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Anionic Calixarene Complexes of Copper(I) and Silver(I) as Cation Receptors

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A tetraphosphonitocalixresorcinarene ligand $(PhCH_2CH_2CHC_6H_2O_2PPh)_4$, bowl, forms tetracopper(I) and tetrasilver(I) complexes $[(bowl)M_4(\mu\text{-}Cl)_4]$, **1**, M = Cu or Ag, and the chloride inclusion compounds $[(bowl)Cu_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)]^-$, **2a**, and $[(bowl)Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]^-$, **2b**. The anionic complexes **2a** and **2b** are now shown to act as hosts for the selective binding of metal cations. This metal cation inclusion is effected by chelation by some or all of the four μ-Cl groups present in **2**. Isolated complexes have the formula [**2**·M] (**3**, M = Na, K, Rb, Cs) for M^+ ions and either [**2**·MCl] (**4**, M = Zn, Cd) or [**2**$_2$·M] (**5**, M = Hg, Pb) for M^{2+} ions. The complexes [(**2a**·Cs)$_2$], **3d**, and [**2b**$_2$·Hg], **5a**, have been characterized by X-ray structure determinations [**3d**·solvate; triclinic, $P1$, $a = 16.5142(1)$ Å, $b = 25.8269(2)$ Å, $c = 26.3615(4)$ Å, $\alpha = 61.785(1)°$, $\beta = 80.403(1)°$, $\gamma = 72.533(1)°$, $Z = 2$; **5a**·solvate; monoclinic, $P2_1/n$, $a = 13.4174(2)$ Å, $b = 43.2897(7)$ Å, $c = 15.7462(3)$ Å, $\beta = 98.734°$, $Z = 2$]. In both **3d** and **5a**, the metal ions are sandwiched between two units of the corresponding anionic complex **2**. In the 2:2 complex **3d**, each Cs^+ ion is coordinated by four Cl atoms of one unit of **2a** and by two Cl atoms and a phenyl ring of the second unit of **2a**. In the 2:1 complex **5a**, the Hg^{2+} ion is coordinated by one Cl atom of one unit of **2b** and by two Cl atoms (with a weak bond to a third Cl atom) of the second unit of **2b**. The metal cation complexation also influences the binding of the occluded chloride anion in **3d**. Both the guest cation and the guest anion can migrate easily between donor and acceptor sites, respectively, such that the host−guest complexes appear to have 4-fold symmetry as characterized by ^1H or ^{31}P NMR. Overall, the formation of **3d** and **5a** from **1** may be considered to occur by salt inclusion.

Introduction

There has been much interest in the use of macrocyclic ligands for complexing either cations or anions, with potential applications for ion sensing, storage, transport, and separation.[1−6] Calixarenes have the ability to transport alkali cations only in strongly basic solution, and usually exhibit selectivity for less strongly hydrated metal ions such as Cs^+.[6−13] In simple calixarenes, the bonding to metal cations is probably mostly electrostatic, but calixarenes have been derivatized with more covalent binding donors, and these can show affinity for alkali metal cations under neutral conditions.[14,15] These calixarene derivatives are considered to be analogs of crown ethers.[15,16] Most of these metal cation receptors act as alkali metal or alkaline earth metal cation receptors when O or N donor atoms are present or as transition metal cation receptors when N, P, or S donor atoms are present.[6−16] There are few derivatives known which can act as hosts for both cations and anions.[17] In earlier papers, we have reported the calixarene complexes

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(1) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021.

(2) Gutsche, C. D. *Calixarenes*, The Royal Society Monographs in Supramolecular Chemistry, Cambridge, 1989.

(3) (a) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 892. (b) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.

(4) (a) Bohmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713. (b) Roundhill, D. M. *Prog. Inorg. Chem.* **1995**, *43*, 533.

(5) Andreetti, G. D.; Ugozzoli, F.; Ungaro, R.; Pochini, A. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: New York, 1991; Vol. 4, Chapter 3.

(6) (a) Koide, Y.; Oka, T.; Imamura, A.; Shosenji, H.; Yamada, K. *Bull. Chem. Soc. Jpn*. **1993**, *66*, 2137. (b) Araki, K.; Yanagi, A.; Shinkai, S. *Tetrahedron* **1993**, *49*, 6763. (c) Takeshita, M.; Shinkai, S. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 1088. (d) Yamamoto, H.; Ueda, K.; Suenaga, H.; Sakaki, T.; Shinkai, S. *Chem. Lett.* **1996**, 39. Note that, in the present case, the complexes with alkali metal cations are neutral and the picrate is probably extracted as the pyridinium salt. Nevertheless, it is clear that picrate extraction accompanies metal cation extraction.

(7) An, H.; Bradshaw, J. S.; Izatt, R. M. *Chem. Rev.* **1992**, *92*, 543.

(8) Hyatt, J. A. *J. Org. Chem.* **1978**, *9*, 1809.

(9) Izatt, R. M.; Lamb, J. D.; Hawkins, T.; Brown, P. R.; Izatt, S. R.; Christensen, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 1782.

(10) Izatt, S. R.; Hawkins, R. T.; Christensen, J. J.; Izatt, R. M. *J. Am. Chem. Soc.*, **1985**, *107*, 63.

(11) Perez-Jimenez, C.; Harris, S. J.; Diamond, D. *J. Chem. Soc., Chem. Commun.* **1993**, 480.

(12) Goldman, H.; Vogt, W.; Paulus, E.; Bohmer, V. *J. Am. Chem. Soc.*, **1988**, *110*, 6811.

(13) (a) Harrowfield, J. M.; Ogden, M. I.; Richmond, W. R.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1159; *J. Chem. Soc., Dalton Trans.* **1991**, 2153. (b) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *10*, 1709.

(14) (a) Weiss, E.; Koster, H. *Chem Ber.* **1977**, *110*, 717. (b) Denamor, A. F. D.; Gil, E.; Tanco, M. A. L.; Tanaka, D. A. P.; Salazar, L. E. P.; Schulz, R. A.; Wang, J. J. *J. Phys. Chem.* **1995**, *99*, 16776. (c) Beer, P. D.; Chen, Z.; Gale, P. A.; Heath, J. A.; Knubley, R. J.; Ogden, M. I.; Drew, M. G. B. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *19*, 343. (d) Shibutani, Y.; Yoshinaga, H.; Yakabe, K.; Shono, T.; Tanaka, M. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *19*, 333. (e) Asfari, Z.; Astier, J. P.; Bressot, C.; Estienne, J.; Pepe, G.; Vicens, J. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *19*, 291. (f) Loeber, C.; Wieser, C.; Matt, D.; De Cian, A.; Fischer, J.; Toupet, L. *Bull. Soc. Chim. Fr.* **1995**, *132*, 166.

(15) (a) Andreetti, G. D.; Calestani, G.; Ugozzoli, F.; Arduini, A.; Ghidini, E.; Pochini, A.; Ungaro, R. *J. Inclusion Phenom.* **1987**, *5*, 123. (b) Calestani, G.; Ugozzoli, F.; Arduini, A.; Ghidini, E.; Ungaro, R. *J. Chem. Soc., Chem. Commun.* **1987**, 344. (c) Beer, P. D.; Chen, Z.; Drew, M. G. B.; Gale, P. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2207. (d) Delaigue, X.; Hosseini, M. W.; Kyritsakas, N.; Decian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1995**, 609. (e) Yordanov, A. T.; Mague, J. T.; Roundhill, D. M. *Inorg. Chim. Acta* **1995**, *240*, 441. (f) Matsumoto, H.; Shinkai, S. *Tetrahedron Lett.* **1996**, *37*, 77. (g) Koh, K. N.; Araki, K.; Shinkai, S.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **1995**, *36*, 6095. (h) Asfari, Z.; Wenger, S.; Vicens, J. *Pure Appl. Chem.* **1995**, *67*, 1037.

(16) (a) Shimizu, H.; Iwamoto, K.; Fujimoto, K.; Shinkai, S. *Chem. Lett.* **1991**, 2147. (b) Soedarsono, J.; Burgard, M.; Asfari, Z.; Vicens, J. *Solvent Extr. Ion Exch.* **1995**, *13*, 755. (c) Deligoz, H.; Yilmaz, M. *Solvent Extr. Ion Exch.* **1995**, *13*, 19.

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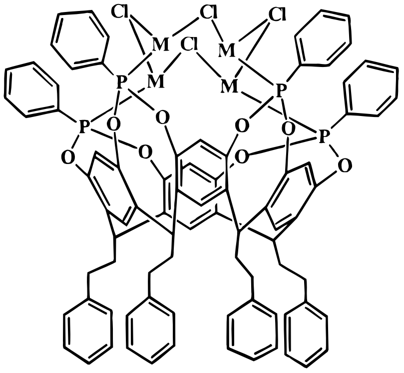
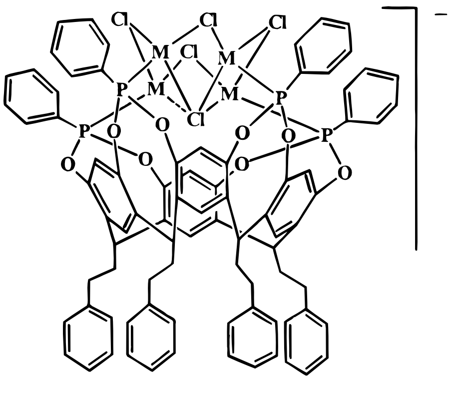
[(bowl)$M_4(\mu\text{-}Cl)_4$], **1**, and the more readily accessible halide inclusion complexes [(bowl)$M_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)$] (M = Cu) or [(bowl)$M_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)$] (M = Ag), **2**, in which the central chloride ion is weakly coordinated to the array of copper(I) or silver(I) acceptors.[18] In the anions **2**, the four μ-Cl groups at the bowl rim appear to be oriented so that two, three, or all four of them could chelate to a metal ion. In principle, therefore, the neutral complexes **1** would be acting as a host for salt inclusion with chloride in the bowl center complexed to the array of four copper(I) or silver(I) acceptors, and a cation at the top of the bowl complexed by the array of μ-Cl donors. This paper reports a study of metal ion complexation by the complex anions **2**. As far as we are aware, this is the first study of the use of chloride donors in calixarenes for complexing metal cations and the reaction is equivalent to overall salt inclusion by **1**.



1a, M = Cu
1b, M = Ag



2a, M = Cu, μ3-Cl present
2b, M = Ag, μ4-Cl present

Results and Discussion

Liquid−Liquid Metal Cation Extraction by Compounds 2. In order to test the ability of **2** to act as metal cation receptors, some preliminary studies on liquid−liquid extraction of several alkali metal, alkaline earth metal, and transition metal cations have been carried out. The method is based on extraction of the metal picrate, followed by estimation of the picrate concentration by colorimetry.[6] The method is thus indirect and susceptible to systematic error, but the results presented in Table 1 show clearly that both **2a** and **2b** are able to extract metal cations from aqueous solution into dichloromethane. The selectivities displayed are unusual: for example, **2b** has a strong affinity for Li^+, which is seldom extracted by other calixarene derivatives.[2,5,6,16] In this case, it is possible that the Li^+ ion (van der Waals radius = 0.7 Å) may be small enough to penetrate the small channel composed of four μ-Cl atoms and also bind to the occluded Cl^- ion.

Table 1. Extraction of Metal Picrates from Aqueous Solution into CH_2Cl_2 at 25 °C by Pyridinium Salts of **2a** and **2b**[a]

ligand	picrate salt extracted (%)					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
2a	7.0	25.1	39.5	30.1	21.8	31.8
2b	62.0	61.6	59.3	52.8	48.1	40.0
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Zn^{2+}	Cd^{2+}
2a	31.2	7.4	9.7	5.0	19.9	30.7
2b	48.4	33.2	37.4	37.0	40.1	59.0
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Pb^{2+}	
2a	10.7	43.0	48.4	23.6	27.6	
2b	42.1	47.0	37.1	81.2	52.4	

[a] Aqueous phase: metal chloride concentration = 0.1 M; metal picrate concentration = 8.3 × 10^{-5} M. Organic phase: ligand concentration = 8.3 × 10^{-5} M. No picrate extraction was observed in the absence of **2a** or **2b**.

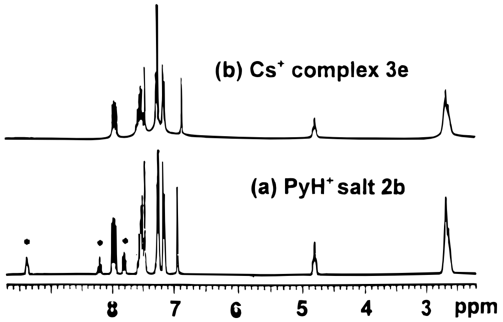


Figure 1. ^1H NMR spectra of compound **4** and cation complex **6a** (notice the disappearance of pyridinium cation resonances which are marked with an asterisk in the lower spectrum).

Attempts have been made to isolate the metal complexes of **2**, and several, though by no means all, could be prepared in analytically pure form.

Formation and Structures of Complexes of 2 with Alkali Metal and Alkaline Earth Metal Cations. The alkali metal cations usually interact with calixarenes through the oxygen donor atoms, and since it is proposed that the derivatives **2** will interact through the μ-Cl donors, it was considered important to isolate at least one example and determine the connectivity by X-ray structure determination. The isolation of alkali metal complexes of formula [**2**·M′], **3**, was achieved by treatment of a slurry of complex **2a** or **2b** at room temperature with an excess of the alkali metal salt (M = Ag, M′ = Na, **3a**; M = Ag, M′ = K, **3b**; M = Ag, M′ = Rb, **3c**; M = Cu, M′ = Cs, **3d**; M = Ag, M′ = Cs, **3e**) in acetone. The cation replacement was clearly indicated by the complete disappearance of the pyridinium cation resonances, which are easily identified in the ^1H NMR spectrum of **2** in the corresponding spectra of **3** (Figure 1). The products were then purified by recrystallization. The only alkali metal which did not yield a pure complex with either **2a** or **2b** was lithium.

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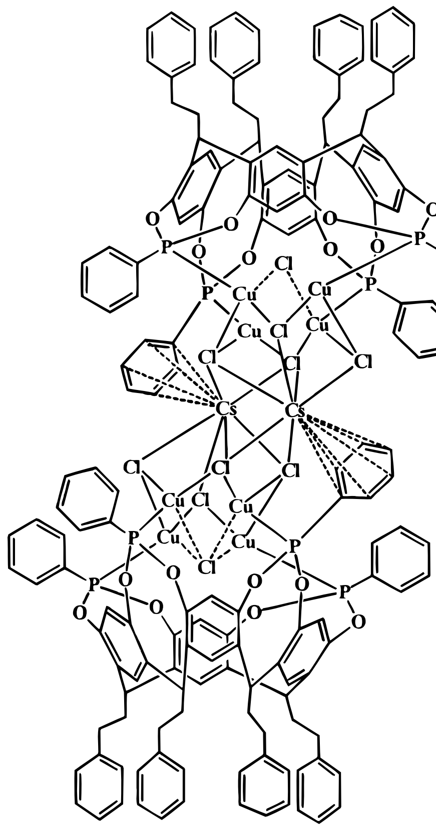
[17] (a) Beer, P. D.; Drew, M. G. B.; Knubley, R. J.; Ogden, M. I. *J. Chem. Soc., Dalton Trans.* **1995**, 3117. (b) Nagasaki, T.; Fujishima, H.; Takeuchi, M.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1883. (c) Rudkevich, D. M.; Mercer-Chalmers, J. D.; Verboom, W.; Ungaro, R.; Dejong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 6124.

[18] (a) Xu, W.; Rourke, J. P.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1993**, 145. (b) Xu, W.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 6456. (c) Xu, W.; Rourke, J. P.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1995**, *34*, 323. (d) Xu, W.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8362.



3d

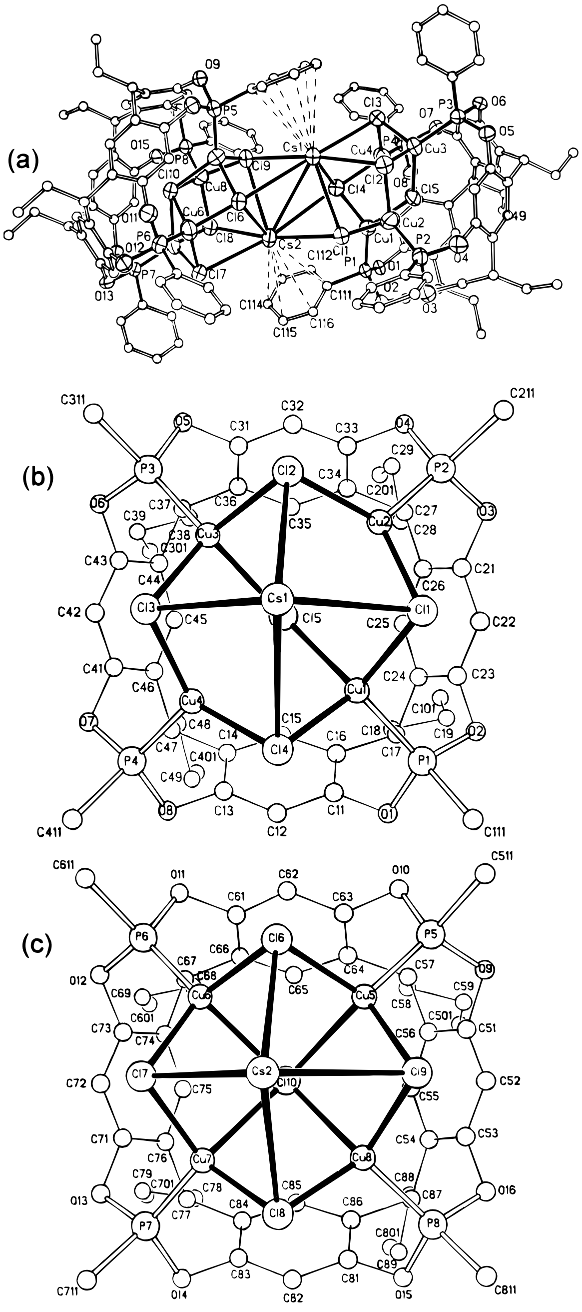


Figure 2. (a) View of the molecular structure of **3d** showing that the two cesium cations are sandwiched by two anionic bowl ligands. (The phenyl rings on the CH_2CH_2Ph groups and all hydrogens have been omitted for clarity.). (b) and (c) Views of the cesium chloride coordination in the two halves of **3d**, showing that one occluded chloride bridges two and the other bridges four copper atoms.

Crystals of **3d** suitable for X-ray analysis were obtained with difficulty by recrystallization from a solvent mixture containing MeCN, Me_2CO, and $CHCl_3$. The structure is shown in Figure 2, and selected bond distances and angles are in Tables 2 (comparison of bowl parameters in **3d** with those of the parent **2a**) and 3 (parameters of bonds to cesium in **3d**). The structure is best considered as a ball-shaped 2:2 dimer [$\mathbf{2a}_2Cs_2$] in which two cesium ions are sandwiched between two units of **2a**.

Each Cs^+ ion in **3d** is coordinated by four μ-Cl units of one unit of **2a** and more weakly by two μ-Cl units and an η-arene group of the other unit of **2a**. The shorter Cs−Cl distances [Cs(1)Cl(1)−Cs(1)Cl(4); Cs(2)Cl(6)−Cs(2)Cl(9)] fall in the range 3.413(4)−3.558(4) Å, and the mean Cs−Cl distance (3.47 Å) is similar to that in cesium chloride (3.45 Å).[19] The longer CsCl distances [Cs(1)Cl(6), Cs(1)Cl(9), Cs(2)Cl(1), Cs(2)Cl(4)] fall in the range 3.525(4)−3.814(4) Å with mean Cs−Cl = 3.65 Å. All these CsCl interactions are considered to be mainly electrostatic in nature. The cesium−carbon distances to the closest phenyl substituent [e.g. Cs(1)C(511)−Cs(1)C(516) = 3.56(1)−4.52(1) Å] are similar to those in related compounds for which weak Cs^+ arene bonding is thought to be present.[13] The shortest CsC separation is very close to the Cs−C distance of 3.53 Å found for methylcesium.[14] The long interatomic distance of Cs^+ to the occluded Cl^- (e.g., Cs(1)Cl(5) = 3.90 Å) is considered to be nonbonding as is a long CsCl contact of 3.92 Å to a chlorine atom of a neighboring chloroform molecule. Thus, the Cs^+ cation is encapsulated in a cage formed by six coordinated chloride ligands and one phenyl ring. It is reasonable to assume that the chloride−phenyl ring cage provides a particularly good environment for a Cs^+ ion after it has lost its hydration shell.[13] The $Cs^+\cdots Cs^+$ separation in the sandwich arrangement is 4.280(2) Å, and the pattern of CsCl distances suggests that this reflects a weak repulsion between the Cs^+ cations; similar distances are common in other cesium sandwich structures.[19,20]

Does the coordination of cesium in **3d** lead to changes in the structure of the component bowl complex **2a**? A comparison of the bond parameters of **2a** and the two independent units of **2a** present in **3d** is given in Table 2. At first glance, the changes appear minor. The mean nonbonding distances between adjacent P, Cu, and μ-Cl atoms are slightly greater in **3d** than in **2a** (Table 2), leading to a minor enlargement of the cavity between the four μ-Cl atoms. This is presumably to allow the maximum bonding of the μ-Cl atoms to Cs^+. However, there are some interesting effects on the binding of the guest chloride

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[19] (a) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (b) Schulz, L. G. *Acta Crystallogr.*, **1951**, *4*, 487. (c) Baldas, J.; Colmanet, S. F.; Williams, G. A. *J. Chem. Soc., Chem. Commun.* **1991**, 955.

[20] Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

Table 2. Selected Bond Distances and Angles in the Anions **2a** and **2b** and in the Complexes **3d** and **5a**[a]

	2a	**3d**, Cu1−Cu4	**3d**,[a] Cu5−Cu8	**2b**	**5a**		**2a**	**3d**, Cu1−Cu4	**3d**,[a] Cu5−Cu8	**2b**	**5a**
M(1)−X(1)	2.374(5)	2.466(4)	2.406(6)	2.56(1)	2.570(6)	M(4)−X(4)	2.306(6)	2.375(4)	2.394(4)	2.61(1)	2.644(7)
M(1)−X(4)	2.405(5)	2.437(4)	2.382(4)	2.57(1)	2.665(7)	M(4)−X(5)	2.983(5)	2.866(5)	2.557(5)	2.69(1)	2.702(5)
M(1)−X(5)	2.512(5)	2.401(4)	2.598(4)	2.72(1)	2.693(6)	M(1)−P(1)	2.177(6)	2.199(4)	2.196(4)	2.41(1)	2.364(6)
M(2)−X(1)	2.348(5)	2.355(4)	2.387(4)	2.59(1)	2.569(6)	M(2)−P(2)	2.177(5)	2.196(4)	2.196(4)	2.40(1)	2.357(5)
M(2)−X(2)	2.386(5)	2.322(4)	2.375(4)	2.58(1)	2.583(6)	M(3)−P(3)	2.181(5)	2.203(4)	2.193(4)	2.39(1)	2.378(6)
M(2)−X(5)	2.548(6)	2.999(6)	2.652(4)	2.76(1)	2.762(5)	M(4)−P(4)	2.168(6)	2.205(4)	2.204(5)	2.37(1)	2.372(5)
M(3)−X(2)	2.410(5)	2.432(4)	2.371(4)	2.60(1)	2.592(7)	P···P[b]	6.04(1)	6.16(1)	6.09(1)	6.29(1)	6.30(1)
M(3)−X(3)	2.369(5)	2.418(4)	2.374(4)	2.62(1)	2.612(6)	M···M[b]	3.33(1)	3.44(1)	3.32(1)	3.48(2)	3.48(1)
M(3)−X(5)	2.467(5)	2.472(4)	2.637(4)	2.69(1)	2.742(6)	X···X[b]	3.74(1)	3.85(1)	3.82(1)	4.24(2)	3.99(1)
M(4)−X(3)	2.294(6)	2.348(4)	2.385(4)	2.59(1)	2.533(7)						
X(4)−M(1)−X(1)	107.5(2)	105.3(1)	103.5(2)	108.5(4)	102.4(2)	X(3)−M(3)−X(2)	106.6(2)	108.1(1)	108.3(2)	108.8(5)	98.5(2)
X(5)−M(1)−X(1)	95.4(2)	98.9(2)	94.1(1)	96.4(4)	95.1(2)	X(5)−M(3)−X(2)	96.7(2)	97.0(2)	94.4(1)	97.6(4)	95.6(2)
X(5)−M(1)−X(4)	100.6(2)	99.8(2)	94.6(1)	98.4(4)	96.2(2)	X(5)−M(3)−X(3)	96.9(2)	88.5(1)	95.3(1)	96.7(4)	94.0(2)
P(1)−M(1)−X(1)	114.7(2)	110.0(1)	115.7(2)	114.6(4)	125.7(2)	P(3)−M(3)−X(2)	110.7(2)	110.2(2)	114.2(2)	114.2(4)	119.5(2)
P(1)−M(1)−X(4)	109.7(2)	109.4(2)	115.6(2)	114.3(4)	108.1(2)	P(3)−M(3)−X(3)	114.0(2)	113.2(1)	115.1(2)	114.7(4)	122.3(2)
P(1)−M(1)−X(5)	126.7(2)	130.7(1)	128.6(1)	122.1(3)	124.1(2)	P(3)−M(3)−X(5)	129.2(2)	129.1(1)	126.3(1)	122.5(3)	120.8(2)
X(2)−M(2)−X(1)	105.5(2)	107.7(1)	107.8(1)	111.8(4)	96.7(2)	X(4)−M(4)−X(3)	110.0(2)	106.5(1)	107.4(1)	110.9(4)	104.9(2)
X(5)−M(2)−X(1)	95.1(2)	86.5(1)	93.2(1)	94.9(3)	93.5(2)	X(5)−M(4)−X(3)	88.5(1)	97.2(1)	97.2(4)	96.4(2)	88.5(1)
X(5)−M(2)−X(2)	95.1(2)	86.3(1)	93.9(1)	96.2(4)	95.8(2)	X(5)−M(4)−X(4)		89.4(1)	95.4(2)	98.3(3)	96.4(2)
P(2)−M(2)−X(1)	117.6(2)	121.9(2)	117.0(2)	115.8(4)	127.8(2)	P(4)−M(4)−X(3)	121.1(2)	119.8(2)	113.3(2)	113.8(5)	125.5(2)
P(2)−M(2)−X(2)	114.0(2)	122.3(2)	115.3(2)	115.7(4)	116.8(2)	P(4)−M(4)−X(4)	120.3(2)	122.4(2)	112.9(2)	113.6(4)	104.5(2)
P(2)−M(2)−X(5)	125.6(2)	122.0(1)	125.5(1)	119.3(3)	119.3(2)	P(4)−M(4)−X(5)		122.2(1)	127.8(2)	121.1(3)	124.3(2)

[a] X = Cl, M = Cu in **2a** and **3d** or Ag in **2b** and **5a**. For the second anion in **3d**, the correct numbering is obtained by the relationships M(*n*+4) = M(*n*), P(*n*+4) = P(*n*), and X(*n*+5) = X(*n*). [b] Mean of four values.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Cesium Coordination in **3d**

Cs(1)−Cl(1)	3.486(4)	Cs(1)−Cl(2)	3.422(4)	C(112)−Cs(2)	3.66(1)	C(113)−Cs(2)	3.76(1)
Cs(1)−Cl(3)	3.413(4)	Cs(1)−Cl(4)	3.505(4)	C(114)−Cs(2)	3.89(1)	C(116)−Cs(2)	3.83(1)
Cs(1)−Cl(6)	3.708(4)	Cs(1)−Cl(9)	3.525(4)	Cs(2)−Cl(1)	3.546(4)	Cs(2)−Cl(4)	3.814(4)
Cs(1)−Cl(15)#1	3.92(7)	Cs(1)−C(511)	3.91(1)	Cs(2)−Cl(6)	3.495(4)	Cs(2)−Cl(7)	3.452(4)
Cs(1)−C(512)	4.38(1)	Cs(1)−C(513)	4.52(1)	Cs(2)−Cl(8)	3.427(4)	Cs(2)−Cl(9)	3.558(4)
Cs(1)−C(514)	4.22(1)	Cs(1)−C(515)	3.73(1)	Cs(1)−Cs(2)	4.280(2)		
Cs(1)−C(516)	3.56(1)	C(111)−Cs(2)	3.70(1)				
Cl(3)−Cs(1)−Cl(2)	70.15(9)	Cl(3)−Cs(1)−Cl(1)	103.68(8)	Cu(4)−Cl(4)−Cs(2)	158.8(2)	Cu(1)−Cl(4)−Cs(2)	79.2(1)
Cl(2)−Cs(1)−Cl(1)	66.28(8)	Cl(3)−Cs(1)−Cl(4)	66.28(9)	Cs(1)−Cl(4)−Cs(2)	71.44(8)	Cl(8)−Cs(2)−Cl(7)	67.99(9)
Cl(2)−Cs(1)−Cl(4)	103.92(9)	Cl(1)−Cs(1)−Cl(4)	67.78(9)	Cl(8)−Cs(2)−Cl(6)	102.29(9)	Cl(7)−Cs(2)−Cl(6)	67.25(9)
Cl(3)−Cs(1)−Cl(9)	112.65(9)	Cl(2)−Cs(1)−Cl(9)	172.51(9)	Cl(8)−Cs(2)−Cl(1)	169.46(9)	Cl(7)−Cs(2)−Cl(1)	120.81(9)
Cl(1)−Cs(1)−Cl(9)	106.23(9)	Cl(4)−Cs(1)−Cl(9)	71.91(9)	Cl(6)−Cs(2)−Cl(1)	77.72(8)	Cl(8)−Cs(2)−Cl(9)	66.89(9)
Cl(3)−Cs(1)−Cl(6)	174.4(1)	Cl(2)−Cs(1)−Cl(6)	114.17(9)	Cl(7)−Cs(2)−Cl(9)	101.54(8)	Cl(6)−Cs(2)−Cl(9)	64.44(9)
Cl(1)−Cs(1)−Cl(6)	75.70(8)	Cl(4)−Cs(1)−Cl(6)	108.63(9)	Cl(1)−Cs(2)−Cl(9)	104.25(8)	Cl(8)−Cs(2)−Cl(4)	106.48(9)
Cl(9)−Cs(1)−Cl(6)	62.60(9)	Cu(2)−Cl(2)−Cs(1)	93.6(1)	Cl(7)−Cs(2)−Cl(4)	169.54(8)	Cl(6)−Cs(2)−Cl(4)	106.51(9)
Cu(3)−Cl(2)−Cs(1)	87.9(1)	Cu(3)−Cl(3)−Cs(1)	88.4(1)	Cl(1)−Cs(2)−Cl(4)	63.85(8)	Cl(9)−Cs(2)−Cl(4)	68.00(8)
Cu(4)−Cl(4)−Cs(1)	91.2(1)	Cu(1)−Cl(4)−Cs(1)	88.7(1)				

[a] Symmetry transformations used to generate equivalent atoms: 1, *x* − 1, *y*, *z*; 2, *x* + 1, *y*, *z*.

ion. In **2a** there are three shorter bonding Cu−Cl(5) distances of 2.467(5)−2.548(6) Å and one longer distance of 2.983(5) Å, which is considered nonbonding. Thus, the guest chloride is present as μ_3-Cl. In **3d**, the two units of **2a** are quite different in terms of the binding of the guest chloride. Thus, for the unit containing the copper atoms Cu(1)−Cu(4), there are two shorter [Cu(1)Cl(5) = 2.401(5), Cu(3)Cl(5) = 2.472(4) Å] and two longer [Cu(2)Cl(5) = 2.999(6), Cu(4)Cl(5) = 2.866(5) Å] CuCl(5) distances, so that Cl(5) is best considered as μ_2-Cl. In contrast, for the unit containing the copper atoms Cu(5)−Cu(8), the distances CuCl(10) are all in the range 2.557(5)−2.652(4) Å, so that Cl(10) is best considered as μ_4-Cl. The chloride anion appears to be too small to bind strongly to all four copper(I) atoms, and so it either binds weakly to all four or binds more strongly to only two or three copper(I) atoms. The structures of **2a** and **3d** contain all three of these bonding modes! In the less symmetrical unit of **2a** present in **3d**, the atoms Cu(1) and Cu(3) have approximate tetrahedral stereochemistry whereas Cu(2) and Cu(4) are approximately trigonal planar. This is clearly seen by comparing the magnitudes of the PCu(μ-Cl) and (μ-Cl)Cu(μ-Cl) angles for these atoms (Table 2).

The complexes **3** have limited solubility in acetone but are appreciably soluble in CH_2Cl_2 and $CHCl_3$, which is an unusual property for alkali metal salts.[21] It is interesting to question whether the observed solid state structure for **3d** is retained in solution. The ^{31}P NMR spectra of complex **3d** in CD_2Cl_2 solution contains only one resonance either at room temperature or at −70 °C whereas, according to the structure in the solid state, at least three such resonances would be expected. This indicates either that **3d** dissociates to monomeric units of **2a**·Cs having 4-fold symmetry in solution or that the units of **2a** rotate rapidly with respect to the cesium ions to give effective 4-fold symmetry. In either case, the guest chloride ion must be present as μ_4-Cl or be able to migrate easily between copper atoms so as to give effective 4-fold symmetry. Complete dissociation to Cs^+ and **2a** is ruled out since the ^{31}P and ^1H NMR parameters are different from those of **2a**. Since both the guest anion and the guest cation are weakly bonded, it is not surprising that they exhibit easy fluxionality. It was shown previously that the guest chloride in **2a** is present as a μ_3-Cl group, but that the NMR spectra indicate 4-fold symmetry in

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(21) Schmidtchen, F. P. *Nachr. Chem., Tech. Lab.* **1988**, *36*, 8.

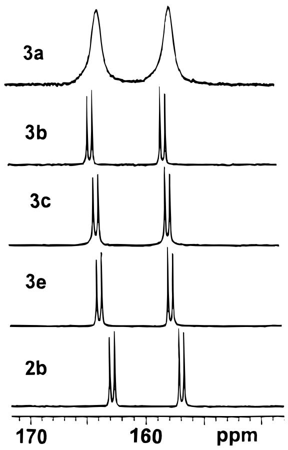


Figure 3. ^{31}P NMR spectra of compound **2b** and complexes **3a**−**c**, **3e**.

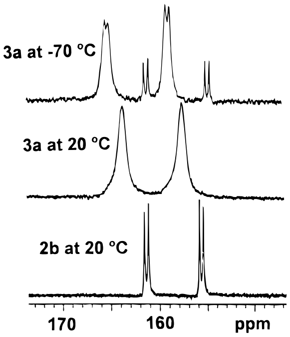


Figure 4. ^{31}P NMR spectra of (a) complex **2b**, (b) complex **3a** at room temperature, and (c) complex **3a** at −70 °C.

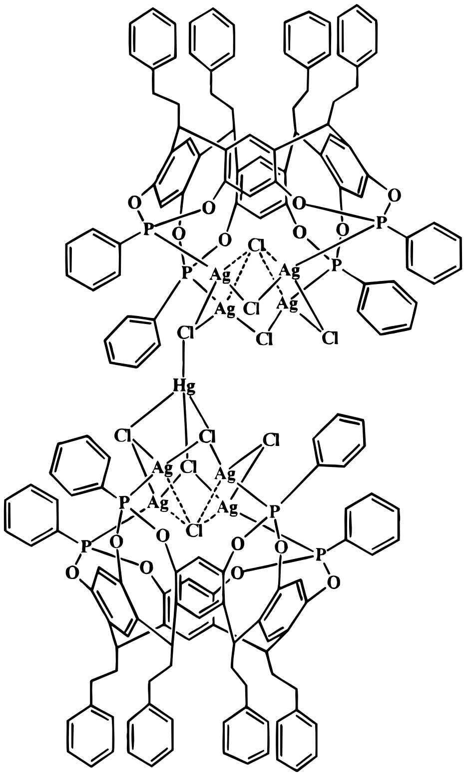
solution, and this was suggested to be due to fluxionality though the presence of μ_4-Cl in solution cannot be discounted.[18]

A more detailed solution study has been made of the alkali metal complexes of **2b**, since for these compounds both the ^{31}P chemical shift and the coupling constant ^1J(AgP) should change on complexation, thus yielding more information. The complexation between **2b** and alkali metal cations led to obvious chemical shift changes in the ^{31}P NMR spectra as shown in Figure 3. For the complexes with the cations K^+, Rb^+, and Cs^+, the ^{31}P NMR spectra at room temperature and at −60 °C are the same and only one resonance is observed. The spectral parameters are concentration independent. Again, therefore, there is effective 4-fold symmetry in solution and it is likely that the sandwich structures are maintained.

Figure 3 shows that the resonances in the ^{31}P NMR spectrum of the Na^+ cation inclusion complex **3a** were broad and concentration dependent at room temperature. A low-temperature (−70 °C) ^{31}P NMR experiment was carried out and showed two sets of doublets at low temperature, one of which has the same chemical shift and coupling constant as free **2b** (Figure 4). It is likely therefore that in this case there is an equilibrium between **3a** and free **2b** and Na^+ in solution. The easier dissociation for the smaller alkali metal Na^+ could be due to steric interactions between the two units of **2b** in **3a** with the smaller bridging metal ion. It is also possible that the Na^+ complex does not dimerize in the way in which the Cs^+ complex does. Recall that no pure complex of either **2a** or **2b** with the smaller ion Li^+ could be isolated. The ^{31}P NMR spectra of products of reaction of LiCl with **2b** contained several broad resonances. Thus, **2b** does react with Li^+, but the nature of the product is not clear.

It is interesting to note here that when compound **2b** was treated with salts of the alkaline earth metal ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in acetone, no metal cation inclusion was observed.

Formation and Structures of Complexes of 2 with Cations, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. The compounds **2** show affinity for the environmentally important main group metal cations Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. Treatment of **2a** or **2b** in acetone with $ZnCl_2$ or $CdCl_2$ gave isolable products of formula [**2b**·ZnCl] = **4a**, [**2a**·CdCl] = **4b**, and [**2b**·CdCl] = **4c**, but similar reactions with $HgCl_2$ and $PbCl_2$ were unsuccessful. However, reaction of **2b** with $Hg(CN)_2$ and $Pb(NO_3)_2$ in acetone did give isolable products of formula [$\mathbf{2b}_2$Hg] = **5a** and [$\mathbf{2b}_2$Pb] = **5b**. The key to successful synthesis of pure complexes appears to depend on a combination of the leaving-group ability of X^- in the salt MX_2 used and the solubility of MX_2 in acetone. The structures of the complexes cannot be determined from the spectroscopic data, and since crystals of most complexes did not diffract strongly enough for X-ray structure determination, there is some uncertainty about the coordination geometries. Fortunately, complex **5a** did give single crystals which were just adequate for an X-ray structure determination. The structure is shown in Figure 5, and bond distances and angles are in Tables 2 (a comparison of the bowl parameters with those of **2b**) and 4 (the coordination of mercury).



5a

The structure of **5a** is confirmed as having a mercury atom sandwiched between two units of **2b** (Figure 5). There is a crystallographically imposed center of symmetry and so the two units of **2b** are structurally identical. However, the mercury atom is not situated at the center of symmetry, but occupies equivalent positions on either side of this center, each having 50% occupancy (Figure 5). Thus, the Hg^{2+} ion connects the two units of **2b** together, but the two bowls are offset, probably to minimize steric hindrance between the phenyl rings on the upper rim of the calixresorcinarene bowl while providing strong coordination to mercury.

The mercury(II) is, as expected, complexed by μ-Cl ligands of **2b**. The shortest bond is Hg(1)−Cl(4A) = 2.474(6) Å, but

Table 4. Selected Bond Distances (Å) and Angles (deg) for Mercury Coordination in **5a**

Hg(1)−Cl(4)#1	2.474(6)	Hg(1)−Cl(1)	2.624(7)	Hg(1)−Cl(3)	2.691(8)	Hg(1)−Cl(2)	2.930(9)
Cl(4)#1−Hg(1)−Cl(1)	111.9(2)	Cl(4)#1−Hg(1)−Cl(3)	96.1(2)	Ag(2)−Cl(2)−Hg(1)	75.4(2)	Ag(3)−Cl(2)−Hg(1)	74.8(2)
Cl(1)−Hg(1)−Cl(3)	150.8(2)	Cl(4)#1−Hg(1)−Cl(2)	113.2(3)	Ag(4)−Cl(3)−Hg(1)	83.6(2)	Ag(3)−Cl(3)−Hg(1)	79.4(2)
Cl(1)−Hg(1)−Cl(2)	87.6(2)	Cl(3)−Hg(1)−Cl(2)	89.0(2)	Hg(1)#1−Cl(4)−Ag(4)	115.7(3)	Hg(1)#1−Cl(4)−Ag(1)	129.1(3)
Ag(2)−Cl(1)−Hg(1)	81.3(2)	Ag(1)−Cl(1)−Hg(1)	85.2(2)				

[a] Symmetry transformations used to generate equivalent atoms: 1, $-x - 1$, $-y$, $-z$.

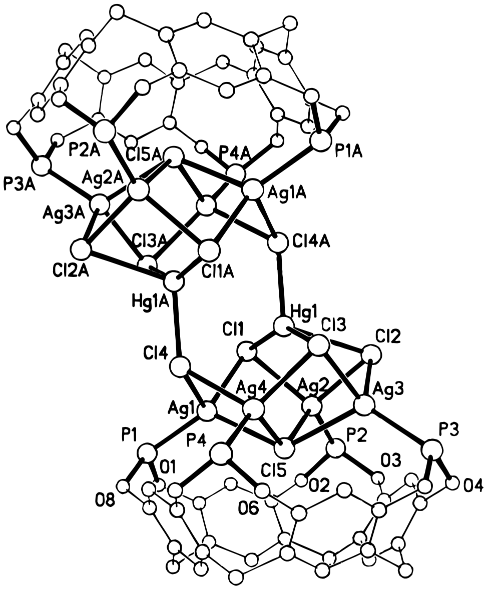


Figure 5. A view of the molecular structure of **5a**. Note that there is only one mercury cation which is disordered in two positions and is sandwiched by two anionic bowl ligands and that both occluded chlorides are μ_4. The CH_2CH_2Ph groups, phenyl groups on phosphorus, and all hydrogens have been omitted for clarity.

there are also strong bonds to two μ-Cl ligands of the second unit of **2b**, with Hg(1)−Cl(1) = 2.624(7) and Hg(1)−Cl(3) = 2.691(8) Å, and there is a much longer distance to a third μ-Cl of this unit of **2b** with Hg(1)−Cl(2) = 2.930(9) Å. The Hg(1)Cl(1)Cl(3)Cl(4A) atoms are essentially coplanar (sum of angles about Hg = 358.8°), and so the mercury is best considered three coordinate with trigonal planar stereochemistry. However, the individual angles Cl(1)HgCl(4A), Cl(3)HgCl(4A), and Cl(1)HgCl(3) of 111.9(2), 96.1(2), and 150.8(2)°, respectively, are far from the ideal value of 120°. The large angle Cl(1)Hg(1)Cl(3) is presumably a result of the large separation between these μ-Cl atoms (5.14 Å) on opposite sides of the crown.

The data in Table 2 show that the average distance between nonbonded adjacent phosphorus, silver, and μ-Cl atoms is similar in **2b** and **5a**. Hence, in contrast to the case of formation of **3d** from **2a**, it is not necessary to open up the bowl structure to accommodate the “guest” mercury ion. Indeed, Cl(1) and Cl(3) move *inward* to some extent to allow them to chelate to mercury. Hence, the transannular distance Cl(1)···Cl(3) = 5.14 Å is considerably less than Cl(2)···Cl(4) = 6.07 Å; Cl(4) is actually moved out toward the periphery of the bowl, presumably to allow better binding to mercury. The “guest” chloride is present as μ_4-Cl in both **2b** and **5a**. This is expected for the larger ion Ag^+, since chloride can bind to all four silver(I) ions without undue strain, in contrast to the situation in the copper(I) complexes **2a** and **3d**.

The ^1H and ^{31}P NMR spectra of complex **5a** at both room temperature and at −70 °C indicate effective 4-fold symmetry. For example, the ^{31}P NMR spectrum in CD_2Cl_2 solution contains only one resonance though the solid state structure should give three such resonances. Nevertheless, the chemical shift and $^1J(AgP)$ coupling constant are significantly different from those of **2b** and so indicate that the mercury(II) ion does not dissociate in solution. As for the alkali metal complexes, therefore, it seems clear that the guest mercury atom can migrate easily between the μ-Cl groups at the bowl rims to give effective 4-fold symmetry.

Table 5. ^{31}P NMR Chemical Shifts and Coupling Constants $^1J(Ag-P)$ in CD_2Cl_2

complex	$\delta(^{31}P)$, ppm	$^1J(^{109}AgP)$, Hz	$^1J(^{107}AgP)$, Hz
$[C_5H_5NH]$[**2b**]	157	766	664
3b	161	798	691
3c	160	783	679
3e	161	786	680
4a	162	822	712
4b	160	874	759
5a	162	823	713
5b	162	821	712

Since each of the metal ions M^{2+} used has a different coordination chemistry, it is not possible to deduce the detailed stereochemistry of the other derivatives **4** and **5** by analogy with that of **5a**. One can speculate that the ions Zn^{2+} and Cd^{2+} may be too small to form a sandwich complex analogous to **5a** and that they therefore form the derivatives **4**, and the individual geometry of M^{2+} in **4** could be tetrahedral (Zn^{2+} and Cd^{2+} rarely form trigonal planar complexes) with coordination by the chloride ion and three μ-Cl atoms of **2a** or **2b**. It is more difficult to predict the stereochemistry of Pb^{2+} in **5b**, since lead(II) has a stereochemically active lone pair of electrons and is unlikely to bridge between units of **2b** in the same way as mercury(II) in **5a**. All the complexes **4** and **5** *appear* to have 4-fold symmetry as probed by NMR spectroscopy, but as discussed above for **3d** and **5a**, this is deceptive and the true structures almost certainly have lower symmetry. Easy fluxionality can explain the phenomenon.

Some insight into the nature of the coordination of **2b** to different metal ions can be obtained from the changes in magnitude of the coupling constant $^1J(AgP)$ in different complexes (Table 5). We suggest that stronger binding of the μ-Cl ligands to the guest metal ion leads to weaker binding of the μ-Cl ligands to silver(I). In turn, this leads to some rehybridization at silver(I) with greater concentration of s-character of silver in the Ag−P bond and less in the AgCl bonds. In agreement, the mean angles PAg(μ-Cl) and (μ-Cl)Ag(μ-Cl) are larger and smaller, respectively, in **5a** compared to **2b** (Table 2). Hence, as more of the μ-Cl ligands are involved in binding to the guest metal and as the degree of covalency in this coordinate bond increases, the magnitude of $^1J(AgP)$ is expected to increase.[22,23] For the isolated complexes which are thought to maintain their structures in solution, the trend in $^1J(AgP)$ is **2b** ≪ **3c** (Rb^+) < **3e** (Cs^+) < **3b** (K^+) ≪ **5b** (Pb^{2+}) < **4a** (Zn^{2+}) < **5a** (Hg^{2+}) < **4b** (Cd^{2+}) (Table 5). The clear trend is that the free anion **2b** has the smallest value, the alkali metal

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(22) Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: New York, 1987; Vol. 2, p 948.

(23) Yuan, Z.; Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Can. J. Chem.* **1994**, *72*, 1605.

complexes have intermediate values, and the M^{2+} ions have the highest values of ^1J(AgP), as would be expected in terms of the above theory. There are no clear trends within the group of alkali metal ions or M^{2+} ions, which may be an indication that the coordination numbers of the metal ions are not the same within each series.

Conclusion

It is shown that the anionic calixarene derivatives **2** are able to act as powerful receptors for several M^+ and M^{2+} metal ions. Several such complexes have been isolated, and the structures of two such complexes have been determined crystallographically. The guest metal cations are shown to bind to some or all of the μ-Cl ligands present at the upper rim of the bowl complexes **2**. The new complexes represent the first examples of sandwiched metal cations in this new class of cation receptor and the first examples of metal cation inclusion by a receptor with chloride donor atoms. NMR studies indicate that complexation also occurs in solution, but the compounds are fluxional, and so it is not obvious if the structures are the same as those established in the solid state. The new complexes are soluble in organic solvents, and it is also shown that the metal ion extracted from aqueous solution into an organic solvent containing the receptor. The unusual selectivity observed suggests potential applications in the extraction, separation, or purification of metal ions. Although the new complexes **3**−**5** have been prepared by cation inclusion from the anionic complexes **2**, containing a guest chloride ion, their formation can also be considered to occur by salt inclusion of MCl or MCl_2 by the neutral receptors **1**. Since anion inclusion by **1** has already been shown to occur selectively[18] and it is now shown that cation inclusion by **2** is also selective, it follows that salt inclusion by **1** will also occur selectively.

Experimental Section

The complexes **2a** and **2b** were prepared as their pyridinium salts as described previously.[18,24] All experiments were carried out by using standard Schlenk techniques. NMR spectra were recorded by using a Varian Gemini 300MHz spectrometer. ^{1}H NMR chemical shifts were measured relative to deuterated solvent peaks, but were reported relative to tetramethylsilane. ^{31}P NMR chemical shifts were determined relative to 85% H_3PO_4 as the external standard. IR spectra were recorded on a Bruker IFS32 FTIR spectrometer with Nujol mulls. UV−vis measurements were recorded by using a Varian CARY 2290 spectrophotometer.

Complex 3a. A slurry of $NaBPh_4$ (0.2 g, 0.58 mmol) and [C_5H_5NH][**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL) was stirred at room temperature for 24 h. The slurry was filtered, and the solid was washed with acetone (2 × 5 mL), dried under vacuum, and then extracted with CH_2Cl_2 (5 mL). The solution was filtered to remove excess Na[BPh_4]. The product was obtained as a crystalline, white solid by diffusion of MeCN (10 mL) into the filtrate. It was isolated by filtration, washed with MeCN, and dried under vacuum. Yield: 0.072 g, 65.8%. Anal. Calcd for $C_{84}H_{68}Ag_4Cl_5NaO_8P_4{\cdot}2H_2O$: C, 50.8; H, 3.6. Found: C, 50.3; H, 3.5. NMR in CD_2Cl_2: 20 °C, $\delta(^{31}P) = 160.7$ [d, br]; −70 °C, $\delta(^{31}P) = 156.8$ [2 × d, $^1J(^{109}Ag-^{31}P) = 828$ Hz, $^1J(^{107}Ag-^{31}P) = 716$ Hz]; $\delta(^1H) = 1.75$ [s, br, 4H, H_2O], 2.72 [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.82 [br, 4H, C*H*(CH_2)$_2$Ph], 6.84 [s, 4H, Ar*H*, ortho to O], 7.16−7.32 [m, 20H, C_6H_5], 7.54 [s, 4H, Ar*H*, meta to O], 7.55−7.65 [m, 12H, PC_6H_5, para and meta to P], 7.94−8.02 [m, 8H, PC_6H_5, ortho to P].

Complex 3b. This was prepared in a similar way, from a slurry of KPF_6 (0.1 g, 1.17 mmol) and [C_5H_5NH][**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.084 g, 76.1%. Anal. Calcd for $C_{84}H_{68}Ag_4Cl_5KO_8P_4{\cdot}2H_2O$: C, 50.1; H, 3.6. Found: C, 49.8; H, 3.4. NMR in CD_2Cl_2: $\delta(^{31}P) = 160.9$ [2 × d, $^1J(^{109}Ag-^{31}P) = 798$ Hz, $^1J(^{107}Ag-^{31}P) = 691$ Hz]; $\delta(^1H) = 1.70$ [s, br, 4H, H_2O], 2.64 [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.74 [br, 4H, C*H*(CH_2)$_2$Ph], 6.74 [s, 4H, Ar*H*, ortho to O], 7.10−7.13 and 7.17−7.23 [m, 20H, C_6H_5], 7.48 [s, 4H, Ar*H*, meta to O], 7.51−7.57 [m, 12H, PC_6H_5, para and meta to P], 7.87−7.93 [m, 8H, PC_6H_5, ortho to P].

Complex 3c. This was prepared in a similar way from a slurry of RbCl (0.1 g, 1.17 mmol) and [C_5H_5NH][**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.070 g, 61.5%. Anal. Calcd for $C_{84}H_{68}Cl_5Ag_4O_8P_4Rb{\cdot}3H_2O$: C, 48.9; H, 3.5. Found: C, 48.5; H, 3.4. NMR in CD_2Cl_2: $\delta(^{31}P) = 160.4$ [2 × d, $^1J(^{109}Ag-^{31}P) = 783$ Hz, $^1J(^{107}Ag-^{31}P) = 679$ Hz]; $\delta(^1H) = 1.70$ [s, br, 6H, H_2O], 2.73 [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.84 [br, 4H, C*H*(CH_2)$_2$Ph], 6.84 [s, 4H, Ar*H*, ortho to O], 7.16−7.28 [m, 20H, C_6H_5], 7.50 [s, 4H, Ar*H*, meta to O], 7.54−7.62 [m, 12H, PC_6H_5, para and meta to P], 7.96−8.05 [m, 8H, PC_6H_5, ortho to P].

Complex 3d. This was prepared in a similar way from a slurry of $CsNO_3$ (0.1 g, 0.51 mmol) and [C_5H_5NH][**2a**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.085 g, 78%. Anal. Calcd for $C_{84}H_{68}Cl_5CsCu_4O_8P_4{\cdot}2MeCN.1/2Me_2CO$: C, 53.6; H, 3.9. Found: C, 53.7; H, 4.0. NMR in CD_2Cl_2: $\delta(^{31}P) = 138.0$ [s, br]; $\delta(^1H) = 1.99$ [s, 6H, C*H*$_3$CN], 2.13 [s, 3H, $(CH_3)_2CO$], 2.70 [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.81 [br, 4H, C*H*(CH_2)$_2$Ph], 6.94 [s, 4H, Ar*H*, ortho to O), 7.18−7.29 (m, 20H, C_6H_5], 7.50 [s, 4H, Ar*H*, meta to O], 7.51−7.60 [m, 12H, PC_6H_5, para and meta to P], 8.00−8.07 [m, 8H, PC_6H_5, ortho to P].

Complex 3e. This was prepared in a similar way from a slurry of $CsNO_3$ (0.1 g, 0.51 mmol) and [C_5H_5NH][**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.090 g, 79.7%. Anal. Calcd for $C_{84}H_{68}Ag_4Cl_5CsO_8P_4$: C, 48.7; H, 3.3. Found: C, 48.3; H, 3.2. NMR in CD_2Cl_2: $\delta(^{31}P) = 160.8$ [2 × d, $^1J(^{109}Ag-^{31}P) = 786$ Hz, $^1J(^{107}Ag-^{31}P) = 680$ Hz]; $\delta(^1H) = 2.69$ [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.81 [br, 4H, C*H*(CH_2)$_2$Ph], 6.88 [s, 4H, Ar*H*, ortho to O], 7.14−7.32 [m, 20H, C_6H_5], 7.47 [s, 4H, Ar*H*, meta to O], 7.50−7.61 [m, 12H, PC_6H_5, para and meta to P], 7.94−8.01 [m, 8H, PC_6H_5, ortho to P].

Complex 4a. This was prepared in a similar way from a slurry of $ZnCl_2$ (0.1 g, 0.74 mmol) and [C_5H_5NH][**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.072 g, 69%. Anal. Calcd for $C_{84}H_{68}Ag_4Cl_6O_8P_4Zn{\cdot}MeCN$: C, 49.8; H, 3.5. Found: C, 49.7; H, 3.4. NMR in $CDCl_3$: $\delta(^{31}P) = 161.9$; [2 × d, $^1J(^{109}Ag-^{31}P) = 822$ Hz, $^1J(^{107}Ag-^{31}P) = 712$ Hz]; $\delta(^1H) = 1.92$ [s, 3H, C*H*$_3$CN], 2.70 [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.80 [br, 4H, C*H*(CH_2)$_2$Ph], 6.86 [s, 4H, Ar*H*, ortho to O], 7.11−7.33 [m, 20H, C_6H_5], 7.48 [s, 4H, Ar*H*, meta to O], 7.50−7.58 [m, 12H, PC_6H_5, para and meta to P], 7.90−8.02 [m, 8H, PC_6H_5, ortho to P].

Complex 4b. This was prepared in a similar way from a slurry of $CdCl_2$ (0.1 g, 0.55 mmol) and [C_5H_5NH][**2a**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.065 g, 66%. Anal. Calcd for $C_{84}H_{68}CdCl_6Cu_4O_8P_4.(CH_3)_2CO$: C, 53.2; H, 3.8. Found: C, 53.5; H, 3.9. NMR in CD_2Cl_2: $\delta(^{31}P) = 141.5$ [s, br]; $\delta(^1H) = 2.16$ [s, 3H, $(CH_3)_2CO$], 2.69 [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.81 [br, 4H, C*H*(CH_2)$_2$Ph], 6.82 [s, 4H, Ar*H*, ortho to O), 7.16−7.29(m, 20H, C_6H_5], 7.45 [s, 4H, Ar*H*, meta to O], 7.52−7.62 [m, 12H, PC_6H_5, para and meta to P], 7.92−8.05 [m, 8H, PC_6H_5, ortho to P].

Complex 4c. This was prepared in a similar way from a slurry of $CdCl_2$ (0.1 g, 0.55 mmol) and [C_5H_5NH][**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.044 g, 41%. Anal. Calcd for $C_{84}H_{68}Ag_4CdCl_6O_8P_4$: C, 48.5; H, 3.3. Found: C, 48.9; H, 3.5. NMR in $CDCl_3$: $\delta(^{31}P) = 159.6$ [2 × d, $^1J(^{109}Ag-^{31}P) = 874$ Hz, $^1J(^{107}Ag-^{31}P) = 759$ Hz]; $\delta(^1H) = 2.68$ [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.79 [br, 4H, C*H*(CH_2)$_2$Ph], 6.89 [s, 4H, Ar*H*, ortho to O], 7.13−7.16 and 7.25−7.31 [m, 20H, C_6H_5], 7.45 [s, 4H, Ar*H*, meta to O], 7.46−7.59 [m, 12H, PC_6H_5, para and meta to P], 7.84−7.98 [m, 8H, PC_6H_5, ortho to P].

Complex 5a. This was prepared in a similar way from a slurry of $Hg(CN)_2$ (0.2 g, 0.79 mmol) and [C_5H_5NH][**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.081 g, 53.6%. Anal. Calcd for $C_{168}H_{136}Ag_8Cl_{10}HgO_{16}P_8$: C, 49.5; H, 3.4. Found: C, 49.8; H, 3.6. NMR in $CDCl_3$: $\delta(^{31}P) = 161.9$; [2 × d, $^1J(^{109}Ag-^{31}P) = 823$ Hz, $_1J(^{109}Ag-^{31}P) = 713$ Hz]; $\delta(^1H) = 1.75$ [s, br, 2H, H_2O], 1.95 [s, 6H, C*H*$_3$CN], 2.68 [br, 16H, C*H*$_2$C*H*$_2$Ph], 4.79 [br, 4H, C*H*(CH_2)$_2$Ph], 6.84

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[24] Tunstad, L. M.; Tucker, J. A.; Dalcanale, E.; Weiser, J.; Bryant, J. A.; Sherman, J. C.; Helgeson, R. C.; Knobler, C. B.; Cram, D. J. *J. Org. Chem.* **1989**, *54*, 1305 and references cited therein.

Table 6. Crystal Data for **3d**$\cdot$2.5$CH_3CN\cdot$0.75$CHCl_3\cdot$1.25$(CH_3)_2CO\cdot$0.25H_2O and **5a**$\cdot$2.0$CH_3CN\cdot$0.5$CHCl_3\cdot$1.0H_2O

formula	$C_{168}H_{136}Cl_{10}Cs_2Cu_8O_{16}P_8\cdot 2.5CH_3CN\cdot 0.75CHCl_3\cdot 1.25(CH_3)_2CO\cdot 0.25H_2O$	$C_{168}H_{136}Ag_8Cl_{10}Hg_1O_{16}P_8\cdot 2.0CH_3CN\cdot 0.5CHCl_3\cdot 1.0\ H_2O$
fw	4044.59	4236.39
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	16.5142(1)	13.4174(2)
b, Å	25.8269(2)	43.2897(7)
c, Å	26.3615(4)	15.7462(3)
α, deg	61.785(1)	
β, deg	80.403(1)	98.734(1)
γ, deg	72.533(1)	
V, Å^3	9446.2(2)	9039.9(3)
d(obs)(calc) g cm^{-3}	1.59(1.42)	1.59(1.56)
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	1.56	1.992
R1[a]	0.1470	0.1686
$_{w}$R2[a]	0.2679	0.3597

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $_{w}R2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

[s, 4H, Ar*H*, ortho to O], 7.13−7.17 and 7.24−7.29 [m, 20H, C_6H_5], 7.48 [s, 4H, Ar*H*, meta to O], 7.49−7.53 [m, 12H, PC_6H_5, para and meta to P], 7.93−8.01 [m, 8H, PC_6H_5, ortho to P].

Complex 5b. This was prepared in a similar way from a slurry of $Pb(NO_3)_2$ (0.2 g, 0.60 mmol) and $[C_5H_5NH]$[**2b**] (0.1 g, 0.0545 mmol) in acetone (20 mL). Yield: 0.091 g, 82%. Anal. Calcd for $C_{168}H_{136}Ag_8Cl_{10}O_{16}P_8Pb$: C, 49.5; H, 3.4. Found: C, 49.8; H, 3.9. NMR in $CDCl_3$: $\delta(^{31}P) = 162.1$ [2 × d, $^1J(^{109}Ag-^{31}P) = 821$ Hz, $^1J(^{109}Ag-^{31}P) = 712$ Hz]; $\delta(^1H) = 1.75$ [s, br, 2H, H_2O], 2.14 [s, 3H, $(CH_3)_2CO$], 2.69 [br, 16H, CH_2CH_2Ph], 4.78 [br, 4H, $CH(CH_2)_2Ph$], 6.80 [s, 4H, Ar*H*, ortho to O], 7.14−7.18 and 7.24−7.29 [m, 20H, C_6H_5], 7.48 [s, 4H, Ar*H*, meta to O], 7.51−7.52 [m, 12H, PC_6H_5, para and meta to P], 7.94−7.98 [m, 8H, PC_6H_5, ortho to P].

X-ray Structure Determinations. The crystals of **3d** or **5a** were obtained with difficulty by slow diffusion of MeCN and Me_2CO into a solution of **3d** or **5a**, respectively, in CH_2Cl_2 and $CHCl_3$. The densities were determined by neutral buoyancy. The crystals lost solvent rapidly on removal from the mother liquor, and so the data crystals were sealed inside Lindemann glass capillary tubes. Preliminary diffraction experiments were carried out on a Siemens P4 diffractometer equipped with scintillation counter detector using graphite monochromated Mo Kα radiation, but only a partial structure could be determined due to weak diffraction. The final X-ray data were obtained by using a Siemens P4 four-circle diffractometer equipped with a CCD X-ray detector using graphite monochromated Mo Kα radiation. Even with these data, large residuals were observed, due at least in part to the weak diffraction and to the severe solvent disorder. A total of 52 791 reflections were collected in the θ range 0.93−29.09° ($-21 \le h \le 18$, $-34 \le k \le 33$, $-21 \le l \le 35$) for **3d** and 35 463 reflections in the θ range 0.94 to 26.02° ($-16 \le h \le 16$, $-45 \le k \le 50$, $-17 \le l \le 18$) for **5a**. The software ASTRO[25] was used for the best data collection strategy, SMART[25] for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT[25] for integration of intensity of reflections and scaling, and SHELXTL[26] for data reduction, absorption correction, space group determination, structure determination, structure refinement, graphics, and structure reporting. For **3d**, a Gaussian absorption correction was applied to the data after indexing the faces of the data crystal and measuring the distances between them while; for **5a**, an empirical absorption correction was applied to the data. The maximum and minimum transmission factors are 0.832 and 0.592 for **3d** and 0.897 and 0.638 for **5a**, respectively.

For **3d**, the triclinic system was found, and, for $Z = 2$, the space group $P\bar{1}$ was chosen. The atoms Cs, Cu, Cl, P, O and all the non-phenyl carbon atoms of the calix[4]arene molecules were refined anisotropically. The isotropic thermal parameters were refined for the carbon atoms of the phenyl rings. Totally, 2.5 acetonitrile, 0.75 chloroform, 1.25 acetone, and 0.25 water molecules were located in the difference Fourier routines. The occupancy factors were assigned on the basis of the relative electron densities obtained in the difference Fourier maps. Anisotropic thermal parameters were assigned and refined for the non-hydrogen atoms of one of the acetonitrile molecules, and the hydrogen atoms were included in the calculated positions. One CH_3CN was found to be disordered (occupancies: 0.65 and 0.35). In one region, CH_3CN and $(CH_3)_2CO$ (occupancies: 0.25 and 0.25) shared the space. Chloroform molecules were located in two regions (occupancies: 0.5 and 0.25). One acetone molecule was found to be 4-fold disordered. Ideal geometries were imposed on these solvent molecules, and common isotropic thermal parameters were refined for each fragment of the solvents. Nine bad reflections close to the beam stop were omitted in the least-squares cycles. In the final least-squares refinement cycles on F^2, the model converged at $R1 = 0.1470$, $_{w}R2 = 0.2679$, and Goof = 1.106 for 19 290 reflections with $F_o \ge 4\sigma(F_o)$ and 1081 parameters, and $R1 = 0.2460$ and $_{w}R2 = 0.3221$ for all 37 244 data. The final difference Fourier synthesis the electron density fluctuates in the range 1.492 to −0.840 e Å^{-3}. The maximum shift and shift/esd in the final cycles were 0.00 and −0.005, respectively. An extinction correction was refined to 0.000 12(5). The crystal data are given in Table 6, and complete positional and thermal parameters, bond distances and angles, anisotropic thermal parameters and hydrogen atom coordinates have been included in the Supporting Information.

For **5a**, the space group $P2_1/n$ was determined from the systematic absences. The atoms Hg, Ag, Cl, P, O and all the non-phenyl carbon atoms (not disordered) of the calix[4]arene molecules were refined anisotropically. Although all the phenyl carbon atoms attached to P atoms show relatively large thermal motions, satisfactory disorder models could not be achieved except for one phenyl ring. A disorder model with two different orientations of C(111)−C(116) (occupancies 0.65/0.35) attached to P(1) was successfully resolved, and the positional coordinates were refined in the least-squares cycles. All the dangling phenyl groups (C(101) to C(406)) as well as C(29) and C(49) were found to be disordered. In each case, two different orientations (occupancies 0.5/0.5) were resolved and the positional parameters were refined. The occupancy factors were assigned on the basis of the relative electron densities obtained in the difference Fourier maps. Common isotropic thermal parameters were assigned and refined for the disordered phenyl ring carbon atoms while individual isotropic thermal parameters were refined for the carbon atoms of the nondisordered phenyl rings. In the asymmetric unit, for $Z = 2$, 1 molecule of acetonitrile, 0.25 molecule of chloroform, and 0.5 water molecules were located in the difference Fourier routines. The chlorine atoms of the $CHCl_3$ were disordered along the C_3 axis of the molecule. Two sets of chlorine atoms were used in the models with the occupancy factors of 0.125 each. Ideal geometries were imposed on these solvent molecules and common isotropic thermal parameters were refined for each of the solvents. Seven bad reflections close to the beam stop were omitted in the least-squares cycles. In the final least-squares refinement cycles on F^2, the model converged at $R1 = 0.1686$, $_{w}R2 = 0.3597$, and Goof = 1.180 for 8487 reflections with $F_o \ge 4\sigma(F_o)$ and

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(25) Software packages ASTRO, SMART, and SAINT, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.

(26) *SHELXTL*, Version 5.0 Reference Manual; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1994.

659 parameters and R1 = 0.2360 and $_{w}R2$ = 0.4001 for all 14 440 data. The final difference Fourier synthesis the electron density fluctuates in the range 1.194 to −0.802 e Å^{-3}. The top peak was found to have associated with Hg(1) at a distance of 1.19 Å. The maximum shift and shift/esd in the final cycles were 0.0012 and 0.002, respectively. An extinction correction was refined to 0.000 24(9). The crystal data are in Table 6, and the positional and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates tables have been included in the Supporting Information.

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Supporting Information Available: Tables of X-ray methods, atomic coordinates, bond distances and angles, H atom positional parameters, and torsion angles for **3d** and **5a** (34 pages). Ordering information is given on any current masthead page.

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