

Electrical Properties of Some Divalent Transition Cupferrone Complexes

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From the temperature dependence of the electrical resistivity of the divalent Mn, Co, Ni, Cu and Zn cupferrone complexes it is concluded that these compounds behave as semiconductors. It is also found that the charge transference (CT) energy as calculated from the UV absorption CT bands is always larger than that derived from the electrical resistivity.

Cupferrone (nitrosophenyl hydroxylamine) is a well known chelating agent with many applications in quantitative and qualitative analysis. From the IR, UV and visible spectra of selected divalent cupferrone complexes^{1, 2} it was evident that these complexes are of the charge transfer type. Therefore we decided to measure the electrical conductivities of these compounds and to compare the obtained information with the charge transfer bands obtained in the UV absorption spectra.

Experimental

All chemicals used were A. R. grade, B. D. H. Label. The ammonium salt of cupferrone was ob-

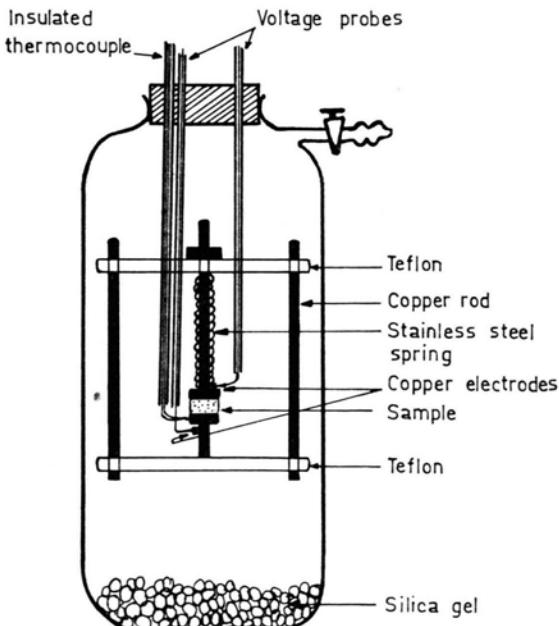


Fig. 1. The Electrical Conductivity Cell.

tained from "Renal" Finomvegyszergyar. The different metal cupferrone complexes were prepared and analysed as previously reported¹. The UV absorption spectra of the different compounds were measured in dioxan using a Unicam Sp 800 recording spectrophotometer. The D.C. resistivities of the samples were measured on discs of 13 mm diameter and 3–5 mm thickness, prepared under a pressure of 12,000 kg/cm². The measuring cell is shown in Figure 1. The cell was enclosed in an evacuated pyrex tube containing silica gel to keep the cell dry. A temperature controlled electric furnace was placed around the device. The current was measured with a VA-J-52 electrometer.

Results and Discussion

At room temperature, the electrical resistivities (ρ) of the investigated compounds were found to be of the order 10^{13} – 10^{15} Ω cm. Linear relationships were obtained between $\log \rho$ and $1/T$. The thickness of the samples had no effect on the measured resistivities, as is exemplified in Figure 2.

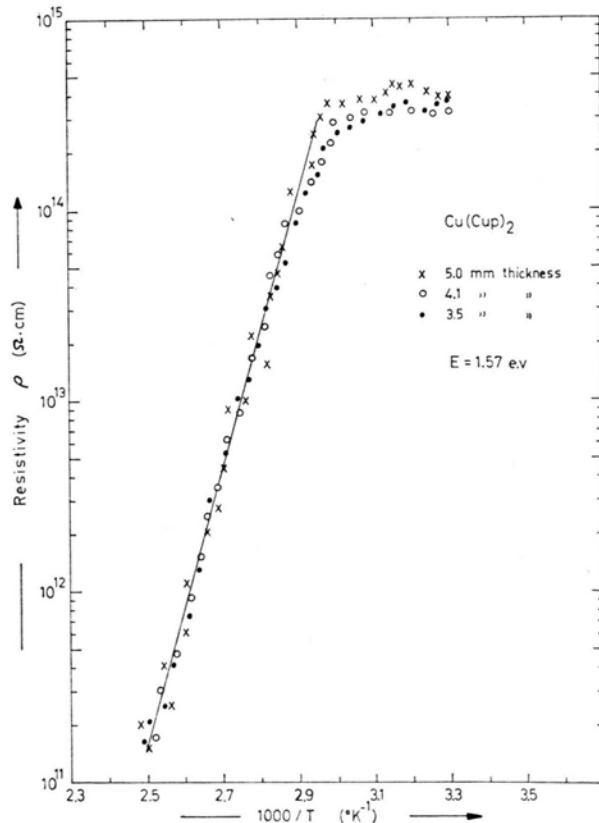


Fig. 2. Resistivity of $\text{Cu}(\text{cup})_2$.

This proves that these compounds are intrinsic semiconductors obeying the relation (3):

$$\varrho = \varrho_0 \exp \{E/kT\}$$

where E is the activation energy of electrical conduction.

The experimental values of ϱ_0 and E are given in Table 1.

In a previous work¹ it was found that the studied compounds are charge transfere (CT) complexes. The electronic absorption bands corresponding to

Table 1. Activation and charge transfere energies for the different cupferrone compounds.

Complex	ϱ_0 Ωcm	λ_{CT} nm	E_{CT} e.V.	E e.V.
Mn(cup) ₂	1.2×10^9	307	4.30	1.15
Co(cup) ₂	8.1×10^9	275	4.35	1.75
Ni(cup) ₂	7.0×10^9	257	4.70	1.30
Cu(cup) ₂	6.1×10^9	255	4.62	1.57
Zn(cup) ₂	0.25×10^9	305	4.32	2.01

¹ A. H. Abou-El Ela, F. M. Abdel-Kerim, H. H. Afifi, and H. F. Aly, Z. Naturforsch. **28b**, 610 [1973].

² A. H. Abou-El Ela and H. H. Afifi, Z. Naturforsch. **29a**, 719 [1974].

³ Y. Ocamoto and W. Brenner, *Organic Semiconductor*, Reinhold, New York 1964.

the CT transitions in dioxan solution at room temperature are given in Table 1, together with their CT energies. If the band model for intrinsic semiconductors is extended to charge transfer complexes, one may expect coincidence of the energy gap ($\varepsilon = 2E$) with the charge transfer energy (E_{CT}). However, this may not be valid if the charge carrier is not produced directly through such an excitation process. Kuroda et al.^{4,5} put

$$\varepsilon = E_{\text{CT}} - \delta$$

where δ was found to be in the order of 1 eV for trinitrobenzene complexes. In the present investigation, the δ values encountered were between 0.3 and 2.1 eV. Since E_{CT} was taken in dioxan, the δ -values observed may be mainly due to the medium effect.

Acknowledgement

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⁴ H. Kuroda, M. Kabayashi, M. Kinoshita, and S. Takamoto, J. Chem. Phys. **36**, 457 [1962].

⁵ H. Kuroda, K. Yoshihara, and H. Akamatu, Bull. Chem. Soc. Japan **35**, 1604 [1962].