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THERMAL AND ANALYTICAL STUDIES ON Co, Ni, Cu AND Pd COMPLEXES OF ISATIN ISONICOTINOYL HYDRAZONE

BY

E. El-Shereafy*, R.M. El-Bahnasawy and T.I. Kashar

Chemistry Department, Faculty of Science,

Menoufia University, Egypt.

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ABSTRACT

The complexes of Co, Ni, Cu and Pd of isatin isonicotinoyl hydrazone have been prepared from neutral solutions. The complexes have been characterised by elemental analysis, IR and UV spectroscopy, magnetism and thermal studies (DTA). IR spectral studies revealed that this hydrazone acts as a bidentate ligand coordinating through azomethine and pyridine nitrogens. From magnetic and electronic spectral data, it was found that the coordination number is six. The X-ray diffraction pattern of the ligand has been compared with those of the corresponding metal complexes. The DC electrical conductivity of the compresses powder samples has been investigated as a function of temperature. The activation energy for conduction (ΔE) has been calculeated for the ligand and the complexes.

INTRODUCTION

In continuation of our earlier studies on the thermo-conductimetric properties of solid metal complexes [1-6], isonicotinoyl hydrazone complexes with Co, Ni, Cu and Pd were subjected to thermal and analytical investigations. These complexes are known for their antibacterial and antitubercular activities [7-9]. On the other hand, several

hydrazones of isatin exhibit anticonvulsant [10] and antibacterial [11] activities. Despite much work has been made on hydrazone of INH derived from aldehydes and Ketones [12,13], only few studies have been made on hydrazone (INH) of diketone [2].

In the present work, the synthesis, structural investigations, the DC electrical conductivity and thermal analysis of some complexes of isatin isonicotinoyl hydrazone have been carried out and their activation energies for conduction have been evaluated.

EXPERIMENTAL

The isatin isonicotinoyl hydrazone ligand, was prepared according to Sacconi [14]. The complexes were prepared by mixing together ethanolic solutions of metal chloride or Na_2PdCl_4 and the ligand in equimolar ratio. The resulting solution in each case was heated on a water bath for about one hour. The precipitate thus formed was filtered, washed repeatedly with hot ethanol and dried under vacuum. The analysis of metals was carried out as given by Vogel [15]. Determination of H_2O was made by heating a weighed amount of the sample in a drying oven at different temperatures (120 - 270 ^{0}C) for at least two hours at each temperature.

Differential thermal analysis (DTA) was carried out on a Shimadzu XD-30 thermal analyzer from room temperature to 750 ^{0}C at a rate of 10 ^{0}C/min. in ambient atmosphere. IR spectra were recorded using a Perkin Elmer 598(4000 - 200 cm^{-1}) infrared spectrophotometer and electronic spectra were

recorded by a Perkin Elmer 550 S spectrophotometer. Magnetic susceptibility was measured using Johnson Matthy magnetic susceptibility balance. The X-ray diffraction patterns were recorded using a Shimadzu diffractometer XD-3 in the range $2\theta = 2 - 60^0$. The DC electrical conductivity was measured as given previously [1-6].

RESULTS AND DISCUSSION

The analytical data (Table 1) of the complexes indicate a 1:3 metal to ligand stoichiometry with a general formula $[ML_3]Cl_2 . xH_2O$ but cobalt complex was oxidized to Co(III) and forms the complex $[CoL_3]Cl_3 . 2H_2O$. The complexes are insoluble in water and organic solvents such as methanol, ethanol, acetone, chloroform and benzene but are soluble in coordinating solvents like DMF, DMSO and pyridine.

The magnetic and electronic spectral studies (Table 2) showed that Pd chelate is diamagnetic. For Ni chelate, μ_{eff} is 2.95 B. M. revealing octahedral field with a non degenerate ground state $^3A_{2g}$ $(t^6_{2g} . e^2_g)$ with no contribution from spin-orbit coupling [16] very close to the spin only value. μ_{eff} of Cu chelate (1.64 B.M.) is in the range normaly accepted for Cu(II) complexes. Value of μ_{eff} for Co chelate (5.44 B.M.) is accepted for octahedral symmetry [17]. The electronic spectral data of prepared chelates in pyridine are shown in Table (2). The spectra manifest two absorption bands at 330 and (340-350) nm due to $\pi - \pi^*$ transitions of the C=N groups. Also a band at (380-390) nm is displayed and is attributed to charge transfer [18].

The important IR spectral bands of the free ligand and its complexes are given in (Table 3). The ligand which is basically substituted pyridine derivative exhibits four υ(C = N) and υ(C=C) skeletal vibrations appearing as band-I (1620), band-II (1560), band-III (1485) and band-IV at (1405) cm^{-1} and a band due to ring breathing mode at 990 cm^{-1} [18] and also in plane and out-of-plane deformation modes at 665 and 440 cm^{-1} respectively [19]. The ligand also shows imide group frequencies at 1270, 1545 and 1300 cm^{-1} [20]. The bands at 3230 and 1700 cm^{-1} may be attributed to υNH and υC = O of the isatin part [21]. The bands at 1670 and 880 cm^{-1} may be assigned to the central υC = N and υN-N respectively [18].

In the spectra of these complexes, pyridine bands II and IV, ring breathing mode and also ring deformation modes occurring at 665 and 440 cm^{-1} all have been shifted to higher frequencies indicating that pyridine ring nitrogen takes part in coordination [18].

Although no observed shift in υC=O of both the imide and of the isatin part, negative shifts were shown in the υC=N with a positive shift in υN=N bands suggesting that nitrogen of the azomethine group is coordinated to the metal ion.

Based on analytical and physicochemical results (magnetic and spectral data), the following formula may be suggested for the prepared complexes.

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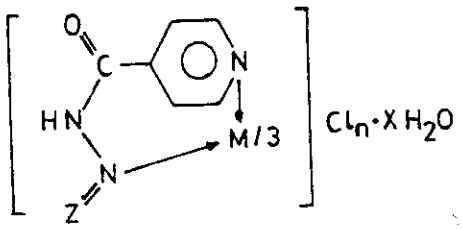
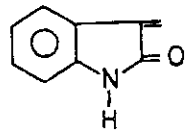


	n	X
Cu & Pd	2	0
Ni	2	4
Co	3	2

Z =



From Fig. (1) it is clearly shown that a strong exothermic peak appears at 410^{0}C in the DTA curve of Ni complex, may be due to rearrangement before decomposition as a result of nitrogen libration before decomposition. Such exothermic peak was shown to appear at lower temperature (300^0 C) in case of Co and Cu complexes.

The X-ray diffraction patterns of Ni and Pd complexes were undertaken as an illustration for complex formation as shown in Fig. (2).

The results obtained indicated disappearance of the characteristic peaks in the X-ray patterns of the organic ligand throughout complexation.

The DC electrical conductivity of the investigated complexes and the ligand show semiconducting behaviour in the temperature range above 150^0 as shown in Fig. (3). The activation energy for conduction was calculated from the known Arrhenius relation $\sigma = \sigma_0 e^{-\Delta E/2kT}$ [3].

The energy gap Eg(eV) of the ligand is 0.28 eV, which is

lower than that of any of the prepared complexes as shown from Table 4. This could be ascribed on the basis that complexation may stabilize the molecular orbitals throughout the complex molecules.

From Table 4 it can easily be seen that the energy gap decreases with increasing the number of d-electrons, which is supported by the proposition that the d-electrons participate in the electronic conduction process. Such mechanism suggests the promotion of electrons from the uppermost filled molecular orbital to the lowest vacant molecular orbitals which include both the ligand and the transition metal [22].

Table (1): Analytical data of isatin isonicotinoyl hydrazone and its compolexes prepared from neutral solutions.

Compound	Colour	Found (calc.)					
		C%	H%	N%	Cl%	M%	H_2O%
$L(C_{14}H_{10}N_4O_2)$	Orange	63.2 (62.5)	3.8 (4.4)	21.0 (20.6)	— —	—	—
$[CoL_3]Cl_3.2H_2O$	Orange	49.9 (50.3)	3.5 (3.2)	16.7 (16.8)	10.2 (10.6)	6.9 (5.9)	3.9 (3.9)
$[NiL_3]Cl_2.4H_2O$	Yellow	50.0 (50.4)	3.1 (3.6)	16.0 (16.8)	6.8 (7.1)	5.6 (5.9)	7.5 (7.2)
$[PdL_3]Cl_2$	Pale brown	50.7 (51.6)	3.6 (3.0)	17.3 (17.2)	6.9 (7.2)	10.1 (10.9)	—
$[CuL_3]Cl_2$	Brown	54.7 (54.0)	3.1 (3.2)	18.0 (18.6)	7.3 (7.6)	6.8 (6.8)	—

Table (2): Electronic splectral data and magnetic moments of isatin isonicotinoyl hydrazone complexes prepared from neutral solutions.

Compound	$\lambda_{max.}$, nm and ($\epsilon \times 10^{-4}$)		μ_{eff} (B.M.)	Assignment
	$\pi - \pi^*$ (C = N)	C.T.		
$[CoL_3]Cl_3.2H_2O$	330 (3.1), 350 (8.5)	380 (0.6)	5.44	octahedral Co(III)
$[NiL_3]Cl_2.4H_2O$	330 (0.6), 340 (0.5)	390 (1.1)	2.95	octahedral Ni(II)
$[PdL_3]Cl_2$	330 (0.7), 340 (0.7)	390 (1.0)	0.00	octahedral Pd(II)
$[CuL_3]Cl_2$	330 (0.9), 340 (0.8)	380 (0.4)	1.64	octahedral Cu(II)

Table (3): Important IR bands (cm^{-1}) and assignment of isatin isonicotinoyl hydrazone and its complexes prepared from neutral solutions.

Compound	Pyridine ring (C=C) and (C=N) I	II	III	IV	Ring breathing mode	isatin υNH	υ CO	amide υ CO	υ C = N pyridine	central	υN – N	Py.ring υC–C deformation. OOP*	in-plane
Ligand L	1620	1560	1485	1405	990	3230	1695	1725	1620	1670	880	440	665
$[CoL_3]Cl_3 .2H_2O$	1600	1582	1485	1420	1060	3210	1695	1725	1600	1610	930	450	680
$[NiL_3]Cl_2.4H_2O$	1600	1585	1495	1420	1065	3210	1700	1725	1600	1620	920	450	680
$[PdL_3]Cl_2$	1600	1585	1480	1420	1060	3210	1300	1725	1600	1620	920	450	680
$[CuL_3]Cl_2$	1600	1585	1490	1420	1060	3210	1700	1725	1600	1620	920	450	680

* Out of plane.

Table (4): Values of the obtained energy gap Eg(eV) of the organic ligand and its corresponding complexes.

Compound	ΔE, eV
Ligand	0.28
$[CoL_3]Cl_3 . 2H_2O$	1.10
$[NiL_3] Cl_2.4H_2O$	0.80
$[CuL_3]Cl_2$	0.55
$[PdL_3]Cl_2$	0.94

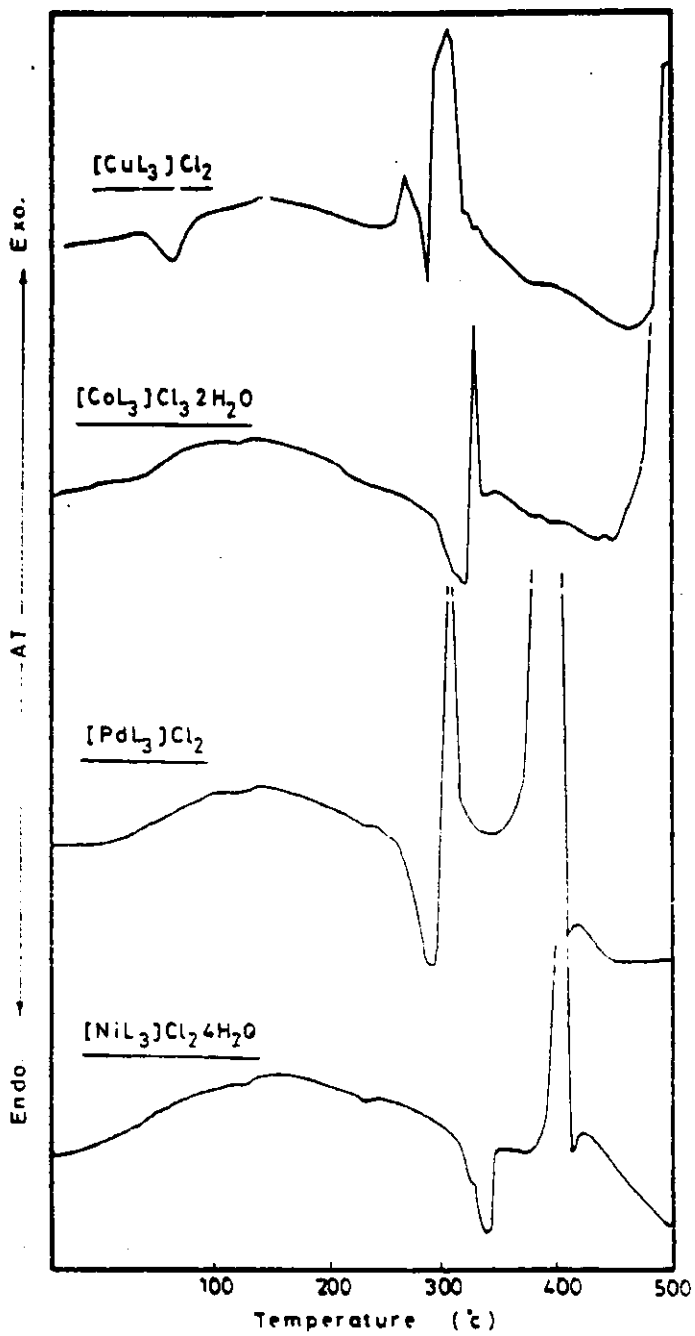


Fig. 1. DTA of Ni-, Pd-, Co- and Cu-complexes prepared in neutral solution.

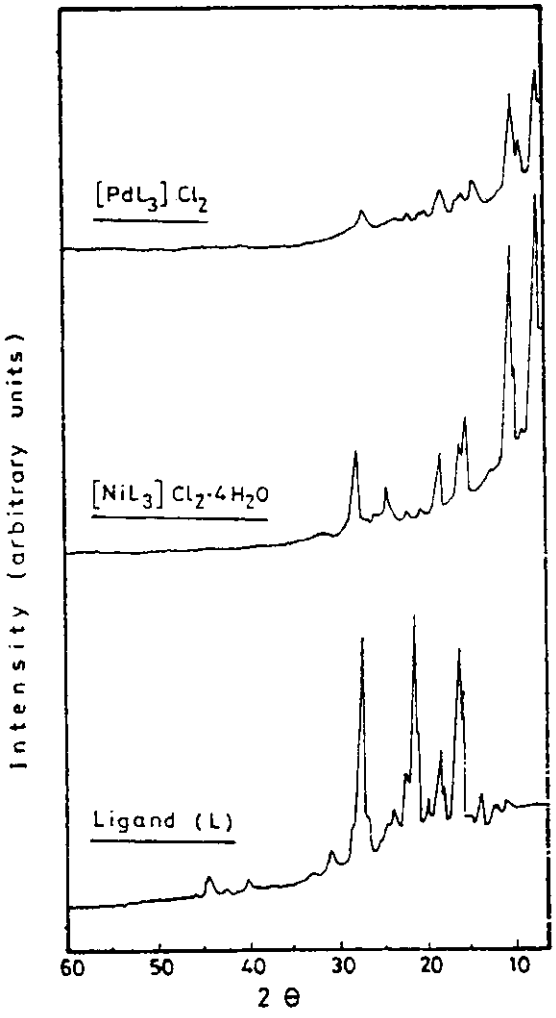


Fig.2. The room temperature X-ray diffraction patterns of the organic ligand (L_4) and its Ni- and Pd- complexes perpared in neutral solution.

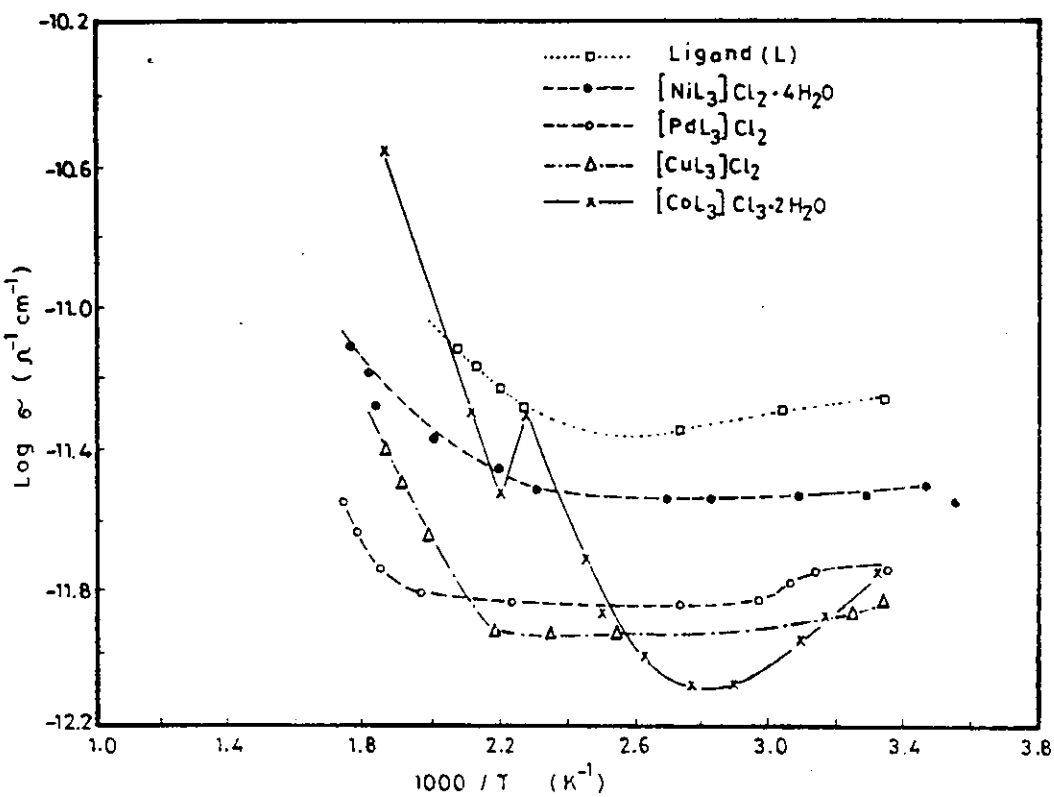


Fig. 3. The variation of log electrical conductivity of various complexes in neutral solution Vs reciprocal of absolute temperature (1000 / T K^{-1}) .

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الملخص العربى

دراسات حرارية وتحليلية على متراكبات الكوبلت والنيكل والنحاس والبلاديوم مع هيدرازون الإسانين أيزونيكوتينويل

السيد الشريفى - رمضان البهنساوى - نهانى كشر
قسم الكيمياء – كلية العلوم – جامعة المنوفية

تم تحضير متراكبات لفلزات الكوبلت والنيكل والنحاس والبلاديوم مع هيدرازون الإسانين أيزونيكوتينويل من محاليل متعادلة – وقد تم تشخيص المتراكبات بدراسة طيف الإمتصاص للأشعة تحت الحمراء وكذا الأشعة فوق البنفسجية وكذلك دراسة الخواص المغناطيسية والتحليل الحرارى التفاضلى ٠

وقد أظهرت دراسة طيف الإمتصاص للأشعة تحت الحمراء أن الهيدرازون يرتبط بالفلز من خلال ذرتى النيتروجين (الأروميثين والبيريدين) ٠ وأظهرت دراسة الخواص المغناطيسية وطيف الإمتصاص للأشعة فوق البنفسجية أن عدد التناسق فى هذه المتراكبات هو ستة ٠

وقد أجريت فحوص الحيود للأشعة السينية – وكذلك أجريت دراسة التحليل الحرارى وقياس التوصيل الكهربى فى درجات حرارة متغيرة ومن ثم تم حساب طاقة التنشيط الخاصة بالتوصيل الكهربى ٠