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Preliminary communication

ANOMALOUS TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY OBSERVED IN MIXED-VALENCE BIFERROCENIUM SALTS

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Summary

The plot of the logarithm of electrical conductivity (σ) vs. $1/T$ for the mixed-valence type salt 1′,1‴-diethylbiferrocenium$^+$ I_3^- displays two inflection points at temperatures around 230 and 275 K. The temperature dependence is concluded to be connected with the valence-state change of the salt with rising temperature, from a trapped-valence state to an averaged-valence one, while the triiodide salt of unsubstituted biferrocene shows a normal linear-relationship between log σ and $1/T$.

Much of the interest in mixed-valence compounds is connected with the attempts to synthesize new electrically semiconducting and conducting materials. In fact, it is noticed that mixed-valence plays an essential role in the high conductivities of "synthetic metals" such as partially-oxidized platinum salts and charge-transfer complexes of TCNQ analogues [1].

In the field of mixed-valence ferrocene chemistry, on the other hand, recent research has revealed that the monocation salts of binuclear ferrocenes can be classified into two categories, trapped-valence and averaged-valence types, by means of Mössbauer spectroscopy [2, 3]. The compounds of the former type (e.g. biferrocenium$^+$ I_3^- [4]) have two kinds of valence state of the iron atoms, corresponding to iron(II) and iron(III), while those of the latter type (e.g. biferrocenylenium$^+$ I_3^- [4]) have only an equivalent state of the iron atom averaging over the two kinds of valence state on the Mössbauer time scale, as a result of strong Fe—Fe interactions.

In this article, we report the electrical conductivity behaviour of some of the salts of biferrocene and 1′,1‴-diethylbiferrocene in order to ascertain whether or not the trapped- and averaged-valence states have a different influence on the

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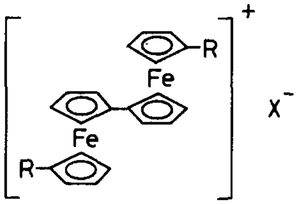
electrical conductance of the system. 1',1'''-Diethylbiferrocenium$^+$ I_3^- (II) is a very suitable compound for this purpose, because the salt is known to change its valence state from a trapped-valence state to an averaged-valence one with increase of temperature [5].

Biferrocenium$^+$ I_3^- (I) and 1',1'''-diethylbiferrocenium$^+$ I_3^- (II) were prepared by the method described in the literature [4, 5]. 1',1'''-Diethylbiferrocenium$^+$ $(TCNQ)_2^{-\cdot}$ (III) was synthesized according to the procedure used for the preparation of 1',1'''-dipropylbiferrocenium$^+$ $(TCNQ)_2^{-\cdot}$ [5]. The samples compressed at a pressure of 6000 kg/cm^2 were set in a Helitran liquid transfer refrigerator (Air Products) and their electrical conductivities were measured in vacuo (ca. 10^{-3} Pa), by using the two-probe d.c. method. Contacts were made with gold paste (Tamura Kaken L-100).



Compound	R	X^-
I	H	I_3^-
II	C_2H_5	I_3^-
III	C_2H_5	$(TCNQ)_2^{-\cdot}$

Cowan and Kaufman have already reported that biferrocenium$^+$ picrate$^-$ behaves as a semiconductor, while ferrocene and ferrocenium$^+$ picrate$^-$ are virtual insulators [6, 7]. In the present work, it was found that biferrocenium$^+$ I_3^- (I) is also semiconducting in the 197—313 K range. This salt is known to be of the trapped-valence type in the 4.2—300 K range, by means of Mössbauer spectroscopy [4]. The electrical conductivity data of I are listed in Table 1 together with the data of the other compounds. The specific electrical conductivity (σ) of I at 300 K (Table 1) was recognized to be more than five orders of magnitude larger than that of biferrocene. While ferrocenium$^+$ I_3^- is known to have a relatively large σ value (1×10^{-9} S cm^{-1} at room temperature) compared with ferrocene itself and other ferrocenium salts such as ferrocenium$^+$ picrate$^-$ [7], the σ value of I is still much greater than that of ferrocenium$^+$ I_3^-.

TABLE 1

CONDUCTIVITY DATA

Compound	σ at 300 K (S cm^{-1})	E (eV)
Biferrocene	$<10^{-11}$	
I	4.8×10^{-6}	0.35
II	1.0×10^{-5}	0.20 (275—309 K) 0.25 (193—233 K)
III	1.5	0.064

The temperature dependence of σ obtained for I is shown by line (a) of Fig. 1; the plot of log σ vs. $1/T$ is approximately linear, that is, the σ value of I follows the equation:

$$\sigma = \sigma_0 \exp(-E/kT)$$

which is observed for most organic and inorganic semiconductors, where E is the activation energy for electrical conduction, and σ_0 is a constant.

On the contrary, the log σ vs. $1/T$ plot for II was not straight, as shown by line (b) in Fig. 1. The log σ value increased in a manner similar to that of I, until the temperature reached about 230 K. However, the slope of the plot increased to some extent above this temperature, and decreased again above ca. 275 K, that is, two inflection points around 230 and 275 K were observed in line (b). The temperature dependence of the σ value was reproduced on lowering the temperature.

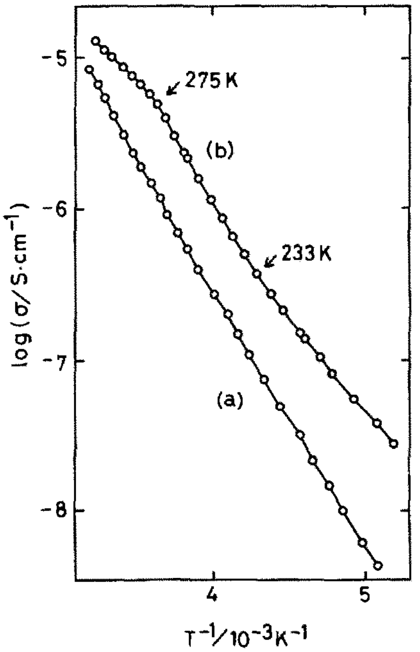


Fig. 1. Variation of electrical conductivity with inverse temperature. (a) Biferrocenium$^+$ I_3^- (I); (b) 1′,1‴-diethylbiferrocenium$^+$ I_3^- (II).

This anomalous feature of the log σ vs. $1/T$ plot seems to be ascribable to the temperature-dependent valence state of II. Mössbauer spectroscopy has revealed that the valence state of II changes from a trapped-valence state to an averaged-valence one with increase of temperature, and that the change starts at about 220 K and the transition from the trapped- to the averaged-valence state finishes completely near 275 K [5]. It can therefore be presumed that the two inflection points around 230 and 275 K observed in this work correspond to the starting and ending points of the change from the trapped- to the averaged-valence state, respectively. In addition, line (b) shows that the E value for the salt in the averaged-valence state is smaller than that in the trapped-valence state. Therefore, the averaged-valence state is favourable to the electrical conduction compared with the trapped-valence state. The *E* values of the averaged- and trapped-valence states were calculated to be 0.20 and 0.25 eV, respectively, by using the data in the temperature range of 275—309 K for the former and those of 193—233 K for the latter. The σ value of II at 300 K (1.0×10^{-5} S cm^{-1}) was about two-fold that of I at the same temperature.

The 1′,1‴-diethylbiferrocenium salt with tetracyanoquinodimethane (TCNQ) (III) gave an extremely large σ value (1.5 S cm^{-1} at 300 K). As to the temperature dependence of σ, III, like I, followed the above equation as well (125—300 K). An *E* value of 0.064 eV was obtained for III, which is less than one-third of the *E* value for II being in the averaged-valence state. Since 1′,1‴-dipropylbiferrocenium$^+$ $(TCNQ)_2^{\dot{-}}$ is known to be in an averaged-valence state that does not depend on the temperature [5], there is a possibility that III is also a salt of the averaged-valence type. However, it seems that the high conductivity of III is due to the presence of $(TCNQ)_2^{\dot{-}}$ rather than to the valence state of the iron atoms, because ferrocenium$^+$ $(TCNQ)_2^{\dot{-}}$ has been reported [8] to exhibit an electrical conductivity (4.2 S cm^{-1} for a single crystal at room temperature) comparable to that of III.

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