

NOTE

Synthesis and Characterization of Some Copper(II) Complexes of Hydrazines

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Some Cu(II) complexes of hydrazine and *p*-chloro phenylhydrazine have been isolated and characterized on the basis of chemical analysis, magnetic susceptibility, infrared and electronic spectral studies.

Key words: Copper(II), Complexes, Hydrazine, *p*-chloro phenylhydrazine

In view of the biochemical relevance of copper(II) complexes, the author has studied the synthesis and characterization of copper(II) complexes of hydrazine (hy) and *p*-chloro phenylhydrazine (*p*-Cl-Phhy)

Hydrazine and *p*-chloro phenylhydrazine (Fluka) and other reagents of reagent grade were used in the present work. The solvents were freshly distilled before use.

All the copper(II) complexes were synthesized by mixing the copper(II) salt in ethanol with corresponding ligand in the same solvent in equimolar ratio in a round bottom flask. On refluxing the reaction mixture for 2 h, and then concentrating the reaction mixture and cooling at room temperature, the desired complexes separated out. These were filtered and dried in vacuum over P₄O₁₀.

The analytical data of all the copper(II) complexes are presented in Table-1. All the complexes have the general composition Cu(L)₂X₂ (X = Cl, Br, SCN or CH₃COO, L = hy or *p*-Cl-Phhy). The compounds are stable, non-hygroscopic and do not change colour on storing. They are found to be soluble in acetonitrile, DMSO and DMF, but are insoluble in water, benzene, etc. The molar conductance values of complexes (10⁻³ M in acetonitrile) were found to be in the range 16–25 ohm⁻¹ cm² mol⁻¹ suggesting the nonionic nature of the present complexes. The magnetic susceptibilities of copper(II) complexes at room temperature (310 K) are found to be in the range 1.74–1.80 BM (Table-1). The possibility of having a tetrahedral structure is excluded and lower magnetic moment values suggest that the forces are operating very strongly to maintain planarity for axial elongation towards D_{4h} symmetry¹.

TABLE-1
ANALYTICAL DATA OF COPPER(II) COMPLEXES

Complex (Colour)	% Analysis: Found (Calcd.)			Decomp. (°C)	μ_{eff} (BM)
	Cu	N	Anion		
Cu(hy) ₂ Cl ₂ (Blue)	31.70 (32.00)	27.93 (28.20)	35.44 (35.76)	130	1.74
Cu(hy) ₂ Br ₂ (Green)	21.87 (22.09)	18.66 (19.47)	54.93 (55.65)	135	1.76
Cu(hy) ₂ (SCN) ₂ (Green)	25.30 (26.07)	33.83 (34.49)	46.84 (47.63)	130	1.78
Cu(hy) ₂ (CH ₃ COO) ₂ (Bluish green)	24.79 (25.85)	21.96 (22.80)	—	115	1.75
Cu(<i>p</i> -ClPhhy) ₂ Cl ₂ (Blue)	14.88 (15.14)	12.66 (13.34)	35.92 (33.84)	130	1.76
Cu(<i>p</i> -ClPhhy) ₂ Br ₂ (Green)	11.75 (12.49)	10.84 (11.01)	44.86 (45.42)	220	1.80
Cu(<i>p</i> -ClPhhy) ₂ (SCN) ₂ (Green)	13.60 (13.67)	23.77 (24.10)	23.85 (24.97)	265	1.76
Cu(<i>p</i> -ClPhhy) ₂ (CH ₃ COO) ₂ (Bluish green)	12.82 (13.61)	11.76 (12.00)	—	186	1.76

TABLE-2
ELECTRONIC SPECTRAL DATA OF Cu(II) COMPLEXES

Complexes	Band (kK)	10 D _q
Cu(hy) ₂ Cl ₂	13.27	6.63
Cu(hy) ₂ Br ₂	13.41	6.72
Cu(hy) ₂ (SCN) ₂	13.54	6.26
Cu(hy) ₂ (CH ₃ COO) ₂	13.40	6.70
Cu(<i>p</i> -ClPhhy) ₂ Cl ₂	22.10	11.10
Cu(<i>p</i> -ClPhhy) ₂ Br ₂	21.84	10.84
Cu(<i>p</i> -ClPhhy) ₂ (SCN) ₂	20.70	10.40
Cu(<i>p</i> -ClPhhy) ₂ (CH ₃ COO) ₂	21.34	10.66

The infrared studies suggest that both the ligands are bidentate in nature. The electronic spectral data show that normally copper(II) complexes have three bands in 12540–12400, 16440–16300 and 21900–21800 cm⁻¹ region, which may be attributed to ²B_{1g} → ²B_{1g}, ²B_{1g} → ²A_{1g} and ²B_{1g} → ²E_g transitions respectively^{2,3}. The data suggest the square-planar geometry of copper(II) in these complexes. An approximate value of D_q may be obtained from the following expression:

$$10D_q = \nu_3 - \frac{1}{2}\nu_1 - \frac{1}{3}(\nu_3 - \nu_2)$$

If it is assumed that the splitting of the states occurs due to tetragonal field, then they follow a baricentre rule^{4,5}. Assigning all the three transitions to a single energy gives an approximate value of 10D_q^{6,7}

In these complexes the states increase with the tetragonal components of the crystal field. As the energy of ²A_{1g} state increases, a situation may arise in which this state is sufficiently close to ²B_{2g} and ²E_g states for the three transitions not

to be resolved in the spectrum. Thus from the appearance of a single broad band in the spectra of most of the complexes studied herein, it is concluded that all the three transitions lie within this one broad envelope and that the distortion is not large from octahedral symmetry. However, the extent of distortion is not known with certainty.

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