The electronic transport properties of the [Co$_2$(L)L′(dioxane)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ complex

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Abstract

The temperature dependence of the electrical conductivity, microstructure and crystal structure properties of the [Co$_2$(L)L′(dioxane)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ complex was investigated. The X-ray diffraction showed that the [Co$_2$(L)L′(dioxane)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ has a triclinic structure. Temperature dependence of the conductivity curve of the complex exhibited two conduction regions, and while increase of conductivity with temperature in the first region is of hopping conduction which takes place in localized states, the conduction in the second region is of Arrhenius-type. These conduction mechanisms are related to intermolecular and intramolecular conduction progresses. The electrical conductivity of the [Co$_2$(L)L′(dioxane)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ complex was 2.57×10^{-7} (S/cm) at room temperature with activation energy of 0.46 eV which showed semiconductivity behavior.
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1. Introduction

The semiconducting metal complexes are interesting as new materials [1–9]. The remarkable growth of interest in the physics and chemistry of the semiconducting metal complexes is reflected by a steady increase in the number of published investigations. It is an interdisciplinary field which combines the related works of chemists and physicists. Semiconducting solid materials are frequently grouped into the categories of molecular crystals, charge transfer complexes and polymers.

In a series of papers [2–9], temperature dependences of the electrical conductivity, thermal conductivity, crystal structure, microstructure and optical properties a large number of new semiconducting metal complexes which showed typical semiconducting characteristics were studied. The values of some characteristic parameters (activation energy, concentration, mobility, optical band gap, etc.) of the studied metal complexes have been determined [2–9].

In the present paper, the crystal and microstructure and electronic transport properties of [Co$_2$(L) L′(dioxane)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ complex are discussed.

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2. Experimental

2.1. The synthesis of $[Co_2(L)L'(dioxane)_2(NO_3)_2](NO_3)_2$ complex

The ligand 1,2-*O*-cyclohexiliydine-4-aza-7-aminoheptane (2.0550 g, 9 mmol) was dissolved in 40 ml methanol in a 50-ml round bottom flask. A solution of metal salt $Co(NO_3)_2 \cdot 3H_2O$ (0.7145 g, 3 mmol) in 20 ml methanol was added dropwise in a 180-min period with continuous stirring at reflux temperature. At the end of the reaction, the product was filtered and washed with hot water. The produced complex was filtered, washed with 1,4-dioxane and ether and dried in a vacuum at 70 °C [2]. The chemical structure of the synthesized and characterized metal complex, i.e., found to be in the form of $[Co_2(L)L' (dioxane)_2(NO_3)_2](NO_3)_2$ [9], is given in Fig. 1.
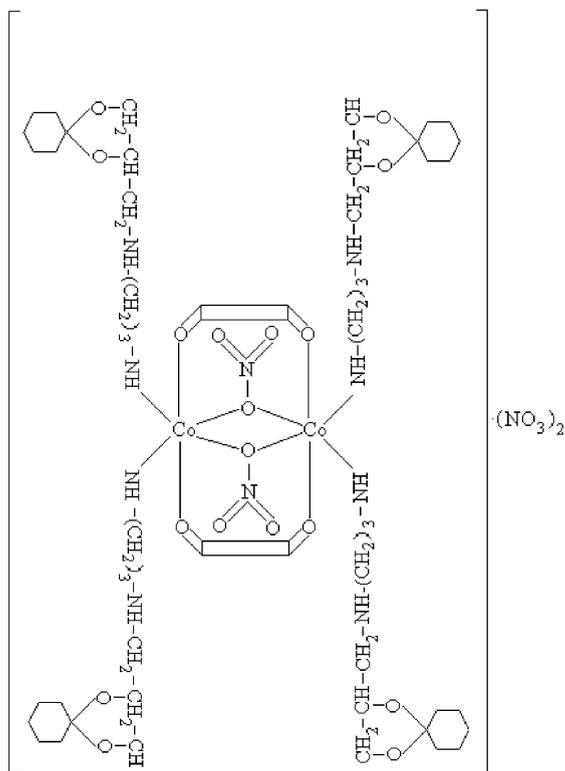
Fig. 1. The chemical structure of the Co(II) complex.

2.2. Physical measurements

X-ray diffraction (XRD) pattern of the complex was recorded with a Rigaku Geigerflex X-ray diffractometer. The diffraction pattern was obtained by using $CuK_{\alpha 1}$ radiation with a graphite monochromator at 5°/min scanning rate. The electrical conductivity of the prepared complex was measured by using standard dc method with a Keithley 197/3A auto ranging multimeter [2–9]. The morphology of surface was investigated by a scanning electron microscope.

3. Results and discussion

3.1. X-ray diffraction characterization and microstructure

X-ray pattern of the Co(II) complex is given in Fig. 2. The crystal structure of complex was determined by using trial and error method [9]. The unit cell parameters were calculated, and by using such parameters, the calculated diffraction data, i.e., 2θ (observed), $\Delta 2\theta$ and indices of the Co(II) complex, are reported in Table 1. The X-ray diffraction shows that the system of the Co(II) complex is triclinic with calculated unit cell parameters. Scanning electron micrographs for the complex are presented in Fig. 3a–b. It was seen that the surface is not uniform. In the structure, there are swellings and the grains are not observed.

3.2. Electrical conductivity

Temperature dependence of the electrical conductivity measurements was performed and conductivity was measured during heating. The conductivity data are shown in the form of $\ln\sigma$ vs. $1/T$ in Fig. 4, and there are two conductivity regions. While the first region indicates a hopping conduction region, the second region is conduction by extended states. The conductivity is the sum of two components,

$$\sigma = \sigma_{hop} + \sigma_{ext} \tag{1}$$

where σ_{hop} is the contribution of conduction due to hopping between the localized states and σ_{ext} is the contribution of conduction between the extended states. In the hopping conduction, when the temperature is low enough to so that carriers cannot be
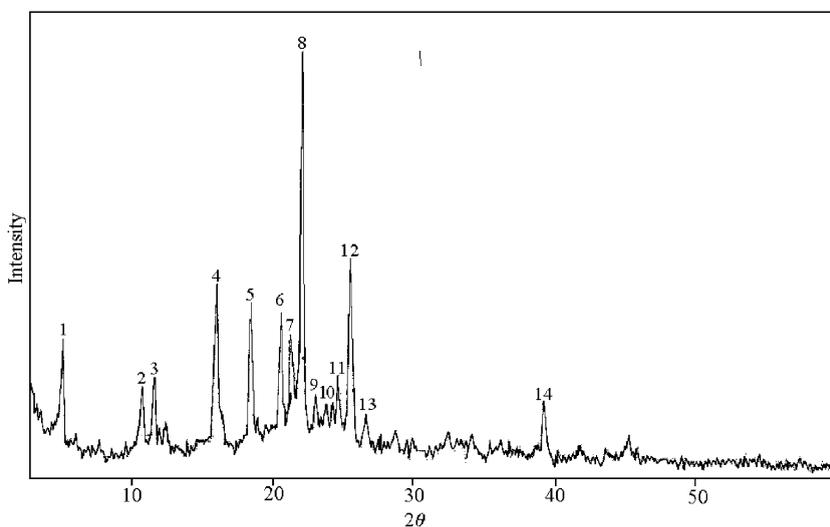
Fig. 2. The X-ray pattern of the Co(II) complex.

excited into one of allowed bands, the dominant conduction takes place via hopping. In the first region, the conduction occurs via variable hopping conductions of the charge carriers in the localized states near the Fermi level and the localized states are characterized according to Mott and Davis [10]. Mott and Davis' analyses are as follows: considering hops over a spatial distance, $\overline{R_0}$, and an energetic distance, $\overline{\Delta E}$, a carrier starting at the Fermi level finds on the average

$$n_s = \frac{4\pi}{3}\overline{R_0^3}N(E_F)\overline{\Delta E} \tag{2}$$

sites. n_s must be at least in order to have one site to hop. This criterion relates the average energy difference to the average hopping width,

$$\overline{\Delta E} = \frac{3}{4\pi N(E_F)\overline{R_0^3}} \tag{3}$$

Optimizing the mean hopping frequency directly leads to an optimized hopping frequency,

$$v = v_0\exp(-(T_0/T)^{1/4}) \tag{4}$$

Table 1
Observed and calculated X-ray diffraction data for Co(II) complex

System: Triclinic, $a=8.2052$ Å, $b=16.6022$ Å, $c=5.8363$ Å, $\alpha=90.119°$, $\beta=95.272°$, $\delta=94.983°$, $V=788.66$ Å^3						
Peak no.	d (observed)	d (calculated)	I/I_0	2θ (observed)	2θ (calculated)	$\Delta 2\theta$	(hkl)
1	16.5386	16.5386	26.1	5.34	5.34	0.000	010
2	8.1392	8.1392	15.7	10.86	10.86	0.000	100
3	7.5696	7.5696	17.2	11.68	11.68	0.000	$\bar{1}$10
4	5.5002	5.5002	41.0	16.10	16.10	0.000	0$\bar{1}$1
5	4.8020	4.8020	35.8	18.46	18.46	0.000	$\bar{1}$11
6	4.3121	4.3121	30.6	20.58	20.58	0.000	111
7	4.1641	4.1668	17.9	21.32	21.31	0.014	$\bar{1}2\bar{1}$
8	4.0263	4.0199	100	22.06	22.09	−0.035	03$\bar{1}$
9	3.8497	3.8739	8.2	23.08	22.94	0.146	210
10	3.7354	3.7679	5.2	23.80	23.59	0.208	$\bar{1}$31
11	3.6069	3.6046	12.7	24.66	24.68	−0.016	$\bar{1}$3$\bar{1}$
12	3.4929	3.4884	46.3	25.48	25.51	−0.033	$\bar{2}$01
13	3.3482	3.3530	9.0	26.60	26.56	0.038	041
14	2.2950	2.2968	14.9	39.22	39.19	0.31	$\bar{2}$32
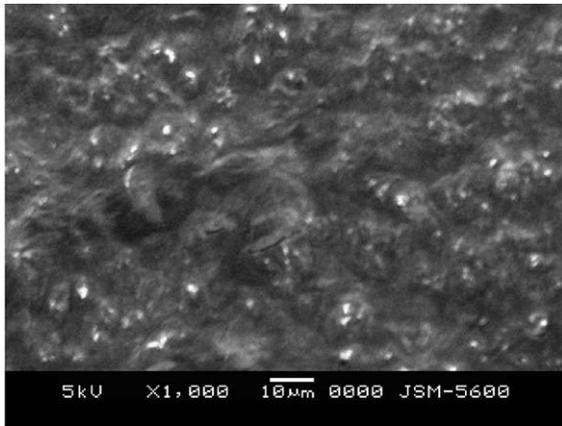
-a-
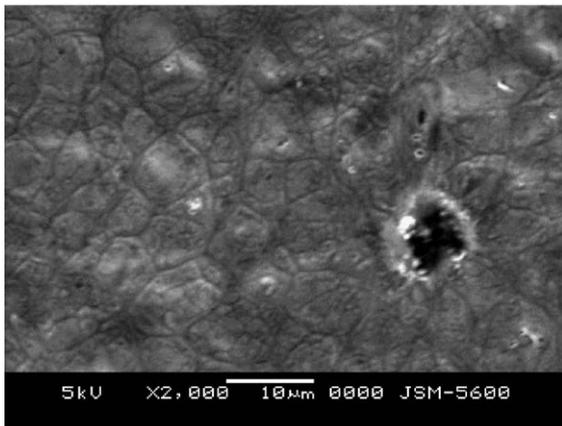
-b-

Fig. 3. SEM micrographs of Co(II) complex.

which shows the strange $T^{1/4}$ law [10,11]. This is related to the dc conductivity,

$$\sigma_{dc}(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)\right]^{1/4} \qquad (5)$$

where T_0 is given by

$$T_0 = \frac{1}{kN(E_F)L_{Loc}^3} \qquad (6)$$

where $N(E_F)$ is the density of localized states at Fermi level, L_{Loc} is the localization length. Fig. 5 shows the hopping conductivity for the complex. It is seen from the figure that the conductivity exhibits three-dimen-

sional variable hopping conduction (VRH) [10]. The parameters of hopping conduction for the complex were calculated using Fig. 5 and Eq. (6), and the calculated values are given in Table 2.

In the extended states of the second region of Fig. 4, the linearity of $\ln\sigma$ vs. $1/T$ indicates that the conductivity exhibits activated behaviour, and can be described by the Arrhenius relation,

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \qquad (7)$$

where σ_0 is the preexponential factor. ΔE is the activation energy for thermally activated process and k is the Boltzmann's constant. The value of electrical conductivity at room temperature, σ_{25}, and activation energy ΔE for each region of the complex are shown in Table 2.

Temperature dependence of the conductivity curve of the complex exhibits two regions, as shown in Fig. 4. In the first region, increase of conductivity with temperature is of hopping conduction type and conduction takes place in localized states. In the hopping model, electron exchange energies are small as compared with the electron–phonon energies, but larger than the phonon dispersion energies. Here, the charge carrier is trapped at each molecule site and moves over the intermolecular barrier via a thermally activated process [10,12]. In the second region, conduction is of typical Arrhenius-type dependence on temperature. The calculated activation energy values for each conduction region show that the lower values of ΔE are associated with the intermolecular conduction process, while the higher values are related to the intramolecular conduction process. In this semiconductor material, there are two stages in the movement of a current carrier motion within the this metal complex, which is macromolecule and passage from one macromolecule to another, that is, the intramolecular and intermolecular transfer of the current carrier. In this metal complex, intramolecular transfer of electrons take place by electrons hopping from one atomic site to another if orbitals with the same energy levels exist between sites. If intermolecular orbital overlap of charges is present, electron or holes can travel from one kind of macromolecule to another. Therefore, π (pi) electrons can transfer also from one type of macromolecule to another by hopping if
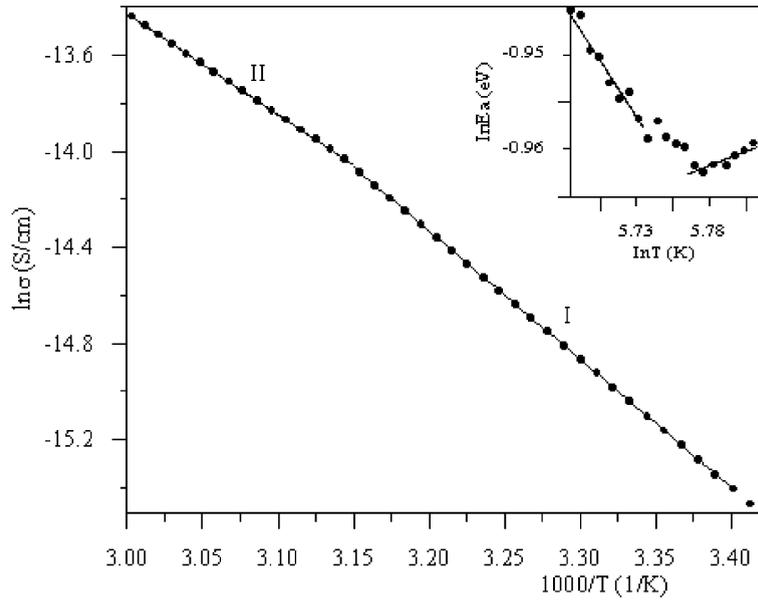
Fig. 4. Temperature dependence of the conductivity of the Co(II) complex.

orbitals with the same energy levels exist between the complex molecule. If we assume that the carriers within intramolecules are excited, then carriers are retarded by the barrier of macromolecules. The acti-

vation energy of intramolecular conduction process is higher. Therefore, the first step of conduction starts between intermolecules, and the lower activation energy corresponds to intermolecular transfer, while
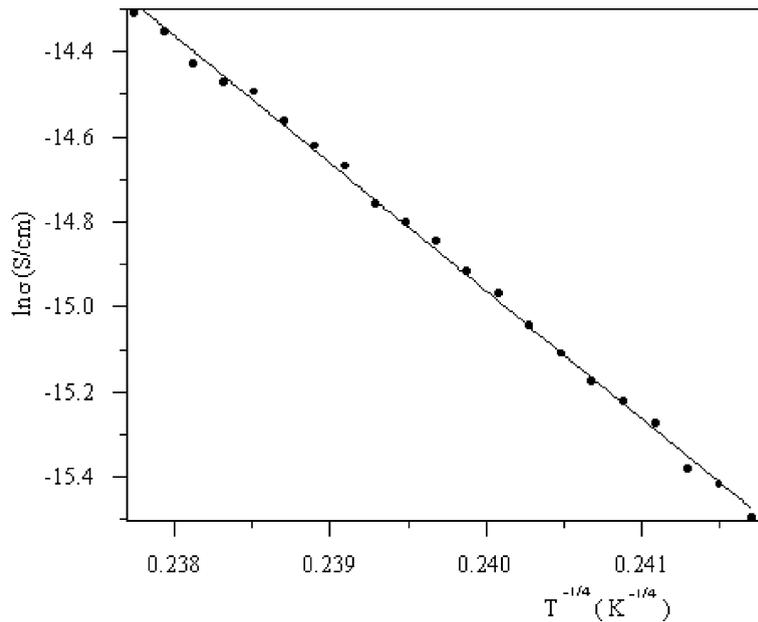
Fig. 5. The hopping conductivity for Co(II) complex.

Table 2
The electronic parameters of the Co(II) complex

σ_{300} (S/cm)	ΔE_1 (eV)	ΔE_2 (eV)	T_0 (K)	$N(E_F)$ (cm^{-3} eV^{-1})	R (nm)
2.57×10^{-7}	0.46	0.36	8.08×10^9	2.35×10^{25}	2.78

the higher activation energy corresponds to intramolecular transfer. However, basically, the conduction process is considered to be both intramolecular and intermolecular. It is considered that while intramolecular conduction process occurs between metal and ligand in this metal complex, intermolecular conduction process occurs from macromolecule metal complex to another [6,9].

4. Conclusions

The electrical conductivity, microstructure and crystal structure properties of the $[CO_2(L)L'(dioxane)_2(NO_3)_2](NO_3)_2$ complex have been investigated. The X-ray diffraction shows that the complex has triclinic structure with unit cell parameters. It is found that while hopping conductivity occurred at low temperatures, the thermally activated conduction mechanism took place at high temperatures. As a result, the $[CO_2(L)L'(dioxane)_2(NO_3)_2](NO_3)_2$ complex is a semiconductor with calculated electronic parameters.

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