

REACTION OF Cu(II) COMPLEX OF PHTHALIC HYDRAZIDE WITH OXYGEN AND NITROGEN DONOR LIGANDS

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The reaction of Cu(II) complex of phthalic hydrazide of type $[\text{Cu}(\text{HPH})_3(\text{H}_2\text{O})_6]\text{H}_2\text{O}$ with acetylacetone (acac), monoethanolamine (MEA) ethylenediamine (en) and bipyridine (bipy) gives mononuclear complexes of types $[\text{Cu}(\text{HPH})_2(\text{acac})_2]\text{H}_2\text{O}$ (I), $[\text{Cu}(\text{HPH})_2(\text{MEA})_2]$ (II), $[\text{Cu}(\text{HPH})_2(\text{en})_2]2\text{H}_2\text{O}$ (III) and $[\text{Cu}(\text{HPH})(\text{bipy})_2(\text{H}_2\text{O})]\text{H}_2\text{O}$ (VI) respectively and with aniline (An) and *p*-phenylenediamine (*p*-Phda) it gives binuclear complexes of types $[\text{Cu}_2(\text{HPH})_2(\text{An})(\text{H}_2\text{O})]\text{H}_2\text{O}$ (IV) and $[\text{Cu}_2(\text{HPH})_2(\text{p-Phda})(\text{H}_2\text{O})]$ (V) respectively. The complexes have been characterized on the basis of IR and electronic spectral and magnetic properties.

Ligand field parameters have been calculated. Analysis of electronic spectra, Dq Value and IR spectra strongly indicate the presence of CuN_2O_4 , CuN_2O_2 and CuNO_4 chromophores.

Key words: Cu (II) Complex, Phthalic hydrazide, Oxygen or nitrogen donor ligands.

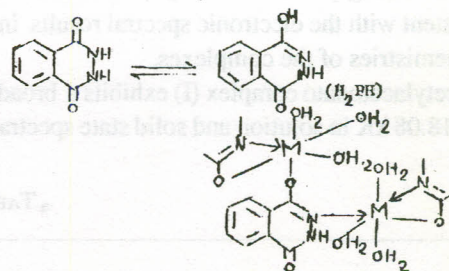
Introduction

The importance of mixed ligand complexes of first row transition metals in biological systems has led to their extensive study [1-9]. The Lewis-acid property studies on Cu(II) β -diketonates [1,2] towards other oxygen and nitrogen donor ligands have been extensively carried out. The heteroaromatic N-bases, possessing good π -accepting properties, have been shown to enhance the affinity of Cu(II) ion towards the oxygen donor sites of anionic ligands [10-11].

The reactions of *bis*-phthalhydrazidato Co(II) [12] and Ni(II) [13] complexes have been reported to form mono and trinuclear *mono*, *bis*, *tris* and *tetrakis*-complexes with acetylacetone and amines, depending on the type of metal ion, adducting ligands and reaction conditions. The mode of bonding of participating ligand and stereochemistries of the complexes have been investigated by IR, and electronic spectral and magnetic property studies. Phthalic hydrazidato ion has been suggested to act as a monoanionic mono- and bidentate ligand, where of the adducting ligands act as neutral mono- and bidentate ligand depending on the type of metal ion, adducting ligand and reaction conditions.

The present paper is an extension of previous studies [13,16] and is concerned with the reaction of *tris*-phthalic hydrazidato Cu(II) complex of type $[\text{Cu}_2(\text{HPH})_3(\text{H}_2\text{O})_6]\text{H}_2\text{O}$ with acetylacetone (acac), monoethanolamine (MEA), ethylenediamine (en), aniline (An), *p*-phenylene diamine (*p*-Phda) and bipyridine (Bipy).

The binuclear parent complex [16] has been reported to possess octahedral geometry around the Cu(II) ions. Phthalic hydrazide (H_2PH) has been suggested to act as a monobasic bidentate chelating and bridging ligand between the Cu(II) ions, coordinating through lactim group [13].



Mode of bonding of (HPH) in parent complex.

Experimental

Preparation of the ligand and complexes. Phthalic hydrazide (H_2PH) was prepared and purified by the methods reported in literature [14,15]. Phthalic hydrazide to Cu(II) complex of type $[\text{Cu}_2(\text{HPH})_3(\text{H}_2\text{O})_6]\text{H}_2\text{O}$, was prepared by the method reported earlier [16].

Mixed complexes of phthalic hydrazide (HPH), $[\text{Cu}_2(\text{HPH})_3 - (\text{H}_2\text{O})_6]\text{H}_2\text{O}$, were obtained by refluxing the suspension of parent complex (1 mM) for 1 hr. in ethanolic solution of acetylacetone (10 mM) or of amine (6 mM). The resulting solution was then filtered and its volume was reduced. The solid complexes were obtained on cooling the solution to room temperature. Complexes were separated and purified by using the method reported for phthalic hydrazidato Ni(II) complexes [13].

Physical measurements. Recording of electronic spectra, IR spectra, magnetic susceptibility measurements and elemental analysis were carried out by methods reported earlier [13].

Results and Discussion

Six coordinate binuclear parent complex, $[\text{Cu}_2(\text{HPH})_3 - (\text{H}_2\text{O})_6]\text{H}_2\text{O}$, forms four coordinate mononuclear *bis*-com-

plexes of type $[\text{Cu}(\text{HPH})_2(\text{acac})_2]\text{H}_2\text{O}$ (I) and $[\text{Cu}(\text{HPH})_2(\text{en})_2]2\text{H}_2\text{O}$ (III) with acetylacetonate and ethylenediamine respectively. It forms six coordinate mononuclear complexes of type $[\text{Cu}(\text{HPH})_2(\text{MEA})_2]$ (II) and $[\text{Cu}(\text{HPH})_2(\text{bipy})_2(\text{H}_2\text{O})]\text{H}_2\text{O}$ (VI) with monoethanolamine and bipyridine respectively whereas with aniline and *p*-phenylenediamine five coordinate binuclear complexes of types $[\text{Cu}_2(\text{HPH})_2(\text{An})(\text{H}_2\text{O})]\text{H}_2\text{O}$ (IV) and $[\text{Cu}_2(\text{HPH})_2(p\text{-Phda})(\text{H}_2\text{O})]$ (V) respectively are obtained. The analytical results are reported in Table 1.

The complexes are stable under laboratory conditions and slightly soluble in methanol, ethanol and ether and insoluble in other organic solvents. The NMR spectra of the complexes could not be recorded due to their poor solubility.

Magnetism and electronic spectra. Magnetic moment of Cu(II) complexes are found in the range of 1.50-1.90 B.M. (Table 2) indicating presence of unpaired electrons and are also consistent with the electronic spectral results in respect of stereochemistries of the complexes.

The acetylacetonato complex (I) exhibits a broad band at 14.90 and 18.08 kK in solution and solid state spectra respec-

tively. The Dq values are consistent with CuN_2O_4 [17,18] and CuN_2O_2 [5,17,18] chromophores in the literature for octahedral and square-planar geometries respectively. The appearance of shoulders at 12.74, 16.13 and 23.53 kK in the solid state spectrum may suggest the tetragonal distortion.

Ethylenediamine complex (III) shows the broad band in 18.00-20.00 kK region in solution and solid state spectra. This suggest the square-planar geometry of the complex. The Dq values are consistent with CuN_2O_2 chromophores in the literature, such as those observed in ethylenediamine complexes of Cu(II)-acetylacetonates [17] and Cu(II) aminoacidates [5].

Aniline and *p*-phenylenediamine complexes (IV and V) exhibit the broad band in 15.00-16.00 kK region. This is indicative of five coordinate distorted square-pyramidal geometry. The complexes seem to be consistent with CuNO_4 chromophores in the literature [6-8]. Appearance of a shoulder in 20.00-29.00 kK region is indicative of the binuclear complexes [4,5,19,20].

Monoethanolamine (MEA) and bipyridine (bipy) complexes (II and VI) show a broad in 15.00-16.00 kK region in-

TABLE 1. ANALYTICAL DATA.

S. No.	Compound	Colour	m.p. (°C)	C		H		N		M	
				Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)
I.	$[\text{Cu}(\text{HPH})_2(\text{acac})_2]\text{H}_2\text{O}$	Blue	360.00	51.87	51.77	4.35	4.29	9.30	9.25	10.55	10.65
II.	$[\text{Cu}(\text{HPH})_2(\text{MEA})_2]$	Brown	380.00	47.28	47.17	4.76	4.70	16.54	16.47	12.57	12.48
III.	$[\text{Cu}(\text{HPH})_2(\text{en})_2]2\text{H}_2\text{O}$	Violet	370.00	44.32	44.41	4.83	5.08	20.67	20.82	11.72	11.58
IV.	$[\text{Cu}_2(\text{HPH})_2(\text{An})(\text{H}_2\text{O})]\text{H}_2\text{O}$	Brown	349.50	45.68	45.84	3.65	3.38	12.10	12.25	21.96	21.78
V.	$[\text{Cu}_2(\text{HPH})_2(p\text{-Phda})(\text{H}_2\text{O})]\text{H}_2\text{O}$	Black	348.50	45.92	45.88	3.50	3.46	14.60	14.38	22.08	22.24
VI.	$[\text{Cu}(\text{HPH})_2(\text{bipy})_2(\text{H}_2\text{O})]\text{H}_2\text{O}$	Brown	235.00	52.12	51.95	5.10	4.88	13.02	12.98	9.84	9.98

TABLE 2. MAGNETIC MOMENTS, ELECTRONIC SPECTRA AND LIGAND FIELD PARAMETERS.

S. No.	Compound	μ_{eff} 298°K B.M.	State	Chromophore	d-d Bands	Dq	L.F.S. Es K.cal/mol
I.	$[\text{Cu}(\text{HPH})_2(\text{acac})_2]\text{H}_2\text{O}$	1.90	Ethanol Mull	CuN_2O_4	14.95 (1.007)	1.49	
				CuN_2O_2	12.74sh, 16.13sh, 18.08br, 23.53		
II.	$[\text{Cu}(\text{HPH})_2(\text{MEA})_2]$	1.87	Water Mull	CuN_2O_4	14.20 (1.55)	1.42	24.343
				CuN_2O_4	13.89sh, 14.96sh, 15.87br, 23.15		
III.	$[\text{Cu}(\text{HPH})_2(\text{en})_2]2\text{H}_2\text{O}$	1.85	Water Mull	CuN_2O_2	18.18br (1.76)		
				CuN_2O_2	13.02sh, 16.95sh, 19.23br, 22.98		
IV.	$[\text{Cu}_2(\text{HPH})_2(\text{An})(\text{H}_2\text{O})]\text{H}_2\text{O}$	1.50	Mull	CuNO_4	12.90sh, 15.87br, 22.99, 27.93sh		
V.	$[\text{Cu}_2(\text{HPH})_2(p\text{-Phda})(\text{H}_2\text{O})]\text{H}_2\text{O}$	1.52	Mull	CuNO_4	12.39sh, 14.82br, 22.99, 26.88sh		
VI.	$[\text{Cu}(\text{HPH})_2(\text{bipy})_2(\text{H}_2\text{O})]\text{H}_2\text{O}$	1.85	Mull	CuN_4O_2	13.12sh, 15.87br, 22.73	1.587	27.21

Note: Band position in kK, log E in parenthesis, $\mu = \mu_{\text{M}}$, $\xi = \text{Epsilon}$.

dicating distorted octahedral geometry [22,23]. The Dq values are consistent with CuN_2O_4 chromophores in the literature such as those in amine complexes of Cu(II)-acetylacetonates [17,18] aminoacidates [5] and carboxylates [6,21].

IR spectra. The ν M-O band of parent complex [16] at 475cm^{-1} like Ni(II) phthalic hydrazidato complexes [13], is shifted to lower frequencies by $10\text{--}5\text{ cm}^{-1}$ in acetylacetonate and amine complexes (I-VI) due to complexation with additional ligand.

The νNH and δNH bands of parent complex [16] at 3137 and 1580 cm^{-1} respectively are shifted to lower frequencies in amine complexes (II-IV) but in the acetylacetonate complex (I) these bands are shifted to higher and lower frequencies respectively. $\nu\text{C}=\text{O}$ band at 1650 cm^{-1} is shifted to lower by $15\text{--}5\text{cm}^{-1}$ in acetylacetonate and amine complexes. These results indicate that NH and C=O groups are not donors in these complexes but are generally involved in hydrogen bonding [13]. In ethylenediamine and bipyridine complexes (III,VI) lower shifted of NH and C=O bands may be the result of hydrogen bonding with coordinated water. In monoethanolamine complex (II) hydrogen bonding with C=O and NH groups

of phthalic hydrazidate ion (HPH). In acetylacetonate complex (I) the lower shift of C=O band may be due to hydrogen bonding with coordinated water, possibly due to axial coordination of water and phthalic hydrazidate ion (HPH).

In binuclear aniline and *p*-phenylenediamine complexes (IV,V) the νNH , $\nu\text{C-N}$ and $\nu\text{C}=\text{O}$ bands of the parent complex [16], are shifted to lower frequencies by $37\text{--}17$, 15 and $10\text{--}5\text{ cm}^{-1}$ respectively. These changes are indicative of the coordination through NH and C=O groups of phthalic hydrazidate ion which may behave as a bridging ligand [13].

The $\nu\text{C}=\text{N}$ band of parent complex [16] at 1606 cm^{-1} is shifted to lower frequencies in mononuclear complexes (I,II,III,VI) where as it is shifted to higher frequencies in binuclear complexes (IV,V). These results suggest the bonding through nitrogen of C=N group of phthalic hydrazidate ion in binuclear complexes where as in mononuclear complexes it is not suggested [13,16].

All above results show that the phthalic hydrazidate ion (HPH) behaves as a monodentate ligand in acetylacetonate, monoethanolamine, ethylenediamine and bipyridine complexes (I,II,III,VI) coordinating through enolic carbonyl

TABLE 3. IR SPECTRAL DATA.

S. No.	Compound	$\nu\text{OH Free}$	$\nu\text{OH Coord}$	νNH_2		νNH	$\nu\text{C}=\text{C}$	$\nu\text{C}=\text{N}$ ($\nu\text{C}=\text{C}-\text{C}=\text{N}$)
				Free	Coord			
I.	$[\text{Cu}(\text{HPH})_2(\text{acac})_2] \cdot \text{H}_2\text{O}$	3720m, br				3120w, br	1665s 1600s	1600s
II.	$[\text{Cu}(\text{HPH})_2(\text{MEA})_2]$						1550Vs	
III.	$[\text{Cu}(\text{HPH})_2(\text{en})_2] \cdot 2\text{H}_2\text{O}$	3710m, br		3450s, br		3100m, br	1635s	1595s
IV.	$[\text{Cu}_2(\text{HPH})_2(\text{An})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	3630m, br	3450s, br		3270s, br	3100m, br	1640vs	1595w
V.	$[\text{Cu}_2(\text{HPH})_2(p\text{-Phda})(\text{H}_2\text{O})]$		3350s, br		3220s	3120m, br	1640s	1605s
VI.	$[\text{Cu}(\text{HPH})(\text{bipy})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	3740m, br	3480vs		3300s, br	3130s, br	1645s	1605s 1575s

(Table 3, Continued.....)

S. No.	Compound	δNH in-plane (NH_2 Sci)	$\nu\text{C}=\text{C}$ (asym $\nu\text{C}-\text{C}-\text{C}$)	$\nu\text{Ring C-O}$ (νRing) (CH_2 Sci)*	$\nu\text{C-N}$ (CH_2 Wagg) ($\nu\text{C}-\text{CH}_3+\text{C}-\text{C}$)	νRing H.Bond δ (CH)	NH_2 Wagg (NH_2 wist) δ (CH)*	$\nu(\text{C}-\text{C} + \text{C}-\text{O})$ CH_2 rock	δNH out of plane
I.	$[\text{Cu}(\text{HPH})_2(\text{acac})_2] \cdot \text{H}_2\text{O}$	1575s	(1505s)	1455s	1375s			(950w)	865w
II.	$[\text{Cu}(\text{HPH})_2(\text{MEA})_2]$	1570s	1510s	1465s	1380s				
III.	$[\text{Cu}(\text{HPH})_2(\text{en})_2] \cdot 2\text{H}_2\text{O}$	1578s (1540w)	1495s	1460s (1445)* (1420)*	1180w(MEA) (1370s) 13753 1085w(en)	110m 1200w (1130w)		870m 885w 870w	855m 850m
IV.	$[\text{Cu}_2(\text{HPH})_2(\text{An})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	1575s	1490vs	1465s	1375s 1280w	(1085w) (1000w)	(1075w) (1075w)* (1000w)*		855m
V.	$[\text{Cu}_2(\text{HPH})_2(p\text{-Phda})(\text{H}_2\text{O})]$	(1575s)	1495vs	1465sm	1375w				850w
VI.	$[\text{Cu}(\text{HPH})(\text{bipy})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	1570s	1490s	1475m (1445s) (1440sh)	1385m	1180w			845w

 $\nu = \text{Nu}; \delta = \text{Delta}$.

(Table 3, Continued...)

S. No.	Compound	Ring vib	ρr (H ₂ O)	NH ₂ rock (CH.O.O.P bond)	$\rho\omega$ (H ₂ O)	Ring def + $\nu M-O$ (δ (Ring))	$\nu M-O$ ($\nu M-O +$ C-CH ₂)	$\nu M-N$
I.	[Cu(HPH) ₂ (acac) ₂] H ₂ O	825w 515w 495w				610w	475w	
II.	[Cu(HPH) ₂ (MEA) ₂]	845m 570w 485m		755m 720m 710m	650w		535w	335
III.	[Cu(HPH) ₂ (en) ₂] 2H ₂ O	830m		795sh 700s		545w 520w	460w	480w
IV.	[Cu ₂ (HPH) ₂ (An)(H ₂ O)] H ₂ O	825m 585w 500m	850w 700m	740m	630w	(620w) (565w) (455w)	470w	375w 370w 300w
V.	[Cu ₂ (HPH) ₂ (p.Phda)(H ₂ O)]	830w	735w		640w	(540w) (530w)	460w	330sh
VI.	[Cu(HPH)(bipy) ₂ (H ₂ O)] H ₂ O	825w 570w 495w		(920w) (890w) (770w) (730w)	630w		470w	290w

s, strong: vs, very strong: m, medium: w, weak: ρr = Rho, $\rho\omega$ = Omega, δ = Delta.

oxygen where as in aniline, *p*-phenylenediamine complexes (IV,V) it acts as a tetradentate chelating and bridging ligand.

The bidentate coordination of acetylacetone is suggested due to appearance of $\nu C=C$, $\nu C-C-C$ and $\nu M-O$ bands at 1550, 1505, and 455 cm⁻¹ respectively as they appear in other acetylacetone complexes [13,24,25].

In monoethanol amine complex (II), the appearance of νOH , νNH , $\nu C-N$ bands at 3470, 3260, 1180 cm⁻¹ respectively as new bands, which are at lower frequencies as compared with that of free amine [13], suggest bidentate coordination of amine with metal ion. Lower shift of C=O band is suggested to be due to hydrogen bonding with C=O and NH groups of phthalic hydrazidato anion. Like other metalamine complexes [26,27] it shows CH₂ rocking, NH₂ rocking bands at 870 and 755 cm⁻¹ respectively. This further support the coordination of amine with metal ion.

The ethylenediamine complex (III), like other metal complexes [17,18,25], exhibits the νNH , CH₂ rocking and $\nu M-N$ bands at 3270-3220, 870, 700 and 480 cm⁻¹ respectively suggesting the bonding of amine with metal ion. The absence of band in the 3400-3300 cm⁻¹ region indicates the bidentate coordination of amine.

The aniline and *p*-phenylenediamine complexes (IV,V) exhibit the νNH and $\nu C-N$ bands in the 3300-3250, 1280-1270 cm⁻¹ region respectively which are at lower frequencies as

compared with free amine [13,28,29]. These results show the bonding of these amines with the metal ion. Appearance of a new band due to free νNH_2 mode at 3400 cm⁻¹ in *p*-phenylenediamine complex (V) is indicative of the monodentate coordination of amine.

The coordination of bipyridine in the bipyridine complex (VI) is suggested by splitting the ν (ring) bands of free bipyridine at 1448 and 1410 cm⁻¹ into 1445, 1440 cm⁻¹ in bipyridine complex and also by splitting the CH of plane bending bands at 753 and 738 cm⁻¹ in the bipyridine complex [30,31].

In amine complexes (IV,V,VI) the appearance of νOH and $\rho\omega(H_2O)$ bands in the 5315-3450, 650-630 cm⁻¹ regions, indicates the presence of coordinated water [32-34].

Conclusion

In all the complexes (I-VI) phthalic hydrazide behaves as a monobasic ligand. It acts also as a monodentate ligand in acetylacetone, monoethanolamine, ethylenediamine and bipyridine complexes (I,II,III) and (VI), occupying possibly trans position of the octahedral framework where as acetylacetone, or amine appears to act as bidentate chelating ligands occupying cis-positions. In aniline and *p*-phenylenediamine complexes (IV and V) it acts as a tetradentate bridging ligand occupying possibly *cis*-positions of square-pyramid while the amines seem to occupy axial positions.

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