A Silver-Linked Supramolecular Cluster Encapsulating a Cesium Cation[†]

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The use of judiciously designed hybrid ligands to form supramolecular assemblies through coordination of two types of metal cations having *incommensurate symmetry* requirements has been successfully demonstrated by us as well as others.[1−18] We have recently reported pentametallic mixed-metal clusters derived from 4-(diphenylphosphino)benzene-1,2-diol (H_2**L**) which can chelate a hard cation through its phenolic oxygens while simultaneously binding a soft metal using its neutral phosphine site.[4,5] Hard metals such as Fe(III), Ga(III), Ti(IV), and Sn(IV) readily form anionic tris-chelates of the type $M\mathbf{L}_3^{n-}$ (M = Fe, Ga, $n = 3$; M = Ti, Sn, $n = 2$) which can serve as precursors to anionic clusters of the type $M_2M'_3\mathbf{L}_6$ where M′ is a soft metal such as Pd(II), Cr(0), Mo(0), and W(0) coordinated to the free phosphine of **L** (Scheme 1). Formation of these C_{3h}-symmetric mesocates is dependent on alkali metal counterions which are incorporated into deep molecular clefts and coordinated to *endo*-catecholate oxygens. Interestingly, no complete encapsulation of these guest cations in our mesocates has yet been found in the solid state.[2,19−25]

Since silver(I) favors lower coordination numbers between 2 and 4 and also prefers relatively soft donors like phosphines, we were interested in exploring the possibility of preparing analogous C_{3h} mesocates with M′ = Ag to form mixed-metal clusters of $M_2Ag_3\mathbf{L}_6$ stoichiometry using these tris-chelate precursors (Scheme 2). We report here the cationic-guest-dependent synthesis, solution spectral characterization, and a single-crystal X-ray structural determination of the resulting Cs[(Sn$\mathbf{L}_3$)$_2$Ag$_3$] cluster (Figure 1).

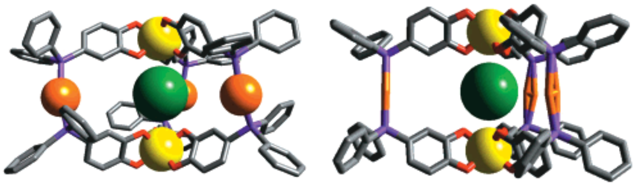

Figure 1. A view of the solid-state structure of each crystallographically independent Cs[(Sn$\mathbf{L}_3$)$_2$Ag$_3$] mesocate viewed along the pseudo mirror plane of the cluster. All solvent molecules and all hydrogen atoms are omitted for clarity. Cesium atoms are green space-filling spheres, silver atoms are orange (spheres at left, wireframe at right to show disorder), Sn cations are yellow spheres, and the ligands are represented as wireframes with carbon gray, oxygen red, and phosphorus purple.

Experimental Section

All operations and manipulations were performed in standard Schlenk glassware under a dry nitrogen atmosphere. Solvents were commercial reagent grade and were deoxygenated before use. The precursor Cs_2[Sn$\mathbf{L}_3$] was prepared as previously reported.[4,5]

All NMR spectra were recorded on a Bruker AM 360 MHz or a JEOL FX-90Q spectrometer. Chemical shifts of proton NMR spectra are referenced to internal TMS. ^{31}P spectra were referenced to external 85% H_3PO_4. Infrared spectra were run on a Nicolet MX-1 FT spectrophotometer using KBr pellets. Elemental analyses were performed by the UNH Instrumentation Center on a Perkin-Elmer 2400 elemental analyzer. FAB mass spectra were run in an NBA matrix and carried out at the UC−Berkeley Mass Spectrometry Facility. Single-crystal X-ray diffraction data were collected on a Siemens SMART diffractometer in the Chexray facility at UC−Berkeley.

Synthesis of Cs[(Sn$\mathbf{L}_3$)$_2$Ag$_3$]. A solution of Cs_2[Sn$\mathbf{L}_3$] (126 mg, 0.100 mmol) and $AgNO_3$ (25.0 mg, 0.150 mmol, an equivalent amount of silver triflate can also be used) in 20 mL of DMF was stirred at ambient temperature in the dark. The initial white turbidity disappeared over 12 h to give a clear, colorless solution. Evaporation of this under reduced pressure yielded a white solid, which was washed three times with water and acetone. The residue was dried in vacuum to give 105 mg of product (86% yield). ^{1}H NMR (360 MHz, d_7-DMF): δ 7.54 (broad multiplet, 6 × 1 phenyl-H), 7.46 (broad, 6 × 4 phenyl-H), 7.36

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[†] Coordination Number Incommensurate Cluster Formation. 20. Part 19: See ref 5.

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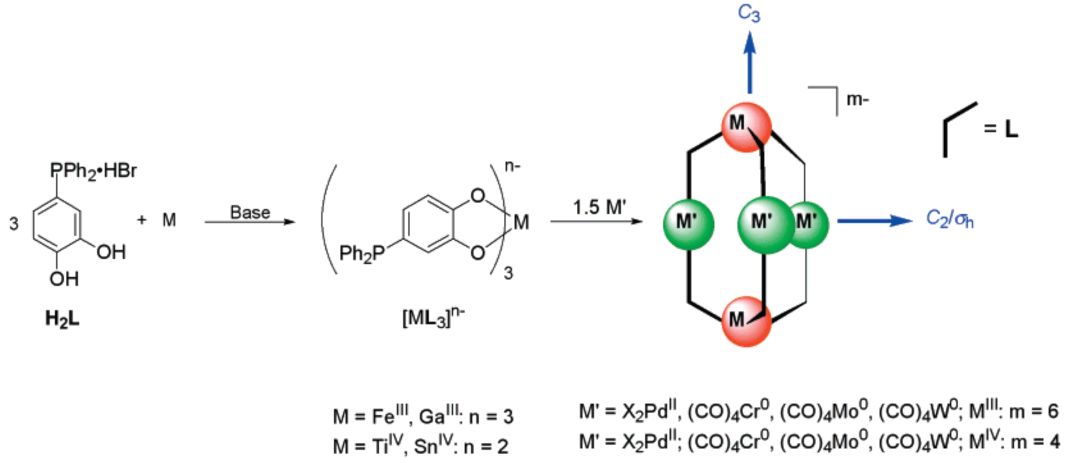
Scheme 1



Scheme 2

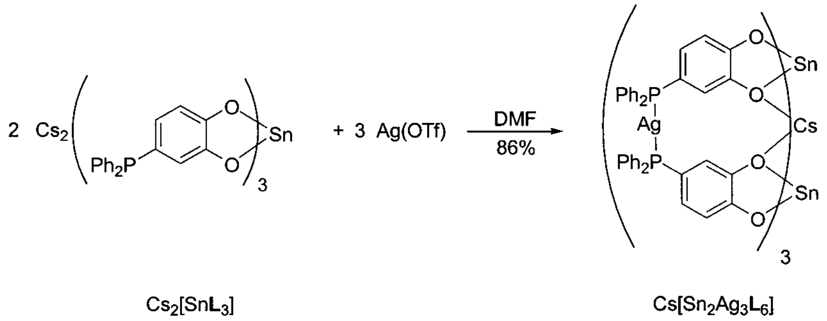


Table 1. Crystallographic Data

	Cs[(Sn**L**$_3$)$_2$Ag$_3$]
fw	3138.24
cryst syst, lattice	trigonal, rhombohedral
space group	$R\bar{3}$ (No. 148)
Z	12
a (Å)	23.7157(3)
c (Å)	88.5147(5)
V (Å^3)	43113.9(8)
temp, °C	-117 ± 1
λ, Å	0.71069
μ, cm^{-1}	11.27
ρ, g cm^{-3}	1.45
R1, wR2 ($I > 2\sigma(I)$)	0.0517, 0.141
R1, wR2 (all data)	0.0858, 0.161
GOF	1.03

(broad triplet,15.8 Hz, 6 × 1 catecholate-H), 6.60 (broad doublet, 7.9 Hz, 6 × 1 cat-H), 6.16 (broad multiplet, 6 × 1 cat-H). $^{31}P\{^1H\}$ NMR (36.3 MHz, d_7-DMF): δ 13.67 (two sets of doublets: $^1J_{107Ag-P} = 497$ Hz, $^1J_{109Ag-P} = 572$ Hz). IR (KBr): C−H bending, 1474 cm^{-1}; $\nu_{(C-O-Sn)}$, 1250 cm^{-1}. Anal. Calcd for $CsSn_2C_{108}H_{78}P_6O_{12}Ag_3$: C, 53.00, H 3.21. Found: C, 52.96; H, 2.96. FAB$^+$ MS (nitrobenzyl alcohol matrix in DMF) (◆ = [CsSn$_2$**L**$_6$Ag$_3$]) species, observed *m/z* (% abundance, calcd *m/z*): [◆ + 2H]$^{2+}$, 1224 (22%, 1224.8); [◆ + H]$^+$, 2448 (100%, 2448.6); [◆ + Cs]$^+$, 2581 (10%, 2580.4). Clear, block crystals for the X-ray diffraction study were grown by diethyl ether diffusion into a DMF solution of this product (Table 1).

X-ray Diffraction Study. Crystal data and details of data collection, structural solution, and refinement are summarized in Table 1. Further details are listed in the Supporting Information.

Results and Discussion

Synthesis and Spectral Data of the Cs[{Sn(4-catecholato-PPh$_2$)$_3$}$_2$Ag$_3$] Cluster. The title cluster was readily prepared from a 2:3 stoichiometric ratio of Cs$_2$[Sn**L**$_3$] and AgNO$_3$ or Ag(triflate) in DMF (Scheme 2). The mesocate can be isolated as a white powder, which surprisingly is not particularly light sensitive. The solid-state IR spectrum (KBr pellet) of this white powder revealed the absence of any nitrate (or triflate) bands, and elemental analysis confirmed its formulation as Cs[(Sn**L**$_3$)$_2$-Ag$_3$]. In DMF solution the proton NMR spectrum is consistent with formation of a species with *at least* (actual or averaged) C_3 symmetry since only a single set of catecholate proton resonances are observed. The $^{31}P\{^1H\}$ NMR spectrum obtained at both 36.3 and 145 MHz confirms coordination of the PPh$_2$ groups and exhibits two doublets of almost equal intensity both centered at δ 13.67 due to ^{31}P-coupling with the two naturally occurring silver isotopes (^{107}Ag, $I = {}^1/_2$, 51.82%; ^{109}Ag, $I = {}^1/_2$, 48.18%). The magnitudes of these coupling constants, 497 Hz ($^1J_{107Ag-P}$) and 572 Hz ($^1J_{109Ag-P}$), are consistent with trans coordination by two PPh$_2$ groups and one or two oxygen atoms.[26-29] Since direct observation of solution Ag−P coupling at ambient temperature is reasonable only with chelating diphosphines,[30-34] retention of the supramolecular nature of this product in solution can be inferred. Furthermore a FAB mass

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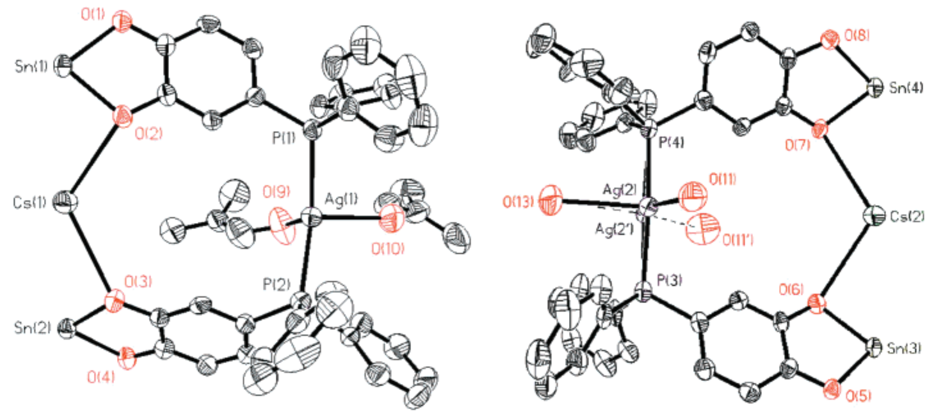

Figure 2. ORTEP view of the asymmetric unit of the solid-state structure of $\{Cs[(Sn\mathbf{L}_3)_2Ag_3]\}_2$. Two clusters make up the asymmetric unit with each complex residing on a 3-fold axis. All hydrogen atoms and the partial occupancy carbon and nitrogen atoms of the disordered DMF solvent ligands are omitted for clarity. Atoms Ag(2) and Ag(2′) represent the major and minor sites, respectively, of the disordered silver(I) ion in one of the clusters. Thermal ellipsoids are at 50% probability.

spectrum of this solution confirmed the presence of $Cs[(Sn\mathbf{L}_3)_2Ag_3]$ clusters (see Experimental Section).

The crucial role played by the Cs^+ counterion in this successful cluster assembly is apparent from numerous failed attempts using NMe_4^+, PPh_4^+, $N(PPh_3)_2^+$, or even Rb^+ salts of the $Sn\mathbf{L}_3^{2-}$ precursor; all resulted in poorly characterized insoluble precipitates. An attempt was made to prepare a tetrahedral $Sn_4Ag_4\mathbf{L}_{12}$ cluster using a 1:1 stoichiometry of $Cs_2[(Sn\mathbf{L}_3)_2Ag_3]$ to $AgNO_3$ in DMF. The rationale here was that the Ag cations could be coordinated by three phosphines and comprise the trigonal faces of a tetrahedron while the $Sn\mathbf{L}_3$ moieties would form the vertices. However, the reaction mixture gave a very complex ^{31}P NMR spectrum with no single dominant species even after extended reaction time. Apparently the coordination of three PPh_2 groups at each Ag(I) center does not produce a unique cluster in the present system.

X-ray Diffraction Study of $Cs[\{Sn(4\text{-catecholato-}PPh_2)_3\}_2Ag_3]$. The complex $Cs[Cs(Sn\mathbf{L}_3)_2Ag_3]\cdot 17.5DMF\cdot x(\text{solvent})$ crystallizes in the rhombohedral space group $R\bar{3}$ containing 12 clusters per unit cell with two crystallographically distinct clusters each residing on 3-fold axes (Figure 2). Each crystallographically unique cluster is a mesocate with one Λ- and Δ-configuration at the two Sn(IV) centers. The silver cations are all linearly coordinated by PPh_2 groups in the solid state, consistent with solution NMR data. Ag(1) is coordinated by two phosphines with a P(1)−Ag(1)−P(2) angle of 156.29(8)° and weakly coordinated by two additional DMF molecules (Ag(1)−O(9) = 2.584(7) Å, Ag(1)−O(10) = 2.611(6) Å). The silver cation in the other cluster is disordered over two sites, Ag(2) (89%) and Ag(2′) (11%). Each of these silver cations is again linearly coordinated by the PPh_2 moieties with an average P−Ag(2)−P angle of 166° and weakly coordinated to two other DMF molecules.

Another observation of interest is the full encapsulation of the Cs^+ cation inside the cluster on the 3-fold axis between the Sn(IV) atoms. Each cation is coordinated by six *endo*-catecholato oxygens with Cs−O bond lengths ranging from 3.050(5) to 3.134(5) Å. The Cs^+ coordination sphere is best described as trigonal prismatic (Figure 2). The Cs^+ cations are shielded from further coordination by the DMF molecules that are bound to the Ag ions. In this respect the Cs^+ cations can be considered part of a host−guest complex. The Sn−Sn distances in this cluster are 7.60 and 7.79 Å (Sn(1)−Sn(2) and Sn(3)−Sn(4), respectively). These are the longest reported for these mesocates[4,5] and presumably result from the positioning of the large Cs^+ cation directly between the Sn^{IV} centers.

In summary, we have prepared and spectrally characterized a new mixed-metal cluster, $Cs(Sn\mathbf{L}_3)_2Ag_3$, based on the hybrid ligand 4-(diphenylphosphino)benzene-1,2-diol (**L**). The mesocate structure of this C_{3h}-symmetric supramolecular complex has been confirmed by a structural study that also revealed a fully encapsulated Cs^+ cation as a guest. The role of this cationic guest appears critical as all other cations tried gave insoluble and intractable products.

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Supporting Information Available: The X-ray structural report of $Cs(Sn\mathbf{L}_3)_2Ag_3$ (including tables of crystal data, data collection parameters, and discussions on modeling of the disorder in the molecules). This material is available free of charge via the Internet at http://pubs.acs.org.

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