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Stoichiometric, Structural and Thermal Investigations on Cu(II), Ni(II) and Co(II) Coordination Compounds of some Acid Hydrazide Bases

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Abstract

Coordination compounds of Cu(II), Ni(II) and Co(II) with terephthalic acid hydrazide-bis-salicylidene (THBS), terephthalic acid hydrazide-bis-2,3,4-trihydroxy phenacylidene (THTP) and terephthalic acid hydrazide-bis-2-hydroxy, 5-carboxy phenacylidene (THHCP) have been synthesized and characterized by analytical, molar conductance, magnetic, spectral and thermogravimetric data. The IR spectra indicate that azomethine nitrogen and phenolic oxygen take part in the coordination. All the Schiff bases act as tetradentate ligands. Square planar polymeric structure for Cu(II) and octahedral polymeric structures for Ni(II) and Co(II) compounds have been assigned.

Introduction

Thiosemicarbazones have been reported [1–5] to form coordination polymers. Intensive studies on this type of coordination compounds have been carried out by Dey, Agarwala and others [6–8]. In recent years, studies on metal complexes of hydrazide Schiff bases [9–13] have been very interesting. This encouraged us to synthesize some new ligands starting from terephthalic acid hydrazide, with the isolation of Cu(II), Ni(II) and Co(II) chelates in the purified solid state. The chelates are characterized by several physico-chemical methods *viz.* analytical, magnetic, molar conductance, spectral (IR and electronic/reflectance) and TG analysis.

Experimental

Materials

All the chemicals used were of Anala R-grade. 2-hydroxy-5-carboxy acetophenone was synthesized following the procedure described earlier [14, 15]. 2,3,4-trihydroxy acetophenone was also prepared by the literature procedure [16]. The ligands THBS, THTP and THHCP were synthesized by refluxing the ethanolic solution of terephthalic acid hydrazide (obtained by the action of hydrazine hydrate on dimethyl terephthalate) with the alcoholic solution of salicylaldehyde, 2,3,4-trihydroxy acetophenone or 2-hydroxy-5-carboxy acetophenone for 4 to 6 h on a water bath. On cooling white or light brown crystals are obtained. The compounds were washed with ethanol and dried. THBS, THTP and THHCP melt at 125, 115 and 130 °C respectively.

Preparation of the Chelates

The methanolic solution of the ligand was mixed with the respective metal salt solution with constant stirring. The mixture was refluxed on a water bath for 30 min. The chelates were isolated in fine crystalline form. They were filtered, washed with ETOH and dried *in vacuo*. The copper chelates were light green, Co(II) chelates were light brown and reddish and nickel chelates were light green and bluish green.

Results and Discussion

The chelates were decomposed by fuming HNO_3 and the metal contents estimated by standard methods. The analytical data (Table I) indicate a 1:1 (M:L) stoichiometric composition for the isolated compounds. The chelates are insoluble in common organic solvents, but were shown to be soluble in DMSO, DMF and dioxan. Their molecular weights could not be determined due to their insolubility in common organic solvents. Calculation of formation constants indicate that these compounds are obtained by the removal of two hydrogen atoms from the ligands. The molar conductances of the chelates in DMSO at the concentration 10^{-3} M fall in the range 2–5 ohm^{-1} cm^2 mol^{-1}, indicating their non-electrolyte nature. The magnetic moment values at 300 K (Table I) are suggestive of a square planar configuration [17, 18] for the Cu(II) complexes and an octahedral configuration for the Ni(II) and Co(II) complexes.

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TABLE I. Thermal, Analytical and Molar Conductance (in DMSO) and Magnetic Moment Data of Cu(II), Ni(II) and Co(II) Chelates

Chelate[a]	Melting point (°C)	Found (Calc.) (%)				Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
		Metal	C	H	N		
CuL	100	12.58 (13.70)	51.98 (56.95)	3.42 (3.45)	12.98 (12.08)	2.8	1.81
CuL′	105	11.76 (11.43)	50.08 (51.84)	3.47 (3.60)	10.95 (10.08)	3.0	1.80
CuL″	125	10.98 (10.96)	52.98 (53.83)	3.51 (3.45)	9.56 (9.66)	3.7	1.79
NiL$(H_2O)_2$	118	10.47 (11.86)	51.94 (53.36)	3.98 (4.04)	10.94 (11.31)	4.8	2.97
NiL′$(H_2O)_2$	120	10.02 (10.00)	52.38 (49.08)	4.29 (4.09)	9.29 (9.54)	5.0	3.04
NiL″$(H_2O)_2$	122	11.04 (9.61)	50.01 (51.08)	4.38 (3.92)	9.86 (9.16)	3.6	2.99
CoL$(II_2O)_2$	140	11.26 (11.90)	51.96 (53.34)	4.32 (4.04)	10.98 (11.31)	2.0	5.14
CoL′$(H_2O)_2$	135	10.26 (10.04)	52.68 (49.06)	4.08 (4.08)	9.48 (9.54)	2.6	5.03
CoL″$(H_2O)_2$	148	10.18 (9.64)	50.01 (51.06)	4.19 (3.92)	9.67 (9.16)	2.9	5.08

[a] L = THBS^{2-}, L′ = THTP^{2-} and L″ = THHCP^{2-}.

Reflectance Spectra

Tetrahedral Cu(II) complexes are expected to give a single broad band in the near IR and no absorption between 16000 and 20000 cm^{-1} whereas the six-coordinated Cu(II) complexes possess two or more bands in the region 5–16K K. The copper chelates under study show the bands characteristic of a square planar geometry. The observed bands may be assigned to the following transitions

$^2B_{1g} \longrightarrow {}^2A_{1g}$ (15 625 cm^{-1})

$^2B_{1g} \longrightarrow {}^2E_g$ (17 850 cm^{-1})

CT band (25 770 cm^{-1})

The bands observed at 10960, 15 320 and 24 860 cm^{-1} in the Ni(II) chelate have been assigned to the following transitions

$^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ (ν_1)

$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ (ν_2)

$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ (ν_3)

The appearance of a band observed at ~19 100 cm^{-1} may be due to spin forbidden transition. The positions of the bands are consistent with the octahedral environment around the central metal ion.

In the spectra of the Co(II) chelate, three bands appeared in the regions 8250–8350, 17 680–19 300 and 20 780–21 430 cm^{-1}. The corresponding transitions are

$^4T_{1g} \longrightarrow {}^4T_{2g}(F)$ (ν_1)

$^4T_{1g} \longrightarrow {}^4A_{2g}(F)$ (ν_2)

$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (ν_3)

The transitions are in close proximity to the reported values for highly distorted Co(II) complexes.

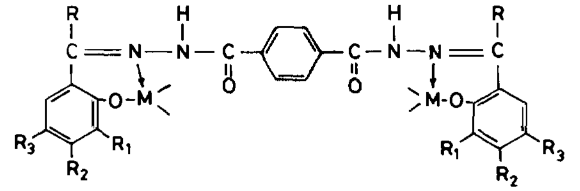
IR Studies

Scrutiny of the IR spectra of the ligands and metal chelates gives valuable information regarding the bond formation of the metal ion with the donor atoms. In the IR spectra of THBS, THTP and THHCP, the band near 1620 cm^{-1} appeared characteristic of the azomethine (C=N) group. The strong absorption in the 3520–3460 cm^{-1} region may be explained by assuming the presence of an intramolecular hydrogen bonded phenolic –OH group.

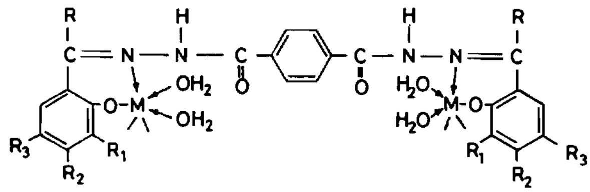
The absence of the band observed at 3520–3460 cm^{-1} in the ligands, indicates the deprotonation and the involvement of hydroxyl oxygen in the chelate formation. The negative shift in the azomethine frequency (~20–40 cm^{-1}) in these compounds, suggests that the nitrogen of this group takes part in bond formation with the metal. New bands around 430 and 530 cm^{-1} observed in the chelates may be due to ν(M–N) and ν(M–O) vibrations respectively. Thus, the –OH group and C=N group are the potential donor centres in the ligands. All the ligands act as tetradentate and each metal ion is coordinated with two nitrogen and two oxygen atoms.

The IR spectra of Ni(II) and Co(II) compounds shows a strong band at approximately 3480 cm^{-1}, which is suggestive of associated water molecules. The occurrence of a new band at ~860 cm^{-1}, in these chelates confirms the presence of coordinated water molecules.

TG analysis of the chelates showed the loss in weight between 110 to 180 °C (in the case of the Co(II) and Ni(II) chelates) to be consistent with the removal of two water molecules. The following tentative coordination polymeric structures may be suggested for the chelates.



(where M = Cu(II), R = H, -CH$_3$, R$_1$ = H, -OH, R$_2$ = H, -OH, R$_3$ = H, -COOH)



(where M = Ni(II), Co(II), R = H, -CH$_3$, R$_1$ = H, -OH, R$_2$ = H, -OH, R$_3$ = H, -COOH)

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