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STUDIES ON COMPLEX ARYLHYDRAZONES, PART V

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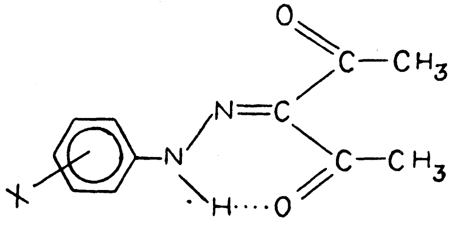
Complexes of the type $[CuL(OH)(H_2O)]$, $[NiL(NH_3)(OH)]$ and $(HgLCl(H_2O)_2]$ where HL = pentane-2,3,4-trioxo-3-phenylhydrazone and six related phenylhydrazones containing electron releasing as well as electron withdrawing substituents in phenyl nucleus were synthesised. Their structures were assigned on the basis of elemental analysis, thermal analysis, magnetic moment, IR, UV-VIS, PMR and ESR spectral data.

INTRODUCTION

The paper discusses the preparation and characterisation of Cu^{+2}, Ni^{+2} and Hg^{+2} complexes with pentane-2,3,4-trioxo-3-phenylhydrazone (HL_1) and six related substituted phenylhydrazones (HL_2–HL_7),



HL

$HL_1 \rightarrow X = H$ $HL_2 \rightarrow X = o\text{-}NO_2$ $HL_3 \rightarrow X = m\text{-}NO_2$ $HL_4 \rightarrow X = p\text{-}NO_2$

$HL_5 \rightarrow X = o\text{-}Me$ $HL_6 \rightarrow X = p\text{-}Me$ $HL_7 \rightarrow X = p\text{-}Br$

Due to presence of several donor atoms, it could act as a good polydentate ligand. The attempt to synthesis Cu^{+2} chelate with ligand LH_1 have already been made by Ghosh and Maulik[1] assuming the azo form of the ligand. However, mode of M-L bonding and structure of the complex have not been described in that work. Recently X-ray studies[2] and ^{13}C NMR spectral studies[3] confirmed the hydrazone form of the ligand. This led us to carry out the complexation of the above ligand with Cu^{+2}, Ni^{+2} and Hg^{+2} ion and investigate the nature of M-L bonding and the structure of chelates.

EXPERIMENTAL

The ligands were synthesised by reported method[4]. To a hot ethanolic or DMF solution of ligand (0.005 mol), aq. solution of copper acetate or nickel sulphate or mercuric chloride (0.005 mol) was mixed and refluxed for 5–8 hrs (12–15 hrs in case of Hg^{+2}) after adjusting the pH 8–9 by NH_4OH. The insoluble product was filtered out, washed with water, hot benzene and recrystallised with nitrobenzene. The absence of free ligand was ascertained by TLC.

RESULTS AND DISCUSSION

The elemental analysis of complexes (Table 1) corresponds to composition $[CuL(OH)(H_2O)]$, $[NiL(NH_3)_2(OH)]$ and $[HgLCl(H_2O)_2]$. Except Ni^{+2} complex with ligand HL_3 (which is partially soluble in $CHCl_3$), all complexes were insoluble in water and common organic solvents.

Ghosh and Maulik[1] have reported CuL_2 type of complex with ligand HL_1. The compound of same characteristic (regarding m.pt., solubility, colour and to some extent elemental analysis) was obtained by us on repeating the experiment too but on TLC. examination, it was found to contain largely ligand and on purification, a new compound, which finally decomposes above 280°C, was obtained. This isolated compound could not conform with the earlier reported complex regarding its stoichiometry and solubility.

The ligands display (N–H) stretch at 3090–3140 cm^{-1} which disappears completely in all Cu^{+2} and Hg^{+2} complexes. This indicates deprotonation of imino group and coordination through deprotonated imino group. All Cu^{+2} complexes display one strong and broad band in the region 1580–1620 cm^{-1} unlike ligand molecules which display two distinct ()C=0) stretch at higher wave numbers and one $\nu_{(C=N)}$ at around 1600 cm^{-1}. The drastic shift of $\nu_{(C=0)}$ vibration to lower frequency unambiguously suggests the coordination of both the carbonyl oxygen atoms to metal atom. The $\nu_{(C=N)}$ of ligand is enveloped in carbonyl group stretching in general and observed at 1570–1600 cm^{-1}. All Cu^{+2} and Hg^{+2} complexes exhibit broad band near 3300–3500 cm^{-1} attributed to coordinated or lattice water molecule[5].

Unlike Cu^{+2} and Hg^{+2} complexs, almost all Ni^{+2} complexes exhibit two distinct (N–H) stretching vibrations in the region 3000–3100 cm^{-1} which suggests the presence of NH_3 group[6–8]. Appearance of two new peaks around 1150 cm^{-1} and 850 cm^{-1} in all Ni^{+2} complexes (which were neither observed in ligand nor in Cu^{+2} and Hg^{+2} complexes) may be attributed to symmetric deformation and rocking mode of NH_3 group respectively[6–8]. The close examination of IR curves of Ni^{+2} and Hg^{+2} complexes shows that on complexation hydrogen bonded $\nu_{(C=O)}$ vibration (observed at 1635 ± 10 cm^{-1} in ligand) is shifted to lower frequency whereas the free $\nu_{(C=O)}$ (observed at 1675 ± 5 cm^{-1} in ligand) as well as $\nu_{(C=N)}$ frequencies registered a small higher shift or remain almost intact. This indicates that chelated)C=0 group in ligand is now involved in coordination, whereas azomethine nitrogen and free carbonyl oxygen are not involved in coordination. All Cu^{+2} and Ni^{+2} complexes exhibit a strong and sharp band at 3270–3340 cm^{-1} characteristic of ν_{O-H} of hydroxy group[9]. Non-electrolytic and polymeric nature have been concluded from insoluble nature of all complexes. Thus it is believed that OH group (in case of Cu^{+2} and Ni^{+2} complexes) and Cl group (in case of Hg^{+2} complexes) are inside the coordination sphere in all complexes.

TABLE 1
MAGNETIC, PHYSICAL AND ANALYTICAL DATA OF COMPLEXES

Name of complex	μ_{eff} in B.M. (at 298°K)	% yield	Colour	% of nitrogen	% of metal	% of chlorine
$CuL_1(OH)(H_2O)$	1.83	70	Dark green	10.10 (9.28)	20.67 (21.05)	—
$CuL_2(OH)(H_2O)$	1.87	40	Black	12.41 (12.11)	18.10 (18.32)	—
$CuL_3(OH)(H_2O)$	1.90	65	Deep brown black	11.89 (12.11)	18.14 (18.32)	—
$CuL_4(OH)(H_2O)$	1.91	40	Brownish black	11.73 (12.11)	17.89 (18.32)	—
$CuL_5(OH)(H_2O)$	1.88	40	Black	8.48 (8.87)	19.69 (20.12)	—
$CuL_6(OH)(H_2O)$	1.88	50	Gray	7.86 (8.87)	20.90 (20.12)	—
$CuL_7(OH)(H_2O)$	1.88	70	Gray	7.01 (7.36)	16.14 (16.69)	—
$NiL_1(NH_3)_2(OH)$	3.12	75	Purple	17.10 (17.89)	17.15 (18.85)	—
$NiL_2(NH_3)_2(OH)$	3.09	40	Black	18.42 (19.55)	15.70 (16.48)	—
$NiL_3(NH_3)_2(OH)$	3.01	90	Deep brown red	19.49 (19.55)	15.98 (16.48)	—
$NiL_4(NH_3)_2(OH)$	3.02	45	Brown	19.12 (19.55)	15.60 (16.48)	—
$NiL_5(NH_3)_2(OH)$	3.14	50	Deep brownish red	16.94 (17.13)	17.67 (18.04)	—
$NiL_6(NH_3)_2(OH)$	3.11	50	Light brownish red	16.83 (17.13)	17.99 (18.04)	—
$NiL_7(NH_3)_2(OH)$	3.15	70	Brownish red	13.87 (14.29)	14.97 (15.05)	—
$HgL_1Cl(H_2O)_2$	Diamagnetic	60	Yellow	5.41 (5.90)	41.28 (42.15)	6.80 (7.50)
$HgL_2Cl(H_2O)_2$	Diamagnetic	45	Yellow	7.60 (7.81)	37.26 (38.50)	6.02 (6.83)
$HgL_3Cl(H_2O)_2$	Diamagnetic	60	Light pinkish yellow	7.85 (7.81)	39.30 (38.50)	6.44 (6.83)
$HgL_4Cl(H_2O)_2$	Diamagnetic	58	Light orange yellow	8.04 (8.08)	37.91 (38.50)	6.01 (6.83)
$HgL_5Cl(H_2O)_2$	Diamagnetic	43	Yellow	6.47 (5.88)	39.12 (41.97)	6.52 (7.45)
$HgL_6Cl(H_2O)_2$	Diamagnetic	45	Light brownish yellow	6.03 (5.88)	40.10 (41.97)	7.20 (7.45)
$HgL_7Cl(H_2O)_2$	Diamagnetic	60	Yellow	4.89 (5.05)	38.70 (36.90)	5.90 (6.40)

Figures within parentheses are calculated values. Estimation of carbon and hydrogen fits well.

The ^1H NMR spectra of ligand HL_3 and its Ni^{+2} complex show that the six methyl and four aromatic proton resonance remain almost intact. Hydrogen bonded imino proton signal at δ 13.5 in free ligand was found to be absent in complex indicating the uninegative behaviour of ligand. Extra signal at δ 5.1 in complex which was not present in the spectra of free ligand suggests the presence of NH_3. Magnetic moment data (Table 1) shows bivalent metal ions in complexes and no antiferromagnetic exchange coupling.

The solid reflectance spectra of Ni^{+2} complexes display two broad bands in the vicinity of 14388–15385 cm^{-1} and 23250–25000 cm^{-1} assignable to the transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively and are labelled as ν_2 and ν_3 respectively. The different ligand field parameters such as 10 Dq, B', β and β° are calculated by Lever's method[10]. The value of 10 Dq and B' are found to be between 7800–9500 cm^{-1} and 700–900 cm^{-1} respectively, which are in good agreement with the reported value of approximate octahedral Ni^{+2} complexes[11]. The variation in covalent character 15–18% in case of electron withdrawing and 22–24% in case of electron releasing substituents in phenyl nucleus is noteworthy because the nature of substituent causes variation in the electron density at phenylimino nitrogen atom.

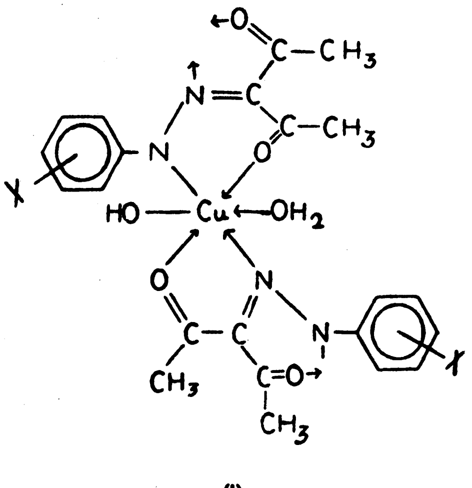
The reflectance spectra of Cu^{+2} complexes exhibit three weak and broad ligand field transitions in the region 12345 ± 150 cm^{-1}, 14875 ± 300 cm^{-1} and 23500 ± 700 cm^{-1} similar to tetragonally distorted octahedral complexes[13]. These bands are tentatively assigned due to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively.

The room temperature ESR spectra of complex $[Cu(L_1)(OH)(H_2O)]$ exhibit two g values spectra ($g_{\|}$ = 2.203, $g_{\perp}$ = 2.043 and g_{av} = 2.096). The energy of electronic transitions in combination with ESR spectral results give spin-orbit coupling constants[12], e.g., for complex $[Cu(L_1)(OH)(H_2O)]$, $(\lambda_{\|}/\lambda)^{1/2}$ and $(\lambda_{\perp}/\lambda)^{1/2}$ are equal to 0.70 and 0.78 respectively, which are in good agreement with the reported values[12]. Absence of signal corresponding to $\Delta m_s = \pm 2$ in ESR spectra rule out any possibility of Cu-Cu interaction[13].

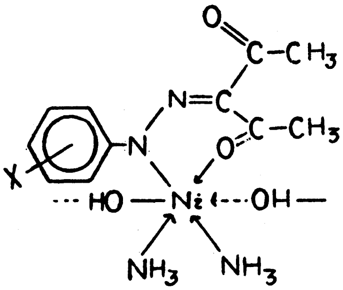
TGA curve of Cu^{+2} and Hg^{+2} complexes (with ligand HL_3 and HL_7) and Ni^{+2} complexes (with HL_2 and HL_5) were obtained. All complexes decompose in two steps. In first step, weight losses were observed in Cu^{+2} and Hg^{+2} complexes between 160–190°C and 180–200°C respectively, which corresponds to one and two water molecules respectively. However, in case of Ni^{+2} complexes, first step decomposition occurs between 230–280°C. It can be presumed that first decomposition corresponds to removal of two NH_3 and substituted phenyl nucleus giving an unstable decomposition intermediate. The thermal decomposition however continues upto 300°C in case of Cu^{+2} complexes and 490°C in case of Ni^{+2} complexes. The residual weight corresponds to metal oxides. The final decomposition product in case of Hg^{+2} complexes should be either HgO or Hg; however, unlike Cu^{+2} and Ni^{+2} complexes, no residue is left in Hg^{+2} complexes, due to volatile nature of mercury at higher temperature.

Due to volatility problem of complexes, no conclusive evidence could be obtained by mass spectra; however, presence of all peaks corresponding to (HL-1) indicates the uninegative character of ligand.

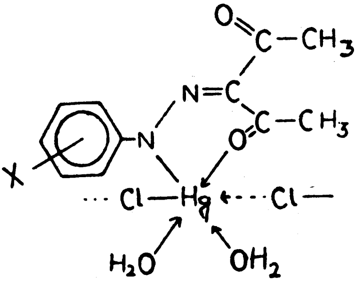
On the basis of above discussion, the following structures (I), (II) and (III) may be assigned to Cu^{+2}, Ni^{+2} and Hg^{+2} complexes respectively.



(I)



(II)



(III)

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