted) since the cage contains four Ni(atu)$_2$ units. In addition, the titration experiment indicated that although the final cage contains only one anion in its cavity, its quantitative formation requires more than 1 equiv of the halide (see Figure 3b).

The sensitivity of the system under study for the "naked-eye" detection of chloride anions was found to be down to ∼1 mM of Cl$^-$ in methanol. On the other hand, spectrophotometric detection allowed sensing down to ∼1 μM of Cl$^-$ in methanol.

Surprisingly, when a crystalline sample of the isolated cage **5** was redissolved in methanol to measure its extinction coefficient, it was noticed that the intensity of the band at 643 nm decreased over time and the dark green color of the solution gradually changed to a less intense coloration. This change in coloration suggests that the cage dissociates partially into the building blocks that form it when it is redissolved in methanol. As can be seen in Figure 4, the intensity of the 643 nm band associated to **5** decreases constantly after dissolution in methanol, reaching equilibrium after approximately 15 min (no further changes were observed for up to 24 h). Dissociation of the cage is first order, giving a $t_{1/2}$ of approximately 4.5 min. Using the data shown in Figure 4 it is possible to extrapolate the curve to $t = 0$, giving an estimated initial absorbance for **5** (at 643 nm) of 1.25 from which the extinction coefficient of the cage can be calculated as ϵ = 417 M^{-1} cm^{-1} (the initial concentration of **5** in this experiment was 0.003 M). Using the extinction coefficient, the concentration of the cage at equilibrium was calculated as 0.0012 M, indicating that only 40% of the initial cage **5** is present when the methanolic solution reaches equilibrium.

The partial dissociation of **5** into its components when redissolved in methanol is not entirely surprising considering that the templating chloride—which keeps the cage together—is strongly solvated in protic polar solvents such as methanol.

Consequently, the chloride is involved in two competing processes: being solvated by methanol or encapsulated by the cage.

To explore this behavior further, a solid sample of **5** was redissolved in a range of solvents and the spectroscopic changes over time investigated. When dissolved in ethanol, the cage behaves in an analogous way to what has been described for methanol. In nonprotic and less polar solvents, namely, acetone and THF, the intensity of the band associated with the cage also decreases with time but the change is far less dramatic.

Influence of the Solvent in the Templation Process. The partial dissociation of **5** when redissolved in methanol prompted us to further investigate the influence of the solvent in the actual templated synthesis of the cage. In one of our earlier communications we reported that the bromide cage [Ni$_6$(atu)$_8$Br][Br]$_3$ (**2**) could only be prepared if a mixture of methanol/acetone was used for its synthesis.[11] Consequently, the templating role of several anions in 1:1 mixtures of methanol/acetone was investigated. Solutions containing 6 equiv of Ni(ClO$_4$)$_2$ and 8 equiv of Hatu in a 1:1 methanol/acetone mixture were prepared; to these solutions 1 equiv of the corresponding anion was added. As expected, the sample containing chloride changed from orange to dark green, indicating the formation of cage **5**. In contrast to the behavior of the system in pure methanol, addition of fluoride or bromide to the Ni(ClO$_4$)$_2$/Hatu mixture also led to a color change of the solution to green, suggesting the formation of the cages with encapsulated fluoride and bromide, respectively. However, addition of other anions (specifically I$^-$, ClO$_4^-$, AcO$^-$, and NO$_3^-$) did not produce any significant color or spectroscopic changes in the reaction mixtures. Analogous reactions in pure acetone (to further check the influence of the solvent in the templating process) could not be carried out due to the insolubility of some of the reagents and intermediate species in this solvent.

It was then possible to prepare and isolate the cage [Ni$_6$(atu)$_8$Br][ClO$_4$]$_3$ (**6**) by reacting 6 equiv of Ni(ClO$_4$)$_2$ with 8 equiv of Hatu in a methanol/acetone mixture (1:3, v/v), followed by addition of 1 equiv of [NBu$_4$][Br]. The bromide-containing cage **6** has a characteristic absorption in the UV−vis spectrum at 655 nm (slightly shifted in comparison to the chloride analogue). To confirm the importance of the solvent in the stability of the cage, a crystalline sample of **6** was redissolved in methanol. As expected, this cage is not stable in methanol and quickly decomposes. This was measured by monitoring the characteristic absorption of the cage at 655 nm, which decreases very quickly with time (leading to a very fast change in color from dark green to orange). In contrast to the behavior of the chloride cage **5**, in this case the cage decomposes completely with an estimated $t_{1/2}$ of approximately 30 s (an accurate value of this measure is difficult to get due to the high instability of the cage in solution).

To explore the scope of this reaction further, a mixture of Ni(ClO$_4$)$_2$ and Hatu in methanol/acetone was reacted with fluoride. Interestingly, this reaction produced a dark green solution with a characteristic absorption band at 603 nm.

Scheme 2

$$4\ Ni(ClO_4)_2 + 8\ Hatu + 2\ [Pt(MeCN)_2Cl_2] \longrightarrow$$
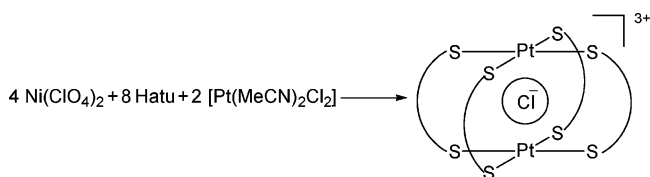
The compound responsible for the green coloration of this solution is likely to be a fluoride-containing cage analogous to **5** and **6**. However, all attempts to isolated this compound and fully characterize it have been unsuccessful (e.g., addition of diethyl ether to help precipitation/crystallization of the compound led to disappearance of the dark green color and formation of an orange solid residue; all attempts to characterize this compound were unsuccessful). Further evidence for the presence of a fluoride-containing cage in solution has been obtained by means of ^{19}F NMR spectroscopy. The spectrum of a mixture containing 6 equiv of $Ni(ClO_4)_2$, 6 equiv of Hatu, and 1 equiv of [NBu$_4$][F] in a mixture of methanol/acetone shows a singlet at −185.2 ppm. This chemical shift is different than that observed for a sample of [NBu$_4$][F] (which appears as a singlet at −145.9 ppm). Addition of a 5-fold excess of fluoride to the reaction mixture led to the presence of both resonances in the ^{19}F NMR spectrum, supporting the idea of having a cage where the encapsulated fluoride is in a different chemical environment than the fluoride anions present outside the cage. Despite these encouraging results, it should be noted that there is not yet enough evidence to be absolutely certain that a fluoride-containing cage is being formed.

Anion Exchange Reaction. The results presented so far clearly indicate the important templating role played by chloride and bromide when the appropriate solvent is used. It also seems evident that there is a degree of dissociation of the cages in solution (see Figure 4). Consequently, it was decided to explore the possibility of exchanging the halides present inside the cages (even though they are completely encapsulated in the corresponding cage once formed). For this, a solution of [Ni$_6$(atu)$_8$Br][ClO$_4$]$_3$ in methanol/acetone (1:1, v/v) was titrated with increasing amounts of a 0.5 M stock solution of [NBu$_4$][Cl] in acetone. One hour was left between each anion addition to ensure equilibration of the systems. The UV−vis spectra recorded after each anion addition showed a shift of the original bands attributed to the bromide containing cage (655 nm) to the characteristic value assigned to the product templated by chloride (643 nm). In contrast, when increasing amounts of bromide where added to a solution of the chloride-containing cage **5**, no significant changes in the UV−vis spectra were observed, suggesting that the chloride cage **5** is more stable than the analogous bromocage **6**.

Anion-Templated Synthesis of [Pt$_2$Ni$_4$(atu)$_8$Cl][ClO$_4$]$_3$. The anion-templated process described for the hexanickel cages **1** and **2** can be extended down group 10 of the periodic table, generating Pd^{II}/Ni^{II} mixed cages. We previously reported in a preliminary communication that when 2 equiv of [Pd(PhCN)$_2$X$_2$] (X = Br, Cl) is added to a mixture containing four equiv of Ni(ClO$_4$)$_2$ and 8 equiv of Hatu, the
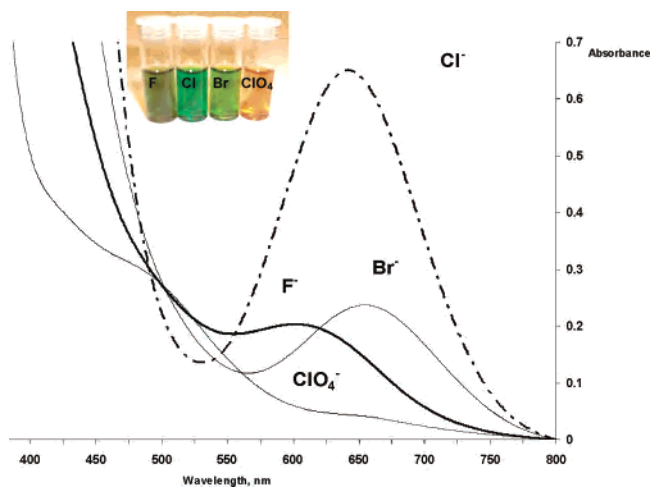

Figure 5. UV−vis spectra of solutions (methanol:acetone 1:1, v/v) containing 6 equiv of Ni(ClO$_4$)$_2$, 8 equiv of Hatu and no halide (—), 1 equiv of chloride (- · -), 1 equiv of bromide (- - -), and 1 equiv of fluoride (—) added as NBu$_4$X salts.
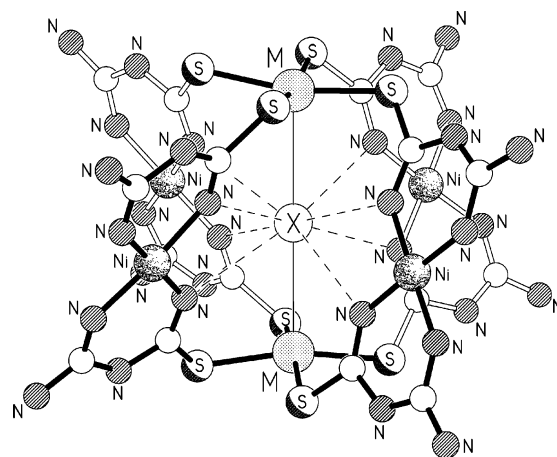

Figure 6. Molecular structure of the cage complexes **1** [M = Ni, X = Cl], **2** [M = Ni, X = Br], **3** [M = Pd, X = Cl], and **7b** [M = Pt, X = Cl].

metallacages [Pd$_2$Ni$_4$(atu)$_8$X][X]$_3$ (X = Cl, **3**; X = Br **4**) are obtained in high yields (see Scheme 1). As an obvious extension, we were interested to see if analogous cages having two platinum(II) centers at the "poles" of the cage bridged by four Ni(atu)$_2$ units could also be prepared. Using a similar approach to the one previously employed to prepare **3** and **4**, the platinum cage [Pt$_2$Ni$_4$(atu)$_8$Cl][ClO$_4$]$_3$ (**7a**) was synthesized. Two equivalents of [Pt(MeCN)$_2$Cl$_2$] was added to a mixture containing four equiv of Ni(ClO$_4$)$_2$ and 8 equiv of Hatu, yielding an orange solid that was isolated and characterized on the basis of spectroscopic, structural, and analytical data as the mixed-metal cage **7a**, Scheme 2. The FAB(+) mass spectrum of this solid was particularly indicative of the formation of the metallacage since a peak (with 98% intensity) corresponding to [**7a** − ClO$_4$] (at 1794 amu) was observed together with a second intense peak (85% intensity) at 1696 amu corresponding to [**7a** − 2ClO$_4$]. The elemental analyses of the bulk sample were consistent with this formulation.

After several attempts, a small number of single crystals suitable for X-ray crystallographic analysis were obtained directly from the reaction mixture from which **7a** is

Table 2. Comparative Selected Geometric Parameters for Complexes **1**, **2**, **3**, and **7b**[a]

	1 [M = Ni, X = Cl]	**2** [M = Ni, X = Br]	**3** [M = Pd, X = Cl]	**7b** [M = Pt, X = Cl]
M−S (min) (Å)	2.2080(14)	2.215(9)	2.315(2)	2.315(5)
M−S (max) (Å)	2.2215(15)	2.243(8)	2.323(2)	2.332(5)
Ni−N (min) (Å)	1.856(5)	1.82(2)	1.847(5)	1.854(14)
Ni−N (max) (Å)	1.878(5)	1.90(3)	1.887(9)	1.892(13)
M···X (min) (Å)	3.1233(13)	3.128(4)	3.1693(15)	3.2565(12)
M···X (max) (Å)	3.1397(14)	3.134(4)	3.1896(15)	b
M···X···M (°)	178.81(5)	178.96(14)	178.49(5)	180.0(2)
M···M (Å)	6.2627(10)	6.262(5)	6.3584(8)	6.513(2)
Ni···X (min) (Å)	4.343(2)	4.400(5)	4.357(2)	4.317(6)
Ni···X (max) (Å)	4.362(2)	4.412(5)	4.390(2)	4.356(3)
N···X (min) (Å)	3.282(4)	3.33(2)	3.285(5)	3.276(15)
N···X (max) (Å)	3.339(4)	3.40(2)	3.390(6)	3.356(14)
ΔM (min) (Å)[c]	0.333	0.340	0.297	0.261
ΔM (max) (Å)[c]	0.336	0.363	0.307	b
$\tau(MS_4/MS_4)$ (deg)[d]	72	68	73	74

[a] The crystallographic data for **1**, **2**, and **3** were deposited with the original communications (see refs 10 and 12) and have CCDC compound codes NUDYAM, NUDYEQ, and JEFJEJ, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44)1223-336033 or deposit@ccdc.cam.uk). [b] Complex **7b** has crystallographic C_2 symmetry and hence only one unique M center. [c] Deviation of the M center from its associated S_4 plane. [d] Rotation of the upper MS_4 unit relative to its lower counterpart about the M···M vector (see text).

obtained. Interestingly, the crystals turned out to be [Pt₂Ni₄(atu)₈Cl][Cl]₃ (**7b**) and not the expected [Pt₂Ni₄(atu)₈Cl][ClO₄]₃ (**7a**), which according to all other spectroscopic and analytic techniques corresponds to the bulk of the sample. This suggests that the crystallization of **7b**, with both "interior" and "exterior" chloride anions, is favored over that of **7a**, which has exterior perchlorates. The reason for this is not immediately apparent.

Structural Characterization of 7b. In all four cage structures determined to date (**1**, **2**, and **3** reported previously and **7b** presented in this paper), the metallacages have very similar overall geometries (see Figure 6 and Table 2). The cages have approximate D_4 symmetry with the encapsulated anion (**X** in the figure) in each case being positioned approximately centrally with respect to the six metal atoms in a pseudo-octahedral fashion. The upper and lower tetrads of sulfur atoms are staggered with respect to each other by ca. 18°, though in reality the donor sulfur atoms from each Ni(atu)₂ unit are rotated by ca. 72° with respect to each other about the **M···M** axis. It is this helical twist[10,14] that results in the aforementioned overall D_4 symmetry, cf. a potential D_{4h} geometry. It is our contention that this helical twist is, to a large extent, anion driven, facilitating the formation of (i) eight N−H···**X** hydrogen bonds from the inwardly directed Ni(atu)₂ imino moieties and (ii) a pair of nonbonded **M···X** interactions.

The **M···X** interactions are accompanied by substantial out-of-plane deviations of the axial metal centers toward the central anion (Table 2). It is interesting to note that in the one example where we have the same cage but anions of significantly different ionic radius [**1** (M = Ni, **X** = Cl) and **2** (M = Ni, **X** = Br)] the **M···X** and **M···M** distances are essentially unchanged. A search of the literature reveals that orthogonal approaches of halide ions to "square-planar" Ni/Pd/Pt metal centers is fairly common, and the metal···halogen

distance is usually in the range 3.0−3.2 Å,[15] values comparable to those observed here. However, in these literature examples there is no deviation of the metal out of its square plane toward the anion. It is only in our cage and box[16] structures, with ligand-controlled dimensional constraints, that achieving this metal···anion separation necessitates an out-of-plane distortion of the square-planar geometry.

Summary

The results presented herein show the important templating role that anions can play in the formation of supramolecular assemblies. In the presence of the spherical chloride and bromide anions, 6 equiv of nickel(II) and 8 equiv of Hatu assemble into the corresponding hexanickel cages with a halide encapsulated at their center. In the presence of other anions such as I⁻, NO₃⁻, OAc⁻, and ClO₄⁻ the formation of the cages is not observed. It has also been demonstrated that the formation of the cages is dependent on the solvent used to carry out the reaction. When protic and polar solvents such as methanol and ethanol are employed, only the chloride cage is formed. In contrast, the bromide cage only forms if less polar solvents such as acetone (or mixtures of acetone and methanol) are employed. The striking color change (from orange to dark green) associated with the formation of the chloride cage **5** in methanol has been successfully employed for the colorimetric detection of micromolar amounts of chloride (even in the presence of several other anionic species). Although the sensitivity of this system is not as good as that reported for other chloride sensors, it demonstrates that templating processes coupled with optical changes can be used as very selective means of detecting anionic species. Further developments will concentrate on improving the sensitivity of the detection (e.g., by incorporating luminescent moieties into the system).

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It has also been shown that mixed-metal (nickel/palladium and nickel/platinum) cages can also be successfully prepared using an anion-templated approach. The X-ray crystal structure of the platinum/nickel cage **7b** showed it to be isostructural to the related nickel and nickel/palladium cages we reported previously.[11,12] The incorporation of two different metals in the same cage provides potential advantages in the construction of sensing metallacages.

Supporting Information Available: Crystallographic information in CIF format and molecular structure of **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049508J