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Structural Investigations of Copper (II), Nickel (II) and Cobalt (II) Complexs of Phenylazoethylacetoacetate.

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Complexs of copper (II), nickel (II) and cobalt (II) of phenylazoethylacetoacetate (HPAEA) (LH) have been isolated in solid state and characterised on the basis of elemental analysis, magnetic, UV-visible and IR-spectral data. Physico-chemical data provide evidences for the existence of octahedral $CuL_2{\cdot}H_2O$, $NiL_2{\cdot}2H_2O$, CoLOAc complexes, square planar dimeric $(CuLOAc)_2$ complex and spin-free square-planar NiLOAc complex.

INTRODUCTION

The chemistry of aryldiazenato complexes is of recent origin. These complexes display much of the expected structural similarity with isoelectronic nitrosyl complexes[1]. The survey of literature indicate that no report on metal complexes of phenylazoethylacetoacetate (HPAEA) have been published. The present work deals with the preparation and structural investigations of transition metal complexes of HPAEA.

EXPERIMENTAL

The ligand phenylazoethylacetoacetate (HPAEA) was prepared as reported earlier[2].

The solid metal chelates were synthesised by refluxing a mixture of respective metal salt (50 ml. 0.01 M) in 75% ethanol and HPAEA (50 ml 0.02 M) in 75% ethanol after raising the pH to the appropriate value (Table 1), for 2–3 hrs. On cooling the mixture, the resulting coloured precipitate was filtered, washed with alcohol and dried around 80°C. In the case of copper (II) acetate and nickel (II) acetate chelates, metal and ligand were mixed in 1:1 molar ratio.

RESULTS AND DISCUSSION

The solid metal chelates do not possess sharp melting point and decomposed in 260–300°C region. These compounds were analysed for C, H, N and metal

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(Table 1). From these data it is evident that the metal chelates possess 1 : 2 (M : L) stoichiometry except in the case of chelates formed by copper (II) acetate and nickel (II) acetate which possess 1 : 1 stoichiometry.

TABLE 1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Sr. No.	Compound	Mol. Wt.	pH of formation	μ_{eff}^{*} (B.H.)	Analysis % : Found/(Calc).			
					C	H	N	Metal
1.	HPAEA $C_{12}H_{14}O_3N_2$	234.0	—	—	62.38 (61.53)	6.92 (5.98)	11.82 (11.96)	—
2.	$CuL_2 \cdot H_2O$ (green)	565.5	4.2	1.92	50.82 (50.92)	5.23 (5.30)	9.84 (9.90)	11.13 (11.22)
3.	CuLOAc (dark green)	355.5	4.8	1.01	47.25 (46.04)	4.51 (5.62)	7.89 (7.52)	17.81 (17.19)
4.	$NiL_2 \cdot 2H_2O$ (green)	560.5	5.1	3.1	51.36 (52.24)	5.35 (5.30)	9.98 (9.84)	10.46 (11.09)
5.	NiLOAc (red)	350.5	7.4	dia. magnetic	47.93 (46.88)	4.56 (4.68)	7.98 (8.18)	16.69 (16.78)
6.	$CoL_2 \cdot 2H_2O$ (brown)	561.0	6.8	5.1	51.34 (50.89)	5.12 (5.34)	9.98 (9.87)	10.59 (10.74)
7.	CoLOAc (green)	351.0	7.2	3.98	47.86 (48.18)	4.55 (4.81)	7.97 (7.18)	16.80 (16.82)

*At 303 K

The solid metal chelates formed by copper (II) acetate and nickel (II) acetate are diamagnetic and the rest of the cheletes are paramagnetic. All these metal complexes were found insoluble in water and most common organic solvents and hence the complexes could not be crystallised.

The paramagnetic copper (II) complex exhibit magnetic moment around 1.92 B.M. (303 K) indicating it to be octahedral or distorted octahedral[3] and copper (II) acetate complex to be a spin-paired and polymeric probably dimeric square-planar complex, suggesting coppr-copper interaction[4,5] in polymeric solid state. The lower value of magnetic moment (1.01 B.M.) of the copper (II) acetate complex also indicates its antiferromagnetic nature[6] involving super exchanging phenomena with oxygen of acetate group bridging copper ions[7,8]. Orange-red colour of nickel (II) acetate chelate and its diamagnetic character are indicative of its square-planar stereochemistry.[9] Metal chelates formed by nickel (II) chloride, cobalt (II) chloride and cobalt (II) acetate are paramagnetic and the μ_{eff} values are given in Table 1. The magnetic moment values suggest that the $NiL_2 \cdot 2H_2O$ and $CoL_2 \cdot 2H_2O$ complexes have octahedral geometry[10] while CoLOAc is tetrahedral[10]. Diffuse reflectance spectra of the paramagnetic copper (II) complex shows a broad diffuse reflectance band around 810 nm, which may be due to the transition $^2E_g \rightarrow {}^2T_{2g}$ suggesting octahedral stereochemistry[10] for the copper (II) chelate, while the copper (II) acetate complex exhibits two bands at 390 and 700 nm and their ratio of the optical densities is nearly 2, a characteristic feature generally exhibited by dimeric square-planer copper (II) complexes[11]. Diffuse reflectance spectra of the orange-red diamagnetic nickel (II) chelate exhibit two bands at 480 and 580 nm, indicating square-planar stereochemistry.[12-14] Cobalt (II) acetate chelate showed bands at 610, 650, 720 nm corrosponding to $^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1$ (F) transition corrosponding to tetrehedral structure[15]. Diffuse reflectance spectra of the cobalt (II) chloride chelate consist of two bands around 1250 and 575 nm which can be assigned to the transitions $^4T_{1g}$ (F) → $^4T_{2g}$ (F) and $^4T_{1g}$ (F) → $^4T_{2g}$ (P). respectively[15]. These bands suggest octahedral stereochemistry for cobalt chloride chelate in confirmity with the conclusions arrived from the magnetic properties. The diffuse reflectance spectra for the paramagnetic nickel (II) chelate obtained from nickel (II) chloride showed two bands around 705 and 400 nm assignable to the transitions $^3A_{2g} \rightarrow {}^3A_{1g}(F)$ and $^3A_{1g} \rightarrow {}^3T_{1g}(P)$ respectively. These bands further suggest octahedral stereochemistry for nickel (II) ions[10]. The ligand HPAEA does not show any band due to OH while strong bands around 3450 cm^{-1} in the nickel (II), copper (II) and cobalt (II) chloride chelates indicate the presence of coordinated water molecule in these complexes[16]. The ligand HPAEA shows the bands at 1705 and 1680 cm^{-1} corresponding to free ester group and $CH_3 - C = O$ group respectively. These bands are found to be shifted lower values in IR spectra of the metal chelates indicating that CH_3—$C = O$ group is involved in the coordination with metal atom. The broad band at 2900–3100 cm^{-1} in the IR spectra of HPAEA is due to N–H of hydrazone (intramolecular hydrogen bonding) group. It is found absent in IR Spectra of chelates, indicating metal atom linked to nitrogen atom of hydrazone group.[17] Some new bands occur in 600–400 cm^{-1} region in all the metal complexes, which are tentatively assigned as ν(M–N) and ν(M–O).[18] The binuclear copper (II) bonded chelate requires the presence of bands due to bonded acetate group and metal - oxygen[18]. Bands at 1603 and 1341 cm^{-1} in the IR spectra of the complex $(CuLOAc)_2$ are assigned to bonded acetate group[18] to the metal atoms forming oxygen bridge between metal atoms in the dimeric copper (II) complex, while the band observed at 555 cm^{-1} in the complex, is attributed to metal-oxygen vibrations[19].

In view of the experimetal evidences the paramagnetic copper (II), nickel (II) and cobalt (II) chelates may be assigned octahedral stereochemistry[20] whereas the copper (II) acetate chelate and orange-red nickel (II) acetate chelate are assigned square-planer stereochemistry while Co (II) acetate complex may be assigned tetrahedral stereochemistry.

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