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Metal Chelates of Heterocyclic Nitrogen-containing Ketones. XIX. Some Acetato– and Nitrato–Copper(II) Complexes of Phenyl-2 picolyl Ketone Hydrazone and Phenyl-2-picolyl Ketone Phenyl Hydrazone

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Abstract

Complexes of phenyl-2-picolyl ketone hydrazone and phenyl-2-picolyl ketone phenyl hydrazone, PPKhy and PPKPhy, respectively, with hydrated copper(II) acetate or hydrated copper(II) nitrate in mole ratio 1:1 or 1:2, metal:ligand, have been prepared. Various physical techniques including molar conductivity, spectral (IR, electronic, ESR and ^{1}H NMR) and magnetic measurements were used to study the nature and structure of the prepared complexes. The data showed that complexes [CuLX$_2$], X = OAc or ONO$_2$ and L = PPKhy or PPKPhy, are trigonal bipyramidal, [Cu(PPKPhy)$_2$](NO$_3$)$_2$ is square planar and [Cu(PPKhy)$_2$](NO$_3$)$_2$ is tetrahedral. The acetate and nitrate groups in the mono-ligand complexes are found to be mono- and bidentate but in the ionized sphere in the bis-ligand complexes. The ligands are present in associated form in solution via intermolecular hydrogen bond and act as neutral bidentate coordinated to the copper(II) via the pyridine and azomethine nitrogen atoms.

Introduction

Heterocyclic nitrogen-containing hydrazones and their metal complexes show very important biological effects [1–3]. Some of these compounds are used in analytical separation of many metal ions in a mixture and as analytical reagents [4–8]. The ligating properties of several hydrazone-containing compounds have been extensively studied [9–12]. In our laboratory, the coordination chemistry of several hydrazone derivatives of heterocyclic nitrogen containing ketones has been studied and reported [13–20]. No studies on the ligating properties of phenyl-2-picolyl ketone hydrazone and phenyl-2-picolyl ketone phenyl hydrazone are reported in literature. In this paper the coordination compounds of these ligands with copper(II) acetate and nitrate are presented. The nature of binding of the acetate and nitrate groups is also discussed.

Experimental

Preparation of the Organic Ligands and their Copper(II) Complexes

The heterocyclic nitrogen-containing ketone was prepared according to the method previously reported [13–15].

The hydrazones were prepared according to the following general method. A solution of phenyl-2-picolyl ketone (0.05 mol) in 50 ml absolute ethanol was treated with excess of the corresponding hydrazine solution (0.08 mol of hydrazine hydrate or 0.06 mol of phenyl hydrazine) in absolute ethanol (20 ml). The reaction mixture was refluxed gently on a water-bath for 5–7 h. On cooling, the corresponding Schiff base separated out. It was filtered, washed with ether several times, dried and recrystallized from absolute ethanol yielding pale yellow needles with melting point (m.p.) 65 °C of PPKhy and with m.p. 86 °C of PPKPhy.

The copper(II) complexes of the general formula [CuLX$_2$], X = OAc or ONO$_2$ and L = PPKHy or PPKPHy, were prepared by treating an ethanolic solution of 0.015 mol of the corresponding copper(II) salt with 0.01 mol of the corresponding ligand in ethanol (20 ml). The reaction mixture was stirred at room temperature for 2–3 h. During this period, the microcrystalline solid in each case was filtered off, washed several times with ethanol followed by ether and dried *in vacuo* over P$_2$O$_5$.

The bis-ligand copper(II) complexes, [CuL$_2$](NO$_3$)$_2$, were prepared according to the general method, *viz.*, to a 0.022 mol of the corresponding ligand in ethanol (25 ml), 0.01 mol of copper(II)

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TABLE I. Analytical Data of Phenyl-2-picolyl Ketone Hydrazone, PPKhy, Phenyl-2-picolyl Ketone Phenyl Hydrazone, PPKPhy, and their Copper(II) Complexes

Compound	Calculated (found) (%)			
	C	H	N	Cu
PPKhy	73.9(73.6)	6.2(6.1)	19.9(20.0)	
$[Cu(PPKhy)(OAc)_2]$	51.8(51.6)	5.1(5.1)	10.7(10.8)	16.2(16.1)
$[Cu(PPKhy)(ONO_2)_2]$	39.1(38.8)	3.3(3.4)	17.6(17.5)	15.9(16.1)
$[Cu(PPKhy)_2](NO_3)_2$	51.2(51.1)	4.3(4.2)	18.4(18.4)	10.4(10.4)
PPKPhy	78.9(78.6)	6.6(6.5)	14.5(14.7)	
$[Cu(PPKPhy)(OAc)_2]$	58.9(58.7)	4.9(4.8)	9.0(8.9)	13.6(13.6)
$[Cu(PPKPhy)(ONO_2)_2]$	60.7(60.5)	3.6(3.5)	14.7(14.7)	13.4(13.4)
$[Cu(PPKPhy)_2](NO_3)_2$	59.9(59.7)	5.0(5.0)	14.7(14.7)	8.3(8.3)

nitrate in ethanol (20 ml) was added. The reaction mixture was stirred for 3–6 h at the room temperature. During this period a precipitate of the corresponding copper(II) complex began to appear. On standing for several hours, microcrystalline solids were formed. The precipitates were filtered off, washed several times with ether and dried *in vacuo* over P_2O_5.

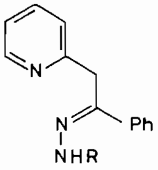
The elemental analyses were determined as previously reported [13] and are given in Table I.

Physical Measurements

All measurements were carried out as reported before [13–18].

Results and Discussion

The interaction of phenyl-2-picolyl ketone with hydrazine hydrate or phenyl hydrazine in ethanol gave the corresponding hydrazone 1. The ^1H NMR spectra of PPKhy and PPKPhy were measured in $CDCl_3$ at room temperature. The spectrum of PPKhy exhibits a broad medium signal centered at δ 6.20 ppm which could be assigned to the $-NH_2$ protons in the hydrazine residue. This signal disappeared on repeating the measurement in the presence of D_2O. The characteristic signal of $-CH_2-$ protons appeared as a strong signal at δ 4.01 ppm. In the region of δ 6.96–8.25 ppm the spectrum displays a multicomponent signal which is attributed to the aromatic protons. On the other hand the spectrum of PPKPhy under the same conditions gave a strong sharp signal at δ 4.08 ppm due to the $-CH_2-$ protons. The aromatic protons are traced from the multicomponent signal in the δ 6.08–8.50 ppm. A moderate broad signal at δ 11.30 ppm appeared in the spectrum, it disappeared on addition of D_2O. This signal is attributed to the imino proton of the hydrazine part. The position of the signal characteristic of the imino protons can be attributed to the effect of the phenyl group on its protons and/or to some sort of molecular association. A third assumption is the presence of this compound in two different tautomeric forms, namely hydrazo-azo structures, Scheme 1. Some authors [21] have reported that the hydrazone form is more stable than the azo-form by 9 kcal/mol, therefore, the tautomeric effect can be ruled out. On recording the spectrum for various concentrations, the position of the iminoproton signal showed upfield shift on lowering the concentration. Accordingly, intermolecular hydrogen-bonding may be assumed which is broken on dilution; this effect may be the pronounced factor. Therefore, structure b in Scheme 1 is the more probable form.



R = H or Ph

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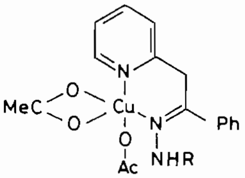

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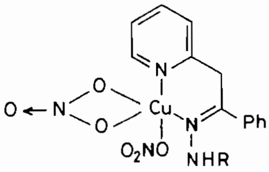

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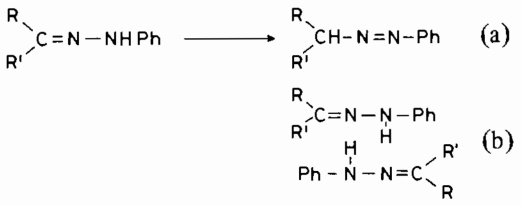

Scheme 1.

TABLE II. Characteristic Infrared Bands (cm^{-1}) of PPKhy, PPKPhy and their Copper(II) Complexes[a]

Compound	ν(C=N) (azometh)	ν(C=N) (arom)	ν(NH)	ν(N–N)	ν(Cu–N)	ν(Cu–Py)
PPKhy	1600s	1580s	3200–3450b	995m		
$[Cu(PPKhy)(OAc)_2]$	1625s	1555s	3300–3460b	1020m	395s	270m
$[Cu(PPKhy)(ONO_2)_2]$	1615m	1565s	3280–3490b	1015m	380m	265m
$[Cu(PPKhy)_2](NO_3)_2$	1620s	1565m	3185–3490b	1020s	390s	260m
PPKPhy	1590s	1575s	3000–3500b	1005s		
$[Cu(PPKPhy)(OAc)_2]$	1610s	1560s	3340–3480b	1020m	340m	245m
$[Cu(PPKPhy)(ONO_2)_2]$	1615s	1560m	3220–3480b	1015s	345m	245m
$[Cu(PPKPhy)_2](NO_3)_2$	1615m	1560m	3180–3490b	1020m	340m	240s

[a] s = strong, m = medium and b = broad.

Infrared Spectra

The infrared spectra of the ligands and their copper(II) complexes with their tentative assignments are given in Table II. The IR spectra of the free ligands exhibit a medium broad band in the 3000–3500 cm^{-1} region due to symmetric and asymmetric vibrational modes of the –NH– grouping. This band is not greatly affected upon complexation. The free ligands exhibit a strong to medium band at 995 and 1005 cm^{-1} for PPKhy and PPKPhy, respectively, characteristic of ν(N–N) frequency [22]. This band exhibits a positive shift in all complexes, indicating its participation in coordination. The strong bands at 1590–1620 and 1570–1580 cm^{-1} were attributed to the different vibrational modes of C=N of pyridine and azomethine, respectively. These bands exhibit opposite shifts in all copper(II) complexes, indicating their participation in coordination. The vibrational frequency of the azomethine C=N is shifted towards higher wave numbers, whereas that due to pyridine C=N exhibits negative shift. Furthermore, the ring breathing frequencies appeared at 1040 and 1030 cm^{-1}, and that due to δPy at 630 and 635 cm^{-1}, respectively. These bands exhibit a positive shift upon complexation indicating the coordination of pyridine to the copper ion.

The acetato–copper(II) complexes, $[CuL(OAc)_2]$, display bands at 1570–1600 and 1415–1425 cm^{-1} due to the asymmetric and symmetric modes of vibration characteristic of CH_3COO, respectively, and with $\Delta\nu = 175–155$ cm^{-1}, which is consistent with the bidentate nature of the acetate group [23]. Another series of bands is displayed at 1595 and 1390 cm^{-1} for PPKhy and at 1635 and 1390 cm^{-1} for PPKPhy, with $\Delta\nu = 205$ and 280 cm^{-1}, respectively, indicating the monodentate nature of this group [23]. Based on the prementioned infrared, analytical and molar conductivity data, structure 2 could be assumed.

With regard to the nitrato-complexes, the IR spectra of the mono-ligand complexes display bands at 1470–1480 (B_2), 1265–1280 (A_1), 1010–1020 (A_2) and 740–760 cm^{-1}, as well as a series of bands at 1340–1350 and 810–816 cm^{-1} which are characteristic of bi- and monodentate coordination of the nitrate group, respectively. Therefore, structure **3** could be assumed.

Conductance, Magnetic and Spectral Data

The molar conductivity of the complexes $[CuLX_2]$, X = OAc or ONO_2 and L = PPKhy or PPKPhy, as 10^{-3} M solutions in nitrobenzene at 26 °C showed that they are non-electrolytes. On repeating the measurements in dimethylformamide solvent under the same conditions, values of 75.52–82.66 ohm^{-1} cm^2 mol^{-1} are obtained. These values are still less than those characteristic of 1:1 electrolytes in this solvent [14–18]. This could be attributed to a partial dissociation and/or partial replacement of the anion by the solvent molecules. The molar conductivity values of $[CuL_2](NO_3)_2$ as 10^{-3} M in nitrobenzene at room temperature are indicative of 1:2 electrolytes.

The room temperature magnetic moments of the complexes under investigation, Table III, are characteristic of one unpaired electron. The magnetic moment values are slightly decreased with decreasing temperature. This temperature effect and the higher value than that of the spin only value (1.73 μB) at room temperature imply the presence of a low-lying excited term which at high temperature is able to mix some of its orbital angular momentum with the spin angular momentum of the ground state via spin–orbit coupling [24–27]. This mixing is quite common for copper(II) complexes with distorted ligand fields [24–26].

The nujol mull electronic spectra of $[CuLX_2]$, L = PPKhy or PPKPhy and X = OAc or ONO_2, are given in Table III. The spectra exhibit a band in the visible region at 13 180–13 000 and 13 350–13 125 cm^{-1} for PPKhy and PPKPhy, respectively, and a shoulder at a lower (11 145–11 000 cm^{-1}) energy side. These spectral features are characteristic of copper(II) in a trigonal bipyramidal ligand field [28, 29]. Assuming a D_{3h} symmetry, the main

TABLE III. Magnetic (μ_B) Electronic Spectral (cm^{-1}) and Electron Spin Resonance Spectral Data of Copper(II) Complexes

Compound	μ_{eff}	Spectral data	ESR data		
			$g_\parallel$	$g_\perp$	g_{av}
[Cu(PPKhy)(OAc)$_2$]	1.78	13180, 11140	2.01	2.19	2.130
[Cu(PPKhy)(ONO$_2$)$_2$]	1.81	13000, 11050	2.02	2.18	2.127
[Cu(PPKhy)$_2$](NO$_3$)$_2$	2.02	18370, 14420, 13490, 12860, 10800	2.26	2.05 2.01	2.119
[Cu(PPKPhy)(OAc)$_2$]	1.78	13350, 11000	2.03	2.18	2.129
[Cu(PPKPhy)(ONO$_2$)$_2$]	1.80	13120, 11100	2.03	2.17	2.122
[Cu(PPKPhy)$_2$](NO$_3$)$_2$	1.81	16810, 14650	2.24	2.05	2.113

band can be assigned to $^2A' \rightarrow {}^2E'$ and the shoulder $^2A' \rightarrow {}^2E''$ transitions. This is similar to the data reported for similar copper(II) complexes with known crystal structure [28, 29].

The electronic spectra of [Cu(PPKPhy)$_2$](NO$_3$)$_2$ either in nujol or in 1,2-dichloroethane are similar and rather consistent with that characteristic of copper(II) in square planar ligand field [30]. The spectrum exhibits a multicomponent band covering the range of 16855–16300 and 15400–14650 cm^{-1} due to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, in a square planar ligand field. The band due to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition can not be identified, but it may be responsible for the asymmetric nature of the second band [30].

The spectrum of [Cu(PPKhy)$_2$](NO$_3$)$_2$ exhibits four bands at 18370, 14420, 13490 and 10870 cm^{-1}. In addition, a weak shoulder at 12860 cm^{-1} was observed, Table III. The spectral features are similar to those reported for copper(II) ion in a tetrahedral environment [18, 30]. The crystal field and molecular orbital calculations for the distorted tetrahedral copper(II) complexes yielded the energy level sequence, $d_{xz} \gg d_{x^2-y^2} > d_{yz} > d_{z^2} > d_{xy}$. Since $d_{x^2-y^2}$ and d_{z^2} orbitals both belong to the a_1 irreducible representation of the C_{2v} point group, the levels are mixed and the indicated energy level sequence denotes the dominant d-orbital percentage of the states [31, 32]. The band at 13490 cm^{-1} is accordingly assigned to $d_{xy} \rightarrow d_{xz}$ promotion and that at 10870 cm^{-1} to $d_{yz} \rightarrow d_{xz}$ transition with the remaining transitions contributing the overall band envelope.

The polycrystalline ESR spectra of [CuLX$_2$], X = OAc or ONO$_2$ and L = PPKhy or PPKPhy, at room temperature are shown in Fig. 1. In all cases, the first derivative ESR spectrum shows only two g-values which are the reverse of these of copper(II) complexes in a normal elongated tetragonal environment [33]; *i.e.*, the [CuLX$_2$] complexes have $g_\perp > g_\parallel$. The analysis of the spectra gave g-values listed in Table III. Since these complexes have a trigonal bipyramidal structure, the g-values are given from the relations [34]: $g = 2.0023 - 6\ \lambda/\Delta$ and $g_\parallel = 2.00$, where Δ is the separation energy, $E(a_1) \rightarrow E(e'')$, analogous to those for compressed tetragonal environment. From the data in Table III, the low $g_\parallel$-values are very close to 2.00 and $g_\perp > g_\parallel$ consistent with $^2A'$ ground state in D_{3h}. The deviation of the lowest g-values from the theoretical value could be due to the distortion from the ideal trigonal bipyramidal configuration for these complexes and also to the exchange coupling effect [12, 16]. The broadening in the spectra could be explained as follows: if the interaction between the individual copper(II) ions is solely dipole–dipole, then each line in the anisotropic ESR spectra is visibly broadened [14, 35]. However, when the interaction involves exchange coupling between crystallographically equivalent sites, then the absorption signals appear sharper, *i.e.*, exchange narrowed.

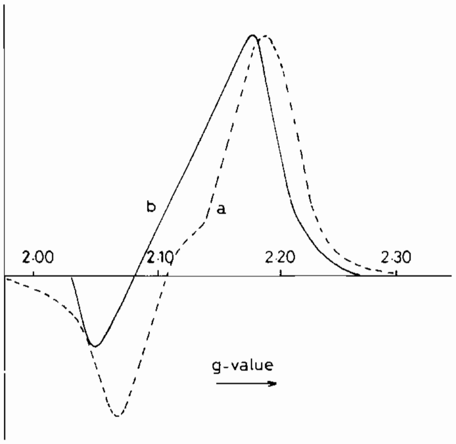

Fig. 1. First derivative ESR spectra of: (a) [Cu(PPKhy)(OAc)$_2$]; (b) [Cu(PPKPhy)(OAc)$_2$] at 25 ± 1 °C.

The room temperature X-band ESR spectrum of [Cu(PPKPhy)$_2$](NO$_3$)$_2$ was found to be of axial type, giving $g_\parallel = 2.24$ and $g_\perp = 2.05$. From the spectrum the copper hyperfine could be determined (189×10^{-4} cm^{-1}) but we could not observe the nitrogen hyperfine lines. On recording the spectrum as CH$_2$Cl$_2$ frozen glass we could determine the nitrogen hyperfine lines to be 15×10^{-4} cm^{-1}; then the aver-

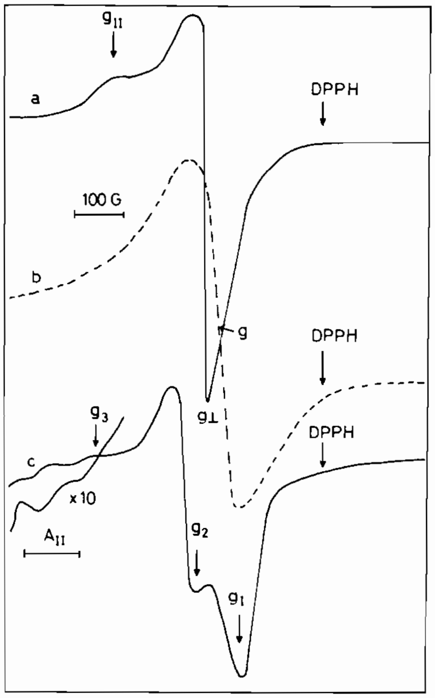

Fig. 2. X-band ESR spectra of [Cu(PPKhy)$_2$](NO$_3$)$_2$ as: (a) polycrystalline at 25 ± 1 °C; (b) CH$_2$Cl$_2$ at 25 ± 1 °C; (c) CH$_2$Cl$_2$ frozen glass.

age hyperfine splitting constant (A) amounts 72.9×10^{-4} cm^{-1}. The resolution of copper hyperfine lines in this complex could be attributed to the decreased dipolar interaction [17, 18, 36]. This reduction may be due to the orientation of the bulky –NHPh group in a manner so as to increase the separation between successive planes containing the planar CuN$_4$ units, such as has been reported in the crystal structure of hexabis(imidazole)copper(II)-(NO$_3$)$_2$. This resulted in partial resolution of the copper hyperfines.

The ESR spectrum of [Cu(PPKhy)$_2$](NO$_3$)$_2$ at room temperature is shown in Fig. 2. The spectrum is typical of tetragonal giving $g_{\perp} = 2.07$, $g_{\parallel} = 2.26$ and $g_{av} = 2.12$. The G-factor calculated from the relation, $G = g_{\parallel} - 2/g_{\perp} - 2$, gives a value of 5.20, indicating the absence of interaction between copper(II) centers in the solid state; the local tetragonal axes have parallel alignment or are slightly misaligned. The improved resolution of the g and hyperfine anisotropy of this copper(II) complex in frozen glass is apparent in Fig. 2. In the spectrum the nitrogen hyperfine lines are absent. The anisotropic coupling could be estimated to 60.5×10^{-4} cm^{-1}, which is uncommon for copper(II) complexes and especially those not containing sulphur donor ligands. On repeating the measurement in CH$_2$Cl$_2$ at room temperature, only a single line spectrum is observed, Fig. 2. Similar spectra for distorted tetrahedral copper(II) complexes are reported [37]. The appearance of a single line spectrum can be attributed to the small anisotropic superexchange value. The small hyperfine coupling constant of this complex could be associated with the metal 4s and 4p admixture into the ground state [13–15].

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