

Square Planar Complexes of Cu(II) and Pd(II) with 2,5-Dihydroxyacetophenone Schiff Bases

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Cu(II) and Pd(II) forms 1 : 2 complexes with 4-methylaminoanil of 2,5-dihydroxyacetophenone (MAADAP) and 2,5-dichloroaminoanil of 2,5-dihydroxyacetophenone (DAADAP). The structures of these complexes have been characterised on the basis of electronic spectra, magnetic moments and ir spectral studies.

CO-ORDINATION ability of Schiff bases derived from 2,5-dihydroxyacetophenone have been studied by various workers¹⁻³. The present work deals with the spectrophotometric study of the complex formation of Cu(II) and Pd(II) with MAADAP and DAADAP.

Experimental

Composition of the complexes : Equimolar solutions of the metal chloride and the ligand in the ratio 2 : 1, 1 : 1, 1 : 2 and 1 : 3 were mixed and the final volume was made to 20 ml by adding required amount of ethanol. The absorption spectra of all the solutions were taken. In all the cases the maximum absorptions were found at 430 nm [with Cu(II)] and 360 nm [with Pd(II)] indicating the formation of only one type of complex with the ligand.

Job's method of continuous variation, molar ratio method and slope ratio method were employed to determine the stoichiometry (metal : ligand) of the complexes. These showed 1 : 2 composition.

Isolation of the complexes : A mixture of the metal salt (CuCl₂ or PdCl₂, A. R. quality) (15 ml., 0.02 M) and ligand (30 ml, 0.02 M), mixed in stoichiometric ratio 1 : 2, was refluxed in alcoholic medium on waterbath for about 2 hrs. On concentration and cooling, coloured crystals separated out

which were washed with water and ethanol and dried in vacuum. The complexes were soluble in DMF and DMSO. A very dilute solution (conc. 10⁻³ M) exhibits 35 Ohm⁻¹ mole⁻¹ cm² molar conductance. The low molar conductance value suggested the non-electrolytic nature of the complexes.

Electronic spectra of the complexes were recorded in nujol mull on a Cary-14 recording spectrophotometer. A Guoy balance was used for magnetic measurement. Infrared spectra of the complexes (KBr disc) were obtained on Perkin-Elmer spectrophotometer model 521.

The colour, elemental analysis and magnetic data of the complexes are listed in Table 1.

Results and Discussion

Copper complexes : The experimental magnetic moment values of the complexes (1.82 B. M. and 1.79 B. M.) are in close agreement to the spin only value (1.78 B. M.), irrespective of the stereochemistry⁴, indicating that the orbital contribution is almost quenched by the crystalline ligand field.

Three bands were mainly observed in the electronic spectra of the complexes. The first two bands in each case involve the transitions ²B_{1g} → ²A_{1g} (16,000 cm⁻¹, 15,800 cm⁻¹) and ²B_{1g} → ²E_g (19,200 cm⁻¹, 19,000 cm⁻¹) whereas the third band

TABLE 1—ELEMENTAL ANALYSIS AND MAGNETIC SUSCEPTIBILITY DATA OF THE METAL CHELATES OF MAADAP AND DAADAP

Compound	Colour	Elemental Analysis					Magnetic Moment B.M.
		C	H	N	Cl	Metal	
		Found (Calcd.)	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)	
MAADAP	Dark	74.54	6.10	5.72	—	—	—
	Brown	(74.70)	(6.20)	(5.80)	—	—	—
DAADAP	Brown	56.50	3.23	4.60	23.72	—	—
		(56.80)	(3.40)	(4.70)	(23.90)	—	—
(MAADAP) ₂ Cu	Black	69.78	5.10	5.21	—	11.50	1.79
	Brown	(69.91)	(5.15)	(5.15)	—	(11.68)	—
(DAADAP) ₂ Cu	Dirty	51.30	2.98	4.26	21.60	9.64	1.82
	Brown	(51.43)	(3.06)	(4.29)	(21.73)	(9.71)	—
(MAADAP) ₂ Pd	Black	61.48	4.68	4.72	—	18.08	Diamagnetic
		(61.39)	(4.77)	(4.77)	—	(18.14)	—
(DAADAP) ₂ Pd	Dull	48.30	2.78	3.98	20.30	15.18	Diamagnetic
	Brown	(48.24)	(2.87)	(4.02)	(20.39)	(15.27)	—

(21,500 cm^{-1} , 21,000 cm^{-1}) is a charge-transfer band⁵. These observations suggest square planar symmetry for these complexes.

Palladium complexes: The diamagnetic Pd(II) complexes are probably square planar⁶ which is the common stereochemistry for the Pd complexes.

In the electronic spectra of Pd(II) complexes, two bands were obtained. The first band was a combination of all the three spin-allowed transition and may be assigned to transitions $^1A_{1g} \rightarrow ^1A_{2g}$, 1E_g , $^1B_{1g}$. The other bands at 48,000 cm^{-1} and 47,200 cm^{-1} have been assigned to the transitions $^1A_{1g} \rightarrow ^1E_u$. The values of ligand field parameters Δ_1 , Δ_2 and Δ_3 derived from d-d spectra of Pd(II) complexes are 34,000, 1,500, 500 and 33,000, 1,500, 500 cm^{-1} respectively for (MAADAP)₂Pd and (DAADAP)₂Pd. The values of Δ_1 were found to be larger than the combined values of Δ_2 and Δ_3 . These observations suggest square planar symmetry for these complexes.

The ir spectra of complexes show that the stretching frequency of azomethine ($-\text{C}=\text{N}-$)

shifted at lower frequency (around 1,580 cm^{-1}) and the band due to (O-H) was found to disappear indicating complex formation through these groups. This view is further supported by the appearance of M-N (490 cm^{-1}) and M-O (460 cm^{-1}) bands.

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