



NOVEL COBALT COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM CARBONYL OXIMES AND DITHIO BIURETS

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ABSTRACT

The synthesis of some Co(II) complexes with acid Schiff bases are reported here. These Schiff bases were derived by condensing carbonyl oximes and amines like Dithio biurets. The characterization of the complexes was done on the basis of elemental analysis, molar conductivity, spectral studies like IR and Electronic and Anti-bacterial activity. On the basis of these analysis it was concluded that Co(II) complexes exhibit Octahedral binuclear geometry with $M_2L_2Cl_2 \cdot 4H_2O$ stoichiometry. The molar conductivity data indicate that the complexes are non-electrolytic in nature. The metal complexes have been screened for their antibacterial activity.

Keywords: Co(II) complexes, Schiff bases, Structural analysis, Antimicrobial studies

1. INTRODUCTION

Schiff bases and their coordination compounds have gained importance recently because of their application as models in biological, biochemical, and analytical, antimicrobial system, anticancer, antibacterial and antifungal activities. Studies of new kinds of chemotherapeutic Schiff bases are now attracted the attention of biochemists^[1-2]. Schiff bases contain azomethine ($>C=N$) group as functional group and hence act as an effective ligand. In addition the presence of nitrogen and oxygen donor atoms in the complexes act as stereospecific catalyst for many reactions like oxidation³, reduction⁴, hydrolysis⁵ and possess antibacterial⁶ activity. In this paper, the synthesis, characterization of some Co(II) complexes with polydentate Schiff base ligands are reported.

2. Materials and Methods

All chemicals used were of A. R. grade purchased from S. D. Fine chemicals (Mumbai) & used without further purification. Distilled solvents were used throughout the experiments. Metal content was determined in the laboratory by the reported methods^[7]. C, H and N analysis were performed at the IIT Mumbai. The infra-red spectra of the ligands and of their metal complexes were recorded in KBr pellets in the 4000-400 cm^{-1} region using a FTIR spectrum one supplied by Perkin Elmer instrument. The electronic spectra were recorded on Beckman Spectrophotometer the diffuse reflectance spectra of solid complexes taken on Carl-Zeiss VSU -2P spectrophotometer. The 1H NMR spectra were recorded on a VXR-300s Varian Super Nuclear Magnetic Resonance spectrophotometer using TMS as an internal standard. TGA analysis was carried out using a Shimadzu DT-30 recording thermal analyse in an inert atmosphere of nitrogen, from room temperature to 900°C.

Colour, , Analytical Data, and**for the Metal Complexes of HPEPDTB**

C	Complex	Colour	Elemental Analysis(%)					
			Found (Calculated)					
			M	C	H	N	S	Cl
	Co ₂ (L) ₂ Cl ₂ .XH ₂ O	Reddish	12.0	41.8	3.0	12.5	12.7	7.0
		Brown	(12.47)	(40.64)	(3.1)	(11.85)	(13.54)	(7.51)

Antimicrobial studies: The *in-vitro* biological screening effects of the investigated compounds were tested against the bacteria *Escherichia coli*, *Staphylococcus*, *B.cereus*, *Bacillus subtilis* were studied on laboratory grown cultures. Stock solutions were prepared by dissolving the compounds in DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC). The nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread over the solid nutrient agar plates with the help of a spreader. Different dilutions of the stock solutions were applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature for 30-36 hrs. The diameter of the inhibition zones was measured in millimetres.

Synthesis and Characterisation of the ligands 5-(2'-hydroxymino-1'-phenyl) ethylidene phenyl/tolyl 2,4,-dithiobiurets

The title ligands have been reported for the first time in the present work. They are obtained as fine powdered solids by the reaction of phenyl/tolyl 2,4-dithiobiuret with isonitrosoacetophenone(HINAP). They are abbreviated as HPEPDTB and HPETDTB respectively. The ligands are insoluble in water but soluble in common organic solvents like chloroform, methanol, carbon tetrachloride etc having varying solubility. The elemental analysis is in agreement with the empirical formulae of the compounds. Table gives colour, m.p. and analytical data of the ligands. The melting point of HPETDTB is greater than that of HPEPDTB, which also reflects the order of thermal stability of the ligands and the strength of the inter-molecular forces.

The complexes are coloured and non-hygroscopic in nature. They are insoluble in water and sparingly soluble in common organic solvents though somewhat more soluble in dimethyl formamide (DMF) at room temperature. They give intense colour with dil. NaOH solution suggesting the presence of a free oxime group in the complexes.

All the complexes are thermally stable at least upto 120°C (Table 5.25, 5.26) indicating fairly high thermal stability and hence a strong metal-ligand bond.

The values of molar conductance of the metal complexes in DMF solution at 10⁻³ M concentration are < 1.0 ohm⁻¹ cm² mole⁻¹ (Table 5.25, 5.26) and are suggestive of the non-electrolytic nature of these complexes.

Owing to the limited solubility of the complexes in suitable organic solvents, determination of their molecular weight by conventional cryoscopic methods was not possible, while the attempts with Rast's method did not yield reproducible results.

Infrared Spectra:

The FT-infrared spectra of the metal chelates (Figs.5.74-5.88) contain large number of bands of varying intensities and are quite complex. However, several structurally important bands, such as those due to $\nu_{(O-H)}$, $\nu_{(C=N)}$, $\nu_{(N-OH)}$, $\nu_{(C=S)}$ etc modes have been identified to derive information regarding the structural features of the ligands and their manner of bonding with the metal ions.

All the metal complexes, show a broad band around 3400-3430 cm^{-1} in their FT-IR spectra. This band may be attributed to O-H stretching mode of water molecules. The centre of gravity of this band near 3420 cm^{-1} implies coordinated nature of these water molecules.

A careful comparison of the spectra of the metal complexes with those of the ligands also reveals that bands due to ν_{N-OH} , and ν_{N-H} in the region around 3200-3300 cm^{-1} are observed for the complexes, which overlap in several cases making their distinction difficult. The -N-H bending vibrations are observed near 1620-1600 cm^{-1} , around the same position as in ligands, indicating that -NH group is not involved in coordination. The presence of free -NOH function in the complexes is also revealed by their solubility in dilute alkali solution.

The azomethine and oximino C=N stretching vibrations are relatively unaffected and are observed at ~1610-14 and 1563-1567 cm^{-1} respectively indicating that the azomethine or oxime nitrogen donors are not involved in bonding.

The C=S stretching frequency of the ligands are found to undergo a negative shift on complexation suggesting that the ligands coordinate to the metal ions through sulphur donors. The C=S stretching bands are observed around 1220-1240 cm^{-1} in the spectra of the complexes.

Another fairly strong band around 725-759 cm^{-1} due to C=S vibrations in ligands is also found to be shifted to lower frequencies between 686-692 cm^{-1} in complexes with medium intensity.

The IR bands due to phenyl ring systems of the ligands observed around 1497, 1450 and 1400 cm^{-1} are found to be almost unaffected in the spectra of the metal complexes.

Absence of -SH band around ~2560 cm^{-1} it shows that the coordination occurs through sulfur atoms and larger low-frequency shift of the C=S stretching frequency may be attributed in part to the change in the symmetry of the ligand from C_s to C_{2v} . Observed decrease in C=S frequencies together with negligible shift or slight increase in C=N stretching frequencies is suggestive of sulphur coordination of the ligands to the metal ion. Similar sulphur coordinated dithiobiuret complexes are reported in the literature.

On the basis of the elemental analysis and results of various physicochemical studies, the bonding in the chloro metal complexes of HPEPDTB and HPETDTB .

Magnetic Susceptibility Measurements:

The room temperature magnetic susceptibility measurements indicate that all the transition metal complexes are paramagnetic in nature.

Co(II) complexes of the two ligands HPEPDTB and HPETDTB show a room-temperature magnetic moment of 4.46 B.M. which is greater than the spin-only moment of 3.87 B.M., expected for the three unpaired electrons in high-spin d^7 configuration. The observed magnetic moment for the Co(II) complexes in the solid state at room temperature is suggestive of their octahedral geometry, though presence of some antiferromagnetic interaction is implied by slightly lower values of the experimental magnetic moments observed and may be expected on account of steric reasons⁴ and the nature of the structures proposed. Alternatively, quenching of the orbital contribution may also be partly responsible for the observed magnetic moment.

The PMR spectra of the ligands, recorded in DMSO- d_6 solution with TMS as a standard, are shown in Figs. A prominent feature of the spectra of HPEPDTB and HPETDTB is the absence of the proton signals due to $-NH_2$ group of the dithiobiurets. This suggests successful schiff base formation by the replacement of $>C=O$ group of the HINAP by the azomethine

UV Spectral Data on Ligands HPEPDTB and HPETDTB

Ligands	Band Position (cm^{-1})	Assignments
HPEPDTB	46,720, 41,660, 37,637	$n-\sigma^*$, $\pi-\pi^*$ transitions
HPETDTB	48,076, 40,650, 34,960	$n-\sigma^*$, $\pi-\pi^*$ transitions

A calculation of S-H distance from the geometry of the molecule reveals that the distance between these two atoms is favourable for hydrogen bond formation. It appears from the spectra that a proton transfers to sulphur as shown by the presence of an absorption bands due to $-SH$ at $\sim 2560\text{ cm}^{-1}$. Important FT-IR spectral bands for HPEPDTB and HPETDTB and their assignments are summarized in Table. On the basis of the analytical and spectral data, the formation and the structure of the schiff base ligands HPEPDTB and HPETDTB may be represented as follows:

Thermal Decomposition Data for

$\text{Co}_2(\text{HPEPDTB})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

	Loss of group	Temperature range(°C)	% weight loss	
			Observed	Calculated
(i)	$4\text{H}_2\text{O}$ $E = 4.99 \text{ k cal mole}$ $N = 1.01$	160	7.0	7.6
(ii)	$2(\text{C}_6\text{H}_5\text{-NH})+$ $2(\text{C}_6\text{H}_5)+2(\text{NOH} = \text{C-H})+$ $4\text{H}_2\text{O}$	530	53.0	52.92
(iii)	$-\text{do}- + \text{Cl}_2 + 2(\text{C}=\text{N})+ 2(\text{N-H})$	800	70.0	69.18

The order of the reaction (n) and the energy of activation (E) for the dehydration step have been calculated and are found to be 1.01 and 4.99 kcal/ mole respectively.

The two Co(II) complexes show a broad band around $7,407\text{-}7,692 \text{ cm}^{-1}$ and a weak shoulder at $15,625\text{-}16,120 \text{ cm}^{-1}$ which can be ascribed to the transitions ν_1 and ν_2 respectively in an octahedral geometry. The ratio of the two band energies¹⁶, ν_2/ν_1 , has diagnostic importance of octahedral Co(II) complexes and is usually found to be much lower than the theoretical value of 2.2. For many octahedral Co(II) complexes the ratio is found to be even lower than 2.0. In the present cases, the values for the ratio ν_2/ν_1 are found to be 2.11 and 2.09 for the octahedral Co(II) complexes of HPEPDTB and HPETDTB respectively, and are well within the range expected and hence are in conformity with the band assignments.

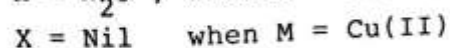
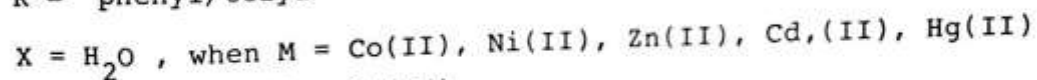
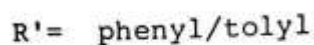
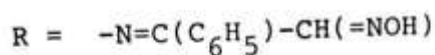
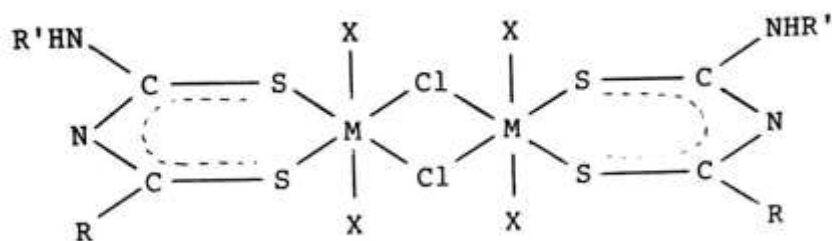
Table summarises the diffuse reflectance spectral data for the Co(II) complexes. The calculated values of the various spectral parameters like $10Dq$, B' and β have been calculated using various equations described by Koing¹⁸ and are presented in the table; these are within the range normally observed. An attempt has also been made to calculate the transition energies by using the equation¹⁸:

$$\nu_2, \nu_3 = 1/2 [15B' + 30 Dq] \pm 1/2 [15B' - 10 Dq]^2 + [15B' \times 10Dq]^{1/2}$$

The values of the calculated transition energies are given in the parantheses and are in fair agreement with the values experimentally observed.

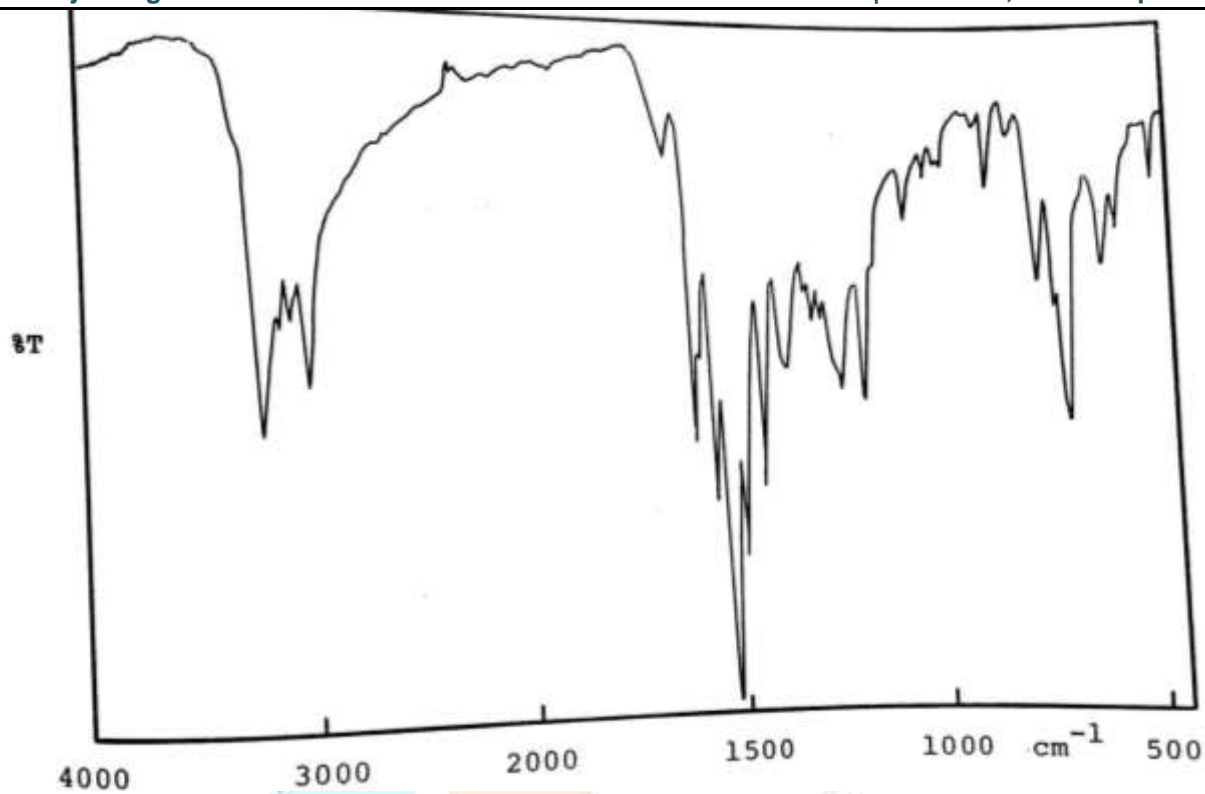
Diffuse reflectance Spectral Data for Co(II) Complexes HPEPDTB and HPETDTB

Assignments	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) (cm^{-1})	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) (cm^{-1})	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ (ν_3) (cm^{-1})	Dq (cm^{-1})	B' (cm^{-1})	β	ν_2/ν_1
Complex							
$\text{Co}_2(\text{L1})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	7,407	15,625 (15,918) 16,129	20,000	822.1	893.6	0.920	2.109
$\text{Co}_2(\text{L2})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	7,692	(14,569)	20,000	843.7	870.2	0.896	2.096

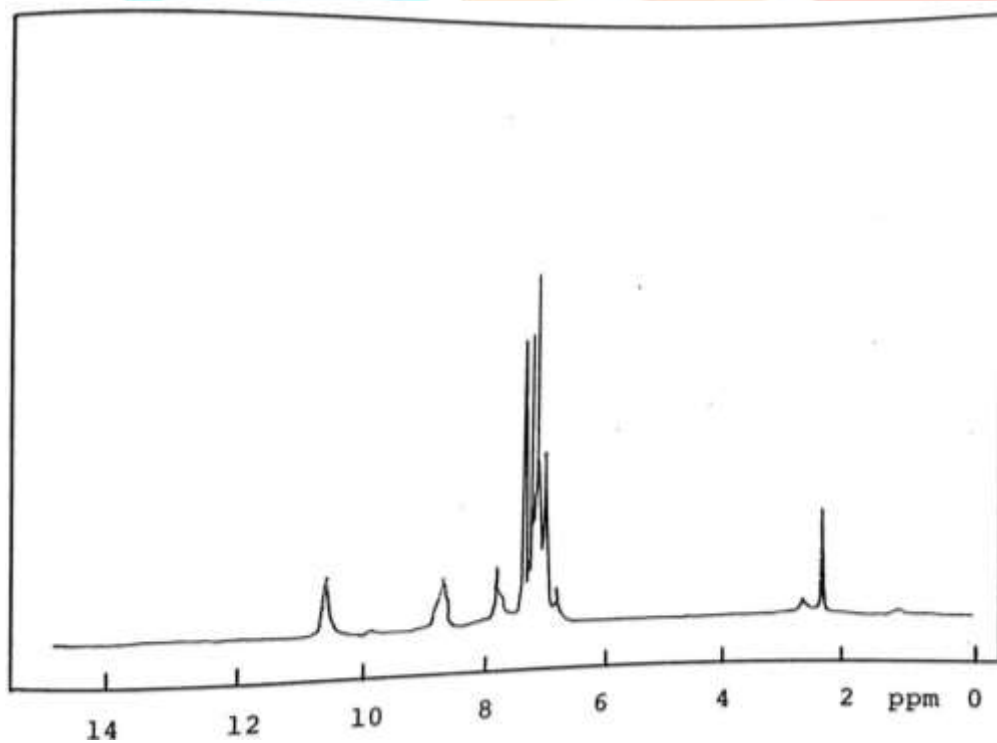


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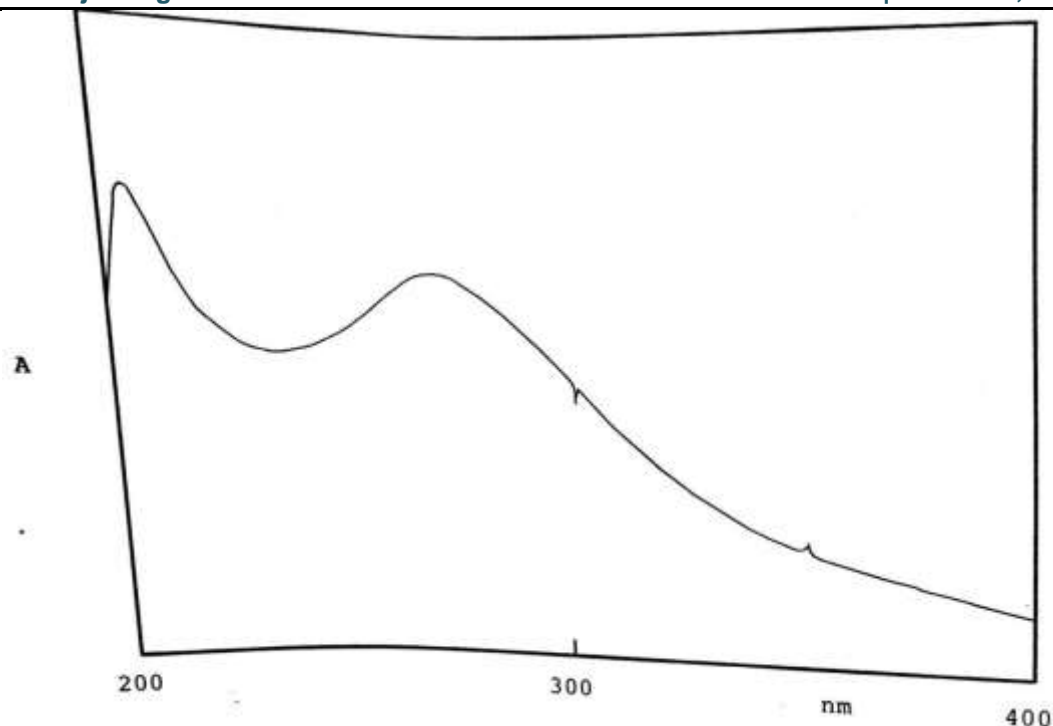
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FTIR Spectrum of HPEPDTB.



PMR Spectra of HPETDTB.



Electronic absorption spectrum of $\text{Co}_2(\text{HPEPDTB})_2 \cdot \text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

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