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Selective Anion Inclusion in Calix(4)arene Complexes Driven by Face-Bridging μ_4-Halide Binding

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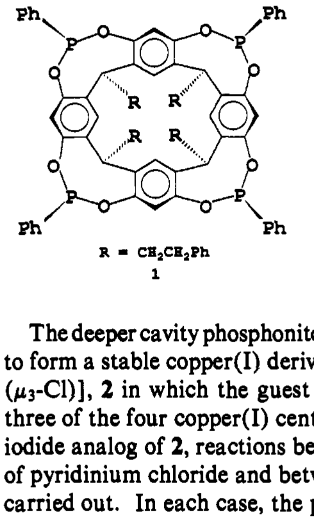
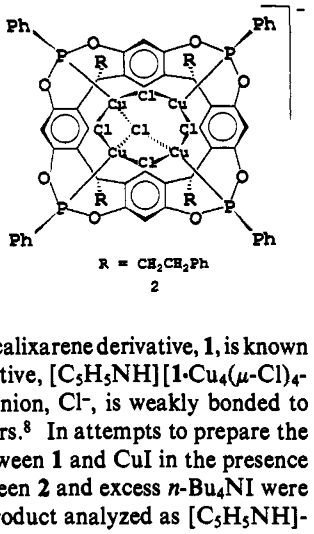
The host–guest chemistry of macrocyclic compounds has developed rapidly in recent years, and now it impinges on wide areas of both chemistry and biochemistry.[1] Calixarenes are bowl-shaped molecules that have a remarkable ability to engulf small guest molecules and cations.[2,3] Although the bottom rim of calixarenes has been derivatized with oxophilic metal centers, the host environment is not fundamentally changed, and inclusion of neutral molecules is still preferred.[4–7] However, when electrophilic metal clusters are incorporated into the upper rim of calixarenes a suitable environment for anion inclusion can be created.[8] It has now been shown that the anion inclusion is selective and that the geometry imposed by the calixarene host can stabilize an unusual μ_4-face bridging binding mode of the guest halide.



R = CH_2CH_2Ph
1



R = CH_2CH_2Ph
2

The deeper cavity phosphonitocalixarene derivative, **1**, is known to form a stable copper(I) derivative, $[C_5H_5NH][\mathbf{1}\cdot Cu_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)]$, **2** in which the guest anion, Cl^-, is weakly bonded to three of the four copper(I) centers.[8] In attempts to prepare the iodide analog of **2**, reactions between **1** and CuI in the presence of pyridinium chloride and between **2** and excess n-Bu_4NI were carried out. In each case, the product analyzed as $[C_5H_5NH][\mathbf{1}\cdot Cu_4I_{3.3}Cl_{1.7}]$, **3**, shows that complete replacement of chloride by iodide is difficult. This was unexpected since copper(I) is a soft metal ion with a strong preference for iodide. Spectroscopic studies of the structure were inconclusive, but an X-ray structure determination (Figure 1) reveals that the I^- is selectively included in the middle of the bowl by weakly bonding to four Cu atoms, while chloride and iodide ions in a ratio of 1.75:2.25 occupy the μ_2-bridging sites in a disordered way.[10] The faced bridged μ_4-I is unprecedented both in metal iodide compounds[11] and in tetranuclear Cu(I) halide derivatives and contrasts with the μ_3-Cl ligand in **2**. Why is it formed? We suggest that copper(I) has a thermodynamic preference for tetrahedral rather than trigonal planar stereochemistry, and this can only be accommodated, given the ligand geometry, by the μ_4-halide binding in **3** (Figure 1). The chloride ligand is too small to bridge between all four copper(I) atoms but can bridge between three of them as in **2**. Hence, in a mixed chloride–iodide complex, the iodide will bind selectively in the center as in **3**. It is less obvious why it is difficult to replace all the μ-Cl groups. The cavity size is determined by the $Cu_4(\mu\text{-}X)_4$ crown structure, and this may be optimized for iodide inclusion when a mixture of μ-I and μ-Cl ligands is present.

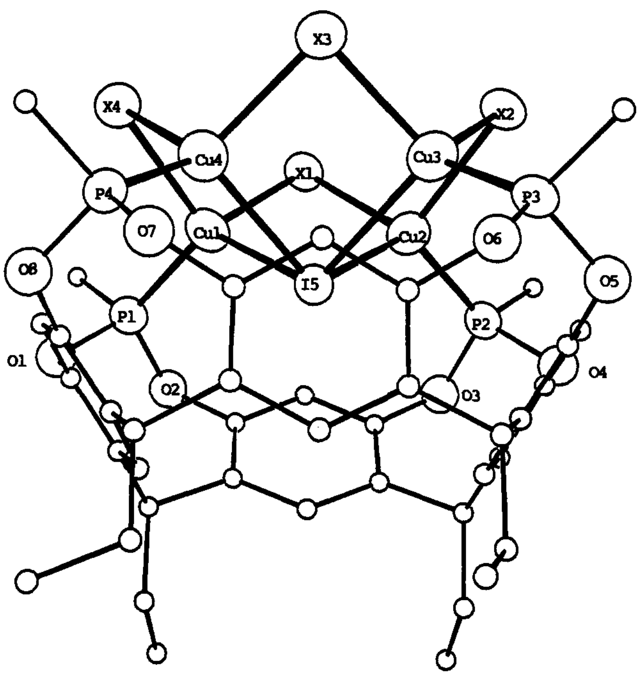


Figure 1. A side view of the molecular structure of **3a**. The phenyl rings on both PhP- and $-CH_2CH_2Ph$ groups have been omitted for clarity, and carbon atoms are assigned arbitrary radii. The central iodide is I(5). Refinement of occupancy factors gave the following ratios I/Cl: X(1) and X(2), 0.625/0.375; X(3), 0.40/0.60; X(4), 0.60/0.40 giving the overall partial formula $[Cu_4I_{3.25}Cl_{1.75}]$, in good agreement with analytical data. Cu–I(5) distances are 2.752(2)–2.845(2) Å, and adjacent nonbonding Cu···Cu distances are 3.275–3.461 Å.

If this interpretation is correct, then a μ_4-Cl group should be possible if copper(I) is replaced by a larger metal ion such as Ag(I). Reaction of **1** with $(AgCCPh)_n$ or $AgNO_3$ in the presence of pyridium chloride gave a new complex $[C_5H_5NH][\mathbf{1}\cdot Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]$, **4a**. The structure of the Me_4N^+ salt of the complex anion is shown in Figure 2. The μ_4-Cl unit is indeed present. In

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(9) Typical spectroscopic data for **3**: $C_{89}H_{74}N_1Cu_4I_{3.3}Cl_{1.7}P_4O_8$; NMR in CD_2Cl_2 δ (^{31}P, ppm) = 132.2 (br), 127.1 (br), 120.7 (br), assigned to PCu units with $PCu(\mu_4\text{-}I)I_2$, $PCu(\mu_4\text{-}I)ICl$, and $PCu(\mu_4\text{-}I)Cl_2$ coordination; δ (^1H) = 2.74 (br, 16H, CH_2CH_2Ph), 4.89 (br, 4H, $CH(CH_2)_2Ph$), 7.05–8.20 (aryl), 9.30 (s, br, 1H, $C_5H_5NH^+$); IR ν_{NH} = 3500 cm^{-1} (w).

(10) Crystal data for **3**: $C_{89}H_{74}N_1Cl_{1.75}Cu_4I_{3.25}P_4O_8\cdot 2CH_3CN$; $M = 2220.2$, triclinic, $P\text{-}1$, $a = 17.830(3)$ Å, $b = 21.321(4)$ Å, $c = 13.779(4)$ Å, $\alpha = 103.3(2)°$, $\beta = 112.5(2)°$, $\gamma = 81.03(1)°$, $Z = 2$, $R = 0.0576$, $R_w = 0.0657$.

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(12) Spectroscopic data for **4a** as the $C_5H_5NH^+$ salt. Anal. Calcd for $C_{89}H_{74}N_1Ag_4Cl_5P_4O_8$: C, 52.97; H, 3.70; N, 0.69. Found: C, 52.66; H, 3.93; N, 0.71. NMR in $CDCl_3$ δ (^{31}P) = 157.0 (dd, $^1J_{Ag(109)\text{-}P}$ = 766.3Hz, $^1J_{Ag(107)\text{-}P}$ = 664.1Hz); δ (^1H) = 1.99 (s, 6H, CH_3CN), 2.67 (br, 16H, CH_2CH_2Ph), 4.84 (br, 4H, $CH(CH_2)_2Ph$), 6.97–8.30 (aryl), 9.32 (s, br, 1H, $C_5H_5N\cdot H^+$); IR ν_{NH} = 3500 cm^{-1} (w).

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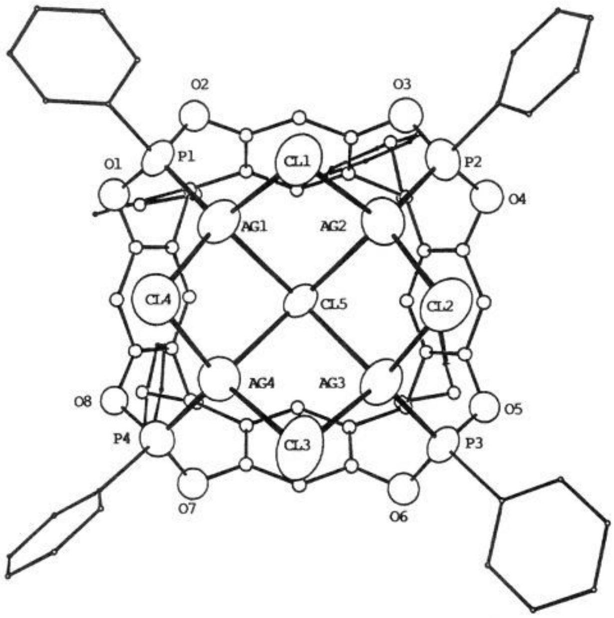

Figure 2. A top view of the molecular structure of **4a**. Distances are Ag–μ-Cl = 2.56(1)–2.62(1) Å, Ag–μ_4-Cl(5) = 2.69(1)–2.76(1) Å, adjacent nonbonding Ag···Ag = 3.415–3.523 Å.

Table I. Extraction of Alkali Metal Picrates from Water into CH_2Cl_2 at 25 °C by **3** and **4a**[a]

ligand	picrate salt extracted (%)					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
3	7.0	25.1	39.5	30.1	21.8	31.8
4a	62.0	61.6	59.3	52.8	48.1	40.0

[a] Aqueous phase: [metal chloride] = 0.1 M; [picric acid] = 2.5×10^{-4} M. Organic phase: [ligand] = 2.5×10^{-4} M. No picrate extraction was observed in the absence of complex **3** or **4a**.

addition, it was easy to replace all chlorides in **4a** to give the corresponding anions $[\mathbf{1}\cdot Ag_4(\mu\text{-}X)_4(\mu_4\text{-}X)]^-$, **4b**, X = Br; **4c**, X = I.

The nature of the unusual $M_4(\mu_4\text{-}X)$ bond in **3** and **4** (Figures 1 and 2) was studied by carrying out extended Huckel MO calculations. The model complex $[Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)(PH_3)_4]^-$, **A**, was considered to be formed from the fragment $[Ag_4(\mu\text{-}Cl)_4(PH_3)_4]$, **B**, by coordination of Cl^-. Both **A** and **B** were built up with ideal C_{4v} symmetry by using average distances and angles based on the X-ray structure determination. Bonding interactions are readily identified by overlap of filled orbitals of Cl^- with acceptor orbitals on silver. There are only three net σ-bonding interactions ($a_1 + 2e$), since one of the four sets of acceptor orbitals (b_{1u}, LUMO in **A**) is nonbonding (Figure 3), and hence the maximum $Ag_4(\mu_4\text{-}Cl)$ total bond order is three rather than four, consistent with the longer Ag–μ_4-Cl distance (average 2.71 Å) compared to the single-bond Ag–μ-Cl distance (average 2.59 Å). The calculated charge on the μ_4-Cl ligand in **A** is –0.498e, indicating that the μ_4-Cl^- ligand is not simply a guest anion but is covalently bonded to the silver(I) centers.

The compounds **3** and **4a** show a strong affinity for alkali metal cations as shown by their ability to extract such cations from aqueous solution into organic solvents containing **3** and **4a** (Table I). Interestingly, **4a** has a strong affinity for Li^+, which can seldom be extracted by other calixarene derivatives.[15,16] Again, size selectivity may play an important role here.

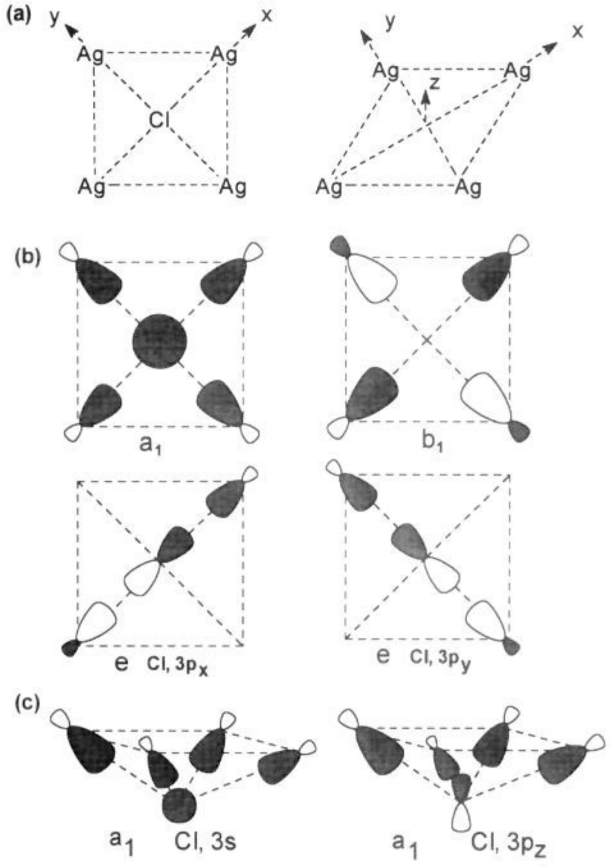

Figure 3. A schematic view of the overlap between the symmetry adapted acceptor orbitals on Ag with the donor orbitals of Cl^-: (a) the axis definition, (b) top view of orbitals involved in bonding (the b_{1u} acceptor orbital is the LUMO in the model complex **A**), and (c) the two components of the a_1 bonding interaction.

In conclusion, this work has demonstrated how metal complexes of phosphonitocalixarene ligands can provide a host for the **size-selective** inclusion of halide ions and that these products can, in turn, act as size-selective hosts for alkali metal cations.

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Supplementary Material Available: Tables of crystal data, bond lengths, and angles for **3** and **4a** (27 pages); tables of observed and calculated structure factors (70 pages). Ordering information is given on any current masthead page.

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[13] Crystal data for **4a** as the Me_4N^+ salt: $C_{88}H_{80}N_1Ag_4Cl_5P_4O_8\cdot 1.5C_2H_5CN$; CH_2Cl_2 $M = 2179.79$, triclinic, $P\text{-}1$, $a = 15.532(4)$ Å, $b = 24.421(8)$ Å, $c = 14.049(8)$ Å, $\alpha = 90.98(4)°$, $\beta = 99.10(4)°$, $\gamma = 99.22(3)°$, $Z = 2$, $R = 0.1075$, $R_w = 0.1188$.

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