

Binary and ternary complexes of copper(II) with some dihydroxycoumarins

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Abstract. The complexation behaviour of copper(II) with a series of selected dihydroxycoumarins has been studied. Copper(II) binary complexes with esculetin, daphnetin and their 4-methyl and 4-phenyl derivatives and ternary complexes having a secondary ligand, ammonia or pyridine have been synthesized. The general composition of binary complexes has been found to be $[\text{Cu}(\text{H}_2\text{O})_2(\text{HL})_2]$ and that of ternary complexes as $[\text{Cu}(\text{L})(\text{X})_4]$ (where $\text{X} = \text{NH}_3$ or $\text{C}_5\text{H}_5\text{N}$). The magnetic studies indicate all the complexes to be monomeric in nature. IR studies show that one of the two phenolic hydroxyl groups present in the ligand is lost during complexation. It is concluded that of the four ligands attached to the copper atom dihydroxycoumarin is bound most firmly.

Keywords. Esculetin; daphnetin; monomeric; dihydroxycoumarins; binary; ternary.

1. Introduction

Copper has considerable biochemical importance in various systems. Besides, many metalloproteins are specifically known to bind metals like Cu^{2+} , Zn^{2+} and Fe^{2+} by forming co-ordinate complexes. In the present paper, we report the formation of Cu(II) binary complexes with some biologically active diphenols and ternary complexes formed in the presence of ammonia or pyridine. The complexes have been prepared at a predetermined pH range necessary for the formation of the neutral complex (Kalra 1972).

The isolated complexes have been characterised on the basis of their elemental analyses, magnetic measurements, electronic and infrared spectra and thermogravimetric analyses.

2. Experimental

2.1. Preparation of ligands

Esculetin and daphnetin and their derivatives have been prepared by condensing hydroxyhydroquinone triacetate or pyrogallol respectively with malic acid or appropriate β -ketonic ester in the presence of sulphuric acid (Pechman 1884).

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2.2. *Isolation of complexes*

The complexes have been prepared by adding an aqueous solution of copper(II) chloride (0.05 mole) to an alcoholic solution of the corresponding ligand in the stoichiometric ratio of 1:2 and subsequently raising the pH of the mixture gradually to 5.0 by adding dilute solution of sodium hydroxide. A green coloured solid separated out. The resultant mixture was refluxed for an hour, cooled, filtered and washed several times with water followed by ethanol to remove unreacted reactants and finally dried under vacuum at room temperature ($\sim 25^\circ\text{C}$) over P_2O_5 .

2.3. *Isolation of mixed ligand complexes*

To an aqueous solution of copper(II) chloride was added an ethanolic solution of the ligand in 1:1 stoichiometric ratio followed by a ten fold excess of secondary ligand, aqueous ammonia or pyridine. On keeping the reaction mixture at 0°C for 24 hr, the complex separated. It was filtered, washed with ethanol and dried in vacuum at room temperature over P_2O_5 .

The formation of the ternary complex is independent of the relative proportions of metal, primary ligand and secondary ligand.

2.4. *Instruments used*

The IR spectra was recorded in cesium iodide pellets on a Perkin-Elmer model 621 IR spectrophotometer. Visible spectra was recorded on a Beckman DU-2 spectrophotometer. ECIL digital pH-meter was used for pH measurements. A Gouy's balance and Setaram thermoanalyser model G-70 was used for magnetic and thermogravimetric studies respectively.

3. Results and discussions

Elemental analyses of Cu(II) binary and ternary complexes prepared above suggest the general composition as $[\text{Cu}(\text{H}_2\text{O})_2(\text{HL})_2]$ and $[\text{Cu}(\text{L})(\text{X})_4]$ where $\text{X} = \text{NH}_3$ or $\text{C}_5\text{H}_5\text{N}$ (tables 1 and 2).

3.1. *Magnetic measurements*

Copper(II) complexes can be divided into two broad classes based on their magnetic behaviour (i) mononuclear complexes having temperature independent magnetic moment in the range of 1.75–2.20 B.M., (ii) complexes having temperature-dependent moment, substantially below the spin only value. Since the room temperature magnetic moments in the present case lie in the range 1.9–2.2 BM (tables 1 and 2), the complexes are supposed to be monomeric in nature.

3.2. *Electronic spectral studies*

All binary as well as ternary complexes of copper isolated are green in colour. A broad absorption band in the 13 kK–16 kK region of the spectrum is usually

Table 1. Elemental analyses, magnetic measurements and electronic spectral data of copper(II)-dihydroxy coumarin complexes.

Complex	Found (Calc.) %			μ_{eff} B.M.	kK
	C	H	Cu		
Diaquo-bis-(esculenato)- copper (II) (Cu-ES.H)	47.2 (47.6)	3.0 (3.1)	13.8 (14.0)	1.88	13
Diaquo-bis-(4-methyl- esculenato)-copper(II) Cu-4ME . H)	49.6 (49.8)	3.5 (3.7)	13.0 (13.2)	1.98	13.2
Diaquo-bis-(4-phenyl)- esculenato)-copper(II) (Cu (4PE . H)	59.2 (59.5)	3.4 (3.6)	10.2 (10.6)	1.98	13.4
Diaquo-bis-(dephneto)- copper(II) (Cu-Da.H)	47.3 (47.6)	2.9 (3.1)	13.7 (14.0)	1.98	13.2
Diaquo-bis-(4-methyl- dephneto)-copper(II)- Cu-4MD . H)	49.6 (49.8)	3.6 (3.7)	13.0 (13.2)	2.10	13.5
Diaquo-bis-(4-phenyl- dephneto) copper(II) (Cu-4PD . H)	59.3 (59.5)	3.4 (3.6)	10.3 (10.6)	2.18	13.8

met within the compounds of this colour. The electronic spectra of all the complexes recorded in nujol mull indicate the presence of one composite band in the region 13 kK–14 kK in binary complexes and in the region 14–16 kK in ternary complexes where the water molecule of the binary complex is replaced by ammonia or pyridine (tables 1 and 2). The λ_{max} values of complexes have been found to be in following order : ammonia > pyridine > water. This order accords with the spectrochemical series assigning magnitude of shifts by replacing one ligand with another (Tuschida 1938).

3.3. Infrared studies

Since all the complexes possess an α -benzopyrone skeleton the spectra of the complexes is almost identical to the spectra of ligand (Bassignana and Cogrossi 1964) except additional bands due to $\nu_{\text{M-O}}$ bonds. In the binary complexes $\rho_{\text{C-OH}}$ bands appearing at 1200–1100 cm^{-1} is shifted by $\pm 30 \text{ cm}^{-1}$ and there is a significant decrease in its intensity. This suggests that the more acidic of the two –OH group, i.e., 7th hydroxyl group (Rastogi 1960) is involved in bond formation through replacement of proton. The pH of the system facilitates the release of proton of 7th –OH group but is not sufficiently high to dissociate the second, considerably weaker, –OH group. This also explains the reduced intensity, whereas the shift in $\rho_{\text{-OH}}$ band is attributed to the involvement of the weaker –OH

Table 2. Elemental analyses, magnetic moments and electronic spectral data of mixed ligand complexes of copper(II).

Complex	Found (Calc.) %				μ_{eff} B.M.	kK
	C	H	N	Cu		
Cu-ES-NH ₃	35.0 (35.1)	5.0 (5.2)	18.0 (18.2)	20.5 (20.7)	1.89	15.7
Cu-4ME-NH ₃	37.0 (37.3)	5.3 (5.6)	17.2 (17.4)	19.4 (19.8)	2.20	15.8
Cu-4PE-NH ₃	46.5 (46.9)	5.0 (5.2)	14.2 (14.6)	16.3 (16.6)	2.20	15.9
Cu-Da-NH ₃	34.9 (33.1)	4.9 (5.2)	18.0 (18.2)	20.4 (20.7)	2.05	15.8
Cu-4MD-NH ₃	37.1 (37.3)	5.2 (5.6)	17.1 (17.4)	19.5 (19.8)	2.10	15.9
Cu-4PD-NH ₃	46.7 (46.9)	5.0 (5.2)	14.3 (14.6)	16.4 (16.6)	2.20	16.0
Cu-ES-Pyr	62.2 (62.4)	4.8 (5.0)	9.8 (10.0)	11.1 (11.4)	1.90	14.2
Cu-4ME-Pyr	62.1 (62.3)	4.5 (4.9)	9.6 (9.8)	11.0 (11.1)	1.98	14.5
Cu-4PE-Pyr	64.0 (64.3)	4.4 (4.6)	8.4 (8.6)	9.2 (9.7)	2.10	14.6
Cu-Da-Pyr	62.2 (62.4)	4.8 (5.0)	9.8 (10.0)	11.0 (11.4)	1.92	14.2
Cu-4MD-Pyr	62.1 (62.3)	4.7 (4.9)	9.6 (8.8)	11.04 (11.1)	2.10	14.4
Cu-4PD-Pyr	64.1 (64.3)	4.2 (4.6)	8.4 (8.6)	9.2 (9.7)	2.20	14.6

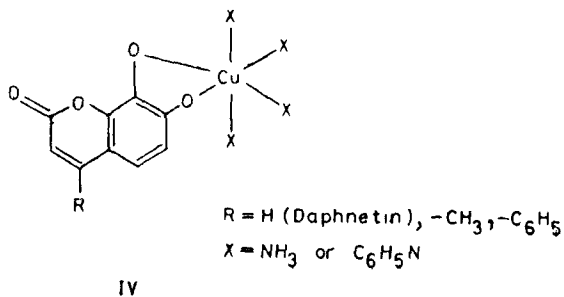
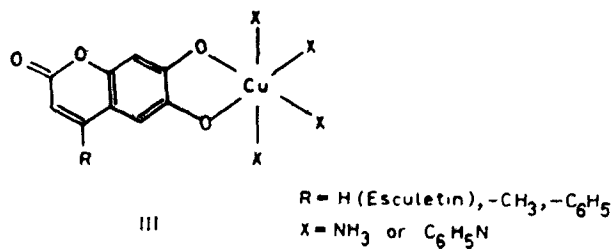
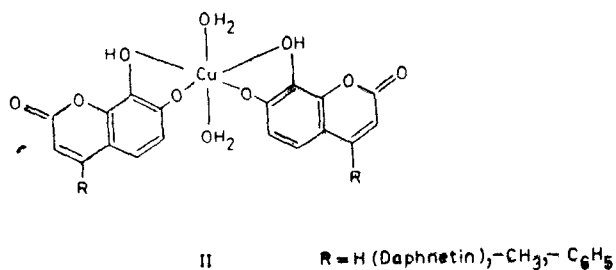
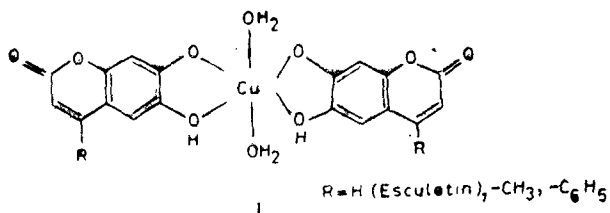
group through donation of the lone pair on oxygen atom. However, on addition of ammonia or pyridine, this proton is also lost. Consequently $\nu_{\text{-OH}}$ band is not observed in the IR spectra of ternary complexes. The broadening of sharp $\nu_{\text{-OH}}$ band in the region $3420\text{--}3300\text{ cm}^{-1}$ and new bands at $900\text{--}850\text{ cm}^{-1}$ and $550\text{--}530\text{ cm}^{-1}$ is attributed to the presence of water molecule, the presence of which is also supported by thermal studies. The ternary complexes show characteristic bands due to ammonia or pyridine.

3.4. Thermogravimetric analysis

During the first step of decomposition at $\sim 150^\circ\text{C}$, the two water molecules of the binary complex are lost. At 260°C , the weight of the residue corresponds to the formation of a 1:1 complex. The final decomposition product at 560° is the stable oxide (Duval 1963). From the course of thermal decomposition it may be inferred that two molecules, each of water and ligand, are attached to the six-coordinated central metal atom.

In the case of ternary complexes, the first decomposition at $50\text{--}90^\circ\text{C}$ results in the loss of four molecules of ammonia/pyridine giving a 1:1 complex. The final product is, however, copper oxide which is formed at 520°C .

On the basis of the above experimental evidences structures I, II and III, IV may be suggested for binary and ternary complexes respectively.



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