stantially longer than normal covalent bonds by 0.32 and 0.24 Å in **1** and **2a**, respectively. The observed lengthening dized with an air stream for a few minutes, until the red color of Mo(II) disappeared and was replaced by a pale blue color. Addition of a saturated solution of K_2SO_4 to this partly oxidized solution precipitated the crystalline blue-gray compound II which was filtered, washed with ethanol, and dried in vacuo over KOH.

Anal. Calcd for $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$: Mo, 25.4; K, 15.5; SO_4, 50.8. Found: Mo, 24.8; K, 15.4; SO_4, 50.0.

The magnetic susceptibility of II was measured by the Faraday method. The magnetic moment of 1.69 BM obtained from this measurement indicated one unpaired electron per $Mo_2(SO_4)_4{}^{3-}$ ion as expected.[1] Raman and ir spectra will be reported separately.

References and Notes

(1) F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Am. Chem. Soc.*, **95**, 4431 (1973).
(2) A. Bowen and H. Taube, *Inorg. Chem.*, **13**, 2245 (1974).
(3) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **95**, 6871 (1973).
(4) The total Mo analysis by permanganatometric titration of Mo(III) to Mo(VI) is based on the fact that all Mo species with an oxidation number greater than 3+ are reduced by a Jones reductor to Mo(III): A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Longmans, London, p 333 (1961). The reduction product is the green binuclear Mo(III) ion.[5] Mo(III) species pass the Jones reductor unchanged.
(5) M. Ardon and A. Pernick, *Inorg. Chem.*, **13**, 2275 (1974).
(6) Arnold Pernick, Ph.D. Thesis, The Hebrew University, Jerusalem, 1974.
(7) Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 767 (1973).

Arnold Pernick, Michael Ardon*

Department of Inorganic and Analytical Chemistry
The Hebrew University of Jerusalem
Jerusalem, Israel

Synthesis, Characterization, and Bonding of Tetrameric Triphenylphosphine Silver Halide Cluster Systems. Evidence of Dictation of Stereochemistries by van der Waals Interactions

Sir:

As part of a continuing effort to elucidate the observed geometrical characteristics of tetrameric cubane-like transition metal cluster systems,[1-6] we report here preliminary results on the solid-state geometries of three tetrameric triphenylphosphine silver halide clusters. This work has unexpectedly revealed a new type of isomerism: the occurrence of $(Ph_3P)_4Ag_4I_4$ in the solid state in both a cubane and chair-like form. Furthermore, this research is of interest in enabling an assessment of the relative importance of the effects of metal–ligand bonding and van der Waals interactions on the stereochemistries of $(Ph_3P)_4Ag_4X_4$ (X = Cl, Br, and I).[6]

Addition of a stoichiometric amount of triphenylphosphine in ether to AgX in a saturated solution of aqueous KX gave $(Ph_3P)_4Ag_4X_4$ (X = Cl, Br, I) as a white precipitate. Slow crystallization of $(Ph_3P)_4Ag_4Cl_4$ (**1**) from $CHCl_3$-ether afforded rectangular crystals which were shown by a complete structural analysis to possess a cubane-like structure defined by two interpenetrating silver and chlorine tetrahedra situated on alternate corners of a highly distorted cube, with each silver atom being further coordinated to a triphenylphosphine ligand (Figure 1a).[7a] A similar crystallization of $(Ph_3P)_4Ag_4I_4$ from $CHCl_3$-ether gave rise to rod-shaped crystals of monoclinic symmetry (**2a**), while crystallization from CH_2Cl_2-ether produced parallelepipeds of triclinic symmetry (**2b**). X-Ray diffraction studies have shown that **2a** possesses a cubane-like structure (Figure 1b)[7b] whereas **2b** adopts a centrosymmetric chair-like configuration (Figure 1c).[7c]
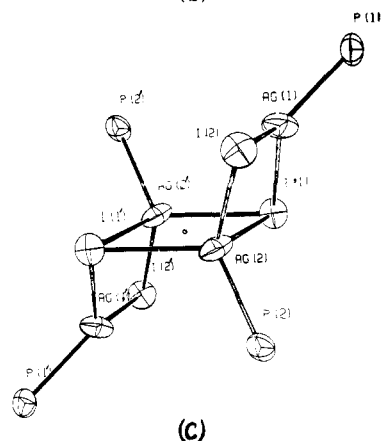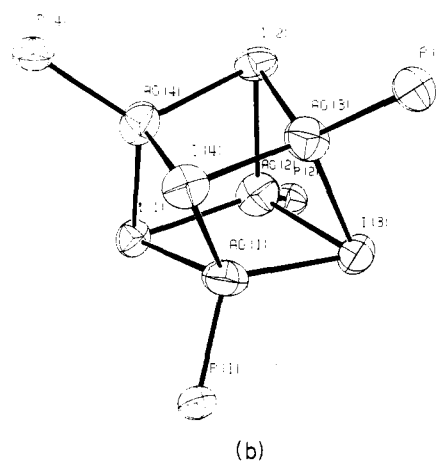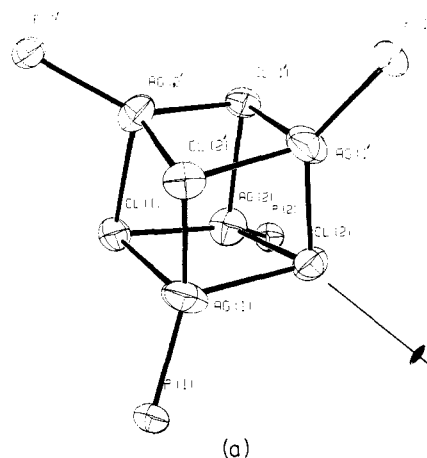

Figure 1. The highly distorted $P_4Ag_4X_4$ core (ORTEP diagram, 50% probability ellipsoids) of the $(Ph_3P)_4Ag_4X_4$ molecules: (a) X = Cl, cubane-like structure with crystallographic C_2-2 site symmetry; (b) X = I cubane-like configuration with no crystallographic constraint; and (c) X = I, chair-like configuration with crystallographic C_i-$\bar{1}$ site symmetry.

The most striking structural feature of the two cubane-like silver tetramers $(Ph_3P)_4Ag_4Cl_4$ (**1**) and $(Ph_3P)_4Ag_4I_4$ (**2a**) is the great deviation of the M_4X_4 core from the idealized T_d geometry. The unusual degree of the *nonsystematic* distortions[9] manifest themselves in the intracluster parameters listed in Table I. Other noteworthy structural characteristics are: (1) the average Ag···Ag distances are 0.74 Å (**1**) and 0.59 Å (**2a**) longer than that in the metal (however, the shortest one in **2a** is only 0.23 Å greater); (2) all X···X contacts are close to or greater than the sum of van der Waals radii; and (3) the average Ag–X distances are sub-

Table I. Selected Molecular Parameters for the Cubane-Like
$(Ph_3P)_4Ag_4X_4$ Clusters (Distances in Å, Angles in Degree)

Parameter		X = Cl	X = I
Ag···Ag	(av)	3.633	3.483
	(min)	3.408 (2)	3.115 (2)
	(max)	3.797 (2)	3.769 (3)
X···X	(av)	3.838	4.583
	(min)	3.652 (6)	4.400 (2)
	(max)	4.033 (4)	4.803 (3)
Ag–X	(av)	2.654	2.911
	(min)	2.532 (3)	2.837 (2)
	(max)	2.761 (3)	3.038 (3)
Ag–P	(av)	2.379	2.461
	(min)	2.372 (3)	2.455 (5)
	(max)	2.386 (3)	2.466 (5)
Ag–X–Ag	(av)	86.46	73.55
	(min)	79.25 (8)	64.46 (6)
	(max)	92.63 (9)	81.08 (6)
X–Ag–X	(av)	92.73	104.08
	(min)	87.21 (9)	97.38 (7)
	(max)	101.22 (9)	115.42 (6)
P–Ag–X	(av)	122.3	114.1
	(min)	109.9 (1)	103.9 (1)
	(max)	138.7 (1)	123.6 (2)

of the Ag···Ag distances and the Ag–X distances are consistent with a bonding model[1,10] in which both the bonding (a_1 + e + t_2) and the antibonding (t_1 + t_2) tetrametal symmetry orbitals and the *partially* antibonding Ag–X (e + t_1 + t_2) orbitals are fully occupied. However, electronic factors alone cannot account for the severe distortions of **1** and **2a** from T_d geometry, or for the *cubane–chair* isomerism of $(Ph_3P)_4Ag_4I_4$. We believe that these effects, as well as the occurrence of *both* cubane and chair-type geometries in the $(R_3Y)_4Cu_4X_4$ series,[4,5] is a consequence of *weak* van der Waals interactions. The latter are evidenced by a wide spectrum of nonbonding intramolecular separations including close (Ph)H···H(Ph) and (Ph)H···X contacts in both **1** and **2a**.

The observed structural variations of the known members of the series $(R_3Y)_4M_4X_4$ can now be rationalized as follows. First, the replacement of the chlorine atoms in **1** by the much larger iodine atoms in **2a** increases the intracluster nonbonding repulsions (I···I, Ag···Ag) as well as other van der Waals interactions (H···I, H···H). As a result, the iodine atoms move outwards, which, in order to maintain reasonable Ag–I bond lengths, causes the silver atoms to move inward toward the centroid of the Ag_4I_4 core; the Ag–P bonds are concomitantly lengthened by 0.08 Å to relieve intensified H···H and H···I interactions. By the same token, a formal transmutation of **1** into the copper analog $(Ph_3P)_4Cu_4Cl_4$[4a] through a replacement of the larger silver atoms with smaller copper atoms also enhances the van der Waals repulsive constraints producing a highly distorted cubane core. Further, substitution of chlorine atoms in $(Ph_3P)_4Cu_4Cl_4$ by larger bromine[4a] or iodine[4b] atoms changes the solid state structure to the chair form, presumably due to even more severe overcrowding. With less bulky terminal ligands such as triethylphosphine and triethylarsine, however, a cubane-like structure is observed in $(Et_3P)_4Cu_4I_4$ and $(Et_3As)_4Cu_4I_4$.[4a]

The fact that $(Ph_3P)_4Ag_4I_4$ is the first determined member of the series which can exist in both cubane and chair-like forms in the solid state suggests that these forms are fairly close in energy with the difference being comparable to van der Waals interactions.

Acknowledgments. We thank Dr. A. P. Ginsberg, Dr. J. W. Koepke, and Dr. D. W. Murphy at Bell Laboratories (Murray Hill) and Professor L. F. Dahl at the University of Wisconsin (Madison) for helpful discussions.

References and Notes

(1) B. K. Teo, Ph.D. Thesis, University of Wisconsin, Madison, 1973.
(2) R. S. Gall, N. G. Connelly, and L. F. Dahl, *J. Am. Chem. Soc.*, **96**, 4017 (1974).
(3) R. S. Gall, C. T.-W. Chu, and L. F. Dahl, *J. Am. Chem. Soc.*, **96**, 4019 (1974), and references cited therein.
(4) (a) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1065, 1427, 1899 (1974), and references cited therein; (b) M. R. Churchill, B. G. DeBoer, and D. J. Donovan, *ibid.*, in press.
(5) (a) N. Marsich, G. Nardin, and L. Randaccio, *J. Am. Chem. Soc.*, **95**, 4053 (1973); (b) W. R. Clayton and S. G. Shore, *Cryst. Struct. Commun.*, **2**, 605 (1973); (c) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **13**, 28 (1960); (d) A. F. Wells, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **94**, 447 (1936); (e) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).
(6) For the first indication of a "cubane-like" structure for $(R_3Y)_4Ag_4I_4$ tetramers (where R = alkyl, L = P, As) see F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937). However, no full structural study was reported.
(7) (a) $(Ph_3P)_4Ag_4Cl_4$ (**1**): orthorhombic *Pbcn; a* = 17.925 (4), *b* = 20.778 (15), *c* = 18.299 (3) Å; *V* = 6815 (5) Å³; and *Z* = 4. Anisotropic least-squares refinement[8] gave R_1 = 4.11% and R_2 = 4.57% for 2059 independent reflections. (b) $(Ph_3P)_4Ag_4I_4$ (**2a**): monoclinic $P2_1/c$; *a* = 24.991 (5), *b* = 12.402 (3), *c* = 25.074 (6) Å, β = 113.30 (2)°; *V* = 7137 (3) Å³, and *Z* = 4. Anisotropic least-squares refinement[8] gave R_1 = 4.94% and R_2 = 5.03% for 3782 independent reflections. (c) $(Ph_3P)_4Ag_4I_4 \cdot xCH_2Cl_2$ (**2b**): triclinic $P\bar{1}$; *a* = 12.126 (7), *b* = 15.107 (7), *c* = 11.977 (7) Å; α = 110.47 (4), β = 96.42 (4), γ = 71.67 (4)°; *V* = 1951 (2) Å³; and *Z* = 1; least-squares refinement in progress.
(8) Hydrogen atoms were calculated at C–H distance of 1.00 Å and assigned constant isotropic thermal parameters of 7.00 Å². For other crystallographic details, see T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, **13**, 1895 (1974).
(9) Nonsystematic variations of 0.1–0.3 Å in metal–metal distances are not uncommon for other cubane-like clusters with no metal–metal bonds.
(10) This bonding scheme is consistent with a preliminary MO calculation on $(H_3P)_4Cu_4Cl_4$ utilizing Fenske's model (M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972)).

Boon-Keng Teo*

Bell Laboratories
Murray Hill, New Jersey 07974

Joseph C. Calabrese

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Effect of Centered Functional Groups on Complexing Properties of Cyclic Polyether Hosts[1]

Sir:

Carboxylic acid and ester groups frequently act as binding sites for complexation by enzymes and antibiotics. Shaping and binding units that control association constants between synthetic multiheteromacrocyclic host and alkylammonium guest compounds have been studied.[2] We report here the syntheses[3] and binding properties toward cations of macrocyclic polyethers whose incorporated 1,3-xylyl unit directs toward the center of the ring, carboxyl, carbomethoxy, or other groups attached to the 2-position.

Cycles **1–4** and **11** were prepared by adding under nitrogen equimolar mixtures of the appropriate dibromide (**16** or 1,3-bis(bromomethyl)benzene) and polyethylene glycol in dry THF over a 3-hr period to a refluxing mixture of THF containing a 3 *M* excess of sodium hydride.[8] For **12–14**, **17–19** were added to the already prepared alkoxides.[8]

The pK_a's (±0.2) of the four cyclic carboxylic acids (**5–8**) and of their open-chain model (**20**) were determined in water at 22°[9] (**5**, 4.8; **6**, 4.8; **7**, 3.8; **8**, 3.4; **20**, 3.3). Thus in acid strength, the five compounds are arranged: zero-membered ring $\gtrsim$ 30-membered ring > 21-membered ring > 18-membered ring ~ 15-membered ring. Two effects explain the acidity order. (1) Molecular models (Corey, Pauling, Koltun or CPK) of the five acids reveal that **5** and **6** are relatively rigid, and their carboxyl groups comfortably hy-