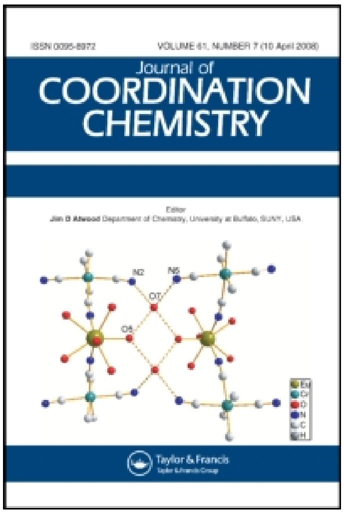

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Cobalt(II) and Copper(II) Complexes of (2-Acetylpyridine)-(5,6-Diphenyl-[1,2,4]Triazin-3-YL) Hydrazone

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COBALT(II) AND COPPER(II) COMPLEXES OF (2-ACETYLPYRIDINE)-(5,6-DIPHENYL-[1,2,4]TRIAZIN-3-YL) HYDRAZONE

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A series of cobalt(II) and copper(II) complexes of (2-acetylpyridine)-(5,6-diphenyl-[1,2,4]triazin-3-yl) hydrazone, APyTHy, L, having the formulae $[LMCl_2]\cdot nH_2O$, $[L_2Cu(H_2O)_2](ClO_4)_2$ and $[L_2M]X_2\cdot nH_2O$ ($X = ClO_4$ or OAc; M = Co or Cu and $n = 0$, 2 or 4) were isolated and characterized by elemental analysis, molar conductance, magnetic moment and IR, electronic and ESR spectral measurements. The IR spectra indicate that APyTHy behaves as a neutral tridentate ligand, coordinating via a triazine-N, azomethine-N and pyridine-N, except for $[LCuCl_2]$ and $[L_2Cu]X_2\cdot nH_2O$ ($X = OAc$ or ClO_4), where it acts as a bidentate, not using the triazine-N in complexation. The magnetic moment and electronic spectral data suggest a distorted octahedral structure for 1 : 2 Co(II) complexes, a tetrahedral geometry for 1 : 2 Cu(II) complexes and a trigonal bipyramidal structure for $[LCu(H_2O)_2](ClO_4)_2$ and $[LMCl_2]\cdot nH_2O$ ($M = Co^{II}$ or Cu^{II}; $n = 0$ or 2) complexes. Upon heating the green $[LCuCl_2]\cdot 2H_2O$, brown square planar $[LCuCl_2]$ was produced. The mixing coefficients and covalency factors for the copper(II) complexes estimated from the combined X-band ESR *g*-values and electronic d–d transitions using Reinen's method imply that the CuN_3X_2 chromophore is considerably distorted towards square pyramidal.

Keywords: Cobalt; Copper; Hydrazone; Triazine

INTRODUCTION

1,2,4-Triazine derivatives are biologically active [1–4] and are used in analytical chemistry for the determination of some metal ions [5–8]. It is known that the activity of some biologically active organic compounds may be modified when their ligating potential to metal ions is utilized. The interaction of copper(II) and cobalt(II), which play vital roles in a number of biological processes, with therapeutically important nitrogen heterocyclic bases is also a subject of considerable interest. In continuation of earlier work on transition metal complexes of 1,2,4-triazines [9,10], we report here the synthesis and structural studies of the cobalt(II) and copper(II) complexes of the

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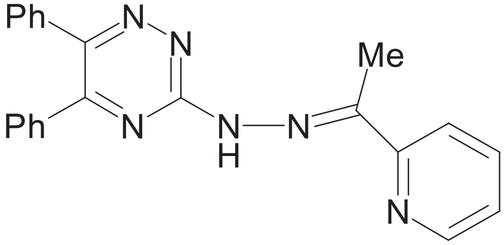


FIGURE 1 Structure of (2-acetylpyridine)-(5,6-diphenyl-[1,2,4]triazin-3-yl) hydrazone.

new potentially biologically active (2-acetylpyridine)-(5,6-diphenyl-[1,2,4]triazin-3-yl) hydrazone, APyTHy, L (Fig. 1).

EXPERIMENTAL

Synthesis of (2-Acetylpyridine)-(5,6-diphenyl-[1,2,4]triazin-3-yl) hydrazone, APyTHy, L

APyTHy was prepared by dropwise addition of an ethanolic solution (30 cm^3) of 2-acetylpyridine (1.21 g, 0.01 mol) to an ethanolic solution (100 cm^3) of 3-hydrazino-5,6-diphenyl-1,2,4-triazine (2.63 g, 0.01 mol), prepared according to the reported method [9]. The reaction mixture was stirred for 1 h at room temperature and the solid product formed on cooling was filtered off, recrystallized from ethanol and dried to give pure APyTHy as yellow crystals with mp 188°C; yield 75%.

Synthesis of the Complexes

Cobalt(II) and copper(II) complexes of L were prepared according to the following procedure: a hot solution of the ligand L (1.71 g, 0.005 mol) in EtOH (50 cm^3) was added to a hot EtOH solution (50 cm^3) of the divalent cobalt(II) and copper(II) salts [$CoCl_2 \cdot 6H_2O$, $Co(OAc)_2 \cdot 4H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, anhydrous $CuCl_2$ and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.005 mol)]. For 1 : 2 (M : L) complex preparation, the same amounts of the metal salts as in the 1 : 1 preparations were added to a hot solution of the ligand (0.01 mol) in EtOH (100 cm^3). The reaction mixture was heated under reflux for 1 h for the copper(II) complexes and 3 h for the cobalt(II) complexes, with occasional stirring. After cooling to room temperature, the precipitated product was filtered off, washed with EtOH followed by Et_2O and dried in vacuum over P_4O_{10}.

Measurements

IR spectra were recorded as KBr discs on a Perkin-Elmer 1430 ratio recording spectrophotometer in the 4000–200 cm^{-1} range. Electronic spectra were recorded on a Shimadzu U 310/PC spectrometer. The mass spectrum of the organic compound was recorded on a Shimadzu GCMS-QP 1000 EX gas chromatograph mass spectrometer. The ion source was set at 25°C and the direct insertion probe (DIP) was gradually heated from 50 to 3000°C. The electron multiplier was maintained at 1500 V and the electron energy was 70 eV. The ^1H NMR spectrum of the ligand was recorded on a

Varian 300-MHz NMR spectrometer in d^6-DMSO as solvent using tetramethylsilane (TMS) as internal standard. The X-band ESR spectra were recorded on a Radiopan SE/X2543 spectrometer with a rectangular TE102 cavity and 100 kHz modulation field (Pazan, Poland) at room temperature (300 K) and liquid nitrogen temperature (LNT) in the solid state and in CH_2Cl_2 solution using DPPH as the *g* marker ($g = 2.0036$). Magnetic susceptibilities were measured by using the Faraday balance technique. Diamagnetic corrections were made using Pascal's constants. Molar conductances in DMF (10^{-3} M solution) were measured at 25°C on a Systronics model 303 conductivity meter. Microanalyses of C, H and N were carried out using a Perkin-Elmer 2400 CHN elemental analyzer. The complexes were analyzed for their metal content by EDTA titration.

RESULTS AND DISCUSSION

Characterization of the Ligand L

The mass spectrum of the free ligand L showed the molecular ion peak M^+ at *m*/*z* 366; and fragments at *m*/*z* 288 (as the base peak) and 351 assignable to molecular weights of cations formed by elimination of pyridine and methyl radicals from the molecular ion, respectively. The ^{1}H NMR spectrum of the ligand L showed chemical shifts (δ/ppm) at 2.4 (3H, CH_3, singlet), 7.5 [12H (10H, two C_6H_5 + 2H, Py–H in positions 4 and 5), multiplet], 8.3 (1H, Py–H in position 3, doublet) and 9 (1H, N–H, singlet). The IR spectrum of L displayed bands at 3229, 1637, 1611, 1545, 1466 and 992 cm^{-1} assigned to ν(N–H), ν(C=N) of the azine, ν(C=N) of the pyridine moiety, ν(C=N) and ν(N=N) of the triazine moiety, and ν(N–N) of the hydrazone, respectively [11–13]. The narrow nature of the ν(N–H) band indicates its existence as a free NH group.

Characterization of the Complexes

Interaction of cobalt(II) and copper(II) salts with L in molar ratios 1 : 1 and 1 : 2 (M : L) in ethanol under refluxing conditions produced complexes with stoichiometries 1 : 1 and 1 : 2 (M : L), respectively, as listed in Table I. Most of the complexes melt above 250°C but a few of them decompose. The complexes are air stable, partially soluble in common organic solvents such as EtOH, MeOH and Me_2CO, but freely soluble in DMF and DMSO. The molar conductances of 10^{-3} M solutions of the complexes in DMSO suggest that the chloro complexes are non-electrolytes but the acetate and perchlorate complexes are 1 : 2 electrolytes [14].

Infrared Spectra

The characteristic IR bands of the free ligand and its metal complexes along with their assignments are given in Table II. The IR spectra of all complexes showed some broadness and a downward shift relative to that of the free ligand L for the band characteristic of ν(N–H), which appeared in the range 3244–3250 cm^{-1}. In some cases it may be overlapped with the ν(OH) of H_2O molecules.

The IR spectra of $[LCoCl_2]$, $[L_2Co](OAc)_2 \cdot 4H_2O$, $[L_2Co](ClO_4)_2 \cdot 2H_2O$, $[LCuCl_2] \cdot 2H_2O$ and $[LCu(H_2O)_2](ClO_4)_2$ showed shifts to lower wavenumbers in the ν(C=N) of

TABLE I Analytical data and some physical properties of L and its metal complexes

Compound	*Colour*	*Found* (*calcd*) (%)				Λ_{eff}[a]	μ_{eff} (BM)	$d \rightarrow d$ *bands*[b] (cm^{-1})
		C	*H*	*N*	*M*			
L	Yellow	72.0	4.9	22.1				
$C_{22}H_{18}N_6$		(72.1)	(4.9)	(22.9)				
$[LCoCl_2]$	Brown	52.9	3.3	16.8	11.8	3.7	3.77	15 700, 17 500, 19 200
$C_{22}H_{18}N_6Cl_2Co$		(53.2)	(3.6)	(16.9)	(11.9)			
$[L_2Co](OAc)_2 \cdot 4H_2O$	Black	58.3	5.0	17.0	6.0	148.6	2.05	9300, 15 600, 17 300, 19 800
$C_{48}H_{50}N_{12}O_8Co$		(58.7)	(5.1)	(17.1)	(6.0)			
$[L_2Co](ClO_4)_2 \cdot 2H_2O$	Black	51.5	4.1	16.6	5.7	157.9	2.28	9300, 15 400, 17 200, 20 200
$C_{44}H_{40}N_{12}O_{10}Cl_2Co$		(51.5)	(3.9)	(16.4)	(5.7)			
$[LCuCl_2] \cdot 2H_2O$	Green	49.6	4.3	15.5	11.7	6.1	1.92	10 400, 13 300, 15 600
$C_{22}H_{22}N_6O_2Cl_2Cu$		(49.2)	(4.1)	(15.7)	(11.8)			
$[LCuCl_2]$	Brown	52.4	3.9	16.7	12.7	3.0	1.78	14 000, 17 000b
$C_{22}H_{18}N_6Cl_2Cu$		(52.7)	(3.6)	(16.8)	(12.7)			
$[L_2Cu](OAc)_2 \cdot 2H_2O$	Green	60.3	4.5	17.8	6.6	150.8	2.13	10 800, 13 460, 14 400, 18 400
$C_{48}H_{46}N_{12}O_6Cu$		(60.7)	(4.8)	(17.7)	(6.7)			
$[LCu(H_2O)_2](ClO_4)_2$	Dark green	39.3	3.6	12.8	9.5	159.1	1.89	10 800, 13 700, 15 800
$C_{22}H_{22}N_6O_{10}Cl_2Cu$		(39.7)	(3.3)	(12.6)	(9.6)			
$[L_2Cu](ClO_4)_2$	Green	51.4	3.5	16.1	6.5	161.6	2.18	10 900, 13 400, 14 400, 18 480
$C_{44}H_{36}N_{12}O_8Cl_2Cu$		(51.3)	(3.6)	(16.9)	(6.4)			

[a] Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) of 10^{-3} M in DMF solution at 25°C. [b] Nujol mull electronic spectra at room temperature.

TABLE II Selected IR spectral bands (cm^{-1}) of L and its metal complexes

Compound	$\nu(NH)$ *and/or* $\nu(OH)$	$\nu(C{=}N)$ *Azomethine*	$\nu(C{=}N)$ *Triazine*	$\nu(C{=}N)$ *Pyridine*	$\nu(N{=}N)$ *Triazine*	$\nu(N{-}N)$ *Hydrazone*	$\nu(M{-}N)$
L	3229s	1637m	1611m	1545s	1466m	992s	
$[LCoCl_2]$	3248m	1622m	1597m	1563s	1441m	1023s	454m 409m 316s
$[L_2Co](OAc)_2 \cdot 4H_2O$	3244m 3420b	1622m	1596m	1566s	1434m	1024s	449m 409m 316s
$[L_2Co](ClO_4)_2 \cdot 2H_2O$	3244m 3414b	1620s	1595s	1564s	1437m	1024m	452w 409w 315s
$[LCuCl_2] \cdot 2H_2O$	3443b	1618s	1600m	1560s	1444m	1021s	454m 408m 317s
$[LCuCl_2]$	3140m	1618m	1598m	1558s	1467m	1025s	461m 407m
$[L_2Cu](OAc)_2 \cdot 2H_2O$	3366b	1619s	1586sh	1558s		1024s	458m 407m
$[LCu(H_2O)_2](ClO_4)_2$	3170m	1624s	1596m	1560s	1438m	1025sh	444m 409m 316s
$[L_2Cu](ClO_4)_2$	3150m	1622s	1596m	1546s	1466m	1022sh	440m 408m

the azomethine of both the hydrazone and triazine moieties by 13–19 and 11–16 cm^{-1}, respectively, and in the ν(N=N) of the triazine moiety by 22–28 cm^{-1} and shifts to higher wavenumbers in the ν(C=N) band of the pyridine ring and in the ν(N–N) hydrazone group by 13–21 and 25–29 cm^{-1}, respectively, when compared with the corresponding values for the ligand. These data, in addition to the appearance of the ν(N–H) band in the complexes, indicate that the ligand L acts as a neutral tridentate ligand bonded to the metal ions via a hydrazone, pyridine and triazine nitrogen atom in these complexes. This result is further supported by the appearance of three new weak bands in the ranges 444–454, 408–409 and 390–395 cm^{-1}, characteristic of ν(M–N) of azomethine, pyridine and triazine nitrogen atoms, respectively, indicating the bonding of the metal ions in these complexes simultaneously to these three nitrogen atoms [15,16].

The spectra of $[LCuCl_2]$, $[L_2Cu](OAc)_2 \cdot 2H_2O$ and $[L_2Cu](ClO_4)_2$ do not show appreciable change in position of the ν(C=N) band of the triazine moiety but shifts to lower and higher wavenumbers in the ν(C=N) of the azomethine of hydrazone and pyridine moieties, respectively, by 12–19 and 10–15 cm^{-1}. These observations suggest participation of azomethine and pyridine nitrogen atoms in bonding to metal ions in these complexes. The ν(N–N) mode, observed at 992 cm^{-1} in the free ligand L, shifts to higher wavenumber by 31–33 cm^{-1} in these complexes, indicating the involvement of one of the nitrogen atoms of the N–N group in bonding, that is the azomethine nitrogen. Accordingly, the ligand L acts as a neutral bidentate ligand coordinated to the copper(II) ion via the azomethine and pyridine nitrogen atoms in these complexes. The spectra of the acetate-containing complexes display relatively strong bands at 1641–1658 cm^{-1}, indicating the ionic nature of the acetate in these complexes [17].

In the perchlorate complexes, two intense bands appear at 1082–1095 and 935–943 cm^{-1}, characteristic of ionic perchlorate [17]. The spectra of $[LCoCl_2]$ show a new weak band at 342 cm^{-1} assigned to ν(Co–Cl) [17]. However, because the organic ligand absorbs strongly below 270 cm^{-1}, no attempts were made to assign the ν(Cu–Cl) band in the spectra of the chloro copper(II) complexes. The fact that the tests for chloride ion with $AgNO_3$ are only given after decomposing the complexes and not in the solutions confirms the presence of the chloride ion in the coordination sphere.

In the IR spectra of the hydrated complexes, broad intense bands centred at *ca.* 3400 cm^{-1} and weak bands at *ca.* 1650 cm^{-1} due to water molecules are clearly seen.

Electronic and Electron Spin Resonance Spectra and Magnetic Moments

The electronic spectra of the organic ligand L and its metal complexes were measured as nujol mulls. The free ligand L showed bands at 39 200 and 30 200 cm^{-1} due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, within the molecule. In the metal complexes, the former band slightly red-shifted while the latter was replaced by intense bands at *ca.* 32 300–30 800 and less intense ones at 25 300–22 500 cm^{-1} that could be assigned to various charge transfer transitions within the complexes. This is in addition to $d \rightarrow d$ transition bands above 20 000 cm^{-1} (Table I).

The magnetic moment for [LCoCl$_2$], 4.21 BM, is in accord with high-spin cobalt(II) complexes [18]. Gupta and Gupta [19] and Sacconi [20] postulated an overall electronegativity scale ($\Sigma\chi$) and an overall nucleophilic reactivity constant scale (Σn°) to estimate the spin state for donors of five-coordinate cobalt(II) complexes with different terdentate ligands. Following these procedures, the estimated values of $\Sigma\chi$ and Σn° for the CoN$_3$Cl$_2$ chromophore in [LCoCl$_2$] are 14.87 and 15.38, respectively, which are consistent with high-spin cobalt(II) complexes. Gillespie's analysis [21] in terms of valence shell electron pair repulsions (VSEPRs) led to the conclusion that the regular trigonal bipyramidal configuration favours low-spin cobalt(II) complexes. Norgett and Venanzi [22] stated that a distortion of the equatorial angles in a trigonal bipyramid decreases the separation between orbitals, favouring a high-spin configuration. These considerations and the magnetic moment value of [LCoCl$_2$] indicate a distorted trigonal bipyramidal configuration for the CoN$_3$Cl$_2$ chromophore in this complex. The nujol mull electronic spectrum of [LCoCl$_2$] exhibits bands in the visible region at 15 700, 17 500 and 19 200 cm^{-1}. This spectrum resembles those reported for distorted trigonal bipyramid cobalt(II) complexes containing the CoN$_3$Cl$_2$ chromophore [23,24].

The magnetic moment values of [L$_2$Co](OAc)$_2 \cdot 4$H$_2$O and [L$_2$Co](ClO$_4$)$_2 \cdot 2$H$_2$O are 2.05 and 2.26 BM, respectively, in the range reported for low-spin six-coordinate cobalt(II) complexes [25]. The electronic spectra of these two complexes display bands at *ca.* 9300 (ν_1) and 15 600 cm^{-1} (ν_2) with a broad-band envelope at *ca.* 19 500 cm^{-1} (ν_3) showing two features at *ca.* 17 200 and 20 000 cm^{-1}. These spectra agree with those published for low-spin distorted octahedral cobalt(II) complexes having effective D_{4h} symmetry [21]. Following the splitting diagram for low-spin d^7 configuration in D_{4h} symmetry, the bands at 15 600, 17 200 and 20 000 cm^{-1} could be assigned to ^{2}A$_{1g} \rightarrow {}^2$E$_g$ (^{2}T$_{2g}$), $\rightarrow {}^2$B$_{2g}$ and $\rightarrow {}^2$A$_{2g}$ transitions, respectively [26].

The room temperature magnetic moment values of the copper(II) complexes (Table I) are in the range 1.78–2.18 BM, characteristic of magnetically dilute copper(II) complexes with one unpaired electron. The large spin-only magnetic moment [1.73 BM per Cu(II)] is due to spin–orbit coupling. The nujol mull electronic spectra of [LCuCl$_2$]$\cdot$2H$_2$O and [LCu(H$_2$O)$_2$](ClO$_4$)$_2$ are similar and display bands in the visible region at 15 600, 13 300 and 15 800, 13 700 cm^{-1}, respectively. These spectral data are consistent with those published for trigonal bipyramidal copper(II) complexes with D_{3h} symmetry [26]. Accordingly, the bands at 15 400, 15 800 and 13 300, 13 700 cm^{-1} can be assigned to symmetry-allowed ^{2}A$_1 \rightarrow {}^2$E and ^{2}A$_1 \rightarrow {}^2$E transitions, respectively, in D_{3h} symmetry.

The X-band ESR spectra of both complexes, measured as powdered samples at 300 K and in CH$_2$Cl$_2$ frozen solution (Table III) are similar and are of rhombic type with $g_x > g_y > g_z$ [27], suggesting that the two complexes are distorted trigonal bipyramids. Following Reinen and co-workers [28–30], it is possible to assess the

TABLE III ESR data for copper(II) complexes of APyDPT (L)

Complex	*State*	g_x *or* $g_\parallel$	g_y $g_\perp$	g_z	$A_z \times 10^4$ (cm^{-1})	$A_x \times 10^4$ (cm^{-1})	g_{iso}	$A_{iso} \times 10^4$ (cm^{-1})
$[\mathrm{LCuCl_2}]\cdot 2\mathrm{H_2O}$	Powder (RT)	2.013	2.09	2.19				
	$\mathrm{CH_2Cl_2}$ (77 K)	2.02	2.10	2.19	90	108		
$[\mathrm{LCuCl_2}]$	Powder (RT)	2.26	2.06					
$[\mathrm{L_2Cu}](\mathrm{OAc})_2\cdot 2\mathrm{H_2O}$	Powder (RT)	2.28	2.06					
	Powder (77 K)	2.27	2.06					
	$\mathrm{CH_2Cl_2}$ (RT)						2.14	83
	$\mathrm{CH_2Cl_2}$ (77 K)	2.06	2.09	2.29				
$[\mathrm{LCu(H_2O)_2}](\mathrm{ClO_4})_2$	Powder (RT)	2.01	2.13	2.22				
	$\mathrm{CH_2Cl_2}$ (77 K)	2.02	2.09	2.23	78	136		
$[\mathrm{L_2Cu}](\mathrm{ClO_4})_2$	Powder (RT)	2.27	2.06					
	$\mathrm{CH_2Cl_2}$ (RT)						2.15	81
	$\mathrm{CH_2Cl_2}$ (77 K)	2.28	2.09	2.05				

RT = room temperature.

distortion of the trigonal bipyramid to a square-based pyramid using the following relations:

$$Qg = (1 + C^2)^{-1/2}\left\{\mathrm{d}_z^2 + C\mathrm{d}_{x^2-z^2}\right\}$$

where Qg is the ground state wave function of pentacoordinate copper(II) complexes with intermediate geometry having C_{2v} symmetry and C is the mixing coefficient; $C = 0$ for D_{3h} (d_z^2 ground state) and $C = (1/3)^{1/2}$ for C_{4v} ($\mathrm{d}_{x^2-y^2}$ ground state). The g-values are expressed as follows:

$$g_z = g_o + 8U_z[C^2/(1 + C^2)]$$

$$g_{x(y)} = g_o + 2U_{x(y)}[C^2/(1 + C^2)][1 \pm (3^{1/2}/C)]^2$$

where g_o is the value of the free electron (2.0023), U_i is the orbital contribution and is defined as:

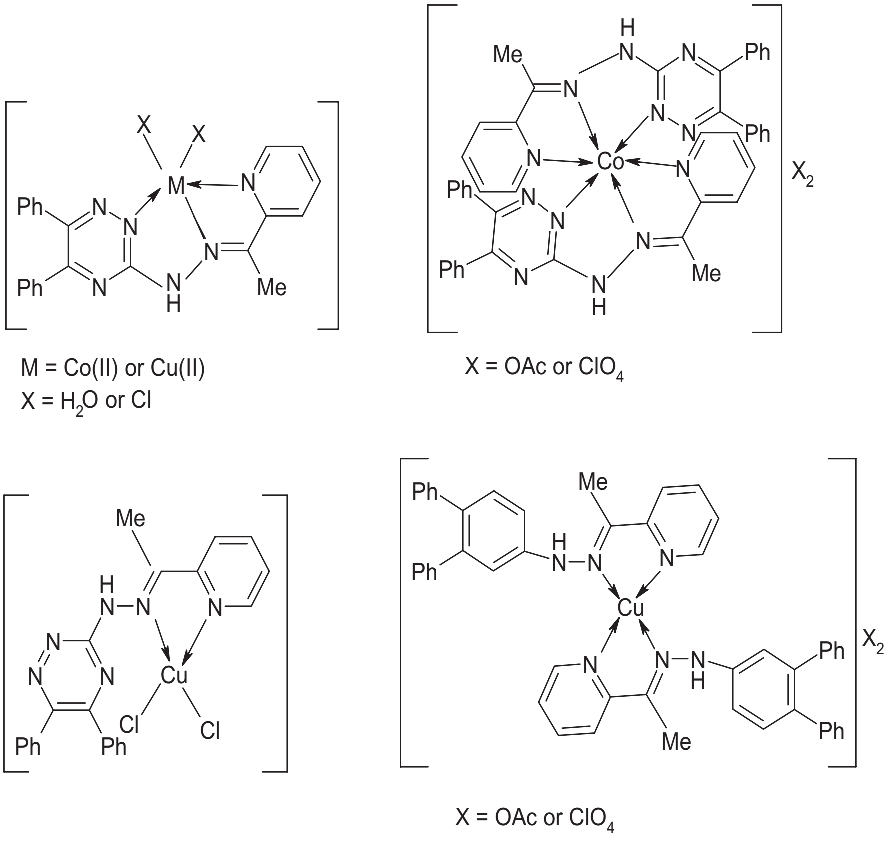
$$U_i = K_i^2|\lambda_o|/\Delta E_i$$

K_i is the covalency factor and $|\lambda_o| = 830\,\mathrm{cm}^{-1}$ is the spin–orbit coupling modulus parameter of the free copper(II) ion. The ΔE_i refers to the d–d transition energies. In C_{2v} symmetry these energies are due to ${}^2\mathrm{A}_1(\mathrm{d}_{x^2-y^2}) \rightarrow {}^2\mathrm{B}_2(\mathrm{d}_{xz}), \rightarrow {}^2\mathrm{B}_1(\mathrm{d}_{xy})$ and $\rightarrow {}^2\mathrm{A}_1(\mathrm{d}_{zy})$ transitions for $i = y$, z and x, respectively [31]. By using the observed ΔE_i energies, the mixing coefficient C and covalency factor K_i can be estimated to reproduce the experimental g-values. By considering the band at $13\,300\,\mathrm{cm}^{-1}$ for the chloro complex and $13\,700\,\mathrm{cm}^{-1}$ for the aquo complex as due to ${}^2\mathrm{A}_1 \rightarrow {}^2\mathrm{B}_1$ transition and those at 15 600 and $15\,800\,\mathrm{cm}^{-1}$ as due to unresolved ${}^2\mathrm{A}_1 \rightarrow {}^2\mathrm{A}_2$, ${}^2\mathrm{B}_2$ transitions in C_{2v} symmetry, a set of $C = 0.18$–0.23 for chloro and 0.26–0.29 for aquo complexes and $K_{\mathrm{av}} = K_x \approx K_y \approx K_z \approx 0.67$ and 0.74, respectively, were obtained, which reproduce the best experimental g-values. This implies that the $\mathrm{CuN_3X_2}$ ($\mathrm{X} = \mathrm{Cl}$ or O) chromophores are considerably distorted to square pyramidal.

The X-band ESR spectrum of polycrystalline [$LCuCl_2$] at 300 K (Table III) is of axial type with $g_{\parallel} = 2.26$ and $g_{\perp} = 2.06$, with no hyperfine structure in the low- and high-field regions. The fact that $g_{\parallel} > g_{\perp} > g_e$ (2.0023) suggests that the $d_{x^2-y^2}$ orbital is most populated in the ground state [27]. The G factor, defined as $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, is > 4, indicating the absence of superexchange interaction between copper(II) centers and that the local axes are aligned parallel or only slightly misaligned [32].

The electronic spectra of [L_2Cu]$(OAc)_2 \cdot 2H_2O$ and [L_2Cu]$(ClO_4)_2$ exhibit four bands at *ca.* 18 400, 14 400, 12 400 and 10 800 cm^{-1} (Table I), in addition to a weak shoulder at 12 800 cm^{-1}. These spectral features are similar to those reported for tetrahedral copper(II) complexes having the CuN_4 chromophore [33–35]. The X-band ESR spectra of both polycrystalline complexes at 300 K (Table III) are of the axial type with two g-values. The fact that $g_{\parallel} > g_{\perp} > g_e$ (2.0023) suggests that the $d_{x^2-y^2}$ orbital is the most populated ground state, which is characteristic of tetrahedral copper(II) complexes [36].

The spectra of both complexes in CH_2Cl_2 at 300 K display isotropic shapes with four hyperfine lines due to the interaction of the unpaired electron with the nuclear spin ($I = 3/2$) of both ^{63}Cu and ^{65}Cu. From these spectra the g-isotropic (g_{iso}) values for [L_2Cu]$(OAc)_2 \cdot 2H_2O$ and [L_2Cu]$(ClO_4)_2$ are 2.14 and 2.15 and the A_{iso} values are 83×10^{-4} and $81 \times 10^{-4}\,cm^{-1}$, respectively. Recording the spectra of both complexes



M = Co(II) or Cu(II)
X = H_2O or Cl

X = OAc or ClO_4

X = OAc or ClO_4

FIGURE 2 Proposed structures of L metal complexes.

as CH_2Cl_2 frozen glass led to anisotropic patterns with three g-values with superhyperfine structure (Table III). The sequence $g_1 > g_2 > g_3 > g_e$ indicates a tetrahedral configuration around copper(II) in these two complexes. The value of R, defined as $R = (g_2 - g_3)/(g_1 - g_2) \sim 0.2$, is less than unity, indicating a $d_{x^2-y^2}$ ground state of the copper(II) ion with both metal 4s and 4p admixture into the ground state [37].

Based on the elemental analysis, conductance, magnetic and spectral studies, the proposed structures for the present complexes are shown in Fig. 2.

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