Cobalt (II), Nickel (II) and Copper (II) Complexes of Carbohydrazide and its Arylidene Derivatives

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Abstract:

Metal complexes formed through the reaction of carbohydrazide and some of it's arylidene derivatives with cobalt (II), nickel (II) and copper (II) ions were prepared and characterized by elemental analysis, conductance measurements, TGA, IR, electronic absorption spectra, X-ray diffraction, The carbohydrazide and it's derivatives coordinate as mono anion tridentate or neutral bidentate ligands. The coordination bond length was determined. The results indicate the higher affinity of metal ions to oxygen than nitrogen. The solid state electrical conductivity of selected complexes was also reported.

Introduction

Hydrazides, of organic acids have found wide application as pharmaceutical agents[1] and in industry [2,3]. The biological activity of the compounds is mainly dependent on their molecular structure. The biological and technical importance of hydrazides is generally based on their ability to form stable metal chelates [4-20]. Also hydrazides of organic acids were found to exhibit antimalarial activity [21] and their chelates could have fungicidal effects [22]. In view of the biological significance and diverse coordinating behaviour of hydrazides as well as the semiconducting properties of some first row transition elements which found to depend on the structure of the complex, it was considered worthwhile to prepare and study some of these compounds.

The aim of the present article is to prepare and characterize cobalt (II), nickel (II) and copper (II) complexes with carbohydrazide and some of it's arylidene derivatives. Elemental analysis, conductance measurements, TGA, magnetic measurements as well as spectroscopic techniques were used to investigate the titled complexes.

Experimental

All compounds used were of analytical reagent grade (BDH products). The arylidene derivatives of carbohydrazide were prepared by refluxing the carbohydrazide (0.01 mol) with the appropriate aldehyde [9] (0.02 mol) dissolved in EtOH (50 mL) for ca 1h . The products were filtered off, washed with EtOH and Et$_2$O and then dried in a vacuum desiccator over silica gel.

The metal complexes were prepared by mixing a hot EtOH solution (30 mL) of the organic ligands (0.01 mol) with a hot EtOH solution (20 mL) of the hydrated metal chloride (0.01 mol). The mixture was refluxed on a water bath for 1-2 hrs. On cooling, the complexes separated were then filtered off, washed with hot EtOH, and dried over P$_4$O$_{10}$.[9].

The ligands included in the present investigation have the general structural formula:

$$(H_2N\text{-}NH)_2CO$$

L1
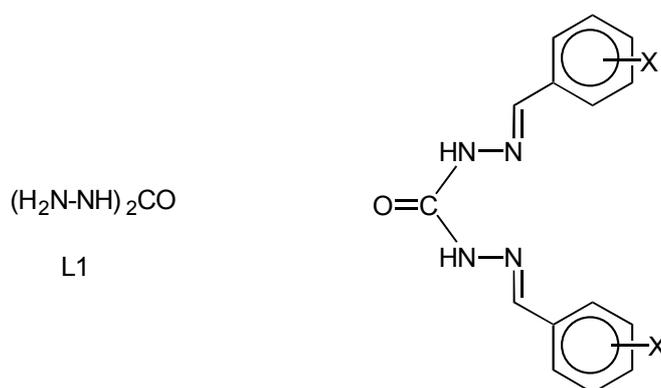
Where x= p-OH (L^2), 3,4-diOH (L^3), p-Cl (L^4), p-Br (L^5) and p-NO$_2$ (L^6).

The Uv-visible spectra (in Nujol) were recorded on a Shimadzu 240 Uv-visible spectrophotometer and the IR spectra on a Perkin Elmer 683 IR spectrophotometer in the 4000-200 cm^{-1} region using KBr optics. Molar conductance measurements were made in DMF using a YSI Model 32 conductance meter. Magnetic moments were determined by the Gouy method (at 25°C) and were corrected for diamagnetism using Pascal's constant. The X-ray powder diffraction patterns were recorded using the

Shimadzu X-ray diffractometer model XD-3. The thermogravimetric analysis (TGA) was achieved using Du Pont 900 Thermal Analyzer.

The electrical resistivity was measured using a super Megohmmeter (Model RM 170) electrometer. The samples were in the form of discs of diameter 13 mm and thickness of 1-3 mm which were pressed under a pressure of ca 300 kgcm^{-2}. Good contact area was achieved by liquid silver painting on the two opposite surfaces of each disc: The temperature was measured in air using Cu-CuNi thermocouple placed close to the sample.

C,H and N content were performed by the aid of the Perkin Elmer 2400 analyser. The analyses for metals and halides were carried out by standard methods [23]. The melting points of all complexes are higher than 350°C.

Results and discussion

The stoichiometry of the complexes formed in solution was first ascertained by applying the conductometric titration. The titration curves display two defined breaks denoting the possible formation of two types of complexes with stoichiometric ratios 1:1 and 2:1 (metal: ligand). The titration curves show a gradual increase in conductance with metal ion concentration. Isolating the solid complexes and their elemental analysis (C,H,N,M and Cl) further supports their stoichiometry. Results of elemental analysis are given in Table 1. The composition and emperical formulae of the complexes under investigation were further confirmed from the values of the molar conductance. The molar conductances in DMF are in 10-18 (ohm^{-1} mol^{-1} cm^2) range. The data suggest that the complexes behave as nonelectrolytes in DMF [24].

Structural investigations by thermogravimetric analysis:

The observed percentage weight loss corresponding to various steps namly, loss of water molecules, loss of chloride as well as the metal content, in the TGA curves were compared with those calculated in the assumption of possible composition of the complexes suggested from the elemental analysis and confirmed latter from IR spectral study.

Table (1)

Elemental Analysis of Co (II), Ni (II) and Cu (II) complexes

No.	Compound	Emperical Formula	Yield %	(% Calc. (Found))						μ_{eff} (B.M)
				C	H	N	M	Cl	H$_2$O	
(1)	[Co L^{1}Cl]	CH$_5$N$_2$OCoCl	72	6.6 (6.5)	2.7 (2.9)	30.5 (30.2)	32.1 (31.5)	19.4 (20.9)	-	-
(2)	[NiL^{1}Cl]	CH$_5$N$_4$ONiCl	70	6.6 (6.8)	2.7 (2.7)	30.6 (31.4)	32.1 (31.7)	19.4 (19.9)	-	-
(3)	[CuL^{1}Cl]	CH$_5$N$_4$OCuCl	73	6.4 (6.3)	2.7 (3.0)	-	33.8 (33.0)	18.9 (20.1)	-	-
(4)	[CoL^{2}Cl$_2$(H$_2$O)$_2$]	C$_{15}$H$_{18}$N$_4$O$_3$CoCl$_2$	75	38.8 (38.9)	3.9 (3.5)	12.1 (11.9)	12.7 (13.0)	-	7.8 (7.3)	4.4
(5)	[NiL^{2}Cl$_2$(H$_2$O)$_2$]	C$_{15}$H$_{18}$N$_4$O$_3$NiCl$_2$	77	38.8 (37.9)	3.9 (4.0)	12.1 (11.7)	13.7 (13.7)	15.3 (14.8)	7.8 (7.5)	2.7
(6)	[CuL^{2}Cl$_2$]	C$_{15}$H$_{14}$N$_4$O$_3$CuCl$_2$	80	41.6 (42.4)	3.2 (3.1)	12.9 (12.1)	14.7 (14.7)	16.4 (15.9)	-	1.9
(7)	[CoL^{3}Cl$_2$(H$_2$O)$_2$]	C$_{15}$H$_{18}$N$_4$O$_7$CoCl$_2$	76	36.3 (35.4)	3.6 (4.0)	11.3 (10.9)	11.9 (11.5)	14.3 (14.0)	7.3 (6.8)	4.8
(8)	[NiL^{3}Cl$_2$(H$_2$O)$_2$]	C$_{15}$H$_{18}$N$_4$O$_7$NiCl$_2$	80	36.3 (36.4)	3.6 (3.8)	11.3 (10.8)	11.9 (12.5)	-	7.3 (7.0)	2.82
(9)	[CoL^{4}Cl$_4$(H$_2$O)$_2$]	C$_{15}$H$_{16}$N$_4$O$_5$CoCl$_4$	82	35.9 (34.9)	3.1 (2.6)	11.2 (11.0)	11.8 (11.6)	28.4 (27.6)	-	5.1
(10)	[NiL^{4}Cl$_4$]	C$_{15}$H$_{12}$N$_4$ONiCl$_4$	84	38.7 (37.9)	2.6 (2.7)	12.1 (11.8)	12.6 (12.5)	-	-	Dia
(11)	[Cu$_2$L^{4}Cl$_3$(H$_2$O)]	C$_{15}$H$_{13}$N$_4$O$_2$Cu$_2$Cl$_5$	79	30.8 (31.3)	2.2 (2.3)	9.6 (9.2)	21.7 (20.8)	30.3 (29.4)	3.1 (2.8)	1.83
(12)	[CoL^{5}Cl(H$_2$O)$_2$]	C$_{15}$H$_{16}$N$_4$O$_3$Br$_2$CoCl$_2$	81	30.5 (30.7)	2.7 (2.4)	9.5 (9.2)	10.0 (9.8)	12.0 (11.9)	6.1 (6.4)	-
(13)	[NiL^{5}Cl$_2$(H$_2$O)$_2$]2H$_2$O	C$_{15}$H$_{20}$N$_4$O$_5$Br$_2$NiCl$_2$	70	28.8 (28.4)	3.2 (3.3)	9.0 (8.9)	9.4 (9.0)	11.4 (10.7)	11.5 (11.7)	-
(14)	[CuL^{5}Cl$_2$(H$_2$O)$_2$]	C$_{15}$H$_{16}$N$_4$O$_3$Br$_2$CuCl$_2$	84	30.3 (30.6)	2.7 (2.4)	9.4 (9.0)	10.7 (10.5)	11.9 (11.2)	6.1 (6.6)	-
(15)	[CoL^6)$_2$]	C$_{30}$H$_{22}$N$_{12}$O$_{10}$Co	80	46.8 (45.9)	2.9 (2.9)	21.9 (22.0)	7.7 (7.2)	-		-
(16)	[Ni(L^6)$_2$]	C$_{30}$H$_{22}$N$_{12}$O$_{10}$Ni	76	46.8 (46.2)	2.9 (2.6)	21.9 (22.0)	7.7 (7.3)	-		-
(17)	[Cu(L^6)$_2$]	C$_{30}$H$_{22}$N$_{12}$O$_{10}$Cu	87	46.5 (46.0)	2.8 (2.7)	21.7 (21.0)	8.2 (8.5)	-		2.71

m.p of all complexes above 350^{0}C

Figure 1 shows thermograms of some solid complexes under investigation. The TGA pattern indicates that the thermal decomposition of the complexes involves mainly three stages. The elimination of lattice water molecule occurs in the range 25-90 ^{0}C (% calc. 2.9 , estimated 2.65) whereas the coordinated water molecules were eliminated within the 125-275^{0}C range (% calc. 6.1-7.8, estimated 5.7-7.4). The chloride content was eliminated in the 275-450 ^{0}C range with an estimated mass loss 12.4-16.0 %, calc. 12.4-16.5 %). The final step of the decomposition occurs within the temperature range 350-650 ^{0}C corresponding to the decomposition of the complexes with the formation of the metal oxide (MO) as a final product from which the metal content was calculated. These values are found in good agreement with the calculated values from the suggested formula listed in Table (1). For some complexes the removal of chloride and the decomposition of the complexes occurred in one step.

On the basis of % loss in weight, the thermal decomposition for the complexes can be formulated as:

$$[MLCl_2(H_2O)_2] \xrightarrow{125\text{-}225°C} MLCl_2 \xrightarrow{275\text{-}450°C} [ML]^{+2} \xrightarrow{350\text{-}650°} MO$$
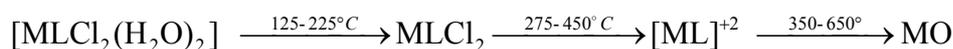
Where L= ligand and MO = metal oxide

The thermal stability for the complexes of the same ligand can be arranged as $Cu^{+2} > Co^{+2} > Ni^{+2}$ complexes.

For the Cu-complex (11) the thermal decomposition can be formulated as:

$$[Cu_2LCl_3(H_2O)] \xrightarrow{100°} [Cu_2LCl_3] \xrightarrow{125\text{-}200°} [Cu_2L]^{+3} \xrightarrow{250\text{-}600°} CuO$$
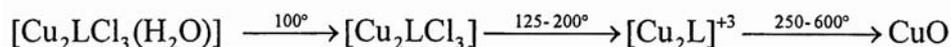
i.e the decomposition involves three main steps; the loss of coordinated water (% calc.3.1, estimated 2.8), loss of chloride (% calc. 18.5, estimated 18.0) and the loss of organic ligand with the formation of CuO from which the Cu content was estimated (21.2 %).

For complexes (15-17) the thermal decomposition involves two steps from which the mental content was calculated and compared with the values listed in Table (1). The thermal decomposition of these complexes can be formulated as:

$$[ML_2] \xrightarrow{up\ 250°} [ML_2] \xrightarrow{250\text{-}375°} [ML] \xrightarrow{>400°} MO$$
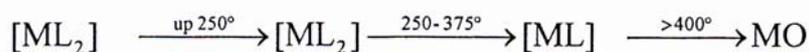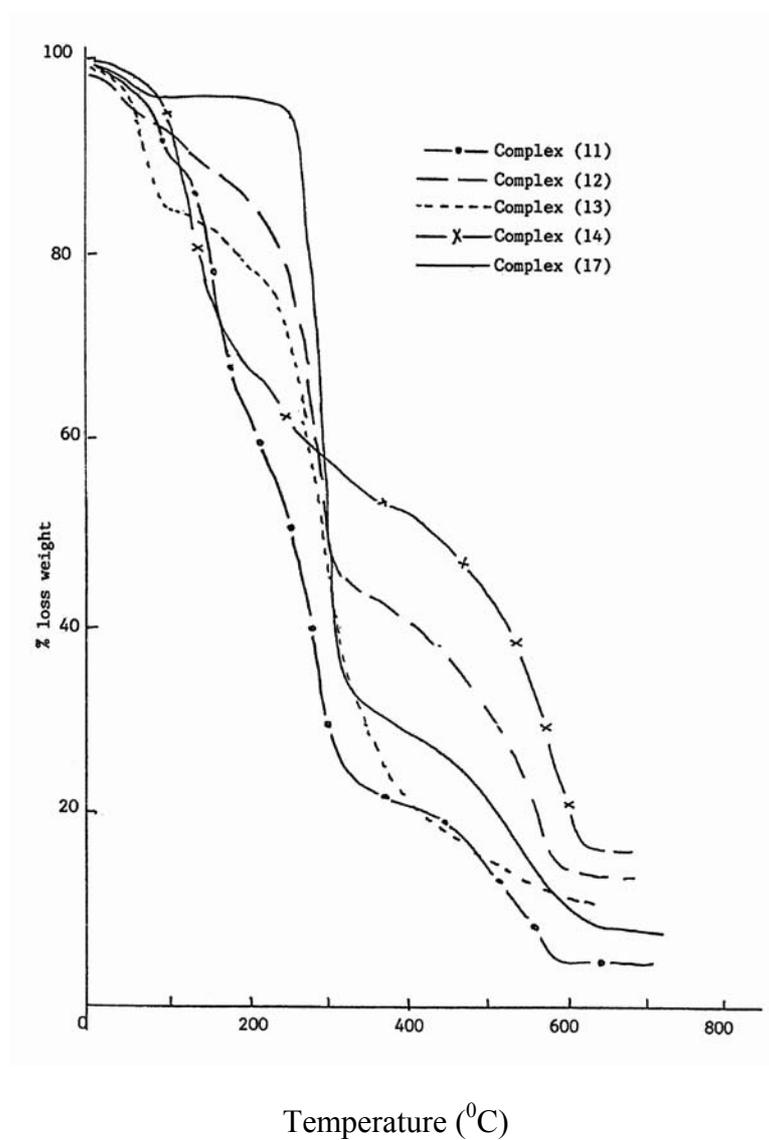
Temperature (^{0}C)
Fig. (1) : TGA of complexes (11-14) and (17)

Structural investigation by IR spectra

The bonding of the ligands to the metal ions under investigation was studied by IR spectroscopy. The IR spectra of the carbohydrazide complexes compared to that of the free ligand reveal the disappearance of the C=O band in the spectra of the carbohydrazide complexes (1, 2 and 3). Some new bands of medium intensity appear in the spectra of the complexes within the 1300- 1230 cm^{-1} range. These bands can be assigned to the stretching mode of the C-O structure [25], formed through enolisation of the amide linkage. This indicates that carbohydrazide acts as a monobasic tridentate ligand through the oxygen and the nitrogen of NH_2 groups as follows:
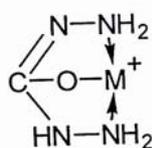
In the complexes (4-10) and (12-14) the hydrazones behave as neutral bidentate ligands via the carbonyl and azomethine groups i.e. in the keto form. This fact is supported by the shift to lower frequency of the carbonyl group and the split of the ν(C=N) band into two bands, one band near the same position of the free ligand and the other shifted to lower frequency. This indicates that one of the C=N groups is involved in the complex formation while the other is non coordinated. This is further supported by the shift of the ν(N-N) to higher frequency [26] as well as by the appearance of new bands in the 470-430 cm^{-1}, 390-350 cm^{-1} and 340-320 cm^{-1} regions assigned to ν(M-O), ν(M-N) and ν(M-Cl), respectively [27].

The above evidence suggests the following structure for the complexes (4-10) and (12-14).
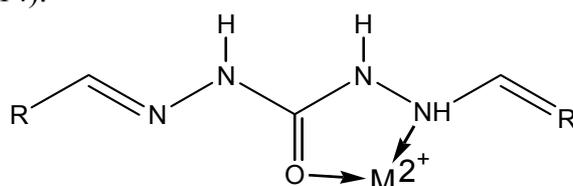
Complexes (4-10) & (12-14)

For the complexes (11 and 15-17) the hydrazone derivatives act as monobasic tridentate ligands coordinating via the azomethine (C=N) and the enol =C-O groups. This chelate mode is supported by the disappearance of the C=O band with simultaneous appearance of a new band in the 1300-1280 cm^{-1} region assigned to ν(C-O) [28]; the shift of ν(C=N) to lower frequency together with the shift of ν(N-N) to higher frequency [26] and the appearance of new bands in the 470-450 cm^{-1} and 390-380 cm^{-1} region due to ν(M-O) and ν(M-N), respectively [27].

Based on the evidence discussed above, the following structures can be proposed about the nature of these complexes.

Complex (11)   Complexes (15-17)
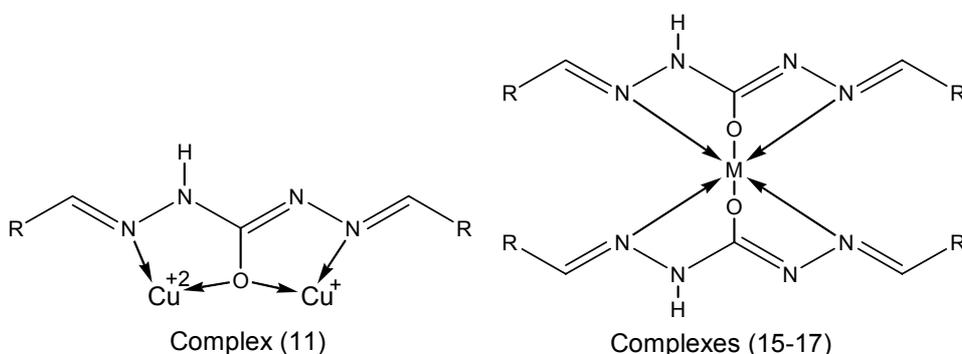
The shift of the C=O and C=N bands due to coordination is further utilised for the determination of the coordination bond length [29]. The values obtained for the coordination bond length amount to 2.48- 3.13 Å for M^{+2}–O= and 2.37- 3.5 Å for the M^{+2} $\leftrightarrow$ N= bonds, respectively. However the values of the coordination bond length (r) for the metal oxygen bond are slightly lower than those of the metal nitrogen bond for all complexes except complexes (4, 5 and 12) indicating that the metal ions under investigation have a higher affinity to oxygen than to nitrogen, (Table 2.).

Table (2)

Band position, band shift and coordination bond length for complexes (4-17)

Compound	M	C=O				C=N			
		ν	$\Delta\nu$	log$\Delta\nu$	r	ν	$\Delta\nu$	log$\Delta\nu$	r
L^2		1665	-	-	-	1648	-	-	-
(4)	Co^{+2}	1648	17	1.231	3.06	1593	55	1.741	2.37
(5)	Ni^{+2}	1650	15	1.176	3.13	1593	55	1.741	2.38
(6)	Cu^{+2}	1650	15	1.176	3.12	1638	10	1.00	3.5
L^3		1670	-	-	-	1645	-	-	-
(7)	Co^{+2}	1648	22	1.343	2.88	1630	15	1.176	3.24
(8)	Ni^{+2}	1650	20	1.301	2.74	1635	10	1.00	3.50
L^4		1674	-	-	-	1620	-	-	-
(9)	Co^{+2}	1644	30	1.477	2.68	1595	25	1.398	2.90
(10)	Ni^{+2}	1654	20	1.301	2.74	1595	25	1.398	2.89
(11)	Cu^{+2}	1649	25	1.398	2.78	1610	10	1.00	3.50
L^5		1685	-	-	-	1655	-	-	-
(12)	Co^{+2}	1648	37	1.568	2.54	1600	55	1.741	2.37
(13)	Ni^{+2}	1645	40	1.602	2.48	1625	30	1.477	2.78
(14)	Cu^{+2}	1655	30	1.477	2.68	1638	17	1.231	3.06
L^6		1690*	-	-	-	1635	-	-	-
(15)	Co^{+2}	-	-	-	-	1625	15	1.176	3.24
(16)	Ni^{+2}	-	-	-	-	1600	35	1.544	2.69
(17)	Cu^{+2}	-	-	-	-	1620	10	1.00	3.50

*enol form (disappearance of C=O band)

Magnetic and Uv- visible spectral studies

The Nujol mull Uv-visible spectra of complexes (1-3) show a broad maximum with λ_{max} at 14925, 15385 and 14815 cm^{-1} for the Co^{+2}, Ni^{+2} and Cu^{+2} complexes, respectively. These bands can be assigned to $^4T_{1g} \rightarrow ^4A_{2g}$ (F), $^3A_{2g} \rightarrow ^3T_{1g}$ (F) and $^2E_g \rightarrow ^2T_{2g}$ Transitions which are characteristic of square planar configurations for Co^{+2}, Ni^{+2} and Cu^{+2} complexes [30].

The magnetic moments for Co^{+2} complexes (4, 7 and 9) are 4.4, 4.8 and 5.1 BM, respectively. The value for complex (4) is lower than that assigned for high spin octahedral Co^{+2} species (4.8- 5.2 BM) [31]. The Nujol mull spectra show bands within the 19608 - 18868 and 15152 – 14706 cm^{-1}

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ranges assigned to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) (ν_3) & $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) (ν_2) [32] respectively. The lowest band (ν_1) could not be observed and is calculated to be within the 6898- 7143 cm^{-1} range. The ν_2 / ν_1 values are 2.12- 2.13 indicating the octahedral structure. The B, β and D_q values are in the ranges 861 and 889, 0.89 and 0.92 and 783- 800 cm^{-1} respectively, supporting the aforementioned geometry.

The observed magnetic moment values for the Ni^{+2} complexes (5, 8 and 16) are 2.7, 2.82 and 2.71 BM, respectively. The electronic spectra of Ni^{+2} complexes show a band within the 14544- 16667 range cm^{-1} assigned to $^3T_{1g} \rightarrow {}^3A_{2g}$ transition indicating octahedral geometry around Ni^{+2} – ion [33]. The Ni(II) complex (10) has diamagnetic character and square planar geometry.

The electronic spectra of Cu^{+2} complexes (6 and 11) exhibit a broad band near 14286 cm^{-1} suggesting square planar stereochemistry [34]. The μ$_{eff}$ values are 1.83 and 1.9 BM supporting the square planar geometry [35]. The other Cu^{+2} complexes exhibit a broad band at 13889 cm^{-1} corresponding to the distorted octahedral structure [36].

X-ray studies

The molecular structure of some complexes under investigation are studied by X-ray powder diffraction. By comparative study of the results obtained with the ligands and their chelates, the following can be pointed out. With respect to ligand (L^3), the peak of the crystalline plane diffraction is observed at 2θ = 27.4°, which can be assigned to the enolic OH (3.2522 Å) as indicated in the ASTM cards. The dihedral angle is found at 22.1 for ligand (L^3), but decreases for the chelates. The M-N distance for the compounds under investigation is about 2.342 Å while the M-O is 2.05- 1.8 Å as indicated from the ASTM cards. The valsue are not much different from those determined from ir-spectra. The shorter M-O bond distance reveals a higher affinity of the metal ions under investigation to oxygen compared to the M-N bond supporting the data obtained from the ir-spectra. For the ligand (L^2) the peak at 2θ =28.2 can be assingned to the OH- group (3.16 Å). For the Ni^{+2} complex (5), the M-N bond distance (at 2θ =30.55) is 2.9237 Å and M-O (at 2θ = 37.45) is 2.3993 Å .The data also indicate the

higher affinity of metal ions to oxygen than nitrogen atom, which is supported form IR spectra.

Electrical conductivity measurements

Figure 2 shows the relation between the solid state electrical conductivity (log σ) and the temperature (1000/T). From the slope of the linear part of the plot, the activation energies of ligand (L^6) and its complexes (16 and 17) are calculated. The resistivities of the metal complexes are higher than for the pure ligand while the corresponding activation energies are lower. This may be due to the increased electron delocalization. The observed activation energy of the complexes (16 and17) follow the order $Cu^{+2} > Ni^{+2}$.

The trend found depends on the ionic radius of the cation and it's ligand fields strength. The calculated activation energies amount to 2.0, 0.79 and 0.37ev for ligand (L^6), Cu^{+2} and Ni^{+2} complexes, respectively.

The inflection observed can be attributed to a change in conduction mechanism. It is assumed that at lower temperatures the conduction process is essentially due to the electronic conduction through π–electron delocalization while the conduction at higher temperatures is due to the excitation of an electron from the upermost filled π–molecular orbital to the lowest unfilled π–molecular orbital of these compounds. However, the electron is assumed to tunnel to an equivalent empty level of a neighbouring molecule in the anodic direction.

When a potential difference (V) is applied to L^6 and its complexes (16 and 17), a current (I) can be measured. The current- voltage (I-V) plots are linear . Hence ligand (L^6) and its complexes obey Ohm's law i.e. Ohmic conduction.
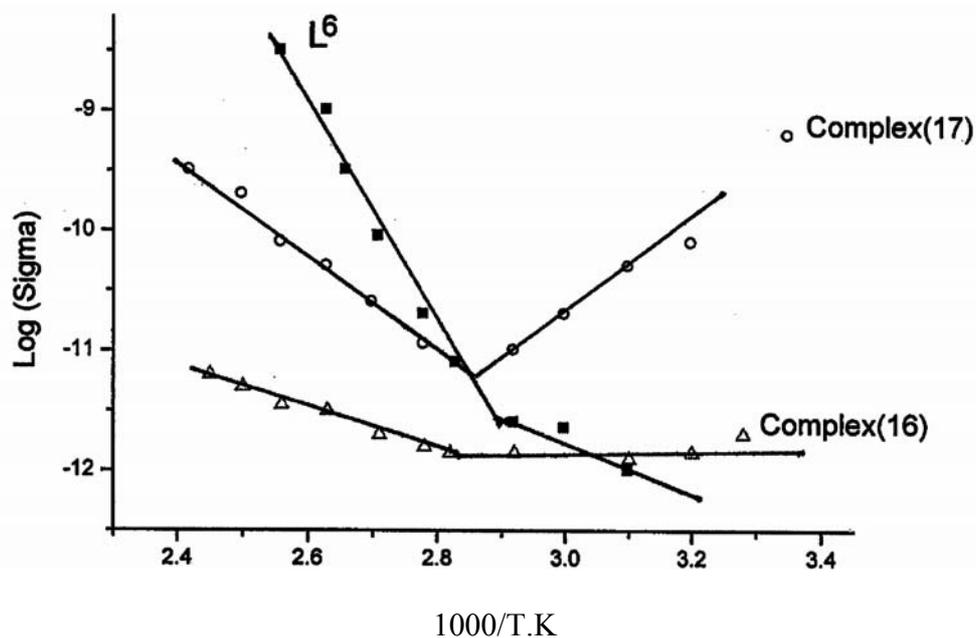
1000/T.K

Fig. 2 : Relationship between electrical conductivity (Loga)
and temperature (1000/T)

References

1.　H. Kala, *De Pharmazie*, 26, 121 (1971), C. A. 75, 295 (1975).

2.　K. Nagano, H. Tsukhara and Z. Tamura; *Chem Pharm. Bull*. (Tokyo), 12, 1198 (1974).

3.　R. C. Agarwal *et al.; J. Inorg. Nucl*, 10, 1183 (1972); 12, 728 (1975).

4.　A. Syamal and M. R. Maurya, *Synth. React. Inorg. Met-Org*. Chem., 16, 39 (1986).

5.　J. S. Chundak, M. V. Leovac and J. L. Bjelica; *Montash. Chem*., 118, 923 (1987).

6.　S. K. Agrawal, D. R. Tutlani, R. Gupta, and S. K. Hajela*; Inorg. Chim. Acta*, 129, 257 (1987).

7.　H. Y. F. El-Baradie, M. Gaber, and Y. M. Issa, *Egypt J. Chem*., 28, 295 (1985).

8.　H. Y. F. El-Baradie, M. Gaber, A. Radwan and H. A. Ibrahim, *Egypt J. Chem*., 32, 265 (1989).

9.　M. Gaber, K. Y. El-Baradie, R. M. Issa and I. El-Mehasseb, *Synth. React. Inorg. Met. Org. Chem*., 22, 1097 (1992).

10.　G. B. El-Hefnawey, M. Gaber, M. M. El-Kersh and K. Y. El-Baradie, *Egypt J. Chem*., 35, 453 (1992).

11.　K. Y. El-Baradie, M. Gaber and I. El-Mehasseb, *Egypt J. Chem*., 37, 441 (1994).

12.　P. Souza, A. I. Matesanz, A. Arquero and V. Fernandez, Z. Naturforsch, B, 49 (5), 665 (1994).

13.　E. Vereda Alonso, M. T. Siles Cordero, A. Garcia de Torres and J. M. Cano Pavon Fresenius, *Journal of Analytical Chemistry*, 351 (8), 802 (1995).

14.　N. K. Singh, N. Singh and G. C. Prasad, *Transition Met. Chem*., 21, 296 (1996).

15.　N. K. Singh, N. Singh, G. C. Prasad, A. Sadhi and A. Shrivastsva, *Transition Met. Chem*., 21. 556 (1996).

16.　M. Gaber, H. E. Mabrouk, Y. M. Shaibi and F. M. El-Azab, *Egypt J. Chem*., 40, 177 (1997).

17.　K. Narang, T. Rao, S. Shrestha and S. Shrestha, *Synth. React. Inorg. Met. Org. Chem.,* 30, 931 (2000).

18.　B. Singh, R. Srivastava and K. Narang, *Synth. React. Inorg. Met. Org ,Chem.,* 30, 1175 (2000).

19. N. K. Singh, S. Kushawaha and A. Dixit, *Synth. React. Inorg. Met. Org. Chem.,* 30, 1237 (2000).

20. N. K. Singh, S. K. Kushawaha and M. J. K. Thomas, *Transition Met. Chem.*, 25, 648 (2000).

21. S. Bahadour and K. Pandey, *J. Ind. Chem. Soc.*, 57, 447 (1980).

22. D. Surage and M. C. Ganekar, *J. Ind. Chem. Soc.*, 57, 95 (1980).

23. A. I. Vogel "Text Book of Quantitative Inorganic Analysis" Longmans, London (1961).p. 433.

24. W. J. Geary, *Coord. Chem. Rev.*,7, 81, (1971).

25. H. Tamada, *Bull Chem. Soc. Japan,* 32, 1051 (1959).

26. D. N. Sathyanarayans and D. Nicholls, Spectrochim. Acta, 34A, 263 (1978).

27. N. Nawar and N. M. Hosny, *Transition Met. Chemi.*, 25, 1 (2000) Transition Met. Chem.

28. N. S. Bairadar, B. R. Patil and V. H. Kulkami, *J. Inorg. Nucl. Chem.*,37, 1901 (1975).

29. R. M. Issa *, M. F. El-Shazzly and M .F. Iskander,* Z. Anorg. *Allg Chem.* 345, 90; 98 (1967); I.M.Issa, R.M.Issa, Y.M.Temerk and M. M. Ghonium, *Montashefte Fur Chemie,* 104, 963 (1973).

30. E. Uhlemann, Z. Naturforsch. Teil B., 21, 592 (1966).

31. A. B. P. Lever, J. Levis and R. S. Syholm, *J. Chem. Soc.*, 1235 (1962).

32. C. K. Jorgenson, *J. Inorg. Nucl. Chem.*, 24, 1521 (1962).

33. L. Sacconi, *Transition Met. Chem.*, 4, 199 (1969).

34. W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, 7, 1835 (1968).

35. L. Sacconi and M. Clapoline, *J. Chem. Soc.*, 278 (1964).

36.   A. B. P. Lever "Inorganic Electronic Spectroscopy" Elsevier Amsterdam, 1968.

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الملخص :

تم تحضير معقدات الكوبلت، النيكل والنحاس الثنائية بتفاعل أيونات هذه
العناصر مع الكربوهيدرازيد وبعض مشتقات الآريليدين، تم تحديد تركيب هذه
المعقدات من تحليل العناصر، درجة التوصيل، قياسات الأشعة تحت الحمراء، الأشعة
السينية والتحليل الحراري الوزني. وقد وجد أن الكربوهيدرازيد ومشتقاته ترتبط
تناسقياً على هيئة أيون أحادي ثلاثي المخلبة أو ثنائي المخلبية متعادل، وقد عين طول
رابطة التناسق من طيف الأشعة تحت الحمراء. النتائج توحي بأن أيون العنصر يميل الى
الإرتباط مع الأكسجين أكثر من النيتروجين. تمت دراسة التوصيل الكهربي لبعض
المعقدات المحضرة في حالتها الصلبة.