

09.5-2 FLUORESCENT COPPER(I) CLUSTER SYSTEMS.

By N. P. Rath, J. Jasinski and E. M. Holt,
Department of Chemistry, Oklahoma State University,
Stillwater, Oklahoma, USA 74078

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 $[(\text{Cu}_2\text{I}_2(\text{CH}_3\text{CN})(p\text{-chloroaniline}))_2]$ 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. By Leh-Yeh Hsu, Wen-Liang Hsu, and Sheldon G. Shore, Department of Chemistry, Ohio State University, Columbus, Ohio 43210, U.S.A.

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". By Robert Bau, Michael Y. Chiang and Elmar Böhlen, Department of Chemistry, University of Southern California, Los Angeles, CA 90089, U.S.A.

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).

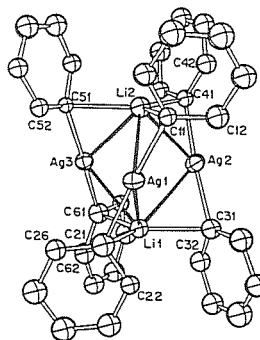


Figure 1: The $[\text{Ag}_3\text{Li}_2(\text{C}_6\text{H}_5)_6]^-$ Anion

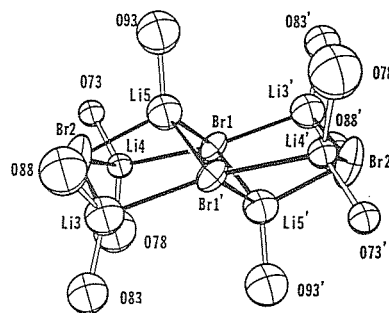


Figure 2: The $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ Cation