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Electronic and Ionic Conductivity in Polyiodine Complexes of Benzophenones and Coumarin

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Complexes of benzophenone, benzophenone derivatives, or coumarin with alkali or ammonium iodides and iodine have been prepared and their conductivities studied. The organic sub-lattices involve six- or four-coordinate cation clathrated by the carbonyl compounds. The iodine sub-lattices consist of I_n chains in which I_3^- and I_5^- ions can be identified. AC (1 KHz) conductivities at room temperature vary from 10^{-1} to 10^{-6} Ω^{-1} cm^{-1}, and are of a mixed ionic and electronic type. The most likely transport mechanism involves hopping processes in the polyiodine sub-lattice.

INTRODUCTION

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 $\sim 10^{-6}$ Ω^{-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 ~ 10 Ω^{-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} Ω^{-1} cm^{-1} depending on both cation and solvent.[2,3] Structural work has indicated that, in most members of this series, the benzophenone

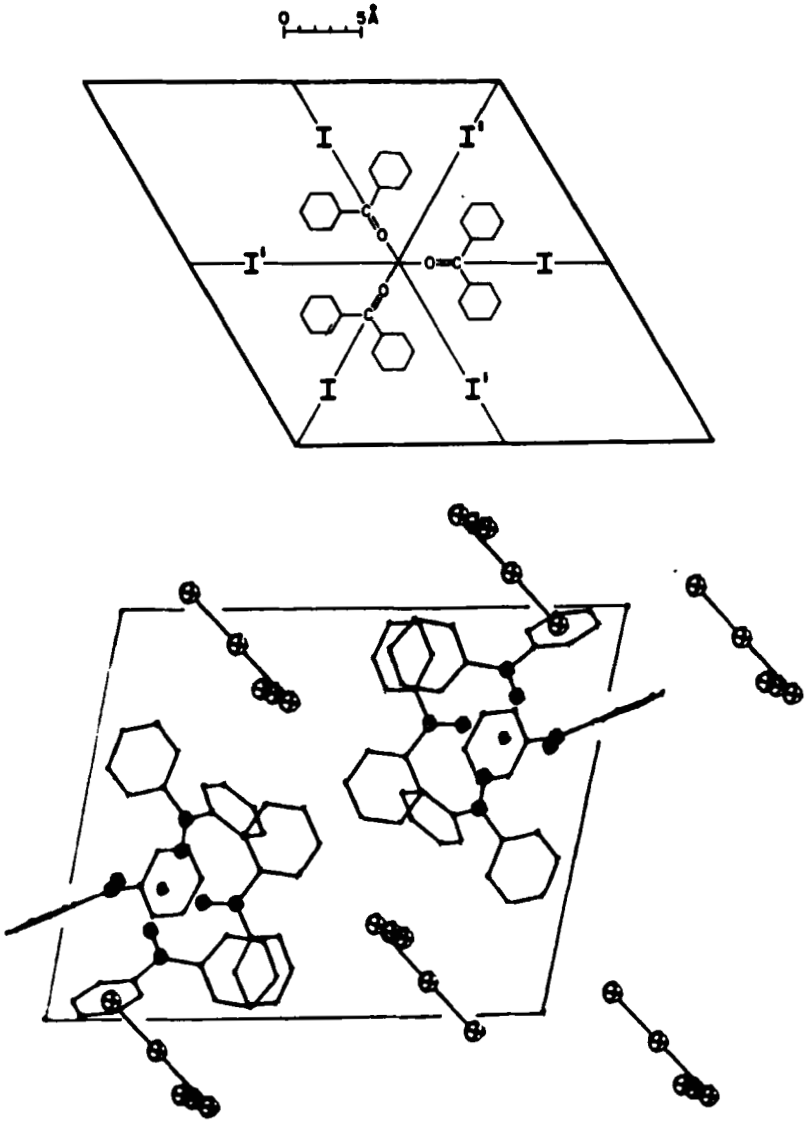

FIGURE 1 (a) Schematic drawing of the (001) projection of the structure of the potassium and ammonium benzophenone iodine complexes. The cations are in a column at the center of the benzophenone oxygen atoms. Benzophenone molecules in a second layer are in staggered positions and complete an anti-prismatic coordination of the cations. The origin of the unit cell is in the center of the drawing. Note that only part of the unit cell is shown; (b) ORTEP drawing of the projection of BILiI looking down the a axis. The large spheres represent the iodine atoms. The unit cell is indicated. Reprinted from reference (5) with permission of the authors.

forms a column in which the cation is six coordinate and the iodine columns are linear,[4] as pictured schematically in Figure 1. 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 as pictured in Figure 1.[5] Raman spectroscopic 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)$_4$RbI$_4$ is $\sim$.04 Ω^{-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.

EXPERIMENTAL: PREPARATION AND STOICHIOMETRY

Benzophenone complexes

Two crystal growth methodologies were employed. In the first, low temperature (−10°C) isothermal diffusion growth was conducted in an apparatus consisting of two bulbs connected by a U-tube solvent column. One bulb contained the benzophenone and 1/2 of the metal iodide; the other contained I_2 and 1/2 of the metal iodide. The usual solvent was chloroform, but ethanol, ethanol-chloroform mixtures, acetonitrile, and other solvents frequently led to good crystal growth. Crystals as large as 1 cm in length and 2–3 mm in cross-section grew over a period of 1–2 weeks.

In the second method, ingredients were simply mixed in the solvent, heated until all ingredients dissolved and allowed to cool slowly to room temperature. Variable size crystal masses grew by this simple method, and crystals large enough to manipulate (3–5 mm in length × 1 mm in cross-section) could be selected from the mass. Crystals were stored in sealed ampoules in air and were quite stable.

These methods are essentially variations on procedures used by Clover in 1904.[7] We will use the abbreviation BIMI to designate these complexes where M is the cation. BIKI has also been studied by

TABLE I

Stoichiometry and analysis of BIMI and CIMI complexes

Cation	Stoichiometry	Analysis %C Theor.	%C Found	%H Theor.	%H Found	%O Theor.	%O Found	%I Theor.	%I Found	%Cation Theor.	%Cation Found
Li	B_4LiI_5	45.57	46.93	2.92	3.11	4.67	4.99	46.33	43.98	0.50	0.49
Na	$B_9Na_2I_9 \cdot CHCl_3$	48.09	48.01	3.11	3.07	4.89	5.18	38.75	38.81	1.56	1.40
K	$B_9K_2I_9 \cdot CHCl_3$	47.57	48.17	3.08	3.09	4.83	4.34	38.33	37.87	2.62	2.51
NH_4	$B_9(NH_4)_2I_9 \cdot CHCl_3$	48.25	48.19	3.40	3.33	4.90	4.95	38.89	38.89	0.95[a]	0.93[a]
Li	$C_6LiI_7 \cdot CHCl_3$	39.41	40.94	2.19	2.41	11.68	11.99	46.30	43.94	0.42	0.41
Li	$C_6Li_2I_8 \cdot EtOH$	34.42	35.13	2.15	2.28	10.65	10.20	52.00	51.41	0.72	0.68
Na	C_4NaI_5	34.78	35.46	1.93	1.94	10.31	9.02	51.13	51.49	1.89	1.87
K	$C_7K_2I_8$	35.75	37.27	2.00	2.12	10.58	10.69	49.97	46.32	3.69	3.64
Rb	C_4RbI_4	36.70	36.51	2.03	2.12	10.87	8.28	43.12	45.67	7.26	7.29
Cs	$C_4Cs_2I_7 \cdot EtOH$	35.12	36.72	2.17	2.22	10.79	9.40	39.95	39.65	11.95	11.75

[a] % Nitrogen.

Kapon[8] who reported a slightly different stoichiometry than that found by Clover[7] or in our work. Analytical data and stoichiometry for the series of complexes are given in Table I. The stoichiometry represents the best fit to a simple ratio. Obviously there is considerable disorder possible in such structures, and no requirement for a simple stoichiometry. Crystal structure data[4,5] confirm the stoichiometry for the Li^+, NH_4^+ and K^+ complexes.

Coumarin complexes

The procedures for the coumarin complexes (CIMI) were very similar. Little success was obtained using diffusion growth. Solution growth was most frequently conducted in ethanol–water mixtures, following suggestions from the literature.[9] The work of Simonis[10] suggests a general stoichiometry for the coumarin complexes of C_4MI_4 with an occasional water of crystallization. Our analyses suggest some variability in the stoichiometry in the series (Table I).

EXPERIMENTAL: MEASUREMENTS

AC(1 KHz) conductivity and temperature dependence

Utilizing a General Radio 1608A impedance bridge at 1 KHz, the total conductivity of single crystals of BIMI and CIMI complexes were measured as a function of temperature by a simple two-probe technique using platinum electrodes and aquadag as the contacting paint. Either a "Displex" closed-cycle helium refrigerator (Air Products CSA 202) or a small Delta Design (Model 2300) environmental chamber were employed as temperature controllers. Temperature limits were imposed at the high end by crystal stability and at the low end by the high impedances.

DC conductivity and faradaic experiments

DC conductivity at room temperature as a function of time was measured using a Keithley 616 electrometer. Faradaic experiments were conducted on $BINH_4I$ compactions. A 13 mm diameter pellet 2.5 cm wide was compacted between two platinum plates. After passing 1–10 coulombs, the pellet was cut into slices. Determinations of iodide (before and after reduction of iodine with sodium thiosulfate) were performed by dissolving the samples in methanol, adding water and inserting an Orion specific iodide electrode (Model 94-53) and reference electrode for a potentiometric measurement.

Proton injecting electrode

Zirconium phosphate hydrate was prepared as described by Hamlen,[11] and compacted into a 13 mm diameter × 1 mm disc. A cell was constructed as follows (using 13 mm compacted discs in a spring-loaded cell):

$$Pt|\ ZrO(H_2PO_4)_2 \cdot XH_2O|\ BINH_4I|\ (CH_3)_4NI_5|\ Pt$$

Alkali metal batteries

Lithium ribbon (Alfa Products) or thin sheets of sodium were prepared in an argon purged glove box. Samples of BIMI dried at 40° were compacted into 13 mm × 3–5 mm discs, introduced into the glove box, and pressed in a spring-loaded clamp against the alkali metals. Measurements were performed on the samples inside the glove box by attaching through feedthroughs to a Keithley 616 electrometer.

Seebeck effect

Single crystals were mounted on a glass plate, both ends of which were heat-sinked with copper foil. A small spot heater (Thermofoil, Minco Products, Inc.) created a variable thermal gradient over the sample whose ambient temperature was controlled by placing it in a Delta Design (Model 2300) chamber.

DISCUSSION

AC(1 KHz) conductivity and temperature dependence

In general, the CIMI series have higher conductivities than the BIMI complexes (Table II). All show evidence for mixed ionic and electronic

TABLE II

AC (1 KHz) conductivity and activation energy of BIMI and CIMI single crystals

Compound	Conductivity (Ω^{-1} cm^{-1}, at 25°C)	E_a(eV)
B_4LiI_5	5.8×10^{-4}	0.15
$B_9Na_2I_9 \cdot CHCl_3$	4.8×10^{-6}	0.83, 0.28
$B_9K_2I_9 \cdot CHCl_3$	4.5×10^{-6}	0.20, 0.05
$B_5Rb_2I_7$[a]	5.5×10^{-5}	0.7
$B_9(NH_4)_2I_9 \cdot CHCl_3$	4.0×10^{-4}	0.45
$C_6LiI_7 \cdot CHCl_3$	3.8×10^{-2}	0.09
C_4NaI_5	1.8×10^{-1}	0.39
$C_7K_2I_8$	4.5×10^{-4}	0.17
C_4RbI_4	4.2×10^{-2}	0.27, 0.10
$C_4Cs_2I_7 \cdot EtOH$	1.3×10^{-2}	0.18

[a] Very poor analytical correspondences were obtained on this complex.

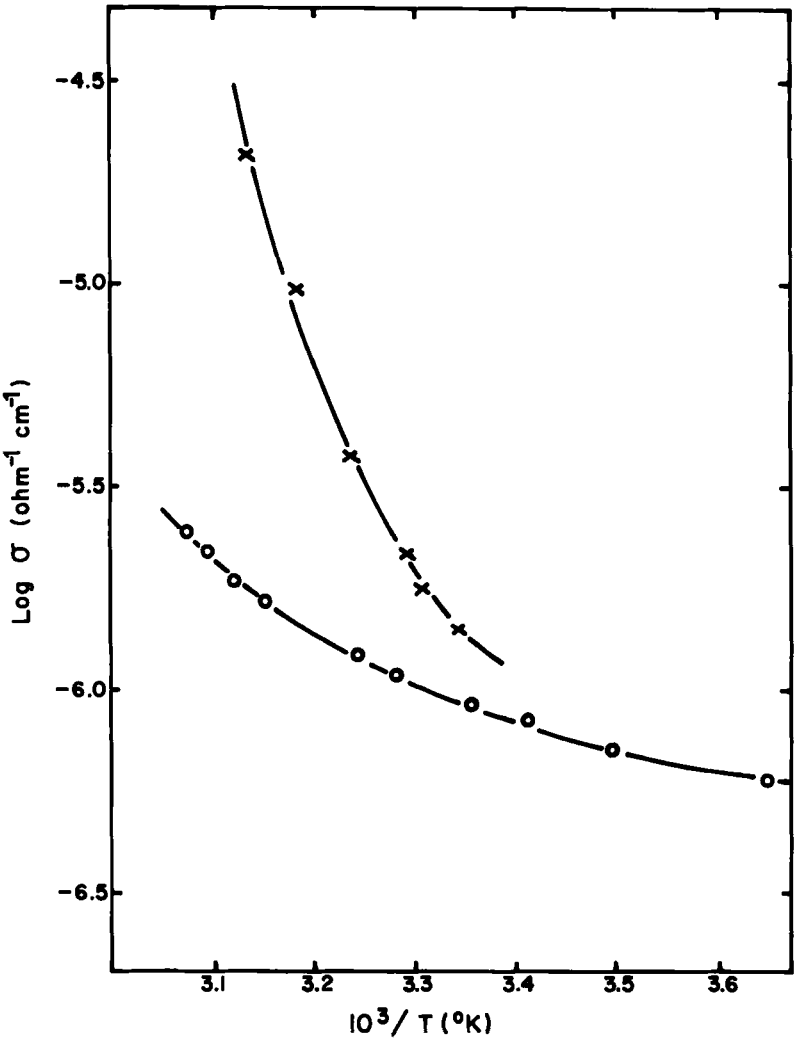

FIGURE 2 Temperature dependent conductivity of $B_9K_2I_9 \cdot CHCl_3$, O; and $B_9Na_2I_9 \cdot CHCl_3$, X.

transport. From the temperature dependence of the ac conductivity, there are several cases in which there are changes in slope of the log σ vs 1/T plot. Figures 2 and 3 illustrate examples from the CIMI and BIMI series. No enthalpic phase transitions are observed by differential scanning calorimetry (Perkin-Elmer DSC2C) in the temperature range in question. A likely cause of this change in slope is the dual nature of the conduction process and the inherently different activation energies of the ionic and electronic process. However, several com-

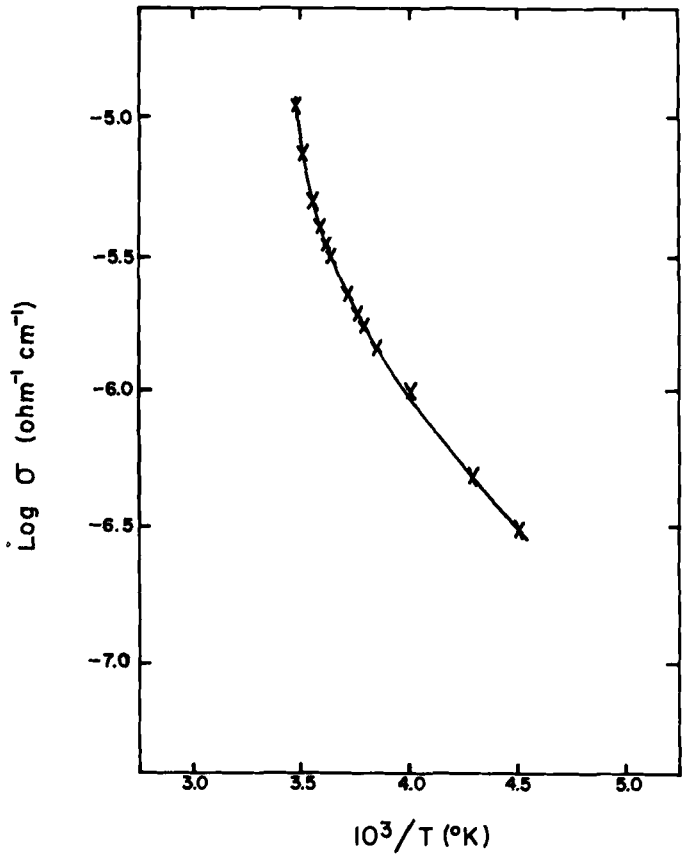

FIGURE 3 Temperature dependent conductivity of C_4RbI_4.

plexes in the series show a linear temperature dependence, with no evidence for low and high temperature processes (Figure 4).

Considerable additional variation in structure of the organic, cationic, and anionic portions of these lattices are possible. Table III lists some preliminary conductivity data (room temperature only) on substituted benzophenone complexes and complexes of the mixed halogenides as anions. For these complexes, the stoichiometries should be considered approximate, since little work was performed on purity-property relationships.

Evidence for ionic conductivity

Both BIMI and CIMI complexes clearly have an ionic component to their conductivity. Under the influence of an applied dc field (Figure

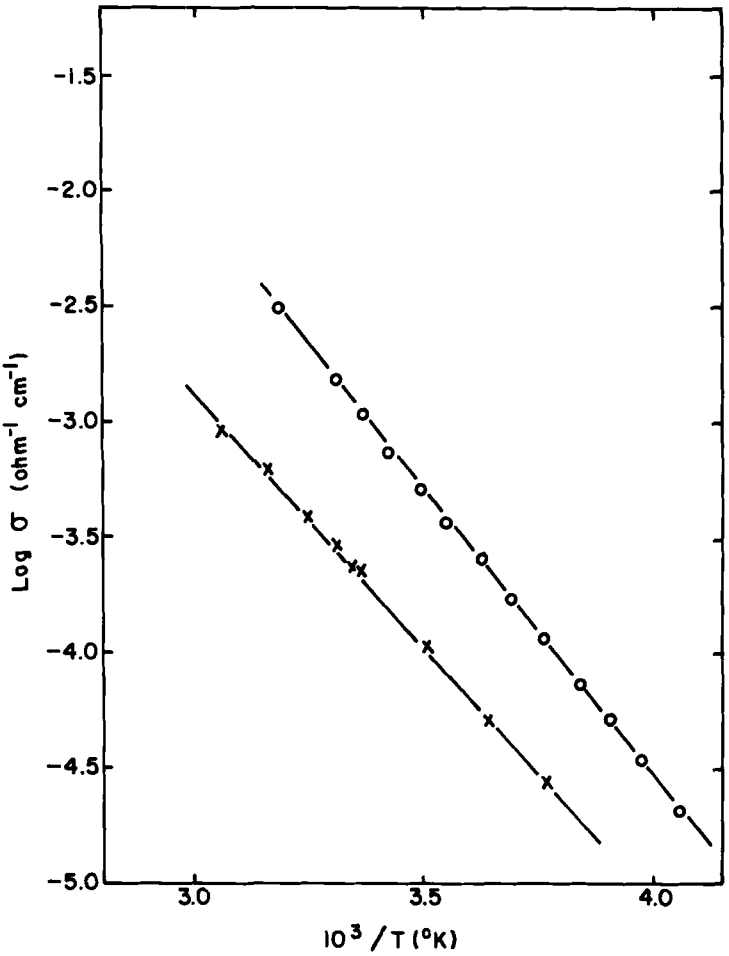

FIGURE 4 Temperature dependent conductivity of $B_9(NH_4)_2I_9 \cdot CHCl_3$ (two different crystals).

5), the dc conductivity of CIMI complexes decreases with time and then levels off. Examination of the electrodes show clear indications of electrochemical events—both platinum electrodes become coated with thin (insulating) layers which limit the conductivity.

Faradaic experiments gave clear qualitative evidence for mass transport, but the degree of transport changed from 5 to 70% from sample to sample and with current density in an irreproducible manner. Again, evidence for electrode products was observed at both anode and cathode. Similar results have been reported for polymer–iodine complexes having an ionic component to their conductivity.[12] Another

TABLE III

AC (1 KHz) conductivity at 25°C of some additional BIMI complexes

Complexes	σ (Ω^{-1} cm^{-1})
$B_{13}LiClI_5$	10^{-6}
$B_9K_2Br_2I_7$	10^{-4}
(Di-2-pyridyl ketone)$_9Rb_2I_9 \cdot CHCl_3$	10^{-6}
(4-methoxy-B)$_9(NH_4)_2 \cdot I_9CHCl_3$	10^{-6}
(4,4'-dimethylamino-B)$_9Rb_2I_9 \cdot CHCl_3$	10^{-6}

approach to examining ionic behavior in these complexes was to use a proton injecting (and electron blocking) electrode.

Zirconium phosphate is known to be a protonic conductor with a $\sigma_{protonic} \sim 10^{-1}\ \Omega^{-1}\ cm^{-1}$.[11] On the assumption that $BINH_4I$ could function as a solid electrolyte transporting protons by a Grotthius type mechanism among the ammonium ions in the columnar array of the

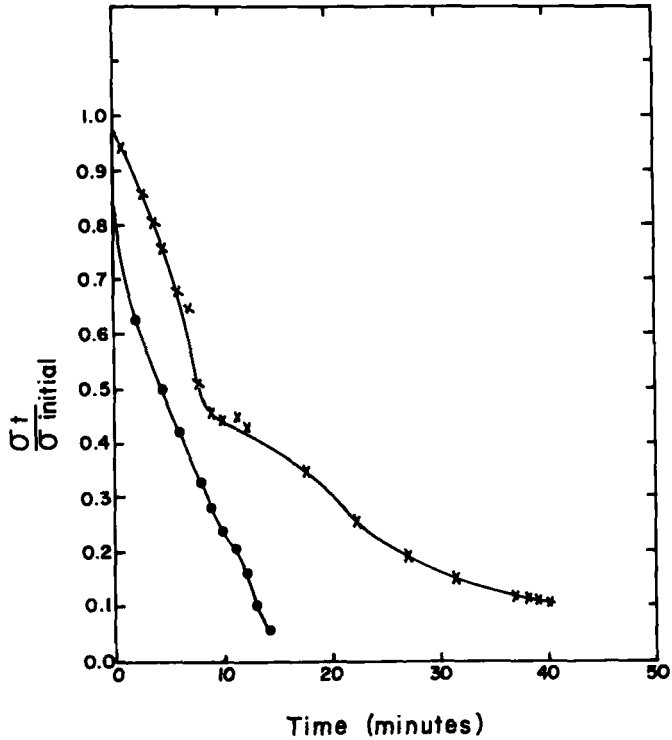

FIGURE 5 Change in conductivity with time upon passing a constant current of 1 μa through C_4RbI_4 crystal, O; 5 ma through $C_6LiI_7 \cdot CHCl_3$ crystal, X.

benzophenone channel, the ionic conductivity was measured for such a cell. σ_{ionic} (average of 5 cells) was found to be $\sim 7.1 \pm 0.4 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, whereas the average σ_{total} (ac) for these five cells was $\sim 6.2 \pm 0.3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$. These same cells functioned as batteries showing an open circuit voltage of ~0.43 to 0.55V at current densities of 3.1 to 3.6 $\mu A cm^{-2}$.

CIMI and BIMI samples can be utilized to construct lithium or sodium batteries by pressing a compaction of the solid against alkali metal ribbons or sheets. A thin film of lithium or sodium iodide is formed and BIMI or CIMI function as an electrode, presumably injecting I^- or $(I_n)^-$ into the electrolyte. Figure 6 shows the open circuit volt-

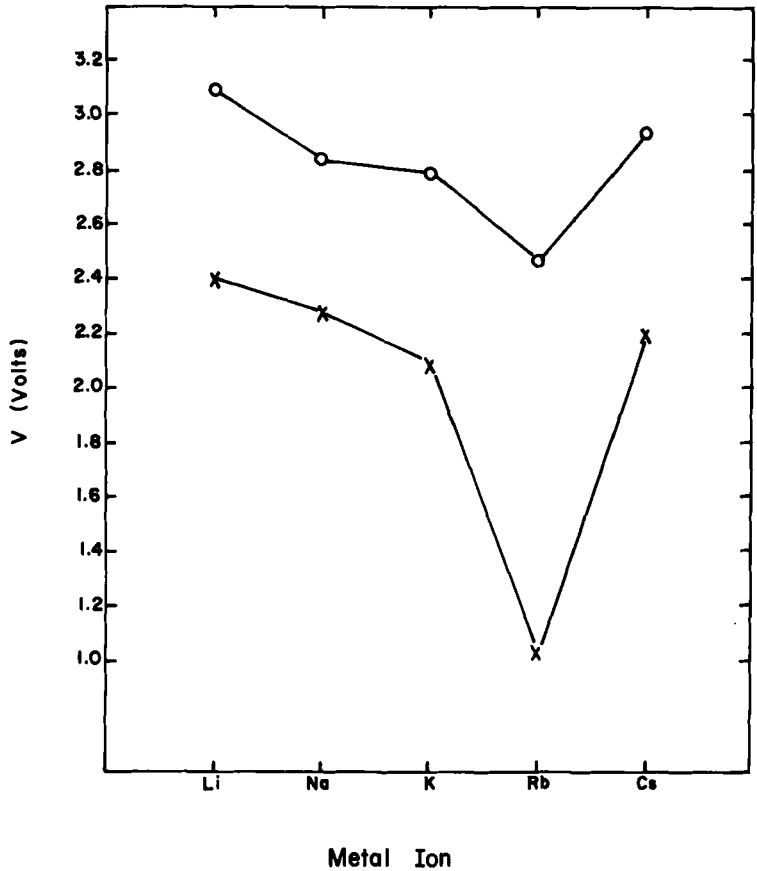

FIGURE 6 Open circuit voltages of Li/BIMI batteries, O; and of Na/CIMI batteries, X; as a function of the nature of the cation M in the complex.

ages of such batteries as a function of the metal ion in the complexes.

It is clear that conduction in these complexes is of a mixed electronic–ionic type, but the precise contributions of both processes has not as yet been determined.

Seebeck effect

A preliminary study of the Seebeck effect was also carried out in CIMI complexes in the hope of unravelling mechanistic questions. The results for C_4RbI_4 are shown in Figure 7. The behavior unfortunately does not allow for a differentiation between electronic and ionic processes, although it does indicate that the majority carriers are either anionic and/or electrons.

Mechanistic considerations

It is tempting to advance a single mechanism to explain the properties of both BIMI and CIMI complexes. Turning to crystal structure con-

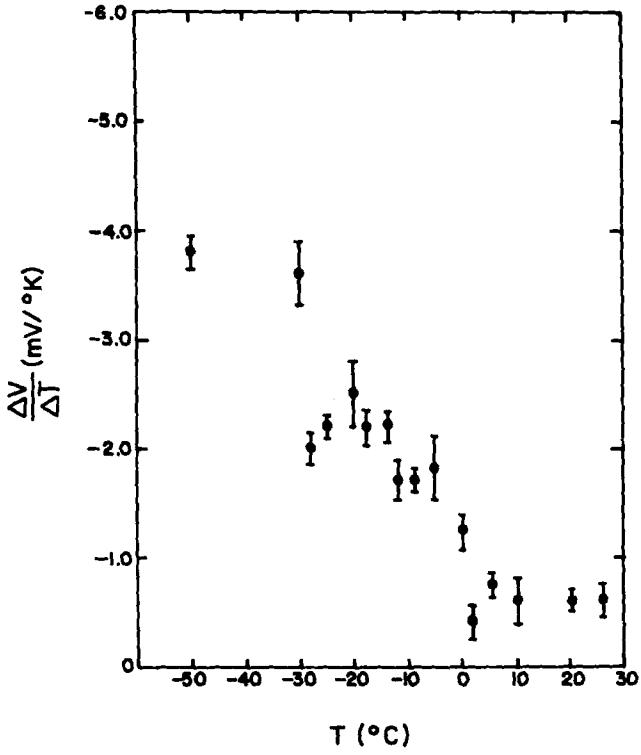

FIGURE 7 Thermoelectric power of C_4RbI_4 as a function of temperature.

siderations, there are a group of BIMI complexes which share a disordered cation stack (Na, K, NH_4 and possibly Rb). For example, in the K^+ complex, out of every three sites in the cation stack, only two are occupied by K^+ and the third site may (or may not) contain solvent molecules. A similarity, therefore, exists between these structures and typical fast-ion conductors where a hopping mechanism would allow for fast-ion transport. This view of the conduction process is, on the other hand, inconsistent with the structural evidence of BILiI in which the Li^+ is tetrahedrally coordinated. Since BILiI shows conductivity characteristics which are very similar to the other members of the series, it is more likely that the transport in these systems occurs primarily in the polyiodine chain. Further, the negative Seebeck coefficient tends to preclude a cationic fast-ion conduction mechanism. Unfortunately the CIMI series crystal structures have not as yet been determined. The stoichiometry C_4MI_4 suggests a tetrahedrally coordinated cation and an iodine stack probably made up of I_3^- and I_5^- units. Thus we tend to favor a hopping mechanism in the iodine chain as the most likely conduction process.

Evidence for ionic conductivity in single crystals of iodine doped with an electron donor, such as *p*-phenylenediamine (PPD), has been presented by Kommandeur and co-workers.[13] The conduction mechanism suggested involves the formation of I_2^- ions followed by an equilibrium forming I_3^- and I^- ions. These studies also report breaks in the conductivity-temperature curves, similar to those found in Figures 2 and 3 of this work, interpreted as the freezing in of ionization equilibria.

The most convincing evidence for ionic transport by iodine ion hopping is the Faradaic evidence cited by Kommandeur *et al;*[13] here the charge transport in PPD doped iodine was convincingly shown to be largely ionic in character. The electrolysis experiments conducted on BIMI and CIMI are indicative of a much more mixed ionic–electronic process. Indeed, if electronic processes can go on in these crystals at all, they must be occurring predominantly in the polyiodine sub-lattice.

In conclusion, conductivity in BIMI and CIMI appears to be associated almost exclusively with the iodine sub-lattices. Both ionic and electronic transport occur. The high ionic conductivities observed at room temperature are leading us to investigate in more detail structural variations and conductivity mechanisms in this type of complex.

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