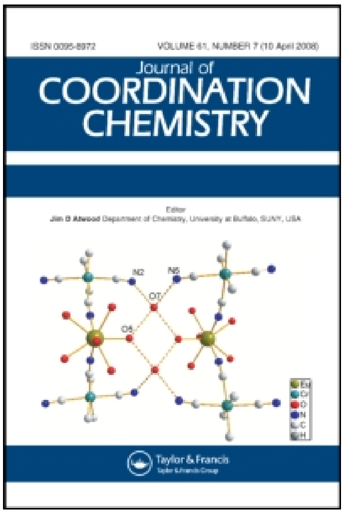

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Versatility in the coordination behavior of a hexatopic compartmental Schiff-base ligand in the architecture of binuclear transition metal(II) complexes

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Versatility in the coordination behavior of a hexatopic compartmental Schiff-base ligand in the architecture of binuclear transition metal(II) complexes

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Condensation of 1*H*-pyrazole-3,5-dicarboxylic hydrazide with 1*H*-indole-2,3-dione (isatin) yield the compartmental ligand, which is capable of encapsulating two transition metal ions namely Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. The ligand is a binuclear hexadentate chelate with N_4O_2 donating sites. The pyrazole core provides the diazine fragment, which serves as an endogenous bridge between the two metal centers. In Co^{II} and Ni^{II} complexes, the ligand is in the imidol form and the subsequent coordination through the imidol oxygen. In other complexes, the lactonic oxygen takes part in ligation. All the complexes are non-electrolytes and soluble in DMSO, DMF, and acetonitrile. Spectral and magnetic studies along with analytical data suggest octahedral geometry for the Co^{II} and Ni^{II} complexes, whereas the Cu^{II} and Zn^{II} complexes are assigned square pyramidal geometry. The Cu^{II} and Ni^{II} complexes show one electron redox behavior and the rest are electrochemically inactive.

Keywords: Pyrazole; Indole; Endogenous; Diazine; Octahedral

1. Introduction

Pyrazole with 1,2-diazine unit provides endogenous bridging between two similar/dissimilar transition/inner transition metal ions [1–6]. With the aid of alkyl or aryl pendent arms at the 3- and 5- positions of the pyrazole core, it can form stable transition metal complexes through chelation. Mixed-valence diazine-bridged coordination compounds involving smaller chloride, bromide, etc., for exogenous bridging are of escalating interest in biology due to the total delocalization of the metal valencies over the cluster, which makes them proficient in electron transfer processes [7–9]. Diazine-bridged compounds have interesting physical properties, such as magnetic behavior, electrical conductivity, stability towards air and moisture, capability of electron transfer, etc., which makes these compounds of preference for applications

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in magnetic materials, metalloenzymes, molecular electronics, and also in the multi-electron transfer processes in biology [10].

1*H*-indole-2,3-dione (isatin) has two dissimilar carbonyl groups, a lactam-carbonyl (α), and a keto-carbonyl (β). The difference in functionality of two carbonyl groups provides many applications in synthetic chemistry [11, 12]. Isatin exhibits versatile biological activities [13] and also is an important biochemical reagent used in the determination of amino acids [14, 15]. Isatin forms Schiff-base ligands by involving β carbonyl with amine functionalities in a selective manner. These ligands, upon interaction with transition metal ions, yield numerous complexes with a variety of physico-chemical properties [16]. Metal–isatin binary complexes were advantageous over simple isatin in chemotherapy and found to act as anticancer agents, especially Schiff-base transition metal complexes derived from isatin [16]. In continuation of our research on the coordination chemistry of pyrazole and isatin, we have synthesized a series of coordination compounds of later first row transition metals.

2. Experimental

1*H*-Pyrazole-3,5-dicarboxylic acid, isatin, hydrazine hydrate, and thionyl chloride were purchased from S.D. Fine Chem. Ltd. and used without purification. Analytical grade absolute ethanol was purchased from the same agency, further dried and distilled before use according to standard procedure. 1*H*-Pyrazole-3,5-dicarboxylic hydrazide was prepared with slight modifications according to the reported method [17]. The preparation of ligand is outlined in figure 1. The estimation of metal(II) ions was carried out by standard methods [18] after decomposing the complexes in nitric acid. The molar conductivity measurements were made on ELICO-CM-82 Conductivity Bridge. Magnetic susceptibility measurements were made on a Faraday balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. ^1H NMR spectra were recorded in DMSO-d_6 on a Bruker-300 MHz spectrometer at room temperature using TMS as internal reference. IR spectra were recorded in a KBr matrix using an Impact-410 Nicolet (USA) FT-IR spectrometer from 4000 to 400 cm^{-1}. The electronic spectra of the complexes were recorded on a Hitachi 150-20 from 1000 to 200 nm. The ESR spectrum of the copper complex was carried out on a Varian E-4X-band EPR spectrometer using TCNE as g-marker. The TG and DTA measurements of the complexes were recorded under nitrogen on a Universal V2.4F TA Instrument keeping final temperature at 800°C and heating rate was $10^\circ C\,min^{-1}$. Cyclic voltammetric studies were performed at room temperature in DMF under O_2 free conditions using CH instruments Electrochemical analyzer, CHI-1110A (USA), using tetramethylammonium chloride as supporting electrolyte. FAB mass spectra were obtained from a JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon (6 kV, 10 mA) as the FAB gas.

2.1. *Preparation of 1H-pyrazole-3,5-dicarbohydrazide*

Pyrazole-3,5-dicarboxylic acid (0.312 g, 0.02 mol) was refluxed with 10 mL of thionyl chloride for about 4 h at 110–115°C under anhydrous conditions. Excess thionyl

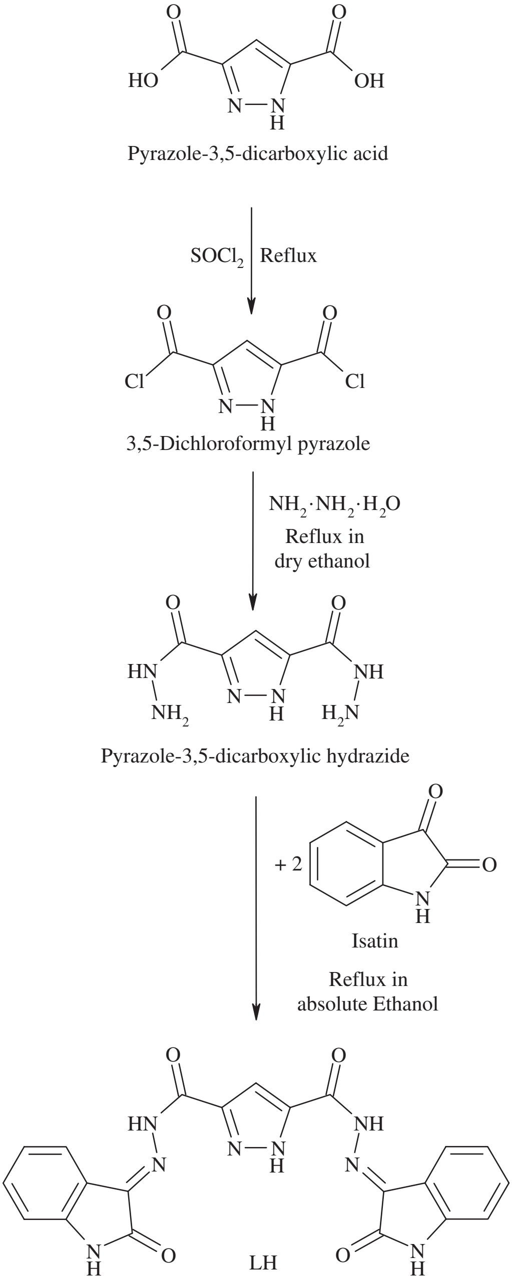


Figure 1. Preparation of LH.

chloride was removed under reduced pressure. The resultant white pasty solid was cooled in an ice bath for 15 min and the hydrazine monohydrate (2.24 mL, 0.04 mol) was added and further refluxed for about 4 h producing a clear colorless solution. The resultant solution was then cooled at 0°C to get colorless solid. Yield: 77%, m.p.: 212–214°C.

2.2. *Preparation of the Schiff-base ligand (LH)*

A mixture of 1*H*-pyrazole-3,5-dicarboxylic hydrazide (1.84 g, 0.01 mol) and isatin (2.94 g, 0.02 mol) in absolute ethanol (50 cm^3) was stirred at room temperature for about 15 min, then refluxed for 3–4 h on a water bath. LH was obtained as a pale yellow precipitate, separated by filtration under suction, washed with ethanol and then air dried. Yield: 84%; m.p. 286–288°C.

2.3. *Preparation of the complexes*

Metal(II) chloride {$CoCl_2 \cdot 6H_2O$ (0.475 g, 0.002 mol), $NiCl_2 \cdot 6H_2O$ (0.474 g, 0.002 mol). $CuCl_2 \cdot 2H_2O$ (0.341 g, 0.002 mol) and $ZnCl_2$ (0.271 g, 0.002 mol)} in EtOH (25 cm^3) was added with stirring to an ethanolic solution (25 cm^3) of LH (0.433 g, 0.001 mol) and refluxed at water bath temperature for 3–4 h. The obtained solid was separated by filtration under suction, washed with hot ethanol and dried *in vacuo*.

3. Results and discussion

Analytical, magnetic, and conductivity data for the complexes are given in table 1. All the complexes are insoluble in water, sparingly soluble in common organic solvents and completely soluble in DMF, DMSO, and acetonitrile.

3.1. *FTIR spectral studies*

Infrared frequencies and their assignments for the different functional groups are given in table 2. The characteristic lactam stretching frequency of the isatin ring system is observed at 1708 and 1679 cm^{-1} as strong bands due to the molecular dissymmetry. It shifts to the lower frequency in Cu^{II} and Zn^{II} complexes and is absent in Co^{II} and Ni^{II} complexes. This shift with reduction in intensity is attributed to the participation of lactam oxygen in coordination; the absence of lactam stretching frequency suggests the imidol form of the ligand with subsequent oxygen coordination. A band at 1665 cm^{-1} in the free ligand assigned to the ν(C=O) of amide remains unchanged in spectra of the complexes. Azomethine and pyrazole ring (C=N) vibrations were observed at 1611 and 1557 cm^{-1}, respectively, in the ligand. Upon complexation, azomethine shifts about 7–14 cm^{-1} to higher frequency, indicating its involvement in coordination [19]. The increase in frequency of ν(N–N) also supports coordination through azomethine nitrogen in all complexes [20]. Pyrazole ring vibrations shift both directions signifying diazine bridging to the metals. The magnitude and direction of shift may be attributed to the extent of overlapping of μ-1,2-diazine lone pair with metal orbitals [21]. The presence of coordinated/lattice waters is confirmed by a band at 3350–3400 cm^{-1}. ν(–NH) appear at 3150 cm^{-1}, unaltered in the complex spectra [22, 23]. The ν(M–N) are observed at 456–466 cm^{-1} [24]. IR spectra of ligand and Cu^{II} complex are provided in Supplementary Material.

Table 1. Analytical, magnetic moment, and conductance data of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} complexes.

Complex	Elemental analysis in %					μ_{eff} in BM	Molar conductance ($Ohm\,cm^2\,mol^{-1}$)
	Metal	Carbon	Hydrogen	Nitrogen	Chloride		
$[Co_2L(\mu\text{-}Cl)(H_2O)_4]$	17.98 (17.65)	38.26 (38.35)	3.01 (2.89)	17.42 (17.04)	5.13 (5.47)	4.23	5.1
$[Ni_2L(\mu\text{-}Cl)(H_2O)_4]$	17.90 (17.53)	37.03 (38.41)	3.05 (2.88)	17.36 (17.03)	5.28 (5.48)	2.98	2.8
$[Cu_2L(\mu\text{-}Cl)Cl_2] \cdot H_2O$	18.04 (18.65)	36.40 (36.73)	2.31 (2.04)	16.15 (16.32)	15.98 (15.59)	1.73	3.8
$[Zn_2L(\mu\text{-}Cl)Cl_2] \cdot H_2O$	19.08 (18.85)	36.23 (36.52)	2.22 (2.02)	16.51 (16.23)	15.22 (15.50)	–	6.1

Calculated values are given in parenthesis.

Table 2. Infrared spectral data of ligand and complexes in cm^{-1}.

Compounds	ν(O–H)	ν(N–H) Isatin	ν(N–H) Amide	ν(>C=O) Lactum	ν(>C=O) Amide	ν(>C=N) Azomethine	ν(>C=N) Pyrazole	ν(N–N)	ν(M–N)
LH	–	3168	3118	1709, 1679	1655	1611	1557	1017	–
$[Co_2L(\mu\text{-}Cl)(H_2O)_4]$	b, 3430	–	b, 3100	–	b, 1660	$1625^{\#}$	1505	1063	461
$[Ni_2L(\mu\text{-}Cl)(H_2O)_4]$	3424	–	b, 3110	–	1657	$1621^{\#}$	1502	1052	466
$[Cu_2L(\mu\text{-}Cl)Cl_2]\cdot H_2O$	3318	3162	3115	1700	s, 1652	1618	1546	1063	458
$[Zn_2L(\mu\text{-}Cl)Cl_2]\cdot H_2O$	b, 3340	b, 3170	b, 3100	1702	1658	1619	1567	1054	456

b: broad band; s: shoulder.

[#] Around 1600 cm^{-1} a shoulder band is observed due to the formation of new azomethine fragment in the isatin ring system.

3.2. ^1H NMR studies

The ^1H NMR spectrum of LH exhibits sharp singlets at 14.7, 14.1, and 10.8 ppm, assigned to pyrazole ring proton (–NH) [21, 25], isatin ring protons (–NH) [16], and amide protons, respectively. Isatin ring protons at such a downfield region confirm its existence as the lactam tautomer. Multiplets at 6.9–7.8 ppm are from aromatic protons.

The absence of pyrazole ring proton (–NH) in the Zn^{II} complex spectrum indicates deprotonation, confirming the endogenous bridging of pyrazole diazine. The other protons experience a small change in the chemical shift values, attributable to the variation in electron density and steric constraints brought about by chelation.

3.3. *Magnetic susceptibility and absorption spectral studies*

Magnetic susceptibility values summarized in table 1 show little or no antiferromagnetic exchange interaction between metal centers. Endogenous diazine bridging can bring the metal ions closer together, but reduction in electron density on the metal centers by electron-withdrawing of bridging exogenous chloride is less favorable for effective spin exchange interactions, hence the exchange interaction decreases [26, 27].

The electronic absorption spectra of the compounds were recorded in DMF at 200–1000 nm. LH shows bands at 313 and 342 nm which correspond to intraligand, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. These transitions have been red shifted by 17–25 and 30–35 nm, respectively, upon complexation indicating coordination of azomethine group. The electronic spectrum of Co^{II} complex shows an intense band at 560 nm, which is a characteristic d–d transition band for Co^{II} complexes with octahedral geometry [28]. Three distinguishable d–d bands at 495, 550, and 665 nm are observed for the Ni^{II} complex suggesting octahedral geometry [29, 30]. The Cu^{II} complex exhibits three main bands at around 615, 350, and 320 nm. The lowest energy asymmetric band is assigned to d–d transition. Broad asymmetric bands at around 600 nm, with a low-energy shoulder band, have been observed for cyclic and acyclic Schiff-base binuclear Cu^{II} complexes with square-pyramidal geometry [31, 32]. Zn^{II} complex shows absorptions around 350–365 nm, which correspond to intraligand transitions. The electronic spectra of ligand and complexes are provided in "Supplementary material".

3.4. *Molar conductivity measurements*

The molar conductance values of complexes were obtained at room temperature in DMSO solution with 10^{-3} mol dm^{-3} concentration. The molar conductivity values of all the complexes (table 1) fall in the range 2.8 to 6.1 Ohm cm^2 mol^{-1}, indicating the non-electrolytic nature of the complexes [33].

3.5. *ESR spectral studies*

X-band ESR spectra of polycrystalline Cu^{II} complex recorded at room temperature shows an isotropic intense broad signal at $g_{iso} = 2.07$ with no response at hyperfine splitting. No half-field absorption rules out the existence of spin–spin interaction, which is further supported by the normal magnetic moment value. The ESR spectrum of the binuclear Cu^{II} complex of this type is characteristic of a square pyramid [27].

3.6. *FAB-mass spectral studies*

The elemental and analytical data suggest $[M_2L] \cdot nH_2O$ for all the complexes; this is supported by FAB mass spectra. The peaks at highest m/z value cannot always be assigned with certainty, but the isotopic pattern is consistent with the binuclear complexes. A peak at m/z 707 was observed in the Cu^{II} complex, which is consistent with the mass of the entire binuclear, monomeric complex including coordinated chloride ions and lattice-celled water molecules. Apart from this, spectrum shows some other peaks which are due to the molecular cations of various fragments of complex. By comparing the analytical and spectral data of cobalt, nickel, and zinc complexes, it is evident that these are monomeric and binuclear complexes.

3.7. *Thermal studies*

Thermogram of $[CoL(\mu\text{-}Cl)(H_2O)_4]$ complex in the range 30 to 800°C under nitrogen shows decomposition in two steps. In the first step, loss of 9.46% was observed at 60–210°C from loss of four coordinated waters and a chloride, confirmed by the appearance of endothermic and exothermic DTA signals at 100 and 210°C, respectively. In the next step, the total weight loss is due to the elimination of ligand and formation of stable metal oxide. Thermograms of the remaining complexes are in agreement with the proposed structures of the complexes.

3.8. *Electrochemistry*

The electrochemical behavior of metal complexes containing two or more chemically equivalent electroactive sites have been the subject of numerous studies. It is reported [34] that for reversible sequential transfer of two electrons (each in oxidation and reduction process) the ΔE_p in the cyclic voltammogram would be 42 mV. In the present investigation the compounds were scanned for the cyclic voltammetric studies. Ligand and its Co^{II} and Zn^{II} complexes are found to be electrochemically innocent in the working potential range (+1 to −1 V); in remaining cases the redox processes are unambiguously metal based.

The typical cyclic voltammogram of Cu^{II} complex is shown in figure 2(a). The present Cu^{II} complex shows one electron transfer redox behavior with oxidation potential at 0.15, 0.16, and 0.17 V and there is no reduction peak observed with varying scan rates of

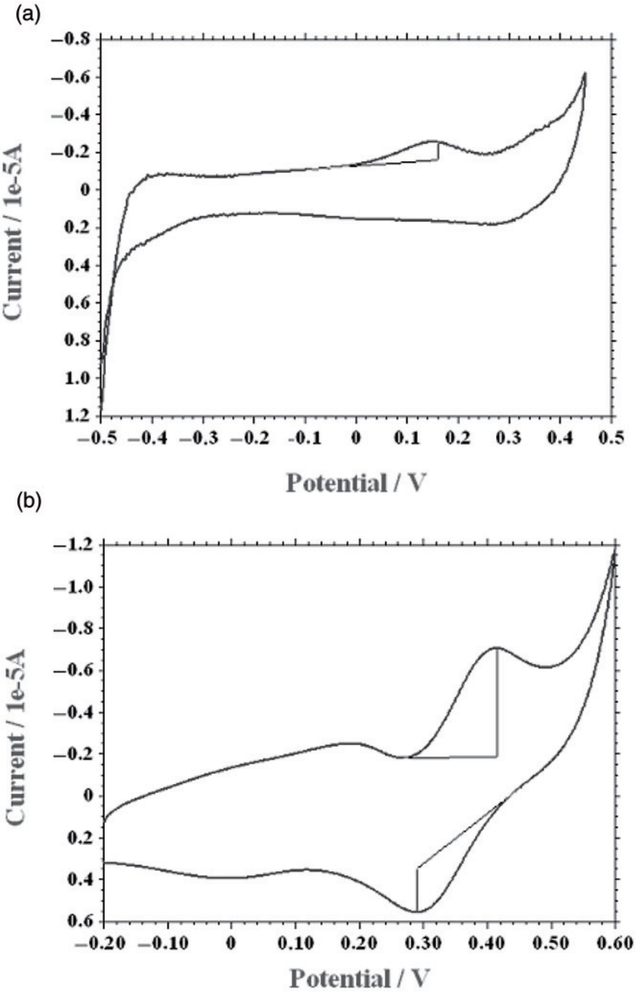
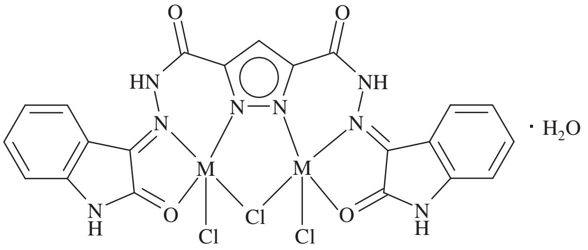
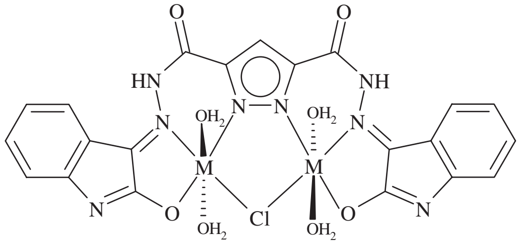


Figure 2. Cyclic voltammogram of Cu^{II} (a) and Ni^{II} (b) complexes at the scan rate of $0.1\,V\,s^{-1}$.

0.05, 0.1, and $0.15\,V\,s^{-1}$, respectively. Analysis of the cyclic voltammogram for Cu^{II}–Cu^{III} oxidation at varying scan rates reveals that it is irreversible one electron transfer. A quasireversible cyclic voltammogram (figure 2b) was obtained for Ni^{II} complex. The oxidation potential is observed at 0.40, 0.41, and 0.42 V and is assigned to Ni^{II}–Ni^{III}. Subsequently in the opposite scan, a peak is observed at 0.28, 0.29, and 0.31 V indicating reduction of Ni^{III}–Ni^{II}. By analyzing the variation of peak position as a function of scan rates, it is possible to predict the nature of the electron transfer behavior. The peak difference in the potential of oxidation and reduction process on average is around 120 mV, suggesting quasireversible redox process. The oxidation step and the corresponding reduction obey the diagnostic criteria that is, I_{pc}/I_{pa} almost constant but not unity which further supports the quasireversible electron transfer process [19, 21].



M: Cu and Zn



M: Co and Ni

Figure 3. Proposed structures of the complexes.

4. Conclusion

Ligand formed by the condensation of 1*H*-pyrazole-3,5-dicarboxylic hydrazide with two equivalent molecules of isatin is a hexadentate chelate towards later first row transition metal ions. All synthesized complexes have [M_2L] composition. The diazine group acts as endogenous bridge between metal centers and successive coordination occurred through the azomethine nitrogen and lactam/imidol oxygen of isatin. Copper and zinc complexes have square pyramidal geometries, while nickel and cobalt complexes are octahedral (figure 3). All complexes are monomers and non-electrolytes. A weak/non-antiferromagnetic interaction is present between the metal ions. An irreversible and quasireversible cyclic voltammograms are obtained for the copper and nickel complexes, respectively.

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