

# Metal Chelates of Some Transition and Non-Transition Metal Ions with Schiff Base Derived from Isatin with *o*-Phenylenediamine

Aly M. A. Hassaan<sup>1,\*</sup> and Mohamed A. Khalifa<sup>2</sup>

<sup>1</sup> Chemistry Department, Faculty of Science, Minia University, El-Minia, Egypt

<sup>2</sup> Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

**Summary.** New Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) chelates of the Schiff base derived from isatin with *o*-phenylenediamine have been synthesized and characterized on the basis of elemental analyses, electronic, IR and <sup>1</sup>H NMR spectra, and also by aid of molar conductivity and magnetic moment measurements. It has been found that the Schiff base behaves as ONNO tetradentate dibasic ligand forming chelates with 1:1 (metal:ligand) stoichiometry. Square planar environment is suggested for nickel(II) chelate. All the metal chelates show non-electrolytic behaviour.

**Keywords.** Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) chelates; Isatin-*o*-phenylenediamine Schiff base.

## Metallchelate einiger Übergangs- und Nichtübergangsmetallionen mit Isatin-*o*-Phenylendiamin-Schiff-Basen

**Zusammenfassung.** Es wurden neue Chelate von Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) und Pb(II) mit Schiff-Basen aus Isatin und *o*-Phenylendiamin hergestellt und mittels Elementaranalysen, Elektronen-, IR- und <sup>1</sup>H-NMR-Spektroskopie, sowie durch Messung der molaren Leitfähigkeit und der magnetischen Momente charakterisiert. Es wurde festgestellt, daß sich die Schiff-Base als vierzähliger zweibasischer ONNO-Ligand verhält, wobei 1:1-stöchiometrische Metall:Ligand-Komplexe gebildet werden. Für das Nickel(II)-Chelat wird eine quadratisch-planare Geometrie vorgeschlagen. Alle untersuchten Metallchelate zeigen ein nicht-elektrolytisches Verhalten.

## Introduction

To our knowledge, no reports can be found in the literature regarding the formation of metal complexes of Schiff bases derived from isatin with aromatic amino compounds.

As a continuation of our interest in the complexation of isatin derivatives [1–6] and concerning the important biological and medical applications of this class of compounds [7–13], we aim now to elucidate the synthesis and characterization of certain metal chelates of *o*-phenylenediamine bis isatin Schiff base with Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II).

## Experimental Part

All chemicals, metal salts, and solvents were either Aldrich or BDH products. Preparation of *o*-phenylenediamine bis-isatin Schiff base ligand was made according to our previous work [5].

### Preparation of the Metal Chelates

The following general procedure was adopted for the preparation of all the metal chelates. Metal salts solution (0.01 mol) of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  in the proper solvent ethanol or water (50 ml) was added dropwise to a solution (0.01 mol) of *o*-phenylenediamine bis-isatin Schiff base ligand in ethanol (100 ml) with constant magnetic stirring. In all cases the resulting mixture was basified by adding an equivalent amount of sodium acetate and heating under reflux for 2 h. The reaction mixture was evaporated to a small volume and left to cool. The precipitate formed in each case was filtered, washed first with water and then with ethanol until the washings were free from the excess sodium acetate and other soluble side products. The metal chelates obtained were recrystallized from chloroform and finally dried in vacuo over phosphorus pentoxide.

### Physical Measurements

Proton nuclear magnetic resonance spectra in deuterated dimethyl sulfoxide were measured on a Varian E.M. 390 NMR Spectrophotometer. Chemical shifts are reported in ppm downfield internal tetramethylsilane ( $\delta$ ). The magnetic measurements were carried out by the Gouy method at room temperature. The apparatus was calibrated with mercury tetrathiocyanato cobaltate(II). Diamagnetic corrections were made using Pascal's constants. Carbon, hydrogen and nitrogen analyses were performed at the microanalysis laboratory, Faculty of Science, Cairo University. Electronic spectra in nujol mull were determined using a Perkin Elmer Lambda 4B UV/Vis spectrophotometer. IR spectra as KBr discs were measured on a Perkin Elmer 1430 Infrared Spectrophotometer and are reported in wave numbers ( $\text{cm}^{-1}$ ). These spectra were calibrated with the  $1601.8 \text{ cm}^{-1}$  absorption of polystyrene film. Molar conductivity measurements in dimethylformamide at room temperature were achieved using a YSI MODEL 35 Conductance Meter.

## Results and Discussion

The colours, analyses, stoichiometries, melting points and molar conductivity values of all the metal chelates under this study are presented in Table 1. These chelates are monomeric and insoluble in water but soluble in most common organic solvents (*EtOH*,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , *DMF*, *Dioxan*, *DMSO*). They are stable towards air and moisture but decompose at higher temperature (290–310 °C). Elemental analyses indicate 1:1 (metal:ligand) stoichiometry for all metal chelates. The suggested general formulae are  $[\text{ML}] \cdot n\text{H}_2\text{O}$  where  $M = \text{Ni(II)}$ ,  $\text{Co(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Pb(II)}$  and  $\text{Mn(II)}$  and  $[\text{CrLNO}_3] \cdot 4\text{H}_2\text{O}$ ;  $L$  stands for the *o*-phenylenediamine bis-isatin Schiff base ligand. The molar conductivities of  $5 \times 10^{-4} \text{ M DMF}$  solutions of these chelates at room temperature were found to be in the range  $5.3\text{--}12.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  revealing their neutrality and non-electrolytic nature. The slightly higher value corresponding to the chromium(III) chelate ( $25.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) than those expected for non-electrolytes indicates the solvation of this complex resulting in a partial displacement of  $\text{NO}_3^-$  anion from the coordination sphere by strong donor *DMF* molecules.

**Table 1.** Physical properties and elemental analyses of the metal chelates

Metal chelate	Colour	M.p. °C	Yield %	% C Found (Calcd.)	% H Found (Calcd.)	% N Found (Calcd.)	$\Lambda$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
[CrLNO <sub>3</sub> ].4H <sub>2</sub> O	pale green	240	58	48.2 (48.0)	3.4 (3.6)	12.9 (12.7)	25.8
[MnL].3H <sub>2</sub> O	yellowish-green	230	56	56.1 (55.8)	3.9 (3.8)	12.1 (11.8)	12.3
[CoL].H <sub>2</sub> O	brown	250	60	60.1 (59.8)	2.9 (3.1)	13.0 (12.7)	9.8
[NiL].H <sub>2</sub> O	green	268	63	60.3 (59.9)	3.3 (3.1)	12.9 (12.7)	5.3
[CuL].H <sub>2</sub> O	deep brown	265	68	59.4 (59.2)	3.5 (3.1)	12.8 (12.5)	8.0
[ZnL].2H <sub>2</sub> O	light yellow	245	55	56.4 (56.7)	3.7 (3.4)	12.4 (12.0)	10.2
[CdL].2H <sub>2</sub> O	white yellow	260	53	51.8 (51.5)	3.0 (3.1)	11.1 (10.9)	9.6
[PbL].3H <sub>2</sub> O	greenish-white	270	54	42.6 (42.2)	3.1 (2.8)	8.8 (8.9)	6.8

### Infrared Spectral Study

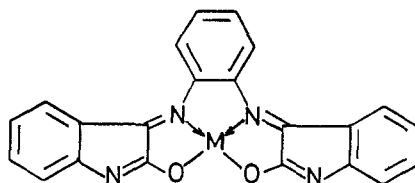
The most important infrared spectral bands of the investigated metal chelates in the present article are summarized in Table 2. As a general remark, a broad band around the 3395–3420 cm<sup>-1</sup> range is observed in all infrared spectra of these chelates. This band may be assigned to water molecule OH stretching frequencies asserting the elemental analysis results that the water molecules are involved in the chemical composition of each metal chelate [14]. The infrared spectrum of the free *o*-phenylenediamine bis-isatin Schiff base ligand is characterized by strong bands at 1715, 1630, 3220 cm<sup>-1</sup> which may be ascribed to the stretching vibrations of C=O, C=N and NH groups, respectively. Upon complexation of this ligand with all the

**Table 2.** Magnetic, IR and electronic spectral data of the metal chelates

Metal chelate	$\nu(\text{C}=\text{N})$ cm <sup>-1</sup>	$\nu(\text{C}-\text{O})$ cm <sup>-1</sup>	$\nu(\text{OH})$ cm <sup>-1</sup>	$\nu(\text{M}-\text{O})$ cm <sup>-1</sup>	$\nu(\text{M}-\text{N})$ cm <sup>-1</sup>	$\lambda_{\text{max}}$ nm	$\mu_{\text{eff}}$ B.M.
[CrLNO <sub>3</sub> ].4H <sub>2</sub> O	1610	1300	3410	540	440	450, 270, 229	3.60
[MnL].3H <sub>2</sub> O	1615	1308	3395	535	443	474, 267, 222	5.70
[CoL].H <sub>2</sub> O	1600	1310	3400	550	470	480, 430, 336	4.50
[NiL].H <sub>2</sub> O	1600	1315	3395	555	480	470, 327, 226	dia
[CuL].H <sub>2</sub> O	1595	1305	3420	560	480	475, 439, 290	1.81
[ZnL].2H <sub>2</sub> O	1610	1300	3398	545	465	223, 267, 438, 359	dia
[CdL].2H <sub>2</sub> O	1620	1315	3405	542	460	265, 343, 439	dia
[PbL].3H <sub>2</sub> O	1620	1320	3420	530	455	220, 270, 340	dia

metal ions, the two bands of both C=O and NH groups of the isatin moiety vanish in all metal chelate spectra which display a new band at 1300–1320  $\text{cm}^{-1}$ ; this band may be due to the stretching frequency of C–O. This result can suggest the deprotonation of NH via the carbonyl oxygen atom of the isatin moiety through its tautomeric lactam-lactim equilibrium which is shifted toward the deprotonation specially in basic medium. The band at 1630  $\text{cm}^{-1}$  due to the stretching mode of the C=N group in the spectrum of the free ligand shows a remarkable negative shift with splittings in the 1595–1620  $\text{cm}^{-1}$  region in all the metal chelate spectra suggesting that the two bridging azomethine nitrogen atoms of the Schiff base are involved in the complex formation. Moreover, a careful inspection of the metal chelate IR spectra in the far zone reveals new bands near the regions of 560–530 and 480–450  $\text{cm}^{-1}$  which may be tentatively attributed to the  $\nu(M-O)$  and  $\nu(M-N)$  modes, respectively [15, 16].

The most important conclusion drawn from the infrared spectral evidence is that the *o*-phenylenediamine bisisatin Schiff base ligand is acting as chelating agent towards the central metal ions as a dibasic ONNO tetradentate ligand via the two coordinating sites of azomethine nitrogen atoms and the two negatively charged oxygen atoms of isatin residues forming three five-membered chelating rings as shown in the formula.



#### *Proton Nuclear Magnetic Resonance Spectra*

Dimethyl sulfoxide was used as a deuterated solvent to measure the  $^1\text{H}$  NMR spectra of the ligand and its metal chelates except those of Cu(II), Co(II), Cr(III), and Mn(II) because of their paramagnetic behaviour.  $^1\text{H}$  NMR spectra of the free ligand may be resolved into three distinct regions (multiplet at 7.2–7.8, triplet at 8.5–8.1 and doublet at 11.8 ppm in a ratio of 4:2:1) corresponding to resonances resulting from the fused aromatic ring protons of isatin moieties, the aromatic ring protons belonging to the *o*-phenylenediamine moiety and the NH protons of the isatin residue. The  $^1\text{H}$  NMR spectra of Ni(II), Zn(II), Cd(II), and Pb(II) chelates show approximately the same peaks identical to those of the free ligand with exception that the peak due to the NH group resonance is absent. This is considered as an additional evidence for the deprotonation of NH.

#### *Electronic Spectra and Magnetic Measurements*

Electronic spectral data and magnetic moments of the investigated metal chelates at room temperature are compiled in Table 2. The magnetic moment of the Cu(II) chelate was found to be 1.81 B.M. which is in agreement with a spin-only value of one unpaired electron [17]. The electronic spectrum of this chelate exhibits two

absorption bands at 475 and 439 nm which may be assigned to d–d transition [18]. The band in the UV region at 290 nm may be ascribed to an intraligand transition. The Ni(II) chelate was observed to be diamagnetic with  $\mu_{\text{eff}}=0$ . The diamagnetism and lack of absorption at the longer wave length region suggest a singlet  $^1A_g$  ground state consistent with a four-coordinate square-planar structure for this chelate. The electronic spectrum shows two bands at 226 and 327 nm assignable to charge transfer transitions. The band at 470 nm may be assigned to a  $^1A_{1g} \rightarrow ^1A_{2g}$  transition. For Cr(III) and Mn(II) chelates, the magnetic moment values are found to be 3.6 and 5.7 B.M. which is slightly less than the spin-only values for three and five unpaired electrons. This suggests the existence of some quenching property. The electronic spectral bands of Cr(III) and Mn(II) chelates in the UV region are to a great extent similar to those bands appearing in spectrum of the free ligand under the same experimental conditions. In addition, spectra of these chelates in the visible region show very weak bands centred at 474 nm for the Mn(II) chelate and at 450 nm for the Cr(III) chelate. This result leads to difficulties in deciding the transition. The Co(II) chelate was found to possess a magnetic moment value of 4.5 B.M. which is consistent with the value required for three unpaired electrons [19]. Its electronic spectrum shows one broad band at 480 nm which may be assigned to a d-d transition. Moreover, the absorption bands at 430 and 336 nm are identical to those observed in the free ligand spectrum but with a slight blue shift. The electronic spectral bands at 223, 267, 359, 438 nm for the Zn(II) chelate, at 220, 270, 340 nm for the Pb(II) chelate, and at 265, 343, 439 nm for the Cd(II) chelate may be attributed to  $L-L^*$  transitions. It is worth mentioning that the data obtained for the chelates prepared by chloride salts of Ni(II), Cu(II), Co(II), and Zn(II) are identical to those obtained for the chelates prepared by acetate salts of the same metal (II) ions indicating their structural identity.

Such coordinative behaviour of the present Schiff base ligand has been observed for several structurally related  $N_2O_2^{2-}$  chromophoric type ligands prepared by condensation of aldehydes or ketones with diamines. In all these systems, the Schiff base acted as tetradentate dibasic ligand via the  $N_2O_2$  ligating atoms towards  $Fe^{3+}$  [20],  $Co^{2+}$  [21–22],  $Co^{3+}$  [23–24],  $Ni^{2+}$  [25, 26],  $Cu^+$  [27],  $Cu^{2+}$  [28–29], and  $Zn^{2+}$  [30]. Furthermore, the complexes of isatin derivatives with linear diamine [6] showed identical behaviour to those reported herein for the rigid complexes of isatin with aromatic diamines. In the case of bis-(isatin)-ethylene-diamine, the ligand acted as dibasic tetradentate ligand enforcing a square planar geometry around the metal ion even though free rotation around the C–C single bond can be expected in the free ligand.

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