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Nanocrystalline Ag from Supramolecular Stabilization of Metals in 4-*tert*-Butylcalix[4]arene Lattices

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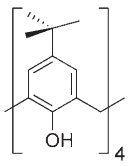
Abstract: Competition between intermolecular forces is a prime method for directing the formation of self-assembled structures without resorting to the use of covalently modified host molecules. In this study, we demonstrate how the competition between hydrogen bonding, coordinate bonding, and van der Waals interactions guides the formation of a complex crystalline clathrate based on a Ag–ethylenediamine coordination complex and 4-*tert*-butylcalix[4]arene. Owing to the coordinative flexibility of Ag and the stabilizing interactions with the calixarene framework, a four-coordinate Ag complex is included in the structure. Subsequent removal of the amine by heating the crystalline inclusion compound results in reduction of the Ag^+ ion such that metallic Ag nanocrystals are formed, thus indicating that this self-assembly approach is a viable method for obtaining simple calixarene frameworks loaded with silver. In the light of the experimental evidence, we comment on how this process relates to the reduction of silver in other systems.

Keywords: calixarenes · host–guest systems · hydrogen bonds · silver · supramolecular chemistry

Introduction

Supramolecular chemistry in the solid state is an incredibly diverse field that ranges from traditional inclusion chemistry to more recent efforts to engage in the rational design of crystalline materials.[1–3] The calixarenes, cyclic bowl-shaped molecules, are frequent organic targets for use in the construction of molecular receptors and supramolecular capsules.[4,5] One of the simplest calixarenes, 4-*tert*-butylcalix[4]arene (**1**), has been studied extensively as a model system for understanding the interplay between various noncovalent forces in guiding the structural motifs of host–guest compounds.[6–8] It is also a favored precursor compound for the synthesis of various functionalized receptor molecules. Despite this, with the exception of recent studies on the gas-adsorption capabilities of the low-density *apo* form of **1**,[9,10] the perceived low solubility and comparative simplicity of the inclusion compounds it forms have caused **1** to be overlooked as a potential building block for noncovalent assembly of functional materials.



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However, early studies by Gutsche et al.[11,12] clearly indicate that amines can effectively solubilize **1** by virtue of the acid–base chemistry of the host and guest, such that a single proton is abstracted from **1** by the amine. In other calixarene-based systems, the inclusion of ammonium cations drives the formation of intriguing capsular assemblies, both in solution[13–16] and in the solid state.[17–20] Similarly, carboxy-substituted calixarenes have been shown to assemble into multidimensional structures through interactions with amines.[21] As such, the inclusion of amines seems a ready route to forming novel inclusion compounds with **1**.

In fact, although the vast majority of inclusion compounds formed by **1** are dominated by van der Waals interactions with the hydrophobic cavity, such that the resulting clathrates have a 1:1 or 2:1 host/guest stoichiometry,[6,22,23] by taking advantage of the acid–base chemistry of aliphatic amines and **1**, the symmetry of the calixarene in the solid state is disrupted, thus precluding the formation of such simple inclusion compounds.[24,25] The resulting competition

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of directional hydrogen bonding between the amine and phenolic hydroxy groups of **1** and van der Waals stabilization of the aliphatic tail by the hydrophobic cavity of the calixarene gives rise to a framework with a 1:3 host/guest stoichiometry, which can then be transformed to the more conventional 1:1 or 2:1.

We recently demonstrated that this strategy of using competing noncovalent forces to guide the self-assembly of larger frameworks of **1** can also be used to incorporate amine clusters coordinated to metal centers, thereby making use of secondary coordination to stabilize such complexes supramolecularly.[26] Such inclusion behavior is a natural extension of the numerous studies of calixarenes as receptors capable of taking up metal cations, either in solution[27–33] or in the solid state.[34–39] However, by relying on moieties that are not bound directly to the calixarene, there exists an opportunity to alter the coordination complexes dramatically by removing the ligands completely from the resulting supramolecular assembly. In particular, thermogravimetric analysis (TGA) of an isopropylamine–silver inclusion compound of **1** suggested that such compounds may be a route to producing simple calixarene-supported metal centers. Such materials could be expected to have catalytic properties similar to those exhibited by other frameworks that support metal centers.

Results and Discussion

Given the apparent preference for a 1:3 host/guest stoichiometry in amine–**1** compounds, we were curious as to how an amine guest that could also serve as a bidentate ligand might influence the packing motif of such compounds. The resulting motif would be representative of the relative importance of the increased coordination of silver (which is well-known to be coordinatively flexible[40,41]) through chelation or formation of coordination polymer versus the formation of an extended hydrogen-bond network in stabilizing such inclusions. Dissolution of $AgNO_3$ and **1** in ethylenediamine (**2**) gives rise to a solution that, upon evaporation of excess solvent, readily produces crystals of a silver–amine calixarene clathrate suitable for single-crystal X-ray diffraction (SCXRD).

The resulting compound **3** has a $\mathbf{1}^-/\mathbf{2}/Ag^+$ stoichiometry of 1:3:0.87; each silver ion is typically coordinated by three molecules of **2** (Ag···N distances 2.23–2.58 Å for majority positions; see Figure 1). As predicted from previous solution[11,12] and solid-state studies,[26,42] the calixarene serves as the counteranion, with a single proton abstracted from one of the phenol groups. Given previous studies of amine–Ag clathrates,[26] this proton is presumably borne by the excess amine left behind as solvent when the silver is present. When the silver is absent, the proton is likely to be borne by one of the *exo* amines, but the disorder in the guest prevents the exact localization of the moiety that bears the proton.[25,42]

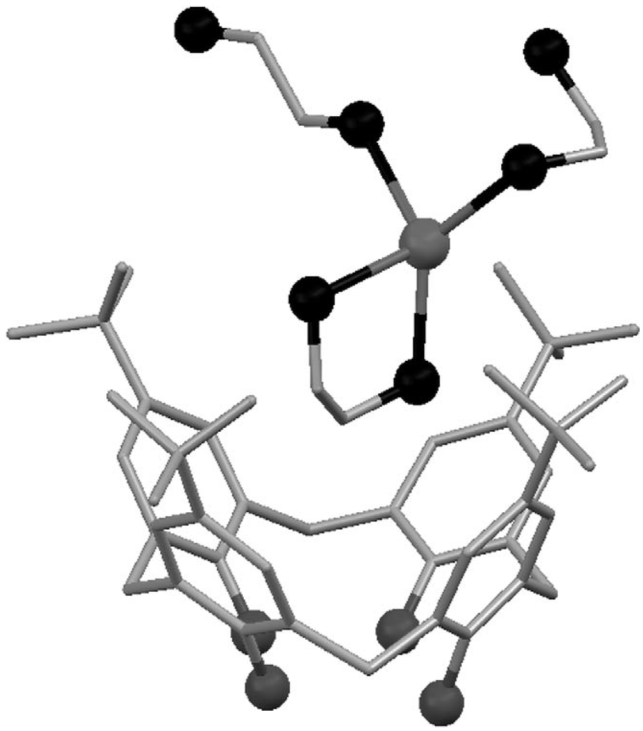

Figure 1. Asymmetric unit of **3** depicting the distorted coordination geometry of silver. All molecules are shown in majority positions, with hydrogen atoms omitted for clarity. N atoms are depicted as black spheres, Ag and O atoms as gray spheres.

The coordination of silver to three molecules of **2** gives rise to a distorted tetrahedral coordination geometry (Figure 1). As a result, rather extensive disorder is observed in the structure. The silver center is disordered over three positions (48:32:7 distribution), along with one of the *exo* amines (67:27:6 distribution), whereas the *endo* amine is disordered over two positions (72:28 distribution). The latter also appears to induce disorder in at least one of the *tert*-butyl groups (two-fold disorder with 72:28 distribution). The two singly coordinated molecules of **2** are found outside the calixarene cavity (*exo*), whereas the single bidentate-chelating molecule of **2** resides within the calixarene (*endo*).

The complex is further stabilized through a network of hydrogen bonds not unlike that seen in previous amine–metal–calixarene compounds[26] and silver coordination polymers[43–45] (Figure 2). The coordinating amines interact with the phenolic hydroxy groups of the calixarene framework (N···O distances 2.94, 2.98, 3.03, 3.09 Å). The free amino groups of the two *exo* molecules of **2** form weak hydrogen bonds to an adjacent silver–amine unit (N···N distance 3.51 Å). In conjunction with the altered geometry of the silver–amine complex, this gives rise to a dramatic distortion of the capped structural motif previously observed for amine–**1** complexes, with the cavities of the terminal calixarenes offset by 7.48 Å.

The hybrid coordination geometry of the guest complex is reminiscent of the calixarene–metal complexes previously reported, in which a range of forces guide the inclusion of

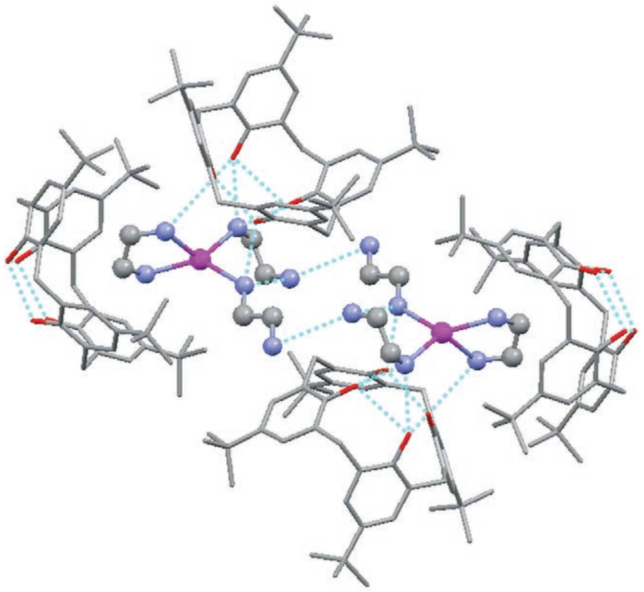

Figure 2. Packing scheme of **3** from a view parallel to the (011) plane. Secondary coordination through hydrogen bonds (light blue) further stabilizes the silver centers. All molecules are depicted in majority positions, with hydrogen atoms omitted for clarity.

the metal. Whereas cesium was shown to form a solid-state complex with the crown conformer **1**,[34] more-complex calixarenes have been typically investigated for the purposes of binding silver. Studies have generally revolved around conformationally immobilized calix[4]arenes arranged in cone, partial cone, or 1,3-alternating conformations suited for binding the cation either in solution or in the solid state.[29–31,38] However, complex coordination spheres of such compounds are based on cation–π interactions, such that the resulting compounds lack any multidimensional supramolecular structure.

By the same token, calixarenes can bear modifications to the phenolic hydroxy groups that make up their bases (such as crown ethers or esters with carbonyl or nitrogen donor atoms[36,46–49]) and render them capable of serving as ligands through nonaromatic interactions. Similarly, calixarenes with a combination of allyl and methoxy groups have been shown to bind metals without polyhapto aromatic coordination owing to self-inclusion of the methoxy obstructing access to the aromatic groups.[35] Even so, these systems still display the absence of extended structures observed in systems that rely on cation–π interactions to bind cations. The covalent modification of the calixarene in these systems is oriented toward producing predictable receptors, such that flexibility in allowing for intermolecular interactions is undesirable. In the present system, by making use of the calixarene itself to stabilize the ligands noncovalently through inclusion (simultaneously leading to obstruction of the calixarene cavity and introducing a suitable alternative binding site), the unmodified hydroxy groups on the base of the calixarene are free to serve as part of a hydrogen-bonding network, such that multidimensional structures are energetically favorable.

More-appropriate structural comparisons can thus be drawn from examinations of other Ag^I coordination compounds, in which self-assembly has long been used to produce multidimensional structures. As mentioned earlier, recent studies have clearly demonstrated that secondary interactions such as hydrogen bonding play a significant role in directing the structure (and therefore the coordination geometry) of various Ag^I coordination polymers.[43–45] Earlier studies of a range of difunctional ligands that rely on nitrogen,[50–55] thioether,[56,57] and sulfonate[53,58,59] donor groups demonstrated how variations in the coordinating group and the use of non- or minimally interacting counteranions are also useful tools in effectively directing the coordination geometry of the Ag^I ion, such that infinite multidimensional structures typically involving two-, four-, or six-coordinate Ag^I centers are observed.

The calixarene is both a hydrogen-bonding partner and noninteracting counteranion, and as such is well-suited to directing the coordination geometry observed for silver. Even so, the included complex is an intriguing contrast to the Ag^I coordination compounds typically formed by **2** and a variety of simple counteranions in the solid state, which generally take the form of coordination polymers in which each Ag^I ion is coordinated by two units of ethylenediamine[60–62] (although exceptions do exist in which chelation is observed[63,64]). It also contrasts with what might be expected based on studies of Ag^I chemistry in pure bases, which showed that Ag halides dissolve in neat monofunctional bases to produce predominantly 1:1 ligand/AgX compounds with tetrahedral geometry.[65,66] One would expect similar geometries to be favored even with crystals derived from neat ethylenediamine, with the difunctional nature of the amine leading to cross-linked polymer chains without any chelation. However, with the calixarene as counteranion, such a structure is not observed.

Ultimately, one must also consider the stabilization offered by inclusion in the calixarene to explain the geometry of the observed complex. Previous studies indicated that tetrahedral amine–Zn clusters[26] cannot be accommodated in a capped structure, so all the amines are found *exo* to the calixarene cavity. Given the fact that similar behavior is observed for clusters composed of amines larger than hexylamine[42] incorporated by **1**, the unusual coordination geometry is, therefore, a structural compromise to allow the formation of a capped motif (albeit in a distorted form). Only small clusters suitable for simultaneous *endo* inclusion and hydrogen bonding to adjacent calixarene units can take full advantage of the calixarene as a secondary ligand, a situation that is allowed for by the coordinative flexibility of Ag^I. This means that the stabilization offered by inclusion and hydrogen bonding with the calixarene can overwhelm the potential for stabilization through the formation of a more-extensive coordination network in which the ethylenediamine molecules each coordinate to two silver centers. However, both the disorder in the structure and the range of

Ag···N distances observed make it clear that a number of energetically equivalent conformations exist for the guest, thus indicating that various subtly different combinations of these forces are suitable for stabilizing this particular motif.

Given that the coordinate interaction is comparable in influence to the hydrogen bonding observed in other amine–**1** compounds, we suspected that we would be able to tune the structure further by heating the clathrate to remove amines from it selectively. TGA of **3** indicated that the guest was lost during three major transitions that are complete at approximately 80–110, 135–150, and 235–260 °C, with the resulting decreases in mass corresponding to the loss of approximately one amine molecule at each step. To understand more fully the structural implications of these transitions, we made use of solid-state NMR spectroscopy and powder X-ray diffraction (PXRD) to monitor these transitions for bulk powder samples of **3**.

The ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra of **3** as synthesized corresponds well with the SCXRD structure (Figure 3 a). The host portion of the spectrum of **3** exhibits a high degree of splitting, which would be expected from the large asymmetric unit found from SCXRD data, in which none of the carbon atoms in the calixarene are crystallographically equivalent. Furthermore, three ethylenediamine peaks are observed at 41.1, 46.8, and 48.4 ppm; the upfield peak is attributed to the shielded *endo* guest (resulting in a complexation-induced shift of −3.77 ppm relative to the solution spectrum[67]) and the downfield peaks are due to the silver-deshielded *exo* amines. These peaks persist upon dipolar dephasing, thus indicating that the crystallographic disorder is probably due to dynamic processes of sufficient amplitude to reduce dipolar coupling to hydrogen.

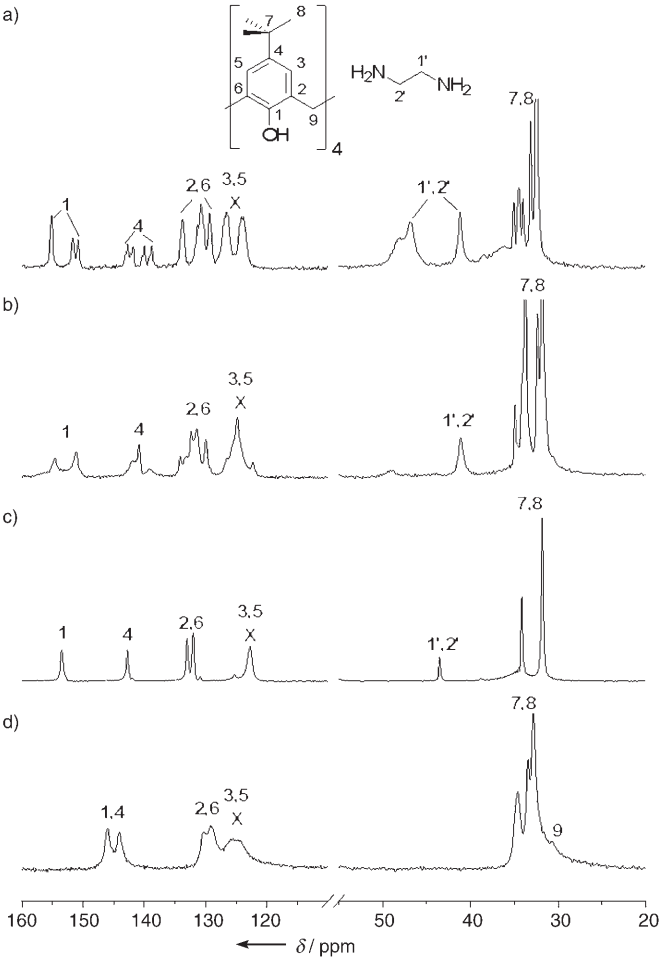

Figure 3. ^{13}C CP/MAS NMR spectra of **3** obtained at room temperature. a) As synthesized; b) after heating to 110 °C; c) after heating to 150 °C; d) after heating to 270 °C. Peaks are assigned according to the figure, with X marking peaks that disappear upon dipolar dephasing.

The spectra clearly indicate that significant structural shifts occur as the amine is removed from the system (Figure 3). After heating to 110 °C, the *exo* amine peaks disappear, but the overall low symmetry of the structure is retained. However, upon heating at 150 °C, peak splittings are no longer observed for the host or guest; the spectrum now reflects those commonly observed for the high-symmetry tetragonal 1:1 host–guest compounds of **1**.[22,68] Furthermore, the guest no longer exhibits a significant complexation-induced shift, suggesting that the amine resides outside the calixarene cavity. The high symmetry appears to be retained upon final removal of the amine guest at 270 °C. Throughout this process, dipolar dephasing indicates that the amine present is undergoing dynamic motion.

These structural shifts are also quite clear from the PXRD data (Figure 4). The powder pattern for the bulk sample of **3** is readily indexed based on the predictions from

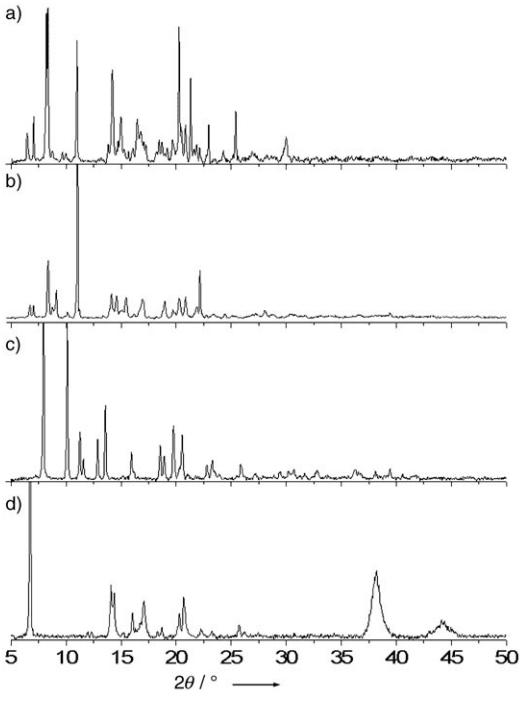

Figure 4. PXRD patterns for **3**. a) Room temperature; b) after heating to 110 °C; c) after heating to 150 °C; d) after heating to 270 °C. See Supporting Information for indexed cell parameters for a)–c).

the SCXRD structure (see Supporting Information). The pattern of the sample heated to 110 °C is also readily indexed to this initial cell, which indicates that the structure of **3** is robust enough to survive the loss of the first amine molecule, as indicated by TGA and NMR spectroscopy. As expected from the NMR spectroscopic data, upon heating to 150 °C, the pattern simplifies considerably. Preliminary indexing of this pattern in the $P4/n$ tetragonal space group suggested by the NMR spectrum and previous studies[7,8,25] yields an expanded cell compared to structures without silver present, with cell axes of $a = b = 13.73$ and $c = 22.08$ Å. However, we cannot rule out at this time the formation of an alternative high-symmetry phase. Given the NMR spectroscopic evidence, this would indicate that the silver clusters are forcing the calixarene layers apart. By the same token, the absence of a complexation-induced shift of the resonance assigned to ethylenediamine for the 1:1 host–guest complex, implies that coordination to silver precludes inclusion. Full removal of the amine gives rise to a relatively simple pattern similar to those observed for amine–**1** complexes,[25,42] with the exception of two broad high-angle peaks at $2\theta = 38.26°$ ($d = 2.35$ Å) and $44.23°$ ($d = 2.05$ Å), which suggest that a second phase is now present.

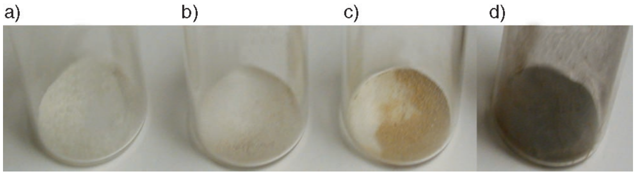

Figure 5. Color change of bulk samples of **3** due to heating. a) Room temperature; b) after heating to 110 °C; c) after heating to 150 °C; d) after heating to 270 °C.

Visual observation of the samples during the heating process provides a reasonable suggestion as to the origin of these high-angle peaks. As shown in Figure 5, as the sample is heated, a dramatic color change in the sample from white to yellow-orange to deep red-brown is observed, suggesting that the silver undergoes reduction. In fact, these reflections can readily be indexed as the 111 and 200 peaks of metallic silver (space group F_{m-3m}). The broad peak widths therefore arise from the small size of the spherical silver crystallites and are representative of the minimum size of the silver clusters (provided each domain is composed of a single cluster). By using the Scherrer equation,[69] the crystallites are found to have an average diameter of 94 Å, which corresponds to a cross-section composed of approximately 29 Ag atoms (based on an atomic radius of 1.6 Å).

The changes in color that are observed on heating raise intriguing questions as to how this reduction might progress. Previous studies showed that silver nanoparticles with comparably simple primary ligands do not exhibit this progression of colors,[70–73] and it is well-known that crystals of amine–silver compounds photoreduce rapidly to produce black, metallic powders. This suggests that the calixarene plays a key role in the reduction process. Two major roles for the calixarene most easily come to mind: 1) that of a reducing agent; 2) that of a framework that isolates the silver complex such that the reduction process is carried out in a novel fashion relative to the aforementioned prior studies.

Given the current data, it is not possible to establish a specific mechanism for the process, although certain routes can be ruled out in the light of the structural evidence available. The oxidation of the hydroxy goups on 4-*tert*-butylcalixarenes to form spirodienone derivatives[74–77] related to calixquinones[78,79] is well-known, and is the most plausible method by which the calixarene reduces the silver centers. Furthermore, such a transformation would likely give rise to the color changes reported. However, as ^{13}C solid-state NMR spectroscopy makes clear, no disruption of the aromaticity related to the formation of an enone occurs, nor is a resonance corresponding to a keto carbon nucleus observed at about 180 ppm. Furthermore, such a transformation would give rise to a massive increase in crystallographic splitting due to the low symmetry of the compound.[75] It therefore appears that the calixarene alone does not reduce the silver center.

Given previous observations suggesting that amine coordination decreases the reduction potential of Ag^I,[73] it seems that a more-complex reduction mechanism involving the amine is at play, such that the calixarene only has a peripheral role that does not result in structural changes. As previously mentioned, one of the roles of the calixarene that satisfies such a restriction would be its role as a framework that isolates the silver centers. In doing so, the resulting environment may be conducive to amine oxidization by the silver ion in a fashion analogous to previously reported catalytic systems involving Ag,[80,81] or chemistry similar to that carried out in biological systems by amine oxidases may occur.[82] Once again, however, the absence of any unassigned resonances in the ^{13}C solid-state NMR spectra indicates that if such chemistry does occur, the amine would also have to be eliminated from the system during oxidation.

On a qualitative level, the color changes observed are quite similar to another supramolecular system in which confinement has been shown repeatedly to give rise to unusual redox chemistry: heat-treated silver-loaded zeolites. In such systems, the silver centers were proposed to undergo partial reduction to form charged silver clusters with covalent character,[83,84] such that a number of competing models for structural features leading to the yellow Ag zeolites have been proposed.[85] At this time, however, we have no direct evidence to confirm any of the models, as the PXRD data provide no evidence of the formation of large covalent clusters (although small clusters would not be observable by this technique).

Structurally, the location of the silver nanoparticles can be partially inferred from the spectroscopic and XRD data. As mentioned above, the final form of the amine-desorbed calixarene is essentially that of the high-symmetry β-*apo* form, indicating that the silver nanoparticles are included in the calixarene matrix such that they do not perturb the favored packing scheme of the pure calixarene. This is not surprising, as the inclusion motifs observed for silver in the various conformationally locked calixarenes previously studied[29–31,38] could not possibly accommodate silver particles of the size predicted from the Scherrer equation. The logical alternative to such an arrangement would be the formation of an intercalated structure, a supposition supported by the PXRD unit-cell expansion along the *c* axis relative to the normal β-*apo* form.[42] In view of this, we are now carrying out further spectroscopic and TEM studies to determine the exact nature of the crystallites formed and the processes leading to them.

Conclusions

The coordinative flexibility of silver and the ability of 4-*tert*-butylcalix[4]arene to serve as a secondary coordinate ligand give rise to a supramolecular framework suitable for stabilizing an unusual amine–silver coordination compound. As predicted, the use of amine guests to bind the silver atom, as opposed to covalently bound moieties or cation–π interactions, results in the coordination compound included having a geometry compatible with the packing needs of the calixarene framework. This is an intriguing role reversal from most metal–organic frameworks, in which the coordination properties of the metal determine the overall packing scheme of the organic subunits in a structure. Finally, the calixarene framework also provides a suitable environment for reduction of the silver ion included to yield metallic nanocrystals of silver. We hope our continuing studies will further clarify the structure and properties of these promising materials.

Experimental Section

Crystals of **3** were prepared by placing **1** (0.840 g, 1.29×10^{-3} mol) in a vial with ethylenediamine (4.5 mL) and heating the mixture at 70 °C until the calixarene was completely dissolved. The solution was allowed to cool, and $AgNO_3$ (0.118 g, 6.98×10^{-4} mol) was then dissolved in it. The vial was then loosely capped and set aside to allow slow evaporation of the amine. After approximately five days, clear crystals were formed.

SCXRD measurements were made on a Bruker SMART 1 K CCD diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å, graphite monochromator) at 173 K. An empirical adsorption correction was applied by using the SADABS program. Structures were solved by direct methods and refined using full-matrix least squares on F^2 with SHELXTL,[86] with all hydrogen atoms placed in calculated positions except for the amino groups of the fully ordered ethylenediamine, which were found from the difference electron-density map. Compound **3** (crystal size $0.48\times0.16\times0.16$ mm): monoclinic, $P2_1/n$, $a = 13.3739(6)$, $b = 21.1368(10)$, $c = 18.5147(9)$ Å, $\beta = 109.652(1)°$, $V = 4928.9(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.242$ Mg m^{-3}, $2\theta_{max} = 29.61°$, $\mu = 0.407$ mm^{-1}, max./min. transmission = 0.9378/0.8287, GoF on $F^2 = 1.033$, residual electron density max. = 0.944, min. = −0.363 e Å^{-3}. Final R indices ($I > 2(I)$): $R_1 = 0.0471$, $wR_2 = 0.1182$ (61 547 reflections total, 13 857 unique). CCDC-603292 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

TGA was carried out by using a TA Instruments TGA 2050 instrument with samples heated from room temperature to 400 °C at a rate of 5 °C min^{-1}. TGA data were interpreted with Universal Analysis for Windows 95/NT suite (version 2.3C; TA Instruments). The overall host/guest ratio n was calculated based on the weight loss prior to decomposition of the host at about 300 °C. Based on this, the molar mass of the inclusion compound and the proportion of amine lost in each step were calculated.

Thermal desorption studies of **3** were carried out in a stepwise fashion by using a vacuum oven to heat bulk samples, with the exception of the 270 °C sample, which was initially heated at 245 °C in the vacuum oven and then transferred to a high-temperature furnace to remove residual amine. In each case, crystals of the clathrate were removed from the mother liquor, blotted dry with filter paper, and gently ground with a mortar and pestle. Samples were heated for 30–45 min at each temperature, and then allowed to cool to room temperature. At each temperature, the samples were analyzed with PXRD and ^{13}C CP/MAS solid-state NMR spectroscopy.

PXRD data were collected at 293 K on a Scintag X-2 Advanced diffractometer ($Cu_{K\alpha} = 1.54178$ Å) equipped with a graphite monochromator, using the θ–θ scan mode. Samples were scanned over a 2θ range of 5–60°, with a scan rate of 0.02° s^{-1} and a count time of 1 s. The resulting diffraction patterns were manually indexed by using the predicted pattern from analogous SCXRD structures (corrected for appropriate wavelength) as a guide, along with the program Crystal Cracker[87] and the Powder 4.0 program suite.[88] Unit-cell parameters were then obtained by fitting the calculated 2θ values to the observed peaks.

^{13}C CP/MAS NMR spectra were collected with a Bruker AMX-300 spectrometer ($^1H = 300.145$, $^{13}C = 75.483$ MHz) and a Doty 5-mm high-speed MAS probe. A pulse delay of 3 s and a contact time of 2 ms were used, with samples spun at approximately 5 kHz. Dipolar dephased spectra were obtained by inserting a 40-μs delay between cross-polarization and acquisition, during which the decoupler was switched off.

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