

Synthesis and characterization of nickel(II), chromium(III), cobalt(II), copper(II), zinc(II) and cadmium(II) complexes with isatin-isonicotinoylhydrazone

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A few metal complexes of isatin-isonicotinoylhydrazone with Ni(II), Cr(III), Co(II), Cu(II), Zn(II) and Cd(II) have been prepared and characterized on the basis of elemental analyses, infrared and electronic spectra as well as ^1H NMR spectra, conductivity and magnetic measurements. In view of the results obtained, it has been found that two molecules of isatin-isonicotinoylhydrazone are chelated to the central metal ion as bis-uninegative ONO tridentate ligand forming non-electrolytic octahedral metal complexes.

In addition to the medical applications of hydrazones¹⁻⁵, they have been investigated as donors because of their varied ligational behaviour towards different metal ions and manifestation of novel structural features in the metal complexes⁶⁻¹². As a part of our programme on the synthesis and characterization of the metal complexes of isatin Schiff bases, the present investigation was undertaken to study the interaction of the Schiff base (I) derived from isatin and isonicotinic acid hydrazide with Ni(II), Cu(II), Cr(III), Co(II), Zn(II) and Cd(II) ions.

Experimental

Metal salts, isatin and isonicotinic acid hydrazide were E Merck or BDH products. The solvents used were of reagent grade.

Synthesis of the Schiff base

It was prepared by refluxing equimolar amounts of isatin and isonicotinic acid hydrazide in 1:1 aqueous methanolic medium for 1 h. The precipitate was filtered off, washed with methanol and dried *in vacuo*.

Synthesis of the complexes

The various metal chlorides (viz, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$) (2.5 mmol) dissolved in 30 ml of

water were added to 70 ml of 1:1 DMF-methanolic solution of isatin-isonicotinoylhydrazone (5 mmol). Then sodium acetate solution (1 ml, 1 M) was added and the contents refluxed for 2 h. On cooling, the products separated out. They were filtered, washed with hot water followed by methanol and dried *in vacuo*.

Conductivity measurements in freshly prepared DMF solutions were made at 25°C using a YSI Model 35 conductance Meter. Electronic spectra of the resulting solid complexes in nujol mull were measured on Shimadzu UV-160 A UV-visible recording spectrophotometer. IR Spectra were measured as KBr discs on Pye Unicam SP 1025 spectrometer. The magnetic susceptibility measurements were carried out by the Gouy method at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant¹³. ^1H NMR spectra in $\text{DMSO}-d_6$ were measured on a Varian E M 390 NMR spectrometer. Chemical shifts are reported in δ ppm downfield from internal TMS.

Results and discussion

The analytical data (Table 1) indicate the formation of 1:2 (M:L) complexes of the general molecular formula $\text{ML}_2 \cdot n\text{H}_2\text{O}$ where $\text{M} = \text{Ni(II)}$, Co(II) , Cr(III) , Cu(II) , Zn(II) and Cd(II) and $\text{LH} = \text{isatin-isonicotinoylhydrazone}$. Molar conductance values (Λ) in DMF solutions ($45.8\text{--}25.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) indicated the complexes to be non-electrolytes although some solvolysis occurred.

In the infrared spectrum of the free ligand, two bands are observed at 1700 and 1680 cm^{-1} assignable to $\nu\text{C}=\text{O}$ of isatin moiety and the amido group of hydrazone chain respectively. In all complexes, the amido $\nu\text{C}=\text{O}$ band disappears and instead a new band due to $\nu\text{C}-\text{O}$ is observed in 1095-1120 cm^{-1} indicating enolization of this group in the presence of metal ion under the reaction conditions. Strong bands at 1700 and 1640 cm^{-1} due to stretching frequencies of $\text{C}=\text{O}$ of isatin moiety and azomethine group $\text{C}=\text{N}$ re-

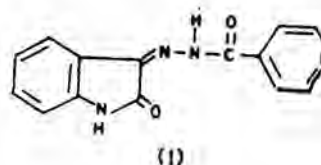


Table I—Characterization data of the complexes

Complex	Found (Calcd.), %			μ_{eff} B M	Λ_M $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
	C	H	N		
$\text{NiL}_2 \cdot 2\text{H}_2\text{O}$	53.83(53.78)	3.68(3.52)	17.85(17.92)	3.20	26.94
$\text{CoL}_2 \cdot 2\text{H}_2\text{O}$	53.64(53.76)	3.74(3.52)	17.98(17.92)	4.81	29.74
$\text{CuL}_2 \cdot \text{H}_2\text{O}$	54.89(54.94)	3.39(3.27)	18.59(18.31)	1.82	40.39
$\text{CrL}_2 \cdot \text{Cl} \cdot 3\text{H}_2\text{O}$	50.38(50.04)	3.42(3.57)	16.42(16.68)	3.43	45.82
$\text{ZnL}_2 \cdot 2\text{H}_2\text{O}$	53.59(53.22)	3.61(3.48)	17.69(17.74)	diamag	25.34
$\text{CdL}_2 \cdot 2\text{H}_2\text{O}$	49.81(49.52)	3.39(3.24)	16.80(16.51)	diamag	38.46

spectively shift (10 cm^{-1}) to lower frequency in spectra of the metal complexes indicating the participation of oxygen atom of the carbonyl group at position 2 of isatin and the nitrogen atom of azomethine group in the complex formation. A strong band at 1545 cm^{-1} in ligand spectrum is assigned to delocalized $-\text{C}=\text{N}-$ vibrations present in isonicotinic ring. This band is not affected in the spectra of all the complexes indicating the non-participation of ring nitrogen atom in coordination. Furthermore, the IR spectra of the metal complexes lack absorption due to $\nu(\text{NH})$, but exhibit a strong band at $1600\text{--}1610\text{ cm}^{-1}$ due to $-\text{C}=\text{N}-\text{N}=\text{C}-$ moiety. Thus the ligand probably acts as a mononegative tridentate ligand chelated to the central metal ion via the azomethine nitrogen, the enolic oxygen of isonicotinoylhydrazone moiety and the isatin carbonyl oxygen atom. In all complexes, bands due to water molecules are observed in the regions $3420\text{--}3380$, $1290\text{--}1275$, $890\text{--}880$ and $780\text{--}765\text{ cm}^{-1}$ attributable to OH stretching, bending, rocking and wagging vibrations respectively.

The proton NMR spectra of the isatin-isonicotinoylhydrazone Schiff base ligand and its $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ complexes were recorded in $\text{DMSO}-d_6$. The spectrum of the free ligand could be resolved into four distinct regions: (multiplets at $\delta 7.2\text{--}7.5$ and $\delta 6.4\text{--}6.8$, two singlets at $\delta 10.4$ and 11.3 ppm) corresponding to resonance resulting from the protons of the fused aromatic rings of isatin moiety, aromatic protons of isonicotinic ring, NH proton of isatin residue and the imino proton of hydrazone moiety respectively. The disappearance of the latter in the ^1H NMR spectra of the metal chelates is considered as an additional evidence of the enolization of the amido group of isonicotinoylhydrazone residue.

The cobalt(II) chelate shows magnetic moment value of 4.81 B.M. which is higher than the spin-

only value and this may be due to orbital contribution. The presence of two bands in the electronic spectrum of this chelate at 21740 and 16390 cm^{-1} due to $^4T_{1g(F)} \rightarrow ^4T_{1g(P)}(\nu_2)$ and $^4T_{1g(F)} \rightarrow ^4A_{2g(F)}(\nu_2)$ respectively, indicate that the $\text{Co}(\text{II})$ chelate has octahedral geometry. This view may be substantiated by the conclusion drawn from magnetic moment value.

The chromium(III) complex shows a magnetic moment value of 3.42 B.M. A band is observed at 11890 , attributable to $^4A_{2g(F)} \rightarrow ^4T_{2g(F)}$ transition in favour of octahedral geometry¹⁴.

The $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ chelates are diamagnetic in nature with no $d\text{--}d$ transitions. The bands appearing in the nujol mull electronic spectra of $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ at 33820 and 23640 cm^{-1} for the former and 31260 and 20680 cm^{-1} for the latter may be assigned to intraligand transitions.

The magnetic moment of nickel(II) complex is found to be 3.20 B.M. in favour of octahedral geometry with $^3A_{2g}$ ground state. Bands at 11240 and 15930 cm^{-1} may be assigned to $^3A_{2g(F)} \rightarrow ^3T_{2g(F)}(\nu_1)$ and $^3T_{2g(F)} \rightarrow ^3T_{1g(F)}(\nu_2)$ transitions respectively.

Copper (II) complex shows magnetic moment at 1.82 B.M. which is close to the spin-only value for a d^9 ion. The electronic spectrum displays a broad band in vicinity of 17980 cm^{-1} which may be assigned to $^2E_g \rightarrow ^2T_{2g}$ transition indicating the presence of copper(II) ion in an octahedral field. The magnetic moment of this complex indicates no copper-copper interaction.

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