

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, $(CuXL)_4$ 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 $(CuIacetonitrile)_4 \cdot dibenzo-18-crown-6$ 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 $[(Cu_2I_2(CH_3CN)(p\text{-chloroaniline})_2)]_2$ 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 $(CuIacetonitrile)_x$, 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, $[crypt\ 222K]_2[Ru_4(CO)_{13}]$ and $[crypt\ 221Na]_2[H_2Ru_4(CO)_{12}]$ will be presented. By comparing the structures of $H_2Ru_4(CO)_{13}$, $HRu_4(CO)_{13}$, and $Ru_4(CO)_{13}^-$, 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, $H_3PhRhOs_3(CO)_9$, $H_2CpIrOs_3(CO)_{10}$, $H_4C_5Me_5RhOs_3(CO)_9$, $H_2(C_5Me_5)_2Rh_2Os_2(CO)_7$, and $H_2Cp_2Rh_2Os_2(CO)_7$, 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 $[Li_6Br_4(Et_2O)_{10}]^{2+}[Ag_3Li_2Ph_6]^-$: 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 $[Cu_5(C_6H_5)_6]^-$ cluster, we have extended this chemistry into silver/phenyl complexes. The $[Ag_3Li_2(C_6H_5)_6]^-$ 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. $[Li_6Br_4(Et_2O)_{10}]^{2+}[Ag_3Li_2Ph_6]^-$ crystallizes in the monoclinic space group $P2_1/n$, 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 $[Ag_3Li_2Ph_6]^-$ cluster (Figure 1) closely resembles the $[Cu_5Ph_6]^-$ cluster mentioned earlier,¹ having the same basic trigonal bipyramidal geometry with lithium atoms in axial positions. The $[Li_6Br_4(Et_2O)_{10}]^{2+}$ cation is extremely unusual: it consists of a $[Li_6Br_4]^{2+}$ 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).

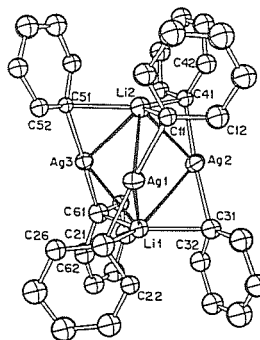


Figure 1: The $[Ag_3Li_2(C_6H_5)_6]^-$ Anion

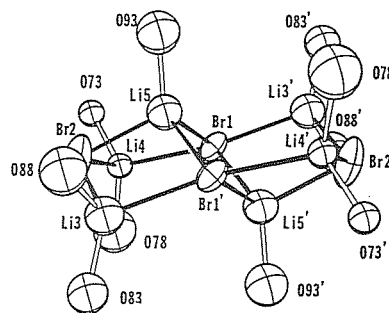


Figure 2: The $[Li_6Br_4(Et_2O)_{10}]^{2+}$ Cation