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Synthesis and Characterization of Copper(II) and Nickel(II) Complexes of Ethyl-2, 3-Dioxobutyrate-2-*o*-Aminophenyl-Hydrazone and Pentane-2,3,4-Trioxo-3-*o*-Aminophenylhydrazone

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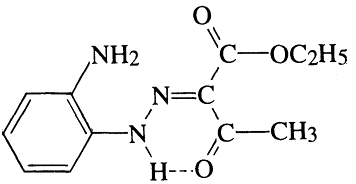
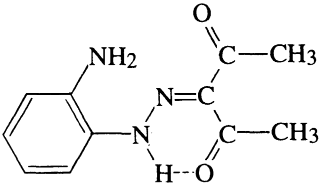
The present work describes the synthesis and characterization of ethyl-2, 3-dioxobutyrate-2-*o*-aminophenylhydrazone and pentane-2, 3, 4-trioxo-3-*o*-aminophenylhydrazone and their polymeric complexes with divalent copper and nickel metal ions. The metal-ligand bonding and geometries of the complexes have been studied from the IR and electronic spectral data.

INTRODUCTION

The coupling products have received considerable attention because of the controversies regarding the structure and the presence of a number of donor sites.[1] Pentane-2,3,4-trioxo-3-phenylhydrazone and its derivative have been utilised by several workers[1–4] for the complexation with different metal ions. Complexes of ethyl-2, 3-dioxobutyrate-2-phenylhydrazones and related phenylhydrazones containing electron releasing as well as electron withdrawing substituents in the phenyl nucleus have also been initially prepared by some workers[3,4] and characterised in our laboratory[1,5,6]. It was thought worthwhile to prepare *o*-amino derivative of ethyl-2,3-dioxobutyrate-2-phenylhydrazone (HL_1) and pentane-2,3,4-trioxo-3-phenylhydrazones (HL_2) and synthesise metal complexes using these amino hydrazones as ligand.


(HL_1)


(HL_2)

EXPERIMENTAL

Synthesis of the Ligand

Ethyl-2, 3-dioxobutyrate-2-*o*-nitrophenylhydrazone and pentane-2,3,4-trioxo-3-*o*-nitrophenylhydrazone were synthesised by coupling benzenediazonium

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chloride with ethyl acetoacetato and acetylacetone respectively in sodium acetate medium.[7,8] 10 gm of ethyl-2, 3-dioxobutyrate-2-*o*-nitrophenylhydrazone was suspended in about 50 ml of water-methanol (200:1; v/v) mixture. Sodium dithionite was added to the suspended solution in very very small parts with constant stirring and warming. Completion of reaction was tested by TLC experiment (About 30–35 gm of sodium dithionite was consumed for complete reduction of nitro group). After complete reduction, the reaction material was allowed to stand for few days for complete dryness. Dried solid mass was then refluxed with petroleum ether (80–100°C). Reaction mixture was filtered while hot. Orange crystals of ethyl-2, 3-dioxobutyrate-2-*o*-aminophenylhydrazone (HL_1) were crystallised out from filtrate after cooling. In a similar manner, ligand HL_2 was synthesised from pentane-2-,3,4-trioxo-3-*o*-nitrophenylhydrazone.

General Method for Preparing the Complexes

An ethanolic solution of the ligand was mixed with an aqueous solution of the copper acetate/nickel sulphate in the molar ratio (1 : 1). The pH of the reaction mixture was adjusted to 7 by dropwise addition of NH_4OH. The black complexes precipitated almost immediately were digested on water bath for 1 h., cooled to room temperature and suction-filtered. The complexes washed with water and ethanol were dried in an oven (50°C).

RESULTS AND DISCUSSION

The analytical data (Table-1) show that the isolated complexes have the general composition $[ML(OH)(H_2O)]$. The insolubility of complexes in polar and non-polar solvents clearly indicate polymeric nature of the complexes.

TABLE 1
ANALYTICAL DATA OF Cu(II) AND Ni(II) COMPLEXES

Name of Complex	μ_{eff} (B.M.)	% Yield	% Found (calc.)	
			N	M
$[CuL_1(OH)(H_2O)]$ (Black)	1.96	68	11.87 (12.11)	18.04 (18.33)
$[CuL_2(OH)(H_2O)]$ (Black)	1.89	72	13.60 (13.26)	19.54 (20.00)
$[NiL_1(OH)(H_2O)]$ (Black)	3.12	54	11.91 (12.29)	17.40 (17.17)
$[NiL_2(OH)(H_2O)]$ (Black)	3.08	69	13.29 (13.47)	19.36 (18.33)

The UV-VIS spectra (in $CHCl_3$) of ligand shows two strong absorption in the vicinity of 210 ± 10 nm and 240 ± 5 mm due to presence of two different type of $> C{=}O$ group[9,10]. Again the absorption in the region 335–360 nm is characteristic of phenylhydrazones ($> N{-}N = C <$)π–π^* transitions.[9,10] In the UV spectra of ligand, the characteristic absorption band of the phenyl azo group in the region 270–280 nm is not observed which is sufficient enough to rule out any possibility of the azo form of the ligand[9,10]. In complexes the absorption bands associated with ligand molecules suffer a blue shift indicative of coordination of ligand molecule with metal atom retaining their hydrazone structure. Thus it is inferred that during complexation, isomeric change in ligand molecule (passing it to azoform) is not taking place even in the pH range 7–8.

In the solid-reflectance spectra of the Cu(II) complexes (ignoring the peak due to ligand part), weak and broad bands seen at around 14500–15200 cm^{-1} and 20000–20500 cm^{-1} are assigned to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ respectively[11]. These suggest a tetrahedrally distorted octahedral geometry for the complexes[11]. In the diffuse reflectance spectra of Ni(II) complexes (ignoring the peak due to ligand part) three weak and broad bands are noticed in the region 10000–10200 cm^{-1}, 15700–16000 cm^{-1} and 24000–24300 cm^{-1} assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_1)$, $^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions respectively[12]. The ratio ν_2/ν_1 of the frequencies of the first and second band maxima lies in the range 1.56–1.57, which is characteristic of all the Ni(II) complexes having octahedral and/or approximate octahedral environments[13]. The different ligand field parameters such as 10 Dq, B′, β and β° were calculated by Drago's method[14]. The value of B′ were found to be between 625–650 cm^{-1} which is in good agreement with the reported value of B′ of octahedral (or distorted) Ni(II) complexes[15]. The values of β (0.59–0.60) and β° (39–41%) suggest the highly covalent character of Ni(II) complexes. The calculated value of ν_2 transition (Drago's method[14] using the energy of ν_1 and ν_3 transitions) are in good agreement with the values obtained from spectra indicating the validity of ligand field parameters.

All Cu(II) complexes are paramagnetic to the extent of one unpaired electron and the μ_{eff} values are around 1.9 B.M. (Table-1). The data suggest that the complexes are devoid of spin-spin interaction. However, one can not set a compromise between the magnetic moments and geometry in the case of Cu(II). However, in view of the electronic spectra it may be concluded that these may have tetragonally distorted octahedral geometry. The magnetic moment value of Ni(II) complexes (Table-1) is similar to octahedral/distorted octahedral complexes[16].

The ligand exhibit strong intensity bands in 3435–3440 cm^{-1} and 3330–3340 cm^{-1} region assigned as asymmetric and symmetric N–H modes (amino group) respectively[17]. The ligands display (N–H) stretching frequency ($\underset{\displaystyle \text{H}}{\underset{|}{\text{—N}}}\text{—N=}$ group) around 3080 cm^{-1} and two >C=O frequencies around 1665–1690 cm^{-1} and 1620 cm^{-1}. The red shift in ν_{N-H} in the present set of ligand molecules can be attributed to intramolecular H-bonding.[18,19] The lowering of two >C=O frequencies in ligand are explain by the presence of α, β-unsaturation in former but α, β-unsaturation and H-bonding in latter.[18,19] The azomethine $\nu_{N=C}$ band is assigned at 1590 cm^{-1}. Thus IR spectra of ligand molecules are characteristic of a hydrazone structure with the free carbonyl, one H-bonded carbonyl, phenyl amino group $(-\underset{\substack{| \\ H}}{N}-N{=}C<)$ alongwith a characteristic $-N{=}C<$ group.

The asymmetric and symmetric N-H modes of $-NH_2$ group suffer an appreciable decrease in frequency as well as in intensity on complexation. The red shift of ν_{N-H} indicates the coordination of $-NH_2$ group to metal ions. In almost all complexes, the N-H band of imino group $(-\underset{\substack{| \\ H}}{N}-N{=})$ disappears. This indicates deprotonation of amino group and coordination through deprotonated amino group. In addition to these, there is a new broad band in the complexes in the region of 3360–3500 cm^{-1} cooresponding to water molecule associated with the complexes[17]. The IR spectra of almost all the complexes display a sharp and medium or strong band around 3300 cm^{-1}, which is neither present in free ligand nor expected for water molecule is assigned to coordinated hydroxy (OH) group[20]. Ferraro[20] has also noted that peak due to O-H (hydroxy group) stretching mode is sharp and usually can be observed even in presence of water. In some complexes ν_{O-H} and ν_{N-H} vibration could not be separated probably due to their coupling and yielded a broad hump in the region 3050–3500 cm^{-1}. The $\nu_{C=O}$ frequency of free carbonyl group remains unaffected in the metal chelates showing non coordination of oxygen atom of free carbonyl group to the metal atoms. The H-bounded >C=O stretch around 1620 cm^{-1} undergo a further lowering and broadening and appears as a broad peak near 1590–1610 cm^{-1} in chelate. This indicates the involvement of oxygen of >C=O group in coordinate bond formation. Pronounced shifting of $\nu_{C=N}$ frequency by 20 cm^{-1} towards lower region in all metal chelates as compared to free ligands suggests the involvement of azomethine nitrogen in coordination. The coordination of metal ion through the O and N donors of free ligand is also confirmed by the appearance of some new bands in the region 500–550 cm^{-1} and 390–420 cm^{-1} which are assinged to ν_{M-O} and ν_{M-N} vibrations respectively in all the complexes[17].

IR spectral pattern has indicated the involvement of amino group, one carbonyl group (H-bonded) azomethine nitrogen and imino nitrogen $(-\underset{\substack{| \\ H}}{N}-N{=})$ after deprotonation in coordination alongwith coordinated hydroxy group. That the water molecule is also present in coordination, is evident from thermal studies where no loss of weight could be recorded below 150°C. Thus it could be inferred that imino nitrogen and one carbonyl oxygen (H-bonded) is coordinated to one metal ion while azomethine nitrogen and amino nitrogen of same ligand molecule is coordinated to another metal ion forming six membered chelate rings. Each metal ion is also coordinated through one hydroxyl group and one water molecule.

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