

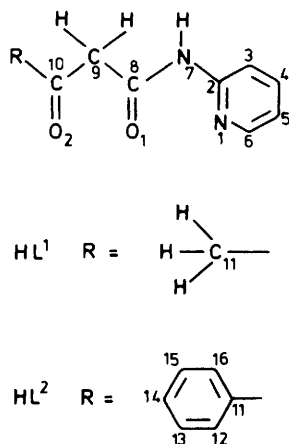
Structural, Spectroscopic, and Magnetic Properties of Mono- and Bi-nuclear Copper(II) Complexes of *N*-(2-Pyridinyl)ketoacetamides †

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The synthesis and properties of two *N*-(2-pyridinyl)ketoacetamide ligands and their mono- and bi-nuclear copper(II) complexes are described. A crystal structure determination for one of the ligands, benzoyl-*N*-(2-pyridinyl)acetamide, HL² (as its hydrochloride hydrate), shows that it belongs to the orthorhombic space group $P2_12_12_1$, with $a = 16.224(9)$, $b = 12.045(6)$, and $c = 7.415(4)$ Å. The β -diketone moiety exists in the enol tautomeric form with unequal C–O bond lengths [1.24(1) and 1.37(1) Å] and other geometric features similar to those in related β -diketones. In solution the ligands display keto–enol tautomerism. Mononuclear copper(II) complexes of type $[CuL_2]$ display spectral and magnetic properties typical of square-planar copper(II) β -diketone chelates. In contrast, binuclear species of type $[Cu_2L_2(CIO_4)_2]$ display very strong antiferromagnetic coupling. The crystal structure of one example involving the *N*-(2-pyridinyl)-acetoacetamide ligand, *viz.* $[Cu_2L_2(CIO_4)_2] \cdot 2H_2O$, shows that it belongs to the triclinic space group $P\bar{1}$, with $a = 10.522(6)$, $b = 9.132(5)$, $c = 8.346(5)$ Å, $\alpha = 102.38(12)$, $\beta = 121.86(14)$, and $\gamma = 93.75(10)^\circ$. The binucleating ligands, L¹, are disposed *trans* to each other in a planar arrangement about the two Cu atoms. The pyridine N and keto O atoms are co-ordinated to each Cu with the amide O acting as a bridging atom. The Cu–Cu distance [3.022(2) Å] and Cu–O–Cu angle [102.0(2)°] can be correlated with the size of the exchange constant, $2J = -588 \text{ cm}^{-1}$, in a similar manner to the values for related μ -alkoxo-copper(II) complexes. The perchlorate groups are weakly co-ordinated to each Cu atom in a bridging bidentate manner.

As part of a wide study of homobinuclear and heterobinuclear complexes of copper(II)^{1–5} we are investigating compounds formed by ligands of the type HL¹ and HL², shown below in the keto tautomeric formulation. This ligand type can be viewed



either as a keto-substituted *N*-2-pyridinylacetamide or as a 2-pyridinylamino-substituted β -diketone.⁶ In either case it involves the little studied 2-pyridinylamido moiety within a potentially binucleating ligand and thus allows comparisons with triketones⁷ and related compartmental ligands⁸ and their binuclear copper(II) compounds. Since the present ligands contain both O,O and O,N donor sets within six-membered

chelate rings, it is possible, in principle, to obtain homo- and hetero-binuclear metal complexes. In the present paper we describe the synthesis, crystal structure, and magnetic properties of homobinuclear copper(II) complexes. Such compounds show very strong antiferromagnetic coupling *via* superexchange within an essentially coplanar *trans*- $[Cu_2L_2]^{2+}$ moiety.

Experimental

All chemicals were of laboratory grade and were used without further purification. Copper(II) perchlorate hexahydrate was obtained from Fluka, Switzerland, and was stored under vacuum over silica gel. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points were measured on a Büchi SMP-20 apparatus and are uncorrected.

Infrared spectra were recorded on a Jasco IRA-1 diffraction-grating spectrophotometer as Nujol mulls: s = strong, m = medium, w = weak, br = broad, and sh = shoulder. Proton n.m.r. spectra were recorded on a Brüker WH90 spectrometer with SiMe₄ as internal reference, ¹³C n.m.r. spectra on a Brüker HX90R spectrometer with SiMe₄ as internal reference. E.s.r. spectra were recorded on a Varian E12 spectrophotometer on frozen glasses and powdered samples at liquid-nitrogen temperature. U.v.–visible spectra were recorded on a Varian Superscan 3 spectrophotometer. Copper analyses were performed by atomic absorption spectroscopy using a Varian AA-1475 instrument.

Synthesis of Ligands HL¹ and HL².—The ligands were prepared by the reaction of 2-aminopyridine with the appropriate ester, ethyl acetoacetate and ethyl benzoylacetate respectively, as described previously.⁹ Both ligands were recrystallized from warm 95% ethanol. Analytical and spectroscopic data are given in Tables 1 and 2.

Synthesis of Mononuclear Complexes $[CuL_2]$ and $[CuL_2]_2$.—Solutions of the appropriate ligand (0.2 mol) and copper(II) acetate monohydrate (0.1 mol) were mixed together in the

† Supplementary data available (No. SUP 56403, 7 pp.): thermal parameters, H-atom co-ordinates, least-squares plane. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: G = 10⁻⁴ T.

Table 1. Analytical and physical data of the ligands and their copper(II) complexes

Ligand or complex	Appearance	M.p./°C	Analysis ^a /%				
			C	H	N	Cl	Cu
HL ¹	White flakes	113—114	60.3 (60.7)	5.70 (5.65)	15.75 (15.70)	—	—
HL ²	White flakes	111—112	70.3 (70.0)	4.90 (5.05)	11.55 (11.65)	—	—
[CuL ¹ ₂]	Dark green microcrystals	210—211	52.0 (51.7)	4.65 (4.35)	13.15 (13.40)	—	14.5 (15.2)
[CuL ² ₂]	Shiny brown microcrystals	242—244	62.0 (62.0)	4.25 (4.10)	10.25 (10.35)	—	11.7 (11.7)
[Cu ₂ L ¹ ₂ (ClO ₄) ₂].2H ₂ O	Dark green crystals	<i>b</i>	30.7 (30.2)	3.05 (3.10)	8.05 (7.80)	9.9 (9.9)	18.0 (17.7)
[Cu ₂ L ² ₂ (ClO ₄) ₂]	Dark green crystals	<i>b</i>	41.7 (41.8)	2.80 (2.75)	6.70 (6.95)	9.0 (8.8)	15.5 (15.8)

^a Calculated values in parentheses. ^b Explodes at *ca.* 260 °C.

Table 2. Spectroscopic and magnetic data

Ligand or complex	I.r. (cm ⁻¹)	U.v.-visible ^a		$\mu_{\text{eff.}}^b$
		$\lambda_{\text{max.}}/\text{nm}$	$\epsilon_{\text{max.}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	
HL ¹	v(CO) 1 725s, 1 670s	199	6 358	—
	v(NH) 3 260m(br), 3 100m, 3 040m	236	11 946	
		275	9 393	
HL ²	v(CO) 1 620—1 640s(br)	208	11 007	—
	v(NH) 3 200w	239	14 169	
		279	9 446	
[CuL ¹ ₂]	v(CO) 1 660(sh), 1 610s(br) v(NH) 3 380w(br), 3 200w(br)	311	11 726	1.82
[CuL ² ₂]	v(CO) 1 620s(br) v(NH) 3 360w(br), 3 120w			1.80
[Cu ₂ L ¹ ₂ (ClO ₄) ₂].2H ₂ O ^d	v(CO) 1 640s(br)	202	25 075	0.82
	v(NH) 3 300m, 3 180m	252	15 937	
	v(ClO ₄) 1 125s, 1 100s(br), 1 055s	286	33 937	
	v(H ₂ O) 3 550m, 3 480m(br)	317	53 167	
		380(sh)	3 394	
		400(sh)	370	
[Cu ₂ L ² ₂ (ClO ₄) ₂] ^e	v(CO) 1 630s	200	42 672	0.93
	v(NH) 3 260w, 3 160w	254br	25 533	
	v(ClO ₄) 1 140s, 1 110s, 1 045s(br)	339	61 560	
		400(sh)	5 596	
		440(sh)	577	
		742	148	

^a (2—5) × 10⁻⁴ mol dm⁻³ solutions in 95% ethanol. ^b Per copper(II) ion at 295 K. ^c Insoluble in 95% ethanol. ^d $g = 2.02 \pm 0.01$, $J = -294 \pm 1 \text{ cm}^{-1}$; 0.09% monomer. ^e $g = 2.00 \pm 0.01$, $J = -262 \pm 1 \text{ cm}^{-1}$; 0.22% monomer.

minimum volume of warm 95% ethanol. The complexes precipitated rapidly as green and brown microcrystals respectively. The products were filtered off, washed with 95% ethanol, and dried in air. Identical products were obtained when the ligand to metal molar ratio was changed to 1:1.

Synthesis of Binuclear Complexes [Cu₂L¹₂(ClO₄)₂].2H₂O and [Cu₂L²₂(ClO₄)₂].—Solutions of the appropriate ligand (0.1 mol) and copper(II) perchlorate hexahydrate (0.1 mol) were mixed in the minimum volume of warm 95% ethanol. The complexes precipitated rapidly as green powders which were filtered off and dried in air. Recrystallization from large volumes of warm 95% ethanol yielded small dark green crystals in both cases. Crystals suitable for X-ray structure determination were obtained only for [Cu₂L¹₂(ClO₄)₂].2H₂O and were grown from a 1:1 solution of 95% ethanol-acetone.

Crystallography.—*Crystal data.* HL².HCl.H₂O, C₁₄H₁₅ClN₂O₃, $M = 294.8$, orthorhombic, $a = 16.224(9)$, $b = 12.045(6)$, $c = 7.415(4)$ Å, $U = 1 449.0$ Å³, $F(000) = 616$ (by least-squares refinement on diffractometer angles for 24 automatically centred reflections, $\lambda = 1.5418$ Å), space group $P2_12_12_1$ (no. 19), $D_m = 1.38(2)$ g cm⁻³ (floatation), $Z = 4$, $D_c = 1.35$ g cm⁻³, pale lemon needles, crystal dimensions (distance to faces from centre) 0.106(001,001) × 0.05(210,210) × 0.038(110,110) mm, $\mu(\text{Cu-K}\alpha) = 23.9 \text{ cm}^{-1}$.

[Cu₂L¹₂(ClO₄)₂].2H₂O, C₁₈H₂₂Cl₂Cu₂N₄O₁₄, $M = 716.44$, triclinic, $a = 10.522(6)$, $b = 9.132(5)$, $c = 8.346(5)$ Å, $\alpha = 102.38(12)$, $\beta = 121.86(14)$, $\gamma = 93.75(10)^\circ$, $U = 649.7$ Å³, $F(000) = 362$ (by least-squares refinement on diffractometer angles for 24 automatically centred reflections, $\lambda = 1.5418$ Å), space group $P\bar{1}$ (no. 2), $D_m = 1.83(2)$ g cm⁻³ (floatation), $Z = 1$, $D_c = 1.83$ g cm⁻³, dark green prolate crystals of dimensions

Table 3. Positional parameters ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
(a) HL²·HCl·H₂O							
Cl	1 607(1)	260(2)	6 127(3)	C(8)	491(5)	3 154(7)	6 549(11)
O(1)	-1(3)	3 934(4)	6 386(8)	C(9)	1 046(5)	2 988(7)	8 026(10)
O(2)	563(3)	4 645(5)	9 519(8)	C(10)	1 060(5)	3 727(6)	9 428(11)
N(1)	-526(3)	3 035(5)	3 349(9)	C(11)	1 578(4)	3 604(5)	11 036(11)
C(2)	68(4)	2 262(6)	3 695(10)	C(12)	1 585(5)	4 439(6)	12 346(11)
C(3)	257(4)	1 436(6)	2 424(11)	C(13)	2 055(5)	4 335(7)	13 905(14)
C(4)	-179(5)	1 427(7)	827(12)	C(14)	2 528(5)	3 406(7)	14 148(14)
C(5)	-774(5)	2 224(6)	475(12)	C(15)	2 532(5)	2 551(7)	12 878(12)
C(6)	-943(5)	3 000(7)	1 746(11)	C(16)	2 064(5)	2 658(6)	11 324(11)
N(7)	508(4)	2 298(5)	5 276(8)	O(3)	3 505(3)	295(4)	15 322(7)
(b) [Cu₂L¹₂(ClO₄)₂·2H₂O							
Cu	728(1)	309(1)	-1 077(1)	C(9)	1 153(6)	-3 010(6)	1 895(8)
Cl	2 869(2)	2 636(2)	4 073(2)	C(10)	217(6)	-2 819(6)	2 582(8)
N(1)	2 191(4)	-661(4)	-1 469(6)	C(11)	24(6)	-3 896(6)	3 591(9)
C(2)	2 739(5)	-1 849(5)	-813(7)	O(1)	779(4)	-951(4)	539(5)
C(3)	3 716(6)	-2 532(6)	-1 199(8)	O(2)	-569(4)	-1 762(4)	2 416(6)
C(4)	4 153(6)	-1 976(7)	-2 306(9)	O(3)	2 536(6)	2 464(6)	2 120(7)
C(5)	3 590(6)	-766(6)	-2 984(9)	O(4)	1 550(6)	1 906(6)	3 920(7)
C(6)	2 624(6)	-141(6)	-2 560(8)	O(5)	3 285(6)	4 226(6)	5 089(9)
N(7)	2 340(5)	-2 466(5)	305(6)	O(6)	4 126(7)	1 944(7)	5 082(10)
C(8)	1 402(5)	-2 116(5)	901(7)	O(7)	3 647(5)	4 966(5)	1 178(6)

(distance to faces from centre) 0.027(100,100) \times 0.056(010, 010) \times 0.10(001,001) mm, $\mu(\text{Cu-K}\alpha) = 45.7 \text{ cm}^{-1}$.

Data collection and processing.¹⁰ HL²·HCl·H₂O. Philips PW1100 diffractometer, ω -2 θ scan mode with ω scan width = 1.5 + 0.2 tan θ , and scan speed 0.04° s⁻¹, graphite-monochromated Cu-K α radiation; 1 265 unique data collected ($3 \leq \theta \leq 60^\circ$, hkl), absorption corrected (maximum, minimum transmission factors = 0.733, 0.581), giving 850 data with $I \geq 3\sigma(I)$. Three standard reflections monitored every 4 h showed no significant variation in intensity over the data-collection period.

[Cu₂L¹₂(ClO₄)₂·2H₂O. As above but scan speed 0.05° s⁻¹. 1 940 Unique data collected ($3 \leq \theta \leq 60^\circ$, $\pm h$, $\pm k$, l), absorption corrected (maximum, minimum transmission factors = 0.802, 0.528), giving 1 680 data with $I \geq 3\sigma(I)$. Three standard reflections monitored every 4 h showed no significant variation in intensity over the data-collection period.

Structure analysis and refinement. HL²·HCl·H₂O. Direct methods. Full-matrix least-squares refinement with chlorine and ligand oxygens anisotropic and hydrogen in calculated positions (except the enol hydrogen, which was located from a Fourier difference synthesis; hydrogens of water not included) with one overall thermal parameter [$U = 0.103(9) \text{ \AA}^2$]. With the data weighted as $[\sigma^2(F)]^{-1}$ the refinement converged at $R = 0.064$, $R' = 0.065$. Inversion of the atomic co-ordinates to check the absolute configuration gave $R = 0.055$, $R' = 0.056$ at convergence. Final atomic parameters given in Table 3 are for this refinement. Programs (DEC VAX 11/780 computer) used and sources of scattering-factor data are given in ref. 11.

[Cu₂L¹₂(ClO₄)₂·2H₂O. Direct methods. Full-matrix least-squares refinement with copper and the atoms of the perchlorate ion anisotropic and hydrogen in calculated positions (except those of water, which were not included) with one overall thermal parameter [$U = 0.05(1) \text{ \AA}^2$]. With the data weighted as $[\sigma^2(F)]^{-1}$ the refinement converged at $R = 0.053$, $R' = 0.059$. Final atomic parameters are given in Table 3. Programs, computer, and sources of scattering-factor data as above.

Magnetic Measurements.—Room-temperature magnetic susceptibilities were determined by the Faraday method on an

instrument described previously.¹² Variable-temperature magnetic susceptibilities were measured over the temperature range 4.3–300 K on a modified Oxford Instruments Faraday balance¹³ using a main field of 10 and/or 40 kG and a gradient field of 1000 G cm⁻¹. The samples (*ca.* 20 mg for the mononuclear complex and *ca.* 60 mg for the binuclear complexes) were placed in a gold bucket which was suspended by a fine quartz fibre from a Sartorius electronic microbalance. The initial measurements between 4.3 and 20 K were made manually and automatic data-logging equipment was used for measurements at higher temperatures. The antiferromagnetism of the binuclear complexes was interpreted in terms of the Bleaney-Bowers expression¹⁴ for a spin-coupled $S = \frac{1}{2}$ system in which the triplet-singlet separation is $2J$. The observed data were fitted using least-squares methods allowing for the presence of monomeric impurity.¹⁵

Results and Discussion

Ligands HL.—We have embarked on an extensive study of the binucleating properties of ligands of types HL¹ and HL² and of various analogues. It is pertinent therefore to describe the spectroscopic and structural properties of these ligands in some detail. The i.r. spectrum of a Nujol mull of HL¹ shows C=O stretching frequencies at 1 725 and 1 670 cm⁻¹, the former due to the CH₃C=O moiety and the latter to the amido C=O (Table 2). In contrast, HL² shows a broad C=O band at 1 620–1 640 cm⁻¹. The move to lower frequency compared with HL¹ is a consequence of replacing methyl with phenyl together with a greater contribution from the enol tautomer. Ligand HL² displays weaker N–H stretching bands than does HL¹, suggesting some intramolecular hydrogen bonding in the former case.

In chloroform solutions both ligands display keto \rightleftharpoons enol tautomerism as judged by ¹H and ¹³C n.m.r. spectroscopy (Table 4). The keto form, shown below, predominates in both cases. A large deshielding effect is exerted by the amido oxygen, O(1), on the enol proton, O(2)H, *via* hydrogen bonding, with the resonance occurring at *ca.* 14 p.p.m. Emsley¹⁶ has recently

Table 4. Chemical shifts (p.p.m. relative to SiMe₄) of the ligands in CDCl₃(a) ¹H

Ligand	Tautomer	Methyl	C(9)H	N(7)H	O(2)H	Pyridyl			Phenyl
						H(5)	H(4)	H(3,6)	
HL ¹	Keto (87%)	2.32	3.62	9.70					
	Enol (13%)	1.97	5.06	9.59	13.5	6.94—7.13	7.61—7.80	8.12—8.32	
HL ²	Keto (73%)		4.17	9.98					
	Enol (27%)		5.79	9.48	14.0	6.93—7.07	7.38—8.31		7.38—8.31

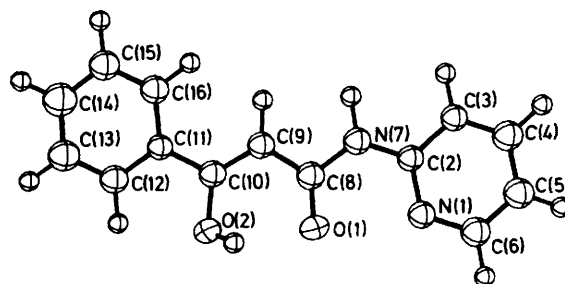
(b) ¹³C

Ligand	Tautomer	Methyl	Pyridyl			Phenyl			Others					
			C(9)	C(8)O	C(10)O	C(2)	C(3)	C(4)		C(5)	C(6)	C(11)	C(14)	
HL ¹	Keto		51.6		203.3									
	Enol	30.8	91.7		*	151.4	114.7	138.6	120.2	147.8				
HL ²	Keto		47.0		194.7									
	Enol		89.3	165.1	*	151.4	115.0	138.4	120.0	147.9	136.1	134.1	125.9, 128.9	

* Not observed.

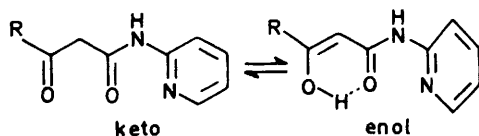
Table 5. Selected bond lengths (Å) and angles (°) for HL²·HCl·H₂O

N(1)—C(2)	1.36(1)	C(9)—C(10)	1.37(1)
N(1)—C(6)	1.37(1)	C(10)—O(2)	1.37(1)
C(2)—C(3)	1.41(1)	C(10)—C(11)	1.47(1)
C(2)—N(7)	1.37(1)	C(11)—C(12)	1.40(1)
C(3)—C(4)	1.38(1)	C(11)—C(16)	1.40(1)
C(4)—C(5)	1.39(1)	C(12)—C(13)	1.39(1)
C(5)—C(6)	1.36(1)	C(13)—C(14)	1.37(1)
N(7)—C(8)	1.40(1)	C(14)—C(15)	1.39(1)
C(8)—C(9)	1.43(1)	C(15)—C(16)	1.39(1)
C(8)—O(1)	1.24(1)	O(2)—H[O(2)]	0.95(1)
		O(1)···O(2)	2.64(1)
		O(1)···H[O(2)]	1.99(1)
Hydrogen bond distances			
Cl···H[N(7)]	2.02	Cl···O(3')	3.18
Cl···N(7)	3.10	O(3)—N(1)	2.74
Cl···O(3)	3.14	O(3)—O(1)	2.89
C(9)—C(10)—O(2)	123.6(7)	C(8)—N(7)—C(2)	126.1(7)
C(10)—C(9)—C(8)	120.0(7)	C(10)—O(2)—H[O(2)]	102.1(5)
C(9)—C(8)—O(1)	125.9(8)		

**Figure 1.** Molecular structure of HL²·HCl·H₂O with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, except for hydrogens which have been reduced for clarity. Water and chloride ions [O(3) and Cl] not included

The crystal structure of HL² has been solved (Figure 1). Pertinent bond lengths and angles are given in Table 5. From the positions of hydrogen atoms seen in a Fourier difference synthesis it was clear that the compound exists in the enol form shown in Figure 1 in which hydrogen is attached to O(2). The unequal bond lengths of C(10)—O(2) and C(8)—O(1), and other dimensions in the β-diketone ring, fit the patterns observed in other β-diketone structures.¹⁶ As seen later this asymmetry is removed in the structure of the dicopper complex. It is noteworthy that the conformation adopted by HL² is ideally suited to the formation of two six-membered chelate rings with a pair of metal ions.

The crystals* used in the structure analysis contained a



discussed δ(OH) shifts of this magnitude in the *cis*-enol tautomers of various β-diketones in relation to substituent and solvent effects on the hydrogen bonding. In the ¹³C n.m.r. spectra the ketonic carbon resonances of C(10) occur at much lower field than the amido carbon resonances of C(8). The latter resonances are in a similar position to those in related *N*-(2-pyridinyl)amides which do not contain a keto substituent, such as *N*-(2-pyridinyl)benzenecarboxamide.¹⁷

* Obtained as a result of hydrolysis of a thionate derivative of HL² and not as described in the Experimental section. The same material, in the form of a hydrochloride hydrate, can be obtained by treating HL² in ethanol with concentrated hydrochloric acid. The i.r. spectra of HL² and HL²·HCl·H₂O are identical except that bands at 3 340 and 1 240 cm⁻¹ are present for the latter.

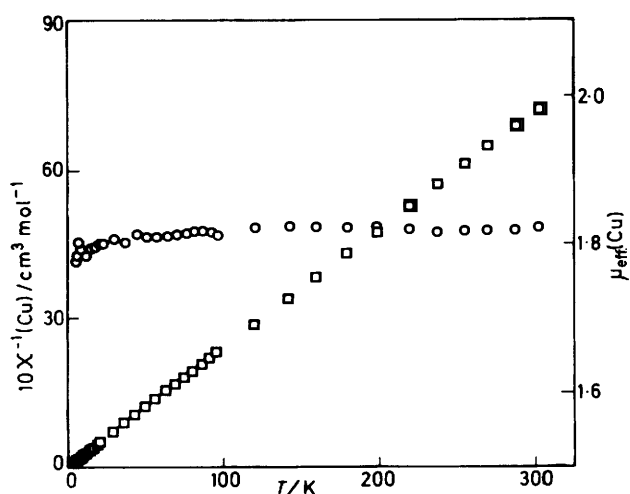


Figure 2. Temperature dependence of the magnetic moments (○) and reciprocal susceptibilities (□) for $[\text{CuL}^1_2]$

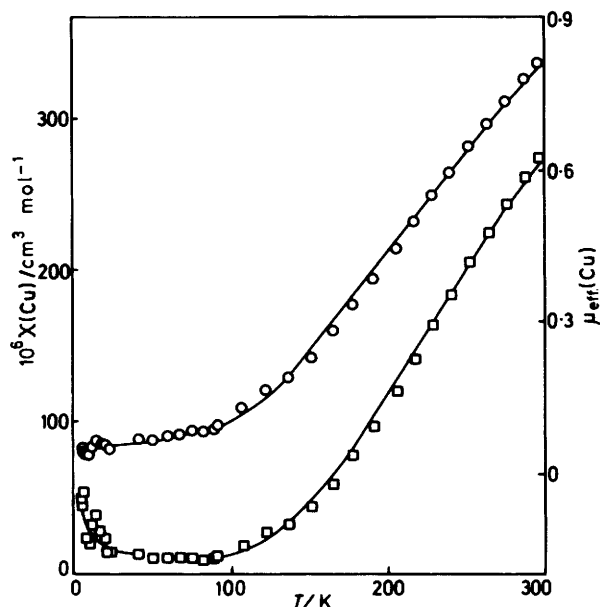


Figure 3. Temperature dependence of magnetic susceptibilities (□) and magnetic moments (○) for $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$. The solid line is the best-fit calculated curve using the parameters given in Table 2

molecule of HCl and a molecule of H_2O in the lattice. These give hydrogen-bonded interactions with each other and with N(7), N(1), and O(1) (Table 5).

Mononuclear Complexes $[\text{CuL}_2]$.—The mononuclear complexes, $[\text{CuL}^1_2]$ and $[\text{CuL}^2_2]$, were obtained in almost quantitative yields on treating copper(II) acetate with ligand in 1:2 molar ratio. Their i.r. spectra (Table 2) show lower C=O stretching frequencies when compared with those of the free ligands. The C=O stretching bands occurring at 1610 cm^{-1} in the spectrum of $[\text{CuL}^1_2]$ are considerably lower than those of the free ligand HL¹ at 1725 and 1670 cm^{-1} . Similarly for $[\text{CuL}^2_2]$ a lower C=O stretching band at 1620 cm^{-1} is observed in comparison with that of the free ligand HL². This shift suggests that the copper is co-ordinated *via* the two carbonyl groups and not by the pyridine nitrogen. Weak broad bands

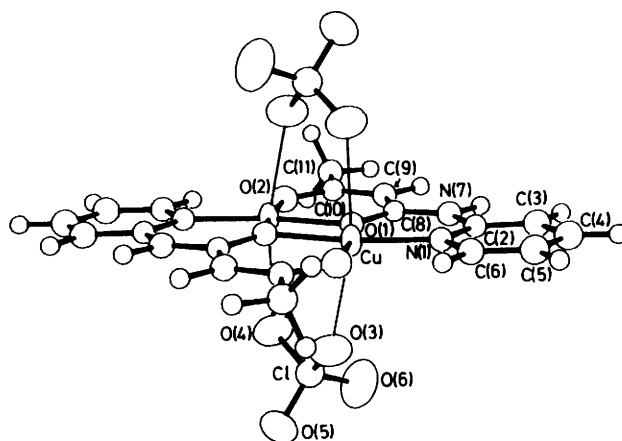


Figure 4. Molecular structure of $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$ with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, except for hydrogens which have been reduced for clarity

have also been observed in the N–H stretching region for both complexes.

The room-temperature magnetic moments of 1.82 and 1.80 observed for $[\text{CuL}^1_2]$ and $[\text{CuL}^2_2]$ respectively are in the range expected for simple mononuclear four-co-ordinate copper(II) complexes. As seen in Figure 2, the magnetic moment of $[\text{CuL}^1_2]$ remains essentially constant between 300 and 4.3 K with the complex showing Curie-like behaviour over the entire temperature range. This magnetic behaviour suggests a planar geometry about the copper ion which would give rise to an orbitally non-degenerate ground state.

Binuclear Complexes $[\text{Cu}_2\text{L}_2(\text{ClO}_4)_2]$.—The binuclear complexes $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{L}^2_2(\text{ClO}_4)_2]$ were obtained in almost quantitative yields by treating copper(II) perchlorate with ligand in 1:1 molar ratio.

The lowering of the C=O stretching bands in the i.r. spectra of $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{L}^2_2(\text{ClO}_4)_2]$ compared with those of the free ligands HL¹ and HL² suggests involvement of the carbonyl groups in co-ordination (Table 2). The shift in frequency is not as large as with the mononuclear complexes, indicating, as expected, stronger C=O character in the carbonyl bonds of the co-ordinated ligand in the binuclear complexes. The i.r. spectra of both complexes show weak bands due to NH stretching vibrations. In addition, strong broad bands related to the perchlorate groups are observed at *ca.* 1100 cm^{-1} . The presence of three distinct bands in this region for both complexes suggests the perchlorate groups are not ionic but in fact are co-ordinated to the copper ions in a bidentate manner. The spectrum of $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$ exhibits bands at *ca.* 3500 cm^{-1} due to the hydrate water molecules.

The u.v.–visible spectra of ethanolic solutions of $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{L}^2_2(\text{ClO}_4)_2]$ show absorbances at 730 (130) and 742 nm ($148\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) respectively, which are attributed to *d-d* transitions. In addition, strong absorbances are observed in the u.v. region which are characteristic of charge-transfer bands.

The low magnetic moments at room temperature of 0.82 for $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$ and 0.93 for $[\text{Cu}_2\text{L}^2_2(\text{ClO}_4)_2]$ indicate that strong antiferromagnetic coupling exists between the two copper(II) ions in each binuclear unit. The variation of magnetic susceptibility with temperature for the two complexes is typical of such strong coupling (Figure 3). The increase in molecular susceptibility at the lowest temperatures is commonly observed^{1,2} in strongly coupled systems and is attributed to the presence of small amounts of monomeric impurity. The

Table 6. Selected bond lengths (Å) and angles (°) for $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2]\cdot 2\text{H}_2\text{O}$

Cu-N(1)	1.961(4)	C(2)-C(3)	1.377(7)	C(2)-N(7)	1.404(7)	Cu(1)-Cu(2)	3.022(2)
Cu-O(1)	1.936(3)	C(3)-C(4)	1.393(8)	N(7)-C(8)	1.348(6)	Cl-O(3)	1.444(5)
Cu-O(1')	1.954(3)	C(4)-C(5)	1.376(8)	C(8)-C(9)	1.384(7)	Cl-O(4)	1.429(5)
Cu-O(2')	1.871(4)	C(5)-C(6)	1.361(8)	C(8)-O(1)	1.293(6)	Cl-O(5)	1.420(5)
Cu-O(3)	2.551(4)	N(1)-C(6)	1.363(7)	C(9)-C(10)	1.380(7)	Cl-O(6)	1.422(5)
Cu-O(4')	2.602(4)			C(10)-C(11)	1.492(7)	O(3)-O(4)	2.344(1)
N(1)-C(2)	1.347(6)			C(10)-O(2)	1.295(6)		
Cu(2)-O(2)-C(10)	126.1(5)	O(1)-C(8)-N(7)	118.9(4)	C(3)-C(4)-C(5)	119.0(6)	O(4')-Cu(1)-O(2')	100.4(2)
O(2)-C(10)-C(9)	125.6(5)	C(8)-N(7)-C(2)	131.9(4)	C(4)-C(5)-C(6)	119.4(6)	O(3)-Cu(1)-O(2')	87.2(2)
O(2)-C(10)-C(11)	114.1(5)	N(7)-C(2)-N(1)	121.6(4)	C(6)-N(1)-C(2)	117.9(4)	O(4')-Cu(1)-O(1')	84.3(2)
C(10)-C(9)-C(8)	126.0(5)	Cu(1)-N(1)-C(2)	124.5(3)	O(3)-Cl-O(4)	109.4(3)	O(3)-Cu(1)-O(1')	81.6(2)
C(9)-C(8)-O(1)	122.4(4)	O(1)-Cu(1)-N(1)	92.0(2)	O(3)-Cl-O(5)	108.7(3)	O(4)-Cu(1)-O(1)	83.2(2)
C(8)-O(1)-Cu(2)	126.5(4)	N(1)-C(2)-C(3)	122.2(5)	O(3)-Cl-O(6)	108.1(4)	O(3)-Cu(1)-O(1)	87.3(2)
Cu(1)-O(1)-Cu(2)	102.0(2)	C(2)-C(3)-C(4)	118.9(5)	O(2')-Cu(1)-N(1)	97.1(2)	O(4')-Cu(1)-N(1)	91.5(2)
O(1)-Cu(1)-O(1')	78.0(2)			O(3)-Cu(1)-O(3')	126.0(1)	O(3)-Cu(1)-N(1)	101.2(2)
Cu(1)-O(1)-C(8)	130.5(5)			O(1')-Cu(1)-O(2')	93.1(2)		

Table 7. Comparisons with related binuclear copper(II) complexes

Complex	$r(\text{Cu}-\text{Cu})/\text{Å}$	Angle/°		J/cm^{-1}	Ref.
		CuOCu	OCuO		
$[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2]\cdot 2\text{H}_2\text{O}$	3.02	102.0	78.0	-294	This work
$[\text{Cu}_2\text{L}^3_2(\text{py})]$	3.05	103.0	77.0	-345	19
$[\text{Cu}_2\text{L}^4_2(\text{H}_2\text{O})_2]$	3.06	103.7	75.1	-370	18
$[\text{Cu}_2\text{L}^5_2(\text{py})_2]$	3.06	103.4	76.6	-370	18
$\alpha\text{-}[\{\text{Cu}(\text{teen})(\text{OH})\}_2][\text{ClO}_4]_2$	2.98	103.0	77.0	-205	25
$[\{\text{Cu}(\text{tmen})(\text{OH})\}_2\text{Br}_2]$	3.00	104.1	75.9	-255	26

py = pyridine, L^3 = heptane-2,4,6-trionate dianion, L^4 = 2,5-bis(trifluoroacetyl)cyclopentanone dianion, L^5 = *N,N'*ethylenebis(benzoyl-acetylacetoneimine) dianion, teen = *N,N,N',N'*-tetraethylethylenediamine, and tmen = *N,N,N',N'*-tetramethylethylenediamine.

monomer is also detected in the e.s.r. spectra of powder or frozen acetonitrile samples as well resolved signals with $g_{\parallel} = 2.29$, $A_{\parallel} = 171 \times 10^{-4} \text{ cm}^{-1}$, and $g_{\perp} = 2.07$, whereas the exchange-coupled copper(II) pairs produce very broad signals at $g \text{ ca. } 2$ and $g \text{ ca. } 4$. The observed susceptibility data were fitted by the Bleaney-Bowers expression¹⁴ and the best-fit magnetic parameters for both complexes are also shown in Table 2. The $2J$ values are in the range -524 to -588 cm^{-1} . In order to correlate structural features with antiferromagnetic coupling of this magnitude a crystal structure analysis was carried out on $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2]\cdot 2\text{H}_2\text{O}$.

The crystal structure confirms that the complex is binuclear with a *trans* arrangement of the *N*-(2-pyridinyl)acetoacetamide ligands (Figure 4). The two copper atoms are bridged by the amido oxygen atoms [O(1) and O(1')] of each ligand, forming a coplanar Cu_2O_2 moiety. Bond lengths and angles are given in Table 6. The Cu-Cu separation is 3.022(2) Å and the Cu-O-Cu angle is 102.0(2)°. These compare well with the known values for binuclear copper(II) complexes of 1,3,5-triketones^{18,19} (Table 7), ligands which co-ordinate in a similar planar fashion.

An approximate square-planar geometry is observed about each of the copper atoms in their co-ordination to the equatorial binucleating ligands. Thus Cu(1) is co-ordinated to the amido oxygen O(1) and pyridine nitrogen N(1) of one ligand [Cu-O(1) 1.936(3) and Cu-N(1) 1.961(4) Å] as well as to the ketonic oxygen O(2') and amido oxygen O(1') of the other [Cu-O(2') 1.871(4) and Cu-O(1') 1.954(3) Å]. The Cu-O bond distances agree well with those observed in binuclear copper(II) complexes of 1,3,5-triketones (1.88–1.97 Å).^{18,19} The Cu-N(1) distance is similar to that observed for binuclear copper(II) complexes of a ligand containing 2-aminopyridine groups in which co-ordination is *via* the pyridine nitrogen (1.95 and 1.96 Å).²⁰

Two perchlorate groups bridge the copper atoms *via* two oxygen atoms each directly above and below the dimeric plane. The perchlorate groups are weakly co-ordinated with an average Cu-O distance of 2.58 Å. The perchlorate bite [O(3)-O(4) separation] of 2.344(1) Å is significantly less than the Cu-Cu distance of 3.022(2) Å leading to axial Cu-O bonds which are not perpendicular to the dimeric plane and which complete a distorted octahedral geometry about each copper atom. Intramolecular perchlorate bridging of this type has previously been reported for some di- μ -hydroxo-dicopper(II) complexes.^{21,22}

The organic ligands are arranged approximately coplanar to the central Cu_2O_2 moiety and show some deviation from the dimeric plane as the distance from the internuclear axis increases. Atoms such as O(2) and N(1), for example, deviate less (0.14 and 0.11 Å respectively) than C(11) and C(3) (0.50 and 0.37 Å respectively). The result is that the ligands deviate slightly from the dimeric plane, one above and one below. Details of the deviations from the best plane are given in Table 8.

The J value of -294 cm^{-1} for $[\text{Cu}_2\text{L}^1_2(\text{ClO}_4)_2]\cdot 2\text{H}_2\text{O}$ compares well (Table 7) with the observed correlations between J and Cu-O distance, CuOCu and OCuO angles found in related binuclear systems.^{18,19,23-27} It would appear from a comparison with the triketone complexes that the trigonal-planar O(1) and O(1') bridging atoms provide the dominant contribution to the superexchange pathway between the Cu($d_{x^2-y^2}$) magnetic orbitals. Substitution of a terminal RC=O group in a triketone by the *N*-(2-pyridinyl) group as in the present compounds gives a small reduction in $r(\text{Cu}-\text{Cu})$, angle CuOCu, and in $-J$. The bridging perchlorate groups probably play a minor role in the exchange-coupling mechanism since they are weakly co-ordinated in the z direction with respect to Cu. Thompson *et al.*²⁰ reached similar conclusions in a study of

Table 8. Deviation (Å) of atoms from Cu(1)–Cu(2) plane of

equation = $-0.2862x - 0.4933y - 0.8214z = 0$

C(6)	0.110(6)	C(9)	0.333(6)
C(5)	0.228(6)	C(10)	0.307(5)
C(4)	0.360(6)	C(11)	0.500(6)
C(3)	0.369(6)	N(1)	0.108(4)
C(2)	0.241(5)	N(7)	0.262(5)
C(8)	0.197(5)	O(2)	0.141(4)

μ -hydroxo- μ -phthalazine complexes of type $[\text{Cu}_2(\text{pap})(\text{OH})\text{Y}]^{n+}$ where Y is a bridging anion such as SO_4^{2-} , NO_3^- , IO_3^- , or ClO_4^- and pap = 1,4-bis(2-pyridylamino)-phthalazine. However, these workers found that variation in Y could finely tune the geometry of the bridging moiety and the resulting J value. We are investigating whether similar variations occur in the present systems when the ClO_4^- group is replaced by other bridging anions.

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