

Structural Characterization of Closely Related Mononuclear Cu^{II} Complexes of 5-Nitrosooxime Pyrimidines. A Combined X-Ray and EPR Study

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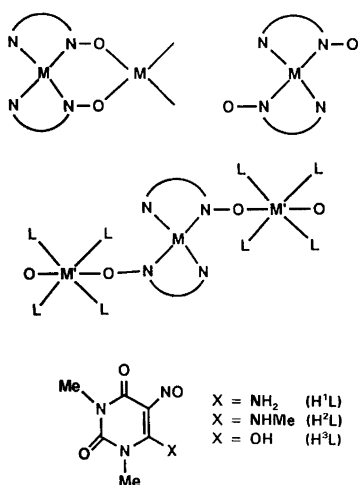
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In reactions of *trans*-bis(oximato)complexes [¹L₂Cu(H₂O)₂] and [²L₂Cu(H₂O)₂] (H¹L = 6-amino-1,3-dimethyl-5-nitrosouracil and H²L = 6-methylamino-1,3-dimethyl-5-nitrosouracil) with [Cu(bipy)₂]²⁺, one of the pyrimidine ligands was replaced by bipy (bipy = 2,2'-bipyridine) affording mononuclear mixed-ligand complexes of the type [LCu(bipy)X] (X is H₂O, EtOH or Cl⁻). Under the reaction conditions, the 6-methylamino group of H²L undergoes hydrolysis leading to violuric acid (5-nitroso-2,4,6-trioxypyrimidine; H³L). Three closely related mononuclear copper(II) complexes, [Cu(¹L)(bipy)(H₂O)]ClO₄·H₂O (1), [Cu(³L)(bipy)(EtOH)][Cu(³L)(ClO₄)(bipy)(EtOH)]ClO₄ (2) and [Cu(³L)Cl(bipy)]·0.5H₂O (3), have been prepared, their crystal structures were determined and an EPR study was carried out.

Mononuclear copper(II) complexes containing two oximato groups in *cis* positions have been successfully used as precursors for homo- and heteropolynuclear complexes in which oximato groups bridge two metal ions (Scheme 1).^{1,2} However, as far as we know, no attempts

have been made with mononuclear *trans*-dioximato precursors. It should be noted that nitrosopyrimidine ligands coordinate to transition metal ions in their iminoxime form, through the oxime N atom and the N atom of the vicinal amino group, to afford mononuclear complexes with two oximato groups in *trans* positions (*cf.* Scheme 1).³ In principle, the deprotonated nitrosooxime groups might also coordinate to another metal ion or metal complex with empty coordination sites to form polynuclear metal complexes. Related to this, it has recently been reported that the nitrosooximato group of 5-nitrosopyrimidine derivatives is able to bridge two metal ions.^{1h,2g,4}

In an attempt to prepare polynuclear complexes, *trans*-bis(oximato)complexes [¹L₂Cu(H₂O)₂] and [²L₂Cu(H₂O)₂]³ (H¹L = 6-amino-1,3-dimethyl-5-nitrosouracil and H²L = 6-methylamino-1,3-dimethyl-5-nitrosouracil) were reacted with [Cu(bipy)₂]²⁺ (prepared *in situ* from Cu^{II} and bipy; bipy = 2,2'-bipyridine). Because of the interligand steric repulsion within the latter complex, we expected that one of the bipy ligands might be replaced by the oximato oxygen atoms of two mononuclear precursors. However, in all cases, one of the pyrimidine ligands was instead replaced by a bipy ligand, affording mononuclear complexes of the type



Scheme 1.

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[LCu(bipy)X] (X is H₂O, EtOH or Cl⁻). It is interesting to note that, under the reaction conditions, the 6-methylamino group of the H¹L ligand undergoes hydrolysis leading to violuric acid (5-nitroso-2,4,6-trioxypyrimidine; H³L). This paper reports the synthesis, structure and EPR studies on three such complexes: [Cu(¹L)(bipy)(H₂O)]ClO₄·H₂O (1), [Cu(³L)(bipy)(EtOH)]ClO₄(ClO₄)(bipy)(EtOH)]ClO₄ (2) and [Cu(³L)Cl(bipy)]·0.5H₂O (3).

Experimental

The ligand H¹L was prepared by nitrosation of 6-amino-1,3-dimethyluracil (Aldrich) with NaNO₂ and acetic acid in water.⁵ The ligand H²L was obtained by reaction of 6-chloro-1,3-dimethyluracil (Sigma) with a solution of CH₃NH₂ in water (40% w/w), and nitrosation of the isolated 6-methylamino-1,3-dimethyluracil as described⁵ for H¹L.

Preparation of the complexes.

Complex 1. Two synthetic approaches were adopted. (a) A mixture of [Cu(¹L)₂(H₂O)₂] (0.466 g, 1 mmol), 2,2'-bipyridine (0.312 g, 2 mmol) and Cu(ClO₄)₂·6H₂O (0.371 g, 1 mmol) in methanol/water (80%, w/w) was stirred until gentle reflux for 15 min. The resulting black solution was left at room temperature and black prisms formed within 72 h. These were washed with methanol and diethyl ether. (b) To a solution of H¹L (0.184 g, 1 mmol) in water (50 ml) Cu(ClO₄)₂·6H₂O (0.186 g, 0.5 mmol) was added. The reaction mixture was gently heated to give a dark-green solution, after which a solution of Cu(ClO₄)₂·6H₂O (0.371 g, 1 mmol) and 2,2'-bipyridine (0.312 g, 2 mmol) was added. The resulting black solution, kept at room temperature, afforded black crystals of the compound. Anal. Calcd. for C₁₆H₁₉N₆O₉CuCl: C, 35.70; H, 3.56; N, 15.61; Cu, 11.80. Found: C, 35.95; H, 3.71; N, 15.90; Cu, 11.61.

Complex 2. The ligand H²L (0.199 g, 1 mmol), Cu(ClO₄)₂·6H₂O (0.566 g, 1.5 mmol) and 2,2'-bipyridine (0.312 g, 2 mmol) were reacted in ethanol, using procedure (b). The black crystals thus formed were washed with ethanol and diethyl ether. Anal. Calcd. for C₁₈H₂₀N₅O₉CuCl: C, 39.35; H, 3.67; N, 12.75; Cu 11.57. Found: C, 39.49; H, 3.64; N, 12.23; Cu, 12.01.

Complex 3. This complex was prepared according to method b for 1, but using CuCl₂·2H₂O instead of Cu(ClO₄)₂·6H₂O. Black crystals formed from the solution and were washed with methanol and diethyl ether. Anal. Calcd. for C₃₂H₃₀N₁₀O₉Cu₂Cl₂: C, 42.87; H, 3.37; N, 15.62; Cu, 14.17. Found: C, 42.56; H, 3.35; N, 15.45; Cu, 14.01.

X-Ray crystallography. For each compound, the unit cell parameters were calculated by least-squares refinement of 25 well centered reflections, and the data were collected by ω–2θ scan mode on a Rigaku AFC-7S diffractometer. Intensities of three reflections monitored periodically

during the data collections exhibited no significant variation. The data were corrected for Lorentz and polarization effects, and in the case of 1, an empirical absorption correction was performed (ψ scans, T=0.94–1.00). The structures were solved by direct methods using SHELXTL/PC⁶ and subsequent Fourier syntheses. Refinements with full-matrix least-squares on F² were carried out using SHELXL93.⁷

In 1, the N(5)–O(5) nitrosooxime group is disordered on two sets of crystallographic positions, N(5a)–O(5b) and N(5b)–O(5b) with site occupation factors 0.43(2) and 0.57(2), respectively. The disordered atoms were refined with isotropic displacement parameters, but the rest of the non-hydrogen atoms with anisotropic displacement parameters. Hydrogen atoms were placed at their calculated positions or were included into idealized rotating groups with tetrahedral angles (CH₃ and H₂O).

For 2, all non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed at their calculated positions or were included in idealized rotating groups with tetrahedral angles (CH₃ and OH).

The structure of 3 consists of two crystallographically independent enantiomeric [Cu(³L)Cl(bipy)] molecules and one crystal water molecule. Carbon atoms were refined with isotropic displacement parameters and the remaining non-hydrogen atoms with anisotropic parameters. Hydrogen atoms of the crystal water molecule could not be positioned, but the rest of the hydrogen atoms were placed at their calculated positions or were included into idealized rotating groups with tetrahedral angles (CH₃).

Crystal and structure refinement data for 1–3 are summarized in Tables 1–4.

Results and discussion

Crystal and molecular structures.

Crystal structure of 1. The asymmetric unit of the structure contains one [Cu(¹L)(bipy)(H₂O)]⁺ cation, one perchlorate anion and one non-bonded molecule of water. In the crystal the ions and molecules are linked together by an extended hydrogen bond network. A perspective view of the complex unit together with an atomic labelling scheme is given in Fig. 1, and selected bond lengths and angles are listed in Table 5. The pyrimidine ligand is coordinated in bidentate fashion through the N(6) atom of the deprotonated amino group and the N(5)–O(5) nitrosooximate group disordered on two sets of crystallographic positions, N(5a)–O(5a) and N(5b)–O(5b). The nitrosooximate group exhibits two different bonding conformations, one through the N(5a) atom and the other through the O(5b) atom, giving rise to five- and six-membered chelate rings, respectively. The Cu^{II} atom exhibits a 4+1 coordination environment consisting of the N(7) and N(18) atoms of the bipy ligand, the N(6) and N(5a) or O(5b) atoms of the

Table 1. Crystal data and structure refinement for complexes 1–3.

Compound	1	2	3
Formula	C ₁₆ H ₁₉ ClCuN ₆ O ₉	C ₃₆ H ₄₀ Cl ₂ Cu ₂ N ₁₀ O ₁₈	C ₁₆ H ₁₅ ClCuN ₅ O _{4.5}
Formula weight	538.36	1098.76	448.32
Temperature/K	293(2)	173(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2 ₁ /c (No. 14)	P2 ₁ /n (No. 14)	Pbca (No. 61)
a/Å	7.915(2)	16.187(9)	13.813(5)
b/Å	13.165(3)	12.811(7)	40.529(14)
c/Å	20.065(4)	21.501(9)	12.404(4)
β/°	93.49(3)	101.18(4)	90
V/Å ³	2086.9(8)	4374(4)	6944(4)
Z	4	4	16
D _{calc} /Mg m ⁻³	1.713	1.668	1.715
μ/mm ⁻¹	1.239	1.183	1.451
F(000)	1100	2248	3648
Crystal size/mm	0.30 × 0.30 × 0.25	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.20
Crystal colour and habit	Violet prism	Black prism	Violet prism
Θ _{max} /°	25.0	25.0	22.5
Index ranges	0 < h < = 9 0 < k < = 16 -25 < l < = 25	0 < h < = 19 0 < k < = 15 -25 < l < = 25	0 < h < = 14 0 < k < = 43 0 < l < = 13
Reflections collected	3715	7708	4527
Independent reflections	3267	6416	4527
Observed reflections [I > 2σ(I)]	1965	4035	1693
Refinement on	F ²	F ²	F ²
Data/restraints/parameters	3263/7/314	6416/5/625	4527/0/340
Goodness-of-fit on F ²	1.041	1.087	0.757
Final R-indices	R1 = 0.0743, wR2 = 0.1581	R1 = 0.0808, wR2 = 0.1738	R1 = 0.0685, wR2 = 0.1140
Δ _{max} and Δ _{min} /e Å ⁻³	0.538, -0.615	0.683, -0.718	0.430, -0.394

Table 2. Selected atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for 1.

Atom	x	y	z	U(eq) ^a or U(iso)
Cu(1)	2121(1)	659(1)	2244(1)	33(1)
O(2)	-1990(8)	3526(5)	190(3)	42(2)
O(4)	1392(9)	4550(5)	1979(3)	57(2)
O(5A) ^b	3001(19)	2764(10)	2652(6)	27(5)
O(5B) ^c	2282(15)	1982(9)	2673(6)	48(4)
N(5A) ^b	2077(22)	2226(13)	2243(10)	30(5)
N(5B) ^c	1886(21)	2806(12)	2411(7)	42(4)
C(5)	980(10)	2784(7)	1816(4)	34(2)
N(6)	302(10)	1059(6)	1611(4)	41(2)
C(6)	73(11)	1997(7)	1442(4)	33(2)
N(7)	2087(9)	-849(5)	2080(3)	26(2)
C(12)	2986(11)	-1382(6)	2536(4)	31(2)
C(13)	3851(11)	-805(7)	3088(4)	32(2)
N(18)	3591(8)	222(5)	3041(3)	32(2)
O(19)	4351(8)	913(5)	1614(3)	44(2)
O(20)	2971(10)	4639(5)	3314(3)	51(2)

^aU(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. ^bSite occupation parameter 0.43(2), isotropic refinement. ^cSite occupation parameter 0.57(2), isotropic refinement.

pyrimidine ligand and, at a longer distance, the O(19) atom of the water molecule.

As expected, bond parameters of the disordered NO group deviate from the values observed for ordered NO groups in 2 and 3 (*cf.* Table 5), but the parameters agree

with those found for disordered bridging groups in dinuclear copper(II) and copper(II)–nickel(II) complexes of related nitrosopyrimidine ligands.^{2b,4} The two different bonding conformations of the nitrosooximate group lead to CuN₄O and CuN₃O₂ coordination polyhedra, both exhibiting a geometry very close to square-pyramidal (SP) with τ-values⁸ of 0.06 and 0.07, respectively (τ = 0 for SP and 1 for TBP). The copper atom is lifted 0.064(6) and 0.185(5) Å from the mean basal planes N₄ and N₃O, toward the apical position. It should be pointed out that recently the X-ray structure was reported⁹ for the closely related complex [Cu(¹L)(bipy)(EtOH)]NO₃; in this complex the nitrosooximate group is not disordered and the pyrimidine ligand is coordinated in a five-membered mode.

Crystal structure of 2. The asymmetric unit of the structure consists of two non-equivalent complex units, [Cu(³L)(bipy)(EtOH)]⁺ (molecule 2a) and [Cu(³L)(ClO₄)(bipy)(EtOH)] (molecule 2b), and one non-coordinated perchlorate anion. A perspective drawing of 2b is given in Fig. 2, and selected bond lengths and angles for both complex units are collected in Table 5.

In both molecules the pyrimidine ligand is coordinated in a bidentate five-membered chelate fashion through the N(5) atom of the oximate group and the O(6) atom of the carbonyl group. The hydrolysis of the 6-methylamino group in the formation of 2 is not unexpected.

Table 3. Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**.

Atom	x	y	z	$U(\text{eq})^a$
Cu(1)	9711(1)	-743(1)	6073(1)	30(1)
Cu(2)	6914(1)	4266(1)	5378(1)	30(1)
Cl(2)	7072(2)	3049(2)	3204(1)	41(1)
O(2)	11 586(4)	-3422(5)	8300(3)	45(2)
O(4)	10 173(5)	-4533(6)	6378(4)	52(2)
O(5)	9380(5)	-2880(6)	5635(4)	61(2)
N(5)	9763(5)	-2309(7)	6045(5)	44(2)
C(5)	10 255(6)	-2722(7)	6576(4)	28(2)
O(6)	10 576(4)	-961(5)	6843(3)	33(2)
C(6)	10 652(5)	-1901(7)	6995(5)	29(2)
N(7)	9857(5)	777(6)	6119(4)	30(2)
C(12)	9406(6)	1315(7)	5643(5)	30(2)
C(13)	8941(6)	661(8)	5117(5)	36(2)
N(18)	9012(5)	-380(6)	5235(4)	34(2)
O(19)	8636(4)	-806(5)	6617(3)	35(2)
C(20)	7937(6)	-78(9)	6574(6)	48(3)
C(21)	8152(7)	837(9)	7008(6)	55(3)
O(32)	4453(5)	1538(6)	3479(4)	63(2)
O(34)	6551(5)	480(5)	5073(4)	55(2)
O(35)	7471(4)	2145(5)	5704(4)	47(2)
N(35)	6957(6)	2705(6)	5369(4)	37(2)
C(35)	6324(6)	2280(7)	4925(5)	34(2)
O(36)	5958(4)	4024(5)	4678(3)	32(2)
C(36)	5824(6)	3066(7)	4560(5)	31(2)
N(37)	6738(5)	5797(6)	5301(4)	36(2)
C(42)	7252(6)	6366(7)	5758(5)	31(2)
C(43)	7755(6)	5728(8)	6261(4)	34(2)
N(48)	7712(5)	4692(6)	6165(4)	35(2)
O(49)	7989(4)	4203(6)	4791(3)	43(2)
C(50)	8644(6)	4943(8)	4803(5)	43(3)
C(51)	8373(8)	5845(9)	4365(6)	57(3)
O(52)	5784(5)	3739(6)	6120(4)	56(2)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

In fact, complex **2** can also be obtained from the complex $[\text{Cu}(\text{H}^4\text{L})]\text{ClO}_4$ [$\text{H}_2^4\text{L} = \alpha, \omega$ -bis(1,3-dimethyl-5-nitrosouracil-6-ylamino)butane, a pseudomacrocyclic ligand in which the amino groups of two 6-amino-1,3-dimethyl-5-nitrosouracil molecules are connected by a butane chain].¹⁰

In molecule **2a** the coordination environment of copper(II) is slightly distorted square-pyramidal ($\tau = 0.08$), with the N(5) and O(6) atoms of the pyrimidine ligand and the nitrogen atoms of bipy forming the basal plane, and the oxygen atom of the ethanol molecule occupying the apical position. In molecule **2b** the five closest atoms of copper are the same as in **2a**, but the oxygen atom O(52) of perchlorate anion in the axial position creates a distorted octahedral coordination environment for Cu(2). In fact, the Cu(2)–O(52) distance is long [2.735(7) Å], and the perchlorate anion can be considered semicoordinated. If the semi-bond is ignored, the coordination stereochemistry of the remaining CuN_3O_2 chromophore is slightly distorted square-pyramidal ($\tau = 0.03$).

In addition to the different number of coordinating atoms there are other significant differences between the

Table 4. Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**.

Atom	x	y	z	$U(\text{eq})^a$
Cu(1)	-157(1)	4340(1)	1327(1)	41(1)
Cu(2)	2846(1)	2158(1)	162(1)	41(1)
Cl(1)	1435(2)	4614(1)	1563(2)	38(1)
Cl(2)	1385(2)	2352(1)	-547(2)	44(1)
O(2)	-2081(5)	5550(1)	3550(5)	65(2)
O(4)	-832(5)	4631(1)	5155(5)	67(2)
O(5)	-133(5)	4182(1)	3628(5)	69(2)
N(5)	-423(6)	4371(2)	2913(6)	48(2)
C(5)	-833(7)	4668(2)	3179(7)	46(3)
O(6)	-1002(5)	4744(1)	1344(5)	53(2)
C(6)	-1174(7)	4847(2)	2307(7)	41(3)
N(7)	-284(5)	4313(2)	-274(5)	36(2)
C(12)	-71(7)	4020(2)	-708(7)	39(3)
C(13)	162(7)	3761(2)	101(8)	48(3)
N(18)	181(5)	3862(2)	1133(6)	46(2)
O(19)	2648(6)	4057(2)	329(6)	91(3)
O(32)	5356(4)	3241(1)	-2014(4)	50(2)
O(34)	3973(5)	3252(2)	1289(5)	73(2)
O(35)	2783(5)	2694(2)	1669(5)	67(2)
N(35)	3141(5)	2598(2)	828(5)	43(2)
C(35)	3774(6)	2764(2)	228(7)	36(2)
O(36)	3912(4)	2302(1)	-892(4)	43(2)
C(36)	4148(7)	2591(2)	-712(7)	45(3)
N(37)	2823(5)	1712(2)	-506(5)	30(2)
C(42)	2687(6)	1459(2)	154(7)	34(2)
C(43)	2621(6)	1541(2)	1294(7)	34(2)
N(48)	2683(5)	1884(2)	1512(5)	36(2)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. ^bSelected bond lengths (in Å) and angles (in °) for **1–3**.

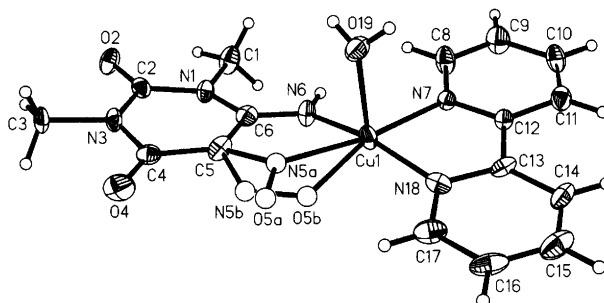


Fig. 1. Perspective view of the $[\text{Cu}^{\text{I}}(\text{L})(\text{bipy})(\text{H}_2\text{O})]^+$ cation in **1**. Displacement ellipsoids are shown with 30% probability level.

two molecules: deviations of copper(II) atoms from the basal N_3O planes toward the apical ethanol oxygen atoms are 0.146(4) and 0.094(4) Å for **2a** and **2b**, respectively; the axial Cu–O(EtOH) distance is shorter in **2a** [2.278(7) Å] than in **2b** [2.340(7) Å]; and the orientation of the O(5) and O(35) atoms with respect to the basal N_3O planes is different, so that in molecule **2a** O(5) does not deviate from the plane, and in molecule **2b** O(35) deviates by 0.184(14) Å.

Bond lengths and angles in the coordination polyhedra compare reasonably well with those found for other Cu^{II} complexes formed by H^2L and closely related nitrosopyrimidine ligands.^{1h,2g,4,11} As previously reported by us,

Table 5. Selected bond lengths (in Å) and angles (in °) for 1–3.

Complex	1	2a	2b	3a	3b
Cu–O(5)	1.944(12)	—	—	—	—
Cu–N(5)	2.06(2)	2.009(8)	2.001(8)	2.006(7)	2.008(7)
Cu–atom(6)	1.934(7)	1.970(6)	1.962(6)	2.009(6)	2.054(6)
Cu–N(7)	2.012(6)	1.962(8)	1.984(8)	1.997(7)	1.986(6)
Cu–N(18)	2.003(7)	1.988(8)	1.995(8)	2.007(7)	2.022(6)
Cu–O(19)	2.258(6)	2.278(7)	2.340(7)	—	—
Cu–Cl	—	—	—	2.480(3)	2.337(3)
Cu–O(ClO ₄)	—	—	2.735(7)	—	—
O(5)–N(5)	1.28(2), 1.24(2)	1.218(10)	1.222(10)	1.238(8)	1.219(8)
O(5)–C(5)	1.39(2), 1.36(2)	1.367(12)	1.372(12)	1.371(10)	1.330(10)
N(5)–Cu–atom(6)	73.4(6)	81.8(3)	81.9(3)	80.3(3)	82.2(2)
N(5)–Cu–N(7)	170.4(6)	170.9(3)	172.7(4)	164.3(3)	169.2(3)
N(5)–Cu–N(18)	107.3(6)	103.1(4)	105.2(4)	102.7(3)	99.8(3)
Atom(6)–Cu–N(7)	99.1(3)	92.3(3)	90.8(3)	90.3(3)	90.2(2)
Atom(6)–Cu–N(18)	167.2(3)	169.0(3)	167.9(3)	157.2(3)	139.7(3)
N(7)–Cu–N(18)	81.3(3)	81.6(3)	81.9(3)	81.2(3)	81.1(3)
O(19)–Cu–N(5)	82.2(5)	91.2(3)	85.9(3)	—	—
O(19)–Cu–atom(6)	99.7(3)	93.0(3)	98.0(3)	—	—
O(19)–Cu–N(7)	93.3(3)	96.1(3)	95.7(3)	—	—
O(19)–Cu–N(18)	93.1(2)	96.7(3)	92.3(3)	—	—
Cl–Cu–N(5)	—	—	—	91.2(2)	91.8(2)
Cl–Cu–atom(6)	—	—	—	98.6(2)	106.5(2)
Cl–Cu–N(7)	—	—	—	102.8(2)	97.8(2)
Cl–Cu–N(18)	—	—	—	103.9(2)	113.6(2)
O(5)–N(5)–C(5)	114.4(14), 117.5(13)	120.4(8)	120.7(8)	120.3(7)	125.7(8)

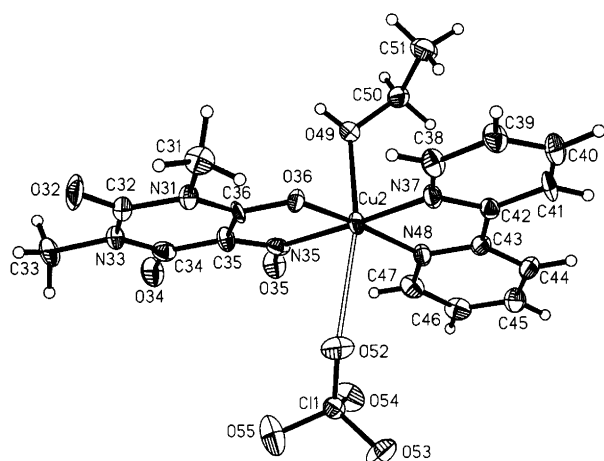


Fig. 2. Perspective view of molecule **2b**, [Cu(3L)(ClO₄)-(bipy)(EtOH)]. Displacement ellipsoids are shown with 30% probability level.

replacement of the N(6) atom by the O(6) atom causes slight lengthening (0.035 Å) of the Cu–atom(6) distance in comparable copper(II) complexes.¹² The difference in the Cu–atom(6) bond lengths between **1** and **2** is somewhat similar to that reported earlier, but for **3** the lengthening is very significant.

In both complex units of **2** the ethanol molecules bonded to copper(II) atoms are involved in hydrogen bonds with oxygen atoms of neighbouring perchlorate anions.

Crystal structure of 3. The asymmetric unit of the structure consists of two enantiomeric complex units, [Cu(3L)Cl(bipy)] (molecules **3a** and **3b**), and one crystal

water molecule. A perspective drawing of **3b** is given in Fig. 3, and selected bond distances and angles for both molecules are listed in Table 5.

In **3a**, the copper(II) atom is in a distorted square-pyramidal environment ($\tau = 0.12$), while the coordination geometry of **3b** is halfway between square-based pyramid and regular trigonal bipyramid ($\tau = 0.48$). Using square-pyramidal description for both complex units, two nitrogen atoms of bipy and the O(6) and N(5) atoms of the pyrimidine ligand occupy the equatorial positions; a chloride anion is coordinated at the axial position.

The basal N₃O plane is more planar in molecule **3a** than molecule **3b**, the maximum deviation from the plane being 0.072(4) Å in **3a**. In **3a**, the copper(II) atom is lifted 0.314(4) Å from the basal plane towards the chloride atom in the apical position, and the dihedral angle between the O(6)Cu(1)N(5) and N(7)Cu(1)N(18) planes is 24.5(3)°. In good accordance with the marked distortion of molecule **3b** from the square-pyramidal

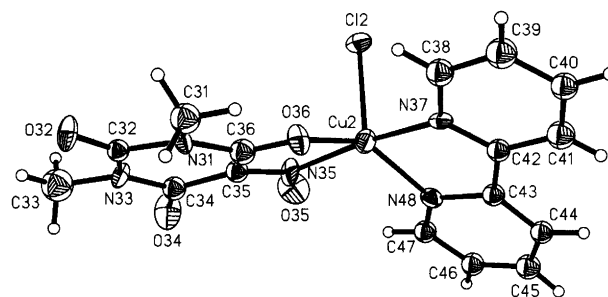


Fig. 3. Perspective view of molecule **3b**, [Cu(3L)Cl(bipy)]. Displacement ellipsoids are shown with 30% probability level.

geometry, the atoms forming the basal plane are pairwise distorted [maximum deviation 0.275(4) Å]. In **3b**, the copper(II) atom is shifted 0.433(3) Å above the basal plane towards the chloride ion and the corresponding OCuN/NCuN dihedral angle is 40.1(3)°.

The Cu–N(5) distances of **3** are the same as those of **2**, but there are significant differences in the Cu–O(6) bond lengths, the distances in **3** being clearly longer than in **2**. The most remarkable differences in the bond lengths between the two molecules of **3** are in the Cu–Cl and Cu–O(6) distances. The Cu–Cl distance in **3a** [2.480(3) Å] is significantly longer than in **3b** [2.337(3) Å], but the Cu–O(6) distance in **3b** [2.054(6) Å] is more lengthened than in **3a** [2.009(6) Å], compared with the corresponding values in **2**.

EPR spectroscopy. The EPR spectra of polycrystalline samples **1–3** at 298 and 77 K (Table 6) are closely similar and resemble the spectrum of an axial doublet with $d(x^2 - y^2)$ ground state. This would be in agreement with the distorted square-pyramidal geometry observed in the crystallographic study.¹³ Hyperfine coupling due to the metal ion (A_{Cu}) could not be resolved even at room temperature, probably because of the insufficient magnetic dilution. The increase in the principal g -components when the temperature was lowered to 77 K might indicate small changes in the molecular conformation. The g_{\parallel} and A_{\parallel} values increase in the order **1** < **2** < **3**, which can be correlated with the distortion from square planarity of the basal plane on going from **1** to **3**.¹⁴ As expected, the values for **1** and **2** are closely similar, in accordance with the structural results, and indicate that both complexes are slightly distorted from the square-pyramidal geometry.

EPR spectra of **1–3** in frozen DMSO solutions at 77 K are characterized by axial g - and A -tensors. Three of the four parallel hyperfine features are well resolved, while the fourth is overlapped by g_{\perp} features, which are partially resolved. From these spectra the parallel components of the spin Hamiltonian parameters, g_{\parallel} and A_{\parallel} , can be readily calculated. The average g_0 and A_0 values were determined from the solution EPR spectra at room temperature (random motion). The spectra at 77 K exhibit, in the g_{\perp} positions, sharp nitrogen nuclear superhyperfine structure on the high-field copperlines. More than the theoretical number of lines are observed (nine

for **1** and seven for **2** and **3**), most likely because of the interaction with the copper atom as well as with the spin of nitrogen nuclei.

It is worth noting here that the EPR spectra of complexes **2** and **3** in solution are almost identical in spite of the significant differences in geometry in the solid state. Perhaps **2** and **3** give rise to the same complex in DMSO solution, formed by coordination of two molecules of DMSO in axial positions on the copper atom to give a distorted octahedral arrangement. In fact, the observed A_{\parallel} would be in accordance with a highly elongated tetragonal geometry around copper.¹⁵

The tendency of g_{\parallel} to decrease and A_{\parallel} to increase, with a greater relative variation of A_{\parallel} than g_{\parallel} , has previously been used as a measure of the strength of in-plane ligand fields under tetragonal geometry in Cu^{II} complexes.¹⁶ Bearing this in mind and assuming also for **1** an elongated tetragonal geometry in DMSO solution, the higher A_{\parallel} value observed for **1** than for **2** and **3** suggests that the in-plane ligand field strength of H¹L is greater than that of H³L. This is in agreement with the replacement of an equatorial nitrogen atom in the coordination polyhedron of **1** by a weaker oxygen, and thus going from **1** to **2** and **3**. We previously reported a similar result for two closely related Cu^{II} complexes with distorted square-pyramidal CuN₄O and CuN₃O₂ chromophores.¹²

Work is in progress to obtain polynuclear complexes from mononuclear *trans*-oximate copper(II) precursors and square-planar [M(L–L)₂] complexes with empty coordination sites (L–L = hexafluoroacetylacetonate or acetylacetonate).

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Supporting information available. Tables for non-hydrogen and hydrogen positional and isotropic displacement parameters, anisotropic displacement parameters, interatomic distances and angles, and least-squares planes for **1** (10 pp.), **2** (15 pp.) and **3** (12 pp.) can be obtained from the authors on request.

References

- (a) Okawa, H., Koikawa, M., Kida, S., Luneau, D. and Oshio, H. *J. Chem. Soc., Dalton Trans.* (1990) 469; (b) Luneau, D., Oshio, H., Okawa, H. and Kida, S. *J. Chem. Soc., Dalton Trans.* (1990) 2283; (c) Luneau, D., Oshio, H., Okawa, H., Koikawa, M. and Kida, S. *Bull. Chem. Soc. Jpn.* 63 (1990) 2212; (d) Chaudhuri, P., Winter, M., Della Vedova, B. P. C., Bill, E., Trautwein, A., Gehring, S., Fleischauer, P., Nuber, B. and Weiss, J. *Inorg. Chem.* 30 (1991) 2148; (e) Ruiz, R., Sanz, J., Cervera, B., Lloret, F., Julve, M., Bois, C., Faus, J., and Muñoz, M. C. *J. Chem. Soc., Dalton Trans.* (1991) 1623; (f) Ruiz, R., Sanz, J., Lloret, F., Julve, M., Faus, J., Bois, C. and Muñoz, M. C.

Table 6. EPR parameters (A -values are given in G).

		Powder Sample		DMSO Solution	
		298 K	77 K	298 K	77 K
Complex 1	g_{\parallel}	2.18	2.26	g_0 2.08	g_{\parallel} 2.31
	g_{\perp}	2.06	2.14	A_0 78	A_{\parallel} 185
Complex 2	g_{\parallel}	2.20	2.27	g_0 2.10	g_{\parallel} 2.33
	g_{\perp}	2.06	2.14	A_0 62	A_{\parallel} 167
Complex 3	g_{\parallel}	2.34	2.37	g_0 2.11	g_{\parallel} 2.33
	g_{\perp}	2.05	2.15	A_0 61	A_{\parallel} 166

- J. Chem. Soc., Dalton Trans.* (1993) 3035; (g) Ruiz, R., Lloret, F., Julve, M., Muñoz, M. C. and Bois, C. *Inorg. Chim. Acta* 219 (1994) 179; (h) Colacio, E., Dominguez-Vera, J. M., Escuer, A., Klinga, M., Kivekäs, R. and Romerosa, A. *J. Chem. Soc., Dalton Trans.* (1995) 343.
- (a) Chaudhuri, P., Winter, M., Fleischauer, P., Haase, W., Florke, U. and Haupt, J. *J. Chem. Soc., Chem. Commun.* (1990) 1728; (b) Basu, P., Pal, S. and Chakravorty, A. *J. Chem. Soc., Dalton Trans.* (1991) 3217; (c) Pal, S., Mukherjee, R., Tomas, M., Falvello, L. R. and Chakravorty, A. *Inorg. Chem.* 25 (1986) 200; (d) Zhong, Z. J., Okawa, H., Matsumoto, N., Sakiyama, H. and Kid, S. *J. Chem. Soc., Dalton Trans.* (1991) 497; (e) Lloret, F., Ruiz, R., Julve, M., Faus, J., Yournaux, Y., Castro, I. and Verdager, M. *Chem. Mat.* 4 (1992) 1150; (f) Birkelbach, F., Winter, M., Florke, U., Haupt, H. J., Burtzloff, C., Leugen, M., Bill, E., Trautwein, A. X., Wieghart, K. and Chaudhuri, P. *Inorg. Chem.* 33 (1994) 3390; (g) Colacio, E., Dominguez-Vera, J. M., Escuer, A., Kivekäs, R. and Romerosa, A. *Inorg. Chem.* 33 (1994) 3914; (h) Lloret, F., Ruiz, R., Cervera, B., Castro, I., Julve, M., Real, J. A., Sapiña, F., Journaux, Y., Colin, J. C. and Verdager, M. *J. Chem. Soc., Chem. Commun.* (1994) 2615.
 - Salas, J. M., Romero, M. A., Sanchez, M. P., Moreno, M. N., Quiros, M., Molina, J., Faure, R. *Polyhedron* 11 (1992) 2177.
 - Dominguez-Vera, J. M., Colacio, E., Escuer, A., Klinga, M., Kivekäs, R. and Romerosa, A. *Polyhedron* 16 (1997) 281.
 - Fuchs, H., Gottlieb, M. and Pleiderer, W. *Chem. Ber.* 111 (1978) 982.
 - Sheldrick, G. M. *SHELXTL/PC*. Version 4.4 Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 - Sheldrick, G. M. *SHELXL93*. Program for the Refinement of Crystal Structures. University of Göttingen, Germany, 1993.
 - Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. and Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* (1984) 1349.
 - Ferguson, G., Low, J. N., Quiros-Olazabal, M., Salas-Peregrin, J. M., Hueso-Ureña, F., Moreno-Carretero, M. N. *Polyhedron* 15 (1996) 3233.
 - Colacio, E., Dominguez-Vera, J.M., Moreno, J. M., Escuer, A., Klinga, M., Kivekäs, R. and Romerosa, A. *Manuscript in preparation*.
 - Romero-Molina, M. A., Martin-Ramos, D., Lopez-Gonzalez, J. D., Valenzuela-Calahorra, C. *An. Quim.* 79 (1983) 200.
 - Moreno, J. M., Ruiz, J., Dominguez-Vera, J. M., Colacio, E., Galisteo, D., and Kivekäs, R. *Polyhedron* 13 (1994) 203.
 - Hathaway, B. J. *Struct. Bonding* 57 (1984) 55.
 - Yokoi, H. and Addison, A. W. *Inorg. Chem.* 16 (1977) 1341.
 - (a) Reinen, D., Ozarowski, A., Jacob, B., Pebler, J., Stratmeier, H., Wieghardt, K. and Tolksdorf, I. *Inorg. Chem.* 26 (1987) 4010; (b) Koch, R., Wilk, A., Wannowius, K. J., Reinen, D. and Elias, H. *Inorg. Chem.* 29 (1990) 3799.
 - Miyoshi, K., Tanaka, H., Kimura, E., Tsuboyama, S., Murata, S., Shimizu, H., Ishizu, K. *Inorg. Chim. Acta* 78 (1983) 23.

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