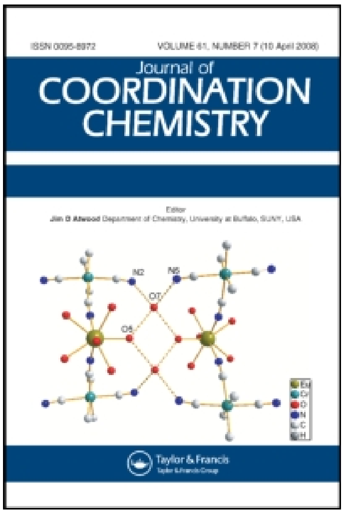


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Cobalt(II) and copper(II) complexes of (2-thiophene)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone

Ali El-Dissouky[a]; Othman Al-Fulij[a]; Samir S. Kandil[b]
[a] Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969 Safat, State of Kuwait [b] Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

To cite this Article El-Dissouky, Ali , Al-Fulij, Othman and Kandil, Samir S.(2004) 'Cobalt(II) and copper(II) complexes of (2-thiophene)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone', Journal of Coordination Chemistry, 57: 7, 605 — 614
To link to this Article: DOI: 10.1080/00958970410001701026
URL: http://dx.doi.org/10.1080/00958970410001701026

J. Coord. Chem., Vol. 57, No. 7, 10 May 2004, pp. 605–614

Taylor & Francis
Taylor & Francis Group

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

ALI EL-DISSOUKY[a], OTHMAN AL-FULIJ[a] and SAMIR S. KANDIL[b,*]

[a]*Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969 Safat, 13060, State of Kuwait;* [b]*Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt*

(Received 10 September 2003; Revised 16 October 2003; In final form 19 March 2004)

New complexes having the formulae [L_2CoX_2] and [$LCuCl_2$], [LCuCl] and [LCu](ClO_4)$_2$ where L = (2-thiophene)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone TDPTH; X = Cl, OAc or ClO_4 have been synthesized and characterized on the basis of elemental analyses, conductance, magnetic moments and infrared, electronic and ESR spectral data. The IR spectra indicate that TDPTH is a neutral bidentate ligand, coordinating *via* a triazine-N and azomethine-N in [L_2CoX_2] and [$LCuCl_2$] with the thiophene-S not coordinated but is tridentate in [LCuCl] and [LCu](ClO_4)$_2$ through the same two nitrogen atoms and thiophene-S. The magnetic moment and electronic spectral data suggest a distorted octahedral structure for Co(II) complexes, a dimeric square pyramidal geometry for [$LCuCl_2$] through chloride bridges and a dimeric diamagnetic, four-coordinate copper in [LCu](ClO_4)$_2$ through thiophene-S bridges. The X-band ESR spectra of Co(II) complexes, in the solid state, are rhombic with three g values consistent with a high-spin distorted octahedral structure. The X-band ESR spectrum of the powdered sample of both [$LCuCl_2$] $\cdot$ $2H_2O$ and [LCu](ClO_4)$_2$ at room temperature and at 77 K showed only one broad signal due to $\Delta M_s = \pm 1$ transition and a weak signal due to the forbidden $\Delta M_s = \pm 2$ transition, indicating an antiferromagnetic interaction between copper(II) centers whereas [LCuCl] is ESR silent, indicating a monovalent copper ion in this complex.

Keywords: Cobalt; Copper; Hydrazone thiophene

INTRODUCTION

1,2,4-Triazine derivatives exhibit a wide range of biological activity such as in antiviral, antibacterial, antimalarial and anti-inflammatory agents [1–4]. The existence of metal ions bonded to biologically active materials may enhance activity. Metal-binding compounds may render remarkable enhancement of biological activity by changing the electronic and structural properties. Recent studies [5,6] have demonstrated that (2-furan)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone, FDPT and (2-acetylpyridine)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone, APyDPT showed different coordination modes toward cobalt and copper. In the FDPT complexes the ligand is bidentate, using two nitrogen atoms, one of triazine-N and one of hydrazone-N but not the furan-O; in the corresponding APyDPT complexes, the coordination is tridentate or

---

*Corresponding author. E-mail: kandilsamir@hotmail.com

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001701026

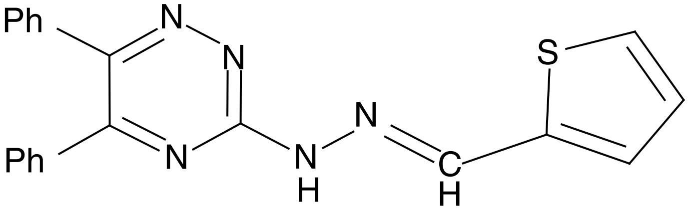


FIGURE 1 (2-Thiophene)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone, L.

bidentate with pyridine-N participating in coordination in both cases. In continuing investigations of 1,2,4-triazine derivatives as ligands [5–7] we report here the synthesis and characterization of the new, potentially biologically active (2-thiophene)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone L, Fig. 1, and its cobalt(II) and copper(II) complexes. This work studies the coordination of the thiophene group.

EXPERIMENTAL

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

(2-Thiophene)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone L (1 : 1, M : L) was prepared by dropwise addition of an ethanolic solution (30 cm^3) of thiophene-2-carboxyaldehyde (1.12 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 [5]. The reaction mixture was stirred for 1 h at room temperature and the solid product, which formed on cooling, was filtered off, recrystallized from ethanol and dried to give pure (2-thiophene)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone, L, as a yellow crystalline product with m.p. 264°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 (1.785 g, 0.005 mol) in ethanol (50 cm^3) was added to a hot ethanol 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 amount of the metal salt as in 1 : 1 preparations was added to a hot solution of the ligand (0.01 mol) in EtOH (100 cm^3). The reaction mixture was refluxed for 1 h for copper(II) complexes and 3 h for 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 ^{1}H NMR spectrum of the ligand was recorded on a Varian-300 MHz NMR spectrometer in d^6-DMSO using tetramethylsilane (TMS) as an 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), at liquid nitrogen temperature (LNT) and at liquid helium temperature in the solid state using DPPH as the g marker ($g = 2.0036$). Magnetic susceptibilities were measured by a Faraday balance. 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 made 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 357 and fragments at m/z 274, 248 and 178 (as base peak) assignable to cations formed by elimination of thiophene, thiophenylidene and radicals from the molecular ion, respectively. The ^{1}H NMR spectrum of the ligand L showed chemical shifts (δ/ ppm) at 3.23 {1H, –H=CH, s}, 6.90–8.41 {13H (10 H, two C_6H_5 and 3 H of the thiophene ring), m}, 11.70 (1H, N–H, s). The IR spectrum of the free ligand L displays bands at 1633, 1597, 1447 and 933 cm^{-1}, assigned to ν(C=N) azomethine, ν(C=N) triazine, ν(N=N) triazine and ν(N–N) hydrazino moieties, respectively [8–10]. The asymmetric and symmetric vibration bands of C–S–C of thiophene ring appeared at 1349 and 1273, respectively, in the free ligand L [11].

Characterization of the Complexes

The reaction of cobalt(II) salts with L in a mole ratio 1 : 2 (M : L) in ethanol under refluxing conditions produced thermally stable violet complexes, listed in Table I. The complexes are air-stable for long times, soluble in DMF, DMSO and pyridine, and partially soluble in nitrobenzene and slightly soluble in EtOH. The molar conductances were measured for 10^{-3} M solutions of these complexes in nitrobenzene and DMF at 25°C. The molar conductances in nitrobenzene indicate a nonelectrolytic nature for all complexes, except $[LCu](ClO_4)_2$ which behaves as 1 : 2 (cation : anion), Table I. The conductance data indicate a partial displacement of Cl and OAc and total for ClO_4 by DMF. This indicates weak Co(II)–X (X = Cl, OAc or ClO_4) bonds presumably due the steric effect of the two ligands. Reaction of anhydrous $CuCl_2$ with L in a mole ratio 1 : 1 gave $[LCuCl_2] \cdot 2H_2O$ which is black and has a melting point of 156°C; the 1 : 2 mole ratio preparation results in a red complex having stoichiometry [LCuCl] with melting point > 210°C. The latter complex appears to be Cu(I) from its diamagnetism and elemental analysis. The formation of this copper(I) complex may result from the reducing action of excess L. On the other hand, interaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with L gave only $[LCu](ClO_4)_2$ in both 1 : 1 and 1 : 2 preparations.

TABLE I Elemental analysis and some physical properties of L and its metal complexes

Compound	*Color*	*M.p.* (°C)	*Found* (*calcd*) (%)				Λ_m[a] *PhNO₂* *DMF*
			C	*H*	*N*	*M*	
L $C_{20}H_{15}N_5S$	Yellow	264–265	66.8 (67.2)	4.2 (4.2)	19.4 (19.6)		
$[L_2CoCl_2]\cdot 2H_2O$ $C_{40}H_{34}N_{10}O_2S_2C_{12}Co$	Violet	> 300	54.2 (54.6)	4.3 (3.9)	16.0 (15.9)	6.3 (6.7)	9.05[b] 86.08[c]
$[L_2Co(OAc)_2]$ $C_{44}H_{36}N_{10}O_4S_2Co$	Violet	> 300	59.0 (59.3)	3.6 (4.0)	15.7 (15.7)	6.6 (6.6)	10.30 [b] 69.86[c]
$[L_2Co(ClO_4)_2]$ $C_{40}H_{30}N_{10}O_8S_2Cl_2Co$	Violet	> 300	49.3 (49.4)	3.5 (3.1)	14.5 (14.4)	5.9 (6.1)	8.56[b] 130.61[c]
$[LCuCl_2]\cdot 2H_2O$ $C_{20}H_{19}N_5O_2SCl_2Cu$	Black	155–157	45.4 (45.5)	3.9 (3.6)	13.4 (13.3)	11.9 (12.0)	3.02[b] 3.08[c]
[LCuCl] $C_{20}H_{15}N_5SclCu$	Red	> 210	52.9 (52.6)	3.0 (3.3)	15.5 (15.4)	13.9 (13.9)	1.72[b] 1.95[c]
$[LCu](ClO_4)_2$ $C_{20}H_{15}N_5O_8SCl_2Cu$	Violet	210–213	38.3 (38.7)	2.2 (2.4)	10.8 (11.3)	10.4 (10.3)	160.85[b] 166.45[c]

[a] Molar conductance ($\Omega\,cm^2\,mol^{-1}$) of 10^{-3} M solutions of complexes in $PhNO_2$[b] and DMF[c] at 25°C.

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

Compound	*ν(NH) and/ or ν(OH)*	*ν(C=N) azomethine*	*ν(C=N) triazine*	*ν(N=N) triazine*	*ν(N–N) hydrazone*	*ν(M–N)*
L	3208s 3403b	1633m	1597m	1447m	993s	
$[L_2CoCl_2]\cdot 2H_2O$	3429b	1620m	1573m	1477m	1019s	478m 410m
$[L_2Co(OAc)_2]$	3460b	1623m	1574m	1478m	1020s	478m 410m
$[L_2Co(ClO_4)_2]$	3470b	1624s	1570s	1479m	1021m	478m 409w
$[LCuCl_2]\cdot 2H_2O$	3208m 3432b	1623s	1567m	1482m	1021s	462m 409m
[LCuCl]	3173m 3442m	1622s	1569m	1488m	1027s	462m 407m
$[LCu](ClO_4)_2$	3182m 3468m	1622s	1569m	1494m	1025sh	411m

Infrared Spectra

The main IR bands of L and its metal complexes as KBr discs, with tentative assignments, are given in Table II. Coordination of L to the metal ion results in lowering of ν(C=N) of azomethine and the triazine ring by 9–13 and 23–30 cm^{-1}, respectively, and upward shifts of ν(N=N) triazine and ν(N–N) hydrazino linkage by 30–47 and 26–34 cm^{-1}, respectively, in all complexes implying coordination of the triazine-N^3 and azomethine-N atoms to the metal ions. These conclusions are further supported by the appearance of medium-weak bands at 462–478 and 407–411 cm^{-1} in the spectra of the complexes that could be attributed to ν(M–N) of azomethine and triazine, respectively. The positions of bands due to ν(C–S–C) of thiophene are only changed significantly in $[LCu](ClO_4)_2$ (1322 and 1280 cm^{-1}) suggesting coordination of thiophene sulfur to copper(II) in this complex. The spectrum of $[L_2Co(OAc)_2]$ displays bands at 1641 and 1363 cm^{-1} due to ν_{as}(OCO) and ν_s(OCO), respectively, of the acetato ligand. The wavenumber separation value between these two bands $\Delta\nu = 278\,cm^{-1}$, is characteristic of a monodentate acetato ligand in this complex [12].

The spectrum of $[LCoCl_2]$ shows a new weak band at 335 cm^{-1} assigned to ν(Co–Cl) [12]. 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 chloro copper(II) complexes. Tests for chloride ion with $AgNO_3$ are only positive after decomposition of the complexes, not in solutions, confirming coordination of chloride. The spectrum of $[LCu](ClO_4)_2$ exhibited new bands at 1180 (s,b) (ν_3), 936 (ν_1) and 621 (ν_4) cm^{-1} characteristic of T_d symmetry of perchlorate and indicated the ionic nature of this complex [12]. The spectrum of $[L_2Co(ClO_4)_2]$ showed a split for $\nu_3(ClO_4)$ at 1059 and 1045 cm^{-1} due to a lowering of symmetry in ClO_4 from T_d to $C_{3\nu}$, indicative of unidentate coordination of perchlorate. This is further supported by the appearance of a band due to ν(Co–O) at 557 cm^{-1}. Finally, coordination of the N–H to the metal ion is unlikely in all complexes, since the ν(N–H) band remains nearly stationary and in some cases overlaps with ν(O–H) of water molecules.

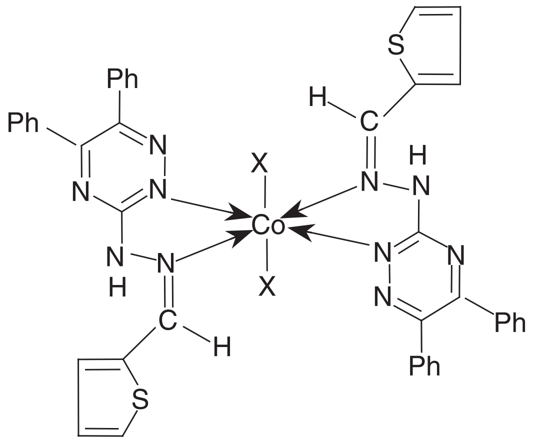
Electronic Spectra

The magnetic moment values of cobalt(II) complexes, Table III, are in the range reported for high-spin, six-coordinate cobalt(II) complexes [13,14]. Electronic spectra

TABLE III Magnetic moment and electronic spectral data for cobalt(II) and copper(II) complexes of L

Complex	μ_{eff}	*Electronic spectral data*				
		State	*d–d Transitions* (cm^{-1})	*10Dq* (cm^{-1})	*B′* (cm^{-1})	*β* (cm^{-1})
$[L_2CoCl_2]\cdot 2H_2O$	4.45	Nujol mul	8300, 17 700, 19 100, 22 000	9600	790	0.702
		H_2O	8400, 17 600, 18 000, 21 000			
$[L_2Co(OAc)_2]$	4.58	Nujol mull	8100, 17 300 18 800, 21 800	9500	783	0.692
		H_2O	8400, 17 600 18 000, 21 050			
$[L_2Co(ClO_4)_2]$	4.47	Nujol mull	8000, 16 800 18 600, 21 000	9050	778	0.692
		H_2O	8350, 17 600 21 000			
$[LCuCl_2]\cdot 2H_2O$	1.20	Nujol mull	12 700, 15 200, 18 500			
		DMSO	12 300, 14 850, 17 800			
		Py	12 450, 15 100, 18 020			
		β-pic	12 600, 15 200, 18 400			
		Im	12 800, 15 400, 18 550			
[LCuCl]	0.3	Nujol mull	20 000, 25 000, 29 400, 33 300			
$[LCu](ClO_4)_2$	0.0	Nujol mull	18 100, 25 000, 28 600, 33 300			
		EtOH	9600, 19 400, 25 400, 29 000, 33 300			
		DMSO	12 400, 25 000, 29 200, 33 300			

of the three cobalt(II) complexes show three bands at 8000–8300 (ν_1), 16 800–17 700 (ν_2) and 18 600–19 100; 2100–22 000 (ν_3) cm^{-1} consistent with those reported for octahedral cobalt(II) complexes containing the CoN_4X_2 chromophore. According to the energy level diagram for high-spin, octahedral cobalt(II) complexes, these bands are assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1), ${}^4T_{1g} \rightarrow {}^4A_{1g}$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions [13]. The splitting of ν_3 is due to the lower symmetry as consequence of the *trans* structure. Since the in-plane ligand field is constant with the N_4 chromophore for the three complexes, the ν_1 varies slightly with the field strength of the monodentate ligands in the order Cl > OAc > ClO_4, Table III. The coordination field parameters Dq, B' and β were calculated according to Lever [14] and the results are given in Table III. Observed ν_2 values are in agreement with the calculated ones. This indicates that the assignments are reasonable and are additional evidence for octahedral structure (**II**). In addition, the values of β are ~0.7 showing that the bonding in cobalt(II) complexes is moderately covalent [13].



X = Cl, OAc or ClO_4

(**II**)

The X-band ESR spectra of $[L_2CoX_2] \cdot nH_2O$, X = Cl, OAc or ClO_4 and n = 2, 0 or 0, respectively, as polycrystalline samples are similar and display three g values (5.72, 4.56 and 2.21 for X = Cl; 5.03, 4.08 and 2.22 for X = OAc; 5.00, 4.01 and 2.19 for X = ClO_4, Table IV). These data are similar to those reported for purely high-spin, distorted

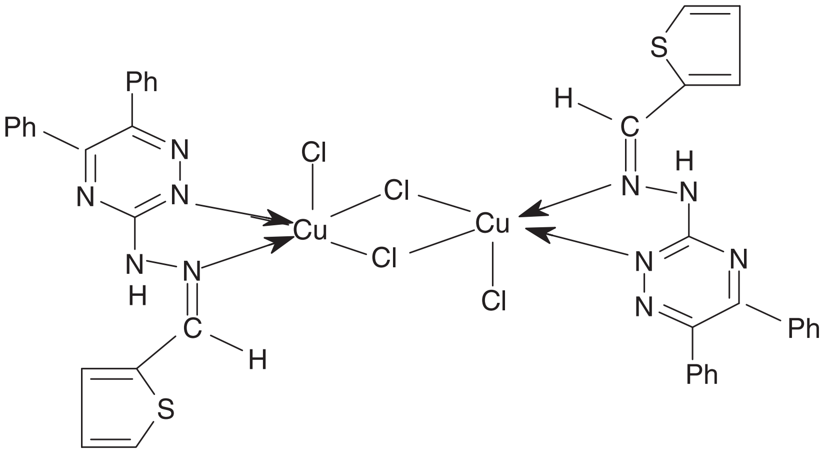
TABLE IV ESR data for cobalt(II) and copper(II) complexes of L

Complex	*State*	$g_\perp$			$g_\parallel$			$\Delta M_s = \pm 2$
		g	g_1	g_2	g_3	$g_1 - g_2$	g	
$[L_2CoCl_2] \cdot 2H_2O$	Solid (8 K)	5.14	5.72	4.56	2.21	1.16		
$[L_2Co(OAc)_2]$	Solid (8 K)	4.56	5.03	4.08	2.22	0.95		
$[L_2Co(ClO_4)_2]$	Solid (8 K)	4.51	5.00	4.01	2.19	0.99		
$[LCuCl_2] \cdot 2H_2O$	Powder (r.t.)						2.13	4.18
	Powder (77 K)						2.19	3.98
$[LCu](ClO_4)_2$	Powder (r.t.)						2.11	4.14
	Powder (77 K)						2.18	3.98

octahedral cobalt(II) complexes corroborating the relative weakness of the spin-quartet and -doublet mixing [15,16]. The values of $g_{\perp} = 1/2(g_1 + g_2) > g_{II}$ show that the axial deformation is an elongation and may indicate the $^4A_{2g}$ state lies lower. The rhombicity $g_1 - g_2$ is in the order $Cl > ClO_4 \geq OAc$. However, the small differences in value infer the similarity of the equatorial environment and that the structural change from $X = Cl$ to OAc to ClO_4 is very small in the three cobalt(II) complexes.

The room temperature magnetic moment values of the three copper complexes $[LCuCl_2] \cdot 2H_2O$, [LCuCl] and $[LCu](ClO_4)$ are 1.2, 0.3 and 0.0, respectively. The anomalous moments for $[LCuCl_2] \cdot 2H_2O$ and $[LCu](ClO_4)$ could be attributed to molecular association and/or strong anti-ferromagnetic interaction between copper(II) centers, occurring through either Cu–Cu bonding or through a bridging ligand. The elemental analysis suggests that copper exists in the oxidation state of +II in both complexes, excluding the possibility of direct Cu–Cu bonding. On the other hand, the moment for [LCuCl] along with the elemental analysis can be taken as an evidence for the formation of Cu(I) in this complex.

The Nujol mull electronic spectrum of $[LCuCl_2] \cdot 2H_2O$ showed a broad band at $15\,200\,cm^{-1}$ and two shoulders at 12 700 and $18\,500\,cm^{-1}$. Such spectral features are consistent with copper(II) square-based pyramidal complexes of C_{4v} symmetry [13]. According to this symmetry, three bands are expected. Thus, the main band at $15\,200\,cm^{-1}$ can be assigned to a $^2B_1 \rightarrow {}^2B_2$ transition while the shoulders at 12 700 and $18\,500\,cm^{-1}$ are due to $^2B_1 \rightarrow {}^2A_1$ and $^2B_1 \rightarrow {}^2E_1$ transitions, respectively. Based on the magnetic and electronic spectral data and the bidentate nature of L, the square pyramidal structure can be assumed to be obtained *via* the chloride bridge structure (**III**).



(III)

The electronic spectrum of $[LCuCl_2] \cdot 2H_2O$ in pyridine (Py), β-picoline (β-Pic), imidazole (Im) or dimethylsulphoxide (DMSO), displayed bands (Table III), characteristic of five-coordinate copper(II) complexes. Argentometric titration of these solutions consumed $AgNO_3$ corresponding to 1 : 2 (complex : $AgNO_3$) supporting the electrolytic nature of these complexes in solutions of coordinating solvents. Thus, formation of five-coordinate copper(II) complexes can be explained from of the following equation:

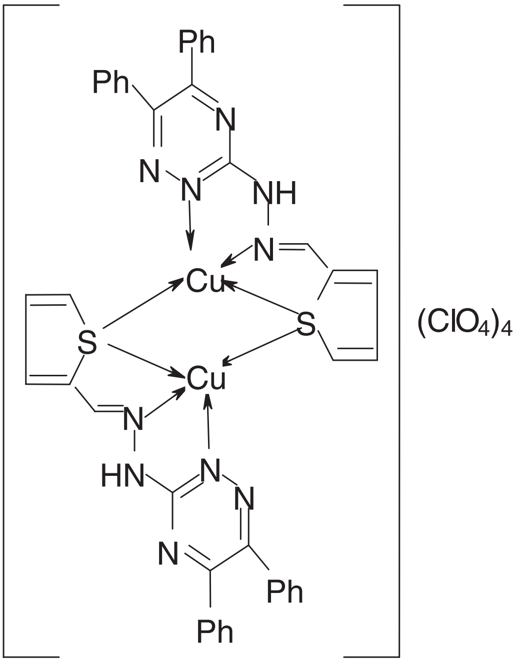
$$[LCuCl_2]_2 + Ls \rightleftarrows [L_2CuLs] + CuCl_2 \qquad (1)$$

The data given in Table III indicate that the LF absorptions in solutions of these complexes have blue shifted relative to those in Nujol mull due to the higher energy of the Cu(II) d vacancy ($d_{x^2-y^2}$) as an expected consequence of increasing in-plane ligand field and/or the differing structure of the Cu(II) chromophore. The transition energies of the adducts are in the order Im > β-Pic > Py > DMSO, indicating that coordination of the nitrogen donors introduces a stronger ligand field than oxygen donors, which results in the shifting of the absorption maxima to higher energies for the nitrogen adducts [17,18].

The room temperature X-band ESR spectrum of the powdered sample of $[LCuCl_2]\cdot 2H_2O$ shows one broad peak (peak separation = 210 G) with $g_{av} = 2.13$, and a weak signal at 1590 G ($g = 4.18$) due to the forbidden $\Delta M_s = \pm 2$ transition characteristic of dimeric copper(II) complexes [19]. Recording the spectrum of the sample at 77 K, gave the same peaks with lower intensity and g_{av} became 2.19, while g at the half field became 3.98. These observations suggest that the antiferromagnetic spin coupling between the copper(II) centers increases with lowering temperature.

The electronic spectrum of [LCuCl] displayed bands at 29 400 and 25 000 cm^{-1} and a new intense shoulder at 20 000 cm^{-1}; no other bands are observed down to 9000 cm^{-1}. These spectral features are similar to those of the free ligand except for shifts especially for the band at 29 400 cm^{-1} (28 600 cm^{-1} in the free ligand). This $\pi \rightarrow \pi^*$ transition is lowered in the complex as a consequence of overlapping of p-orbitals of the ligand with d-orbitals of the metal. The new shoulder at 20 000 cm^{-1} can be assigned to a Cu → Cl charge transfer transition. These observations, along with the fact that the complex is ESR silent, can be taken as evidence for a monovalent copper(I) complex.

The Nujol mull electronic spectrum of $[LCu](ClO_4)_2$ displayed intraligand bands at 33 300, 28 600 and 25 000 cm^{-1} and a new shoulder at 18 100 cm^{-1}, and no bands are located in the lower energy side of the visible region. The shoulder could be assigned to MLCT and/or not d–d transitions. Such spectral features and the almost zero magnetic moment observed for this complex suggest either the existence of copper as copper(II) in agreement with the diamagnetic copper(II) complexes reported by Tsuchida *et al.* [20] or reduction of copper(II) to copper(I) by the ligand. Elemental analysis and electronic spectral data support the existence of copper(II) in this complex. A similar phenomenon has been reported for several copper(II) complexes with sulfur-containing ligands in which the paramagnetism is almost quenched at room temperature through strong spin–spin interaction between copper(II) centers in the solid state at room temperature [21–24]. This interaction may take place either through formation of a σ or δ bond by overlap of the two d-orbitals or through overlap of the extended molecular orbitals of two copper(II) centers simultaneously with one of the ligand donor orbitals [21]. This involves copper(II) being simultaneously attached to one ligand atom; the sulfur atom is a good candidate. Accordingly, structure **(IV)** is suggested for this complex.



(IV)

A saturated EtOH solution spectrum of the complex, Table III, displayed a broad band at $19\,400\,\mathrm{cm}^{-1}$ and a very weak one at $9600\,\mathrm{cm}^{-1}$, characteristic of tetrahedral copper(II) complexes [13]. This structure change in solution may proceed according to the following equations:

$$[\mathrm{LCu}]_2(\mathrm{ClO}_4)_4 \xrightarrow{\mathrm{EtOH}} [\mathrm{L}_2\mathrm{Cu}](\mathrm{ClO}_4)_2 + \mathrm{Cu}(\mathrm{ClO}_4)_2 \tag{2}$$

or

$$[\mathrm{LCu}]_2(\mathrm{ClO}_4)_4 + 2\mathrm{EtOH} \rightarrow [\mathrm{LCu}(\mathrm{EtOH})]_2(\mathrm{ClO}_4)_4 \tag{3}$$

In Eq. (2) a tetrahedral bis-chelate is formed through removal of one Cu(II) ion from the dimer and a breakdown of one ligand–metal bond, presumably Cu–S. In Eq. (3), a tetrahedral complex is achieved through solvent ligation with the breakdown of one of the three bonds between the metal and each ligand (L). The DMSO solution spectrum of the complex gave only one broad absorption band at $12\,400\,\mathrm{cm}^{-1}$, Table III, characteristic of distorted octahedral copper(II) complexes [13]. This can be achieved by the axial ligation of the dimeric structure or by the dissociation of the dimer followed by DMSO axial ligation.

The X-band ESR spectrum of a powdered sample of $[\mathrm{LCu}](\mathrm{ClO}_4)_2$ at room temperature, Table IV, displayed one strong signal with $g_{\mathrm{av}} = 2.11$ and a weak signal at 1608 G due to the forbidden $\Delta M_{\mathrm{s}} = \pm 2$ transition, characteristic of dimeric copper(II) complexes.

References

[1] S. Saxena, M. Verma, A.K. Saxena and K. Shanker, *Arzneim. Forsch.* **44**, 766 (1994).
[2] A.K. Mansour, S.B. Awad and S. Antown, *Z. Naturforsch., Teil B.* **29**, 792 (1974).
[3] Z. El-Gendy and R.M. Abdel-Rahman, *Indian J. Heterocycl. Chem.* **4**, 293 (1995).
[4] N.I. Korotkikh, G.A. Losev, V.F. Lipnitsky, S.G. Kalistratov, A.S. Sokolova and O.P. Shvaika, *Khim.-Farm. Zh.* **27**, 51 (1993); *Chem. Abstr.* **122**, 81223n (1995).
[5] S.S. Kandil, G.Y. Ali and A. El-Dissouky, *Transition Met. Chem.* **27**, 398 (2002).
[6] S.S. Kandil, A. El-Dissouky and G.Y. Ali, *J. Coord. Chem.* **57**, 105 (2004).
[7] S.S. Kandil, N.R. El-Brollosy and A. El-Dissouky, *Synth. React. Inorg. Met.-Org. Chem.* **30**, 979 (2000).
[8] R.M. Silverstein, G.C. Bassler and T.C. Morrill, *Spectrometric Identification of Organic Compounds* (New York: John Wiley & Sons, 1991).
[9] D. Heinert and A.E. Martell, *J. Am. Chem. Soc.* **84**, 3257 (1962).
[10] D.N. Sathanarayana and D. Nicholls, *Spectrochim. Acta A.* **34**, 263 (1978).
[11] V.A. Mukhedkar, U. Bhagwat and A.J. Mukhedkar, *J. Chem. Soc. Dalton Trans.* 1899 (1982).
[12] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley-Interscience, New York, 1986).
[13] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd Edn. (Elsevier, Amsterdam,1986).
[14] A.B.P. Lever, *J. Chem. Educ.* **45**, 711 (1968).
[15] J. Zarembowitch and O. Kahn, *Inorg. Chem.* **23**, 589 (1984).
[16] P. Thuery and J. Zarembowitch, *Inorg. Chem.* **25**, 2001 (1986) and references therein.
[17] R.B. Martin and R.J. Sunderberg, *Chem. Rev.* **74**, 471 (1974).
[18] R.G. Bhirud and T.S. Srivastava, *Inorg. Chim. Acta.* **173**, 121 (1990).
[19] A. El-Dissouky, A.M. Hindaway and A. Abdel-Salam, *Inorg. Chim. Acta.* **118**, 109 (1986).
[20] Y. Yamada, H. Nakamura and T. Tsuchida, *Bull. Chem. Soc. Jpn.* **31**, 303 (1958); **33**, 1278 (1960).
[21] B.J. Hathaway, In: G. Wilkinson, R.D. Gillard and J.A. Cleverty (Eds.), *Comprehensive Coordination Chemistry* (Pergamon, Oxford, 1987), Vol. 5, p. 533.
[22] K.Z. Ismail, A.K. Shehata and A. El-Dissouky, *Polyhedron* **16**, 2909 (1997).
[23] R.N. Patel, H.C. Pandey and K.B. Pandeya, *Transition Met. Chem.* **22**, 575 (1997).
[24] M.F. El-Shazly, T.M. Salem and M.A. El-Sayed, *Inorg. Chim. Acta* **29**, 155 (1978).