COPPER(II) COMPLEXES WITH 1-PHENYL-4,6-DIMETHYLPYRYMIDINE-2-THIONE. CHEMICAL, SPECTROSCOPIC, MAGNETIC, CONDUCTIVITY AND POLAROGRAPHIC STUDIES

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New copper(II) complexes of general composition: $CuLX_2.nH_2O$ ($X = Cl^-$, $n = 0{\cdot}25$; $X = NO_3^-$, $n = 0{\cdot}5$), $Cu_2L_3Cl_4.2\,H_2O$, $CuL_2X_2.H_2O$ ($X = ClO_4^-$, BF_4^- and NO_3^-) and $Cu_2L_7X_4$ ($X = ClO_4^-$, BF_4^- and NO_3^-), where L = 1-phenyl-4,6-dimethylpyrimidine-2-thione, have been isolated. Chemical and thermal analyses, conductivity, magnetic susceptibility, infrared and ligand field spectroscopic data and, for the perchlorate complexes also polarographic studies, are reported. Diagnostic IR bands frequencies of counter-ions, ν(Cu–X) modes and ligand field spectra for the mono- and bis-ligand compounds, having an equatorial $[CuNSCl_2]$, $[CuNSO_2]$ and $[CuN_2S_2]$ microsymmetry, indicate a coordinating character of some anions, suggesting an elongated octahedral geometry for these complexes. For the $[Cu_2L_7]X_4$ ($X = ClO_4^-$, BF_4^- and NO_3^-) complexes, which exhibit at room temperature subnormal magnetic moments, a polynuclear structure with the copper(II) in a roughly square-pyramidal environment, is proposed. Polarographic data for the perchlorate complexes and for the $Cu(ClO_4)_2$–L system at various ligand concentrations, have shown that in DMF solution the prevailing species are $[CuL_2]^{2+}$, $[CuL_3]^{2+}$ and $[Cu_2L_7]^{4+}$ confirming the oxidation state II for the copper ions in the $[Cu_2L_7]X_4$ complexes.

It is well documented that pyrimidine and purine bases and their derivatives, play a significant role in many biological systems, the ring system being a component of nucleic acids, several vitamins, co-enzymes etc. and provide potential binding sites for metal ions. As a part of our research program concerning studies on the coordinating behaviour of oxo- and thio-pyrimidine analogues with metal ions, in this communication, we report the preparation and physico-chemical characterization of some new copper(II) complexes with 1-phenyl-4,6-dimethylpyrimidine-2-thione.

Recently it has been reported that, in aqueous or in non-aqueous solution, the interaction of copper(II) salts with 4,6-dimethylpyrimidine-2(1*H*)-thione[1] and 1,4,6-trimethylpyrimidine-2-thione[2] yields copper(I) and copper(II) complexes respectively independently of the anion, whereas the reaction with 1-methylpyrimidine-2-thione leads, depending on the counter-ion to the formation of copper(II)[3] and copper(I)[4] complexes. From the above results, it can be inferred that the coordinating properties of the counter-ion together with the chemicals environment of the thioamido group thione ⇄ thiol equilibrium, the solubility of the reaction products and the effect of the mutual influence between the ligands (MIL)[5], play an important role in determining the stoichiometry, the coordination stereochemistry and the stabilization of a preferred oxidation state of the central copper ion.

As for ligands containing a $H-\overset{|}{N}-\overset{|}{C}=S$ group, the interaction of cupric–cuprous and thioamide–disulphide redox couples, with the formation of transient intermediates of unusual purple colour[6], is often formulated in terms of thiol structure $=N-\overset{|}{C}-SH$ of the thioamido group[7], we have studied the interaction of copper(II) salts with 1-phenyl-4,6-dimethylpyrimidine-2-thione which allow no thione ⇄ thiol tautomerism. This seems interesting also considering the few comparative studies on copper(I) and copper(II) complexes with N–H, and N-alkyl or N-aryl substituted pyrimidinethiones.

EXPERIMENTAL

The 1-phenyl-4,6-dimethylpyrimidine-2-thione (L) was prepared by the method reported[8] previously.

Preparation of Complexes

$[CuLCl_2].0{\cdot}25\,H_2O$: To a MeOH (15 cm^3) solution of $CuCl_2.2\,H_2O$ (3 mmol), 3 mmol of the solid L were added with stirring at room temperature. The green product obtained was filtered off and washed with ether.

$[Cu_2L_3Cl_4].2\,H_2O$: Solid $CuCl_2.2\,H_2O$ (2 mmol) was added to a suspension of the complexing agent (4 mmol) dissolved in EtOAc (25 cm^3) and acetone (5 cm^3). The initial yellow suspension under reflux for 1 h, turned to violet and a brown compound deposited. After three days the compound was filtered, washed with copious amounts of EtOAc and Et_2O.

$[CuL(NO_3)]NO_3.0{\cdot}5\,H_2O$: The compound was prepared dissolving with stirring at room temperature the the solid L (5 mmol) in a triethylothoformate (TEOF) (7 cm^3) and EtOAc (15 cm^3) solution containing the stoichiometric amount (5 mmol) of $Cu(NO_3)_2.5\,H_2O$. The green precipitate deposited was filtered, washed with EtOAc and EtO_2.

$[CuL_2(H_2O)]X_2$ ($X = ClO_4^-, BF_4^-$) and $[CuL_2(NO_3)]NO_3.H_2O$: Two milliomoles of hydrated salt were dissolved in 5 cm^3 of TEOF and 15 cm^3 of EtOAc. On the addition of the solid L (4 mmol) under stirring at room temperature for 8 h, the initial light blue solutions immediately turned to green-olive and the green or red-brown (nitrate) complexes deposited.

$[Cu_2L_7]X_4$ ($X = ClO_4^-, BF_4^-, NO_3^-$): A solution of the appropriate hydrated salt (1·25 mmol) in 5 cm^3 of TEOF was added to a suspension of L (5 mmol) in 20 cm^3 of EtOAc. The green products initially formed turned to purple (maroon the nitrate) under stirring at room temperature for 8 h. After three days the solid compounds were filtered off and washed with EtOAc and Et_2O.

All the above reported compounds were dried in vacuo over P_4O_{10}.

Analyses and Apparatuses

Copper was determined by complexometric titration with EDTA after destruction of the compounds with H_2SO_4 conc. and aqua regia. Carbon, hydrogen, nitrogen and sulphur were analyzed using a C. Erba 1106 Elemental Analyzer. Conductivity measurements were performed on freshly 10^{-3} mol dm^{-3} solutions in DMF at 25°C with a WTW conductivity bridge. Thermogravimetric studies on the hydrated compounds, were carried out on a Mettler TG 50 Thermobalance in conjunction with a direct Mettler TC 10 TA processor recorder.

IR spectra were recorded (4 000—500 cm^{-1}) in KBr pellets and in Nujol mulls on polyethylene sheets (500—50 cm^{-1}) on a Perkin-Elmer 180 spectrophotometer.

Solid state electronic spectra were performed with a Shimadzu MPS-50L spectrophotometer as Nujol mulls on filter paper.

Magnetic susceptibilities at room temperature, were measured by the Gouy method. The diamagnetic corrections for each compound was estimated by conbining the experimentally determined value of $-121 . 10^{-6}$ c.g.s. units for the complexing agent with Pascal's constants for the other atoms.

The polarographic measurements were carried out in purified DMF (Merck-Uvasol), using an Amel Multipolarograph model 472, under a nitrogen atomosphere. A satured Ag|AgCl, KCl, DMF electrode was used as a reference. All half-wave potentials were referred to a saturated calomel electrode (SCE). The measurements were performed at constant temperature (25 ± 0·1°C) and drop times were 0·5, 1·0, and 2·0 s. The polarographic behaviour of the complexes, $Cu(ClO_4)_2$, and of the ligand, was examined in the 10^{-4}—10^{-3} mol dm^{-3} concentration range. The $Cu(ClO_4)_2$ was recrystallized from DMF. Sodium perchlorate was used as base electrolyte and the ionic strength of the solutions was kept constant (0·1 mol dm^{-3}). The reversibility of the electrode reactions was tested by semlog analysis of the polarographic waves. By using the dependence of the current values on the drop times and the depolarizer concentrations, it was determined that all the reduction processes were diffusion controlled. The number of the electrons involved in the reduction process of $Cu(ClO_4)_2$, determined by the Ilkovič equation, is two whereas one electron only is involved in the ligand reduction[8].

RESULTS AND DISCUSSION

General

All the compounds prepared are listed in Table I together with their colour, elemental and thermal analyses and molar conductivities in DMF. Analytical results demonstrate that, under experimental conditions, 1-phenyl-4,6-dimethylpyrimidine-2--thione, forms 1 : 1 and 2 : 3 copper(II) complexes with $CuCl_2.2 H_2O$, 1 : 2 and 2 : 7 complexes with copper(II) perchlorate, tetrafluoroborate and nitrate. A 1 : 1 complex was also obtained with copper(II) nitrate.

All the solid microcrystalline or powder-like complexes, are sensitive to the atmospheric moisture, but are stable in an inert atmosphere or in vacuo over P_4O_{10}, with exception of the mono-ligand nitrate complex, which slowly decomposes with loss of NO_2 and probable oxidation of the ligand to sulfenate or sulfinate anions[9].

The molar conductivities in DMF of the complexes, referred to their formula weights, show that $[Cu_2L_3Cl_4].2 H_2O$ and $[CuLCl_2].0{\cdot}25 H_2O$ behave as 1 : 1 and non-electrolytes respectively; the 2 : 7 complexes as 1 : 3 electrolytes, while the mono-ligand nitrate and all the bis-ligand complexes have conductivities intermediate between the values corresponding to 1 : 1 and 1 : 2 electrolytes[10].

The good agreement between the thermogravimetric dehydration results and the expected weight losses confirms the compound stoichiometries (Table I). For all the hydrated complexes, except $[CuL(NO_3)]NO_3.0{\cdot}5\,H_2O$ which began to decompose before deaquation was complete, water loss occurs gradually in a single step up to ca 140°C.

With regard to the unusual stoichiometry of magnetically anomalous $[Cu_2L_7]X_4$ ($X = ClO_4^-, BF_4^-, NO_3^-$) complexes, for which repeated attempts to obtain single crystals suitable for X-ray structure determination have so far failed, the IR spectral data tend to exclude the presence of non-coordinated ligand molecules merely incorpored in the crystal lattice, as have been spectroscopically inferred for complexes related[11] and established[12] using X-ray analysis, as well as the possibility that the compounds may be formulated as $[Cu^I_2L_5]X_2.2\,LHX$ ($X = ClO_4^-, BF_4^-, NO_3^-$) complexes, (there is not evidence for the presence of $\nu(\overset{+}{N}\text{–}H)$ modes).

TABLE I

Colour, analytical data and molar conductivities, Λ_M ($\Omega^{-1}\,mol^{-1}\,cm^2$) in DMF solution ($c = 1\,.\,10^{-3}\,mol\,l^{-1}$) at 25°C of copper(II)–L complexes

Complex	Colour	Calculated/Found						
		%C	%H	%Cu	%N	%S	%H_2O	Λ_M
$[CuLCl_2].0{\cdot}25\,H_2O$	green	40·5	3·5	17·9	7·9	9·0	1·3	16
		40·6	3·5	17·8	7·9	9·0	1·3	
$[Cu_2L_3Cl_4].2\,H_2O$	brown	45·3	4·2	13·3	8·8	10·0	3·8	70
		45·3	4·2	13·2	8·8	10·0	3·7	
$[CuL(NO_3)]NO_3.0{\cdot}5\,H_2O$	green	34·9	3·2	15·4	13·6	7·8	dec.	111
		34·8	3·1	15·4	13·6	7·7		
$[CuL_2(NO_3)]NO_3.H_2O$	red-brown	45·1	4·1	9·9	13·2	10·0	2·8	118
		45·1	4·1	9·9	13·1	9·9	2·8	
$[CuL_2(H_2O)](ClO_4)_2$	green	40·4	3·7	8·9	7·8	9·0	2·5	134
		40·4	3·7	8·9	7·7	8·9	2·5	
$[CuL_2(H_2O)](BF_4)_2$	green	41·9	3·8	9·2	8·1	9·3	2·6	146
		41·8	3·8	9·2	8·1	9·3	2·6	
$[Cu_2L_7](NO_3)_4$	maroon	53·4	4·5	6·7	13·3	11·9		182
		53·3	4·5	6·7	13·3	11·9		
$[Cu_2L_7](ClO_4)_4$	violet	49·4	4·1	6·2	9·6	10·9		222
		49·2	4·1	6·2	9·6	10·9		
$[Cu_2L_7](BF_4)_4$	violet	50·7	4·3	6·4	9·9	11·3		229
		50·7	4·2	6·3	9·8	11·2		

Moreover polarographic studies of the perchlorate complexes, pointing to the formation of the $[Cu_2L_7]^{4+}$ species in DMF solution, show that the solid $[Cu_2L_7]X_4$ complexes are not a mechanical mixture of $[CuL_4]^{2+}$ and $[CuL_3]^{2+}$ cations in equimolecular ratio and mainly that the oxidation state for the copper ions is II.

IR *Spectral Studies*

The analysis of the ligand bands in the range 1 600 – 1 300 cm^{-1}, assigned to a combination of stretching vibrations of the C=C, C=N, C–C and C–N bonds which do not form part of an "aromatic skeleton" (ref.[8]), shows (see Table II) that in the spectra of the complexes these bands are shifted to low- and high-frequency sides indicating that the non-substituted ring nitrogen atom takes part in the complexation. The salient feature of the IR spectra of the complexes, is the perturbation of the ligand bands at 1 235 and 1 200 cm^{-1}, which are assigned to a prevailing $\nu(C{=}S)$ contribution. Furthermore, the ligand band at 473 cm^{-1}, considered to have significant contribution from $\delta(C{=}S)$ in-plane deformation, in the spectra of almost all the complexes, appears split into higher and lower frequencies because of N,S-bridging or chelating effect of the ligand.

The IR absorptions due to the perchlorate and tetrafluoroborate anions (Table III) in the spectra of $[CuL_2(H_2O)]X_2$ and $[Cu_2L_7]X_4$ and $[Cu_2L_7]X_4$ ($X = ClO_4^-, BF_4^-$) complexes, are intermediate in character between those expected for the coordinated as well as those of the free ions[13]. In each spectrum the ν_3 (in T_d symmetry) band shows some evidence of splitting and ν_1 and ν_2 modes are obscured by ligand absorptions or occur albeit weakly. Such spectra are typical of complexes in which the anions are weakly coordinated as observed in $[Cuen_2]X_2$ ($X = ClO_4^-, BF_4^-$)[14], or distorted from T_d symmetry by lattice requirements, by site-symmetry effects or by hydrogen bonds with water molecules. All the spectra of nitrate complexes show evidence in favour of both ionic and coordinated NO_3^-: each of the ν_3, ν_4 and ν_2 (in D_{3h} symmetry) modes are triply or doubly split, while ν_1 is IR active[14]. However, only the mono- and bis-ligand nitrate complexes show, in the low frequency IR region, an intense broad band at 335 – 320 cm^{-1} (Table IV), which can be resolved into two contributions, assignable to $\nu(Cu–O)$ anion modes[15]. Moreover, among all the water-containing complexes, only the $[CuL_2(H_2O)]X_2$ ($X = ClO_4^-$, BF_4^-) ones show, in the far-IR spectra, a medium band in the range 400 – 380 cm^{-1} assignable to $\nu(Cu–O)_{aqua}$ mode[16].

Even though metal-ligand vibrations are often difficult to assign on an empirical basis, from a comparison between the far-IR spectra of the free ligand and those of its metal complexes, the new bands between 320 – 285 cm^{-1} and 270 – 240 cm^{-1}, may be tentatively assigned to the $\nu(Cu–N)$ and $\nu(Cu–S)$ respectively. These values are in agreement with those reported for copper(I)[1,8] and copper(II)[17,18] complexes with similar ligands.

TABLE II

Principal IR bands (cm^{-1}) of L and its copper(II) complexes

Assignments	L	[CuLCl$_2$]. .0·25 H$_2$O	[Cu$_2$L$_3$Cl$_4$]. .2 H$_2$O	[CuL(NO$_3$)]. .NO$_3$.0·5 H$_2$O	[CuL$_2$(NO$_3$)]. .NO$_3$.H$_2$O
ν(O–H)		3 450 m, br	3 450 m, br	3 540 m, s	3 530 m, s
				3 460 m, s	3 440 m, s
ν(ring)	1 615 vs	1 615 vs	1 614 vs	1 612 vs	1 615 vs
	1 527 vs	1 519 vs	1 521 vs	1 522 vs	1 524 vs
	1 428 s	1 432 vs	1 435 s, br	1 440 vs	1 440 s
	1 348 vs	1 340 w, sh	1 345 w	1 323 m	1 330 m, sh
	1 337 s		1 324 w	1 305 s, sh	1 325 m, sh
ν(C=S) + ν(NCN) + ν(NCS)	1 275 vs	1 290 vs	1 272 s	1 280 vs	1 275 vs
	1 252 w	1 248 w	1 250 w, sh	1 248 m, sh	1 245 vs
	1 235 vs	1 214 m, w	1 228 s	1 212 m, s	1 218 m, sh
	1 200 m, w	1 183 w	1 180 w	1 180 m	1 184 m
δ(C=S) + π(ring)	473 s	496 s		496 m, s	496 m, s
		468 w, br	473 m, br	474 m	478 m
		458 m, sh	462 m, sh	454 w	464 m, sh

TABLE II

(*Continued*)

[CuL$_2$(H$_2$O)]. .(ClO$_4$)$_2$	[CuL$_2$(H$_2$O)]. .(BF$_4$)$_2$	[Cu$_2$L$_7$].(NO$_3$)$_4$	[Cu$_2$L$_7$].(ClO$_4$)$_4$	[Cu$_2$L$_7$].(BF$_4$)$_4$
3 460 m, s	3 445 s, br			
1 614 vs	1 610 vs	1 612 vs	1 610 vs	1 610 vs
1 525 vs	1 522 vs	1 520 vs	1 520 vs	1 520 vs
1 438 s	1 435 s, br	1 430 s	1 430 s, br	1 430 s, br
1 340 w, sh		1 345 vs	1 337 m	1 340 m, sh
	1 305 w, sh	1 315 m, sh	1 310 w, br	1 305 w
1 284 vs	1 276 vs	1 270 vs	1 270 vs	1 268 vs
1 244 m, w	1 238 m, s	1 240 s	1 238 s	1 236 s
1 214 m	1 210 m, w	1 220 m, sh	1 218 m, sh	1 210 m, sh
1 182 m	1 180 m, w	1 185 w	1 180 w, sh	1 180 w, sh
496 m, s	497 m, s			
472 w	471 w	477 m, s	480 m, w	478 s
460 w	460 w, sh	468 m, sh	460 m, w	463 s

TABLE III

IR bands wavenumbers (cm^{-1} attributed to the ClO_4^-, BF_4^- and NO_3^- groups of copper(II)-L complexes

Assignments for $XY_4(T_d)$	$[CuL_2(H_2O)]X_2$		$[Cu_2L_7]X_4$		$[CuL(X)]X$ $.0{\cdot}5\ H_2O$ $X = NO_3^-$	$[CuL_2(X)]X$ $.H_2O$ $X = NO_3^-$	$[Cu_2L_7]X_4$ $X = NO_3^-$	Assignments for $NO_3^-(D_{3h})$
	$X = ClO_4^-$	$X = BF_4^-$	$X = ClO_4^-$	$X = BF_4^-$				
ν_3 $\nu_d(XY)$	1 140 s	1 105 vs, sh	1 130 s, sh	1 110 vs, br	1 768 mw	1 770 mw	1 745 m	$\nu_1 + \nu_4$
	1 110 vs, sh	1 080 vs	1 115 vs, sh	1 080 vs, sh	1 715 m, br	1 738 m		
	1 090 vs, br	1 060 vs	1 090 vs, br	1 060 vs				
ν_1 $\nu_s(XY)$	940 vw	masked	930 vw	masked	1 745 vs	1 475 m, sh	1 455 m, sh	$\nu_d(NO)$ ν_3
					1 385 vs	1 390 vs	1 385 vs	
ν_4 $\delta_d(YXY)$	635 m	522 s	636 mw	520 vs	1 290 s, sh	1 285 s	1 315 m, sh	
	625 s		622 s					
ν_2 $\delta_d(YXY)$	masked	353 mw	masked	352 m	1 008 s	1 010 m	1 005 m	$\nu_s(NO)$ ν_1
					833 ms	835 mw	838 w	$\pi(NO_3)$ ν_2
					807 ms	810 mw	826 w	
					738 w	740 w	718 w	$\delta_d(ONO)$ ν_4
					728 w	720 w		
					718 w	715 w		

TABLE IV

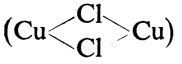
Far-IR spectral bands (400—80 cm^{-1}) of the copper(II)-L complexes and their tentative assignments

Assignments	L	$[CuLCl_2]$. .0·25 H_2O	$[Cu_2L_3Cl_4]$. .2 H_2O	$[CuL(NO_3)]$. .NO_3.0·5 H_2O	$[CuL_2(NO_3)]$. .NO_3.H_2O
ν(Cu-OH_2)					
ν(Cu-X)		339 vs	328 vs	335 vs, br	335 vs, br
		314 ms	281 vs	320 vs, sh	324 vs, sh
ν(Cu-N)		300 ms	300 vs	298 s	314 m, sh
			294 m		302 s
ν(Cu-S)		256 m	264 m, sh	265 m, sh	250 m, w
			246 m, sh		
Ligand and other bands	330 m, w		334 s, sh	328 s, sh	326 s, sh
	282 m	284 m, sh		278 m	272 m, sh
	228 m	231 m, w	227 m	228 w, br	225 w, br
	217 m	212 m, sh	215 m, sh	212 w, sh	216 w
		202 m	202 m		
		174 w, br	178 m, br	173 m, sh	170 w
		155 m, sh	150 m	164 m, br	150 w
		141 s	144 m	150 m, sh	139 w
	87 m, br	106 m, br	106 m, br	100 m, br	102 m, br

For the mono-ligand chloride complex, the presence of a doublet at 339, 314 cm^{-1} in the metal-halogen stretching region, ($\nu_{as}(B_1) + \nu_s(A_1)$ in C_{2v} symmetry group), strongly suggests an essentially *cis*-planar $[CuNSCl_2]$ arrangement around the copper(II) ion, but with probably long Cu–Cl bond interaction from adjacent units along the z axis as frequently observed in planar copper(II) halide complexes[3,19]. For $[Cu_2L_3Cl_4]$.2 H_2O, the far-IR spectrum shows two strong bands at 328 and 281 cm^{-1}, which can be assigned to terminal and bridging ν(Cu–Cl) modes respectively, by analogy with other complexes of copper(II) chlorides[20]. In fact, the frequency position of these bands together with the magnetic moment (1·64 B.M.) and ligand field absorptions[21], tend to exclude the presence of discrete more or less distorted tetrahedral or planar $[CuCl_4]^{-2}$ units and therefore the possibility that the compound may be formulated as $[CuCl_4][CuL_3]$.2 H_2O, as reported for $[M_2L_3X_4]$ (M = Co, Hg; X = Cl, Br) complexes with 1-methyl- and 1,4,6-trimethylpyrimidine-2-thione[2]. Although for compounds of the type $[Cu_2L_3X_4]$ (X = halide)[22] there are not reliable models for which the crystal structure has been resolved, all

TABLE IV
(*Continued*)

$[CuL_2(H_2O)].(ClO_4)_2$	$[CuL_2(H_2O)].(BF_4)_2$	$[Cu_2L_7](NO_3)_4$	$[Cu_2L_7](ClO_4)_4$	$[Cu_2L_7](BF_4)_4$
384 w, br	395 m, w			
319 ms	317 m	300 ms	302 m	303 m
296 vs	296 s	288 ms	288 m	289 m
245 m	250 w	261 m	266 m	266 m, w
		245 w, br	245 m	246 m
334 m, sh	330 m	324 w	334 w	334 w
277 m, sh	276 m	278 m, sh	278 m	279 m, sh
226 w	222 w, sh	222 w, sh	224 m	223 m
214 w				
202 w	202 m	206 m	205 m	209 m, w
177 w	178 w	169 m	174 m, br	175 m, br
150 m, w	152 w	151 m	150 m	151 w
138 w	140 w	138 m	139 m	140 w
98 m, br	98 m, br	102 vs, br	110 s	109 m, br

the data of the $[Cu_2L_3Cl_4].2\ H_2O$, are consistent with a copper(II)–chlorine bridged  $(\mathrm{Cu}{<}^{\mathrm{Cl}}_{\mathrm{Cl}}{>}\mathrm{Cu})$ binuclear structure.

Magnetic Moments and Reflectance Spectra

Room temperature magnetic moments and diffuse reflectance spectral bands energies are listed in Table V. The electronic spectra were recorded only in the solid phase because possible ligand exchange or solvolysis of the complexes in solution occur. The magnetic properties of the complexes were observed to be significantly different according to the metal–ligand ratio. The 1 : 1, 2 : 3 and 1 : 2 copper(II)–L derivatives (except $[CuLCl_2].0{\cdot}25\ H_2O$, $\mu_{\mathrm{eff}} = 1{\cdot}85$ B.M.), show room temperature magnetic moments like or a bit lower than that expected for spin-only for copper(II) ion; whereas the 2 : 7 complexes are some of relatively few copper(II) compounds in which the effective magnetic moment per copper(II) atom, is almost or completely quenched at room temperature[23–30].

A literature survey[23,31,32], reveals that the room temperature subnormal magnetic moments found for the 2 : 7 complexes, lie in the range generally reported for molecular associations forming bi-, tri- or poly-nuclear copper(II) species through mono-atom bridges[23,28,29] or through bridging diamagnetic ligands containing bidentate groups which form part of a mobile π-system[24–26,32–33].

As pyrimidinethiones are quite versatile in their coordination behaviour[34,35], the very low magnetic moments more than to direct spin–spin interaction arising from metal–metal bond, might be ascribed tentatively to a magnetic super-exchange[23,36] mechanism operating through the $=N-\overset{|}{C}=S$ group or exocylic S-atom of bridging ligand involved in essentially co-palnar $Cu(NCS)_2Cu$[24,37] or $Cu(S)_2.Cu$[28,38–40] rings respectively. However, due to the impossibility to obtain crystallographic data together with the absence of magnetic data over a temperature range, definite conclusions can not be drawn.

The reflectance spectra of the $[CuLX_2].nH_2O$ ($X = Cl$, $n = 0{\cdot}25$; $X = NO_3^-$, $n = 0{\cdot}5$) and $[CuL_2X_2].H_2O$ ($X = ClO_4^-, BF_4^-, NO_3^-$) complexes, showing no bands above 1 000 nm indicative of tetrahedral stereochemistry[41] and displaying two well separated absorption envelopes of moderate intensity in the ranges 585 to 630 nm and 720−800 nm, are consistent with a presence of an equatorial more or less co-planar $[CuNSCl_2]$, $[CuNSO_2]$ and $[CuN_2S_2]$microsymmetry[42,43] respectively, but with probable axial interaction giving rise to a somewhat elongated octahedral geometries[44,45].

The most striking feature of the reflectance spectra of the violet $[Cu_2L_7]X_4$ ($X = ClO_4^-, BF_4^-$) complexes, is the intense "blue band" envelope, comparable to those found for the blue copper(II) protein centres[46], with a maximum at ca 580 nm and a pronounced shoulder on the high frequency side; a broad weak band is also present at ca 825 nm. In spite of its high intensity, by analogy with the position of the main *d–d* band of moderate intensity observed in the spectra of the other complexes, it seems reasonable to assume that the "blue band" is basically *d–d* in origin[47] even if its exact assignment is uncertain and object of discussion at the present[41,48]. The position and the intensity of the bands displayed by the violet compounds are in agreement with those reported for five-coordinated square-pyramidal[49] copper(II) complexes with N,S-donor ligands[50–52].

The brown $[Cu_2L_7](NO_3)_4$ and $[Cu_2L_3Cl_4].2\,H_2O$ compounds, show a set of *d–d* bands similar to that of the violet complexes but with the intensity of the main band considerably smaller. This change in intensity is probably not indicative of a gross structural change as the band maxima do not appear to be significantly shifted.

Polarographic Studies in DMF

In this work, the polarographic studies have been used to evaluate the stability

TABLE V

Solid state (Nujol mull) electronic spectra (nm) and magnetic moments μ_{eff} (B.M.) at room temperature of the copper(II)–L complexes

Compounds	Ligand and CT bands			*d–d* bands		μ_{eff}
L	370 vs, br	395 s, sh				
[$CuLCl_2$).0·25 H_2O	355 vs	432 vs, br		585 m	720 m	1·85
[$Cu_2L_3Cl_4$].2 H_2O	360 vs, br	440 s, sh	538 m	585 m	825 m, sh	1·65
[$CuL(NO_3)$]NO_3.0·5 H_2O		422 vs, br		600 m	770 m, sh	1·70
[$CuL_2(NO_3)$]NO_3.H_2O	375 vs, br	440 vs, sh		580 m	800 m, br	1·65
[$CuL_2(H_2O)$]$(ClO_4)_2$	375 vs, br	430 vs, sh		590 m	760 m	1·68
[$CuL_2(H_2O)$]$(BF_4)_2$	385 vs, br	440 s, sh		630 m, br	795 m	1·74
[Cu_2L_7]$(NO_3)_4$	380 vs, br		540 m, sh	575 m	825 m, sh	0·69
[Cu_2L_7]$(ClO_4)_4$	385 vs, br		545 vs, sh	583 vs	825 m, sh	0·80
[Cu_2L_7]$(BF_4)_4$	390 vs, br		543 vs, sh	578 vs	820 m, sh	0·70

TABLE VI

Polarographic data of $Cu(ClO_4)_2$, of ligand and of the [$CuL_2(H_2O)$]$(ClO_4)_2$ and [Cu_2L_7]$(ClO_4)_4$ complexes (in DMF solution) at 25 ±·10°C drop time = 1 s

Species	Conc. 10^{-4} mol. $.l^{-1}$	Wave O		Wave I		Wave II		Wave III		Wave IV	
		$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA
$Cu(ClO_4)_2$	10·0	0·030	7·1								
Ligand (L)	10·0									1·710	4·0
[$CuL_2(H_2O)$]$(ClO_4)_2$	5·0	0·035	0·8	0·230	2·6					1·725	1·0
[Cu_2L_7]$(ClO_4)_4$	5·0			0·250	2·0	1·210	1·4	1·350	3·7	1·710	1·6

constants of the $[CuL_2(H_2O)](ClO_4)_2$ and $[Cu_2L_7](ClO_4)_4$ complexes and mainly to determine the oxidation state of the copper ion in the 2 : 7 compound. We have compared the polarographic behaviours of the $[Cu_2L_7](ClO_4)_4$, $[CuL_2(H_2O)].(ClO_4)_2$ complexes and of the $Cu(ClO_4)_2$–L system at increasing L concentration with those of $Cu(ClO_4)_2$, of free ligand (Tables VI, VII) and particularly with those of $[Cu^IL]ClO_4$ and $[Cu^I_2L_5](ClO_4)_2$ compounds[8].

The polarographic reduction of the Cu^{2+} ion to Cu(Hg) shows only one wave, the process is bielettronic quasi-reversible and diffusion controlled[53]. The reduction of the ligand is one-electron process, diffusion controlled and reversible[8].

Comparing the polarographic behaviour of the $[CuL_2]^{2+}$ species with that of Cu^{2+} ion and of the free ligand (Table VI and Fig. 1), it appears that the $[CuL_2]^{2+}$ complex (wave I) is partially dissociated in Cu^{2+} ions (wave 0) and free ligand (wave IV).

More complicated is the electrochemical reduction of the $[Cu_2L_7]^{4+}$ species since its polarographic curve shows four waves (Table VI and Fig. 1). The wave I and wave IV correspond to the reduction of the $[CuL_2]^{2+}$ and of the free ligand respectively. The waves II and III are due to the reduction of the complexed species, which can be characterized by means of the dependence of $E_{1/2}$ and i_d on the experimental parameters (depolarizer concentration, drop time, etc.) and by the semlog analyses of the polarographic curves.

The amount of i_d values of the waves I, II, and III (Table VI), corresponds to the i_d value of the reduction of the free Cu^{2+} ion; this proves that the copper is present in all species always as copper(II). The wave I and II correspond to two-electrons, quasi-reversible and diffusion controlled processes; the wave III arises from a two-electrons irreversible and diffusion controlled process. To assign the stoichiometry to the compounds corresponding to the waves I, II, and III and to

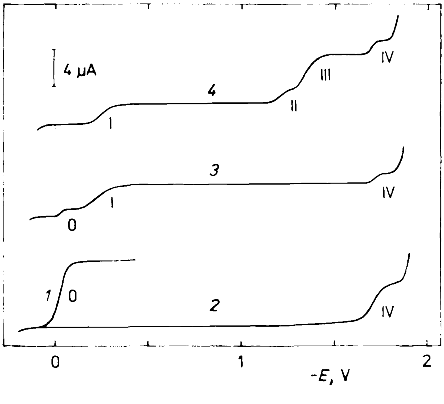


FIG. 1

DC polarographic curves (in DMF) of $Cu(ClO_4)_2$ (1), of the ligand (2), and of $[CuL_2(H_2O)](ClO_4)_2$ (3) and of $[Cu_2L_7].(ClO_4)_4$ (4) complexes. The waves are denoted by Roman numerals. (For experimental conditions see Table VI)

TABLE VII

Polarographic data for the $Cu(ClO_4)_2$–thione system in DMF solution, $C(Cu(ClO_4)_2) = 1{\cdot}0 \, . \, 10^{-3}$ mol l^{-1}, $T = 25 \pm 0{\cdot}1$°C, drop time = = 1 s. Lover lines correspond to data obtained six days later

Thione	Wave O		Wave I		Wave II		Wave III		Wave IV	
conc. 10^{-3} mol l^{-1}	$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA	$-E_{1/2}$ V	i_d μA
0·0	0·030	7·1								
2·0	0·030	1·6	0·240	3·8	1·225	0·5	1·380	1·1	1·710	1·1
	0·035	1·0	0·230	3·7	—	—	1·365	2·1	—	—
4·0	0·030	1·1	0·280	3·0	1·230	1·5	1·360	1·1	1·720	6·9
	—	—	0·280	2·5	1·240	1·1	1·365	3·4	1·715	4·2
6·5	0·030	0·9	0·320	2·9	1·230	1·5	1·370	1·8	1·716	16·5
	—	—	0·325	2·5	1·225	0·5	1·360	4·0	1·705	15·0
7·5	0·035	0·6	0·340	2·5	1·220	1·4	1·350	2·5	1·715	19·5
	—	—	0·335	2·5	—	—	1·335	4·6	1·700	18·0
10·0	0·030	0·3	0·360	2·1	1·210	1·1	1·340	3·4	1·700	29·0
	—	—	0·365	1·8	—	—	1·335	5·1	1·705	27·5

determine their physico-chemical properties, we have examined the polarographic behaviour of the system $Cu(ClO_4)_2$–L at increasing ligand concentration. The experimental data (Table VII), show that the wave 0, corresponding to the reduction of the free Cu^{2+} ion, disappears in the time with the increasing ligand concentration ,whereas all the other waves above described appear. The $E_{1/2}$ of the wave I decreases with the increasing L concentration, while the $E_{1/2}$ values of the waves II and III can be considered constant. The dependence of the $E_{1/2}$ of the wave I on the L concentration, suggests that in solution are present more types of complexes in equilibrium. Since this wave corresponds to a quasireversible and diffusion controlled reduction process, by using the Ayabe–Matsuda method[54], the $E^r_{1/2}$ (reversible half-wave potential) values were determined, and by applying the simplified equation of DeFord–Hume[55] were identified two complexes $[CuL]^{2+}$ and $[CuL_2]^{2+}$, whose overall stability constants are $\beta_{[CuL]^{2+}} = 2{\cdot}5 \,.\, 10^5$ and $\beta_{[CuL_2]^{2+}} = 3{\cdot}1 \,.\, 10^8$, respectively. The dependence of $E^r_{1/2}$ vs log C_L shows that the $[CuL]^{2+}$ is present until a Cu^{2+}/L ratio of 1 : 2. The DeFord–Hume equation and the meaning of the parameters were reported and discussed in a previous paper[8]. The $E_{1/2}$ values of the waves II and III, remaining nearly constant with the increasing L concentration, indicate that to each wave corresponds the reduction of a compound of established composi-

TABLE VIII

Comparison between the free thione concentration values $C'_{L(free)}$ calculated from the solution composition and $C''_{L(free)}$ calculated from the i_d of the wave IV (C^0_L initial thione concentration; C_{Lc} complexed thione concentration). All concentrations are in 10^{-3} mol l^{-1}. Lover lines correspond to values calculated from i_d data determined six days later

C^0_L	C_{Lc} [a]	$C'_{L(free)}$ [b]	$C''_{L(free)}$
2·0	1·8	0·2	0·3
	2·05	—	—
4·0	2·1	1·9	1·7
	2·88	1·1	1·05
6·5	2·34	4·2	4·1
	2·9	3·6	3·7
7·5	2·6	4·8	4·9
	3·0	4·4	4·5
10·0	2·8	7·2	7·2
	3·1	6·9	6·9

[a] $C_{Lc} = [[CuL_2]^{2+}] + [[CuL_3]^{2+}] + [[Cu_2L_7]^{4+}]$; [b] $C'_{L(free)} = C^0_L - C_{Lc}$

tion. The stoichiometry and the overall stability constant of the complexes were determined using the Elenkova and Nedelkeva equation[56] applied to each wave at increasing ligand concentration.

$$\log \beta + q \log C_\mathrm{L} = \log \left\{ \frac{i_\mathrm{d} - i}{i} - \left[\frac{C_\mathrm{L}(0, t_1)}{C_\mathrm{L}} \right]^{q-p} \exp \frac{\alpha n F}{RT} \left[E - (E_{1/2})_\mathrm{irr} \right] \right\} - \frac{nF}{2 \cdot 3RT} (E - E^0_\mathrm{Cu}) = f(C_\mathrm{L})$$

The characteristics of the equation and the meaning of the all parameters mentioned have been reported and discussed previously[8].

The waves II and III correspond to the reduction of the species $[\mathrm{CuL}_3]^{2+}$ and $[\mathrm{Cu}_2\mathrm{L}_7]^{4+}$ which overall stability constant values are: $\beta_{[\mathrm{CuL}_3]^{2+}} = 1 \cdot 0 \,.\, 10^{46}$ and $\beta_{[\mathrm{Cu}_2\mathrm{L}_7]^{4+}} = 1 \cdot 6 \,.\, 10^{52}$, respectively. It is evident that in solution prevail the same complexes reported as solid compounds. Therefore the equilibria and the electrochemical mechanisms can be summarized as below:

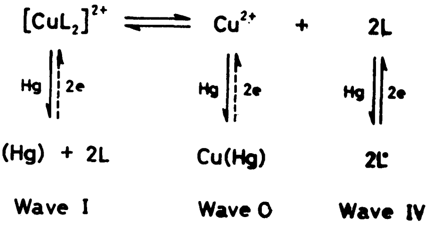
$$2\mathrm{Cu}^{2+} + x\mathrm{L} \rightleftharpoons \underbrace{[\mathrm{CuL}]^{2+} + [\mathrm{CuL}_2]^{2+}} \xrightleftharpoons[\mathrm{Hg}]{2e} 2\mathrm{Cu(Hg)} + 3\mathrm{L} \quad \text{Wave I} \quad (A)$$

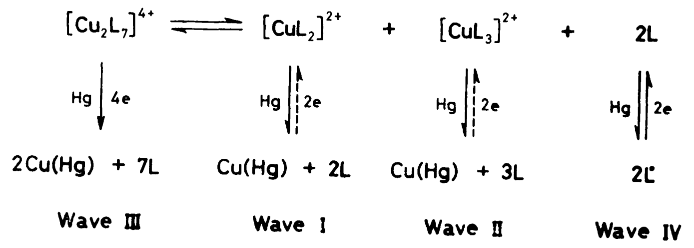
$$[\mathrm{CuL}_2]^{2+} + x\mathrm{L} \rightleftharpoons [\mathrm{CuL}_3]^{2+} \xrightleftharpoons[\mathrm{Hg}]{2e} \mathrm{Cu(Hg)} + 3\mathrm{L} \quad \text{Wave II} \quad (B)$$

$$2[\mathrm{CuL}_3]^{2+} + x\mathrm{L} \rightleftharpoons [\mathrm{Cu}_2\mathrm{L}_7]^{4+} \xrightleftharpoons[\mathrm{Hg}]{4e} 2\mathrm{Cu(Hg)} + 7\mathrm{L} \quad \text{Wave III} \quad (C)$$

$$\mathrm{L} \xrightleftharpoons[\mathrm{Hg}]{e} \mathrm{L}^{\bullet} \quad \text{Wave IV} \quad (D)$$

Polarographic reduction mechanisms of $[\mathrm{CuL}_2]^{2+}$ ana $[\mathrm{Cu}_2\mathrm{L}_7]^{4+}$ complexes:





Finally, in Table VIII are reported the free ligand concentration values calculated:

1) from the i_d values of the reduction wave of the copper(II) compounds taking into account their stoichiometry and supposing that the copper ion is bivalent in each complex;

2) from i_d values of the wave IV which are due to the free ligand reduction. Both the $C'_{L_{free}}$ and $C''_{L_{free}}$ calculated values agree at each ligand concentration and these results are a further evidence that the copper ion in the magnetically subnormal $[Cu_2L_7]^{4+}$ complex is bivalent.

The IR *spectra were recorded in the Centro Interdipartimentale Grandi Strumenti of University of Modena.*

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