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IONIC AND ELECTRONIC CONDUCTIVITY IN COUMARIN AND BENZOPHENONE COMPLEXES WITH ALKALI POLYIODIDES*

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A group of clathrated metal polyiodides has been prepared using the carbonyl compounds benzophenone, some of its derivatives, or coumarin as the organic "host" and alkali or ammonium iodide-iodine mixture as the "guest". We first reported[1] on the conductivity and optical properties of single crystals of $(benzophenone)_9(KI)_2I_7CHCl_3$, which have a golden, metallic reflection on the crystal surface parallel to the polyiodine chain axis. DC conductivity was $\sim 10^{-6}\ \Omega^{-1}cm^{-1}$ at room temperature, along this axis, and about one order of magnitude lower across the needle axis, whereas the (contactless) microwave conductivity was $\sim 10\ \Omega^{-1}cm^{-1}$ at room temperature. The cation M^+ was then varied to be Li^+, Na^+, Rb^+, Cs^+, NH_4^+ and R_4N^+, solvent of crystallization was varied, and it became clear that the conductivity was a mixture of ionic and electronic conductivity, the total varying from 10^{-2} to $10^{-6}\ \Omega^{-1}cm^{-1}$ depending on both cation and solvent.[2,3] Structural work has indicated that, in most members of this series, the benzophenone forms a column in which the cation is six coordinate and the iodine columns are linear.[4] However, when the cation is Li^+, it is tetrahedrally coordinated to four oxygens of four benzophenone molecules. The columns of iodine are made up of I_5^- anions each of which is bent at the central iodine atom.[5] Raman spectro-

scopic data confirm aspects of the iodine chain structure in these complexes.[6]

In this paper, details of the conductivity behavior of these benzophenone complexes are presented, together with an investigation of a family of more stable, more conductive complexes of coumarin with alkali iodides-iodine. All ac conductivity measurements were made along the needle axis of single crystals. For example, the ac (1 KHz) conductivity of the complex $(coumarin)_4RbI_4$ is $\sim .04\ \Omega^{-1}cm^{-1}$. Data are also presented on a group of measurements attempting to distinguish between ionic and electronic processes in these crystals. Because of similarities in the optical and electrical behavior of all these complexes, a common transport mechanism, associating the conductivities with the iodine sub-lattices exclusively, is advanced.

In general, the coumarin complexes have higher conductivities than the benzophenone complexes. Their stoichiometry is in the approximate ratio coumarin:alkali ion:iodine = 4:1:4 to 5. Crystal structures are not known as of this writing. Both series of complexes clearly have an ionic component to their conductivity as indicated by their dc behavior, Faradaic experiments, and their abilities to function as electrodes for alkali batteries.

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