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A New Class of Mixed Ionic-Electronic Conductor: Anthrone-Iodine-Alkali Iodide Complexes

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A New Class of Mixed Ionic-Electronic Conductor: Anthrone-Iodine-Alkali Iodide Complexes

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Complexes of anthrone (A) with iodine (I) and alkali iodide (MI, M = Na, K, Rb, or Cs) have been prepared for the first time. These complexes (abbreviated AIMI) yield lustrous, rectangular crystals from acetone. At room temperature, the dc conductivity along the longitudinal direction of the entire series of the AIMI crystals decreases initially with time for about twenty minutes, but remains unchanged afterward. This indicates that the conduction is ionic as well as electronic in character. Their ac (1 kHz) conductivity, by contrast, is independent of time and is in the order of 10^{-6} to 10^{-3} Scm^{-1}, varying systematically with the cation size in the following order: AICsI < AIRbI < AIKI < AINaI. It is concluded that AIMI complexes are a new class of mixed ionic and electronic conductor.

Keywords: anthrone complexes, ionic-electronic conductor

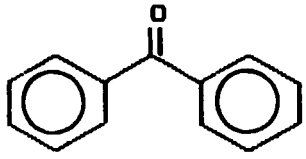
INTRODUCTION

It is well known that complexes of benzophenone (**I**) with iodine and alkali iodide can be obtained from chloroform.[1–6] The unusual electrical features of these complexes (BIMI) are that they show both ionic and electronic conductions[2–5] and behave as one-dimensional fast cationic conductors[5] with microwave conductivities[2] as high as 10 Scm^{-1}.

By using a benzophenone analog, such as 9-fluorenone or 5-dibenzosuberenone, to substitute benzophenone in the BIMI complexes, we[7,8] have obtained two new classes of complexes from chloroform, denoted as FIMI and DIMI, respectively. Interestingly, both FIMI and DIMI complexes have only electronic conduction and show no evidence for ionic transport.[7,8] Thus, it seems clear that a small change in the benzophenone skeleton has led to a dramatic difference in the conduction behavior of the resulting complexes. Because the structural information on the FIMI and DIMI complexes is not yet available, the reason for their different behavior is not clear.

In this paper, we present a new class of mixed ionic and electronic conductor

which contains iodine, alkali iodide and anthrone (**II**), also a benzophenone analog. The electrical properties of this new class of complexes are reported.



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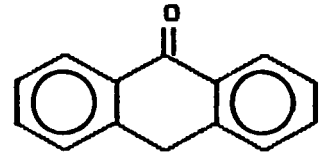

II

EXPERIMENTAL

AIMI complexes were prepared by dissolving 3 mmol of anthrone, 3.5 mmol of iodine and 1 mmol of alkaline iodide in 50 ml of acetone. The solution was refluxed for one hour and allowed to cool. It was then poured into a flask and allowed evaporation of the solvent to dryness at room temperature. The flask was covered with three pieces of filter paper for slow evaporation. Shiny, rectangular crystals were yielded after about two weeks. The melting point of the obtained crystals was recorded with a Du Pont 9900 thermal analysis system or a Perkin-Elmer Model 2C differential scanning calorimeter.

All the conductivity measurements were conducted with current passing through the longitudinal direction of the crystals. Mounting and electrode attachment employed a simple two-probe technique. Gold wires with a diameter of 1 mil served as electrode connectors and were attached to the samples using graphite aquadag as the contacting paint.

Employing a Hewlett-Packard Model 6181C as constant dc current source, the room temperature dc conductivity as a function of time was obtained by measuring voltage with a Keithley Model 617 electrometer. Due to ionic contribution, ac current (1 kHz) was supplied by a Gen Rad Model 1657 RLC Digibridge for measuring the temperature dependence of conductivity from about 250 to 300 K. Temperature was controlled with a Haake Model F-3Q circulator and monitored by a copper-constantan thermocouple connected to a Keithley Model 177 digital multimeter.

RESULTS AND DISCUSSION

In appearance, the AIMI crystals are blackish in color and rectangular in shape with dimensions of about $10 \times 3 \times 1$ mm^3. All the crystals have a metallic luster along the longitudinal direction and are stable in the air for about one week. For longer periods, they must be kept in closed vials; otherwise, the crystals gradually lose their metallic luster due to sublimation of the iodine from the complexes. The melting points for AINaI, AIKI, AIRbI, and AICsI are 187, 181, 203, and 207°C, respectively.

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TABLE I

Analytic data of AIMI complexes

Cation	Best formula		C%	H%	I%	M%
Na	$A_3NaI_3 \cdot 2H_2O$	Found	48.91	3.31	37.10	2.32
		Calcd.	49.34	3.35	37.23	2.25
K	$A_3KI_3 \cdot H_2O$	Found	49.24	3.14	36.38	3.74
		Calcd.	49.43	3.16	37.31	3.83
Rb	A_3RbI_3	Found	47.86	2.91	36.20	8.18
		Calcd.	48.10	2.88	36.30	8.15
Cs	A_3CsI_3	Found	45.77	2.82	34.80	12.85
		Calcd.	46.02	2.76	34.73	12.45

Table I presents elemental analyses and stoichiometries of AIMI complexes. It is clear that these complexes have a general stoichiometry $(anthrone)_3MI_3 \cdot nH_2O$ with $n = 2$ or 1 for the smaller cations, and $n = 0$ for the larger cations. Water molecules are probably absorbed by the iodide salts from the atmosphere during preparations of the complexes. The presence of water is confirmed by the Karl Fischer method.[9] There is no evidence for the presence of solvent molecules in the AIMI complexes. This is in contrast to the BIMI complexes in which solvent molecules are incorporated into the crystals.[2,3,10]

Figure 1 shows room temperature dc conductivity as a function of time during the passage of 1 μA current through the AIMI and DIRbI crystals. It is evident that for the DIRbI complex which exhibits only electronic conduction, the conductivity is essentially unchanged with time. On the contrary, for the entire AIMI series, the conductivity decreases progressively for about 20 minutes, but levels off afterward. The decrease in the dc conductivity is most likely due to the polarization at the electrodes resulting from ionic migrations. The reason for leveling off in conductivity is presumably because the electronic conduction, which does not depend on time, is still somehow operative after ionic migrations have stopped in these complexes. These results indicate that the electrical conduction in all the AIMI complexes is both ionic and electronic in character. A similar behavior[4,10] has been observed for some of mixed ionic and electronic conductors, such as BIKI and BIRbI crystals of the chloroform series.[10]

As shown in Figure 1, the extent of decrease in the room temperature dc conductivity varies systematically with the cation size in the following order: AICsI < AIRbI < AIKI < AINaI. Since a change in the cation size has such a profound effect on the dc conductivity, it is suggested that the ionic conduction is probably dominated by the cationic transport and the contribution of ionic conduction in each AIMI complex is probably increased in the same order as above.

It is noted that the more ionically conducting complexes, such as AINaI and AIKI, are also hydrated as shown in Table I. However, it appears that in the solid states only the positively charged cations themself are moving under the influence of an applied dc field and the water molecules in the complexes do not have much

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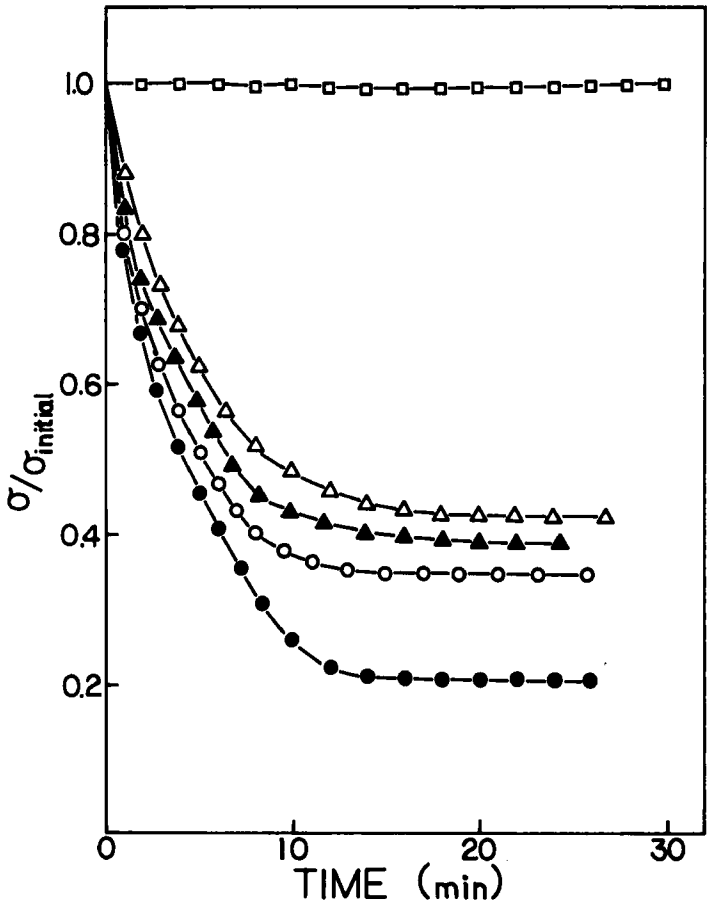

FIGURE 1 Change in dc conductivity as a function of time during the passage of a constant current of 1 μA through the crystal of DIRbI (□), AICsI (△), AIRbI (▲), AIKI (○), and AINaI (●). The DIRbI complex is included for comparison.

effect on the cationic movement, according to the results shown in Figure 1, which clearly indicates that the extent of decrease in the dc conductivity is greater for the hydrated complexes. Moreover, the interaction between the water molecules and anionic iodide ions, if it exists, would also make the movement of water molecules difficult. As discussed above, the decrease in the dc conductivity is most likely due to polarization at the electrodes as a result of ionic migration, it is therefore suggested that the mobility of the ion in the solid states is greater for the smaller cations. This is probably the reason why the extent of decrease in the dc conductivity is greater for the hydrated complexes.

Figure 2 shows the reciprocal temperature (1/T) dependence of the ac conductivity (σ) of the AIMI complexes. For the temperature range studied, these complexes behave clearly as typical semiconductors exhibiting a linear dependence of log σ on 1/T. It is best described by the well known Arrhenius equation: $\sigma = \sigma_0$

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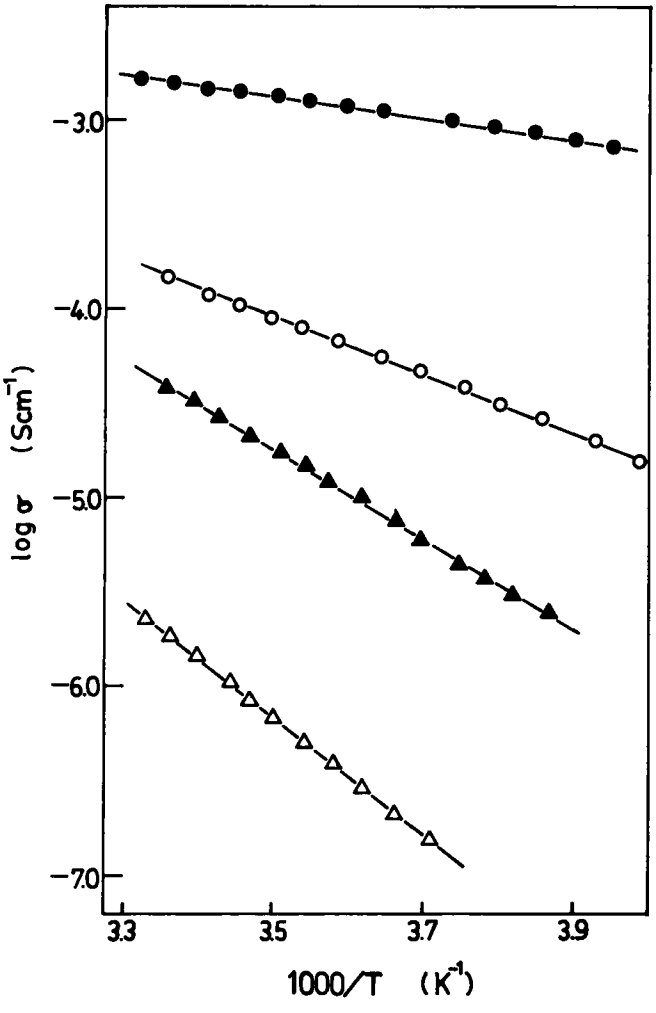

FIGURE 2 The reciprocal temperature dependence of ac conductivity of AINaI (●), AIKI (○), AIRbI (▲), and AICsI (△).

exp $(-Ea/kT)$, where σ_0 is a constant, Ea is the activation energy for conduction and k is the Boltzmann's constant. From the Arrhenius plots, which give straight lines having the slope $-Ea/k$, the activation energy for conduction can be obtained.

Table II lists the activation energy and room temperature ac conductivity of AIMI complexes. As shown in Figure 3, it can be seen that an increase in the cation size gives rise to a decrease in the conductivity accompanied by an increase in the activation energy. The inverse relationship between the conductivity and the activation energy is not unexpected because the lower conductivity at room temperature usually, but not always, implies the higher activation energy. It is of interest that only one activation energy is obtained for all the AIMI complexes, although the conductivity is composed of both ionic and electronic processes. These

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TABLE II

AC (1 kHz) conductivity and activation energy of AIMI complexes

Complex	Conductivity (Scm^{-1}, at 300 K)	Activation energy (eV)
AINaI	1.7×10^{-3}	0.11
AIKI	1.6×10^{-4}	0.29
AIRbI	4.5×10^{-5}	0.48
AICsI	2.3×10^{-6}	0.60

results suggest that within the temperature range studied only one process is predominant. For some of the mixed ionic-electronic conductors, such as BIRbI and BICsI complexes,[2,3] the results of only one activation energy have also been reported.

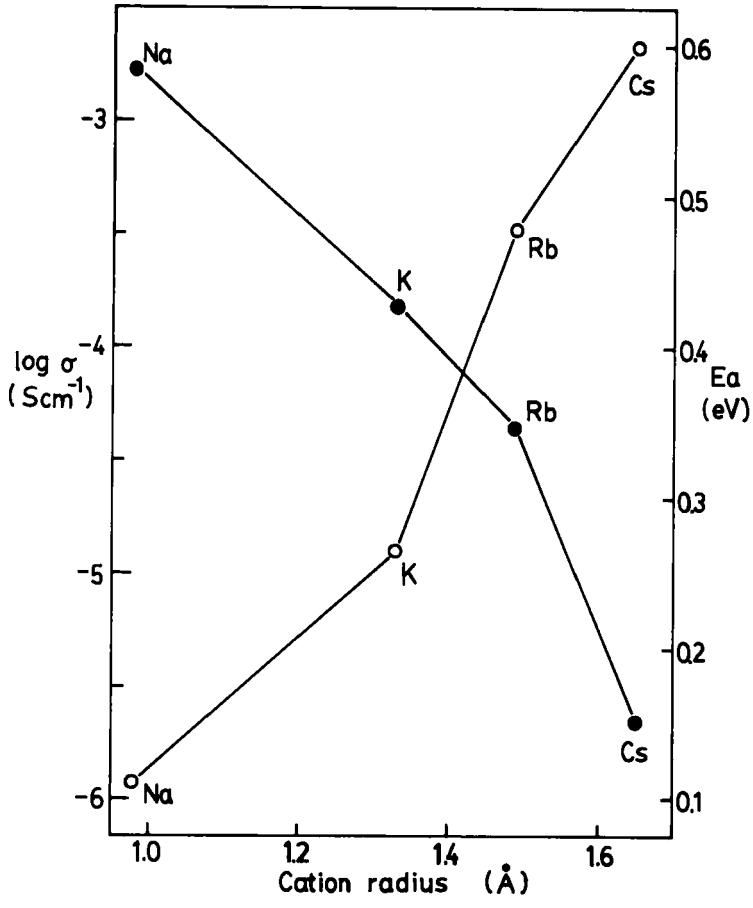

FIGURE 3 Cation dependence of ac conductivity (●, ordinate scale on left) and activation energy (○, ordinate scale on right) of AIMI complexes where M = Na, K, Rb, or Cs.

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In the absence of the structural information on AIMI complexes, it appears somewhat difficult to understand the correlation between the cation and the conductivity. However, it is of particular interest to note that a similar correlation has been observed for complexes of the planar 9-fluorenone molecule[11] with iodine and alkali iodide.[7] In contrast, for the nonplanar carbonyl compounds such as benzophenone[12] or 5-dibenzosuberenone[13] complexed with iodine and alkali iodide, the correlation between the conductivity and the cation size is not found.[4,8] Therefore, it seems most likely that the planarity of the carbonyl compound plays a significant factor in understanding the correlation. A reasonable assumption is that the nearly planar anthrone molecules[14] are arranged in columnar stacks with π-molecular overlap along the stacking direction and the cations are located in a fashion similar to the potassium ion in the structure of the BIKI complex.[6] In such stacks, it is conceivable that the intrastack distance between anthrone molecules is of importance for the electronic conduction. Thus, the larger cations, which tend to increase the spacing between anthrone molecules along the stack, would decrease the intrastack interactions, and hence result in lower electronic conductivity. For the ionic process, the larger cations, as suggested earlier, also tend to lower the conductivity. Taken both the electronic and ionic contributions together, the conductivity of the AIMI complexes is consequently decreased with increased cation size.

In conclusion, a new class of anthrone complexes with a mixed ionic and electronic conduction has been obtained. It is found that their conductivity and activation energy can be correlated with the cation size. Although the cationic transport is probably predominant in the ionic process, the relative contribution between the ionic and electronic processes is yet to be determined.

Acknowledgments

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References

1. A. M. Clover, *Am. Chem. J.*, **31**, 256 (1904).
2. M. M. Labes, M. Jones, H. I. Kao, L. Nichols, C. Hsu and T. O. Poehler, *Mol. Cryst. Liq. Cryst.*, **52**, 115 (1979).
3. H. I. Kao, *Tamkang J.*, **18**, 231 (1981).
4. C. Wu, B. Kim, H. I. Kao, C. W. Griffin, M. Jones and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **88**, 317 (1982).
5. C. Wu and M. M. Labes, *J. Phys. Chem.*, **90**, 4199 (1986).
6. P. Coppens, P. C. W. Leung, R. Ortega, W. S. Young and C. Laporta, *J. Phys. Chem.*, **87**, 3355 (1983).
7. H. S. Yang and C. M. Wang, *J. Chin. Chem. Soc.*, **34**, 301 (1987).
8. H. S. Yang and C. M. Wang, *Mol. Cryst. Liq. Cryst.*, **159**, 315 (1988).
9. J. Mitchell, *Anal. Chem.*, **23**, 1069 (1951).

10. C. M. Wang, S. F. Wang and H. Chang, *J. Chin. Chem. Soc.*, in press (1989).
11. R. Luss and D. L. Smith, *Acta. Cryst.*, **B28**, 884 (1972).
12. E. B. Fleischer, N. Sung and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968).
13. H. Shimanouchi, T. Hata and Y. Sasada, *Tetrahedron Lett.*, 3573 (1968).
14. S. N. Srivastava, *Acta Cryst.*, **17**, 851 (1964).

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