Low-lying Electronic States in μ-Phenolato Copper(II) Binuclear Compounds with Hydroxo, Ethanolato, Azido, and Cyanato Exogenous Bridges: Crystal Structures, Magnetic Properties, and Interpretations

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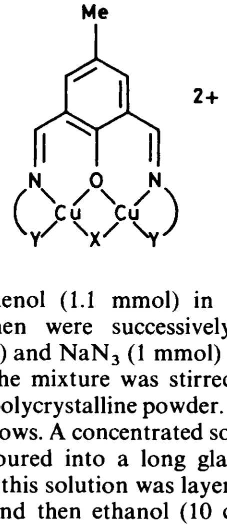
Four novel μ-phenolato copper(II) binuclear complexes with exogenous bridges were synthesized, namely $[Cu_2L^3(X)][ClO_4]_2$, X = N_3 (**1**) or OCN (**2**), and $[Cu_2L^4(X)][ClO_4]_2{\cdot}H_2O$, X = C_2H_5O (**3**) or N_3 (**4**), L^3 is the binucleating ligand 4-methyl-2,6-bis[*N*-(2-pyridylethyl)formimidoyl]phenolate and L^4 = 4-methyl-2,6-bis[*N*-(2-methylthioethyl)formimidoyl]phenolate. The four crystal structures were determined. Compounds (**1**) and (**2**) are isomorphous: space group *Cc*, *a* = 12.723(9) and 12.773(5), *b* = 32.125(7) and 32.167(5), *c* = 8.987(7) and 8.980(4) Å, β = 130.39(5) and 130.35(5)°, and *Z* = 4. Compounds (**3**) and (**4**) are not isomorphous but have rather similar structures: space group $P2_1/c$, *a* = 9.346(2) and 9.669(2), *b* = 32.517(4) and 30.860(4), *c* = 8.866(6) and 8.717(3) Å, β = 97.04(3) and 98.08(2)°, and *Z* = 4. In (**1**)—(**4**), the copper(II) ions of the binuclear unit are bridged by the phenolic oxygen atom and by the exogenous ligand X in an end-on fashion. In (**3**), OCN^- bridges by its oxygen atom. In (**1**) and (**2**) the copper(II) is in a classical 4 + 2 environment but in (**3**) and (**4**) this environment is strongly distorted with the sulphur atom displaced by *ca*. 0.6 Å from the basal plane. The magnetic properties of compounds (**1**)—(**4**) were investigated and revealed a spin-singlet ground state in all cases. The singlet–triplet energy gaps were found as −278(2) for (**1**), −12.9(3) for (**2**), −850(10) for (**3**) and −408(4) cm^{-1} for (**4**). The low-lying states in μ-phenolato compounds with exogenous ligands are discussed.

We have recently undertaken a study, in relation to the molecular structures, of the magnetic properties of copper(II) binuclear compounds with two dissimilar bridges.[1–3] One of the bridges is a phenolato group and remains constant, the other is hydroxo, azido, or cyanato. The former bridge may be defined as endogenous and the latter as exogenous. So far, we have investigated two series of compounds containing binuclear cations of the type $[Cu_2L(X)]^{2+}$ with X = OH, N_3, or OCN and Y = $CH_2CH_2NMe_2$ (L^1) or 2-pyridylmethyl (L^2), *i.e.* $[Cu_2L^1(X)][ClO_4]_2{\cdot}H_2O$ (**A**) and $[Cu_2L^2(X)][ClO_4]_2$ (**B**). This paper completes and terminates this study. It is devoted to two novel series noted $[Cu_2L^3(X)][ClO_4]_2$ (**C**) and $[Cu_2L^4(X)][ClO_4]_2{\cdot}H_2O$ (**D**) where Y = 2-(2′pyridyl)ethyl or 2-methylthioethyl respectively. In series (**C**), two compounds have been investigated with X = N_3 (**1**) or OCN (**2**). The compound with X = OH has been reported, as well as its magnetic properties, but its structure has not been solved.[4,5] In series (**D**), two compounds have been studied with X = C_2H_5O (**3**) or N_3 (**4**). We have not been able to synthesize the cyanato compounds in this series.

First we describe the crystal structures of the compounds, then their magnetic properties. Finally, we attempt to rationalize the magnetic properties of the compounds belonging to the four series (**A**)—(**D**). In conclusion, we will summarize the main information arising from this work.

Experimental

Syntheses.—Compounds (**1**) and (**2**) were synthesized as follows. 2-Aminoethylpyridine (2 mmol) was added to 2,6-diformyl-4-methylphenol (1.1 mmol) in ethanol–acetonitrile (1:1, 50 cm^3). Then were successively added copper(II) perchlorate (2 mmol) and NaN_3 (1 mmol) for (**1**) and NaNCO (1 mmol) for (**2**). The mixture was stirred and filtered. Slow evaporation gave a polycrystalline powder. Single crystals of (**1**) were obtained as follows. A concentrated solution (5 cm^3) of (**1**) in methanol was poured into a long glass tube of 1 cm in diameter. On top of this solution was layered very slowly pure methanol (2 cm^3) and then ethanol (10 cm^3). The tube was plugged. Dark green crystals appeared within a few days (Found: C, 36.85; H, 3.30; Cl, 9.50; Cu, 17.00; N, 12.90; O, 19.55. Calc. for $C_{23}H_{23}Cl_2Cu_2N_7O_9$: C, 37.35; H, 3.15; Cl, 9.60; Cu, 17.20; N, 13.25; O, 19.45%). Single crystals of (**2**) were obtained in a similar way using diethyl ether instead of methanol (Found: C, 38.20; H, 3.20; Cl, 9.50; Cu, 17.00; N, 9.00; O, 21.70. Calc. for $C_{24}H_{23}Cl_2Cu_2N_5O_{10}$: C, 38.95; H, 3.15; Cl, 9.60; Cu, 17.20; N, 9.45; O, 21.65%).



Compounds (**3**) and (**4**) were synthesized as follows. 1-Amino-2-methylthioethane (2 mmol) prepared as previously described,[6] was added to 2,6-diformyl-4-methylphenol (1.1 mmol) in ethanol (50 cm^3). Then were successively added copper(II) perchlorate (2 mmol) and LiOH (1 mmol) for (**3**) and NaNCO

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Details of data collection and structure refinement for compounds (**1**) and (**2**)*

	(**1**)	(**2**)
Formula	$C_{23}H_{23}Cl_2Cu_2N_7O_9$	$C_{24}H_{23}Cl_2Cu_2N_5O_{10}$
μ(Mo-K_α)/cm^{-1}	18.3	18.2
a/Å	12.723(9)	12.773(5)
b/Å	32.125(7)	32.167(5)
c/Å	8.980(7)	8.980(4)
β/°	130.39(5)	130.35(5)
U/Å^3	2 795(7)	2 812(5)
Scan range/°	2.1 + 0.345 tanθ	1.65 + 0.345 tanθ
Reflections collected	2 449	2 471
Reflections kept for refinement [$F > 3\sigma(F)$]	1 530	1 750
Average shift/e.s.d. in last cycle	0.015	0.035
Scale factor	0.51	0.55
R	0.043	0.038
R'	0.046	0.041
Number of data per variable	4.4	4.2

* Details common to both compounds: colour, dark green; D_c = 1.75 × 10^3 kg m^{-3}; crystal system, monoclinic; space group *Cc*: $Z = 4$; Nonius CAD4 diffractometer; graphite monochromator; Mo-K_α radiation (λ = 0.710 70 Å); 24 °C; ω scan type: 2θ range 2—50°; scan speed dependent upon reflections; background, half of scan time, in fixed position before and after every scan; two standard reflections, measured every other hour; reflections measured, two octants; computer program, CRYSTALS, J. Carruthers and D. C. J. Watkin, Chemical Crystallography Laboratory, University of Oxford; atomic form factors, 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4; function minimized $R' = [\Sigma w_i(F_o - F_c)^2/\Sigma w_iF_o]^{\frac{1}{2}}$; no secondary extinction observed; no absorption correction applied (flat ψ scan); unit weights.

Table 2. Details of crystallographic data collection and structure refinement for compounds (**3**) and (**4**)*

	(**3**)	(**4**)
Formula	$C_{17}H_{28}Cl_2Cu_2N_2O_{11}S_2$	$C_{15}H_{23}Cl_2Cu_2N_5O_{10}S_2$
D_c/kg m^{-3}	1.73 × 10^3	1.79 × 10^3
μ(Mo-K_α)/cm^{-1}	20.4	21.3
a/Å	9.346(2)	9.669(2)
b/Å	32.517(4)	30.860(4)
c/Å	8.866(6)	8.717(3)
β/°	97.04(3)	98.08(2)
U/Å^3	2 674(3)	2 575(2)
2θ range/°	3—46	3—50
Reflections collected	4 094	5 141
Reflections kept for refinement	1 759 [$F > 3\sigma(F)$]	1 893 [$F > 2\sigma(F)$]
Number of data per variable	5.4	5.8
Scale factor	0.44	0.43
R	0.0413	0.0473
R'	0.0445	0.0508

* Details common to both compounds: colour, crystal system, Z, diffractometer, monochromator, radiation, temperature, scan speed, background, standard reflections, reflections measured, computer program, form factors, functions minimized, secondary extinction, and weighting scheme as in Table 1; space group *P*2/*c*; scan type ω/1.33θ; scan range, 1.5 + 0.345 tanθ; average shift/e.s.d. 0.07.

(1 mmol) for (**4**). The mixture was stirred and filtered. Slow evaporation afforded polycrystalline powders. Single crystals were obtained by recrystallization from hot ethanol [Found: C, 30.80; H, 4.10; Cl, 9.65; Cu, 18.25; N, 3.90; O, 26.45; S, 8.80. Calc. for $C_{17}H_{28}Cl_2Cu_2N_2O_{11}S_2$ (**3**): C, 29.25; H, 4.05; Cl, 10.15; Cu, 18.20; N, 4.00; O, 25.20; S, 9.20. Found: C, 26.35; H, 3.65; Cl, 10.85; Cu, 17.65; N, 9.75; O, 22.15; S, 9.20. Calc. for $C_{15}H_{23}Cl_2Cu_2N_5O_{10}S_2$ (**4**): C, 25.90; H, 3.35; Cl, 10.20; Cu, 18.25; N, 10.05; O, 23.00; S, 9.20%].

Crystal Data Collection and Refinement.—The structures of compounds (**1**)—(**4**) were determined by *X*-ray diffraction. Preliminary Laue and precession photographs assigned monoclinic unit cells for the four compounds. The space groups [*Cc* for (**1**) and (**2**), $P2_1/c$ for (**3**) and (**4**)] were deduced from systematic absences. Cell dimensions were obtained by least squares from the setting angles of 25 reflections. Data collection and structure refinement details are given in Table 1 for (**1**) and (**2**), Table 2 for (**3**) and (**4**).

Compounds (**1**) *and* (**2**). All non-hydrogen atoms were refined with anisotropic thermal parameters, except the oxygen atoms of perchlorate anions, in order to get a higher number of data per variable. For the same reason, hydrogen atoms were added in calculated positions with fixed isotropic thermal parameters. Tables 3 and 4 show the atomic parameters, 5 and 6 the main interatomic distances and bond angles.

Compounds (**3**) *and* (**4**). All atoms except hydrogens were refined with anisotropic thermal parameters. Hydrogen atoms were added as for (**1**) and (**2**). Tables 7 and 8 show the atomic parameters, 9 and 10 the main interatomic distances and bond angles.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Magnetic Measurements.—These were carried out with a Faraday-type magnetometer equipped with a continuous-flow cryostat. In order to minimize the amount of paramagnetic impurities, *ca.* 10-mg samples were prepared by selecting single crystals under a binocular lens. The independence of the magnetic susceptibility *versus* the magnetic field was verified at room temperature. The diamagnetic correction was estimated as -280×10^{-6} cm^3 mol^{-1} for (**1**) and (**2**) and -260×10^{-6} cm^3 mol^{-1} for (**3**) and (**4**).

Results

Description of the Structures.—*Compounds* (**1**) *and* (**2**). These two compounds are isomorphous. The unit cell contains two binuclear $[Cu_2L^3(X)]^{2+}$ cations and four perchlorate anions. The unit for (**2**) is shown in Figure 1, with the atom labelling. The two copper atoms are connected by a double bridge: the oxygen atom of the phenolato ligand and the co-ordinated X_p atom of the second bridging group. The copper(II) ions are in 4 + 2 surroundings. Each basal plane is made up of two nitrogen atoms, the oxygen atom of the ligand L^3, and the bridging atom of the exogenous ligand. Both apical positions are occupied by oxygen atoms of perchlorate anions with Cu–O(perchlorate) distances ranging from 2.60(1) to 2.79(1) Å in (**1**) and from 2.606(8) to 2.82(1) Å in (**2**). Around Cu(1), the mean deviation of the atoms N(11), N(12), O(1), and X_p from the mean-square basal plane is 0.102 Å for (**1**) and 0.112 Å for (**2**). Around Cu(2), the mean deviation of the atoms Cu(2), N(21), N(22), O(1), and X_p from the mean-square basal plane is 0.043 Å for (**1**) and 0.056 Å for (**2**). The two basal planes make a dihedral angle across the O(1)X_p edge of 175.6° for (**1**) and 175.0° for (**2**).

In compound (**1**) the bridging angles are Cu–O–Cu 99.4(6)° and Cu–N–Cu 106.1(6)°. The Cu(1)···Cu(2) separation is

Table 3. Atomic parameters for compound (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.1000	0.094 60(5)	0.1000	C(27)	0.105(2)	0.185 8(5)	−0.329(3)
N(11)	−0.082(1)	0.067 6(3)	−0.086(2)	C(28)	0.505(1)	0.181 3(4)	0.447(2)
N(12)	0.140(1)	0.068 0(3)	0.331(2)	C(29)	0.489(1)	0.153 3(5)	0.553(2)
C(11)	−0.121(2)	0.030 7(5)	−0.064(2)	C(30)	0.596(1)	0.151 0(5)	0.751(2)
C(12)	−0.014(2)	0.010 4(5)	0.134(2)	N(1)	0.106(1)	0.119 8(4)	−0.083(2)
C(13)	0.040(2)	0.037 7(5)	0.303(2)	N(2)	0.053(2)	0.108 4(6)	−0.234(4)
C(14)	−0.247(2)	0.013 7(5)	−0.200(3)	N(3)	−0.008(3)	0.094 6(8)	−0.413(3)
C(15)	−0.343(2)	0.033 2(6)	−0.379(3)	O(1)	0.265(1)	0.129 8(3)	0.269(1)
C(16)	−0.306(1)	0.070 9(5)	−0.403(2)	C(1)	0.370(1)	0.128 2(4)	0.460(2)
C(17)	−0.178(1)	0.086 4(4)	−0.257(2)	C(2)	0.593(1)	0.121 5(5)	0.868(2)
C(18)	0.254(1)	0.071 8(5)	0.507(2)	C(3)	0.715(2)	0.117 6(7)	1.084(3)
C(19)	0.369(1)	0.099 5(5)	0.579(2)	Cl(1)	−0.046 4(4)	0.199 2(1)	−0.046 0(6)
C(20)	0.479(2)	0.097 4(5)	0.777(2)	Cl(2)	−0.643 5(4)	0.050 7(1)	−0.932 2(6)
Cu(2)	0.261 0(2)	0.156 98(5)	0.062 7(3)	O(11)	−0.536(2)	0.023 2(6)	−0.858(3)
N(21)	0.231(1)	0.182 2(4)	−0.162(2)	O(12)	−0.710(1)	0.040 4(4)	−0.854(2)
N(22)	0.432(1)	0.187 1(3)	0.264(2)	O(13)	−0.746(1)	0.049 6(4)	−1.138(2)
C(21)	0.335(2)	0.194 4(4)	−0.155(2)	O(14)	−0.585(1)	0.092 7(4)	−0.869(2)
C(22)	0.475(2)	0.193 6(5)	0.036(3)	O(21)	0.088(1)	0.210 0(3)	0.027(1)
C(23)	0.481(2)	0.216 0(4)	0.196(2)	O(22)	−0.034(1)	0.161 1(3)	0.057(2)
C(24)	0.313(2)	0.208 7(5)	−0.319(2)	O(23)	−0.101(1)	0.232 4(4)	−0.005(2)
C(25)	0.183(2)	0.209 7(6)	−0.491(3)	O(24)	−0.134(1)	0.192 1(3)	−0.248(1)
C(26)	0.075(2)	0.198 5(5)	−0.501(2)				

Table 4. Atomic parameters for compound (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.1000	0.094 91(4)	0.1000	C(27)	0.101(1)	0.185 9(4)	−0.335(2)
N(11)	−0.084 8(8)	0.067 4(3)	−0.089(1)	C(28)	0.506(1)	0.181 8(3)	0.448(2)
N(12)	0.142(1)	0.068 3(3)	0.335(1)	C(29)	0.487(1)	0.153 6(4)	0.552(1)
C(11)	−0.121(1)	0.030 2(3)	−0.064(2)	C(30)	0.595(1)	0.150 3(4)	0.752(2)
C(12)	−0.014(1)	0.010 5(4)	0.135(2)	O	0.102 0(8)	0.118 6(3)	−0.095(1)
C(13)	0.040(1)	0.037 8(4)	0.302(2)	C	0.048(2)	0.104 9(5)	−0.259(3)
C(14)	−0.246(1)	0.013 0(4)	−0.199(2)	N	−0.009(2)	0.092 9(5)	−0.424(2)
C(15)	−0.341(1)	0.032 7(4)	−0.373(2)	O(1)	0.265 1(8)	0.130 2(2)	0.270(1)
C(16)	−0.308(1)	0.071 1(4)	−0.406(2)	C(1)	0.369(1)	0.127 6(3)	0.459(1)
C(17)	−0.178(1)	0.086 8(3)	−0.258(2)	C(2)	0.594(1)	0.121 8(4)	0.868(2)
C(18)	0.255(1)	0.072 3(4)	0.508(2)	C(3)	0.717(1)	0.118 7(5)	1.087(2)
C(19)	0.368(1)	0.099 1(4)	0.579(2)	Cl(1)	−0.046 7(3)	0.199 02(8)	−0.047 2(4)
C(20)	0.480(1)	0.096 6(4)	0.780(2)	Cl(2)	−0.643 4(3)	0.050 9(1)	−0.931 8(5)
Cu(2)	0.259 4(2)	0.156 60(4)	0.061 9(2)	O(11)	−0.537(2)	0.022 5(4)	−0.856(2)
N(21)	0.228 0(9)	0.182 4(3)	−0.163(1)	O(12)	−0.706(1)	0.040 6(3)	−0.850(1)
N(22)	0.429 5(9)	0.186 8(3)	0.264(1)	O(13)	−0.744(1)	0.048 5(3)	−1.136(2)
C(21)	0.332(1)	0.194 0(3)	−0.156(2)	O(14)	−0.589(1)	0.092 2(3)	−0.871(1)
C(22)	0.475(1)	0.193 2(4)	0.036(2)	O(21)	0.089 4(8)	0.209 3(2)	0.026(1)
C(23)	0.478(1)	0.216 0(3)	0.192(2)	O(22)	−0.036 6(9)	0.161 3(2)	0.052(1)
C(24)	0.312(1)	0.208 1(4)	−0.321(2)	O(23)	−0.098(1)	0.232 5(3)	−0.001(1)
C(25)	0.179(2)	0.209 7(5)	−0.498(2)	O(24)	−0.136 2(8)	0.192 5(3)	−0.250(1)
C(26)	0.073(2)	0.198 5(4)	−0.501(2)				

3.035(2) Å. The almost linear azido group makes an angle of 26.5° with the plane of the ligand L^3.

In (**2**), OCN^- is found to bridge the copper atoms through its oxygen atom. Indeed, we compared the *R* and B_{eq} values assuming successively an O and a N co-ordination. These two tests are in favour of O co-ordination, as summarized below.

	O co-ordination	N co-ordination
R	0.038	0.039
$B_{eq}/Å^2$	O 0.045	N 0.027
	C 0.087	C 0.086
	N 0.078	O 0.120

The bridging angles are Cu–O(phenolato)–Cu 98.5(3)° and Cu–O(OCN)–Cu 101.7(4)°. The Cu(1) ··· Cu(2) separation is 3.017(2) Å. The OCN group is almost linear and makes an angle of 28.5° with the plane of the ligand L^3. The perchlorate anions provide additional bridges on each side of the molecular skeleton, so that each binuclear unit is well isolated from its neighbouring units in the crystal lattice.

Compound (**3**). The unit cell contains four $[Cu_2L^4(C_2H_5O)]^{2+}$ binuclear units, eight perchlorate anions, and four water molecules. The binuclear unit is represented in Figure 2, with the atom labelling. The two copper atoms are doubly bridged by the oxygen atom of the phenolato and the oxygen atom of the ethanolato groups. These copper atoms are in highly distorted 4 + 2 surroundings. The Cu(1), N(11), O(1), and O(3) atoms on the one hand, and Cu(2), N(21), O(1), and O(3) on the other, are almost perfectly coplanar. These two mean planes make a dihedral angle of 169.6°. The deviation of S(1) from the former plane is 0.301 Å and that of S(2) from the latter plane is 0.726 Å. If the four co-ordinated atoms are included in the basal plane,

Table 5. Main interatomic distances (Å) and bond angles (°) for compound (**1**)

In binuclear unit			
Cu(1) ··· Cu(2)	3.035(2)		
Copper surroundings			
Cu(1)–N(11)	1.97(1)	Cu(2)–N(21)	1.97(1)
Cu(1)–N(12)	1.98(1)	Cu(2)–N(22)	1.96(1)
Cu(1)–N(1)	1.88(1)	Cu(2)–N(1)	1.92(1)
Cu(1)–O(1)	1.97(1)	Cu(2)–O(1)	2.01(1)
Cu(1)–O(22)	2.60(1)	Cu(2)–O(21)	2.63(1)
Cu(1)–O(12)	2.79(1)	Cu(2)–O(14)	2.64(1)
N(12)–Cu(1)–N(11)	93.7(5)	N(22)–Cu(2)–N(21)	96.0(5)
N(1)–Cu(1)–N(11)	97.8(5)	N(1)–Cu(2)–N(21)	97.3(5)
O(1)–Cu(1)–N(12)	91.2(5)	O(1)–Cu(2)–N(22)	90.7(5)
O(1)–Cu(1)–N(1)	78.3(5)	O(1)–Cu(2)–N(1)	76.2(5)
Cu(1)–N(1)–Cu(2)	106.1(6)	Cu(1)–O(1)–Cu(2)	99.4(5)
Cu(1)–N(11)–C(11)	127.2(11)	Cu(2)–N(21)–C(21)	122.9(11)
C(1)–O(1)–Cu(1)	130.8(9)	C(1)–O(1)–Cu(2)	127.3(9)
Azido bridge			
N(1)–N(2)	1.11(3)	N(2)–N(3)	1.33(3)
N(1)–N(2)–N(3)	178.9(25)		

Table 6. Main interatomic distances (Å) and bond angles (°) for compound (**2**)

In binuclear unit			
Cu(1) ··· Cu(2)	3.017(2)		
Copper surroundings			
Cu(1)–N(11)	2.012(8)	Cu(2)–N(21)	1.974(9)
Cu(1)–N(12)	2.005(9)	Cu(2)–N(22)	1.963(9)
Cu(1)–O	1.926(8)	Cu(2)–O	1.963(8)
Cu(1)–O(1)	1.973(7)	Cu(2)–O(1)	2.008(7)
Cu(1)–O(22)	2.611(8)	Cu(2)–O(21)	2.606(8)
Cu(1)–O(12)	2.82(1)	Cu(2)–O(14)	2.63(1)
N(12)–Cu(1)–N(11)	93.8(4)	N(22)–Cu(2)–N(21)	96.2(4)
O–Cu(1)–N(11)	96.0(3)	O–Cu(2)–N(21)	95.3(4)
O(1)–Cu(1)–N(12)	90.6(3)	O(1)–Cu(2)–N(22)	89.9(3)
O(1)–Cu(1)–O	80.7(3)	O(1)–Cu(2)–O	78.9(3)
Cu(1)–O–Cu(2)	101.7(4)	Cu(1)–O(1)–Cu(2)	98.5(3)
Cu(1)–N(11)–C(11)	125.9(7)	Cu(2)–N(21)–C(21)	121.9(8)
C(1)–O(1)–Cu(1)	129.8(7)	C(1)–O(1)–Cu(2)	128.7(7)
Cyanato bridge			
O–C	1.23(2)	C–N	1.22(2)
O–C–N	177.3(19)		

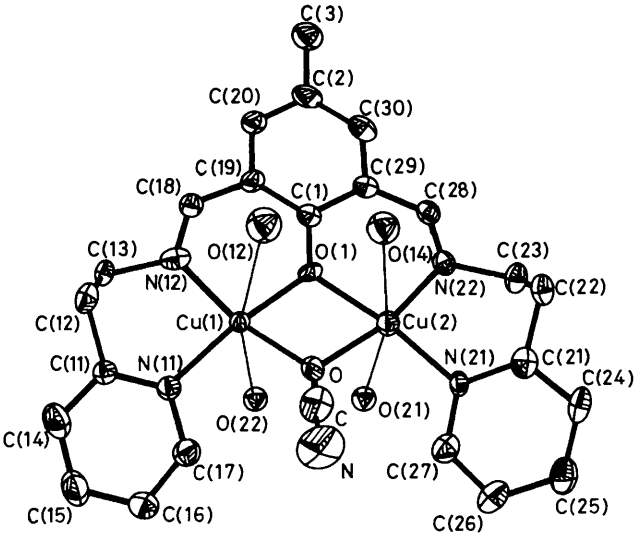

Figure 1. Perspective view of the binuclear cation $[Cu_2L^3(OCN)]^{2+}$ in (**2**)

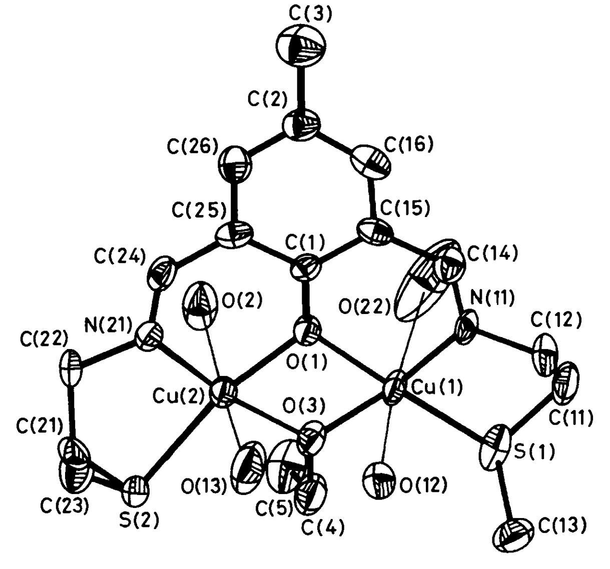

Figure 2. Perspective view of the binuclear cation $[Cu_2L^4(C_2H_5O)]^{2+}$ in (**3**)

which then is Cu(1), N(11), O(1), O(3), and S(1) for the first one, and Cu(2), N(21), O(1), O(3), and S(2) for the second, the distances of atoms to these least-squares planes are: first plane, Cu(1) −0.035, N(11) −0.059, O(1) 0.090, O(3) −0.063, and S(1) 0.066; second plane, Cu(2) −0.169, N(21) −0.097, O(1) 0.211, O(3) −0.105, and S(2) 0.160 Å. The Cu(1)–S(1) and Cu(2)–S(2) distances are 2.301(3) and 2.321(3) Å, respectively. The two apical positions around Cu(1) are occupied by oxygen atoms of perchlorato groups with Cu–O distances around 2.70 Å. One of the apical positions around Cu(2) is occupied by an oxygen atom of another perchlorate anion with a Cu(2)–O(13) distance of 2.836(9) Å, the other apical position being occupied by a water molecule with a much shorter Cu(2)–O(2) distance, 2.379(7) Å.

The bridging angles are Cu–O(phenolato)–Cu 100.4(3)° and Cu–O(ethanolato)–Cu 103.1(3)°. The Cu(1) ··· Cu(2) separation is 2.985(2) Å. The C(4)–O(3) direction within the ethanolato bridge makes an angle of 8.2° with the Cu(1)O(1)O(3)Cu(2) mean plane of the bridging network.

One of the perchlorate anions bridges the two metal ions on one side of the molecular skeleton. The other ClO_4^- group is terminal, as well as the co-ordinated water molecule. This perchlorate group participates in a long four-atom bridge between Cu(1) and Cu(2) through an intramolecular hydrogen bond between the non-co-ordinated O(21) atom of the Cu(1)-co-ordinated perchlorate and O(2) of the Cu(2)-co-ordinated water molecule, with O(2)–O(21) 2.93 Å.

Compound (**4**). Although compounds (**3**) and (**4**) are not isomorphous, their crystal and molecular structures are rather similar. The unit cell of (**4**) also contains four units

Table 7. Atomic parameters for compound (3)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.454 1(1)	0.369 54(4)	0.529 4(1)	C(16)	0.219(1)	0.245 4(3)	0.590(1)
Cu(2)	0.226 9(1)	0.408 58(4)	0.690 7(1)	C(21)	−0.049(1)	0.455 1(4)	0.689(1)
O(1)	0.282 4(7)	0.354 9(2)	0.618 1(7)	C(22)	−0.056(1)	0.417 7(3)	0.785(1)
O(3)	0.408 2(7)	0.419 9(2)	0.622 5(8)	C(23)	0.167(1)	0.495 0(4)	0.881(1)
C(4)	0.486(1)	0.455 6(4)	0.640(1)	C(24)	0.012(1)	0.349 7(4)	0.744(1)
C(5)	0.556(1)	0.464 0(5)	0.793(2)	C(25)	0.095(1)	0.314 7(3)	0.697(1)
S(1)	0.672 4(3)	0.386 2(1)	0.450 4(3)	C(26)	0.037(1)	0.275 3(4)	0.713(1)
N(11)	0.468 2(9)	0.315 6(3)	0.441 0(8)	Cl(1)	0.155 3(4)	0.416 5(1)	0.277 3(3)
S(2)	0.130 7(3)	0.474 39(9)	0.691 0(3)	O(11)	0.073(1)	0.415 2(4)	0.138(*1*)
N(21)	0.046 9(8)	0.387 1(3)	0.740 5(9)	O(12)	0.273(1)	0.389 2(2)	0.278 2(9)
C(1)	0.222(1)	0.319 0(3)	0.627(1)	O(13)	0.076(1)	0.408 0(4)	0.393(1)
C(2)	0.101(1)	0.240 4(4)	0.666(1)	O(14)	0.215(2)	0.456 4(3)	0.299(2)
C(3)	0.041(1)	0.198 0(4)	0.693(2)	Cl(2)	0.632 6(3)	0.322 0(1)	0.894 9(3)
C(11)	0.709(1)	0.335 1(5)	0.396(1)	O(21)	0.489 8(9)	0.319 1(3)	0.925(1)
C(12)	0.576(1)	0.311 5(4)	0.335(1)	O(22)	0.641(1)	0.337 5(6)	0.758(1)
C(13)	0.634(2)	0.410 6(4)	0.271(1)	O(23)	0.699(2)	0.286 6(4)	0.917(3)
C(14)	0.399(1)	0.285 0(3)	0.477(1)	O(24)	0.715(1)	0.346 7(4)	0.994(1)
C(15)	0.280(1)	0.283 3(3)	0.566(1)	O(2)	0.333 1(8)	0.103 5(3)	0.444 6(8)

Table 8. Atomic parameters for compound (4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.452 3(1)	0.365 28(4)	0.561 3(2)	C(16)	0.183(1)	0.248 9(4)	0.706(1)
Cu(2)	0.266 3(1)	0.422 70(4)	0.722 0(2)	C(21)	0.021(1)	0.482 6(5)	0.726(2)
O(1)	0.297 9(6)	0.361 0(2)	0.681 5(7)	C(22)	0.015(1)	0.447 9(4)	0.845(2)
N(1)	0.433 0(9)	0.424 0(3)	0.620(1)	C(23)	0.265(2)	0.523 2(5)	0.869(2)
N(2)	0.525(2)	0.451 1(6)	0.638(3)	C(24)	0.049(1)	0.372 7(4)	0.826(1)
N(3)	0.631(2)	0.471 4(7)	0.691(3)	C(25)	0.107(1)	0.331 0(3)	0.789(1)
S(1)	0.593 7(3)	0.374 6(1)	0.371 2(4)	C(26)	0.036(1)	0.294 0(4)	0.825(1)
N(11)	0.454 7(9)	0.303 9(3)	0.527(1)	Cl(1)	0.158 3(3)	0.402 9(1)	0.280 4(3)
S(2)	0.196 3(4)	0.494 8(1)	0.693 4(4)	O(11)	0.225(1)	0.437 4(3)	0.211(1)
N(21)	0.094 8(9)	0.410 2(3)	0.803(1)	O(12)	0.251(1)	0.366 9(3)	0.310(1)
C(1)	0.225(1)	0.326 7(3)	0.713(1)	O(13)	0.116(1)	0.417 3(3)	0.424(1)
C(2)	0.071(1)	0.253 0(4)	0.786(1)	O(14)	0.037(1)	0.391 0(3)	0.180(1)
C(3)	−0.011(1)	0.214 0(4)	0.828(2)	Cl(2)	0.657 0(3)	0.339 0(1)	0.915 2(4)
C(11)	0.576(1)	0.318 7(5)	0.312(2)	O(21)	0.519 7(9)	0.329 7(4)	0.941(1)
C(12)	0.565(1)	0.288 7(4)	0.440(2)	O(22)	0.671(1)	0.346 5(8)	0.773(1)
C(13)	0.774(1)	0.378 2(5)	0.458(2)	O(23)	0.746(1)	0.310 3(6)	0.988(2)
C(14)	0.372(1)	0.275 7(3)	0.577(1)	O(24)	0.702(3)	0.373 5(7)	0.999(2)
C(15)	0.262(1)	0.285 0(4)	0.665(1)	O(2)	0.396 8(8)	0.074 8(3)	0.471 0(9)

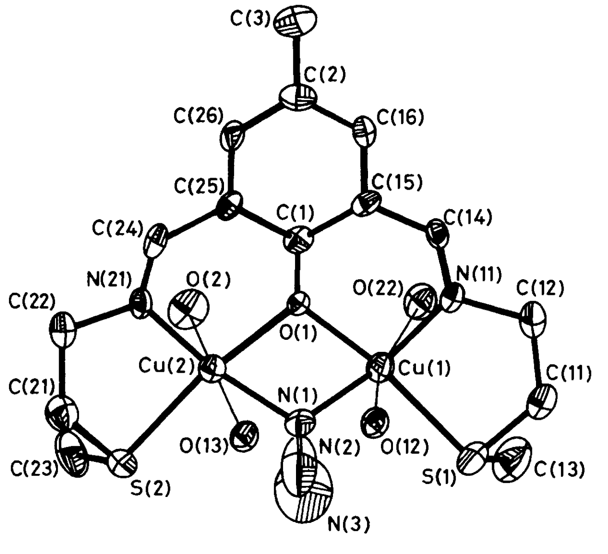

Figure 3. Perspective view of the binuclear cation $[Cu_2L^4N_3]^{2+}$ in (4)

$[Cu_2L^4(N_3)(H_2O)][ClO_4]_2$. The binuclear cation is shown in Figure 3, with the atom labelling. The copper atoms are in highly distorted 4 + 2 surroundings. The Cu(1), N(11), O(1), and N(1) atoms on the one hand, and Cu(2), N(21), O(1), and N(1) on the other, are coplanar and the two mean planes make a dihedral angle of 171.5°. The deviation of S(1) from the former plane and S(2) from the latter is 0.6 Å. If the four co-ordinated atoms are included in the basal plane, which then is Cu(1), N(11), O(1), N(1), and S(1) for the first one and Cu(2), N(21), O(1), N(1), and S(2) for the second one, the distances of atoms to these least-square planes are: first plane, Cu(1) 0.09, N(11) 0.107, O(1) −0.178, N(1) 0.115, and S(1) −0.134; second plane, Cu(2) −0.165, N(21) −0.065, O(1) 0.169, N(1) −0.071, and S(2) 0.132 Å. The Cu(1)–S(1) and Cu(2)–S(2) distances are 2.310(3) and 2.328(3) Å, respectively. The Cu–S distance range in (3) and (4) is 2.29—2.34 Å. These values are not different from those observed for other copper(II) compounds containing thioether ligands. For instance, 2.33 Å was found for μ-2-[(2-dipropylaminoethyl)thio]ethanolato-N,S,μ-O-dicopper(II).[7] Moreover, Glick and co-workers,[8] while studying the structures of various copper(II) complexes with 12—16-membered cyclic tetrathia ethers, compared Cu–S distances in the CuS_4 basal plane of the square-pyramidal copper(II) environment. They found that the

Table 9. Main interatomic distances (Å) and bond angles (°) for compound (**3**)

In binuclear unit			
Cu(1) ··· Cu(2)	2.985(2)		
Copper surroundings			
Cu(1)–O(1)	1.928(6)	Cu(2)–O(1)	1.957(6)
Cu(1)–O(3)	1.903(6)	Cu(2)–O(3)	1.910(6)
Cu(1)–S(1)	2.301(3)	Cu(2)–S(2)	2.321(3)
Cu(1)–N(11)	1.932(8)	Cu(2)–N(21)	2.924(8)
Cu(1)–O(12)	1.705(9)	Cu(2)–O(13)	2.836(9)
Cu(1)–O(22)	2.71(1)	Cu(2)–O(2)	2.379(7)
O(3)–Cu(1)–O(1)	78.3(3)	O(3)–Cu(2)–O(1)	77.4(3)
S(1)–Cu(1)–O(3)	100.5(2)	S(2)–Cu(2)–O(3)	100.6(2)
N(11)–Cu(1)–O(1)	92.3(3)	N(21)–Cu(2)–O(1)	91.6(3)
N(11)–Cu(1)–S(1)	89.2(3)	N(21)–Cu(2)–S(2)	89.1(3)
Cu(1)–O(1)–Cu(2)	100.4(3)	Cu(1)–O(3)–Cu(2)	103.1(3)
Cu(1)–S(1)–C(11)	94.1(4)	Cu(2)–S(2)–C(21)	92.2(4)
C(1)–O(1)–Cu(1)	129.4(6)	C(1)–O(1)–Cu(2)	130.2(6)
Ethanolate bridge			
O(3)–C(4)	1.38(1)	C(4)–C(5)	1.48(2)
C(5)–C(4)–O(3)	114.5(11)		

Table 10. Main interatomic distances (Å) and bond angles (°) for compound (**4**)

In binuclear unit			
Cu(1) ··· Cu(2)	3.007(2)		
Copper surroundings			
Cu(1)–O(1)	1.945(6)	Cu(2)–O(1)	1.968(7)
Cu(1)–N(1)	1.898(9)	Cu(2)–N(1)	1.949(7)
Cu(1)–S(1)	2.310(3)	Cu(2)–S(2)	2.328(3)
Cu(1)–N(11)	1.918(9)	Cu(2)–N(21)	1.930(9)
Cu(1)–O(12)	2.72(1)	Cu(2)–O(13)	2.797(9)
Cu(1)–O(22)	2.67(1)	Cu(2)–O(2)	2.354(8)
N(1)–Cu(1)–O(1)	79.0(3)	N(1)–Cu(2)–O(1)	77.2(3)
S(1)–Cu(1)–N(1)	99.4(3)	S(2)–Cu(2)–N(1)	100.3(3)
N(11)–Cu(1)–O(1)	92.6(3)	N(21)–Cu(2)–O(1)	92.1(3)
N(11)–Cu(1)–S(1)	89.4(3)	N(21)–Cu(2)–S(2)	88.7(3)
Cu(1)–O(1)–Cu(2)	100.4(3)	Cu(1)–N(1)–Cu(2)	102.8(4)
Cu(1)–S(1)–C(11)	92.5(4)	Cu(2)–S(2)–C(21)	92.8(4)
C(1)–O(1)–Cu(1)	129.7(6)	C(1)–O(1)–Cu(2)	129.5(6)
Azido bridge			
N(1)–N(2)	1.22(2)	N(2)–N(3)	1.24(2)
N(1)–N(2)–N(3)	162.4(29)		

Cu–S bond length is almost constant, with average values ranging from 2.30 to 2.36 Å. The occupations of the apical positions around Cu(1) and Cu(2) are the same as in (**3**) with a Cu(2)–O(2) distance involving a water molecule [2.354(8) Å] much shorter than the Cu–O distances involving perchlorate anions [ranging from 2.72(1) to 2.797(9) Å].

The bridging angles are Cu–O–Cu 100.4(4)° and Cu–N–Cu 102.8(3) Å and the Cu(1) ··· Cu(2) separation is 3.007(2) Å. As usual the N_3^- bridge is almost linear. Its direction makes an angle of 27° with the mean plane of the bridging network Cu(1)O(1)N(1)Cu(2).

Contrary to compound (**3**), an intermolecular hydrogen bond exists between two different units, involving O(2) of the Cu(2)-co-ordinated water molecule and O(11) of the Cu(1)-co-ordinated perchlorate belonging to another unit (*c* translation along this axis), with O(2)–O(11) 2.87 Å.

Magnetic Properties.—The temperature dependence of the molar magnetic susceptibility χ_M for a copper(II) binuclear compound is expected to obey equation (1) where J is the

$$\chi_M = \frac{2N\beta^2 g^2}{kT}[3 + \exp(-J/kT)]^{-1}(1 - \rho) + \frac{C}{T}\cdot\rho \quad (1)$$

singlet–triplet (S–T) energy gap arising from the intramolecular interaction and ρ the eventual proportion of uncoupled copper(II) contained in the sample. The other symbols have their usual meanings. If we assume that the uncoupled impurity has the same molecular weight as the actual compound, $C = N\beta^2g^2/2k$. The parameters J, g, and ρ were determined by minimizing R defined as $\Sigma(\chi_M^{\text{obs.}} - \chi_M^{\text{calc.}})^2/\Sigma(\chi_M^{\text{obs.}})^2$.

Compound (**1**). The plot of χ_M *versus* T shown in Figure 4 exhibits a maximum around 248 K, which is characteristic of an intramolecular antiferromagnetic interaction. The fitting of the experimental data in the range 28—300 K leads to $J = -278(2)$ cm^{-1}, $g = 2.077(5)$, and $\rho = 0.020$; $R = 5.9 \times 10^{-6}$ (for 135 experimental points).

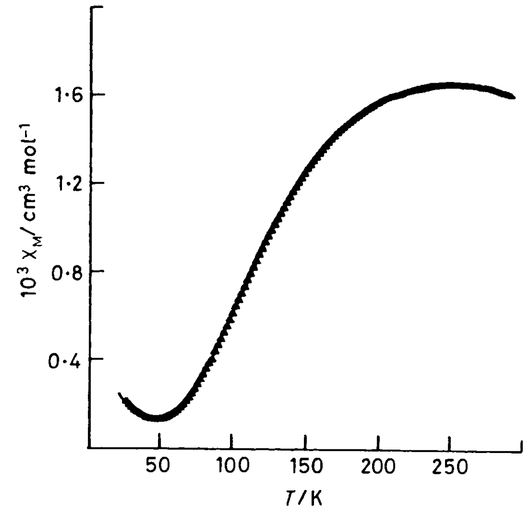

Figure 4. Experimental and calculated temperature dependences of the molar magnetic susceptibility for $[Cu_2L^3(N_3)][ClO_4]_2$ (**1**)

Compound (**2**). The situation for this compound is more complicated. Plots of both χ_M and χ_MT *versus* T are given in Figure 5; χ_M continuously increases upon cooling, but slower than would be expected for the Curie law, especially below *ca.* 50 K. As for χ_MT, it is equal to 0.775(2) cm^3 K mol^{-1} at 288 K, which corresponds well to the high-temperature limit expected for a copper(II) pair ($\chi_MT = N\beta^2g^2/2k$). Upon cooling, χ_MT continuously decreases and reaches 0.37(1) cm^3 K mol^{-1} at 10 K and 0.14(1) cm^3 K mol^{-1} at 3 K. Extrapolating χ_MT towards 0 K, we obtained a value close to zero. Therefore, it is clear that the compound has a spin-singlet ground state with a weak S–T energy gap. However, the fitting of the experimental data in the range 3—300 K with expression (1) was not satisfactory. It led to $J = -13.2$ cm^{-1}, $g = 2.00$, and $\rho = 0.2$ with $R = 2.84 \times 10^{-3}$ (for 148 experimental points). The ρ value is unreasonable and the R value is two orders of magnitude higher than in the previous case. The same results were obtained for three different samples, all prepared by carefully selecting single

Table 11. S–T Energy gap (cm^{-1}) for μ-phenolato-copper(II) binuclear compounds with an X^- exogenous ligand

X	L^1 (**A**)	L^2 (**B**)	L^3 (**C**)	L^4 (**D**)
OH	-367^a	-364	-385^b	-850^c
N_3	-86.5	-161	-278	-408
OCN	-3.8	$+43$	-12.9^d	

[a] A J value of -288 cm^{-1} has also been reported for a compound with the same formula.[20] [b] See ref. 5. [c] $X = C_2H_5O$. [d] Below 13 K, the magnetic susceptibility does not follow the law expected for this J value (see text).

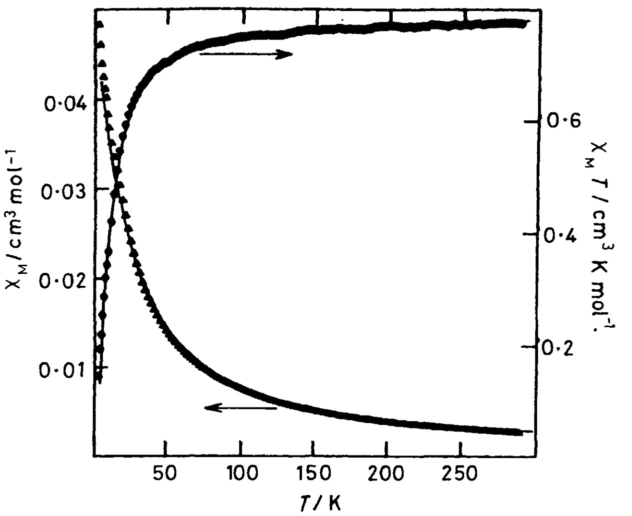

Figure 5. Experimental and calculated temperature dependences of the molar magnetic susceptibility χ_M and of $\chi_M T$ for $[Cu_2L^3(OCN)][ClO_4]_2$ (**2**)

crystals under a binocular lens. Actually, with such a J value, a maximum of χ_M is expected around 11 K, which is not observed. If we consider only the experimental data above 13 K, an excellent fit is obtained with $J = -12.9(3)$ cm^{-1}, $g = 2.046(4)$, and $\rho = 0.021$; $R = 3.67 \times 10^{-6}$. Below 13 K, the experimental susceptibilities are higher than the calculated ones. Owing to the care taken in this investigation, we think that this behaviour is a characteristic feature of the compound. Apparently, the S–T energy gap is constant and equal to -12.9 cm^{-1} in the range 13—300 K and decreases (in absolute value) upon cooling below 13 K. Perhaps compound (**2**) provides a new example of exchange elasticity.[9–11]

Compound (**3**). The molar magnetic susceptibility of compound (**3**) at room temperature is very low, 195×10^{-6} cm^3 mol^{-1}, and decreases upon cooling to *ca.* 160 K (see Figure 6). This behaviour is characteristic of a large S–T energy gap. At 300 K, the excited triplet state is very weakly populated. The increase of χ_M below 160 K, in a temperature range where the triplet state is totally depopulated, is due to the proportion ρ of uncoupled copper(II). The fitting of the experimental data in the range 50—292 K led to $J = -850(10)$ cm^{-1}, $g = 2.08(1)$, and $\rho = 0.011$; $R = 1.87 \times 10^{-4}$ (for 121 experimental points).

Compound (**4**). The plot of χ_M *versus* T for compound (**4**) is shown in Figure 6; χ_M continuously decreases upon cooling from 300 to 70 K. The fitting of the experimental data in the range 34—300 K led to $J = -408(4)$ cm^{-1}, $g = 2.061(6)$, $\rho = 0.0080$, and $R = 1.75 \times 10^{-6}$ (for 130 experimental points).

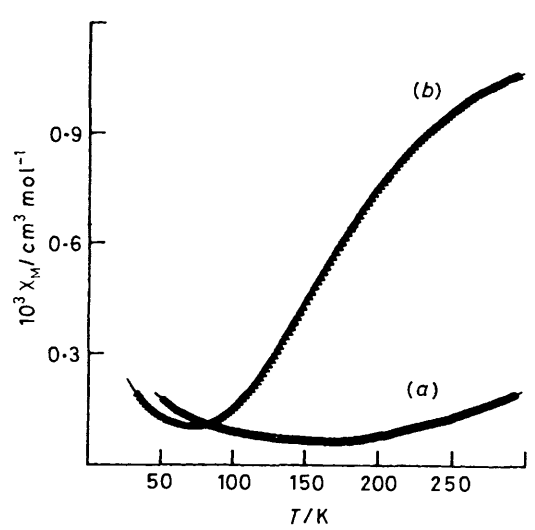

Figure 6. Experimental and calculated temperature dependences of the molar magnetic susceptibility for (*a*) $[Cu_2L^4(C_2H_5O)][ClO_4]_2 \cdot H_2O$ (**3**) and (*b*) $[Cu_2L^4(N_3)][ClO_4]_2$ (**4**)

The X-band powder e.s.r. spectra of compounds (**1**)—(**4**) have been recorded at several temperatures. They are typical of triplet states but poorly resolved. Probably, the zero-field splitting tensor D and the tensor g are not coaxial so that their principal cannot be deduced from powder data.

Discussion

We would like to propose a qualitative rationalization of the magnetic properties of the compounds belonging to the four series: $[Cu_2L^1(X)][ClO_4]_2 \cdot xH_2O$, (**A**), $[Cu_2L^2(X)][ClO_4]_2$ (**B**), $[Cu_2L^3(X)][ClO_4]_2$ (**C**), and $[Cu_2L^4(X)][ClO_4]_2 \cdot H_2O$ (**D**), with X = OH [or C_2H_5O for (**3**)], N_3, or OCN. The S–T energy gaps for the compounds are listed in Table 11. First, we will summarize briefly the key concepts which will be utilized. All these concepts have been discussed thoroughly in several papers and reviews.[12–15]

(*i*) In a copper(II) binuclear system, each magnetic centre has an unpaired electron described by a magnetic orbital (M.O.), of which the energy and the orientation depend on its environment.[13,16]

(*ii*) The first approximation consists of assuming that all the electrons of the binuclear system are passive, except for those two occupying the magnetic orbitals. In this active-electron approximation, the S–T energy gap J arising from the intramolecular interaction appears as the result of a competition between a ferromagnetic component governed by the two-electron exchange integral j between the M.O.s and an antiferromagnetic contribution governed by the overlap integral S and the transfer integral β. This latter term, to the first order, is proportional to the energy gap Δ between the two molecular orbitals (m.o.) transforming as irreducible representations of the molecular symmetry group and constructed by combining the two M.O.s.[16] This active-electron approximation seems qualitatively valid when the bridging atoms are oxygens, *i.e.* with X = OH or C_2H_5O, and the peripheral atoms bound to copper are nitrogens [series (**A**)—(**C**)]. In that case, the antiferromagnetic contribution is expected to increase (in absolute value) with the value of the CuOCu bridging angle.[16–21]

(*iii*) When the copper(II) ions are bridged by two different bridges X and Y, these can exert a complementary or an anti-complementary effect.[22–24] This latter situation is encountered if the overlaps between the two M.O.s around each of the bridges, S_X and S_Y, are of opposite sign.[2] A similar way to describe this

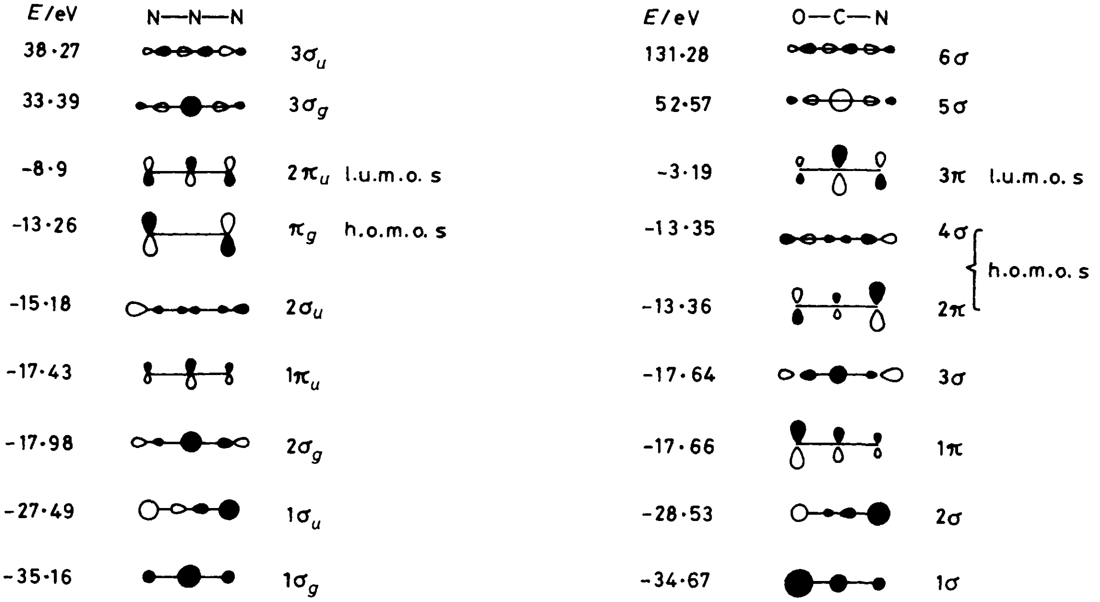

Figure 7. Comparison of the m.o. energy diagrams for N_3^- and OCN^- as obtained by the extended Hückel method; eV ≈ 1.60×10^{-19} J

anticomplementary effect is that one of the bridges destabilizes one of the two m.o.s obtained by combining the M.O.s and the other bridge the other m.o., so that Δ may be very small.

(*iv*) When the highest occupied molecular orbitals (h.o.m.o.s) of the bridging and (or) the terminal ligands are not very low in energy with respect to the M.O.s the active-electron approximation is no longer valid and additional terms must be taken into account in the expression of J, which may even become preponderant. In a perturbational development of J, these terms are assigned to double spin polarization (d.s.p.), ligand-to-metal and metal-to-ligand charge transfers (l.m.c.t. and m.l.c.t.) and kinetic exchange + polarization (k.e. + P).[25–29] In particular, it has been established that the l.m.c.t. terms favour the antiferromagnetic interaction.[26] The physical meaning of these additional terms is difficult to specify. In one case, however, a qualitative picture has been proposed.[30] This concerns the spin polarization effect exerted by N_3^- that favours an antiferromagnetic interaction when bridging in an end-to-end fashion and a ferromagnetic interaction when bridging in an end-on fashion.

Let us return to the experimental data and look first for the role of X within the same series, then for the role of the geometry when X remains constant. Finally, we will discuss the specificity of the compounds of the series (**D**) [(3) and (4)] with the sulphur-containing ligand L^4.

Role of X.—In the series (**A**), (**B**), and (**C**), $J(X = OH) < J(X = N_3) < J(X = OCN)$ and in the series (**D**), $J(X = C_2H_5O) < J(X = N_3)$. As already mentioned, the fact that the μ-hydroxo compounds are more antiferromagnetically coupled than the μ-(1,1) azido is consistent with the ferromagnetic contribution exerted by N_3^-.[1,3,31] In none of the azido compounds, however, does this ferromagnetic contribution compensate the strong antiferromagnetic contribution due to the phenolato bridge. More surprising is the situation of the μ-cyanato compounds. In each series (**A**)—(**C**) the cyanato compound has the less negative J value. The coupling was even found to be ferromagnetic ($J > 0$) for $[Cu_2L^2(OCN)][ClO_4]_2$.[3] We notice first that, *in each series, the* average value $\bar{\alpha}$ of the bridging angles is smaller with X = OCN than with X = N_3[(**A**) 98.70 and 99.35; (**B**) 98.65 and 100.10; (**C**) 100.10 and 102.75°]. Moreover, the larger $\Delta\bar{\alpha} = \bar{\alpha}(X = N_3) - \bar{\alpha}(X = OCN)$ is, the more negative $\Delta J = J(X = N_3) - J(X = OCN)$ is. The average value of $\Delta J/\Delta\bar{\alpha}$ is -122 cm^{-1} per degree. This clearly indicates that the differences in bridging angle values contribute to the differences in S–T energy gaps between azido- and cyanato-bridged compounds. This factor, however, does not seem to be the only one. In any case, the magnitude of the interaction in cyanato compounds appears weak. For instance, $J = -161$ cm^{-1} for $[Cu_2L^2(N_3)][ClO_4]_2$ and -12.9 cm^{-1} for $[Cu_2L^3(OCN)][ClO_4]_2$ whereas $\bar{\alpha} = 100.10°$ for both compounds. We ascribe this difference between azido and cyanato compounds to an effect rather similar conceptually to the anticomplementarity.

Indeed, the h.o.m.o.s π_g in N_3^- are well separated in energy from the m.o.s immediately above or below. In contrast, the h.o.m.o.s 2π and 4σ in OCN^- are quasi-degenerate, as shown in Figure 7, which compares the electronic structures of the two ligands as obtained by the extended-Hückel method. If we assume that the binuclear units have a mirror-plane perpendicular to the molecular skeleton (which is not rigorously exact), then the two m.o.s constructed from the *xy*-type magnetic orbitals will be symmetric (φ_s) and antisymmetric (φ_A), respectively, with regard to this mirror plane. Whatever X may be, owing to the large value of the Cu–O(phenolato)–Cu angle, the d_{xy}(Cu)–2*p*(phenolato oxygen) interaction destabilizes φ_A more than φ_S. For X = N_3, the $d_{xy}(Cu)-\pi_g(N_3)$ interaction exerts an additional destabilization of φ_A, hence N_3^- and O(phenolato) act in a complementary way. When X = OCN, for the same values of the bridging angles, the d_{xy}(Cu)–4σ(OCN) interaction exerts a specific destabilization of φ_S, so that $\Delta_{OCN} = \varepsilon(\varphi_A) - \varepsilon(\varphi_s)$ may be expected to be smaller than Δ_{N_3}, as schematized in Figure 8. It follows that, everything else being unchanged, the variation of the antiferromagnetic contribution which varies as Δ is less pronounced for X = OCN.

Role of the Geometry.—Since the structure of $[Cu_2L^3(OH)][ClO_4]_2$ is not known, we focus on the azido and cyanato compounds of the series (**A**)—(**C**). For the same exogenous ligand X, the only significant structural changes involve the bridging angles (average value $\bar{\alpha}$) and the angle θ of the N_3 or OCN direction with the molecular mean plane. For both X = N_3 and OCN, J increases when α decreases, as already

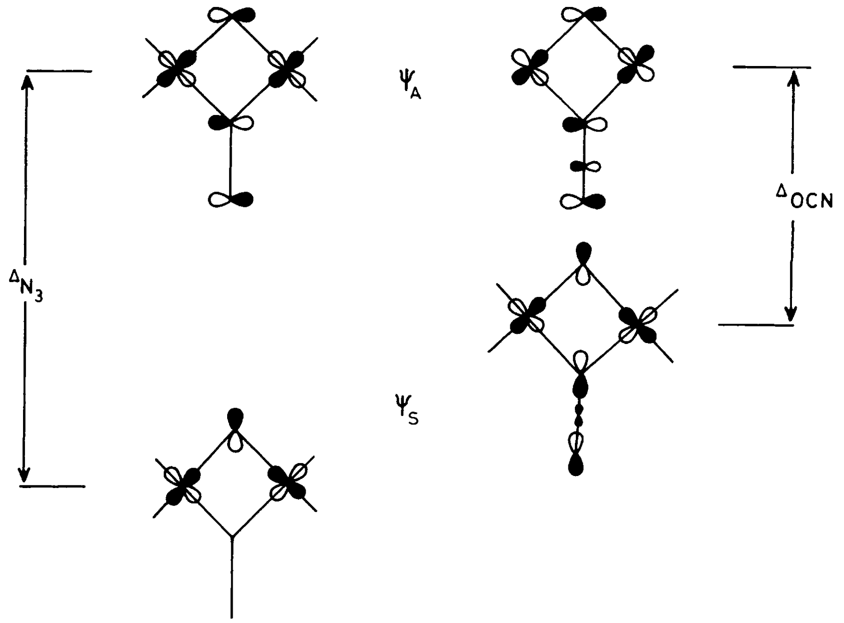

Figure 8. Schematic diagram showing the two singly occupied m.o.s (in the low-lying triplet state) for μ-phenolato-μ-azido (left) and μ-phenolato-μ-cyanato (right) copper(II) binuclear compounds (see text)

established and rationalized in several other cases.[12–16] The role of θ {which reaches 43° in $[Cu_2L^1(N_3)]^{2+}$}, is not clear from the available data.

Specificity of the $[Cu_2L^4(X)][ClO_4]_2\cdot H_2O$ *Compounds.*—The presence of sulphur-containing terminal ligands in the co-ordination sphere of the copper atom, everything else being unchanged, considerably increases the magnitude of the antiferromagnetic interaction. An analogous conclusion might be drawn from the study of copper(II) binuclear compounds with 2-[2′-(dialkylamino)ethylthio]ethanol performed by Kida and co-workers[32] and from a recent report by Latour and co-workers.[33] Actually, this result is rather important since it shows that not only the nature and the geometry of the bridging network plays a role in the magnitude of the interaction, but also the nature of the peripheral ligands. For compounds (**3**) and (**4**), J is roughly twice as large as it would be with peripheral chains co-ordinating only through nitrogen atoms [as in series (**A**)—(**C**)].

The role of the sulphur atoms in bridging ligands, for instance when S replaces O or NR, has been rationalized in terms of the enhancement of the overlap between M.O.s.[13,16] The same explanation cannot easily be extended to the case where the sulphur atoms are located in the periphery of the binuclear unit. Probably the correct interpretation has to be sought again beyond the active-electron approximation, maybe in the l.m.c.t. terms. Each of these terms appearing in the perturbational development of J is inversely proportional to the energy gap ΔE between the l.m.c.t. state and the ground state.[25–29] The replacement of NR_3 by SR_2 makes the copper(II) ion more reducible, and hence lowers the energy of the S→Cu c.t. state. It enables an enhancement of the S→Cu c.t. term, which has been seen to be necessarily an antiferromagnetic contribution.

The average values of the bridging angles in compounds (**3**) and (**4**) are very close (101.7 and 101.6°) and a comparison of the magnetic data confirms again that the exogenous bridge N_3^-, when in an end-on mode, decreases the magnitude of the antiferromagnetic interaction with respect to hydroxide or ethanolate.

Conclusions

Since this paper terminates our work dealing with the μ-phenolato copper(II) compounds with exogenous ligands, we summarize the main conclusions as follows.

(*i*) From a structural viewpoint, we have characterized the first compounds in which the cyanato ligand bridges by its oxygen atom.

(*ii*) In any series, the μ-azido compound is much less antiferromagnetically coupled than the μ-hydroxo (or ethanolato), irrespective of the structural details. This is consistent with the fact that N_3^- tends to exert a ferromagnetic contribution when bridging in an end-on fashion, owing to a spin-polarization effect.

(*iii*) The μ-cyanato compounds are all weakly coupled with either a singlet or a triplet ground state. We have suggested that two factors could account for the difference between μ-azido and μ-cyanato compounds: first, the bridging angles are systematically smaller in μ-cyanato compounds; secondly, the energy gap Δ_X between singly occupied molecular orbitals of highest energy (in the triplet state) is expected to be reduced with X = OCN with respect to X = N_3 (assuming that the bridging angles are unchanged), due to an effect conceptually similar to the anticomplementarity. In other respects, we assume that the spin polarization favouring the triplet state is also valid with X = OCN.

(*iv*) The replacement of NR_3 by SR_2 in the lateral chains, everything else being unchanged, considerably increases the magnitude of the antiferromagnetic interaction. It is suggested that the origin of this phenomenon should be sought, beyond the active-electron approximation, in the additional second-order terms appearing in a perturbational development of J. Maybe, the l.m.c.t. terms have to be invoked. Anyhow, this result shows that any kind of magneto structural correlation should exclusively concern series of related compounds in which the metal ions are surrounded by the same bridging as well as terminal atoms. In this frame, the decrease of J when the average value of the bridging angles increases seems valid, not only for X = OH, but also for X = N_3 on the one hand and for X = OCN on the other.

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