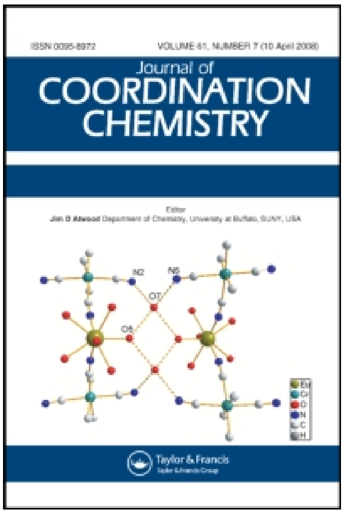

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N-COORDINATED COPPER(II) COMPLEXES WITH 2-*S*-METHYL-5, 5-DIMETHYLIMIDAZOLIN-4-ONE (L). CRYSTAL STRUCTURE OF $[CuL_4H_2O][CuCl_4]$

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The reaction between CuX_2 (X = Cl, Br, NO_3, ClO_4) and 2-*S*-methyl-5,5-dimethylimidazolin-4-one (L) yields complexes having stoichiometry $CuL_2Cl_2 \cdot 1/2H_2O$ (**1**), CuL_2Br_2 (**2**), $CuL_4X_2 \cdot 2H_2O$ [X = NO_3 (**3**), ClO_4 (**4**)]. The X-ray crystal structure solved for **1** showed that it contains discrete $[CuL_4 \cdot H_2O]^{2+}$ and $[CuCl_4]^{2-}$ ions, separated by normal van der Waals contacts. The $[CuL_4H_2O]^{2+}$ cation has crystallographic C_4 symmetry, with the copper atom and the oxygen of the water molecule lying on a four-fold axis of the space group *P4/n* and the metal atom in a square-pyramidal coordination geometry, obtained by a square basal plane defined by four N atoms and the apex occupied by the water molecule. The $[CuCl_4]^{2-}$ anion shows a very flattened tetrahedral geometry. FT-IR and FT-Raman spectra of **1–4** show that **2,3** and **4** also are N(3)-coordinated to copper; nitrate and perchlorate do not coordinate. The ν(CuO) vibrations are present at about 380 cm^{-1} for **3** and **4**, while for **2** ν(CuBr) are at 224 and 215 cm^{-1}. Esr data for **1–4** recorded on solid samples highlight a $d_x{}^2 - y^2$ ground state for the cation of **1**, **3**, and **4** which is typical for tetragonally elongated monomeric copper(II) complexes. Compound **2** exhibits two couples of g values characteristic of two independent copper centres both with compressed tetrahedral geometry. The deconvoluted reflectance spectra of **1–4** substantially confirm the presence of CuN_4 and $CuBr_4$ chromophores in **2** and a *trans*-CuN_4O_2 chromophore in **3** and **4**. For the latter complexes an orbital sequence $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xy}, d_{yz}$ is also suggested on the basis of the similarity between L and imidazole type ligands.

KEYWORDS: Copper(II), complexes, 2-*S*-methyl-5,5-dimethylimidazolin-4-one, X-Ray structure, FT-IR, FT-Raman, Esr.

INTRODUCTION

2-*S*-methyl-5,5-dimethylimidazolin-4-one (L) can be obtained[1] in two annular desmotropic Δ^1 and Δ^2 isomers.

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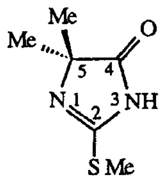
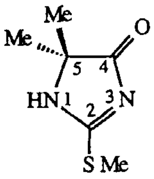


Δ1



Δ2

According to Lempert *et al.*,[2] who solved the X-ray structures of two desmotropes of the *S*-Me derivative of 5,5-diphenylthiohydantoin, solvent polarity is the crucial factor in obtaining one of the two isomers. Apolar solvents, such as carbon tetrachloride or benzene stabilize the Δ^1 isomer, polar solvents such as water stabilize the Δ^2 isomer, while a mixture of the two isomers is always present in intermediate dielectric constant solvents.

From a biological point of view, L can be considered an interesting ligand since its imidazoline skeleton is close to that of imidazole which is widely investigated[3] as a ligand for copper(II). The presence in L of a carbonyl, an *S*-methyl and two methyl groups in the ring positions 4, 2 and 5, respectively, would confer ligand properties towards metal ions which are peculiar with respect to imidazole. Pursuant to our interest[4] in the coordinating abilities of heterocyclic pentaatomic ligands we have undertaken a study of the reaction between L and copper(II) chloride, bromide, nitrate and perchlorate in isopropanol solutions.

EXPERIMENTAL

Materials

2-*S*-methyl-5,5-dimethylimidazolin-4-one was prepared as previously described and recrystallized from benzene.[1] All the solvents and copper salts used in the synthesis of **1**–**4** were purchased from Aldrich and used without any further purification.

$[CuL_4H_2O][CuCl_4]$ (**1**)

A mixture of $CuCl_2$ (0.269 g, 0.002 mol), 2-*S*-methyl-5,5-dimethylimidazolin-4-one (0.632g, 0.004 mol) and isopropanol (100 cm^3) was reacted at room temperature for 15 mins. By adding petroleum ether to the mixture a green, microcrystalline solid was formed (70% yield). This green precipitate, which was recrystallized from isopropanol, had m.p. 158 °C; anal. % (calcd. for $C_{24}H_{42}Cl_4Cu_2N_8O_5S_4$): C, (31.3) 31.6; H, (4.6), 4.9; N, (12.2) 12.1; S, (14.0) 14.3; IR (KBr pellet): ν(OH) 3450sbr; ν(NH) 3187s; ν(CO) 1734s, 1710mw; ν(CN) 1519vs cm^{-1}.

CuL_2Br_2 (**2**)

A mixture of $CuBr_2$ and 2-*S*-methyl-5,5-dimethylimidazolin-4-one (1/4 molar ratio) and methanol was reacted at room temperature for 20 mins. The violet precipitate isolated by centrifugation (30% yield) was recrystallized from methanol and isopropanol (1:1 v/v) to give a microcrystalline powder having m.p. 131°C; anal. % calcd. for $C_{12}H_{20}Br_2CuN_4O_2S_2$): C, (26.7) 26.5; H, (3.7) 3.8; N, (10.4) 10.4; S, (11.9) 11.8; IR (KBr pellet): ν(OH) absent; ν(NH) 3195m; ν(CO) 1734s, 1711mw; ν(CN) 1517vs cm^{-1}.

$CuL_4(H_2O)_2(NO_3)_2$ (**3**) *and* *$CuL_4(H_2O)_2(ClO_4)_2$* (**4**)

A solution of $Cu(NO_3)_2 \cdot xH_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ (1 equivalent) in isopropanol/ethanol (1/1 v/v) was added dropwise to a solution of 2-*S*-methyl-5,5-dimethyl-imidazolin-4-one (4 equivalents) in isopropanol. The mixture was stirred for 10 mins at 60°C; the lilac precipitate formed was filtered, washed and recrystallized from isopropanol (20% yield). **3** had: m.p. 172 °C; anal. % (calcd. for $C_{24}H_{44}CuN_{10}O_{12}S_4$) C, (33.7) 33.7; H, (5.2) 5.1; N, (16.3) 16.3; S, (15.0) 14.9; IR (KBr pellet); ν(OH) 3495w, 3440m; ν(NH) 3360m, 3090mbr; ν(CO) 1728vs; ν(CN) 1522vs; $\nu_2(NO_3^-)$ 840-831, $\nu_3(NO_3^-)$ 1380 cm^{-1}. **4** had: m.p. 202°C; anal.% (calcd. for $C_{24}H_{44}Cl_2CuN_8O_{14}S_4$): C, (31.6) 32.0; H, (4.6) 4.5; N, (12.3) 12.4; S, (14.3) 14.4; IR (KBr pellet): ν(OH) 3498w, 3445m; ν(NH) 3350m, 3080m; ν(CO) 1725vs; ν(CN) 1523vs; $\nu_3(ClO_4\ )$ 1088-1117, $\nu_4(ClO_4\ )$ 630 cm^{-1}.

Spectroscopic Measurements

IR spectra were recorded as KBr pellets (4000–400cm^{-1}) using a Perkin-Elmer 983 instrument and a Perkin-Elmer 7500 Data Station. FT-IR spectra were recorded as polyethylene pellets (3500–50cm^{-1}) by means of a Bruker IFS55 Fourier transform infrared spectrometer. The FT-Raman spectra were recorded on a Bruker RFS100 Fourier transform Raman spectrometer operating with an exciting frequency of 1064 nm (Nd: YAG laser). The detection of the signal was made with an indium-gallium-arsenide detector operating at room temperature. The samples were packed as powder into a suitable cell and then fitted into the compartment designed for use with 180° scattering geometry. Reflectance spectra were recorded on a Cary 5 Uv-Vis-NIR Varian spectrophotometer using a disk of polyethylene as support. X-Band esr spectra were obtained at room temperature on solid samples with a Varian E9 spectrometer.

Data Treatment

The electronic spectrophotometric reflectance data were analysed with a calculation program, SPECPEAK, developed in our Department.[5] SPECPEAK allows the breakdown of a spectrum into Gaussian component bands by a non-linear least-squares calculation of the maximum wavelengths and the half bandwidths of each peak and a linear least-squares calculation of heights. The reliability of each deconvoluted spectrum is defined by a parameter, RP (Reliability Parameter), reported in Table V for **1–4**. RP is calculated as $[\Sigma R^2/(Nexp\text{-}Npar)]^{1/2}$ where R are the residuals, Nexp the number of experimental points and Npar the number of optimized parameters (three for each peak).

X-Ray Data Collection and Structure Determination of [CuL$_4$H$_2$O][CuCl$_4$] (**1**)

The solid obtained by adding petroleum ether to the reaction mixture yielded crystals of **1** suitable for an X-ray structure determination. Crystallographic data and other experimental details are summarized in Table I. The diffraction experiment was carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature and using Mo-Kα radiation (λ = 0.71073Å). The diffracted intensities were corrected for Lorentz, polarization and absorption (empirical correction).[6] Scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 7. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\Sigma w(F_O - k|F_C|)^2$. All calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.[8] Anisotropic thermal factors were refined for all non-hydrogen atoms. All hydrogen atoms, with the exception of those of the water molecule, were detected in a difference Fourier map and refined. The final difference Fourier synthesis showed maximum residuals of 0.3–0.5 eÅ^{-3} corresponding to disordered positions of the hydrogen atoms of the water molecule; the remaining residuals were less than 0.3 eÅ^{-3}. Atomic coordinates are listed in Table II.

RESULTS AND DISCUSSION

2-*S*-methyl-5,5-dimethylimidazolin-4-one (L) has been used as Δ^1 since it was better purified in a low polar solvent and in this form it was made to react in isopropanol with the copper(II) salts. Halide complexes were obtained with stoichiometry

Table I Crystallographic data for the chloride complex, **1**.

FORMULA	$C_{24}H_{40}Cl_4Cu_2N_8O_4S_4 \cdot H_2O$
F.W.	919.80
Crystal system	tetragonal
Space Group	*P*4/*n*
a (Å)	15.833 (3)
c (Å)	7.664 (2)
U (Å^3)	1921(1)
Z	2
D_{calc} (gcm^{-3})	1.590
μ(Mo-K$_\alpha$) (cm^{-1})	16.43
Min. transmission factor	0.86
Scan mode	ω
ω-scan width (°)	1.8 + 0.35tanθ
θ-range (°)	3–23
octants of reciprocal space explored	+*h*, +*k*, +*l*
measured reflections	1341
unique observed reflections with $I > 3\sigma(I)$	828
Final *R* and R_w indices*	0.032, 0.035
No. of variables	148
ESD**	1.056

* $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$; $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}$.
** ESD = $[\Sigma w(F_o - k|F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$; $w = 1/(\sigma(F_o))^2$; $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/{}^2F_oLp$.

Table II Positional parameters and their estimated standard deviations for **1**.

Atom	*x/a*	*y/b*	*z/c*
Cu(1)	0.250	0.250	0.7635(2)
Cu(2)	0.250	-0.250	0.500
Cl	0.14455(8)	-0.16730(7)	0.4002(2)
S(6)	0.29089(8)	0.09692(8)	0.4376(2)
O(W)	0.250	0.250	1.0517(8)
O(7)	0.1253(2)	0.1189(2)	0.9843(5)
N(1)	0.1758(2)	0.0051(2)	0.6147(5)
N(3)	0.2109(2)	0.1274(2)	0.7400(5)
C(2)	0.2227(3)	0.0739(3)	0.6047(6)
C(4)	0.1525(3)	0.0897(3)	0.8502(6)
C(5)	0.1278(3)	0.0038(3)	0.7754(6)
C(8)	0.0329(3)	0.0004(4)	0.7365(7)
C(9)	0.1555(3)	-0.0682(3)	0.8935(7)
C(61)	0.2606(3)	0.0215(3)	0.2737(7)
H(8A)	0.015(3)	0.047(2)	0.678(5)
H(8B)	0.021(3)	-0.048(3)	0.665(7)
H(8C)	0.003(3)	-0.005(3)	0.845(6)
H(9A)	0.213(3)	-0.069(3)	0.920(5)
H(9B)	0.142(3)	-0.124(3)	0.838(6)
H(9C)	0.126(4)	-0.069(4)	1.002(9)
H(10)	0.184(3)	-0.036(4)	0.545(6)
H(61A)	0.205(3)	0.030(3)	0.244(6)
H(61B)	0.275(3)	-0.037(3)	0.323(6)
H(61C)	0.297(3)	0.037(4)	0.180(7)

$CuL_2Cl_2 \cdot 1/2H_2O$ (**1**) and CuL_2Br_2 (**2**) while nitrate and perchlorate salts with stoichiometry $CuL_4X_2 \cdot 2H_2O$ [$X = NO_3$ (**3**), ClO_4 (**4**)] were isolated.

1 was obtained in a crystalline form suitable for an X-ray structural investigation from which it was shown to be formed by discrete $[CuL_4H_2O]^{2+}$ cations and $[CuCl_4]^{2-}$ anions. The shortest interaction between cations and anions was Cl···H(10) (2.436(1)Å). Selected distances and angles in the complex are reported in Table III; an ORTEP drawing of the $[CuL_4H_2O]^{2+}$ cation is reported in Figure 1. The $[CuL_4H_2O]^{2+}$ cation has crystallographic C_4 symmetry, with the copper atom and the oxygen of the water molecule lying on a four-fold axis of the space group *P*4/*n*. Only one ligand is crystallographically independent, the remaining three being generated by the C_4 axis.

The copper atom displays square-pyramidal coordination geometry where the square basal plane is defined by the N(3) atoms of the four L molecules and the apex is occupied by the water molecule. As expected[9] the copper atom Cu(1) is slightly displaced from the basal plane (0.18 Å) towards the water molecule. This was also found[10] in pentacoordinate chloro(ethylendiamine)histaminecopper(II) chloride where the copper atom is 0.13Å above the N_4 plane towards the coordinated chloride.

The arrangement of the ligands about the copper atom is determined by steric repulsions among the methyl groups and by intramolecular hydrogen bonds between the water molecule and the O(7) atoms of the four L molecules [O(7)···O(W) 2.910(4)Å]. The five-membered ring of the ligand is essentially planar; deviations from the best plane are: N(1) 0.021(4), C(2) -0.013(4), N(3) -0.002(3), C(4) 0.014(5), C(5) -0.020(5) Å. O(7) and S(6) atoms are 0.040(3) and

Table III Geometrical data for **1**.

Selected distances (Å) and angles (°)			
Cu(1)-N(3)	2.045(4)	Cu(1)-O(w)	2.209(7)
N(1)-C(2)	1.321(6)	C(2)-N(3)	1.352(6)
N(3)-C(4)	1.388(6)	C(4)-C(5)	1.528(7)
C(5)-N(1)	1.447(6)	C(4)-O(7)	1.206(6)
C(5)-C(8)	1.533(7)	C(5)-C(9)	1.519(7)
C(2)-S(6)	1.714(5)	S(6)-C(61)	1.798(6)
Cu(2)-Cl	2.255(1)		
N(3)-Cu(1)-N(3)^{i}	169.9(2)	N(3)-Cu(1)-N(3)^{ii}	89.56(2)
Cu(1)-N(3)-C(2)	128.3(3)	Cu(1)-N(3)-C(4)	123.8(3)
N(1)-C(2)-N(3)	113.2(4)	C(2)-N(3)-C(4)	106.8(4)
N(3)-C(4)-C(5)	109.0(4)	C(4)-C(5)-N(1)	99.9(4)
C(5)-N(1)-C(2)	110.9(4)	C(5)-C(4)-O(7)	124.8(5)
N(3)-C(4)-O(7)	126.2(4)	N(1)-C(5)-C(8)	110.5(4)
N(1)-C(5)-C(9)	111.5(4)	C(4)-C(5)-C(8)	110.8(4)
C(4)-C(5)-C(9)	111.7(4)	C(8)-C(5)-C(9)	111.9(4)
N(1)-C(2)-S(6)	125.0(4)	N(3)-C(2)-S(6)	121.8(3)
C(2)-S(6)-C(61)	102.3(2)	N(3)-Cu(1)-O(W)	95.0(1)
Cl-Cu(2)-Cl^{iii}	96.61(3)	Cl-Cu(2)-Cl^{iv}	140.35(8)
Torsion angles (°)			
C(61)-S(6)-C(2)-N(1)	13.4	C(61)-S(6)-C(2)-N(3)	- 165.2
S(6)-C(2)-N(3)-C(4)	- 180.0	S(6)-C(2)-N(1)-C(5)	177.8
C(2)-N(1)-C(5)-C(4)	3.8	N(1)-C(5)-C(4)-N(3)	- 3.0
C(5)-C(4)-N(3)-C(2)	- 1.2	C(4)-N(3)-C(2)-N(1)	1.3
N(3)-C(2)-N(1)-C(5)	- 3.5	C(2)-N(1)-C(5)-C(8)	120.5
C(2)-N(1)-C(5)-C(9)	- 114.4	C(2)-N(3)-C(4)-O(7)	- 179.2
N(1)-C(5)-C(4)-O(7)	177.5	C(9)-C(5)-C(4)-O(7)	- 64.5
C(8)-C(5)-C(4)-O(7)	61.0		

Symmetry codes: i) 1/2-*x*, 1/2-*y*, *z*; ii) 1/2-*y*, *x*, *z*; iii) *y*-1/2, -*x*, 1-*z*; iv) 1/2-*x*, -1/2-*y*, +*z*.

–0.035(1)Å out of the plane, respectively. The coordination of L to Cu(1) occurs through the N(3) atom, meaning that L acts as a Δ^2 desmotrope in isopropanol according to the polarity of this solvent.

The [CuCl$_4$]$^{2-}$ anion lies on a $\bar{4}$ crystallographic symmetry element and shows a very flattened tetrahedral geometry with two Cl-Cu(2)-Cl angles of 140.35(8)° and four of 96.61(3)°. The structure of this ion has been reported to be very sensitive to its surroundings.[11–14] The Cu(2)-Cl distance [2.255(1)Å] and the Cl-Cu(2)-Cl bond angles in this compound are comparable with those reported in literature.[15] Since for the other complexes a structural X-ray investigation was not possible, copper(II) surroundings have been suggested by FT-IR, FT-Raman, electronic and esr spectroscopies carried out on solid samples of **2–4**, on the basis of the results for **1**.

The shifts of the IR bands ν(NH), ν(CO) and ν(CN) with respect to those of the free ligand, recorded on samples of **1–4** as KBr pellets in the range 4000–500 cm^{-1}, are the same for all copper(II) complexes thus indicating that ligand coordination always involves the N(3) atom (see Experimental). Further, the ν_2 and ν_3 vibrations of nitrate ion in **3** fall at 840–831 and 1380 cm^{-1} respectively, while ν_3 and ν_4 of perchlorate ion in **4** at 1088–1117 and 630 cm^{-1} respectively, thus excluding these ions in copper coordination. Better evidence of their non-coordination comes from a comparison between the FT-IR and FT-Raman spectra of **3** and **4** with those of KNO$_3$ and KClO$_4$ recorded as polyethylene pellets and reported in Table IV. At

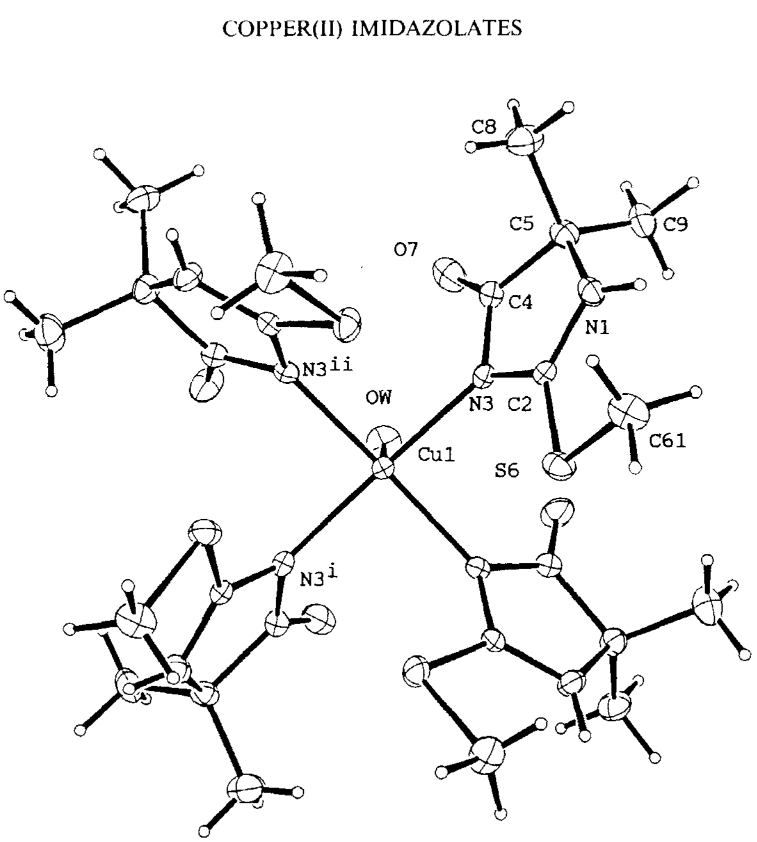


Figure 1 ORTEP drawing of the $[CuL_4 \cdot H_2O]^{2+}$ cation seen almost along the C_4 axis. Thermal ellipsoids are drawn with 30% probability.

Table IV IR and Raman assignments (cm^{-1}) for KNO_3, **3**, $KClO_4$ and **4**.

Compound		$\nu_1 + \nu_4$	ν_1	ν_2	ν_3	ν_4
KNO_3	IR	1763mw		826m	1368m[a]	730s
	R		1049s		1358w	715w
3	IR	1737m	1042vw	829vw	1372w	730s
	R	1736m	1042s		1372	707m
		1718m				
$KClO_4$	IR		939w	463vw	1080sbr	625ms
	R		941s	463s	1086w	628m
					1123w	
4	IR		932ms	478w	1080sbr	624m
	R		932vs	479s	1122w	637m

[a] Polyethylene 1368 cm^{-1}.

1763 cm^{-1} potassium nitrate exhibits a combination IR band which, according to Lever,[16] could be used to distinguish the various coordination modes of the nitrate group. Unfortunately, the presence of a carbonyl group which absorbs in th FT-IR spectrum of **3** at 1737 cm^{-1} does not allow any speculation whenever this band is split at 1736 and 1718 cm^{-1} in the FT-Raman spectrum. Table IV shows for KNO_3 the theoretical bands assigned to a D_{3h} symmetry. A lowering to C_{2v} symmetry should require that ν_1 and ν_2 be both IR and Raman active and that ν_3 andν_4 split both in IR and in Raman. For **3**, only ν_1 is present as an IR band at 1042 cm^{-1} with very weak intensity. Potassium perchlorate for ν_1 and ν_2 shows weak IR absorptions and a split of the ν_3 Raman active band. However this behaviour could be due to a slight distortion from T_d symmetry. The same trend is substantially observed for **4** (see Table IV). Therefore, nitrate and perchlorate ions are to be excluded from possibly coordinating in **3** and **4**, respectively. Conductivity measurements could support this analysis but **3** and **4** are practically insoluble in non-coordinating solvents. The environment of the cation in **1** includes a water molecule as evidenced by a strong broad ν(OH) band at 3450 cm^{-1} in its IR spectrum. Otherwise, according to their stoichiometry, in the range 3500–3000 cm^{-1}, **3** and **4** exhibit ν(OH) at 3495w, 3440m and 3498w, 3445m respectively. The FT-IR and FT-Raman spectra for **3** and **4** in the 400–100 cm^{-1} range are practically superimposable, indicating a strict structural analogy for the two complexes. Hypothesizing a local D_{4h} symmetry for **3** and **4** with a *trans*-N_4O_2 chromophore, three bands due to ν(Cu-N), two Raman and one IR active, and two ν(Cu-O) bands, one IR and one Raman active, would be present. However, the FT-IR and FT-Raman spectra of **3** and **4** exhibit only one IR active band, which is not present in the FT-Raman spectrum, at about 380 cm^{-1}. This agrees with the literature[17] which gives ν(CuO) within 356–282 cm^{-1}, and could be attributed to ν_{as}(CuO). As far as the ν(CuN) modes are concerned, they are given[17] within 275–292 cm^{-1}. Unfortunately many other bands, both in the FT-IR and FT-Raman spectra, are present for **1–4**, and it is difficult to make unambiguous assignments. However, in this range, absorptions at 287 and 257 cm^{-1} for **1**, and at 224 and 215 cm^{-1} for **2** could be assigned to the ν(Cu-Cl)[15] and ν(Cu-Br)[18] modes, respectively. Hence, on the basis of the IR and Raman spectroscopies, **3** and **4** contain the CuN_4O_2 chromophore. The ligand field bands and esr data of **1–4** recorded as solid samples at room temperature are reported in Table V. The $g_\perp$ and $g_\parallel$ values for the cation of **1**, **3** and **4** are characteristic of tetragonally elongated monomeric copper(II) complexes with $d_{x^2-y^2}$ ground state with CuN_4O or CuN_4O_2 chromophores.[19] The couple of $g_\perp$ and $g_\parallel$ values, related to the **1** anion, agrees well with a flattened tetrahedral geometry.[15] Also, **2** exhibits two couples of $g_\perp$ and $g_\parallel$ that are both typical of compressed tetrahedral geometry[19] in agreement with the presence of two independent copper(II) centres. The electronic spectra for **1** and **2** were recorded in the range 200–2200 nm; for **3** and **4** within 200–800 nm. For the anion of **1**, $[CuCl_4]^{2-}$, the deconvoluted d-d bands are six *i.e.* 6.0, 7.1, 7.7, 8.2, 8.9 and 10.4 kK. Evaluating a distortion angle θ of 19.8° for $CuCl_4$ from the structural data, as suggested by Hitchman, the following transition energies, 7.8 (d_{xy}), 8.2, 9.3 (d_{xy}, d_{yz}) and 11.5 (d_{z^2}) kK for a $d_{x^2-y^2}$ ground state, are deduced from Figure 4 of reference 20, in agreement with what was found by deconvoluting the d-d bands of $[CuCl_4]^{2-}$. The bands at 7.1 and 6 kK should be attributed to overtones of ν(OH) and ν(NH) vibrations. The deconvoluted bands due to the cation of **1** as shown in Table V fall at 12.3, 14.8 and 17.2 kK as expected for a square-based pyramidal stereochemistry with the one electron orbital sequence $d_{x^2-y^2}>d_{z^2}>d_{xy}>d_{xz},d_{yz}$. These absorptions fall practically at the same wavenumbers as those found in the pentacoordinated chloro(ethylendiamine)histaminecopper(II) chloride complex[10] for which the following absorptions were identified and assigned: 12.4(d_{z^2}),

Table V Ligand field (LF), epr, deconvoluted LF bands and assignments for **1–4**.

Compound	Ligand Field λ(nm) (kK)	E.p.r.		Gaussian component bands				
		$g_{\perp}$	$g_{\parallel}$	RP[a]	λ(nm)	ν(kK)	$\delta_{1/2}$(nm)[b]	
cation of **1**	630,860	2.067	2.240	0.010	812	12.3	153	d_{z^2}
	(15.9,11.6)				677	14.8	136	d_{xy}
					580	17.2	137	d_{xz}, d_{yz}
anion of **1**	1100,1230,1380	2.062	2.300		1674	6.0	422	
	(9.1,8.1,7.2)				1415	7.1	280	
					1305	7.7	170	d_{xy}
					1220	8.2	125	d_{xz},
					1118	8.9	157	d_{yz}
					961	10.4	204	d_{z^2}
cation of **2**	High Intensity Bands	2.162	2.355	0.008	793	12.6	306	
					568	17.6	179	
					503	19.9	67	
anion of **2**	1030,1420,1730	2.157	2.376		2091	4.8	570	
	(9.7,7.0,5.8)				1698	5.9	426	
					1455	6.9	271	
					1239	8.1	323	
					1000	10.0	283	
3	528,648	2.050	2.210	0.017	652	15.3	153	d_{xy}
	(18.9,15.4)				533	18.8	100	d_{z^2}
					470	21.3	61	d_{xz},d_{yz}
4	538,660	2.048	2.230	0.007	675	14.8	191	d_{xy}
	(18.6,15.1)				538	18.6	110	d_{z^2}
					474	21.1	65	d_{xz},d_{yz}

[a] RP Reliability Parameter defined as in the Experimental section. [b] Half-width at $\varepsilon_{max}/2$.

15.2(d_{xy}), 17.2(d_{xz}), 19.1(d_{yz}) kK. In $[CuL_4H_2O]^{2+}$, the d_{xz} and d_{yz} orbitals are degenerate, since this cation has the local symmetry C_{4v}. The lack of d_{xz} and d_{yz} orbital degeneration in chloro ethylendiamine histamine copper(II) chloride is due to a local C_{2v} symmetry due to the diversion of the Cu-N bond lengths.

For **2** the d-d transitions below 700 nm are hidden by high intensity bands. However, deconvolution of the spectrum shows three bands at 12.6, 17.6 and 19.9 kK and five at 10.0, 8.1, 6.9, 5.9 and 4.8 kK which should be attributed as follows: the former to d-d bands of a CuN_4 chromophore and the latter to a $CuBr_4$ chromophore.

By assuming a similarity between imidazole-like ligands and L, the d-d transitions of **3** and **4** can be compared with those of *trans-O-tetrakis*(imidazole)complexes extensively studied by Su *et al.*[14,21] Typical of these *tetrakis* complexes is the $d_{xy} \rightarrow d_{x^2-y^2}$ transition which always falls at about 15 kK. Since the non-bonding d_{xy} level should be weakly affected by exchanging imidazole with L, we believe that the deconvoluted bands at 15.3 and 14.8 kK in **3** and **4** can be attributed to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. From the structure model of $[CuL_4H_2O]^{2+}$ it is easy to see that to reach a *pseudo*-octahedral geometry around copper(II) the sixth position is sterically hindered by the four *S*-Me groups. Consequently the entrance of the second water molecule in **3** and **4** should occur by a 180° rotation of two L molecules, in order to have two *S*-Me groups on top and two at the bottom of the plane containing CuN_4. This hypothesis allows hexacoordination in the copper(II) complexes and the transitions at 18.8 and 18.6 kK in **3** and **4**, respectively, related to $d_{z^2} \rightarrow d_{x^2-y^2}$ should indicate a higher stabilization of the d_{z^2} level than in

$[CuL_4H_2O]^{2+}$. The degenerate transitions $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, at 21.3 and 21.1 in **3** and **4** respectively indicate a real D_{4h} local symmetry for them.

As far as regards the high intensity bands present in the spectra, the two groups of deconvoluted bands around 260 and 336 nm common to all complexes are due to the ligand. In addition, **3** exhibits a band at 225 nm due to nitrate ion, while **1** and **2** have two CT bands due to the $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ anions at 409 and 564 nm respectively.

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SUPPLEMENTARY MATERIAL

Tables providing complete listings of bond lengths and angles, positional and displacement parameters with e.s.d.'s., general temperature factor expressions, and observed and calculated structure factors (13 pages) are available upon request from the authors.

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