BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2322—2325 (1971) [Vol. 44, No. 9

Electron-transfer Phenomena in Some Three-dimensional Complex Thiocyanate Semiconductors

Masao HASHIMOTO,* Shichio KAWAI, and Ryôiti KIRIYAMA
Institute of Scientific and Industrial Research Osaka University, Suita-shi, Osaka

(Received February 3, 1971)

Measurements of the electrical conductivity, the photoconductivity, the electronic spectra, and the magnetic susceptibility were carried out with powder samples of $CuHg(SCN)_4$ and $(Cu_xZn_{1-x})Hg(SCN)_4$. The electrical conductivity (σ) of the compounds has been found to obey the usual exponential equation of electrical conduction, $\sigma=\sigma_0\exp(-E_t/KT)$. It was found that there was a close relation between the photocurrent spectra and the electron-transfer bands in both compounds. In terms of the band model, the nature of the semiconductivity and the photocurrent in their intrinsic region are discussed in connection with the electron-transfer phenomena.

The $M(II)Hg(SCN)_4$ series of compounds has been known for many years.[1)] In $ZnHg(SCN)_4$ the zinc ion is surrounded by a slightly distorted tetrahedron of four nitrogen atoms,[2–4)] while green $CuHg(SCN)_4$ has a quite different structure,[5)] in which copper ions are surrounded octahedrally by four nitrogens and two sulfurs. However, their polymeric structure are similar. The structure of mixed crystals of $(Cu_xZn_{1-x})Hg(SCN)_4$ composition, with x smaller than 0.22, is also isomorphous with $ZnHg(SCN)_4$, and their color changes from pale pink to dark purple depending on the relative concentration of Zn^{2+} and Cu^{2+}.[6)] The color of the mixed crystals is caused by the intense electron-transfer bands at about 330 and 550 mμ; green $CuHg(SCN)_4$ has also an electron-trasfer band at about 430 mμ.[6)]

The present experiments were undertaken in order to elucidate the relation between the electron-trasfer phenomena and the semiconduction in inorganic complex salts with a three-dimensional framework. Braterman *et al.* have investigated the electrical conductivity of some complex cyanides and found no equality between the activation energy for the semiconduction and the optical absorption energy of the electron-transfer band.[7)] Our present results, however, will show that the mechanism of intrinsic semiconduction in $CuHg(SCN)_4$ and $(Cu_xZn_{1-x})Hg(SCN)_4$ is closely related to the nature of their electron-transfer bands.

Experimental

Materials. The green compound, $CuHg(SCN)_4$, was prepared by mixing aqueous solutions of copper(II) sulfate and potassium mercury tetrathiocyanate. The precipitate was filtered off, washed with cold water, and dried at about 100°C in an air thermostat. The crystalline powder of $ZnHg(SCN)_4$ was obtained by a similar method of preparation. The purple mixed compounds $(Cu_xZn_{1-x})Hg(SCN)_4$ were prepared by adding mixed aqueous solutions of zinc and copper sulfate to aqueous solutions of potassium mercury tetrathiocyanate. The mole fractions of the copper ion in the products were assumed to be the same as those of the starting mixed solutions. All the materials thus obtained were identified by means of an X-ray diffractometer using Cu$K\alpha$ radiation.

Electrical Conductivity. The electrical conductivity measurements were carried out in a vacuum with pellets of the compounds. The electrode assembly used for our measurements is shown in Fig. 1. The electrical current at a constant field strength was measured with a Toa Dempa Model PM 18 microvolt-ammeter, capable of measuring currents down to 10^{-12} A. The field strengths were in the region between 100 to 450 V/cm. In order to prevent thermal decomposition under these experimental conditions, the measurements were carried out at temperatures below about 420°K.

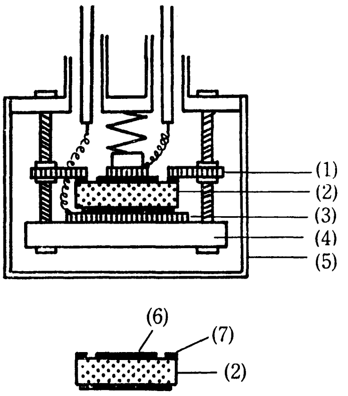

Fig. 1. Electrode assembly.

(1) Copper ring(guard electrode), (2) Specimen, (3) Copper plate, (4) Steatite, (5) Shield box, (6) Central electrode (evapolated gold), (7) Guard electrode(evapolated gold)

For the measurements of the photocurrent, a DC electric field was applied between the guard electrode and the central electrode of a pellet (Fig. 1). The surface between these two electrodes was then exposed to light. The photoconductivity was excited by a monochromatic light from a quartz prism monochrometer. A xenon-lamp was employed as the light source. The photocurrent was measured with the microvolt-ammeter mentioned above at field strengths ranging from 100 to 450 V/cm. The measurements were carried out at room temperature over the 380—1000 mμ spectral region. On the assumption that the photoconductivity is

---

* Present address: Department of Chemistry, Faculty of Science, Kobe University, Rokkodai-cho, Nada-ku, Kobe.

1) A. Rosenheim and Cohn, *Z. Anorg. Allg. Chem.*, **27**, 280 (1901).

2) W. Stahl and M. Staraumamis, *Z. Phys. Chem.* (Leipzig), **193**, 121 (1943—1944).

3) J. W. Jeffery, *Nature*, **159**, 610 (1947).

4) J. W. Jeffery and K. M. Rose, *Acta Cryst.*, **B24**, 653 (1968).

5) A. Korczyski, *Roczniki Chem.*, **36**, 1539 (1962).

6) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 823 (1965).

7) P. S. Braterman, P. B. P. Phipps, and R. T. P. Williams, *J. Chem. Soc.*, **1965**, 6164.

linearly related to the intensity of the light, the spectral response of photocurrent was determined; that is, the measured values of the photocurrent were divided by the relative intensity of the light.

Electronic Spectra. The diffuse reflectance (R_d), *i.e.*, the ratio of the quantity of light reflected by a powdered sample to the quantity of light reflected by magnesium carbonate, was measured with a Shimadzu Spectrophotometer, with its integration attachment, in the visible region. In presenting the data of the reflectance measurements, it seems convenient to use Kubelka and Munk's expression,[8] $f(R_d)=(1-R_d)/2R_d$, for there is a certain parallel between this quantity and the extinction coefficient of the crystal.

Magnetic Susceptibility. The magnetic susceptibility of $ZnHg(SCN)_4$ and $(Cu_xZn_{1-x})Hg(SCN)_4$ were obtained by the Gouy method in the temperature range from 118 to 300°K. The Gouy tube was calibrated with a standard aqueous solution of nickel(II) chloride. The diamagnetic corrections were estimated from the observed magnetic susceptibility of $ZnHg(SCN)_4$.

Results

Electrical Conductivity. The electrical conductivity (σ) of the compounds was found to obey the usual exponential relation to the temperature:

$$\sigma = \sigma_0 \exp\left(-E_t/kT\right),$$

where σ_0 is a constant and where E_t is the thermal activation energy for the electrical conduction. The values of the specific conductivity at about 373°K (σ_{373}) are listed in Table 1, together with the thermal activation energy (E_t) as calculated from $\log\sigma$ *vs.* $1/T$ plots. It can be seen in Fig. 2 that the $\log\sigma$ *vs.* $1/T$ plots of $(Cu_xZn_{1-x})Hg(SCN)_4$ give two strainght lines, with a break around 393°K. The two notations, E_t^e and E_t^i, in Table 1 denote the activation energy for the lower (extrinsic) and the upper (intrinsic) part of the break respectively.

TABLE 1. SPECIFIC CONDUCTIVITY AT 373°K (σ_{373}) AND THERMAL ACTIVATION ENERGY MEASURED WITH PELLETS OF $(Cu_xZn_{1-x})Hg(SCN)_4$

x	σ_{373} $\mho$/cm	E_t^e eV	E_t^i eV
0.0	1.8×10^{-14}	1.2	1.6
0.03	3.3×10^{-13}	1.1	1.6
0.1	7.7×10^{-12}	0.9	1.5
0.2	9.3×10^{-11}	0.6	1.6
1.0	$1\ \times10^{-10}$	—	2.2

It is noticeable that the conductivity of (Cu_xZn_{1-x})-$Hg(SCN)_4$ increases with an increase in the copper concentration. This shows that the increase in the copper concentration causes an increase in the number of charge carriers required for electrical conduction. Furthermore, the value of E_t^e gradually increases with a decrease in the copper concentration, while the value of E_t^i is almost constant, regardless of the relative concentrations of Cu^{2+} and Zn^{2+}. The lower activation energy (E_t^e) must result from the presence of lattice imperfections introduced by the doping of copper ions in the $ZnHg(SCN)_4$ lattice.

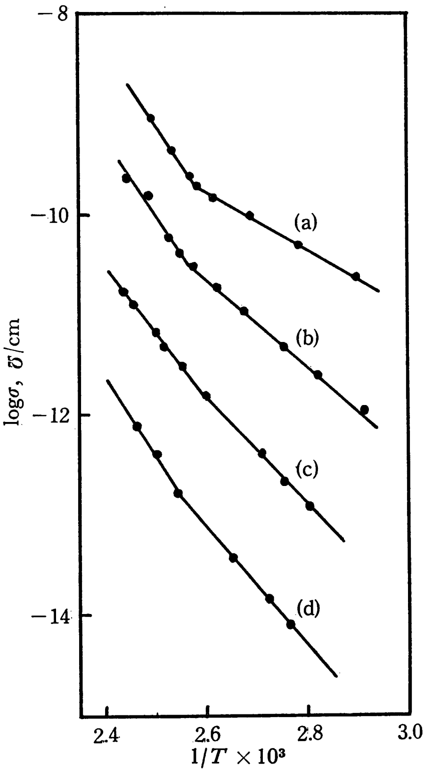

Fig. 2. Temperature dependence of specific conductivity (σ) of $(Cu_xZn_{1-x})Hg(SCN)_4$.
(a), x=0.2; (b), x=0.1; (c), x=0.03; (d), x=0

Electronic Spectra. In order to clarify the relation between the electrical conductivity and the depth of the characteristic color of $(Cu_xZn_{1-x})Hg(SCN)_4$, the electronic spectra of a series of the mixed crystals were measured in the visible region. Our results, obtained by diffuse reflectance (Fig. 3), are essentially in agreement with the spectrum of $(Cu_{0.14}Zn_{0.86})Hg(SCN)_4$ reported by Forster *et al.*[6] The band at 560 mμ has been identified as an electron-transfer band. It can be seen in Fig. 3 that the absorbance of the spectra

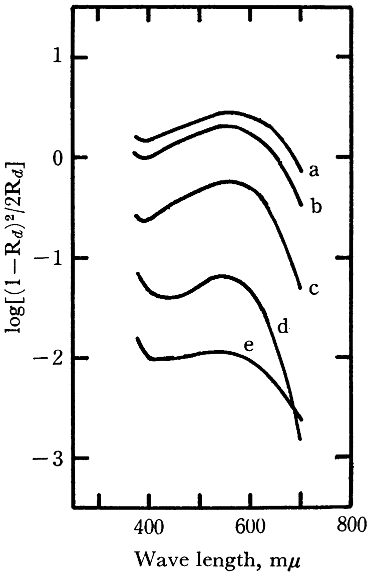

Fig. 3. Curves of $\log[(1-R_d)^2/2R_d]$ for $(Cu_xZn_{1-x})Hg\ (SCN)_4$
a), x=0.2; b), x=0.1; c), x=0.03; d), x=0.003; e), x=0.

---

[8] P. Kubelka and F. Munk, *Z. Tech. Phys.*, **12**, 593 (1931).

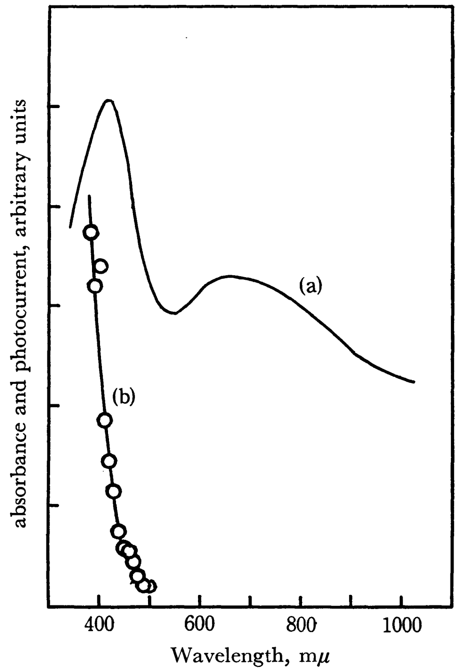

Fig. 4. Absorption and photocurrent spectra of $\mathrm{CuHg(SCN)_4}$. (a), absorption spectrum(Ref. 6); (b), photocurrent spctrum.

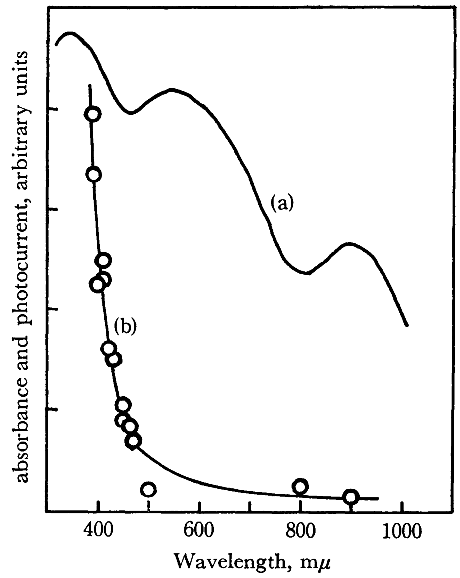

Fig. 5–a. Absorption and photocurrent spectra of $\mathrm{(Cu_xZn_{1-x})Hg(SCN)_4}$. (a), absorption spectrum of $\mathrm{(Cu_{0.14}Zn_{0.86})Hg(SCN)_4}$(Ref. 6); (b), photocurrent spectrum of $\mathrm{(Cu_{0.03}Zn_{0.97})Hg(SCN)_4}$.

increases with an increase in the copper concentration. This must be closely related to the fact that the electrical conductivity increases with an increase in the copper concentration.

Photocurrent Spectra. It seems to be of paticular interest that the inorganic complex salts, $\mathrm{CuHg(SCN)_4}$ and $\mathrm{(Cu_xZn_{1-x})Hg(SCN)_4}$, exhibit photoconductivity.

The photocurrent spectrum of $\mathrm{CuHg(SCN)_4}$ is shown in Fig. 4, together with its electronic spectrum. The threshold energy of the photocurrent (E_o) is about 2.8 eV, slightly larger than the energy of the absorption edge of the electron-transfer band with its absorption peak at about 430 m*μ*. Although the threshold energy of the photocurrent (E_o) does not agree well with the energy of the absorption edge of the band at about 430 m*μ*, the photoconductivity response found for $\mathrm{CuHg(SCN)_4}$ may be caused by the electronic transitions associated with the electron-transfer band at 430 m*μ*.

The photocurrent spectra of $\mathrm{(Cu_{0.03}Zn_{0.97})Hg(SCN)_4}$, $\mathrm{(Cu_{0.1}Zn_{0.9})Hg(SCN)_4}$, and $\mathrm{(Cu_{0.2}Zn_{0.8})Hg(SCN)_4}$ are shown in Fig. 5, together with the electronic spectrum. What is evident on comparing the photocurrent and electronic spectra is that the photocurrent spectra are closely related to the electron-transfer band with its absorption edge at about 450 m*μ*. It is noticeable that the threshold values of the photocurrents are almost equal to about 450 m*μ* (E_o=2.8 eV) for all these three compounds. However, the tail of the photocurrent spectrum of $\mathrm{(Cu_xZn_{1-x})Hg(SCN)_4}$ in the 450—600 m*μ* region seems to shift to the long-wavelength side, depending on the relative concentrations of $\mathrm{Cu^{2+}}$ and $\mathrm{Zn^{2+}}$. As well as the thermal activation energy for electrical conduction in the extrinsic region (E_t^e), these tails are associated with the electronic levels of several sorts of lattice imperfections, which were probably introduced by the doping of $\mathrm{Cu^{2+}}$ in the $\mathrm{ZnHg(SCN)_4}$ lattice.

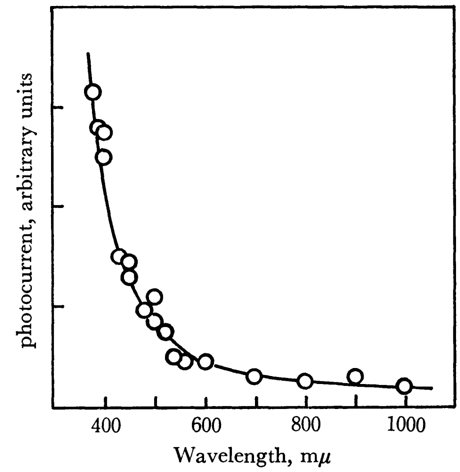

Fig. 5–b. Photocurrent spectrum of $\mathrm{(Cu_{0.1}Zn_{0.9})Hg(SCN)_4}$.

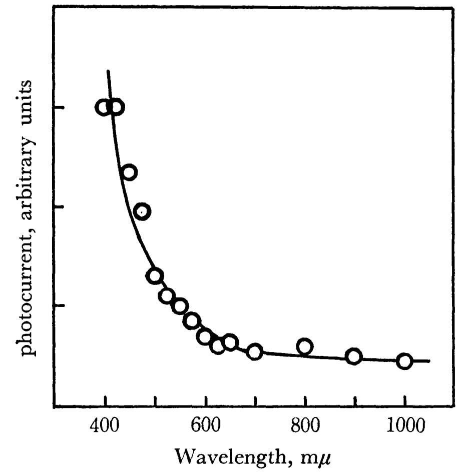

Fig. 5–c. Photocurrent spectrum of $\mathrm{(Cu_{0.2}Zn_{0.8})Hg(SCN)_4}$.

TABLE 2. EFFECTIVE MAGNETIC MOMENT (μ_{eff}) OF Cu(II) IN $(Cu_xZn_{1-x})Hg(SCN)_4$ LATTICE AT ROOM TEMPERATURE

Compound	μ_{eff} B.M.
$(Cu_{0.1}Zn_{0.9})Hg(SCN)_4$	2.0
$(Cu_{0.2}Zn_{0.8})Hg(SNC)_4$	1.9

Magnetic Moments. The magnetic susceptibility of the mixed crystals, $(Cu_xZn_{1-x})Hg(SCN)_4$, obeys the Curier-Weiss law fairly well over the temperature range from 118 to 283°K, with quite a small Weiss constant. The values of the effective magnetic moments (μ_{eff}) of Cu(II) in $(Cu_xZn_{1-x})Hg(SCN)_4$ are listed in Table 2. Figgis has shown that Cu(II) in a perfectly regular tetrahedral environment should have an effective moment of about 2.2 B.M.[9] However, it is well established by measurements that the μ_{eff} of Cu(II) is 1.96—2.00 B.M. for Cs_2CuCl_4, 1.91 B.M. for $(Ph_3MeAs)_2CuCl_4$, and 1.96 B.M. for $(Ph_3MeAs)_2CuBr_4$.[10] In Cs_2CuCl_4, the values of the two Cl–Cu–Cl bond angles are 120° and 104°.[11] The value of μ_{eff} of Cu(II) in $(Cu_{0.1}Zn_{0.9})Hg(SCN)_4$ in this case is almost equal to that in Cs_2CuCl_4. Therefore, the degree of distortion of the CuN_4 tetrahedron in $(Cu_xZn_{1-x})Hg(SCN)_4$ may be expected to be almost identical with that of the $CuCl_4$ tetrahedron in Cs_2CuCl_4. In fact, $ZnHg(SCN)_4$ is isomorphous with $CoHg(SCN)_4$,[2] where the N–Co–N bond angles are 118° and 106°.[3,4] The degree of distortion in $(Cu_{0.2}Zn_{0.8})Hg(SCN)_4$ may larger than that in $(Cu_{0.1}Zn_{0.9})Hg(SCN)_4$, judging from the value of μ_{eff} found for $(Cu_{0.2}Zn_{0.8})Hg(SCN)_4$. Consequently, it follows that the mixed crystal with a higher copper concentration will include a greater amount of lattice imperfections caused by Cu^{2+} doping.

Discussion

Here, we will propose a qualitative discussion of the semiconducting nature of the three-dimensional complex salts studied. However, our discussion will be confined to the case of intrinsic semiconduction, because the experimental data are not sufficient to clarify the latttice imperfections which affect the extrinsic semiconduction in the lower-temperature range.

Measurements of the electrical conductivity and its temperature dependence showed that $CuHg(SCN)_4$ and the mixed crystal, $(Cu, Zn)Hg(SCN)_4$, were semiconductors with quite low conductivities. In the case of the mixed crystals, it may be concluded, from a comparison of their photocurrent spectra with their electronic spectra, that the charge carriers for the intrinsic semiconduction originate from electronic transitions associated with the electron-transfer band at about 330 mμ. It may be seen in Fig. 2 that the intrinsic conductivity of the mixed crystals increases with an increase in the copper concentration. This may be due to the increase in the number of charge carriers. In this case, the absorbance of the electron-transfer band at 330 mμ may be expected to increase. Unfortunately, our spectral data are restricted to the visible region; therefore, the compositional dependence of the absorbance of the band at 330 mμ is obscure.

In general, the electron-transfer processes are of two types: the transfer of an electron from an orbital mainly localized on the ligand(s) to an orbital mainly localized on the metal (abbreviated L→M), and the transfer of an electron in the opposite direction (abbreviated M→L).[12] Forster *et al.* have suggested that the electron-transfer bands of the mixed crystals are analogous to those found for $CuCl_4^{2-}$ and $CuBr_4^{2-}$.[6,13,14] This implies that the electron-transfer bands of the mixed crystals are of the L→M type. If it is possible to consider that the electron-transfer bands of the mixed crystals and $CuHg(SCN)_4$ are of the L→M type, a reasonable account for the intrinsic semiconduction of these compounds may be given on the assumptions that the charge carriers are positive holes originating from the electron transfer from thiocyanate to the copper ion and that the holes are conducted through a valence band formed by electronic levels of thiocyanate ions. This mechanism of semiconduction may well account for the fact that, in the case of the mixed crystals, only the higher-energy electron-transfer band is responsible for the photocurrent; that is, if the lower energy electron-transfer band arises from electronic transitions involving localized orbitals, such as nonbonding orbitals of the ligand, the positive holes in such orbitals are likely to be localized in the ligand, therefore making no contribution to the electrical conductivity. In fact, Ferguson has pointed out that the lowest-energy electron-transfer band of $CuCl_4^{2-}$ probably arises from transitions involving orbitals which are nonbonding in T_d symmetry.[13]

The thermal activation energy (E_t) is related to the optical energy (E_o) by the following expression:

$$E_o/E_t = \varepsilon_s/\varepsilon_o,$$

where ε_s and ε_o are the static and high-frequency dielectric constants respectively. If the interatomic bonding is ionic, E_t is smaller than E_o. For the complex salts studied, the values of E_t^i obtained from $\log \sigma$ *vs.* $1/T$ plots are smaller than the values of E_o obtained from the threshold values of the photocurrent and electronic spectra. This suggests that the chemical bonds between copper and thiocyanate ions are most likely to be electrostatic.[15] Furthermore, the extremely low conductivities of these complex salts may well be due to the strong ionic character of the chemical bonds.

---

[9] B. N. Figgis, *Nature*, **182**, 1568 (1958).

[10] D. M. N. Goodgame and F. A. Cotton, *J. Chem. Soc.*, **1961**, 2298.

[11] L. Helmholz and R. F. Kruth, *J. Amer. Chem. Soc.*, **74**, 1176 (1952).

[12] H. B. Gray, *J. Chem. Educ.*, **41**, 2 (1964).

[13] J. Ferguson, *J. Chem. Phys.*, **40**, 3406 (1964).

[14] P. S. Braterman, *Inorg. Chem.*, **2**, 448 (1963).

[15] S. Yamada and R. Tsuchida, This Bulletin, **28**, 664 (1955).