

ELECTRICAL CONDUCTIVITY OF CHLORO(PHENYL)GLYOXIME AND ITS Co(II), Ni(II) AND Cu(II) COMPLEXESOrhan TURKOGLU^{a1,*}, Mustafa SOYLAK^{a2} and Ibrahim BELENLI^b^a Department of Chemistry, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey; e-mail: ¹ turkoglu@erciyes.edu.tr, ² soylak@erciyes.edu.tr^b Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey; e-mail: belenli@ibu.edu.tr

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Chloro(phenyl)glyoxime, a vicinal dioxime, and its Ni(II), Cu(II) and Co(II) complexes were prepared. XRD patterns of the complexes point to similar crystal structures. IR and elemental analysis data revealed the 1:2 metal-ligand ratio in the complexes. The Co(II) complex is a dihydrate. Temperature dependence of electrical conductivity of the solid ligand and its complexes was measured in the temperature range 25–250 °C; it ranged between 10^{-14} – 10^{-6} $\Omega^{-1} \text{ cm}^{-1}$ and increased with rising temperature. The activation energies were between 0.61–0.80 eV. The Co(II) complex has lower electric conductivity than the Ni(II) and Cu(II) complexes. This difference in the conductivity has been attributed to differences in the stability of the complexes.

Keywords: Electrical conductivity; Cobalt; Nickel; Copper; Chloro(phenyl)glyoxime complexes; Oximes; Dioximes; XRD.

Complexes formed by dimethylglyoxime, *vic*-dioximes and related ligands have been under intensive investigation for a few decades. Research on these materials has gained momentum recently, due to their potential use in trace-metal analysis, electrochemical and electro-optical sensors, as catalysts, and in medical applications^{1–6}. Vicinal dioximes are amphoteric, as they have both acidic hydroxy groups and slightly basic nitrogen atoms, and form complexes with many transition metals such as Ni(II), Cu(II), Zn(II), Pd(II) and Co(II). In the compounds, two *vic*-dioxime molecules coordinate to a metal ion, in a symmetrical or unsymmetrical fashion. Metal ions often bind to four N atoms, facilitating two extra hydrogen bridge bondings, and form complexes with square-planar, square-pyramidal or octahedral geometries. Some ligands, such as substituted aminoglyoxime, react with Co(II) to give octahedral complexes that have two additional water

molecules bound in the axial positions. On the other hand, Ni(II) and Cu(II) ions form square-planar complexes with the same ligands^{3,7-9}.

Electrochemical properties of vicinal dioxime-metal complexes in solution have been reported^{3,10}. To our knowledge, electrical properties of the complexes in the solid state have not yet been published. Herein we report on the syntheses, characterization and solid-state thermo-electric behavior of the chloro(phenyl)glyoxime and its Co(II), Ni(II) and Cu(II) complexes.

EXPERIMENTAL

All the chemicals used were of analytical grade (99.9%, Merck) and used as supplied. For the synthesis of 2-(hydroxyimino)-1-phenylethan-1-one (isonitrosoacetophenone), metallic sodium (2.3 g) in absolute ethanol (100 ml) was cooled to $-10\text{ }^{\circ}\text{C}$. Next, butyl nitrite (11.7 ml) was slowly added to the EtOH solution (*ca* 30 min) upon continuous stirring. The mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for another 20 min, followed by dropwise addition of acetophenone (12 ml). The stirring of the mixture was continued at room temperature for another 30 min. After standing overnight, the resulting red solid was filtered off and washed several times with diethyl ether. The crude product was redissolved in a minimum amount of water and the solution was acidified with acetic acid (1-3 ml). The white precipitate of the product was filtered off, washed twice with water, and recrystallized in ethanol-water (1:2).

In order to form phenylglyoxime, isonitrosoacetophenone (3.11 g) was dissolved in EtOH (20 ml). CH_3COONa (3.20 g) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1.79 g) were dissolved in H_2O (10 ml) and the solution was added to the isonitrosoacetophenone solution. The mixture was refluxed upon stirring at $100\text{--}110\text{ }^{\circ}\text{C}$ for 4 h. After two days, water (60 ml) was added and the mixture was left standing overnight. The product was filtered off, washed twice with water, and stored in a vacuum desiccator.

Chloro(phenyl)glyoxime (L) was prepared from phenylglyoxime. For the synthesis, phenylglyoxime (5 g) was ground in an agate mortar, followed by addition of enough chlorine. Dry chlorine was passed through the suspension exposed to UV radiation for 15-20 min. At the end of the reaction, a white product was obtained. Then, air was passed through the mixture for 30 min to remove excess chlorine.

The solid complexes of the ligand L were prepared by adding (upon continuous stirring) 15-20 ml aqueous solutions of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.119 g, 0.5 mmol), $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.119 g, 0.5 mmol) or $\text{CuCl}_2\cdot 6\text{H}_2\text{O}$ (0.085 g, 0.5 mmol) dropwise to 20 ml of alcoholic solutions of the ligand (0.198 g, 1 mmol); pH of the mixtures was between 3 and 4. For precipitation of the complexes, pH was adjusted to 5.5-6 by dropwise addition of 1% NaOH aqueous solution. The mixtures were stirred on a water bath at $50\text{--}60\text{ }^{\circ}\text{C}$ for 30 min and in an ice bath for another 30 min. The products were then filtered off, washed several times with cold water and diethyl ether, and dried in a vacuum desiccator. Elemental analyses (C, H and N) were performed with a CHNS-932 (LECO) apparatus.

Elemental analyses. The ligand L: for $\text{C}_8\text{H}_7\text{ClN}_2\text{O}_2$ (198.6) calculated: 48.40% C, 3.55% H, 14.11% N; found: 49.01% C, 3.97% H, 14.66% N. The cobalt complex: for $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{CoN}_4\text{O}_6$ (490.2) calculated: 39.22% C, 3.27% H, 11.43% N; found: 39.85% C, 3.31% H, 11.15% N. The nickel complex: for $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{N}_4\text{NiO}_4$ (453.9) calculated: 42.36% C, 2.67% H, 12.35% N; found: 41.87% C, 2.82% H, 12.08% N. The copper complex: for $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{CuN}_4\text{O}_4$ (458.7) calculated: 41.87% C, 2.63% H, 12.22% N; found: 41.95% C, 2.60% H, 12.51% N. The co-

balt, nickel and copper complexes and the ligand are dark brown, green-yellow, black and white, respectively.

X-ray powder diffraction (XRD) data of the complexes and ligand L were recorded with a Bruker AXS D8 advanced diffractometer, using graphite monochromatized $\text{CuK}\alpha$ radiation operated at 40 kV and 40 mA. The bonding of the ligand L in the investigated complexes was examined by FTIR spectroscopy with a Jasco 330 model spectrometer. The recorded FTIR spectra of the complexes (KBr pellets) were compared with that of uncoordinate L. Magnetic moments in the solid state were measured with a Gouy balance at room temperature by the Faraday method, using mercuric tetrathiocyanatocobaltate(II) as a susceptibility standard. Diamagnetic corrections were made from the Pascal's constants. Electronic absorption spectra of the compounds in DMSO solutions were recorded on a Hitachi Model 150-20 UV-VIS double-beam spectrophotometer.

The total electric conductance (σ_T) of the synthesized complexes and the ligand L were measured on sample pellets ($d = 12$ mm, thickness ≈ 1 mm) made in a stainless holder under $ca 5 \times 10^3 \text{ kg cm}^{-2}$ pressure. Disk-shaped pellets were sintered in air at 70–80 °C for 24 h. Scanning electron microscopy (SEM) revealed that the degree of compaction in all cases ranged between 80 and 95%. Silver electrodes were vacuum-deposited as four narrow lines on the flat surface of the pellets by DC sputtering technique. Fine silver wires were attached to the silver-deposited regions using high-conductivity silver paint. After making the four-point contacts, the pellets were heated in air at 70–80 °C for 5 h to make the contacts stronger to handle and to reduce contact resistance. The ohmic character of the contacts was checked prior to each measurement. The electric conductivity was measured in the range between room temperature and $ca 250$ °C by four-probe arrangement. Potential difference E was measured from the inner two probes with a Keithley digital multimeter; the current i was measured with a Keithley digital electrometer. If the distances S between the probes are the same and the ratio L/S is higher than 2, where L is the distance between the end probes and the sample edge, the total electric conductance (σ_T) can be calculated using Eq. (1)¹¹.

$$\sigma_T = \frac{1}{2\pi S} \frac{i}{E} \quad (1)$$

The temperature of the samples during these measurements was determined by placing a thermocouple at about 5 mm from the sample. Temperature increments between the measurements were kept small and the measurements of the samples at each temperature were performed after thermal equilibrium had been reached.

RESULTS AND DISCUSSION

Elemental analyses and other physical data show that the ligand L reacts with metal ions ($M = \text{Cu}^{2+}$, Ni^{2+} or Co^{2+}), producing chelate complexes of the ML_2 type. These complexes are insoluble in water and in most common organic solvents such as ethanol, methanol, acetone, chloroform and benzene, and poorly soluble in DMF and DMSO. The complexes are air-stable solids that gradually decompose, melt and volatilize in the temperature range of 250–340 °C. According to the formulae of the complexes, both

Cu(II) and Ni(II) ions exhibit coordination number 4, whereas Co(II) is hexacoordinate, having two water molecules in the coordination sphere.

The main infrared stretching modes of the free ligand and the ML_2 chelates are shown in Table I. The data show that both ligands are bidentate, and the metal ions bind to two ligand molecules through nitrogen atoms. The ligand O–H stretching vibrations have been observed at 3300 cm^{-1} . This vibration was not observed in the IR spectra of the complexes. The disappearance of this band is due to the formation of M–N and hydrogen bonds. The complexes show IR absorption bands around $1650\text{--}1680\text{ cm}^{-1}$ for stretching modes H–O...H and at about 500 cm^{-1} for M–N stretch. These new bonds cause a shift of the C=N stretching frequencies of the complexes to $1610\text{--}1620\text{ cm}^{-1}$ compared to that of uncoordinate L (1640 cm^{-1}). In the case of the Co(II) complex, the axially bound water molecules can be identified by broad $\nu(\text{OH})$ band around $3400\text{--}3360\text{ cm}^{-1}$ that keeps its intensity even after heating the complex at $125\text{ }^\circ\text{C}$ for 12 h.

Table I also gives the room temperature magnetic moments of the prepared complexes. The magnetic moment of the d^7 Co(II) chelate ($\mu_{\text{eff}} = 4.26\ \mu_{\text{B}}$) is within the range reported for high-spin octahedral Co(II) complexes^{12,13}. The square-planar geometry for the d^9 Cu(II) chelate is also confirmed by its magnetic moment ($\mu_{\text{eff}} = 1.85\ \mu_{\text{B}}$) which falls within the range reported in the literature. For the Ni(II) chelate, the diamagnetic nature is observed, as expected for d^8 -metal ions in a square-planar field^{12,13}. The suggested geometries of the complexes are depicted in Fig. 1. Due to the asymmetry of the ligand, the complexes are expected to exist as *cis*- and *trans*-isomers.

TABLE I
Measured magnetic moments and IR stretching frequencies (cm^{-1}) of the ligand L and its complexes

Compound	$\mu_{\text{eff}} (\mu_{\text{B}})$	O–H	C–H (arom.)	C=N	N–O	H ₂ O	O–H...O	Others
L	Dia	3300	3090–3000	1640	965	–	–	^a
[Co(L) ₂ (H ₂ O) ₂]	4.26	–	3050	1620	940	3400–3360	1680	^{a,b,c}
[Ni(L) ₂]	Dia	–	3040	1610	950	–	1670	^{a,b}
[Cu(L) ₂]	1.85	–	3030	1620	950	–	1650	^{a,b}

^a $\nu(\text{C–Cl})$ bands at $690\text{--}760\text{ cm}^{-1}$. ^b $\nu(\text{M–N})$ bands at *ca* 500 cm^{-1} . ^c $\nu(\text{M–O})$ bands at *ca* 600 cm^{-1} .

The UV-VIS spectrum of the ligand exhibits a band at 266 nm that can be attributed to the $n \rightarrow \pi^*$ transition of the oxime group^{3,12}. Only one absorption band is present in the UV-VIS spectra of the complexes, at 260 nm for Co^{2+} , 264 nm for Ni^{2+} and 279 nm for Cu^{2+} . These spectral data are assigned to the intraligand transition. Lower-lying absorption bands due to $d \rightarrow d$ transitions could not be observed due to the poor solubility of the complexes.

Figure 2 shows X-ray diffraction patterns of the ligand L and the studied complexes at room temperature. The first peak of the ligand is missing in diffractograms of the complexes, but the latter show extra peaks, absent in the XRD pattern of the ligand. These extra peaks prove the coordination of the metal ions. These XRD patterns also indicate that the ligand and complexes are crystalline, with various degrees of crystallinity. In particular, the XRD patterns of the ligand and the Co(II) complex have higher background intensity and reduced sharpness of the peak profiles than the Cu(II) and Ni(II) complexes, thus indicating poorer crystallinity. Broadening of the peak profiles for the Co(II) complex may be due to the two water ligands. The XRD patterns of the Cu(II) and Ni(II) complexes are very similar but that of the Co(II) complex is slightly different, exhibiting some extra peaks and small shifts in all peak positions toward higher angles. The close XRD patterns for the studied complexes point to their similar crystal structures.

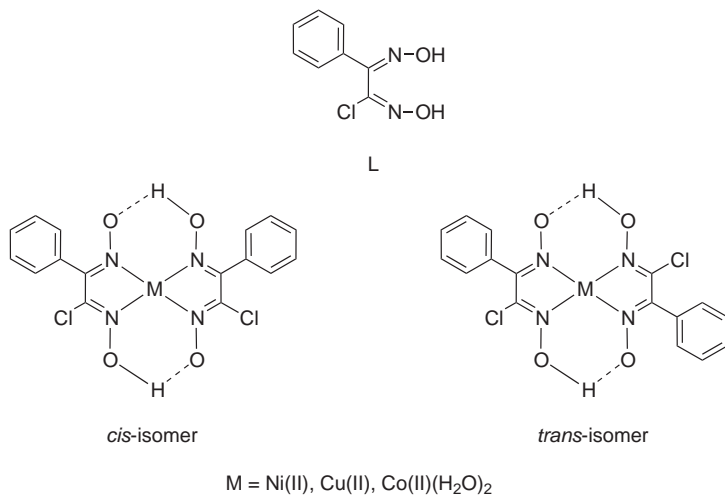


FIG. 1
Proposed structure for ML_2 complexes

Despite many efforts, no single crystals of the complexes were obtained to allow crystal structure determination.

Table II shows activation energies and pre-exponential factors for the ligand L and the complexes under study. Activation energy is lowest for the Cu(II) complex that shows the highest conductivity, and highest for the Co(II) complex that shows the lowest conductivity. The activation energy values do not exhibit large differences, indicating similar forbidden energy gaps for these compounds. Low values of the activation energy, despite very low conductivity, indicate that the conduction is likely to occur *via*

TABLE II
Activation energies (E_a) and pre-exponential factors (σ_0) for the ligand L and its complexes

Compound	E_a , eV	σ_0 , $\Omega^{-1} \text{ cm}^{-1}$
L	0.74	0.49
[Co(L) ₂ (H ₂ O) ₂]	0.80	0.37
[Ni(L) ₂]	0.68	0.54
[Cu(L) ₂]	0.61	0.68

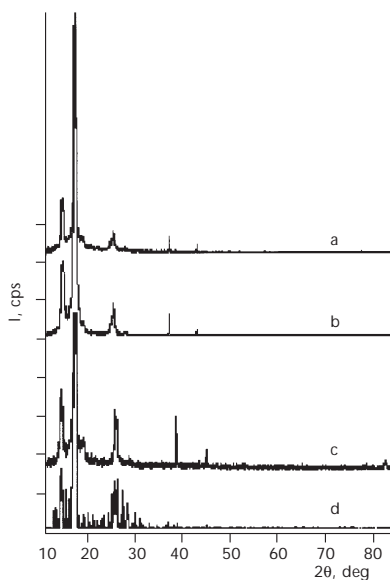


FIG. 2
XRD patterns of Cu(II) (a), Ni(II) (b), Co(II) (c) complexes of chloro(phenyl)glyoxime (d). Count rates are drawn with different offset values

tunneling or hopping of charge carriers between localized states. Electrons thermally excited from uppermost filled molecular orbitals to the lowest unoccupied molecular orbitals are then assumed to tunnel to equivalent empty levels of the neighboring molecules, whereas the positive holes move in the opposite direction, as reported in the literature for similar substances^{7,11,14-17}. In the literature, electric conductivities of some organometallic and polymeric compounds, lying in the same range as those for our complexes and having similar activation energies, have been explained by tunneling or hopping of charge carriers^{7,15,17}.

Figure 3 shows the typical Arrhenius plots of $\log \sigma_T$ vs T^{-1} for the materials. These data have been obtained during repeated heating runs at a constant rate in air. Electric conductance of the ligand L at 37 °C is $7.2 \times 10^{-13} \Omega^{-1} \text{ cm}^{-1}$ and that of its Co(II) complex even lower at the same temperature, *viz.* $5.5 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1}$. The Ni(II) and Cu(II) complexes, on the other hand, show much higher conductances at 37 °C, *viz.* 5.0×10^{-12} and $1.1 \times 10^{-10} \Omega^{-1} \text{ cm}^{-1}$, respectively. The ligand has a quite low conductivity at room temperature because of a very small number of charge carriers. The conductivity increases with rising the temperature up to 150 °C. The maximum conductance for the ligand was $1.25 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$ at this temperature, this value being about four orders of magnitude higher than its room-temperature conductance. Above 150 °C, the ligand started to melt and decompose. The nature of the electric conductivity in the samples is electronic.

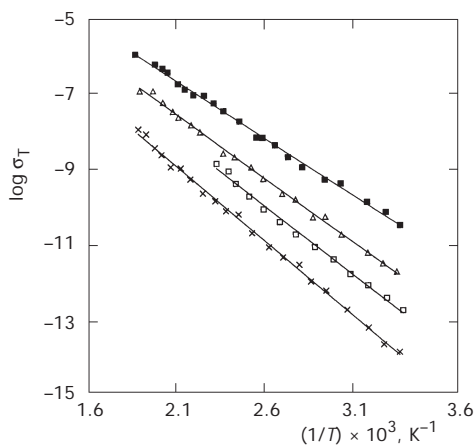


FIG. 3

Temperature dependence of total conductances (σ_T) for chloro(phenyl)glyoxime (L; \square) and its complexes $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$ (\times), $[\text{Ni}(\text{L})_2]$ (Δ) and $[\text{Cu}(\text{L})_2]$ (\blacksquare)

In general, the total conductance is given by $\sigma_T = n |e| \mu$, where n is the number of charge carriers, e is their charge, and μ is their mobility. As shown in Fig. 3, the conductance rises exponentially with temperature. Temperature dependence of the observed electric conductivity obeys the simple Arrhenius equation (Eq. (2)):

$$\sigma_T = \sigma_o \exp(-E_a / kT), \quad (2)$$

where σ_T is the total electric conductance, σ_o the pre-exponential factor, E_a the activation energy, k Boltzmann constant, and T the absolute temperature. It should be noted that the electric conductivity measured in this work is a bulk property including grain boundary effects together with inner grain conductivity. Intrinsic conductivity would be useful if single crystals of these complexes were available; nevertheless, bulk conductivities are also necessary for understanding electric conduction phenomena, being valuable for comparison of complexes.

With rising temperature, the conductivity increases as a result of increasing charge carrier density due to thermal activation. The mobility of the charge carriers is also temperature-dependent (proportional to a power of temperature), but the exponential temperature dependence of the charge carrier density dominates the thermo-electric behavior. In the complexes, the hydrogen bonding may play an intermediary role in the mechanism of the charge transfer between two ligands bound to the central metal ion, leading to enhanced conductivity with a decrease in activation energy. This also indicates the possibility of some degree of delocalization in the excited states.

Differences in the conductivity of the complexes may originate from different electronic configurations of metal ions bound to the ligand molecules. Thermogravimetric (TG) and differential thermal analysis (DTA) measurements have shown that the decomposition and volatilization temperatures of the Co(II) complex are highest and those of Cu(II) complex are slightly lower than for the Ni(II) complex. This suggests that molecular bonding and hence stability differences among the complexes may lead to differences in their charge carrier densities and/or mobilities. On the other hand, different coordination geometry of the complexes and, hence, different molecular packing and intermolecular interactions are probably also responsible for differences in their electrical conductivity. The conductivity of the Co(II) complex is lower than those of the other complexes, indicat-

ing its higher stability and different geometry (Fig. 1). The Cu(II) compound shows, on the other hand, the highest conductivity, which may be explained by a higher charge carrier density due to its square-planar geometry and lower stability. The Cu(II) ion in its complex has one more valence electron than the Ni(II) ion. This extra electron occupies the $d_{x^2-y^2}$ orbital and may take part in intermetallic interactions. These interactions can be expected to take place between adjacent atoms¹⁵.

CONCLUSION

Chloro(phenyl)glyoxime reacts with metal ions ($M = \text{Cu}^{2+}$, Ni^{2+} or Co^{2+}), producing chelate complexes that are insoluble in common organic solvents, and poorly soluble in DMF and DMSO. The complexes are air-stable up to temperatures 290–340 °C. The Cu(II) and Ni(II) complexes have square-planar geometry and the high-spin Co(II) complex octahedral geometry. XRD patterns indicate that the ligand and its complexes have different crystal systems with various degrees of crystallinity. The three studied complexes show very close XRD patterns, suggesting similar crystal structures. Temperature dependence of the electric conductivity of the complexes obeys Arrhenius equation with very low conductance values. Electrical conductivity in the ligand and the complexes can be described by tunneling or hopping of charge carriers between localized sites.

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