

## SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH ETHYLENEDIAMINE BIS-ISATIN TETRADENTATE LIGAND

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**ABSTRACT.** Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with ethylenediamine bis-isatin Schiff base and two bis-pyridine adducts of both Ni(II) and Zn(II) chelates have been prepared and investigated in terms of microanalysis, conductance, <sup>1</sup>H NMR, IR and electronic spectral measurements as well as magnetic moments determination. According to magnetic and electronic spectral data, a square planar structure is suggested for Ni(II) chelate whereas a six-coordinate octahedral geometry is found for its bis-pyridine adduct.

### INTRODUCTION

Although the metal complexes of Schiff bases of isatin with different amino compounds have attracted much attention [1-5], no investigations, however, are known in the literature about the metal complexes of Schiff base derived from isatin with ethylenediamine. In view of the importance of isatins in many scientific fields [6-13], and in continuation to our previous work [14-22], we describe in the present investigation the synthesis and characterization of metal complexes of ethylenediamine bis-isatin Schiff base with Co(II), Ni(II), Cu(II) and Zn(II) and some pyridine adducts.

### EXPERIMENTAL

**Materials.** Isatin, ethylenediamine, metal salts and solvents were of A.R. grade (E. Merck or B.D.H.).

#### *Preparation of ligand*

Ethylenediamine bis-isatin Schiff base ligand was prepared by adding a hot ethanolic solution (100 ml) of isatin (0.02 mol) to an ethanolic solution (50 ml) of ethylenediamine (0.01 mol) and heating under reflux for 2 h during which time a brown product was precipitated. The contents were cooled to room temperature, filtered off, washed with ethanol. The brown

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product was recrystallized from DMF, filtered off, washed with hot ethanol, then with diethylether and dried *in vacuo*.

#### *Preparation of the complexes*

The complexes were prepared by refluxing equimolar amounts ((0.01 mol) of ethylenediamine bis-isatin Schiff base ligand and hydrated metal acetates of Co(II), Ni(II), Cu(II) or Zn(II) in absolute ethanol. The resulting reaction mixtures were basified by adding the equivalent amount of sodium acetate and heated under reflux with constant stirring for 3 h. The reaction mixtures were evaporated to a small volume and left to cool. The complexes that precipitated were filtered, washed with hot distilled water and then with ethanol several times until the washing were free from the excess sodium acetate and other soluble side products. The metal complexes obtained were recrystallized from chloroform and finally dried over  $P_4O_{10}$  in a desiccator.

#### *Preparation of the base-adducts*

Pyridine (0.02 mol) was added to 50 ml of a well-stirred DMF solution of Ni(II) or Zn(II) chelates (0.01 mol). The reaction mixture was heated gently under reflux on water bath with continuous stirring for about one h. The solution was then reduced to small volume and left to cool. The base-adducts which precipitated were filtered off, washed with benzene and then diethylether and dried *in vacuo*.

#### *Apparatus and physical measurements*

IR spectra were measured as KBr discs on Pye Unicam SP 1025 spectrometer. UV-VIS spectra (in DMF) were determined using a Perkin Elmer Lambda 4B UV-VIS spectrophotometer. Carbon, hydrogen and nitrogen analyses were carried out at the microanalysis laboratory, Faculty of Science, Cairo University. Conductivity measurements were made in DMF at rt (25°) using a YSI MODEL 35 conductance meter. The magnetic measurements were performed at 298 K by the Gouy method using  $Hg[Co(NCS)_4]$  as calibrant.  $^1H$  NMR spectra were recorded using a Varian E.M. 390 NMR Spectrophotometer in  $DMSO-d_6$  with TMS as internal standard.

## RESULTS AND DISCUSSION

Elemental analyses data as well as conductivity and magnetic measurements of the complexes synthesised in this study are listed in Table 1. All the complexes are found to be quite stable at room temperature. Elemental analyses data suggested that these complexes have the general formula  $ML$  where  $M = Co(II), Ni(II), Cu(II)$  and  $Zn(II)$ , and  $L$  stands for the deprotonated ethylenediamine bis-isatin Schiff base ligand. Analytical data also suggest formation of bis adducts of  $NiL(py)_2$  and  $ZnL(py)_2$ . The low values of molar conductivities (less than  $20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) in DMF solution at room temperature indicate a non-electrolytic nature for all of the complexes [23] suggesting that the ligand is covalently bonded in all the cases.

*Infrared spectra.* Assignments of the most important bands, which help to understand the mode of bonding in the synthesized complexes, are given in Table 2. The IR spectrum of the



free ligand is characterized mainly by strong bands at 3225, 1720 and 1635  $\text{cm}^{-1}$  which are assignable, respectively, to the stretching frequencies of N-H, C=O and C=N groups. On complexation, with all the metal ions, the bands due to  $\nu\text{C=O}$  and  $\nu\text{N-H}$  of the isatin moieties disappear with simultaneous appearance of a band at 1310-1330  $\text{cm}^{-1}$  which may be assigned to  $\nu\text{C-O}$ , suggesting the deprotonation of the N-H group via the adjacent carbonyl oxygen atom of the isatin residue through its tautomeric lactam-lactim equilibrium (Figure 1) which is shifted toward deprotonation specially in basic medium. The band at 1635  $\text{cm}^{-1}$ , due to the stretching mode of azomethine (C=N) group in the spectrum of the free ethylenediamine bis-isatin Schiff base ligand, shows a remarkable negative shift to the region of 1600-1620  $\text{cm}^{-1}$  suggesting the involvement of the two bridging azomethine nitrogen atoms in the coordination sphere. Furthermore, a careful inspection of the infrared spectra of metal chelates in the far zone exhibits new bands in the vicinity of 530-550 and 460-485  $\text{cm}^{-1}$  which may be tentatively attributable to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  modes, respectively [24]. The IR spectra of Ni(II) and Zn(II) bis adducts exhibit  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  bands at 475 and 535  $\text{cm}^{-1}$ , respectively, for the former and at 485 and 550  $\text{cm}^{-1}$  for the latter. These values are shifted to higher frequencies relative to the parent complexes owing to the increased electron density around the central metal ion as a result of the bis-adduct formation.

Table 1. Analytical, magnetic and conductivity data of the complexes.

Complex	C	H	N	$\mu_{\text{eff}}$ (B.M.)	$\Lambda$ $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
	Found (calcd.) %				
NiL	57.3(57.6)	3.4(3.2)	15.2(14.9)	dia	7.23
CuL	56.4(56.9)	3.3(3.1)	14.8(14.7)	1.80	5.98
CoL	57.8(57.6)	3.1(3.2)	14.6(14.9)	4.58	6.09
ZnL	56.7(56.6)	3.4(3.1)	14.4(14.6)	dia	4.38
NiL(py) <sub>2</sub>	63.4(63.0)	4.5(4.1)	15.9(15.7)	2.93	2.65
ZnL(py) <sub>2</sub>	62.1(62.2)	4.3(4.0)	15.8(15.5)	dia	2.04

The foregoing IR spectral results suggest that the anion of the ethylenediamine bis-isatin base ligand is coordinated to the central metal ions as dibasic ONNO tetradentate ligand through the two coordinative bridging azomethine nitrogen atoms and two anionic oxygen atoms belonging to the isatin residues. Thus three nitrogen atoms and two anionic oxygen atoms belonging to the residues. Comparison of the IR spectra of Ni(II) and Zn(II) chelates with those of their corresponding bis-pyridine adducts reveals that the stretching band of the azomethine group is not, nearly, shifted, but its intensity is increased with splitting. This may be ascribed to a contribution to the C=N stretching from the two added pyridine nuclei. The general suggested structure for the metal chelates is shown in Figure 2.

The attempted assignment of the structures of these new transition metal complexes is based, almost exclusively, on IR spectral evidence. Obviously it would be most desirable to look at the crystal structures of the free ligand and the complexes. Unfortunately the



complexes of the ligand, and of several other very closely related ligands, were isolated as powders and no crystals were obtained.

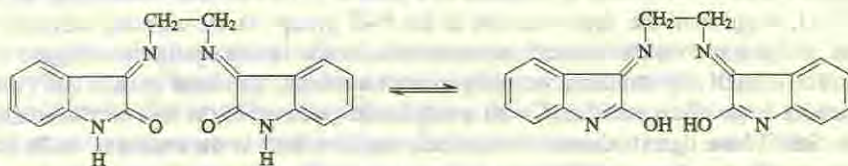


Figure 1. Structure of the lactam-lactim tautomers of the ethylenediamine bis-isatin Schiff base ligand.

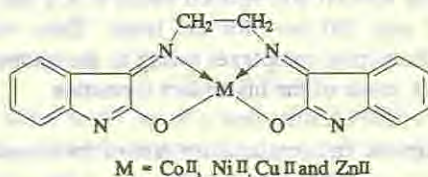


Figure 2. Structure of ethylenediamine bis-isatin complexes.

**<sup>1</sup>H NMR spectra.** The <sup>1</sup>H NMR spectra of the free ligand and its Ni(II) and Zn(II) complexes were measured in DMSO-d<sub>6</sub>. The spectrum of the free ligand could be resolved into three distinct regions: a multiplet at  $\delta$  3.2-3.7, multiplet at  $\delta$  7.1-7.6 and singlet at  $\delta$  11.6, corresponding to resonances resulting from the aliphatic protons of the ethylenic chain bridge, protons of the fused aromatic nuclei of isatin residues and the N-H protons belonging to isatin moieties, respectively. Integration of the above <sup>1</sup>H NMR signals yielded the ratio of 2:4:1, respectively. This is consistent with the above assignments. Comparison of the free ligand spectrum with those of both Ni(II) and Zn(II) chelates showed the disappearance of the peak due to the N-H group. This result supports the foregoing IR spectral evidence of the deprotonation of this group.

The <sup>1</sup>H NMR spectrum of the pyridine adduct of Zn(II) chelates is similar to that of the parent Zn(II) complex with the exception of appearance of a complex group of signals in the aromatic region resulting from the two axial pyridine ligands. It is worth mentioning that in the parent Ni(II) and Zn(II) complexes and that of Zn(II) pyridine adduct, the protons of the ethylenic chain bridge and those of the aromatic fused nuclei of the isatin moieties are far enough from the metal center. Thus, in the <sup>1</sup>H NMR spectra of the chelates, the positions of these signals are hardly changed from those appearing in the spectrum of the free ligand.

**Magnetic moments and electronic spectra.** Magnetic moments and electronic spectral data of the investigated complexes in this study are given in Table 1 and 2. The Ni(II) chelate was found to be diamagnetic. The electronic spectrum of this chelate in DMF solution shows an intense band at 34.5 kK due to C.T. transition and two bands at 28.6 and 21.8 kK assignable to d-d transitions. This magnetic and spectral behaviour suggests a square planar structure for this chelate.



Cu(II) and Co(II) chelates were found to possess magnetic moment values of 1.80 and 4.58 B.M. which are due to the values required for one and three unpaired electrons, respectively [25, 26]. The electronic spectrum of the Cu(II) chelate showed two bands at 32.2 and 22.7 kK and that of the Co(II) chelate exhibited one broad band around 21.7 kK. These absorption bands may be assigned to d-d transition [27].

Two bands are observed at 34.5 and 20.8 kK for ZnL. Likewise ZnL(py)<sub>2</sub> exhibits two bands at 33.2 and 21.6 kK. These bands may be attributed to intraligand transitions. Such coordinative behaviour of the present Schiff base ligand has been observed for several structurally related N<sub>2</sub>O<sub>2</sub> chromophoric type ligands towards many divalent and trivalent transition and non-transition metal ions [28-30]

Table 2. IR and electronic spectral data of the complexes.

Complex	$\nu(\text{C-O})$ (cm <sup>-1</sup> )	$\nu(\text{C=N})$ (cm <sup>-1</sup> )	$\nu(\text{M-O})$ (cm <sup>-1</sup> )	$\nu(\text{M-N})$ (cm <sup>-1</sup> )	$\nu_{\text{max}}(\epsilon_{\text{max}})$ kK mol <sup>-1</sup> cm <sup>2</sup>
NiL	1310	1605	530	460	34.5(4250), 28.6(210), 21.8(125)
CuL	1325	1620	550	480	32.2(190), 22.7(120)
CoL	1330	1615	540	465	21.7(115)
ZnL	1310	1610	545	470	20.8(2105), 34.5(4250)
NiL(py) <sub>2</sub>	1330	1596-1617	535	475	17.0(90), 20.0(180)
ZnL(py) <sub>2</sub>	1315	1610-1618	550	485	32.2(3950), 21.6(1820)

The bis-pyridine adducts of Ni(II) chelate showed paramagnetic character. Its electronic spectrum showed dramatic changes compared to that of the parent complex under the same measurement condition, suggesting the formation of six-coordinate octahedral structure for this base-adduct. The parent Ni(II) chelate was found to be diamagnetic as expected for square planar Ni(II) chelate. On the other hand, Ni(II) bis adduct was found to have a magnetic moment value of 2.93 B.M. at 25° which corresponds to two unpaired electrons in octahedral Ni(II) complexes. This view may be supported by its electronic spectrum which exhibits two bands at 17.0 and 20.0 kK attributable to d-d transitions of an octahedral Ni(II) field.

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