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COORDINATION BEHAVIOR OF N/O DONOR LIGAND WITH SOME TRANSITION METALS

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ABSTRACT

Tridentate Schiff base ligand (4-DMIAB) of complexes: cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), and mercury(II) ions have been prepared by the condensation of 4-Ominoantipyrine, isatin, and 4-amino benzoic acid. The complexes and ligand were characterized by UV-visible, FTIR, elemental analysis, magnetic susceptibility, and molar conductance measurements. It has been found that the Schiff base ligand behaves as neutral tridentate (N,N′,O) forming chelates with (1:2) (metal: ligand) stoichiometry. Octahedral environment is suggested for all metal complexes.

Key words: Schiff base, Isatin tridentate, Metal complexes.

INTRODUCTION

The chemistry of transition metal complexes with multi dentate ligands have attracted attention because these metal ions can exhibit several oxidation states, metal complexes with Schiff base ligands. These have been studied for their application in biological, clinical, analytical and pharmacological areas[1-3]. Reduced Schiff base have recently gained considerable attention, because of the flexibility of Schiff base ligands can be improved by hydrogenation of their C=N bonds, they should thus co-ordinate metal ions move easily[4,5]. Isatin is reported to possess a wide range of central nervous system activities.

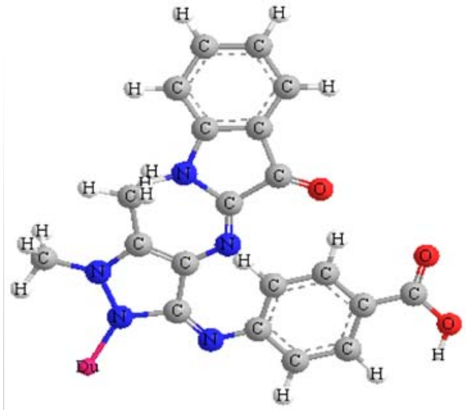

Fig. 1: Molecular structure of li 4-[((3Z)-1,5-dimethyl-2-phenyl-4-{[(3Z)-2-oxo-1,2-dihydro-3H-indol-3-ylidene]amino}-1,2-dihydro-3H-pyrazol-3-ylidene)amino]benzoic acid

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Schiff bases of isatin (1-H-indole-2,3-dione) derivatives were connected with dye synthesis, but more recently these heterocyclic have been shown to demonstrate antiprotozoal, antibacterial, antifungal, antiviral, anti-HIV, anticonvulsant, antitumoral, anti-inflammatory, and antihelminthic activities; influence neurodegenerative diseases; participate in metabolism; acetyl cholinesterase inhibitors; and stimulate the growth of plants[6,7]. In this paper, we reported the preparation, characterization, analytical studies of tridentate Schiff base ligand derived from 4-aminoantipyrine, isatin, and 4-amino benzoic acid. The ligand has both oxygen and nitrogen donor sites. It co-ordinates with the metal ion in a tridentate manner.

EXPERIMENTAL

Materials and methods

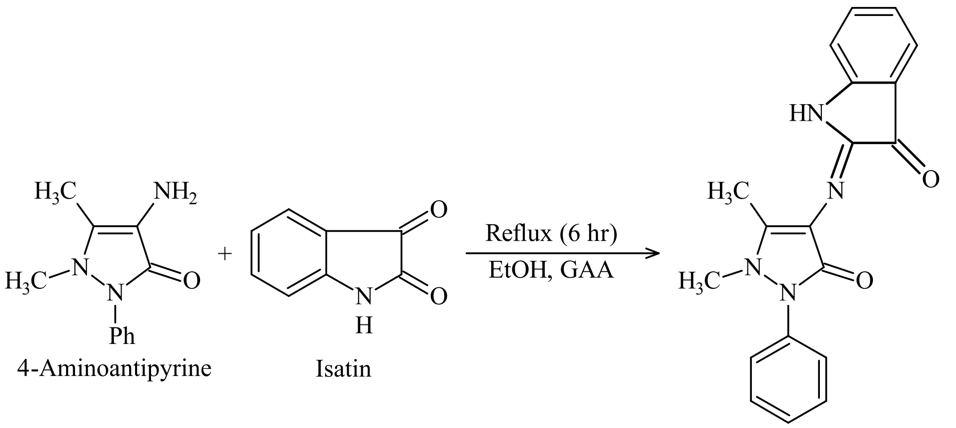
All chemical used were of reagent grade supplied from Merck, Fluka, and Aldrich. FTIR spectra were recorded using KBr discs in 4000-400 cm^{-1} range on FTIR Shimadzu Spectrophotometer model 8400. UV-Vis spectra were recorded in ethanol on Shimadzu Spectrophotometer double beam model 1700 UV-Vis spectrophotometer. Elemental analyses were carried out by measurement of Micro analytical unit of 1108 C.H.N Elemental analyzer. Spectrophotometer Magnetic susceptibilities were measured as powder samples using Faraday method, a Balance magnetic MSB-MKI was employed for this purpose. The diamagnetic corrections were made by Pascal's constants[8]. Molar conductance measurements were determined in DMSO by using an Alpha digital conductivity meter Model 800. The electro thermal melting point Model 9300 was used to measure the melting points of the ligand and its complexes. Physical data, analysis and conductivity of ligand and its complexes are listed in Table 1.

Preparation of Schiff base ligand (4-DMIAB)

The method of preparation

Preparation of compound (I) (4-DMIA)

In a round bottom flask, 4-aminoantipyrine (0.01 mol, 2.03 g) in ethanol (15 mL) and isatin (0.01 mol, 1.47 g) in ethanol (15 mL) added few drops of glacial acetic acid to solution the mixture was refluxed for (6 hr), the product precipitate was obtained by filtration and recrystallized from hot ethanol, and dried over anhydrous $CaCl_2$. m.p (165-168°C) (**Scheme 1**).



4-Aminoantipyrine

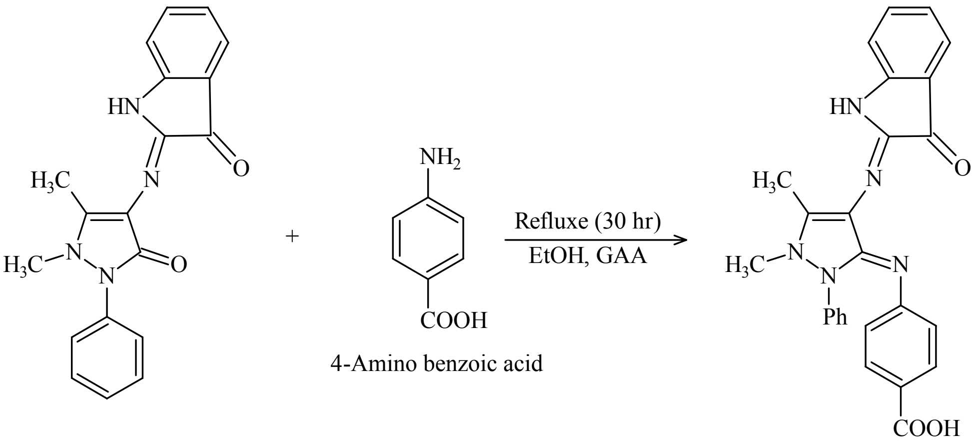
Isatin

(Z)-2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1 *H*-pyrazol-4-ylimino) indolin-3-one
Compound (I)

Scheme 1: Preparation of the ligand (4-DMIA)

Preparation of compound (II) (4-DMIAB)

The Schiff base ligand (4-DMIAB) was preparaed by condensation of compound (I) (0.01 mol, 3.32 g) which was dissolved in 50 mL ethanol and refluxed with (0.01 mol, 1.37 g) of 4-amino benzoic acid for (30 hr) adding three drops from glacial acetic acid, aclear colored solution was obainted. The Schiff base ligand was isolated after the volume of mixture was reduction to half by evaporation and recrystilized by hot ethanol and dried over anhydrous $CaCl_2$ (**Scheme 2**).



(Z)-2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1 *H*-pyrazol-4-ylimino) indolin-3-one
Compound (I)

(Z)-2-(5-Imino-2,3-dimethyl-4-phenylcyclopenta-1,3-dienylimino) indoline-3-one 4-methylbenzoate
Compound (II)

Scheme 2: Preparation of the ligand (4-DMIAB)

Preparation of metal complexes

Metal salt ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2$ and $HgCl_2$) dissolved in hot ethanol (30 mL) was mixed with hot ethanol solution of the ligand (0.002 mol, 0.451 g) and refluxed for (1 hr) on a water bath, on cooling the contents. The complexes separated out in each case. The product was filtered, washed with ethanol and dried under vacuum.

RESULTS AND DISCUSSION

The metal complexes are insoluble in water and soluble in DMSO, DMF, $CHCl_3$, acetone, methanol and ethanol. A series of solutions were prepared having a constant concentration (10^{-3}) of the metal ion and ligand, the M : L ratio was determined from the relationship between the absorption of light and the mole ratio of M : L. The analytical data of the complexes confirm the 1 : 2 metal to ligand stoichiometry. The molar conductance value suggested that the all complexes are electrolytes. The results of complexes formation in solution are listed in Table 1.

Calculation of the metal complexes stability constant

Stability constant are obtained spectrophotometrically by measuring the absorbance of solution of ligand and metal mixture. The degree of formation of the complexes is obtained according to the relationship[9], $\beta = (1-\alpha) / (4\alpha^3c^2)$ and $\alpha = (A_m-A_s) / A_m$, where A_s and A_m the absorbance of the partially and fully formed complex respectively at optimum concentration. The calculated β and log β values for the prepared complexes are recorded in Table 2. The stability follows the sequence; Co(II) < Ni(II) < Cu(II) > Zn(II) > Cd(II) > Hg(II). The sequence of metal ions of the first row transition metal agree with lrving-Williams series of stability constant[9].

Microanalysis

The elemental analysis data the complexes as shown in Table 1, which exhibit the formation 1 : 2 [M : L] ratio. It was found that the theoretical values are in a good agreement with the found data. The purity of the Schiff base ligand were listed by TLC technique and C, H and N elemental analyses.

Table 1: Physical data, analysis and conductivity of ligand and its complexes

Compound	Color	M.P. °C	Analysis : Found (Calc.)%				Yield %	Conductivity S.mol^{-1}. cm^2
			C	H	N	M		
[$C_{26}H_{21}N_5O_3$]	Red	165-168	69.8 (69.1)	4.2 (4.6)	15.7 (15.5)	----	80	----
[$(C_{26}H_{21}N_5O_3)_2$Co]Cl_2	Green	224-225	61.2 (60.4)	4.4 (4.0)	12.9 (13.5)	5.2 (5.6)	74	74.14
[$(C_{26}H_{21}N_5O_3)_2$ Ni]Cl_2	Pale Green	210-212	60.2 (60.4)	4.2 (4.0)	14.3 (13.5)	5.4 (5.7)	72	77.43
[$(C_{26}H_{21}N_5O_3)_2$Cu]Cl_2	Dark green	215-217	62.1 (62.2)	4.0 (4.0)	13.0 (13.5)	6.7 (6.0)	68	72.23
[$(C_{26}H_{21}N_5O_3)_2$Zn]Cl_2	Red	180-183	60.8 (60.0)	4.6 (4.0)	13.0 (13.4)	6.4 (6.3)	76	77.42
$(C_{26}H_{21}N_5O_3)_2$Cd]Cl_2	Red	227-229	57.1 (57.5)	3.4 (3.8)	12.9 (12.9)	9.8 (10.3)	65	76.13
[$(C_{26}H_{21}N_5O_3)_2$Hg]Cl_2	Red	205-207	53.7 (53.1)	3.7 (3.5)	11.3 (11.9)	17.8 (17.0)	62	74.52

Infrared spectra of ligand and complexes

The IR data of the spectra of Schiff base ligand and their complexes are presented in Table 2. The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in chelation. The spectrum of free ligand shows two weak bands 3088 cm^{-1} and 2968 cm^{-1} which due to υ (C-H) aromatic and aliphatic respectively, these bands are in stable in positions in both ligand and chelate complexes. The spectra of the free ligand show band at 3423 cm^{-1}, which can be attributed to NH stretching vibration of isatin[10].

Table 2: Metal : ligand ratios determination by the method of mole ratio and the calculated stability constant values

Ligand	Metal ion	λ_{max} nm	M : L	B	log β
4-DMIAB	Co(II)	445	1:2	**5.7939×10^7**	**7.762**
	Ni(II)	450	1:2	**2.6780×10^8**	**8.427**
	Cu(II)	470	1:2	**8.4256×10^8**	**8.925**
	Zn(II)	348	1:2	**1.3663×10^7**	**7.135**
	Cd(II)	350	1:2	**3.8975×10^7**	**7.590**
	Hg(II)	330	1:2	**4.7939×10^7**	**7.680**

Table 3: Some IR frequencies in (cm^{-1}) of the ligand and its metal complexes

Compound	ν (NH)	ν (C=O)	ν (C=N)	ν (M-O)	ν (M-N)
L = [$C_{26}H_{21}N_5O_3$]	3423	1724	1650	---	---
[CoL_2] Cl_2	3421	1750	1635	569	484
[NiL_2] Cl_2	3417	1735	1625	553	464
[CuL_2] Cl_2	3425	1745	1618	545	476
[ZnL_2] Cl_2	3412	1738	1620	513	457
[CdL_2] Cl_2	3420	1748	1623	532	474
[HgL_2] Cl_2	3418	1742	1630	534	481

Bands of the free ligand at and 1724 cm^{-1}, assignable to stretching vibration due to υ (C=O) groups of isatin, was shifted to higher frequency in the complex, suggesting the involvement of the carbonyl oxygen atom in coordination. The appearance of a new non-ligand band around (569-513) cm^{-1} in all complexes due to υ (M-O) substantiates it[11]. The absorptions at 1650 cm^{-1} in free ligand can be attributed to υ (C=N) stretching vibration of imine nitrogen, which is in agreement with previous observations. This shifts to lower wave numbers, in the complexes suggesting the co-ordination of the azomethine nitrogen to the metal centers[12]. This is further substantiated by the presence of a new band around (484-457) cm^{-1} assignable to υ (M-N)[13]. It is concluded that the ligand behaves as a neutral tridentate ligand coordinated to the metal ions, the nitrogen atoms of azomethine groups, and oxygen atom of the carbonyl group to give five-member chelate ring. Representative example for there is given in Fig. 2. This band remains in the same region in the complexes.

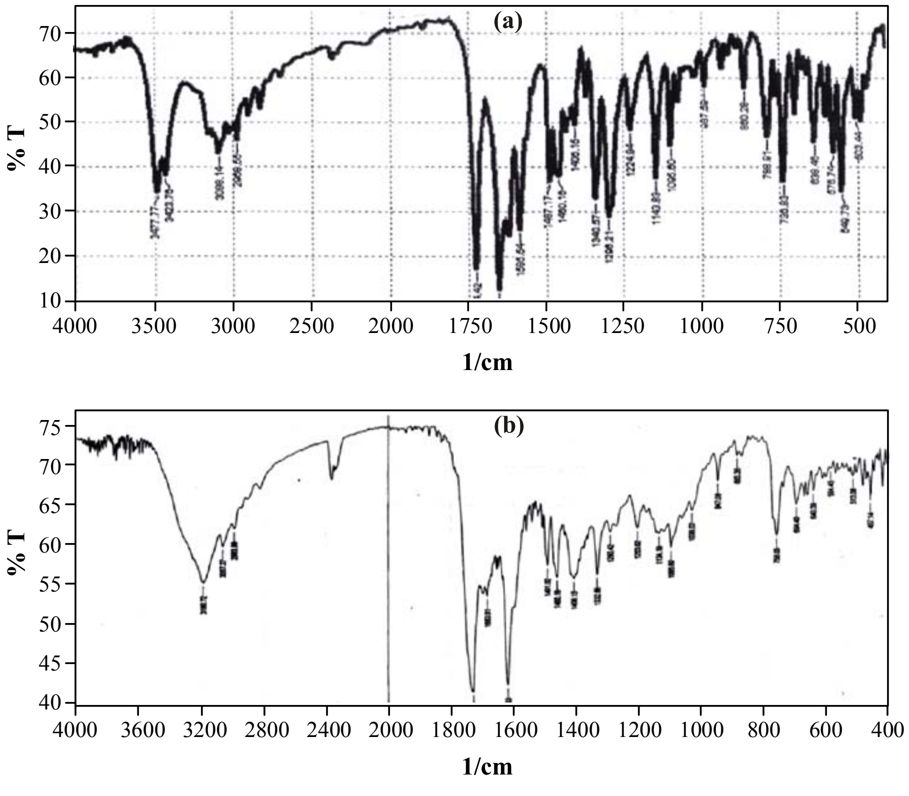


Fig. 2: IR spectra of (a) the ligand (4-DMIAB) & (b) [CoL_2]Cl_2

Magnetic measurement and electronic spectra

The UV-Vis spectrum of the Schiff base ligand is characterized mainly by two absorption bands at 420 nm (23809 cm^{-1}), and 243 nm (41152 cm^{-1}), which may be assigned to $n \rightarrow \pi^*$and $\pi \rightarrow \pi^*$ transitions. These transitions were also found in the spectra of the complexes, but they were shifted towards lower frequencies, confirming the coordination of the ligand to the metal ions (Fig. 3).

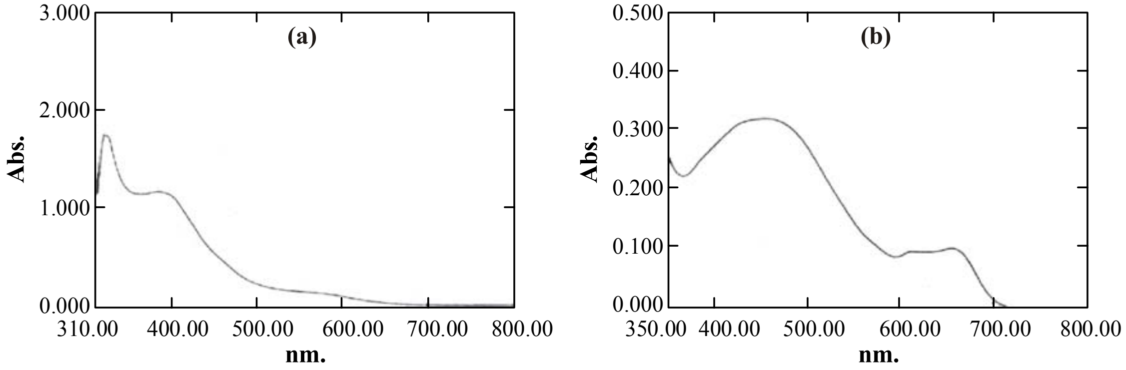


Fig. 3: Electronic spectrum of (a) the ligand (4-DMIAB) & (b) $[CoL_2]Cl_2$

(i) Co(II) complex shows magnetic moment (4.43 B.M) corresponding to three unpaired electrons. The electronic spectrum of the cobalt(II) complex exhibits absorption at 445 nm (22471 cm^{-1}), 286 nm (34965 cm^{-1}) and 278 nm (35971 cm^{-1}). These bands may be assigned to the transitions: ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively. The position of these bands suggests an octahedral environment around the Co(II) ion[14].

(ii) Ni(II) complex shows magnetic moment (3.12 B.M) at room temperature corresponding to two unpaired electrons. The electronic spectrum exhibits three absorption bands at at 450 nm (22222 cm^{-1}), 297 nm (33670 cm^{-1}) ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and 282 nm (35460 cm^{-1}) ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively[15]. Position of these bands indicates an octahedral geometry around the Ni(II) ion[16].

(iii) The magnetic moment value of the copper(II)[17] complex (1.75 B.M) which may suggest an octahedral structure. Its electronic spectrum shows band centered at 470 nm (21276 cm^{-1}) which may assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition in octahedral.

(iv) Zinc(II), cadmium(II) and mercury(II) complexes are diamagnetic moments for d^{10} ions and the electronic spectra there complexes do not show any d-d band[18]. According to these results, the following structure formal of these chelate complexes may be proposed in Fig. 4.

Table 4: Electronic spectra and magnetic moment of complexes

Complexes	Abs. nm (cm^{-1})	Transition	μ_{eff} (B.M)
L= Ligand	243 (41152)	$\pi \rightarrow \pi^*$	——
	420 (23809)	$n \rightarrow \pi^*$	
$[CoL_2]$ Cl_2	445 (22471)	${}^4T_{1g} \rightarrow {}^4T_{1g}(F)$	4.43
	286 (34965)	${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$	
	278 (35971)	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$	

Cont…

Complexes	Abs. nm (cm^{-1})	Transition	μeff(B.M)
$[NiL_2] Cl_2$	450 (22222) 297 (33670) 282 (35460)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	3.12
$[CuL_2] Cl_2$	470 (21276)	$^2E_g \rightarrow {}^2T_{2g}$	1.75
$[ZnL_2] Cl_2$	348 (28735)	CT	Dia
$[CdL_2] Cl_2$	350 (28571)	CT	Dia
$[HgL_2] Cl_2$	330 (30303)	CT	Dia

Conductivity measurement

All chelate complexes prepared in this work showed conductivity values ranged between (72.23-77.43) S. $mol^{-1}.cm^2$ in DMSO at room temperature. These values indicates high conductivity of the complexes[19]. According to these results the structural formula of the metal complexes may be proposed as in Fig. 4.

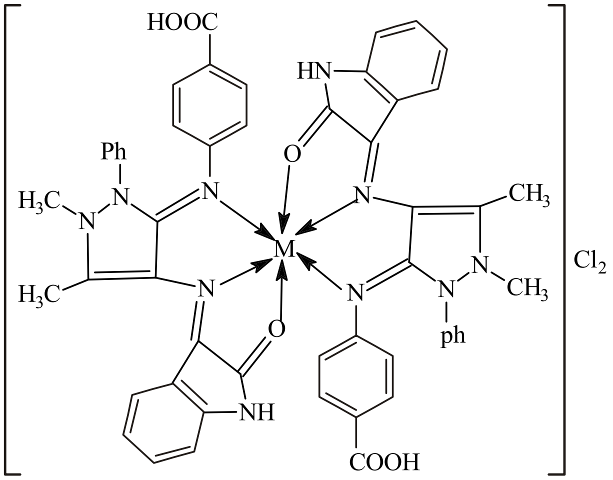


Fig. 4: The proposed structural formula of the metal chelate complexes M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)

CONCLUSION

Schiff base ligand (4-DMIAB) and its chelate complexes have been synthesized. All the complexes are stable and ionic. The geometry is proposed for all complexes show octahedral stereochemistry.

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