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ON THE FORMATION OF MONONUCLEAR AND BINUCLEAR COMPLEXES OF PENTADENTATE N_4O_2 SCHIFF BASE LIGANDS WITH Co(II), Ni(II) AND Cu(II) IONS: TGA, SPECTRAL AND CONDUCTANCE STUDIES

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ABSTRACT

Four types of complexes derived from pentadentate N_4O_2 Schiff base (SB) ligands having the general formulae; $[M(SB)Cl(H_2O)_2]$, $[M_2(SB)Cl_2(H_2O)_5]$ for Co(II) and Ni(II) and $[Cu(SB)Cl]$ and $[Cu_2(SB)Cl_2(H_2O)]H_2O$ were prepared and investigated. The isolated complexes were characterized on the basis of elemental analysis, thermogravimetric analysis (TGA), IR, electronic and electron paramagnetic resonance (EPR) spectra and conductance measurements. The electrical resistivities were measured and the activation energies were calculated for the solid complexes. It was found that the resistivities and activation energies of the complexes based on salicylidene derivatives were higher than those of complexes containing the naphthalidene moiety.

INTRODUCTION

Transition metal complexes of aryl Schiff bases (SB) have wide application in catalysis [1–4] of various chemical and photochemical reactions as

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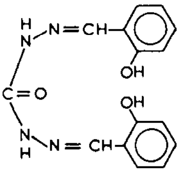
well as in biological systems [5–8]. The applications of such metal chelates to any one system depends to a large extent on its molecular structure.

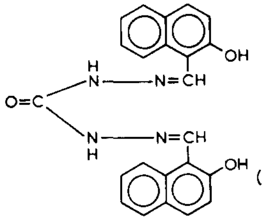
Accordingly, the aim of the present study was to synthesize and characterize some Co(II), Ni(II) and Cu(II) mononuclear and binuclear complexes with Schiff base ligands N_4O_2 derived from carbohydrazide. The complexes were characterized by elemental analysis, thermogravimetric analysis (TGA), spectroscopic techniques and conductance measurements. The electrical resistivities and the activation energies of these complexes were measured and are commented on in relation to molecular structure.

EXPERIMENTAL

The aldehyde and carbohydrazide were obtained from Aldrich chemical company. The ligands were prepared by the method of Diehl and Hach [9]; they have the following structural formulae



(II)



(I)

All other materials were of reagent grade and were used without further purification.

Preparation of $[M(SB)Cl(H_2O)_2]$ complexes

To a stirred solution of the ligand (0.002 mol) dissolved in 100 ml of ethanol was added 0.002 mol of the metal(II) chloride dissolved in 20 ml of distilled water. The mixture was refluxed for about 1 h on a water bath. The solid complex was separated out from the mixture, filtered off, washed with dry ethanol and dried in vacuo.

Preparation of $[M_2(SB)Cl_2(H_2O)_5]$ complexes

0.002 mol of ligand solution dissolved in 100 ml of ethanol, containing 4 mol of sodium acetate, was added dropwise to 0.005 mol of the metal(II) chloride dissolved in 50 ml of distilled water. The mixture was stirred for 3 h in cold conditions. The solid complex separated out from the mixture, was filtered off, washed with dry ethanol and dried in vacuo.

Apparatus and working procedures are the same as those previously described [10].

RESULTS AND DISCUSSION

All the prepared complexes were subjected to elemental microanalysis; the data are listed in Table 1. The results of analysis for the complexes with ligands (**I**) and (**II**) are in accordance with the formation of mononuclear and binuclear complexes of the compositions $[M(SB)Cl(H_2O)_2]$ and $[M_2(SB)Cl_2(H_2O)_5]$, respectively. These results reveal that the ligands behave as monobasic tridentate towards one metal ion or as dibasic pentadentate ones towards two metal ions, forming a binuclear complex.

Figure 1 shows the thermograms of some of the solid complexes with ligand (**I**). One the basis of % loss in weight (Table 2) the thermal decomposition for mononuclear Co(II) or Ni(II) complexes can be formulated as follows

$$\begin{tikzcd}
{[M(SB)Cl(H_2O)_2]} \arrow[r, "-H_2O", "120\text{–}150\,^\circ C"'] & {[M(SB)Cl(H_2O)]} \arrow[r, "-H_2O", "170\text{–}180\,^\circ C"'] & {[M(SB)Cl]} \arrow[d, "310\text{–}315\,^\circ C"', "-Cl"] \\
 & MO & {[M(SB)]^+} \arrow[l, "400\text{–}450\,^\circ C"']
\end{tikzcd}$$

whereas the thermal decomposition for the binuclear Co(II) or Ni(II) complexes can be formulated

$$\begin{tikzcd}
{[M_2(SB)Cl_2(H_2O)_5]} \arrow[r, "-2H_2O", "125\text{–}130\,^\circ C"'] & {[M_2(SB)Cl_2(H_2O)_3]} \arrow[dr, "-3H_2O", "190\text{–}200\,^\circ C"'] & \\
MO & {[M_2(SB)]^{2+}} \arrow[l, "420\text{–}490\,^\circ C"'] & {[M_2(SB)Cl_2]} \arrow[l, "-2Cl", "300\text{–}350\,^\circ C"']
\end{tikzcd}$$

The thermal decomposition for mononuclear Cu(II) complexes with ligand (**I**) can be postulated on the basis of loss in weight as follows

$$[Cu(SB)Cl] \xrightarrow[300\text{–}310\,^\circ C]{-Cl} [Cu(SB)]^+ \xrightarrow[350\text{–}500\,^\circ C]{} Cu_2O \xrightarrow[550\text{–}600\,^\circ C]{} CuO$$

For binuclear Cu(II) complexes the thermal decomposition can be represented as follows

$$\begin{tikzcd}
{[Cu_2(SB)Cl_2(H_2O)]H_2O} \arrow[r, "-H_2O", "50\text{–}60\,^\circ C"'] & {[Cu_2(SB)Cl_2(H_2O)]} \arrow[r, "-H_2O", "150\text{–}170\,^\circ C"'] & {[Cu_2(SB)Cl_2]} \arrow[d, "270\text{–}300\,^\circ C"', "-2Cl"] \\
CuO & Cu_2O \arrow[l, "400\text{–}450\,^\circ C"'] & {[Cu_2(SB)]^{2+}} \arrow[l, "320\text{–}350\,^\circ C"']
\end{tikzcd}$$

On the basis of the above results one can conclude the following: (a) lattice water is removed from the binuclear copper chelates at 50–60 °C, whereas coordinated water could be eliminated from all complexes within the temperature range 120–200 °C; (b) coordinated Cl could be removed within the 270–350 °C range; (c) binuclear Ni(II) or Co(II) complexes are thermally more stable than the mononuclear ones: in addition, the mononuclear Cu(II) complex is more volatile than the binuclear Cu(II) complexes; (d) the thermal stability for mononuclear complexes is $[Cu(SB)Cl] >$

TABLE 1

Analytical, magnetic and conductance data of metal(II)–Schiff base complexes

Complex	Microanalysis results [a]				EPR data				Conductance [b] (ohm^{-1} cm^2 mol^{-1})	E (eV)
	%C	%H	%N	%Cl	%M	$g_{\parallel}$	$g_{\perp}$	g_{eff}		
$[CoL_ICl(H_2O)_2]$	52.1 (52.32)	4.1 (3.98)	10.3 (10.61)	6.4 (6.72)	10.5 (11.18)	1.6612	1.7411	2.2079	12.25	0.492
$[Co_2L_ICl_2(H_2O)_5]$	40.4 (40.83)	3.7 (3.85)	8.0 (8.28)	10.3 (10.50)	17.0 (17.45)	1.6512	1.7441	2.4017	12.98	–
$[CoL_{II}Cl(H_2O)_2]$	43.3 (42.12)	4.1 (3.92)	13.8 (13.10)	8.4 (8.301)	14.7 (13.78)	1.6781	1.7671	2.4369	15.55	–
$[Co_2L_{II}Cl_2(H_2O)_5]$	31.5 (31.30)	4.1 (3.83)	9.4 (9.74)	12.1 (12.35)	19.70 (20.52)	1.6931	1.7862	2.4611	16.13	–
$[NiL_ICl(H_2O)_2]$	53.3 (52.35)	4.00 (3.98)	9.9 (10.60)	7.7 (6.73)	11.9 (11.13)	[c]			17.74	0.286
$[Ni_2L_ICl_2(H_2O)_5]$	40.6 (40.92)	4.2 (4.11)	9.0 (8.32)	10.0 (10.50)	18.0 (17.40)	[c]			18.56	–
$[NiL_{II}Cl(H_2O)_2]$	43.1 (42.13)	4.4 (4.20)	13.8 (13.10)	7.9 (8.30)	13.8 (13.74)	[c]			18.37	–
$[NiL_{II}Cl_2(H_2O)_5]$	31.5 (31.33)	3.9 (3.83)	9.9 (9.74)	13.2 (12.36)	20.9 (20.43)	[c]			[d]	0.571
$[CuL_ICl]$	56.6 (55.70)	3.7 (3.42)	11.1 (11.30)	6.8 (7.16)	13.50 (12.71)	1.4349	1.7457	2.2597	[d]	0.469
$[Cu_2L_ICl_2(H_2O)]H_2O$	43.8 (43.80)	3.9 (3.17)	8.8 (8.88)	10.8 (11.27)	14.4 (20.16)	1.4401	1.7394	2.2585	17.50	–
$[CuL_{II}Cl]$	45.5 (45.30)	4.0 (3.30)	13.9 (14.15)	8.4 (8.97)	15.9 (16.03)	1.4364	1.7511	2.2649	17.42	–
$[Cu_2L_{II}Cl_2(H_2O)]$	36.1 (35.22)	3.5 (2.74)	11.5 (10.95)	13.8 (13.87)	24.2 (24.65)	1.4349	1.7520	2.2646	19.42	–

[a] % Found (% calculated).

[b] 10^{-3} M complex in DMF.

[c] EPR inactive at room temperature as well as liquid N_2 temperature.

[d] Insoluble in DMF.

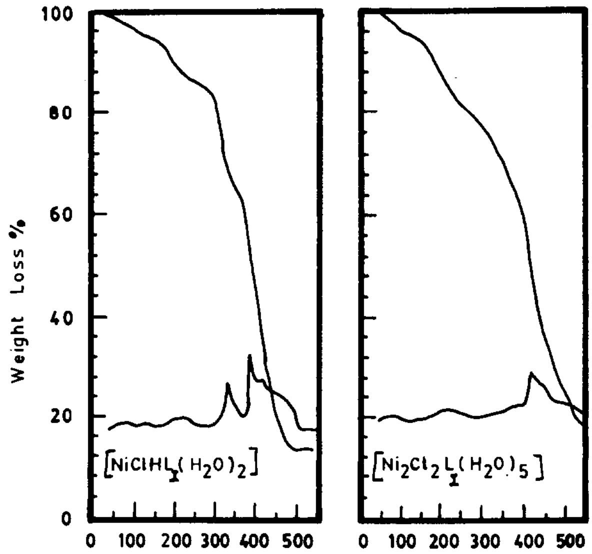


Fig. 1. Thermograms of some solid complexes with ligand (**I**).

TABLE 2

Thermogravimetric analysis of M(II) ions with ligand (**I**)

Complex	% loss in weight [a]	Assignment	Temperature range (°C)
$[CoL_ICl(H_2O)_2]$	3.41 (3.20)	Loss of one coordinated H_2O	120–125
	6.82 (6.60)	Loss of two coordinated H_2O	170–180
	13.55 (13.20)	Loss of one coordinated Cl	310–315
	88.82 (88.10)	Loss of SB ligand	400–450
$[Co_2L_ICl_2(H_2O)_5]$	5.33 (5.00)	Loss of two coordinated H_2O	125–130
	13.31 (13.10)	Loss of three coordinated H_2O	190–200
	23.82 (23.40)	Loss of two coordinated Cl	300–350
	82.54 (82.20)	Loos of SB ligand	420–490
$[Ni_2L_ICl_2(H_2O)_5]$	5.34 (5.10)	Loss of two coordinated H_2O	125–130
	13.35 (13.00)	Loss of three coordinated H_2O	190–200
	23.88 (23.30)	Loss of two coordinated Cl	300–360
	82.79 (82.10)	Loss of SB ligand	430–300
$[CuL_ICl]$	7.15 (6.80)	Loss of coordinated Cl	300–310
	87.19 (86.50)	Loss of SB ligand	350–500
$[Cu_2L_ICl_2(H_2O)]\cdot H_2O$	2.85 (2.40)	Loss of one lattice H_2O	50– 60
	5.71 (5.30)	Loss of one coordinated H_2O	150–170
	16.95 (16.40)	Loss of two coordinated Cl	270–300
	79.87 (79.30)	Loss of SB ligand	320–350

[a] % Calculated (% found).

$[Ni(SB)Cl(H_2O)_2] \simeq [Co(SB)Cl(H_2O)_2]$; (e) the thermal stability for binuclear complexes is $[Co_2(SB)Cl_2(H_2O)_5] \simeq [Ni_2(SB)Cl_2(H_2O)_5] > [Cu_2(SB)Cl_2(H_2O)] \cdot H_2O$.

The conductance vs. molar ratio curves are characterized by two breaks at mole ratios of 1 : 1 and 2 : 1 (M : ligand), respectively. The gradual increase in the conductance can be ascribed to the displacement of protons from the ligand, so that complex formation should take place through a covalent link construction between the metal ion and the oxygen atom of the phenolic OH group. Support for this idea comes from the low conductance values for the DMF solutions of the complexes (Table 1); hence no ionic character is observed. This also indicates the coordinated nature of the Cl^- ions in the mononuclear and binuclear complexes.

The bonding of the ligands to the metal ions was investigated by IR spectroscopy. The IR spectra of mononuclear and binuclear complexes compared with those of the free ligands (Table 2), reveal the following:

(i) In mononuclear complexes the $\nu(C{=}N)$ band is split into two bands; one is in nearly the same position as the free ligand and the other is shifted to a lower frequency (by 30–15 cm^{-1}). This provides evidence that one of the two C=N groups is coordinated to the metal ion and the other is uncoordinated.

(ii) In binuclear complexes one $\nu(C{=}N)$ band is shifted to a lower frequency (by 15–30 cm^{-1}); hence the two nitrogen atoms are contributing to form coordinate bonds with the metal ions.

(iii) The bands corresponding to $\delta(OH)$ and $\gamma(C{-}OH)$ are observed within the 1350–1300 and 1225–1170 cm^{-1} ranges, respectively in the IR spectra of the free ligands. These bands exhibit lower intensity in the IR spectra of the mononuclear complexes and disappear in those of the binuclear complexes.

(iv) The band corresponding to $\nu(C{=}O)$ is shifted to a lower frequency (by 33 cm^{-1}) in the spectra of all chelates on complex formation. This indicates that the C=O group is involved in coordination with the metal ions.

(v) The new bands appearing in the ranges 485–450, 385–360 and 340–320 cm^{-1} are assigned to $\nu(M{-}O)$, $\nu(M{-}N)$ and $\nu(M{-}Cl)$, respectively. Thus, the knowledge gained from IR spectra provides clear evidence that on coordination with the metal ions, the ligands behave as monobasic tridentate in the case of the mononuclear complexes and as dibasic pentadentate in the case of the binuclear complexes.

The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes were studied in DMF; the λ_{max} and ε_{max} values are listed in Table 3. The changes in the λ_{max} values with variation in the metal ions is due to the difference in the perturbing influence of the central metal ions on the ligand groups. The shift of the bands together with the change in colour of the complexes indicates complex formation. Co(II) complexes exhibit four absorption bands with λ_{max} at 380–390, 400–405, 520–525 and 655–660 nm. These

TABLE 3

IR and electronic spectral data for metal(II) ion–Schiff base complexes

Complex or ligand	ν(OH)	IR frequency (cm^{-1})					UV and visible	
		ν(C=O)	ν(C=N)	ν(M–N)	ν(M–O)	ν(M–Cl)	λ_{max} (nm)	$\varepsilon \times 10^4$ ($mol^{-1} cm^{-1}$)
$[CoL_ICl(H_2O)_2]$	3500–3420	1635	1605 1640	355	480	320	390, 405, 525, 665	1.25, 1.24, 0.31, 0.06
$[Co_2L_ICl_2(H_2O)_5]$	450–3400	1640	1610	360	475	325	395, 405, 525, 665	1.28, 0.9, 022, 0.12
$[CoL_{II}Cl(H_2O)_2]$	3500–3400	1630	1605 1625	350	475	325	390, 400, 525, 665	1.32, 0.82, 0.41, 0.08
$[Co_2L_{II}Cl_2(H_2O)_5]$	3460–3380	1635	1605	360	480	320	390, 405, 525, 665	1.12, 0.92, 0.52, 0.21
$[NiL_3Cl(H_2O)_2]$	3450–3300	1640 1625	1600	370	475	320	415, 435, 535, 605	1.38, 1.44, 0.01, 0.006
$[Ni_2L_ICl_2(H_2O)_5]$	3450–3300	1640	1600	365	450	325	414, 430, 545, 605	1.51, 1.84, 1.83, 0.02
$[NiL_{II}Cl(H_2O)_2]$	3460–3340	1640	1605 1620	370	485	325	375, 405, 530, 600	0.83, 1.003, 0.91 0.03
$[Ni_2L_{II}Cl_2(H_2O)_5]$	3480–3380	1640	1595	370	485	325	415, 440, 610	[a]
$[CuL_ICl]$	3330 [b]	1640	1600 1620	355	460	320	405, 430, 645	[a]
$[Cu_2L_ICl_2(H_2O)]H_2O$	3500–3410	1645	1600	360	460	320	405, 425, 450, 475, 610	1.4, 2.0, 1.51, 0.97, 0.05
$[Cu_2L_{II}Cl_2(H_2O)]$	3360	1655	1600	370	485	325	375, 395, 435, 660	0.82, 0.86, 0.26, 0.04
L_I	3330	1675	1650	–	–	–	305, 370, 410	2.7, 3.8, 0.73
L_{II}	3325	1670	1635	–	–	–	275, 290, 325, 370	2.9, 3.5, 4.4, 0.14

[a] Nujol mull.

[b] ν(OH) phenolic.

four bands can be assigned to a $\pi \rightarrow \pi^*$ transition within the aromatic ring system, a $\pi \rightarrow \pi^*$ transition within the C=N group, and ${}^4T_{1g} \rightarrow {}^4T_{1g}(\mathrm{P})$ and ${}^4T_{1g} \rightarrow {}^4A_{2g}(\mathrm{F})$ transitions for the d^7 system, respectively. The Ni(II) complexes exhibit three bands with λ_{max} at 400–475, 500–555 and 600–690 nm which can be assigned to ${}^3A_{2g} \rightarrow {}^1E_g(\mathrm{D})$, ${}^3A_{2g} \rightarrow {}^1A_{1g}(\mathrm{G})$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\mathrm{P})$ transitions, respectively. The Cu(II) complexes show one broad band with λ_{max} at 610–650 nm. The band can be assigned to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The position of λ_{max} and the shape of the band indicate an octahedral structure for Co(II) and Ni(II) complexes and a square planar geometry for Cu(II) complexes.

The X-band electron paramagnetic resonance (EPR) spectra of Co(II) or Cu(II) complexes measured at room temperature exhibit an intense broad signal and no obvious hyperfine structure (Fig. 2). According to ligand field theory [11,12], g values of Cu(II) complexes of axial symmetry may be

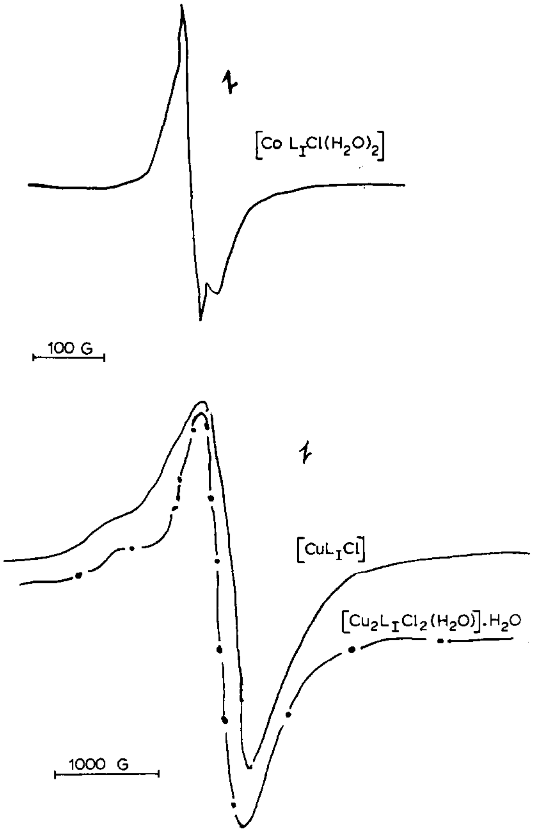


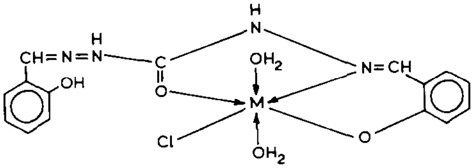
Fig. 2. X-band EPR spectra of some solid Co(II) and Cu(II) complexes.

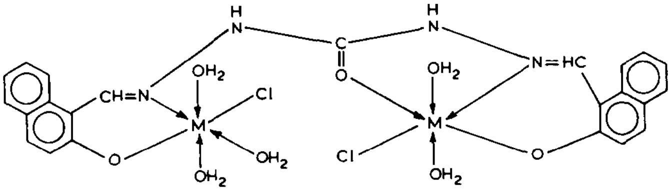
approximated by the equations

$$g_{\|} = 2\left[1 - \frac{4_{\lambda}K_{\|}}{\Delta E(d_{X^2-Y^2} - d_{XY})}\right] \tag{1}$$

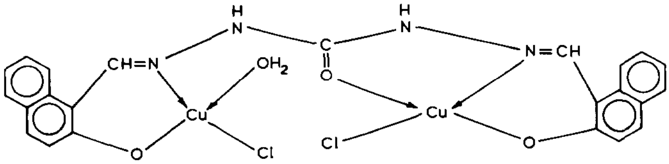
$$g_{\perp} = 2\left[1 - \frac{\lambda K_{\perp}}{\Delta E(d_{X^2-Y^2} - d_{xz})}\right] \tag{2}$$

where λ is the spin-orbit coupling constant of the copper ion and $K_{\|}$ and $K_{\perp}$ are the orbital reduction factors for $\|$ and $\perp$ components respectively. The pattern of the g values for Co(II) complexes may indicate low spin Co(II) complexes of type (**II**) similar to other observations [13] on Co(II) Schiff base complexes. Therefore, the shape of the EPR spectra together with the g_{eff} values (Table 1) may indicate elongated octahedral geometry for Co(II) and square planar geometry around Cu(II). The positive contribution in the g_{eff} value over that of a free electron (2.0023) may indicate an increase in the covalent nature of the bonding between the metal(II) ion and ligand molecule [14,15]. Molecular models indicate that a *trans* structure accommodates the pentadentate ligand with much greater ease than does a *cis* structure. Accordingly, the bonding between Schiff base ligands and the metal ions can be as follows





M = Co(II) or Ni(II)



The resistivities of the complexes varied from 0.9×10^6–4.5×10^{12} ohm cm which is in the range of typical semiconductors [16]. Figure 3 shows log ρ vs. $1/T$. From the slope of the linear parts of the plot the activation

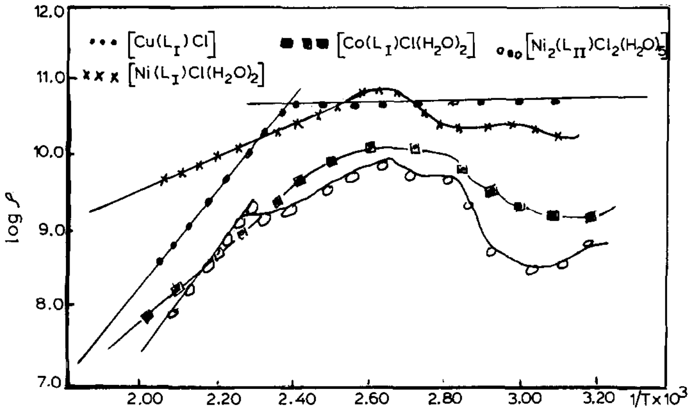


Fig. 3. Electrical resistivities of some solid complexes.

energies have been calculated (Table 1); the observed activation energies of the complexes of ligand (I) follow the order Cu(II) > Ni(II). The trend found depends on the ionic radius of the cation and its ligand field strength. On comparing the resistivities and activation energies of the similar complexes of ligands (I) and (II) one can find that the observed activation energies follow the order (II) > (I) which may be due to longer bonding distances in complexes containing the naphthalidene moiety than those in the complexes containing the salicylidene moiety.

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