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Highly Conductive TCNQ Salts of Copper(II) Complexes with 2,2′-Bipyridine and 1,10-Phenanthroline

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The synthesis of new materials exhibiting high electrical conductivity is currently of great experimental and theoretical interest [1]. 7,8,8,8-Tetracyanoquinodimethane (TCNQ) has a large potential capacity to make highly conductive materials with donar molecules. Some transition metal complexes with TCNQ have been anticipated to have possible high conductivity [2], but no systematic studies have been carried out except for Pt(II)–TCNQ complexes [3]. In the present investigation, we have prepared some Cu(II) complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) incorporating $TCNQ^-$ as anions, and found that they are a new class of highly conductive materials.

The TCNQ salt of mono(bpy)copper(II), $Cu(bpy)(TCNQ)_2$, was prepared by adding a solution of $Cu(bpy)(NO_3)_2 \cdot 3H_2O$ (50 mg) in deaerated water (7 ml) to a solution of Li(TCNQ) (53 mg) in deaerated water (10 ml) with vigorous stirring under a nitrogen atmosphere. Black powders precipitated were collected on a filter, washed with water and dried *in vacuo*. $Cu(bpy)_2(TCNQ)_2$, $Cu(phen)(TCNQ)_2$ and $Cu(phen)_2(TCNQ)_2$ were prepared with the same procedure as for $Cu(bpy)(TCNQ)_2$ by use of the appropriate nitrate, $Cu(bpy)_2(NO_3)_2 \cdot H_2O$, $Cu(phen)(NO_3)_2 \cdot H_2O$ or $Cu(phen)_2(NO_3)_2 \cdot H_2O$, in the place of $Cu(bpy)(NO_3)_2 \cdot 3H_2O$.

The electrical conductivity was determined on the compressed pellets by means of van der Pauw's four-probe method [4]. Figures 1 and 2 show the semilogarithmic plot of the electric conductivity against reciprocal temperature. All of the complexes exhibit the characteristic property of semiconductors. The conductivity σ increases with increasing temperature in accordance with the following equation:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (1)$$

where E_a is the activation energy for the conductivity. The values of E_a are given in Table I along with σ at 300 K and σ_0.

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TABLE I. Conductivity σ at 300 K, Conductivity σ_0 at Infinite Temperature and Activation Energy E_a of Cu(II)–TCNQ Complexes.[a]

Complex	σ/Ω^{-1} cm^{-1}	σ_0/Ω^{-1} cm^{-1}	E_a/eV
$Cu(bpy)(TCNQ)_2$	1.6	6.3	0.036
$Cu(phen)(TCNQ)_2$	1.9	7.9	0.039
$Cu(bpy)_2(TCNQ)_2$	0.040	0.36	0.054
$Cu(phen)_2(TCNQ)_2$	0.23	2.2	0.057

[a]Satisfactory carbon, hydrogen, nitrogen and copper analyses have been obtained on all the complexes.

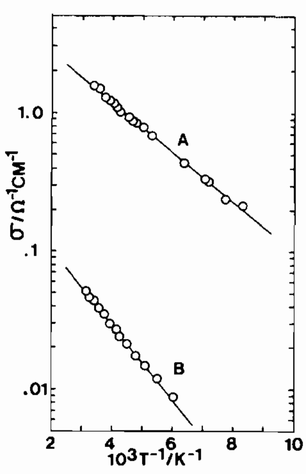

Fig. 1. Temperature dependence of electric conductivity σ (Ω^{-1} cm^{-1}) of $Cu(bpy)(TCNQ)_2$ (A) and $Cu(bpy)_2(TCNQ)_2$ (B).

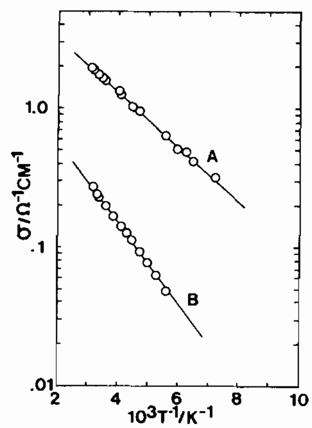

Fig. 2. Temperature dependence of electric conductivity σ (Ω^{-1} cm^{-1}) of $Cu(phen)(TCNQ)_2$ (A) and $Cu(phen)_2(TCNQ)_2$ (B).

The conductivities of Cu(bpy)$(TCNQ)_2$ and Cu(phen)$(TCNQ)_2$ are comparable to those of $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ ($4\ \Omega^{-1}\ cm^{-1}$) [1] and partially oxidized phthalocyanine complexes, $MPcI_x$ (for example, $CuPcI_{1.71}$ has $4.2\ \Omega^{-1}\ cm^{-1}$) [5], which are well known as typical highly-conducting metal complexes. Compressed pellets usually exhibit much smaller conductivities than those of the corresponding single crystals by factors of 10–100, and the E_a values of compressed pellets are much larger than the corresponding single-crystal values: for example, $\sigma = 4\ \Omega^{-1}\ cm^{-1}$ and $E_a = 0.03$ eV have been reported for polycrystalline (quinolinium)$(TCNQ)_2$, but $\sigma = 100\ \Omega^{-1}\ cm^{-1}$ and $E_a \cong 0$ for the single crystal [6]. These strongly suggest that the single crystals of the Cu(II)–TCNQ complexes should have still better electric properties, but unfortunately we have not succeeded in obtaining the single crystal as yet.

The Seebeck coefficient against copper was found to be equal to about $-50\ \mu V/K$ for every complex. The negative sign indicates that the complexes are n-type semiconductors: their high conductivities are due to electrons migrating in the TCNQ stacks.

Cu(II) complexes usually take a coordination number of four or more. Therefore, the chemical composition of Cu(bpy)$(TCNQ)_2$ and Cu(phen)$(TCNQ)_2$ indicates that the TCNQ anions should coordinate to copper atoms in the complexes. This coordination facilitates charge transfer interaction between TCNQ and Cu(II) ions to enhance electric conductivity.

As exemplified above, most of the highly conductive metal complexes already found belong to the category of mixed valent complexes, in which the central metal ions are partially oxidized by halogen. As distinct from these, the Cu(II)–TCNQ complexes studied in the present investigation are a new class of highly conductive materials.

References

1 H. J. Keller (ed.), 'Low-Dimensional Cooperative Phenomena', Plenum Press, New York (1975).

2 L. R. Melby, R. J. Harder, W. R. Hertler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc., 84,* 3374 (1962); D. S. Acker and D. C. Blomstrom, *Chem. Abst., 63,* 549 (1965).

3 H. Endres, H. J. Keller, W. Moroni, D. Nöthe and Vu Dong, *Acta Cryst., B34,* 1882 (1978), and references therein.

4 L. J. van der Pauw, *Philips Res. Rept., 13,* 1 (1958).

5 J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman and T. J. Marks, *J. Am. Chem. Soc., 99,* 286 (1977).

6 W. J. Siemons, P. E. Bierstedt and R. G. Kepler, *J. Chem. Phys. 39,* 3523 (1963); V. Walatka, Jr. and J. H. Perlstein, *Mol. Cryst. Liq. Cryst., 15,* 269 (1971).