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Copper(II) Complexes with 3,8-Diphenyl-3,7-Diene-4,7-Diaza-2,9-Decadihydroximine

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Reaction of the oximine ligand 3,8-diphenyl-3,7-diene-4,7-diaza-2,9-decadihydroximine, H_2peah wih copper(II) acetate yields an inner complex salt of the type [Cu(peah)] in an alkaline alcoholic medium. When [Cu(peah)] and CuX_2 salts are allowed to react in ethanolic medium, a series of binuclear copper(II) complexes of the type [Cu_2(peah)X_2] ($X = Cl^-$, Br^-, NO_3^- or ClO_4^-] have been obtained. When an alcoholic solution of the oximine ligand is allowed to react with an ethanolic solution of copper(II) chloride having a few drops of 6N-HCl, a complex having the formula (Cu(H_2peah)Cl_2] is formed. Magnetic measurements, spectral studies and conductivity data indicate [Cu(peah)] to have square planar geometry whereas [Cu_2(peah)X_2] possess C_2 symmetry. The complex Cu(H_2peah)Cl_2] is expected to have a distorted octahedral geometry.

INTRODUCTION

Metal complexes with oximines have received much attention during recent years[1–5] as the bis complexes with copper(II), nickel(II) and cobalt(II) and tris complexes with iron(II), iron(III) and cobalt(III) have been found to be excellent ligands capable of coordinating further through unused oxygen donor atoms to give homo and hetero polynuclear encapsulation and macrocyclic metal complexes. In continuation of earlier work in the field[6, 7] we report here isolation and characterization of six complexes of copper(II) with the oximine ligand, 3,8-diphenyl-3,7-diene-4,7-diaza-2,9-decadihydroximine, abbreviated hereafter as H_2peah, of the type Cu(peah), Cu_2(peah)X_2 ($X = Cl^-$, Br^-, NO_3^- or ClO_4^-) and Cu(H_2peah)Cl_2.

EXPERIMENTAL

All the chemicals used were BDH reagents except 1,2-diaminoethane which was Loba make and 1-phenyl-1,2-propanedione-2-oxime, an Aldrich reagent.

Preparation of the oximine ligand, H_2peah

The oximine ligand 3,8-diphenyl-3,7-diene-4,7-diaza-2,9-decadihydroximine was prepared by triturating 1,2-diaminoethane and 1-phenyl-1,2-propanedione-2-oxime together in molar ratio 1:2. The mixture first becomes viscous and on cooling to 0°C a light yellow solid was obtained. It was crystallised from an acetone solution and dried under vacuum (m.p. = 170 ± 2°C, yield = 60%).

Preparation of the complexes

3,8-Diphenyl-3,7-diene-4,7-diaza-2,9-decadihydroximinatocopper(II) [Cu(Peah)]

The ligand H_2peah (3.5 g, 0.01 mol) dissolved in about 25 mL hot absolute ethanol was added to an ethanolic solution of copper(II) acetate monohydrate (2.0 g, 0.01 mol) and the mixture was cooled and concentrated at room temperature when greenish yellow crystals were separated. They were filtered and dried *in vacuo.*

Copper(II)(3,8-diphenyl-3,7-diene-4,7-diaza-2,9-decadihydroximinato) copper(II), $[Cu_2(peah)(NO_3)_2]$

3,8-Diphenyl-3,7-diene-4,7-diaza-2,9-decadihydroximinatocopper(II) (1.03 g, 0.0025 mol) was treated dropwise with an alcoholic solution of cupric nitrate hexahydrate (0.73 g, 0.0025 mol) with constant stirring. A bright green crystalline compound appeared immediately and its quantity slowly increased on standing. It was filtered, washed with alcohol, followed by ether dried under vacuum and analysed to have the formula $[Cu_2(peah)(NO_3)_2]$. The remaining three complexes were prepared using similar procedure with corresponding copper(II) salts.

Dichloro(3,8-diphenyl-3,7-diene-4,7-diaza-2,9-decadihydroximine)copper(II) $[Cu(H_2peah)Cl_2]$

The ligand (3.5 g, 0.01 mol) was dissolved in a minimum amount of absolute alcohol on warming and to it an alcoholic solution of cupric chloride dihydrate having a few drops of 6N-HCl was added. The mixture was vigorously shaken. The colour of the mixture solution immediately changed to blue and fine blue crystals were obtained. It was filtered, washed with alcohol and finally with ether and analysed after drying.

The compounds were analysed using standard procedures[8] such as copper iodometrically, halogens as their respective silver halides and carbon, hydrogen and nitrogen by semimicro combustion methods.

The infrared spectra of the ligand and copper(II) complexes were recorded on Beckmann IR-20 spectrophotometer. The conductivity measurements were made on a Systronic conductometer model 303 using dimethyl sulfoxide as a solvent. Magnetic moments were measured by the Gouy method using $Hg[Co(CNS)_4]$ as the calibrant. The absorption spectra of dimethyl sulfoxide solution of these complexes were recorded on a Cary 2390 spectrophotometer using a pair of 1 cm quartz cuvetts. Analytical, conductivity and magnetic moment data are recorded in Table-1. IR spectral data are recorded in Table-2.

RESULTS AND DISCUSSION

Infrared spectra

In the high frequency region the complex of the type $[Cu(H_2peah)Cl_2]$ shows a strong and broad band, the centre of gravity of which lies in the vicinity of 3450 cm^{-1}. The band can be assigned to (O—H) stretching vibration of the N—OH group involved in hydrogen bonding, most probably intramolecular in nature and further suggests that the ligand occurs in its neutral form. Intramolecular hydrogen bonding in oxime complexes where the protons of the N—OH groups have not been ionised or partly ionised such as $Ni(Hdmg)_2$ and related complexes are now well established and have been studied by several workers[9]. Our results are in

TABLE-1
ANALYTICAL, MAGNETIC MOMENT AND CONDUCTIVITY DATA OF THE LIGAND (H_2peah) AND COPPER(II) COMPLEXES

Ligand/Complexes (colour)	% Analysis, Found (Calcd)					μ_{eff} (B.M.)	Λ_m (in ohm^{-1} cm^2 mol^{-1})
	Cu	C	H	N	Halogen		
[H_2peah] (yellow)	—	68.65	6.30	15.98	—	—	—
[$C_{20}H_{22}N_4O_2$]	—	(68.57)	(6.28)	(16.00)	—	—	—
[Cu(peah)]	15.38	58.41	4.90	13.58	—	1.78	15
(greenish yellow)	(15.43)	(58.32)	(4.86)	(13.69)	—		
[Cu($C_{20}H_{20}N_4O_2$]							
[Cu_2(peah)Cl_2]	23.35	44.02	3.65	10.31	13.10	1.15	17
(yellowish green)	(23.26)	(43.95)	(3.66)	(10.25)	(13.00)		
[Cu_2($C_{20}H_{20}N_4O_2$)Cl_2]							
[Cu_2(peah)Br_2]	19.92	37.68	3.16	8.50	25.20	1.14	16
(brownish green)	(20.00)	(37.79)	(3.14)	(8.81)	(25.19)		
[Cu_2($C_{20}H_{20}N_4O_2$)Br_2]							
[Cu_2(peah)$(NO_3)_2$]	21.31	40.12	3.34	14.15	—	1.12	14
(green)	(21.20)	(40.06)	(3.33)	(14.02)	—		
[Cu_2($C_{20}H_{20}N_6O_8$)]							
[Cu_2(peah)$(ClO_4)_2$]	18.90	35.58	2.98	8.32	10.58	1.13	18
(deep green)	(18.84)	(35.61)	(2.96)	(8.30)	(10.53)		
[Cu_2($C_{20}H_{20}N_4O_{10}$)Cl_2]							
[Cu(H_2peah)Cl_2]	13.18	49.62	4.56	11.62	14.68	1.85	20
(blue)	(13.11)	(49.53)	(4.54)	(11.55)	(14.65)		
Cu($C_{20}H_{22}N_4O_2$)Cl_2]							

TABLE-2
IR SPECTRA (cm^{-1}) OF THE LIGAND H_2PEAH AND COPPER(II) COMPLEXES

Complex	$\nu_{(O-H)}$	$\delta_{(O-H)}$	$\nu_{(C=N)}$ (azomethine)	$\nu_{(C=N)}$ (oxime)	$\nu_{(N-O)}$
1. (H_2peah) (ligand)	3450 s, b	1700 s, b	1660 s	1400 s	1010 s
2. [Cu(H_2peah)Cl_2]	3450 s, b	1700 s, b	1600 s	1475 s	1110 s
3. Cu(peah)	—	—	1605 s	1470 s	1100 s
4. Cu_2(peah)Cl_2]	—	—	1610 s	1475 s	1050 s
5. [Cu(peah)Br_2]	—	—	1615 s	1470 s	1055 s
6. [Cu_2(peah)$(NO_3)_2$]	—	—	1610 s	1475 s	1050 s
7. [Cu_2(peah)$(ClO_4)_2$]	—	—	1615 s	1470 s	1050 s

close agreement with earlier reports. The infrared spectrum of 1-phenyl-2-hydroxyimino-propan-2-one shows a group of two bands respectively at 3415 and 3360 cm^{-1} which are fairly broad and strong implying hydrogen bonded structure involving the N—OH group. In the present series of complexes, the above assignment gains further support from the fact that in the complexes of the type [Cu(peah)] and binuclear complexes of the type $[Cu_2(peah)X_2]$, these bands fully disappear where the deprotonation of oxime proton has taken place and the ligand occurs as binegative charged ion.

The spectra of the ligand and the complex of the type $[Cu(H_2peah)Cl_2]$ show an absorption band of medium intensity at *ca.* 1700 cm^{-1} while a common aspect of all the spectra of other types of complexes *i.e.* [Cu(peah)] and $[Cu_2(peah)X_2]$ is the disappearance of this band from this position. These characteristic features lead us to believe that this band arises due to O—H deformation vibration of the N—OH group. Earlier studies on acetylacetonedioximato and diacetylazinedioximato metal chelates containing the ligands in the neutral form also show N—OH deformation vibration around 1700 cm^{-1}. This band disappears from the spectra of the inner complex salts of the types Cu(aado) and Cu(daado). Symbols H_2aado and H_2daado stand for acetylacetonedioxime and diacetylazinedioxime respectively.

The spectrum of the ligand as well as of the copper(II) complexes in the frequency region 1650–900 cm^{-1} are most valuable for the elucidation of structure and bonding. In the spectra of all the copper(II) complexes there appear two sharp bands of medium to strong intensity at about 1600 and 1500 cm^{-1} respectively. Considering their sharpness and intensity, they have been assigned to the $C\overset{...}{=}N$ stretching vibration. As the structure of the ligand shows that the ligand contains two kinds of $C\overset{...}{=}N$ groups relating to azomethine and oxime groups. The location of these bands near 1600 cm^{-1} and 1500 cm^{-1} clearly manifests that the vibrational energies of these groups are significantly different from each other.

Analyses of the available data on structurally related molecules such as H_2dmg and Schiff bases lead us to assign the high frequency and low frequency bands respectively to azomethine and oxime $C\overset{...}{=}N$ groups respectively. The $C\overset{...}{=}N$ stretching band due to >C=N—OH group in H_2dmg appears at 1450 cm^{-1} which shifts to a higher frequency region in the trinuclear dimethylglyoximato complexes and appears in the region 1590–1550 cm^{-1} giving further support to the above assignment.

In the spectrum of the ligand the sharp band at 1450 cm^{-1} is attributed to $\nu_{(C=N)}$ of the oxime group and the band at 1650 cm^{-1} is assigned to $\nu_{(C\overset{...}{=}N)}$ of the azomethine group.

It is conspicuous to observe that in all the copper(II) complexes, while the high frequency $\nu_{(C=N)}$ band has shifted to lower frequency region, the low frequency oxime $C\overset{...}{=}N$ band has undergone a blue shift. These changes in infrared absorptions appear to be caused by change in electronic environment on account of coordination with the metal ions. It is believed that the ligand is bonded to the copper(II) ion with both of the imine and oxime nitrogen atoms by donating its non-bonding electron pairs with the simultaneous metal ligand π-electron interactions. Besides above mentioned bands in the region 1650–900 cm^{-1} whose position and intensity suffers a shift on complexation, there appears a group of three bands in the spectrum of ligand which remains almost unperturbed in the spectra of all the three series of complexes. They appear at 1580 cm^{-1}, 1570 cm^{-1} and 1440 cm^{-1} and are characteristic of phenyl ring breathing modes. The first and last two bands are of medium intensity whereas the second band is very weak and appears in the form of a shoulder. These spectral features lead us to conclude that the ligand and copper(II) coordination compounds of the type Cu(peah) have structures as shown in Figs. 1 and 2 respectively. The complex $[Cu(H_2peah)Cl_2]$ is presumed to have the structure as shown in Fig. 3.

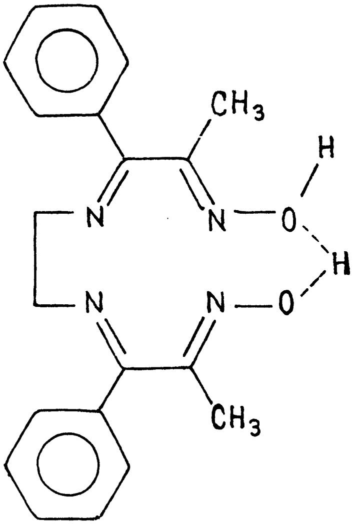

Fig. 1

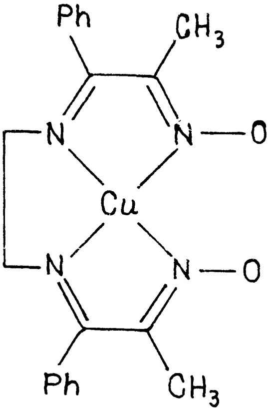

Fig. 2

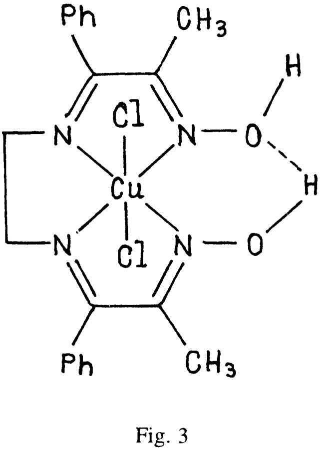

Fig. 3

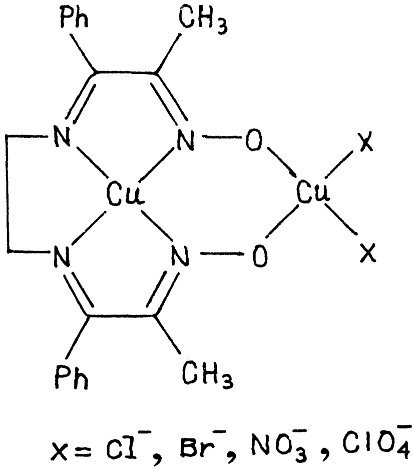

Fig. 4

The band around 1370 cm^{-1} which is present in the spectra of 1-phenyl-2-hydroxyiminopropan-1-one, the ligands [H_2(peah)] and all the three series of copper(II) complexes namely [Cu(peah)], [Cu(H_2peah)Cl_2] and [Cu_2(peah)X_2] are easily recognisable as appearing due to the CH_3 deformation vibration.

The medium intensity bands appearing in the region 1300–1100 cm^{-1} are located at 1300, 1250 and 1200 cm^{-1}. The bands at 1300 and 1200 cm^{-1} may be attributed to C—CH_3 stretching or CH_3 rocking modes when a band at 1250 cm^{-1} may be attributed to C—H in-plane vibration of the phenyl ring.

Another band of considerable intensity which appears in the spectra of ligand as well as all the three series of complexes in the region 800–700 cm^{-1} located at 770 cm^{-1} had been assigned to C—H out-of-plane vibration.

The sharp and intense band at 1010 cm^{-1} in the spectrum of the ligand is assigned to the N—O stretching vibration. This band shifts to 1100 cm^{-1} in the spectrum of the complex [Cu(peah)] as well as in 1110 cm^{-1} in the spectrum of the complex [Cu(H_2peah)Cl_2]. In the spectra of the complexes [Cu_2(peah)X_2] this band appears in the region 1055–1050 cm^{-1}. The shift of this band to higher frequency region in the spectra of [Cu(peah)] and [Cu(H_2peah)Cl_2] in comparison to the spectrum of the ligand is due to coordination of the N-atom of the NO group to the Cu-atom. The downward shift of this band in the spectra of [Cu_2(peah)X_2] in comparison to [Cu(peah)] and [Cu(H_2peah)Cl_2] indicates coordination of the O-atom of the NO group to Cu-atom of CuX_2 salts giving rise to binuclear clusters.

A few sharp and intense additional bands recorded in the spectra of [Cu_2(peah)X_2] and [Cu(H_2peah)Cl_2] in the far infrared region 600–400 cm^{-1} are believed to arise due to $\nu_{Cu—Cl}$, $\nu_{Cu—Br}$ or $\nu_{Cu—O}$ vibrational modes and support coordination of the anions Cl^-, Br^-, NO_3^- and ClO_4^- to the Cu-atom in a monodentate manner. On the basis of these spectral features, complexes of the type [Cu_2(peah)X_2] are assigned to have the structure as shown in Fig. 4.

The magnetic moment, electronic and ESR spectra and conductivity data also support the proposed structures for the complexes[10–12].

Magnetic moment and electronic spectra

The complex [Cu(H_2peah)Cl_2] has the magnetic moment 1.85 B.M. and shows a broad band at 19000 cm^{-1} and another band at 26000 cm^{-1}. The former band corresponds to the transition $^2E_g \rightarrow {}^2T_{2g}$ and the latter to charge transfer respectively. The slightly higher magnetic moment value might be due to spin-orbit coupling and absence of spin-spin interaction. The magnetic moment and electronic spectral data are suggestive of distorted octahedral geometry for the complex[13]. In The ESR spectrum of the complex, the g_{av} value is found to be 2.123. The spectrum is isotopic consisting of a single line characteristic of a regular octahedral geometry. This type of spectrum may result due to the fact that a regular octahedral stereochemistry undergoes a dynamic or pseudo rotational type of Jahn-Teller distortion[14].

The copper complex [Cu(peah)] has been found to have magnetic moment 1.78 B.M. A broad band is observed in the electronic spectrum, the centre of gravity of which lies at 14100 cm^{-1} ($\varepsilon = 15$). It can be attributed to the ligand field band due to the chromophore CuN_4. The broad band shows considerable amount of structure and represents at least two superimposed absorptions assignable to the transitions,

$$^2B_{1g} \rightarrow {}^2A_{1g} \text{ and } {}^2B_{1g} \rightarrow {}^2E_g$$

and leads us to believe that the complex [Cu(peah)] is square planar.

The complexes of the type $[Cu_2(peah)X_2]$ have μ_{eff} in the range 1.12 to 1.15 B.M. per copper atom. The electronic spectra of the complexes consist of two bands, one in the region 13000–12000 cm^{-1} and another in the region 18000–17000 cm^{-1}. The high frequency band arises due to chromophore CuN_4 and the low frequency band originates due to the chromophore CuO_2X_2 both under C_2 symmetry. The lower value of μ_{eff} is due to binuclear nature of the complexes which may be either due to overlap of Cu—Cu orbitals or due to antiferromagnetic exchange between Cu-atoms through the ligand participation. The ESR spectrum of one of the complex $[Cu_2(peah)Cl_2]$ shows one line and the anisotropy of the g-tensors is well resolved. The $g_\perp$ and $g_\parallel$ values are 2.252 and 2.038 respectively at room temperature. These values closely agree with those of the binuclear copper(II) complexes reported earlier[15]

Conductivity data

Molar conductance values for the complexes are found in the range 15–20 ohm^{-1} cm^2 mol^{-1} which support the non-electrolytic nature of the complexes.

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