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Synthesis and Characterization of Mono- and Binuclear CU(II) Complexes with some 4-carboxy-3-hydroxy-phenylhydrazo- β-diketones.

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Summary: Mono- and binuclear Cu(II) complexes of some 4-carboxy-3-hydroxyphenyl-hydrazo-β-diketones are synthesized and characterized by elemental analysis, ir, electronic and epr spectra. The data indicate the in mono-nuclear complexes the ligands behave as dianionic bidentate while in binuclear complexes they act as trianionic tetradentate. The results of epr spectra suggested that Cu(II)- ions are present in a nearly square planar coordination with tetragonal symmetry.

Introduction

As a matter of fact, ligands derived from p-amino-salicyclic acid have found application in biological systems [1,2]. These applications are of great importance if the Cu(II) complexes of such ligands are prepared (3,4]. It is well known, however, that the majority of the biologically important Cu(II) complexes are of tetragonal symmetry or lower. Accordingly, it is always desirable to study some properties of the corresponding Cu(II) complexes such as, stability constants, thermal stabilities as well as spectra in order to obtain a reasonable information about their geometrical structure.

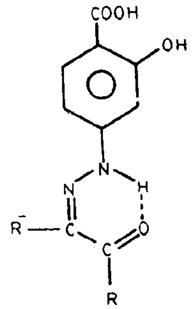
In the present report, the chelating ability of 4-carboxy-3-phenylhydrazo-acetylacetone (CHPHAA), -benzoylacetone (CHPHBA), -dibenzoylmethane (CHPHDBM) and -thienoylmethylketone (CHPHTMK) have been measured. Each compound retains at least a portion of the basic structure of CHPH, namely 4-carboxy-3-hydroxyphenylhydrazo group but different β-diketone.

Experimental

a) Preparation of ligands:

CHPHAA, CHPHBA, CHPHDBM and CHPHTMK were prepared using the same procedures as described previously [5-6]. The purity of the ligands are tested by elemental analysis, ir and ^{1}H nmr spectra and they have the following formulae.

	R	$\bar{R}$
CHPHAA	CH_3	CH_3CO
CHPHBA	C_6H_5	CH_3CO
CHPHDBM	C_6H_5	C_6H_5
CHPHTMK	C_4H_3S	H



b) Preparation of Cu(II) Complexes:

i) 2:1 (M:L) complexes:

The complexes were prepared by dissolving (0.09 mole) KOH in 10 ml of distilled water and mixed with (0.03 mole) of the ligand in 100 ml of EtOH. The mixture was stirred causing the ligand to dissolve and then (0.06 mole) of copper sulfate, dissolved in the least amount of distilled water was added dropwise. On stirring the reaction mixture for about 30 minutes the brown solid Cu(II) complexes was precipitated, then filtered off and recrystalized from H_2O/EtOH (50% v/v). The pure compounds were filtered off, washed with ether and dried *in vacuo*.

ii) 1:1 (M:L) Complexes:

The same procedure as given above was used except that the copper concentration was 0.03 mole.

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Table 1: Analytical and Stability Constants Data for CHPHAA, CHPHBA, CHPHDBM and CHPHTMK Complexes with Cu(II) Ion.

Complex	^a^Result of Microanalysis					EPR data	^b^log K_1
	% C	% H	% N	% S	% Cu	g_{eff}	
$[Cu(CHPHAA)(H_2O)_2]$	40.10 (39.83)	4.20 (3.87)	8.10 (7.75)		17.30(17.66)	2.044	13.58
$[Cu_2(CHPHAA)(H_2O)_4]_2SO_4$	28.20 (28.35)	3.60 (3.35)	5.70 (5.51)	3.00 (3.15)	24.60 (25.00)	2.214	25.78
$[Cu(CHPHBA)(H_2O)_2]$	47.80 (48.17)	3.80 (3.78)	6.50 (6.61)		14.60 (14.99)	2.046	14.05
$[Cu_2(CHPHBA)(H_2O)_4]_2SO_4$	35.40 (35.79)	3.10 (3.33)	5.10 (4.91)	3.10 (2.81)	21.70 (22.08)		24.70
$[Cu(CHPHDBM)(H_2O)_2]$	54.00 (54.38)	3.50 (3.70)	5.60 (5.77)		12.60 (13.08)	2.043	14.60
$[Cu_2(CHPHDBM)(H_2O)_4]_2SO_4$	41.40 (41.77)	3.20 (3.32)	4.30 (4.44)	2.45 (2.53)	20.20 (20.11)	2.232	24.90
$[Cu(CHPHTMK)(H_2O)_2]$	38.50 (38.66)	2.80 (2.97)	6.80 (6.94)	7.80 (7.94)	15.20 (15.74)	2.043	14.82
$[Cu_2(CHPHTMK)(H_2O)_4]_2SO_4$							25.22

[a] % Found (% Calculated); [b] : pK^H_1 pK^H_2 pK^H_3 [16], in 30.06 (w/w) dioxane-water solvent.

	pK^H_1	pK^H_2	pK^H_3
CHPHAA	3.34	6.94	11.60
CHPHBA	2.90	6.70	11.50
CHPHDBM	3.60	7.30	10.32
CHPHTMK	4.04	7.27	10.42

All the prepared complexes were then subjected to elemental analysis; the results obtained are listed in Table-I.

c) Measurements:

Apparatus and working procedures are the same as described previously [7].

Results and Discussion

Complexes in the solid state:

The results of analysis show that all the prepared complexes have two or more water molecules coordinated to the central metal ion, since they are not removed by static vacuum for two hours at room temperature. This conclusion is also suported by the results of TGA which show dehydration of water molecules from the complexes at 120-150°C.

On examining the ir spectra of mono- and binuclear Cu(II) complexes, Table-II, in comparison to those of the free ligand the following can be pointed out:

a) all complexes exhibit a broad band (3300-3400 cm^{-1}) which could be assigned to νOH of water molecules. The presence of coordinated water is further confirmed by the appearance of non-ligand bands in the region 1210-1225 cm^{-1} assignable to rocking mode of water molecules.

b) the shift to higher frequency of the νCO of the carboxyl group on the spectra of complexes indicates the participation of carboxylate group in chelate formation. The shift of the CO band to higher wavenumbers can be explained on the basis that the COOH group is contributing to a hydrogen bonding chelate ring with the O-OH- group. Thus H- bonding causes an obvious shift ofthe CO but to lower wavenumbers, compared to the free CO group. The destruction of the H-bond through proton displacement by the Cu(II) ion causes a shift to higher wavenumbers. The participation of phenolic OH group in chelate formation takes place through H^+ displacement as gathered from the disappearance of δOH at 1370-1365 cm^{-1} and γC-OH at 1080-1075 cm^{-1} for all metal complexes.

c) all metal chelates show new bands at 460-490 cm^{-1}, which are not observed in the spectra of the free ligands, can be assigned to νM-O.

d) the main differences between the ir spectra of mono- and binuclear Cu(II) complexes can be pointed out as follows:

i- the νNH, located at 3100-3200 cm^{-1} in the spectra of the ligands, is observed at the same position in the spectra of mono-nuclear complexes. This band is absent in the spectra of the binuclear complexes, indicating that the ligands attain the hydrazo structure on the formation of the binuclear Cu(II) complexes.

ii- the new band observed at 360-380 cm^{-1} in the spectra of binuclear complexes, which does not appear in the spectra of the mono-nuclear type, can be assigned to νM-N.

iii- the two bands located at 1150 and 1340 cm^{-1} ν_{as} S = O and νs S = O respectively indicating the non-coordinated nature of SO4. This conclusion is also supported from the solution conductance values for binuclear Cu(II) complexes (215- 195 ohm^{-1} cm^2 $mole^{-1}$) which are in agreement with the data obtained by previous authors [8] for 1:2 electrolytes. The conductance values obtained for mono-nuclear complexes (12.0-9.0 ohm^{-1} cm^2 $mole^{-1}$) are too low to account for any ionic character.

The visible spectra of the different Cu(II) complexes show the presence of complex bands in the region 500-600 nm. The intensity of the band is a function of both the molar ratios of Cu:L and the pH of the medium. The general shape and position

Table II: IR Data of CHPHAA, CHPHBA, CHPHDBM and CHPHTMK Ligands and Their Copper (II) Complexes.

Compound	IR (cm^{-1})								
	νOH	νN-H	νC = O	νCOO	νM-OH_2	νM-O	M-N	νs S = O	νas S = O
CHPHAA	3360	3100	1640 1670	1575					
$[Cu(CHPHAA)(H_2O)_2]$	3300	3100	1660 1680	1580	1210	460			
$[Cu_2(CHPHAA)(H_2O)_4]_2SO_4$	3350		1700	1610	1210	470	360	1340	1150
CHPHBA	3400′	3110	1640 1670	1575					
$[Cu(CHPHBA)(H_2O)_2]$	3350	3110	1650 1660	1580	1225	470			
$[Cu_2(CHPHBA)(H_2O)_4]_2SO_4$	3330		1710	1610	1225	480	380	1340	1150
CHPHDBM	3360	3100	1640 1670	1575					
$[Cu(CHPHDBM)(H_2O)_2]$	3300	3100	1640 1680	1575	1220	480			
$[Cu_2(CHPHDBM)(H_2O)_4]_2SO_4$	3300		1700	1600	1220	470	370	1340	1150
CHPHTMK	3400	3110	1640 1670	1575					
$[Cu(CHPHTMK)(H_2O)_2]$	3350	3110	1630 1670	1580	1220	490			
$[Cu_2(CHPHTMK)(H_2O)_4]_2SO_4$	3300		1720	1610	1220	490	375	1340	1150

of such bands are closely similar to those previously measured in case of Cu(II)-Schiff base complexes where Cu(II) was assumed to be in a square planar coordination [9,10].

Therefore, it could be saftely concluded that the Cu(II) complexes under investigation might be present in the same geometrical coordination. Accordingly, the absorption band may be assigned to the transition $^1B_{1g}\,(^2E_g) \longrightarrow {}^2E_g\,(^2T_{2g})$.

Cu(II) complexes are particulrly suitable to an epr study. The X-band epr spectrum of [Cu(CHPHAA) $(H_2O)_2$] or [Cu_2(CHPHBA) $(H_2O)_4]_2$ SO_4 at 300 K, shows an intense broad signal (Fig. 1). The values of $g_{eff} = g_l$ are 2.043-2.046 and 2.214-2.232 for mono- and binuclear Cu(II) complexes respectively (Table-I). Generally, these complexes are not magnetically dilute, therefore exchange [11] and/or dipolar forces are expected to operate in which case the g anisotropy, in case of mono-nuclear complexes, is likely to be reduced. On the other hand, the exchange is taking place in binuclear complexes, and this is shown by the fact that no hyperfine structure is observed [12].

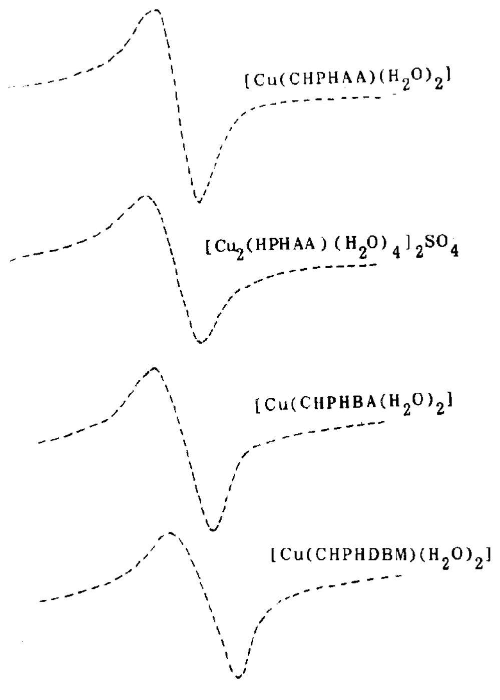
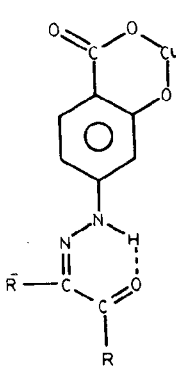
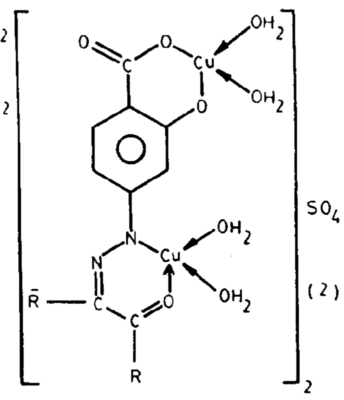


Fig. 1: X-band EPR spectra of some solid Cu(II) complexes.

Moreover, the obvious broadening of the epr signal may be due to an interaction between Cu(II) ions which are probably present in non-equivalent lattice position. The line broading observed and the pattern of the g_{eff} values for mono- and binuclear Cu(II) complexes indicate a square planar geometry around the Cu(II) ion.

On the basis of the above results, mono- and binuclear Cu(II) complexes could be represented by structures (1) and (2) respectively.

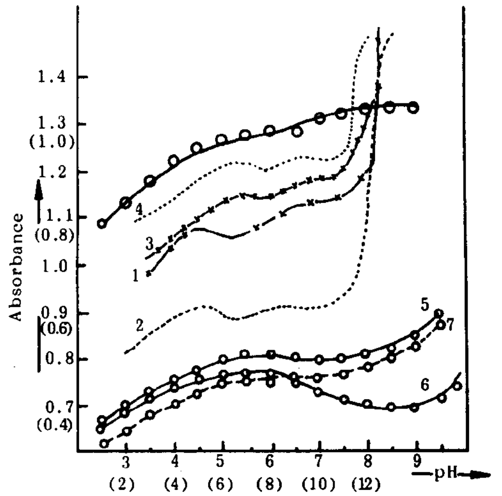

(1)


(2)

Complexes in solutions

The spectra of the ligands under investigation in a series of universal buffer solutions were studied in absence and in presence of Cu(II) ions. The spectra of the ligands display one shoulder at 435-440 nm which does not show apparent variations with pH change 2.0-3.0. This behaviour denotes that one form of the ligands, probably the solvated neutral molecules dominate under such conditions in solution. With increasing pH 3.0-6. the absorbance increases and the change in the spectra can be ascribed to the ionization of COOH group. At pH 7.0 the ionization of the phenolic OH group takes place. The shoulder becomes more defined and the extinction increases with increasing pH tending to attain a limiting value at pH > 7.50-9.00. Above pH 9.50 the ionization ofthe hydrazo group starts and the shoulder situated at 435-440 nm is converted into a well defined band with λ_{max} at 450-460 nm depending on the ligand used. The extinction of the new band increases with increasing pH tending to attain a limiting values at pH 12.0-12.50. The shift in the band with increasing pH can be attributed to the stepwise establishment of the acid-base equilibria between neutral, mono-, di- and trianionic species respectively. The absorbance - pH curves are seen in Fig. 2 display identical character, for the ligands under investigation, where typical dissociation S- shaped curves are obtained in which the curve consists of three steps confirming the dissociation of more than one person.

The spectra of the ligands in presence of Cu(II) ions are completely different with increasing pH of the medium, the absorbance increases while the positions of the band are shifted slightly to shorter wavelength by (15-20 nm). The plot of absorbance as a function of pH yield also a typical dissociation curve (Fig. 2). This behaviour refers to the probable existence of more than one complex species in solution. The increased tendency for complex formation with increasing pH is probably due to the shift in equilibrium in favour of complex compound. This behaviour was explained on the basis that, the reaction between the ligands and Cu(II) ion takes place through displacement of H^+ ions from the ligand on complex formation.



scale between brackets is for free ligands.

Fig. 2: Absorption-pH plots for (1) CHPHAA; (2) CHPHBA; (3) CHPHDBM (4) CHPHTMK (5) Cu-CHPHAA; (6) CU-CHPHBA; (7) Cu-CHPHDBM; (8) Cu-CHPHTMK.

The stiochiometry of the complexes under investigation were studied by applying some of the known spectrophotometric methods namely, molar ratio [13], slope ratio [14] and limiting logarithmic [15] methods. The results proved that Cu(II) forms with CHPHAA, CHPHBA, CHPHDBM and CHPHTMK (1:1) and (2:1) (M:L) complexes.

The stability constants of complexes formed in solutions are determined from the results of the molar ratio method [13]. The results are listed in Table-I. The attempt to rationalize the trend of log K_1 for mono- and binuclear Cu(II) complexes in terms of ligands basicity $\Sigma pk^H_1 + pK^H_2 + pK^H_3$ was unsuccessful. This descrepancy is partly ascribed to the failure of measured pK^H_1 values to account for the intrinsic basicity of the ligand molecules felt by the metal ion. In the case of mono-nuclear Cu(II) complexes the hydrazo nitrogen does not participate in chelate formation i.e. the ligands coordinated to Cu(II) ion through OH and COOH groups after deprotonation. Considering this and eleminating pK^H_3 (dissociation of NH group) from the basicity term ($pK^H_1 + pK^H_2 + pK^H_3$), the representation of $pK^H_1 + pK^H_2$ versus log K_1 yields a straight line whose correlation coefficient equals 0.999. The slope of the straight line equals1.0, this indicates that the effect of changing β-diketone molecule on the ligands on the stability of the metal-ligand complexes, compared to that of proton-ligand complexes is of the same extent. Also, a conclusion could be drawn that CHPHAA, CHPHBA, CHPHDBM and CHPHTMK form the same chelate ring upon complexation with Cu(II) ion.

The representation of log K_1 for binuclear Cu(II) complexes vs. ligand basicity term ($pK^H_1 + pK^H_2 + pK^H_3$) gives a straight line of slope equals unity and correlation coefficient equals 0.99 (Fig. 3). This indicates that CHPHAA, CHPHBA,

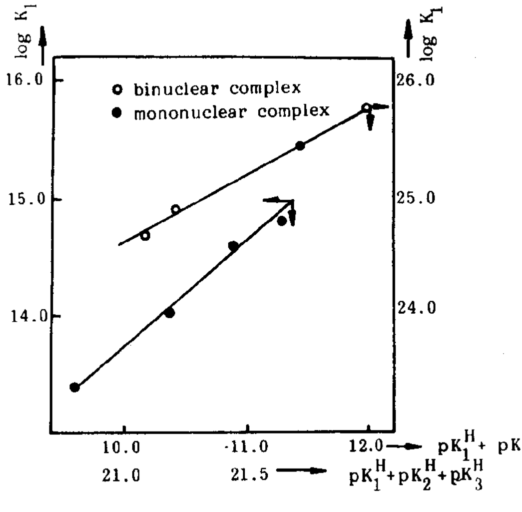


Fig. 3: Relationship between the values of log K_1 for Cu(II) complexes and the basicity; ($\Sigma_1 pk_1 H$) of the ligands.

CHPHDBM and CHPHTMK ligands are coordinated to Cu(II) ion through OH, COOH and NH groups after deprotonation, which is in good agreement with the results of studies of the solid complexes.

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