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NOTE

Synthesis and Characterization of Some Metal Complexes of Cu(II), Cd(II), UO_2(II) and Pd(II) with Anthracene Carboxaldehyde Semicarbazone

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The metal complexes of the type $[CuL_2(H_2O)_2]$, UO_2L_2, PdL_2 and CdL_2 where L = anthracene carboxaldehyde semicarbazone are synthesised. The IR spectral data suggest the coordination of ligand through O and N atom. The analytical, electronic, spectral and magnetic data further confirm the geometry of the complexes.

Transition metal complexes of Schiff bases have occupied a central role in the development of chemistry. Major biochemical interest in Schiff base compounds stems from their suitability in designing metal containing model systems which closely mimic biologically active systems. Zn(II), Cd(II) and Hg(II) chelates of vanillin semicarbazone and thiosemicarbazone have been studied. They were found to possess activity against pathogenic fungi. Uranyl complexes of thiosemicarbazones have been seldom reported. However, a few coordinate complexes of orthovanillin semicarbazone have been reported by Agarwala and co-workers[1]. Dutta and Sengupta have also investigated some uranyl complexes of semicarbazones[2].

Synthesis of the ligand: The starting materials used for the preparation of anthracene carboxaldehyde semicarbazone were anthracene carboxaldehyde, semicarbazide hydrochloride and sodium acetate. The reaction mixture was stirred and refluxed for about 4 h. The crystals of the ligand obtained were recrystallised from alcohol and characterised on the basis of analytical and spectral data.

General Methods for Preparing the Complexes

An aqueous solution of the metallic salt, semicarbazide hydrochloride and sodium acetate was refluxed with hot ethanolic solution of anthracene carboxaldehyde in 1 : 2 molar ratio for about 3 h. After cooling, ammonium hydroxide was added till ammoniacal, and refluxed again for 2 h in the case of Cu(II) complex. In the case of UO_2(II) complexes, refluxing was continued for about 5 h. The coloured complexes were washed with alcohol and dried.

For preparing Pd(II) complexes, conc. hydrochloric acid was added to aqueous palladium chloride solution. Hot solution of this was added to hot ethanolic solution of anthracene carboxaldehyde. After adding semicarbazide hydrochloride and sodium acetate, it was refluxed for about 8 h, cooled and the coloured complexes were washed with water containing dilute hydrochloric acid and alcohol and dried.

For the preparation of Cd(II) complex, aqueous solution of cadmium acetate was added to anthracene carboxaldehyde semicarbazone dissolved in hot ethanol-DMF mixture and refluxed for about 8 h. The solution was kept overnight, concentrated by evaporation, cooled and the reddish yellow precipitate was filtered, washed with DMF-alcohol mixture and dried.

The complexes were characterised on the basis of elemental analysis, conductance measurements, magnetic studies, UV and IR spectral data. Analytical, molar conductance and magnetic data of the complexes are presented in Table-1. The very low values of molar conductance indicate that the complexes are non-electrolytes in nitrobenzene and are neutral in nature. Hence the ligand besides being co-ordinated to the metal ion, also neutralises the charge.

TABLE-1
ANALYTICAL DATA, MOLAR CONDUCTANCE AND MAGNETIC MOMENTS

Complex	Colour	Found (Calcd.) (% metal)	μ_{eff} (B.M.)	Conductance (ohm^{-1} mol^{-1} cm^2)
$[CuL_2(H_2O)_2]$	Greenish yellow	10.19 (10.83)	1.8	0.8
$[PdL_2]$	Brown	16.88 (17.21)	Diamag	1.3
$[CdL_2]$	Yellow	20.90 (21.23)	Diamag	1.2
$[UO_2L_2]$	Yellow	25.10 (26.60)	Diamag	0.6

The observed magnetic moment of 1.8 B.M. for Cu(II) complex indicates the presence of unpaired electrons. The corresponding electronic configuration will be $d^9(t_2g^6\,{}^3eg)$. Complexes of Cd(II) are diamagnetic as expected for d^{10} configuration. The magnetic moment data are not helpful in assigning the structure of Cd(II), UO_2(II) or Pd(II) complexes.

Electronic spectra of the ligand are characterized by two bands lying at 37600 and 24000 cm^{-1} which can be assigned to $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions respectively. These transitions are observed with high intensity. During complex formation, a red shift is detected for these bands which indicates involvement of schiff base in coordination. Spectra of complexes are also characterized by a strong band of maximum absorption at a region of 31000–23000 cm^{-1} which can be assigned to the charge transfer transition from ligand to metal. Cu(II) complex shows two bands with peaks at 22400 cm^{-1} and 14686 cm^{-1}. The band at 14686 cm^{-1} is assigned to d–d transition. The other band is attributed to charge transfer transition[3]. The significant infrared spectral bands of the ligand and the complexes are given in Table-2.

TABLE-2

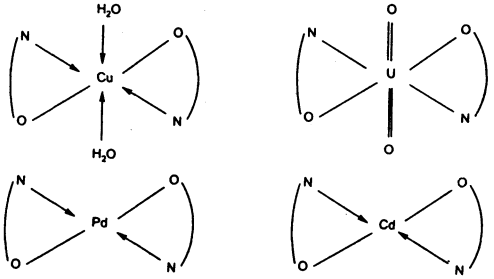
SELECTED INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF ANTHRACENE CARBOXALDEHYDE SEMICARBAZONE AND CHELATES

Complex	ν(C=N)	ν(C=O)	ν(M—N)	ν(M—O)
Ligand	1610	–	–	–
$[CuL_2(H_2O)_2]$	1578	1053	–	–
$[PdL_2]$	1570	1034	524	420
$[CdL_2]$	1558	1034	520	410
$[UO_2L_2]$	1558	1034	524	418

The ligand exhibits bands of high intensity at about 3480, 3300, 3210 and 3120 cm^{-1} due to the —NH—CO—NH_2 group. It has been suggested that the vibrations of the terminal —NH_2 group are responsible for the two bands at higher frequency region, as they are also present in the spectra of complexes at about the same frequencies or a slight shift to the higher frequency region. In the metal complexes, the intensities of these bands are considerably lowered, due to the fact that the hydrazine nitrogen atom of —N—NH—CO participates in coordination.

A strong band in the spectrum of the ligand at 1610–1580 cm^{-1} may be assigned to azomethine stretching modes[4]. In the metal complexes, this band is shifted to lower frequency region indicating the participation of the azomethine nitrogen atom in coordination. However, there is likely to be overlap with aromatic ring absorptions in the region. A broad feature at approximately 3500 cm^{-1} in the spectra of several complexes is attributed to the hydroxyl stretching mode of water molecule. In $[CuL_2(H_2O)_2]$ a strong band at approximately 950–870 cm^{-1} suggests that the water molecules are co-ordinated. All the above observations show that the ligand behaves as univalent bidentate coordinating through the azomethine nitrogen and enolic oxygen atoms.

All these studies suggest octahedral structures for Cu(II) and UO_2(II) complexes, a tetrahedral structure for Cd(II) complex and a square-planar structure for Pd(II) complex as shown below.



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