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Inclusion of Metal Complexes into Cavities of 2D Coordination Networks Built from *p*-Sulfonatothiacalix[4]arene Tetranuclear Clusters

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Reactions of the *p*-sulfonatothiacalix[4]arene salt (Na_4H_4TCAS) and MSO_4 (M = Co, Cu) in the presence of 2,2′-bipyrazine (2,2′-bpz) generated 2D coordination networks formed by tetranuclear cluster subunits, namely $\{[Co(2,2'\text{-bpz})(H_2O)_4]^{2+}\subset[Co_4(TCAS)(\mu_4\text{-}SO_4)(H_2O)_4]^{2-}\cdot 10.75H_2O\}_n$ (**1**) and $\{[Cu(2,2'\text{-bpz})(H_2O)_3]^{2+}\subset[Cu_4(TCAS)(\mu_4\text{-}SO_4)(H_2O)_4]^{2-}\cdot 16H_2O\}_n$ (**2**). X-ray diffraction analyses reveal that both these complexes include metal–2,2′-bipyrazine complexes into the hydrophobic cavities of *p*-sulfonatothiacalix[4]arenes as guests through supramolecular interactions. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Recently, both the fields of host–guest chemistry and coordination polymers have seen rapid progress and continue to receive wide attention in the chemical sciences.[1,2] The overlapping of these two diverse fields occurs when host molecules are employed as building blocks to construct coordination polymers.[3] The incorporation of host molecules into coordination frameworks, which have well-documented inclusion properties, brings out a number of special aspects not necessarily achievable with conventional ligands, such as multiple inclusion behaviors, unusual topologies, and a vast range of intermolecular interactions. In addition, the coordination polymers formed from host molecules may lead to the development of useful chemoselective materials. Water-soluble calixarenes, which show a wide variety of inclusion properties and coordination abilities to both main-group and transition-metal ions,[4–5] are potentially versatile synthons for the syntheses of coordination polymers. Though there are several examples of coordination polymers constructed from water-soluble calixarenes exhibiting the inclusion of large guest molecules, such as [2.2.2]cryptand and crown ether,[3a,3b] coordination polymers of calixarenes incorporating transition-metal complexes as guests are rarely reported.[3g] Recently, *p*-sulfonatothiacalix[4]arene (TCAS), a new member of the calixarene family, has attracted considerable interest in the broad field of supramolecular chemistry.[6] Like its classic counterpart *p*-sulfonatocalix[4]arene (CAS), *p*-sulfonatothiacalix[4]arene possesses strongly hydrophilic upper and lower rims and a strongly hydrophobic conelike cavity that is bound by four phenyl rings. It can change its conformation from C_{4v} to a cleftlike C_{2v} symmetry while keeping a cone conformation to better accommodate many kinds of ionic and neutral guests. However, the introduction of four sulfur atoms into the calix[4]arene skeleton leads to at least two significant changes. Firstly, the electron-rich cavity of thiacalix[4]arene is larger than that of the classic calix[4]arene. Thus, regardless of electron-density effects, *p*-sulfonatothiacalix[4]arene shows a higher inclusion ability to encapsulate aromatic moieties than classic calix[4]arene, which suggests that the size of the cavity is more important in determining the inclusion ability.[7] Secondly, *p*-sulfonatothiacalix[4]arene can bind metal ions not only at the upper and lower rims but also at the linker positions,[8] which makes it a good candidate for constructing polymers. As reported previously, it tends to form tetranuclear bivalent anions with transition metal ions, capture small guests such as water and the pyridinium cation in its hydrophobic pocket, and further extend its structure through metal–sulfonate oxygen bonds into a 2D layer.[9] Based on the above discussion, we reason that divalent metal complexes with aromatic ligands such as 2,2′-bipyrazine are likely to be incorporated into the 2D cavities of thiacalixarenes for the balance of the charge and interactions with aromatic rings,[10] as shown in Scheme 1. Herein, we wish to report two coordination polymers derived from *p*-sulfonatothiacalix[4]arenes, 2,2′-bipyrazine (2,2′-bpz), and MSO_4 (M = Co, Cu), namely, $\{[Co(2,2'\text{-bpz})(H_2O)_4]^{2+}\subset[Co_4(TCAS)(\mu_4\text{-}SO_4)(H_2O)_4]^{2-}\cdot 10.75H_2O\}_n$

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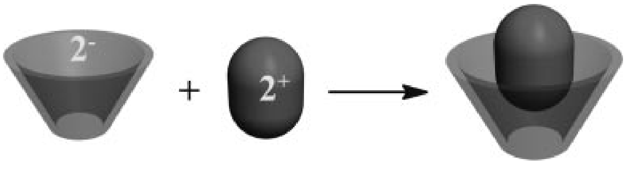
(**1**) and $\{[Cu(2,2'\text{-bpz})(H_2O)_3]^{2+}\subset[Cu_4(TCAS)(\mu_4\text{-}SO_4)(H_2O)_4]^{2-}\cdot 16H_2O\}_n$ (**2**), with an unusual incorporation of the metal–2,2′-bpz complexes into the cavities of the *p*-sulfonatothiacalix[4]arenes.

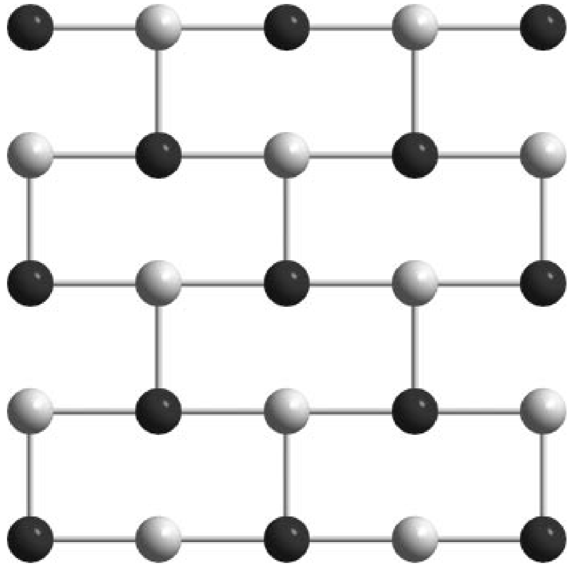


Scheme 1. Schematic representation of the incorporation of the divalent metal complex with aromatic ligands into the bivalent anionic cavity of the *p*-sulfonatothiacalix[4]arene.

Results and Discussion

Crystals of complexes **1** and **2** suitable for X-ray diffraction were obtained by slow diffusion of an MeOH solution of 2,2′-bpz into an aqueous solution of Na_4H_4TCAS and $CoSO_4$, and Na_4H_4TCAS and $CuSO_4$, respectively. Complexes **1** and **2** crystallize in space group $C2/c$ and $P2_1/c$, respectively. They display a very similar structure of a 2D, up–down bilayer arrangement built from $[M_4(TCAS)(\mu_4\text{-}SO_4)]^{2-}$(M = Co for **1**, Cu for **2**) subunits, with inclusion of metal–2,2′-bpz cations into the cavities of the *p*-sulfonatothiacalix[4]arenes as counterions.

In the bowl-like anion subunit, a trapezoid-like tetranuclear cluster is sandwiched between one TCAS unit and one sulfate ligand (Figure 1). The fully deprotonated $TCAS^{8-}$ unit maintains a conventional cone conformation and utilizes its phenoxy groups as μ_2-phenoxy bridges to bind four M^{II} ions. The average $M–O_{(phenoxy)}$ distances are 2.105 Å in **1** and 2.072 Å in **2**. Interestingly, at the lower rim of $TCAS^{8-}$, the SO_4^{2-} anion binds to the four M^{II} ions in a rare tridentate coordination mode to complete the base of the bowl.[9] Two oxygen atoms of the sulfate anion ligate to two metal centers and one acts as a bridge linking the other two metal centres. All of the four cobalt(II) ions in **1** and three of the copper(II) ions (Cu1, Cu2, Cu3) in **2** are in an O_5S octahedral geometry. The oxygen atoms from aqua ligands and the sulfonate groups of adjacent *p*-sulfonatothiacalix[4]arenes complete the six-coordination spheres. Exceptionally, in **2**, Cu4 is in an O_4S square-pyramidal geometry, with an aqua ligand in the equatorial plane. Notably, each $[M_4(TCAS)(\mu_4\text{-}SO_4)]^{2-}$ subunit acts as a three-connector and extends the structure of **1** or **2** into an interesting molecular brick-wall architecture (Scheme 2). Though the aggregation of the tetranuclear clusters in both complexes is directed by the coordination of the sulfonate groups of



Scheme 2. Schematic representation of the brick-wall networks of **1** and **2**.

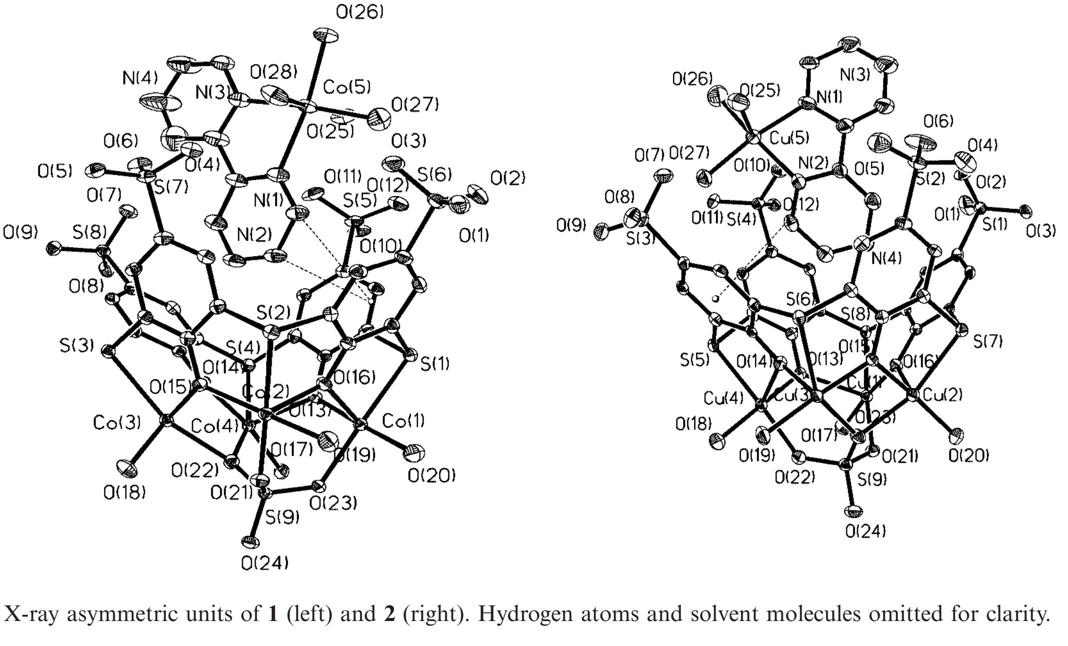


Figure 1. The X-ray asymmetric units of **1** (left) and **2** (right). Hydrogen atoms and solvent molecules omitted for clarity.

$TCAS^{8-}$, there is a slight difference in the coordination modes. In **1**, two sulfonate groups monodentately link the subunits into an infinite chain along the crystallographic *b* axis (Figure 2). Along the crystallographic *a* axis, two sulfonate groups adopt an O,O'-η^1:η^1:μ_2 bridging bidentate mode to connect the two adjacent linear chains into an up–down bilayer structure (Figure 2). In **2**, one sulfonate group adopts an O,O'-η^1:η^1:μ_2 bridging bidentate mode (Figure 3) to join the subunits into an infinite chain along the crystallographic *b* axis. Along the crystallographic *c* axis, two sulfonate groups bind in a monodentate coordination mode and act as chain linkers (Figure 3). Along the third crystallographic axis (*c* axis for **1**, *a* axis for **2**), the layers lie directly above one another to give 1D channels. Large numbers of lattice water molecules (10.75 and 16 in the asymmetric units of **1** and **2**, respectively) fill the channels and interstices between the layers (Figure S1 and Figure S2 in the Supporting Information).

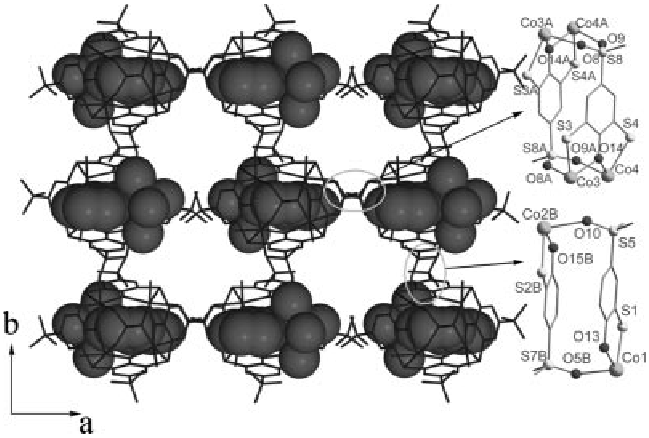


Figure 2. The extended structure of **1** with the incorporation of cobalt–2,2′-bpz cations into the cavities of *p*-sulfonatothiacalix[4]-arenes.

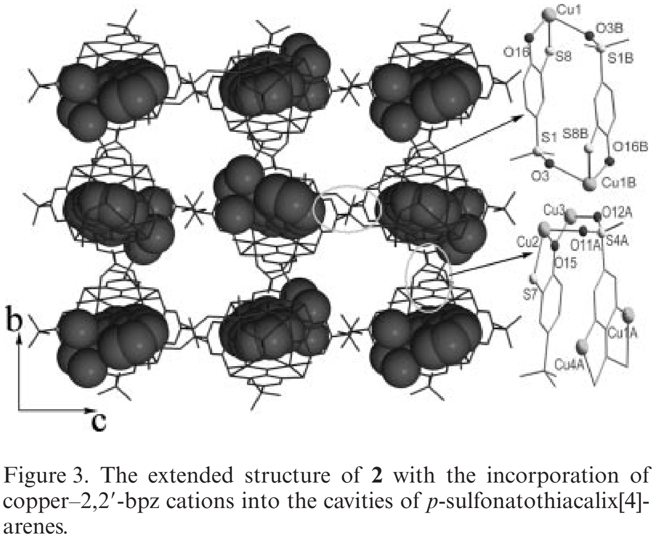


Figure 3. The extended structure of **2** with the incorporation of copper–2,2′-bpz cations into the cavities of *p*-sulfonatothiacalix[4]-arenes.

Despite being fixed by the four metal centers and the SO_4^{2-} anion at the lower rim, the *p*-sulfonatothiacalix[4]arene shows versatility in displaying various conformations and splays its opposite aromatic rings into a cleftlike C_{2v} symmetry to accommodate the guest. Comparatively, the separation distance between the opposite phenyl ring centroids of each *p*-sulfonatothiacalix[4]arene in **1** is much larger (7.5 Å) than that of **2** (6.2 Å). Accordingly, the dihedral angles between the aromatic rings and the plane of the phenolic oxygen atoms are 137.9° (in **1**) and 136.9° (in **2**), which are larger than that of the corresponding coordination polymer that encapsulates the pyridinium cation (133.8°).[9a] The metal–2,2′-bpz cation, as expected, is precariously held in the shallow hydrophobic pocket of the $TCAS^{8-}$ anion as the counterion (Figure 1) by cooperative supramolecular interactions. In **1**, the $[Co(2,2'\text{-bpz})(H_2O)_4]^{2+}$ moiety is held by two CH···π interactions, one involving a *meta* pyridyl hydrogen atom and a phenyl ring of the *p*-sulfonatothiacalix[4]arene with a C–H···Ar centroid distance of 2.926 Å, and the other involving a *para* pyridyl hydrogen atom and the same phenyl ring of the *p*-sulfonatothiacalix[4]arene with a C–H···Ar centroid distance of 3.164 Å, as shown in Figure 1 left. However, in **2**, the $[Cu(2,2'\text{-bpz})(H_2O)_3]^{2+}$ cation uses one of its *meta* pyridyl hydrogen atoms to form a CH···π interaction with a phenyl ring of the *p*-sulfonatothiacalix[4]arene, with a C–H···Ar centroid distance of 2.700 Å (Figure 1 right). Additionally, other intermolecular interactions such as electrostatic attractions, hydrophobic–hydrophobic interactions, and hydrogen bonding may also play important roles in the recognition process between metal–2,2′-bpz cations and $TCAS^{8-}$ anions. The closest O···O separations of the aqua ligands in the metal–2,2′-bpz cations and the oxygen atoms of the sulfonate groups are 2.703 Å in **1** and 2.705 Å in **2**, which shows rather strong hydrogen-bonding interactions between the hosts and guests.

In summary, we have successfully synthesized two tetranuclear cluster coordination polymers, which both include metal–2,2′-bpz complexes as guests through a combination of supramolecular interactions. It further demonstrates that *p*-sulfonatothiacalix[4]arene is a good host molecule with the flexibility to accommodate a range of guests through self-adjustment and that it is a good ligand to construct coordination polymers. Because of the thermal stability of the skeleton, the layer coordination networks built from tetranuclear clusters may prove to be of high interest in separation/absorption applications.[11] Further research is under way and systematic results will be reported later.

Experimental Section

Syntheses of Complexes 1 and 2: A solution of 2,2′-bipyrazine (8 mg, 0.05 mmol) in CH_3OH (4 cm^3) was carefully layered on a solution of Na_4H_4TCAS (45 mg, 0.05 mmol) and $CoSO_4\cdot 6H_2O$ (66 mg, 0.25 mmol) or $CuSO_4\cdot 5H_2O$ (63 mg, 0.25 mmol) in water (4 cm^3, pH = 3.8) using an H_2O/CH_3OH (3 cm^3) buffer. Over a period of about three weeks, red (**1**) or orange (**2**) prism crystals formed, which were suitable for X-ray diffraction analyses. Yield: 26 mg for **1** (30.67 %, based on Na_4H_4TCAS) or 24 mg for **2** (26.95 %, based on Na_4H_4TCAS). **1**, $C_{32}H_{51.50}Co_5N_4O_{38.75}S_9$ (1695.46): calcd. C 22.67, H 3.06, N 3.30; found C 22.81, H 2.98, N 3.36%. **2**, $C_{32}H_{46}Cu_5N_4O_{43}S_9$ (1780.97): calcd. C 21.58, H 2.60, N 3.15; found C 21.69, H 2.53, N 3.19%.

X-ray Structure Determination: Crystal data for **1**: $C_{32}H_{51.50}Co_5N_4O_{38.75}S_9$ (1695.46), monoclinic, space group *C2/c*, T = 173(2) K, a = 22.764(4), b = 18.334(4), c = 30.170(6) Å, β = 95.057 (7), V = 12543(4) Å^3, Z = 8, $d_{calcd.}$ = 1.796 Mg m^{-3}, $F(000)$ = 6884, μ (Mo-K_a) = 1.695 mm^{-1}, red, 0.20 × 0.13 × 0.06 mm, θ range 3.05–27.49°, 46748 reflections collected, 14025 unique (R_{int} = 0.0381). Final *GooF* = 1.074, R_1 = 0.0546, wR_2 = 0.1301, R indices based on 12226 reflections with $I > 2\sigma(I)$ (refinement on F^2), 838 parameters, $(\Delta\rho)_{max}$ = 1.802, $(\Delta\rho)_{min}$ = –0.767 e/Å^{-3}. Crystal data for **2**: $C_{32}H_{46}Cu_5N_4O_{43}S_9$ (1780.97), monoclinic, space group $P2_1/c$, T = 173(2) K, a = 14.981(3), b = 18.407(4), c = 23.447(5) Å, β = 100.571(2), V = 6356(2) Å^3, Z = 4, $d_{cald.}$ = 1.861 Mg m^{-3}, F (000) = 3596, μ = 2.049 mm^{-1}, orange, 0.40 × 0.15 × 0.60 mm, θ range 2.32–27.48°, 47791 reflections collected, 14314 unique (R_{int} = 0.0457), Final *GooF* = 1.161, R_1 = 0.0659, wR_2 = 0.1342, R indices based on 12550 reflections with $I > 2\sigma(I)$ (refinement on F^2), 895 parameters, $(\Delta\rho)_{max}$ = 1.495, $(\Delta\rho)_{min}$ = –0.848 e/Å^{-3}. Data collections for the two compounds were performed with a Rigaku Mercury-CCD diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). The data sets were collected at 173(2) K (ω-scan mode). The structures of the two compounds were solved by direct methods and refined by full-matrix least-squares techniques with the *SHELXTL*-97 program package.[12] All non-hydrogen atoms were refined anisotropically except for several disordered solvent molecules. The organic hydrogen atoms were located at geometrically calculated positions and refined using a riding model [C–H = 0.95 Å $U_{iso}(H) = 1.2U_{eq}(C)$]. The hydrogen atoms on the water molecules were located in difference density maps and were refined as riding using the instruction AFIX 3,[12] and no attempt was made to locate the hydrogen atoms of disorder water molecules.

CCDC-266331 and CCDC-266330 (for **1** and **2**, respectively) 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.

Supporting Information: (see footnote on the first page of this article). Figure S1 – Lattice water molecules occupying the channels and the interstices between the layers in **1**, and Figure S2 – Lattice water molecules occupying the channels and the interstices between the layers in **2**.

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