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Figure 1: Structural formulas A, B, and C shown on the page: chelate polymer structures with pyridine-derived thioamide/dithiocarbamate units, metal centers M, and repeat index n.

Abstract

Full Text

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ELECTRICAL CONDUCTIVITY AND ACTIVATION ENERGY OF CHELATE COMPOUNDS OF DITHIOCARBAMATES AND THIOAMIDES OF PYRIDINE DERIVATIVES

In order to establish the dependence of semiconductor properties on atomic structure, we are carrying out systematic studies of the electrical conductivity and activation energy of polymers ([1,2]).

In the present work, the temperature dependence of the electrical conductivity of chelate polymers of the proposed structures A, B, and C has been measured.

These polymers contain chelate units $2(\mathrm{N},\mathrm{S})M$ with the metals Cu, Co, and Zn. Radicals R were introduced into the polymer chains:

Radicals R:

1. biphenylene radical
2. dimethyl-substituted biphenylene radical
3. dimethoxy-substituted biphenylene radical

For comparison, the electrical conductivity and activation energy were determined for compounds of structures G and D and for a polymer of structure

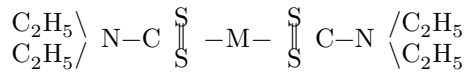
Displayed radical structures R: three biphenyl-type radicals labeled 1, 2, and 3, the second bearing CH_3 groups and the third bearing OCH_3 groups.

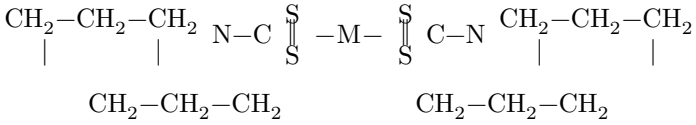
Figure 2: Displayed radical structures R: three biphenyl-type radicals labeled 1, 2, and 3, the second bearing CH_3 groups and the third bearing OCH_3 groups.

Structural formulas G, D, and E shown on the page: pyridine-derived thioamide starting compounds and polymer structure with R, SH, N, and CH_3 substituents.

Figure 3: Structural formulas G, D, and E shown on the page: pyridine-derived thioamide starting compounds and polymer structure with R, SH, N, and CH_3 substituents.

E, which are, respectively, the starting substances for the synthesis of chelate polymers A, B, and C.





Complex compounds of metal dithiocarbamates of structures and with $M =$ Cu, Co, and Zn ([3]) are monomeric analogs of the polychelates studied earlier ([2]).

The results of measurements of electrical conductivity σ and activation energy E are given in Table 1. The compounds studied prove to be insulators at room temperature, $\sigma < 10^{-13}$ ohm^{-1}·cm^{-1}. Therefore, the measurements were carried out at elevated temperature, and the values of σ are given at a temperature of 383°K. The activation energy E was calculated for

$$\sigma = \sigma_0 e^{-E/2kT}.$$

The value of E is reduced by a factor of two if kT, instead of $2kT$, is taken in the denominator of the exponent. The present work confirms the results of ([2]) in that the electrical conductivity depends substantially on the nature of the metal and changes in the series Zn < Cu > Ni > Co. For the previously studied metal polythiooxamides, the electrical conductivity decreases by 8 orders of magnitude on going from the Cu polymer to the Co polymer ([2]). As can be seen from

Fig. 1. Temperature dependence of the electrical conductivity for polymers of structure A with radical (2). 1 —Cu, 2 —Co, 3 —Zn

Figure 4: Fig. 1. Temperature dependence of the electrical conductivity for polymers of structure A with radical (2). 1 —Cu, 2 —Co, 3 —Zn

the data of Table 1, for polychelates of structures , , and with radicals (1), (2), and (3), and for complexes of structures and , the electrical conductivity, depending on the nature of the metals, changes in the same sequence by 1-4 orders of magnitude. Fig. 1 gives the temperature dependence of the electrical conductivity for Cu, Co, and Zn polychelates of structure with radical 2. For Cu polychelates of structures , , and the highest electrical conductivity was observed, equal to 10^{-10}–10^{-11} ohm$^{-1} \cdot$ cm^{-1}. Among complex dithiocarbamates of structures and , the Cu complexes also have an increased electrical conductivity, $\sigma = 10^{-10}$ ohm$^{-1} \cdot$ cm^{-1}. According to ligand-field theory, the stability of complex compounds of transition metals changes in the same order Zn < Cu > Ni > Co. The electron affinity of the metal changes analogously ([4]). Consequently, the value of the electrical conductivity changes regularly depending on the nature of the chemical bonds M—C and M—N in the chelate unit 2(N, S)M. In terms of catalytic activity for the decomposition reaction of hydrazine, the polychelates are arranged in the same series Zn < Cu > Ni > Co ([5]). The luminescent properties of the polychelates change in the reverse order, Zn > Cu ([6]).

Fig. 1. Temperature dependence of the electrical conductivity for polymers of structure with radical (2). 1 —Cu, 2 —Co, 3 —Zn.

Substances of structures and , which do not contain metals, possess lower electrical conductivity than the corresponding polychelates of structures and . Their electrical conductivity is 10^{-13}–10^{-16} ohm$^{-1} \cdot$ cm^{-1}. For the polymer of structure the electrical conductivity is higher than for structures and by 1-4 orders of magnitude. For Cu polychelates, a decrease in electrical conductivity is observed in the series of radicals (1) > (3) > (2). Investigation of dithiocarbamate complex compounds of metals of structures and established that the electrical conductivities and activation energies for complexes with different radicals $R =$ —$(C_2H_5)_2$— and —$(CH_2)_6$— are almost identical (Fig. 2), although the difference in the radicals pri-

Table 1

Structure	Radical	Metal	σ at 383° K, ohm$^{-1}\cdot$cm^{-1}	E, eV	Structure	Radical	Metal	σ at 383° K, ohm$^{-1}\cdot$cm^{-1}	E, eV
A	1	Cu	$1.0 \cdot 10^{-10}$	1.40	D	3	–	$1.0 \cdot 10^{-13}$	2.88

Structure	Radical	Metal	σ at 383° K, ohm$^{-1}\cdot$cm^{-1}	E, eV	Structure	Radical	Metal	σ at 383° K, ohm$^{-1}\cdot$cm^{-1}	E, eV
A	1	Co	$3.4\cdot10^{-13}$	1.42	V	1	Cu	$6.3\cdot10^{-11}$	1.52
G	1	–	$1.25\cdot10^{-13}$	3.60	V	1	Co	$3.8\cdot10^{-12}$	1.40
A	2	Cu	$3.7\cdot10^{-12}$	1.40	V	2	Cu	$5.6\cdot10^{-13}$	1.60
A	2	Co	$5.0\cdot10^{-13}$	1.28	V	2	Co	$2.3\cdot10^{-13}$	1.40
A	2	Zn	$3.0\cdot10^{-14}$	1.32	V	3	Cu	$1.2\cdot10^{-12}$	1.56
G	2	–	$7.9\cdot10^{-13}$	3.04	E	3	–	$2.0\cdot10^{-12}$	2.64
A	3	Cu	$7.3\cdot10^{-11}$	1.40	Zh	–	Cu	$4.0\cdot10^{-10}$	2.20; 1.28
A	3	Co	$2.6\cdot10^{-13}$	1.40	Zh	–	Zn	$3.1\cdot10^{-13}$	3.84
G	3	–	$6.3\cdot10^{-16}$	5.20	Z	–	Cu	$4.3\cdot10^{-10}$	2.20; 1.40
B	1	Cu	$1.7\cdot10^{-11}$	1.88	Z	–	Co	$2.9\cdot10^{-13}$	2.12
B	2	Cu	$2.2\cdot10^{-12}$	1.80	Z	–	Zn	$1.0\cdot10^{-14}$	6.16

leads to different crystal structures. This is a striking example of the fact that electrical conductivity and activation energy are determined mainly by the short-range order, i.e., by the nature of the chemical bonds, and not by the packing of molecules in the crystal. X-ray structural analysis of single crystals showed that these compounds belong to the monoclinic Fedorov group $P2_1/C$ and have different unit cells. The numbers of molecules in the unit cells, equal, respectively, to $Z = 4$ and $Z = 2$, mean that the atoms of the complex with R $= -(C_2H_5)_2$ are located in a general position, whereas in the complex with R $= -(CH_2)_6$ the copper atoms are located at centers of symmetry of the crystal.

In work ([2]) it was reported that, for dithiocarbamate polychelates with phenylene and diphenylene radicals, owing to conjugation of π-bonds it is possible to obtain reduced activation energies of 0.72–0.84 eV at temperature $T < 360°$ K, as compared with activation energies equal to 1.20–1.24 eV at $T > 360°$ K. For the same polymers with hexamethylene radicals the activation energy is already 1.44 eV at $T < 360°$ K.

Fig. 2. Temperature dependence of electrical conductivity for complex compounds. 1 $-(CH_2)_6NCSSCu$, 2 $-(C_2H_5)_2NCSSCu$.

Figure 5: Fig. 2. Temperature dependence of electrical conductivity for complex compounds. 1 $-(CH_2)_6NCSSCu$, 2 $-(C_2H_5)_2NCSSCu$.

Fig. 2. Temperature dependence of electrical conductivity for complex compounds.
1 $-(CH_2)_6NCSSCu$, 2 $-(C_2H_5)_2NCSSCu$

For compounds of structures G, D, and E (without metals), in comparison with the corresponding polymers of structures A, B, and V (with metals), the activation energies are raised to 2.88–5.28 eV. The presence of chelate nodes in polymers A, B, and V substantially lowers the activation energy to 1.40–1.88 eV. For the most highly conducting monomeric dithiocarbamate Cu complexes of structures Zh and Z, activation-energy values equal to 1.28–1.40 eV are established at $T > 410^\circ$ K, while at $T < 410^\circ$ K there are elevated activation energies of 2.20 eV. These data show that activation energies of the same order, 1.3–1.4 eV, as in the polychelates can be obtained also in the case of monomeric complexes, but with the expenditure of a certain amount of thermal energy. The present study agrees with the data of work ([2]) and permits the conclusion that, although the activation energy changes little with variation in the nature of the metals, the presence of chelate nodes in polymers and in complex compounds leads to a decrease in activation energy to 1.2–1.8 eV. For the thirty compounds investigated, having the same $M \ldots S = C - N <$ groupings, a definite value of the activation energy has been established, varying within small limits of 1.2–1.6 eV.

Copper thiocyanate CuSCN is the simplest, in composition, semiconducting polymer containing the $S = C = N$–group [(2)]. We have established that after heat treatment copper thiocyanate has the same order of magnitude of activation energy, 1.20 eV, as the chelate compounds investigated, with

$$S = C - N$$

groups.

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