

09.5-2 FLUORESCENT COPPER(I) CLUSTER SYSTEMS.

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Temperature dependent fluorescence has been previously observed for copper(I) halide clusters of the format, $(\text{CuXL})_4$ where L is an electron pair donating ligand such as phosphine, amine, nitrile or carboxylate. These tetrameric clusters show Cu and I atoms at alternate corners of a distorted cube with each copper atom completing its tetrahedral geometry by electron pair donation from a ligand.

The fluorescent complex $(\text{CuIacetonitrile})_4 \cdot \text{dibenzo-18-crown-6}$ is of this format with the crown ether altering the donicity of the acetonitrile group via a second sphere interaction. The fluorescent mixed ligand cluster $[(\text{Cu}_2\text{I}_2(\text{CH}_3\text{CN})(\text{p-chloroaniline}))_2]$ also displays this cubic cluster geometry with copper atoms on one face ligated to acetonitrile groups and those of the opposite face coordinating to the amine nitrogens of p-chloroaniline groups.

However the parent complex of CuI and acetonitrile is of formulation $(\text{CuIacetonitrile})_x$, displaying folded sheet structure with distorted squares of alternating Cu and I atoms linked together in linear array. Each copper atom has a further ligation to one acetonitrile nitrogen atom. Fluorescence has not previously been associated with structures of this type.

Details of cluster geometry such as bond lengths, nonbonded metal-metal distances, and symmetry elements present or absent in the cluster may be correlated with the observed temperature dependence of the fluorescence.

09.5-3 CRYSTAL STRUCTURES OF RUTHENIUM CLUSTER ANIONS AND OSMIUM-BASED MIXED METAL CLUSTERS.

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Transition metal clusters have been explored because of their unique types of bonding and because of their potential importance to catalytic chemistry such as hydroformylation and Fischer-Tropsch reactions. Although spectroscopic elucidation of the cluster structures are useful, X-ray diffraction has proved to be the most rewarding technique in the determination of their molecular structure.

The crystal structures of the two new ruthenium cluster anions, $[\text{crypt } 222\text{K}]_2[\text{Ru}_4(\text{CO})_{13}]$ and $[\text{crypt } 221\text{Na}]_2[\text{H}_2\text{Ru}_4(\text{CO})_{12}]$ will be presented. By comparing the structures of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$, $\text{HRu}_4(\text{CO})_{13}$, and $\text{Ru}_4(\text{CO})_{13}^-$, it is of interest to note that the number of bridging carbonyls increases with increasing negative charge on the anion.

The crystal structures of five osmium-based bimetallic clusters, $\text{H}_3\text{PhRhOs}_3(\text{CO})_9$, $\text{H}_2\text{CpIrOs}_3(\text{CO})_{10}$, $\text{H}_4\text{C}_5\text{Me}_5\text{RhOs}_3(\text{CO})_9$, $\text{H}_2(\text{C}_5\text{Me}_5)_2\text{Rh}_2\text{Os}_2(\text{CO})_7$, and $\text{H}_2\text{Cp}_2\text{Rh}_2\text{Os}_2(\text{CO})_7$, will also be presented here. The molecular structures of these compounds exhibit the following properties: (i) molecules are based on a distorted tetrahedron, (ii) bridging carbonyls shorten the metal-metal distances, (iii) bridging hydrides elongate metal-metal bonds, and (iv) the ring ligands are displaced from their possible symmetrical apical positions.

09.5-4 PREPARATION AND X-RAY STRUCTURE DETERMINATION OF $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}[\text{Ag}_3\text{Li}_2(\text{C}_6\text{H}_5)_6]^-$: AN UNUSUAL CATION COMPOSED OF A SOLVATED "SALT CLUSTER".

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Following our recent report¹ of the preparation and structure determination of the $[\text{Cu}_5(\text{C}_6\text{H}_5)_6]^-$ cluster, we have extended this chemistry into silver/phenyl complexes. The $[\text{Ag}_3\text{Li}_2(\text{C}_6\text{H}_5)_6]^-$ mixed-metal cluster was prepared by treating a cold suspension (0°C) of AgBr in diethyl ether with solution of freshly prepared phenyl lithium in a 1:3 molar ratio. After removal of half of the solvent, large colorless crystals of the title compound appeared upon standing (a few days of storage) at -15°C. $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ crystallizes in the monoclinic space group $\text{P}2_1/\text{n}$, with $a = 16.497(12)\text{Å}$, $b = 29.790(20)\text{Å}$, $c = 12.792(7)\text{Å}$, $\beta = 100.19(5)^\circ$, $V = 6187(7)\text{Å}^3$, $Z = 2$. The positions of the Ag and Br atoms were determined by direct methods (using the program MULTAN), and the coordinates of the rest of the atoms determined by standard heavy-atom techniques. Least-squares refinement resulted in a final R factor of 0.076 for 4003 reflections with $I > 3\sigma(I)$. The $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ cluster (Figure 1) closely resembles the $[\text{Cu}_5\text{Ph}_6]^-$ cluster mentioned earlier,¹ having the same basic trigonal bipyramidal geometry with lithium atoms in axial positions. The $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ cation is extremely unusual: it consists of a $[\text{Li}_6\text{Br}_4]^{2+}$ salt-like core surrounded by a shell of ten ether molecules. We thank the U.S. National Science Foundation (Grant CHE-81-01122) for support of this research.

- 1) P.G. Edwards, R.W. Gellert, M.W. Marks and R. Bau, *J. Am. Chem. Soc.*, **104**, 2072 (1982).

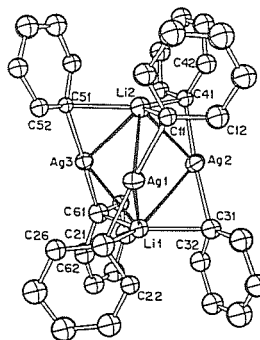


Figure 1: The $[\text{Ag}_3\text{Li}_2(\text{C}_6\text{H}_5)_6]^-$ Anion

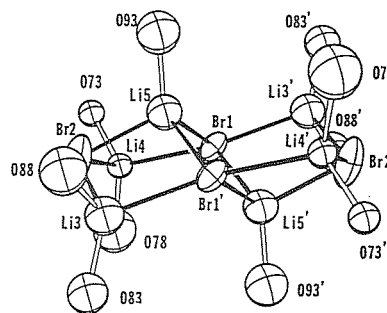


Figure 2: The $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ Cation