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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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SEMICONDUCTOR AND OPTICAL PROPERTIES OF COPPER, NICKEL, ZINC, AND CADMIUM DITHIOCARBAMATES

For the directed synthesis of organic semiconductors, investigation of the dependence of electrophysical properties on atomic structure and the nature of the chemical bond is of great importance. For this purpose we are carrying out studies of a series of chelates and polychelates. Intracomplex compounds represent an interesting, in crystallochemical terms, class of polymeric compounds and their monomeric analogs with little-studied electrophysical properties. Chelate compounds were among the first to find practical application in the field of electronics of organic compounds (for example, copper phthalocyanine possesses photoconductivity and is used in "vidicons" ; chelates of rare-earth metals are being studied for the selection of quantum amplification of radiation in optical generators).

Systematic investigation of chelates and polychelates has made it possible to establish a number of regularities determining the semiconductor parameters of these materials ([1–3]). It was shown earlier that, in the case of chelate compounds with nodes $2(S, N)M$, the electrical conductivity can be changed by 8 orders of magnitude in the series Cu > Ni > Co > Zn, by changing the nature of the metals. In the present work it has been established that the magnitude of the electrical conductivity depends, to an even greater extent than on the nature of the metal, on the concentration of the metal in the sample. This is shown, using the example of the most highly conducting Cu compounds, in the form of a linear dependence of $\ln \sigma$ on the percentage content of Cu in the sample (Fig. 1). This dependence practically covers the entire region of semiconductor materials, since it begins with the pure metal with electrical conductivity $\sigma = 10^{+6}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ and extends all the way to polymeric insulators with $\sigma = 10^{-14}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.

Fig. 1. Dependence of electrical conductivity on the percentage content of copper.

Fig. 2

Figure 2: Fig. 2

Fig. 3. Absorption spectra of copper diethyldithiocarbamate (a), nickel diethyldithiocarbamate (b). 1, 2—as in Fig. 2.

Figure 3: Fig. 3. Absorption spectra of copper diethyldithiocarbamate (a), nickel diethyldithiocarbamate (b). 1, 2—as in Fig. 2.

1 —bis-(azothio)-polychelate of copper (R —methyl); 2 —copper polydithiocarbamate (R —diphenylene); 3 —copper polydithiocarbamate (R —phenylene); 4 — copper dithiooxamide; 5 —copper thiocyanate; 6 —polymeric compound of composition Cu 62.3, N 14.4, S 12.4, C 10.1, H 1.3%; 7 —copper.

Fig. 2. Absorption spectra of zinc diethyldithiocarbamate (a), cadmium diethyldithiocarbamate (b). 1 —in chloroform, 2 —in methanol.

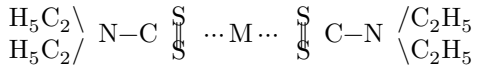
It can be established approximately that increasing the copper concentration by 5% leads to an increase in electrical conductivity by one order of magnitude. In order to verify this dependence experimentally, by thermal treatment of the complex compound $2CuSCN \cdot S = C(NH_2)_2$ at $t = 400^\circ$ for 5 hours, a new material was synthesized with the composition (Cu 62.3%, N 14.4, S 12.4, C 10.1, H 1.3%), which has $\sigma = 10^{-2}\ \Omega^{-1} \cdot \text{cm}^{-1}$ and $E = 0.07$ eV. To establish a more precise quantitative dependence of σ on the percentage content of metals, one should take into account the magnitude of the activation energy E and the different valence states of the copper atoms. The experimental data are still insufficient to distinguish between the behavior of compounds of monovalent and divalent copper. However, one may conclude that the introduction of organic groups makes it possible to vary the electrical conductivity of chelates and polychelates by changing the concentration of the transition metal in the sample.

Fig. 3. Absorption spectra of copper diethyldithiocarbamate (a), nickel diethyldithiocarbamate (b). 1, 2—as in Fig. 2.

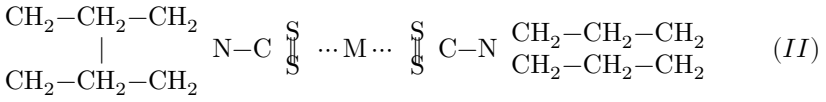
All the chelates and polychelates studied are high-resistance materials. High-resistance parameters are characteristic of luminescent and photoconducting materials (of the "vidicon" type). We have previously shown that the electrical conductivity of chelate compounds increases with increasing electron affinity of the metal. The luminescent properties decrease with increasing electrical conductivity ([3]). For the use of crystalline chelate compounds in the electronics of organic compounds, a rational combination of electrophysical properties with special optical properties is needed.

An interesting result was obtained by comparing the thermal activation energy E_{therm} with the energy scheme of the electronic levels E_{opt}. We established the pattern of electronic levels for each compound from the electronic absorp-

tion spectra, which were measured on an SF-4 spectrophotometer. A series of compounds of the type was studied:



$$M = Zn,\ Cd,\ Cu,\ Ni \qquad (I)$$



$$M = Cu \text{ and } Ni \qquad (II)$$

The results of the measurements are given in Table 1 and in Figs. 2 and 3. The following types of electronic transitions were established in the absorption spectra.

1) Ligand bands, appearing as a result of transitions between the ground and excited states of the electronic system of the dithiocarbamate group ($n-\pi^*, n-\sigma^*, \pi-\pi^*$). These bands are characteristic of all the compounds considered and are located in the ultraviolet region (λ_{max} = 245-320 mμ).

Table 1

Compound	Methanol λ_{max}, mμ	Methanol E	Chloroform λ_{max}, mμ	Chloroform E
Zn (I)	315 S	6,00	315 S	800
Zn (I)	275 S	20,500	280 S	21,000
Zn (I)	260	34,000	263	34,000
Zn (I)	245 S	18,000	245 S	18,000
Zn (I)	$\sim$ 210	15,000		
Cd (I)	320 S	400	320 S	600
Cd (I)	281	20,000	285 S	20,500
Cd (I)	260	36,000	267	36,000
Cd (I)	217	20,000	245 S	21,500
Cu (I)	600 S	1,000	600 S	1,200
Cu (I)	432	13,500	436	13,009
Cu (I)	335	1,000	335 S	1,500
Cu (I)	287	17,500	290	19,500
Cu (I)	269	34,000	271	34,000
Cu (I)	245 S	12,500	245 S	13,500
Cu (I)	218	11,000		

Compound	Methanol λ_{max}, mμ	Methanol E	Chloroform λ_{max}, mμ	Chloroform E
Cu (II)	600 S	1,200	600 S	1,300
Cu (II)	430	15,000	437	13,500
Cu (II)	340 S	1,000	340 S	1,500
Cu (II)	287	10,500	290	12,000
Cu (II)	270	37,000	272	37,000
Cu (II)	245 S	13,000	245 S	14,000
Cu (II)	219	12,500		
Ni (I)	630	180	630	100
Ni (I)	480 S	200	480 S	250
Ni (I)	425 S	1,400	420 S	1,800
Ni (I)	383	5,500	387	5,500
Ni (I)	323	36,500	326	30,000
Ni (I)	245	31,500	247	31,500
Ni (I)	238 S	28,000		
Ni (I)	$\sim$ 223	26,500		
Ni (II)	630	130	630	100
Ni (II)	480 S	300	480 S	250
Ni (II)	420 S	1,900	420 S	2,000
Ni (II)	386	7,000	387	6,500
Ni (II)	323	45,500	326	36,000
Ni (II)	244	37,000	246	37,000
Ni (II)	238 S			
Ni (II)	220			

2) Long-wavelength $d-d$ bands in the visible region, which are observed only in compounds with transition metals (Cu, Ni) (λ_{max} = 480-630 mμ). These bands correspond to electronic transitions between the split levels of the ground state of the central metal atom. In accordance with ligand-field theory ([4]), one $d-d$ band was found for the copper complexes, and two $d-d$ bands for the nickel complexes. The zinc and cadmium complexes have no $d-d$ bands, since the $3d^{10}$ and $4d^{10}$ shells of the Zn and Cd atoms are filled. These compounds are transparent in the visible region.

3) Charge-transfer bands, which correspond to $d-\pi$ transitions between the central metal atom and the ligand atoms (λ_{max} = 326-427 mμ). For the copper complexes only one band of this type is observed, and for the nickel complexes three bands. In the zinc and cadmium complexes these bands are absent.

The activation energies E_{opt}, calculated from the long-wavelength edge of the corresponding absorption bands, and E_{therm}, determined from the slope of straight-line segments of $\lg \sigma \sim 1/T$, agree with each other within the limits of measurement error. A comparison of the optical and thermal activation energies of copper and zinc dithiocarbamates made it possible to determine the nature

of the current carriers in the compounds studied. In the deciphered (together with N. S. Ivanova) structure of zinc diethyldithiocarbamate, two covalent Zn–S bonds were established, corresponding to *sp*-hybridization of the electrons of the zinc atom, while in the structure of copper hexamethylenedithiocarbamate four covalent Cu–S bonds were found, corresponding to dsp^2-hybridization of the electrons of the copper atom. A feature of the structures of copper and zinc diethyldithiocarbamates is the identical packing motif of the structural elements in the unit cells. Copper diethyldithiocarbamate and hexamethylenedithiocarbamate have different crystal structures, but identical σ and E. In ot-

unlike organic semiconductors with conjugated bond systems, where the charge carriers are π-electrons, in intracomplex dithiocarbamate compounds of copper the lowered activation energy $E_{\text{therm}} = 2.4$ eV is due to the interaction of the metal and ligand d- and π-electrons (the third type of band). In the molecular compound zinc dithiocarbamate, the increased activation energy $E_{\text{therm}} = 3.8$ eV is due to ligand electrons–the free electron pair ($3p^2$) of sulfur atoms and the π-electrons of the thiocarbamate group (the first stage of the band). At higher temperature $t > 140°$, copper dithiocarbamates also have an increased activation energy $E_{\text{therm}} = 3.8$ eV (^4). The dependence of the electrical conductivity of Cu compounds on the percentage content of copper is due to the participation of the copper d-electrons in conduction. Therefore ZnS, unlike CuS, which has high conductivity, is an insulator with a forbidden-band width $E = 3.7$ eV. The semiconductor parameters are determined mainly by the nature of the metal-ligand chemical bond, and not by the crystalline structure or superstructure.

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Note: Figure translations are in progress. See original paper for figures.