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Abstract

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CHEMISTRY

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ELECTRICAL CONDUCTIVITY OF CHELATE POLYMERS

At the present time the physicochemical properties of various types of polymeric substances are being widely studied (1,2).

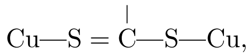
To establish the relationship between the semiconducting properties of chelate polymers and their atomic structure, measurements were made of the electrical conductivity σ and activation energy E of a series of polymers. Polychelates of 7 different structures were investigated; their formulas are given in Table 1.

The polymers were usually synthesized by the interaction of equimolecular aqueous solutions of metal acetates with alcoholic solutions of the corresponding tetrafunctional organic compounds. The substances obtained were amorphous, insoluble, and infusible powders, whose decomposition temperatures lay above 250-350°. More detailed consideration of the synthesis and of a number of physicochemical properties of the substances obtained is the subject of special communications that will be published in forthcoming issues of the journal *Vysokomolekulyarnye soedineniya*.

The samples were prepared in the form of tablets 5-7 mm in diameter, pressed under a pressure of 5000 kg/cm^2. Measurements of electrical conductivity were carried out down to $\sigma = 10^{-13}\ \Omega^{-1} \cdot cm^{-1}$. The electrical conductivity of the polymers varied with temperature according to an exponential relation

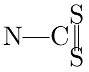
$$\sigma = \sigma_0 e^{-\frac{E}{2kT}}.$$

The results obtained are presented in Table 1. As is evident from the data given, the greatest electrical conductivity was observed for copper polychelates of structure I. The special electrical properties of these substances are in good agreement with the assumption that, in this case, polymers of network structure are formed (3,4). In this process atoms of monovalent copper form linear S–Cu –S bonds. From X-ray diffraction data on the radial distribution curve of the polymers it was established that the distance between the nearest copper atoms,



$$\mathrm{Cu{-}S = \overset{|}{C}{-}S{-}Cu},$$

is 5.8 Å. Participation in the formation of polychelates by radicals with π-bonds of carbon atoms (I, $R = n\text{-}C_6H_4$—and I, $R = n,n'\text{-}(C_6H_4)_2$—) sharply increases the electrical conductivity of copper polymers in comparison with radicals having σ-bonds C–C (I, $R = -(CH_2)_2$—and I, $R = -(CH_2)_6$—). The network structure of the copper polymers makes it possible to create the coplanarity of polymer chains necessary for conjugation of the π-bonds of the atoms



$$N\text{—}C\begin{matrix}S\\ \|\\ S\end{matrix}$$

and of the phenylene rings.

The electrical conductivity of polymers also depends on the nature of the metals. For polymers of structure II the electrical conductivity decreases and the activation energy increases in the series: Co, Zn, Ni. According to ligand-field theory for

Electrical Conductivity of Chelate Polymers

Table 1

Compounds	M	R	σ_{295}, $(\Omega^{-1}\cdot cm^{-1})$	σ_0, $(\Omega^{-1}\cdot cm^{-1})$	E, eV
I –structural formula shown	Cu^{1+}	$—(CH_2)_2—$	$2.0 \cdot 10^{-7}$	$2.1 \cdot 10^{9}$	1.9
I –structural formula shown	Cu^{1+}	$—(CH_2)_6—$	$5.5 \cdot 10^{-9}$	$8.5 \cdot 10^{-1}$	1.31
I –structural formula shown	Cu^{1+}	$n\text{-}C_6H_4—$	$1.65 \cdot 10^{-4}$	$4.0 \cdot 10^{5}$	0.22; 1.71
I –structural formula shown	Cu^{1+}	$n,n' - (C_6H_4)_2—$	$3 \cdot 10^{-5}$	$3.5 \cdot 10^{20}$	0.69; 3.44
II –structural formula shown	Ni^{2+}	$—(CH_2)_2—$	$4 \cdot 10^{-12}$	$1.7 \cdot 10^{3}$	1.64

Compounds	M	R	σ_{295}, $(\Omega^{-1}\cdot\text{cm}^{-1})$	σ_0, $(\Omega^{-1}\cdot\text{cm}^{-1})$	E, eV
II – structural formula shown	Zn^{2+}	$—(CH_2)_2—$	$4 \cdot 10^{-9}$	$4.5 \cdot 10^{-3}$	0.59
II – structural formula shown	Zn^{2+}	$—(CH_2)_6—$	$3 \cdot 10^{-10}$	$9 \cdot 10^{1}$	0.78
II – structural formula shown	Co^{2+}	$—(CH_2)_2—$	$2.5 \cdot 10^{-6}$	$5.5 \cdot 10^{-4}$	0.22
II – structural formula shown	Co^{2+}	$—(CH_2)_6—$	$1 \cdot 10^{-10}$	–	–
II – structural formula shown	Co^{2+}	n-C_6H_4—	$2.5 \cdot 10^{-10}$	$2.5 \cdot 10^{4}$	1.7

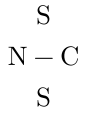
Compounds	M	R	σ_{295}, ($\Omega^{-1}\cdot$cm^{-1})	σ_0, ($\Omega^{-1}\cdot$cm^{-1})	E, eV
II – structural formula shown			For nickel polychelates with $R =$ —$(CH_2)_6$— and $n, n' -$ $(C_6H_4)_2$—; for zinc with $R =$ n-C_6H_4— and $n, n' -$ $(C_6H_4)_2$—; for cobalt with $R = n, n' -$ $(C_6H_4)_2$—, $\sigma_{295} <$ 10^{-13} $\Omega^{-1}\cdot$ cm^{-1}		
III – structural formula shown	Cu^{2+}	–	$6.5 \cdot 10^{-9}$	$4 \cdot 10^{19}$	0.69
III – structural formula shown	Ni^{2+}	–	$4 \cdot 10^{-12}$	$5.6 \cdot 10^{-4}$	0.77
III – structural formula shown			For cadmium polychelates, $\sigma_{295} <$ 10^{-13} $\Omega^{-1}\cdot$ cm^{-1}		
IV – structural formula shown	Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}	–	For all polychelates, $\sigma_{295} <$ 10^{-13} $\Omega^{-1}\cdot$ cm^{-1}		

Compounds	M	R	σ_{295}, $(\Omega^{-1}\cdot\text{cm}^{-1})$	σ_0, $(\Omega^{-1}\cdot\text{cm}^{-1})$	E, eV
IV – structural formula shown	Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}	CH_3—	For all polychelates, $\sigma_{295} < 10^{-13}\ \Omega^{-1}\cdot\text{cm}^{-1}$		
V – structural formula shown	Cu^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}	—	For all polychelates, $\sigma_{295} < 10^{-13}\ \Omega^{-1}\cdot\text{cm}^{-1}$		
V – structural formula shown	Fe^{2+}	2H—	$1.9 \cdot 10^{-11}$	$6.9 \cdot 10^{-7}$	0.47
V – structural formula shown	Fe^{2+}	—$(CH_2)_2$—	$1 \cdot 10^{-12}$	–	–
V – structural formula shown	Fe^{2+}	—$(CH_2)_6$—	$6 \cdot 10^{-8}$	$2 \cdot 10^{-3}$	0.45
V – structural formula shown	Cd^{2+}	*o*-C_6H_4—	$2.2 \cdot 10^{-9}$	$5.6 \cdot 10^{-4}$	0.72

Compounds	M	R	σ_{295}, ($\Omega^{-1}\cdot$cm^{-1})	σ_0, ($\Omega^{-1}\cdot$cm^{-1})	E, eV
V – structural formula shown			For polychelates of copper, nickel, zinc, and cobalt with $R =$ 2H—, —$(CH_2)_2$—, —$(CH_2)_6$—, and o-C_6H_4—; of iron with $R =$ o-C_6H_4—; of cadmium with $R =$ 2H—, $\sigma_{295} < 10^{-13}\ \Omega^{-1}\cdot$ cm^{-1}		
VI – structural formula shown	Ni^{2+}	o-C_6H_4—	$1\cdot10^{-8}$	–	–
VII – structural formula shown	Fe^{2+}	—$(CH_2)_6$—	$3.5\cdot10^{-9}$	$3\cdot10^{-1}$	0.87
VII – structural formula shown	Co^{2+}	—$(CH_2)_2$—	$1\cdot10^{-12}$	$4\cdot10^{24}$	4.52
VII – structural formula shown	Co^{2+}	—$(CH_2)_6$—	$1\cdot10^{-7}$	–	–
VII – structural formula shown	Co^{2+}	o-C_6H_4—	$6\cdot10^{-8}$	$1\cdot10^{10}$	2.2

Compounds	M	R	σ_{295}, $(\Omega^{-1}\cdot\text{cm}^{-1})$	σ_0, $(\Omega^{-1}\cdot\text{cm}^{-1})$	E, eV
VII — structural formula shown			For the iron polychelate with $R =$ o-C_6H_4—, $\sigma_{295} < 10^{-13}\ \Omega^{-1}\cdot\text{cm}^{-1}$		

for the high-spin state of transition metals, in the case of Co^{2+} a tetrahedral (sp^3) bond configuration should be realized, and in the case of Ni^{2+}, a square (sp^2d) bond configuration. X-ray structural analysis of nickel diethyldithiocarbamate, which in a certain sense is a monomeric analog of nickel polychelates of structure II, confirms that the four sulfur atoms are located with the metal atoms in one plane, forming a rectangle around it. In this same plane are found



$$\begin{matrix} & S \\ N - & C \\ & S \end{matrix}$$

bonds (5). According to measurements of magnetic moments μ_B, in polymers of structure II with $R = -(CH_2)_6-$; o-C_6H_4- and n,n'-$(C_6H_4)_2-$, the presence of three unpaired electrons of the Co^{2+} atom has been established, which leads to a tetrahedral configuration of Co—S bonds (μ_B, respectively, equal to 4.71; 4.72 and 4.48 Bohr magnetons) (4). The significant increase in the electrical conductivity of the cobalt polychelate of structure II, $R = -(CH_2)_2-$, to $\sigma_{295} = 2.5 \cdot 10^{-6}\ \Omega^{-1} \cdot \text{cm}^{-1}$, and the decrease in activation energy to $E = 0.22$ eV corresponds to a decrease in the magnetic moment to $2.58\,\mu_B$, owing to an increase in the degree of coplanarity of the chelate units. A certain increase in the electrical conductivity of the nickel chelate polymer of structure II, $R = -(CH_2)_2-$, also corresponds to a decrease in the magnetic moment to $1.11\,\mu_B$, in comparison with the nickel compound II, $R = n,n'$-$(C_6H_4)_2-$, for which μ_B is equal to 2.62. The introduction of $-(CH_2)_2-$ radicals into the chains of cobalt and nickel polymers creates more favorable conditions for the formation of square M—S bonds than the introduction of n,n'-$(C_6H_4)_2-$ radicals. When tetrahedral M—S bonds are formed, the coplanarity of the polymer chains is disrupted, whereas when square M—S bonds are formed, coplanarity is preserved and the electrical conductivity increases.

For copper polychelates of structure I, in the plots of $\lg\sigma$ versus $1/T$, two straight-line segments with different slopes are observed, making it possible to determine two activation energies for each polymer. The electrical conductivity of the copper compound of structure I, $R = n,n'$-$(C_6H_4)_2-$, increases rapidly with temperature owing to the large values $E_2 = 3.44$ eV and $\sigma_0 = 3.5 \cdot 10^{20}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$, and at 125° is equal to $0.5\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. Further investigations of the nature of the activation energies will make it possible to establish whether the presence of E_1 is caused by impurity conduction.

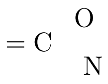
An analogous picture is observed for copper polyrubeanate of structure III. For polyrubeanates having M—S bonds, the electrical conductivity decreases in the series: Cu > Ni > Cd. According to X-ray data, all atoms of the rubeanic acid molecule lie in one plane (^{6}). In copper polyrubeanates the nearest Cu . . . Cu distance is 4.6 Å.

For polychelates of structure IV, geometric analysis shows that the steric hindrances arising owing to the presence of phenylene and pyridine rings disrupt the coplanarity of the polymer chains. Polymers of this type with M = Cu^{2+}, Zn^{2+} and Co^{2+} and $R = n, n'$-$(C_6H_4)_2$— possess reduced electrical conductivity ($\sigma_{295} < 10^{-13}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$) in comparison with polyrubeanates.

All the bis-dioxa-polychelates of structure V that were studied also possess low electrical conductivity ($\sigma_{295} < 10^{-13}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$).

It is known from structural chemistry that the degree of use of the free electron pair of the nitrogen atom in chemical bonds with the formation of additional P_π-bonds is considerably greater than for oxygen atoms. When M—N and M —O bonds are formed in the chelate unit of polymers, an increase in electrical conductivity is observed for iron polychelates of structure VI. The electrical conductivity is especially increased for iron polymers of structure VI, $R = 2\mathrm{H}$—, and VI, $R = -(CH_2)_6-$, for which magnetic data (^{7}) establish a tetrahedral configuration of bonds of the iron atom, in contrast to iron polychelates of structure VI, $R = -(CH_2)_2-$, and VI, $R =$

$= o$-C_6H_4—, for which a square configuration of the bonds was found. According to ligand-field theory, the complex compounds of Fe^{2+} with tetrahedral (sp^3) bonds are more stable. For polar bonds



$$= \mathrm{C}\begin{matrix} \mathrm{O} \\ \mathrm{N} \end{matrix}$$

coplanarity of the chelate rings is no longer a necessary condition for increasing the electrical conductivity of the polymers. Incorporation of a VI phenylene radical into the polymer leads to increased electrical conductivity of the cadmium polychelate. The electrical conductivity of bis-(aza-oxa)-polychelates of iron and cadmium of structure VI is increased in comparison with the corresponding copper polymers.

The nitrogen atom ($\chi = 3.0$) is a more electronegative ligand than the sulfur atom ($\chi = 2.5$), while the atoms Fe^{2+} ($\chi = 1.65$) and Cd^{2+} ($\chi = 1.5$) are more electropositive metals than Cu^{2+} ($\chi = 2.0$). Judging from the literature data (^{8}), the electrical conductivities of free phthalocyanine and copper phthalocyanine are close and equal, respectively, to $6.7\cdot10^{-8}\ \Omega^{-1}\cdot\text{cm}^{-1}$ and $5.0\cdot10^{-8}\ \Omega^{-1}\cdot\text{cm}^{-1}$. Introduction into the phthalocyanine monomer of a more electropositive metal —magnesium ($\chi = 1.2$)—also leads to an increase in electrical conductivity to $1.4\cdot10^{-6}\ \Omega^{-1}\cdot\text{cm}^{-1}$. For the synthesized bis-diaza-polychelates of nickel, iron, and cobalt of structure VII with M—N bonds, where the metal ions occupy voids in the atomic structures of the polymers, enhanced electrical conductivity was observed.

Studies of the electrical conductivity of 48 chelate polymers show that the electrical characteristics of semiconducting polymers, as well as of inorganic semiconductors (^{9}), are determined to a considerable extent by short-range order, i.e., by the nature of the chemical bonds in the chelate rings and in the radicals. To establish more rigorous regularities in the semiconducting properties of polychelates as a function of polymer structure, additional investigations will be carried out.

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CITED LITERATURE

1. A. V. Topchiev, M. A. Geiderikh, B. E. Davydov, V. A. Kargin, B. A. Krentsel, I. M. Kustanovich, L. S. Polak, *DAN*, **128**, No. 2, 312 (1959).
2. E. I. Balabanov, A. A. Berlin, V. P. Parini, V. L. Tal' roze, E. L. Frankevich, M. I. Cherkashin, *DAN*, **134**, No. 5, 1123 (1960).
3. A. P. Terent' ev, E. G. Rukhadze, V. V. Rod' e, High-molecular compounds—in press.
4. A. P. Terent' ev, V. V. Rod' e, E. G. Rukhadze, High-molecular compounds—in press.
5. E. A. Shugam, L. M. Shkol' nikova, *Kristallografiya*, **3**, 749 (1958).
6. B. Long, P. Markey, P. G. Wheatley, *Acta Crystallogr.*, **7**, 140 (1954).
7. V. V. Rod' e, L. I. Nekrasov, A. P. Terent' ev, E. G. Rukhadze, High-molecular compounds, **3**, No. 11 (1961).
8. A. T. Vartanyan, *Izv. AN SSSR, OKhN*, 1952, No. 2, 16.

9. E. V. Zvonkov , *Problems of Physical Chemistry*, **2**, 97 (1959).

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

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