Binuclear Copper(II) Complexes of a New Sulphur-containing Binucleating Ligand: Structural and Physicochemical Properties†

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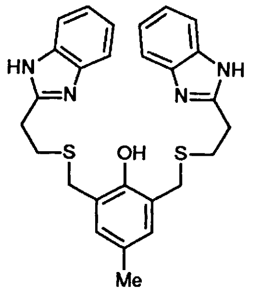
The new ligand HL [2,6-bis{4-(benzimidazol-2-yl)-2-thiabutyl}-4-methylphenol] has been prepared. Its reaction with various copper(II) salts afforded a series of complexes **1**–**6** of general formula $Cu_2L(X)Y_2$ (X = Y = Cl, **1**; X = Y = Br, **2**; X = OH, Y = ClO_4, **3**; X = Y = NO_3, **4**; X = N_3, Y = NO_3, **5**; X = N_3, Y = ClO_4, **6**). The molecular structure of **6** was determined by X-ray diffraction analysis. It exists as a discrete, dinuclear species in the solid state. The two copper sites are related by a symmetry axis and bridged by the phenoxo oxygen and a nitrogen from the μ-1,1-azide. Each copper is in a square-pyramidal environment, the base of which is constituted by an oxygen, a sulphur and a nitrogen from the organic ligand and the bridging azide nitrogen, while a perchlorato oxygen occupies the apical site. All compounds exhibit a high antiferromagnetic coupling which probably results from sulphur ligation. They exchange electrons at moderately positive potentials which reflects the balance between the hard phenoxo oxygen and the soft nitrogen and sulphur donors provided by the ligand.

During the past two decades the chemistry of dinuclear copper species has grown steadily in connection with the surge of interest in the magnetic properties of multinuclear systems and the development of bioinorganic chemistry.[1] Magnetic studies of dicopper(II) complexes have contributed deeply to elaboration of the conceptual framework used to analyse the spin-exchange interactions[2] and a rationale to the design of molecular ferromagnets. On the other hand, understanding the activation of dioxygen by the multicopper proteins (haemocyanins, tyrosinase, laccases and multicopper oxidases) has become a major incentive in the bioinorganic field.[3] Although they undertake different functions, these proteins[4] do have at their active sites a pair of copper(II) ions which exhibit a strong antiferromagnetic coupling and exchange only pairs of electrons at positive potentials of the Cu^I–Cu^{II}. The latter property is undoubtedly related to the need to avoid the formation of superoxide, the one-electron reduced product of dioxygen, which is both thermodynamically unfavourable and potentially damaging to the protein.

In a search for dicopper complexes able to exchange electrons pairwise, in a concerted manner and at a high potential of the Cu^I–Cu^{II} couple, we previously synthesised a series of dicopper complexes of a binucleating ligand potentially providing each copper atom with two thioether sulphur and two benzimidazole nitrogen donors.[5] These complexes exchanged electrons at potentials higher than 1.0 V *vs.* saturated calomel electrode (SCE); however, the two copper(II) ions were independent from each other owing to the failure of an ethylene tetrathioether unit to act as an efficient bridge. Moreover, they were unstable in solution, being rapidly reduced in most solvents. To solve both problems, we relied on the new ligand HL incorporating a phenol unit in addition to the benzimidazole–thioether combination.[6] Introduction of a phenolate bridge was actually supposed to bring the two metals in close proximity (Cu ••• Cu *ca.* 3.1 Å), to furnish an efficient pathway for the magnetic exchange,[7–9] and, at the same time, to stabilize the copper(II) species.[10] In addition, this system was expected to give various complexes differing in the nature of the second, exogenous, bridge, thus allowing one to evaluate the effect of these ligands on the structural, spectroscopic and redox properties.[9] In this report we present the synthesis and spectroscopic and electrochemical properties of a series of binuclear copper complexes of this new ligand in which the exogenous bridge X is Cl^-, Br^-, OH^- or N_3^-. Magnetostructural correlations of three complexes with X = Cl^-, OH^- and N_3^- have been published.[6] In addition, we describe the structural and magnetic properties of a new azido derivative which differs from the preceding one by the nature of the counter anion (NO_3^- instead of ClO_4^-). This subtle change induces a drastic structural rearrangement manifested in a significantly enhanced exchange interaction.



HL

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Experimental

Preparation.—CAUTION: Although no problems were encountered in the preparation of the perchlorate salts **3** and **6**, suitable care should be taken when handling such potentially hazardous compounds.

2,6-*bis*[4-(*benzimidazol*-2-*yl*)-2-*thiabutyl*]-4-*methylphenol* (HL). 3-(benzimidazol-2-yl)propane-1-thiol (11 g, 61.8 mmol) and 2,6-bis(hydroxymethyl)-4-methylphenol (5 g, 29.8 mmol) were mixed in acetic acid (30 cm^3). The solution was refluxed for 3 h. After cooling to room temperature, water (100 cm^3) was added and cautiously ammonia (20%, 80 cm^3). The mixture was then extracted with chloroform (3 × 200 cm^3) and the solvent evaporated. A white fluffy solid (15.5 g) was obtained. It was chromatographed on silica gel (500 g, Merck 70–230 mesh) and the following products were successively eluted with ethyl acetate: 1,3-bis{3-[4-(benzimidazol-2-yl)-2-thiabutyl]-hydroxy-4-methylphenyl}-2-thiapropane (12%) (fast atom bombardment mass spectrum m/z 355, $M^{\cdot +}$), unreacted thiol (8%), HL (26%), and unidentified products. The ligand was identified by NMR spectroscopy ($CDCl_3$–CD_3OD, from $SiMe_4$); ^1H, δ 2.15 (s, 3 H, CH_3), 3.0 (m, 8 H, SCH_2CH_2), 3.75 (s, 4 H, benzylic), 5.04 (s, *ca.* 3 H, NH and OH), 6.81 (s, 2 H, *m*-H of phenyl) and 7.25 (m, 8 H, benzimidazole); ^{13}C, δ 20.5 (CH_3), 30.2, 30.3 (SCH_2CH_2), 30.8 (benzylic), 115.4 (benzimidazole C^5 and C^8), 123.3 (benzimidazole C^6 and C^7), 126.8 (*m*-C of phenyl), 130.4 (*o*-C of phenyl), 131 (*p*-C of phenyl), 139.4 (benzimidazole C^4 and C^9) 151.9 (phenylic COH) and 155.0 (benzimidazole C^2).

Copper complexes. The following general procedure was used. The ligand HL (1 mmol) was first ionized with a base (2 mmol, triethylamine or KOH, for **1**–**4**; NaN_3, for **5** and **6**) in methanol (30 cm^3), and this solution was added to the appropriate copper(II) salt (2 mmol) dissolved in the same solvent (30 cm^3). Crystals of **6** suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether in methanol. Table 1 lists the elemental analyses of all compounds.

X-Ray Data Collection and Structure Determination.—The orthorhombic unit cell was found by taking preliminary Weissenberg photographs. The same crystal was mounted on an Enraf-Nonius CAD-4 four-circle diffractometer equipped with graphite-monochromated Mo-K radiation (λ 0.7107 Å). Accurate cell dimensions were obtained by least-squares fitting of the setting angles of 25 reflections and are reported in Table 2 with other experimental parameters. The space group *Fdd*2 was established from systematic absences. The data were corrected for Lorentz and polarization effects, but not for absorption.

The crystal structure was solved by conventional Patterson and Fourier methods using the SHELX 76 package.[11] The copper positions were determined from sharpened Patterson functions and the phases provided by these heavy atoms were used for successive Fourier difference syntheses which revealed the positions of the remaining non-hydrogen atoms. It was noticed that the two terminal nitrogen atoms of the azido group were not located on the C_2 axis. Furthermore, attempts to refine the structure with these atoms blocked on the symmetry axis led to large anisotropic thermal parameters and unrealistic nitrogen–nitrogen distances. Therefore, it was clear that the azido group was statistically disordered and this group was refined in two symmetrical positions out of the C_2 axis with half occupancy factors. Finally, this model afforded usual N–N distances when corrected for the thermal motions. There was also evidence for a degree of disorder and/or high amplitude thermal motions of the ClO_4^- group. Fourier difference maps did not yield a second well resolved and internally consistent set of oxygen atoms. These maps clearly indicated that the refined positions accounted for the majority of the oxygen atoms. Consequently, no provision for disorder was introduced in the refinement. The difficulty of modelling the ClO_4^- group does not seriously affect the chemically significant features of the structure. Structure refinements included anisotropic thermal parameters for all non-hydrogen atoms. These atoms were introduced in the final refinement model in fixed and idealized positions with isotropic thermal parameters. The functions minimized were $R' = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^{\,2}]^{\frac{1}{2}}$ $[w = 1/(\sigma^2 F + 0.0001\ F^2)]$ and $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. Atomic coordinates of compound **6** are listed in Table 3.

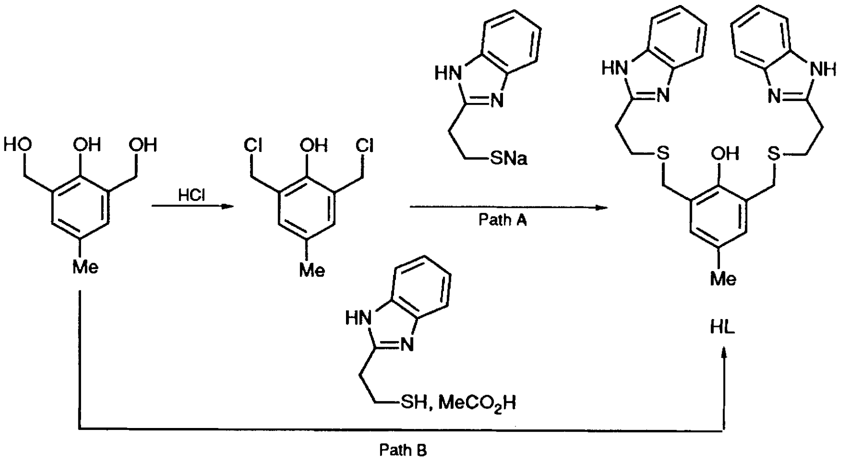
Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Physicochemical Measurements.—The UV/VIS and IR spectra were obtained with Beckman Acta VI and IR 4250 spectrophotometers, respectively. Magnetic measurements were done with a SHE QUID variable-temperature susceptometer as detailed previously.[6] Electrochemical experiments were performed as described elsewhere.[12] Potentials are referenced to the SCE; under the conditions used in the present studies, the potential of the ferrocene–ferrocenium couple was 0.455 V.

Results

Syntheses.—We previously reported[6] that the ligand HL can be synthesised in the two-step procedure illustrated in Scheme 1, path A, which involves reaction of the bis(chloromethyl) derivative with the sodium salt of the thiol. We have found since that substitution of the two benzylic hydroxy groups by the thiol can be effected with a slightly better yield (26 *vs.* 21%) in a single step[13] as depicted in Scheme 1, path B.

This ligand belongs to the class of sulphur-containing Robson type ligands.[3a,8c,14–16] However, like its previously mentioned pyridine analogue,[3a] it differs from most of the other



Scheme 1

Table 1 Analytical data for the complexes $Cu_2L(X)Y_2$ with calculated values in parentheses

Complex			Analysis (%)					
	X	Y	C	H	N	O	S	Cu
1·MeOH[a]	Cl	Cl	44.55 (44.65)	3.80 (4.15)	8.10 (7.45)	3.50 (4.25)	8.65 (8.50)	17.15 (16.85)
2·H_2O[b]	Br	Br	37.10 (37.15)	3.35 (3.35)	6.10 (6.40)	3.95 (3.65)	7.95 (7.35)	14.10 (14.55)
3·MeOH[c]	OH	ClO_4	38.90 (38.90)	3.95 (4.05)	5.90 (6.25)	21.10 (21.45)	7.00 (7.15)	13.70 (14.20)
4·MeOH	NO_3	NO_3	40.20 (40.30)	3.75 (4.10)	11.25 (11.35)	21.85 (22.20)	7.60 (7.40)	14.30 (14.70)
5	N_3	NO_3	41.80 (41.55)	3.55 (3.50)	16.05 (16.15)	14.45 (14.35)	7.85 (8.20)	16.10 (16.30)
6·MeOH	N_3	ClO_4	38.00 (37.90)	3.30 (3.75)	11.05 (11.05)	17.75 (18.00)	7.30 (7.20)	14.50 (14.30)

[a] Cl 14.60 (14.10%). [b] Br 27.50 (27.45%). [c] Cl 8.45 (7.95%).

Table 2 Crystallographic data for complex **6**

Formula	$C_{27}H_{27}Cl_2Cu_2N_9O_9S_2$
M	833.6
Crystal dimensions/mm	0.3 × 0.3 × 0.2
Crystal system	Orthorhombic
Space group	*Fdd*2
a/Å	14.979(8)
b/Å	26.247(1)
c/Å	18.905(1)
U/Å^3	7432.6
Z	8
D_c/g cm^{-3}	1.58
T/°C	20
μ/cm^{-1}	1.5
F(000)	3368.0
Total reflections	2921
Observed reflections [$F > 3\sigma(F)$]	1616
R	0.051
R'	0.061

members[8c,14–16] of this class in that the sulphur atoms are located in an 'internal' position within the complexing side chains. This was specifically designed in order that chelation by the benzimidazole enforces sulphur co-ordination. Thioethers are not strong ligands for copper(II)[17] and their binding is not warranted in solution owing to solvent competition. As detailed below, in the present complexes, the thioethers are bound to the copper atoms in solution as well as in the solid state.

Structure of Compound **6**, $[Cu_2L(N_3)(ClO_4)_2]$.—The molecular structure of the azido derivative **6** is shown in Fig. 1, and bond lengths and angles are collected in Tables 4 and 5, respectively. A crystallographic two-fold axis is present, which passes through the phenoxo atoms C(1), C(4), C(5) and O(1) and the azido nitrogen N(3). The azido ligand is disordered between two positions, symmetrical with respect to the two-fold axis, and the axis passing through the three nitrogens makes an angle of 17.6° with the Cu–O(1)–Cu′–N(3) plane. Both perchlorato anions are disordered also. The two coppers are bridged by the phenoxo oxygen O(1) and nitrogen N(3) from the μ-1,1-azide. The Cu ••• Cu distance is 3.036(1) Å, and the angles within the bridge are Cu–O(1)–Cu 98.4° and Cu–N(3)–Cu 104.6°. Each copper ion is in a square-pyramidal environment whose base is constituted by the thioether sulphur, a benzimidazole nitrogen, the phenoxo oxygen and an azido nitrogen; the apical site is occupied by an oxygen from a perchlorate counter ion. Bond lengths and angles are within the range expected for five-co-ordinate copper(II) complexes.

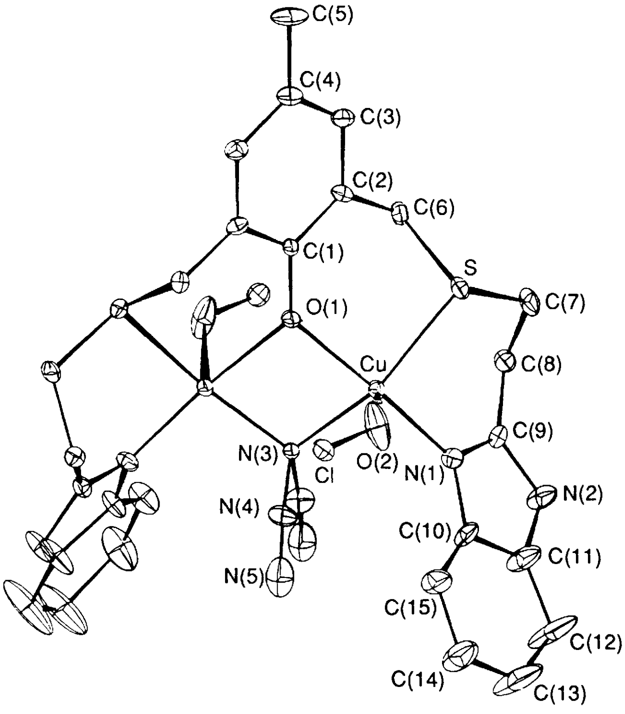
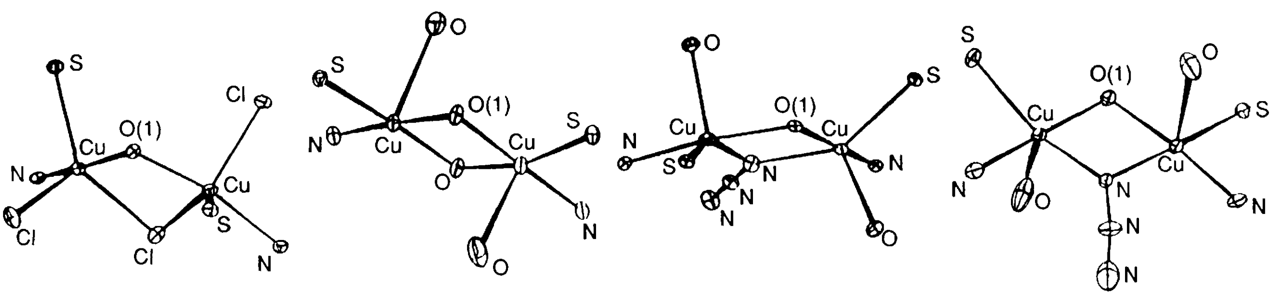


Fig. 1 Molecular structure of compound **6**: ORTEP diagram showing 30% probability ellipsoids and the atom numbering scheme

Spectroscopic Studies.—Fig. 2 depicts the copper co-ordination spheres of the chloro **1**, the hydroxo **3** and the two azido derivatives **5** and **6** whose structures have been solved by X-ray diffraction.[6] In each compound the exogenous ligand forms a second bridge between the two metals. It is likely that the bromide behaves in the same manner since μ-phenoxo-μ-bromo-dicopper derivatives of similar ligands have been characterized.[7,9] To our knowledge, such a bridging co-ordination mode is unknown for the nitrato anion in the present series of complexes built from Robson type ligands. Moreover, a conductimetric measurement indicates that **4** is a 3 : 1 electrolyte pointing to the absence of any bridging anion in the solution state. Thus, it seems most plausible that the two coppers in **4** are singly bridged by the phenoxide, as already observed in several cases.[16,18] Conductivity studies also show that in solution **3**, **5** and **6** loose the perchlorate and nitrate counter ions which are probably replaced by solvent molecules; thus, upon dissolution in dimethyl sulphoxide (dmso) **5** and **6** probably give the same cationic species $[Cu_2L(N_3)(dmso)_x]^{2+}$. The situation is somewhat different for the halides. The chloride **1** behaves as



1 **3** **5** **6**

Fig. 2 Copper co-ordination spheres of complexes **1**, **3**, **5** and **6**

Table 3 Atomic coordinates (× 10^4) of compound **6**

Atom	*x*	*y*	*z*
Cu(1)	429(1)	524(0)	0(0)
S	526(2)	1128(1)	900(2)
Cl	2346(2)	−323(1)	160(2)
O(1)	0(0)	0(0)	693(5)
O(2)	1722(8)	9332(4)	−71(7)
O(3)	3130(7)	−326(4)	−213(7)
O(4)	2524(12)	−401(7)	849(8)
O(5)	1938(6)	168(4)	166(11)
N(1)	722(7)	1022(3)	−707(5)
N(2)	478(9)	1724(4)	−1328(7)
N(3)	0(0)	0(0)	−620(6)
N(4)	176(24)	−103(14)	−1192(13)
N(5)	452(22)	−188(16)	−1702(29)
C(1)	0(0)	0(0)	1410(7)
C(2)	−216(7)	433(4)	1781(5)
C(3)	−204(7)	434(5)	2528(6)
C(4)	0(0)	0(0)	2901(8)
C(5)	0(0)	0(0)	3704(9)
C(6)	−456(8)	915(4)	1404(6)
C(7)	145(11)	1723(4)	517(7)
C(8)	−343(9)	1662(4)	−201(6)
C(9)	271(7)	1461(4)	−726(6)
C(10)	1125(14)	1443(6)	−1681(9)
C(11)	1260(9)	994(5)	−1299(7)
C(12)	1876(12)	628(6)	−1507(9)
C(13)	2341(17)	693(9)	−2132(14)
C(14)	2070(28)	1176(13)	−2555(20)
C(15)	1584(22)	1547(10)	−2303(16)

Table 4 Selected bond lengths (Å) for compound **6**

Cu • • • Cu	3.036(1)	N(1)–C(11)	1.381(16)
Cu–S	2.330(3)	N(2)–C(9)	1.367(16)
Cu–O(1)	2.005(6)	N(2)–C(10)	1.389(22)
Cu–O(5)	2.466(9)	C(1)–C(2)	1.375(12)
Cu–N(1)	1.922(8)	C(2)–C(3)	1.412(14)
Cu–N(3)	1.919(7)	C(2)–C(6)	1.496(14)
Cl–O(2)	1.372(11)	C(3)–C(4)	1.375(13)
Cl–O(3)	1.371(11)	C(4)–C(5)	1.518(22)
Cl–O(4)	1.345(15)	C(7)–C(8)	1.552(18)
Cl–O(5)	1.429(10)	C(8)–C(9)	1.453(16)
S–C(6)	1.841(12)	C(10)–C(11)	1.397(20)
S–C(7)	1.813(12)	C(10)–C(15)	1.389(35)
O(1)–C(1)	1.355(16)	C(11)–C(12)	1.389(21)
N(3)–N(4)	1.416(28)	C(11)–C(13)	1.382(31)
N(4)–N(5)	1.072(58)	C(13)–C(14)	1.553(43)
N(1)–C(9)	1.336(13)	C(14)–C(15)	1.306(47)

Table 5 Selected bond angles (°) for compound **6**

S–Cu–O(1)	90.5(2)	Cu–N(3)–N(4)	132.1(18)
S–Cu–O(5)	96.2(4)	N(3)–N(4)–N(5)	170.6(41)
S–Cu–N(1)	91.8(2)	O(1)–C(1)–C(2)	120.7(6)
S–Cu–N(3)	162.8(1)	C(2)–C(1)–C(2)	118.6(12)
O(1)–Cu–O(5)	87.2(3)	C(1)–C(2)–C(3)	120.6(9)
O(1)–Cu–N(1)	174.2(3)	C(1)–C(2)–C(6)	120.9(9)
O(1)–Cu–N(3)	78.5(3)	C(3)–C(2)–C(6)	118.5(9)
O(5)–Cu–N(1)	97.9(4)	C(2)–C(3)–C(4)	121.0(10)
O(5)–Cu–N(3)	96.5(3)	C(3)–C(4)–C(3)	118.3(14)
N(1)–Cu–N(3)	97.9(3)	C(3)–C(4)–C(5)	120.9(7)
Cu–S–C(6)	97.0(3)	S–C(6)–C(2)	108.1(7)
Cu–S–C(7)	105.9(4)	S–C(7)–C(8)	114.2(7)
C(6)–S–C(7)	102.5(6)	C(7)–C(8)–C(9)	109.7(10)
O(2)–Cl–O(3)	114.5(7)	N(1)–C(9)–N(2)	110.1(9)
O(2)–Cl–O(4)	110.2(9)	N(1)–C(9)–C(8)	128.0(10)
O(2)–Cl–O(5)	107.8(6)	N(2)–C(9)–C(8)	121.9(9)
O(3)–Cl–O(4)	109.2(9)	N(2)–C(10)–C(11)	107.5(13)
O(3)–Cl–O(5)	112.1(7)	N(2)–C(10)–C(15)	130.4(17)
O(4)–Cl–O(5)	102.4(11)	C(11)–C(10)–C(15)	122.1(18)
Cu–O(1)–Cu	98.4(4)	N(1)–C(11)–C(10)	106.8(12)
Cu–O(1)–C(1)	130.8(2)	N(1)–C(11)–C(12)	130.8(12)
Cu–O(5)–Cl	137.2(6)	C(10)–C(11)–C(12)	122.2(14)
Cu–N(1)–C(9)	119.3(7)	C(11)–C(12)–C(13)	119.4(16)
Cu–N(1)–C(11)	131.4(7)	C(12)–C(13)–C(14)	114.2(22)
C(9)–N(1)–C(11)	108.6(9)	C(13)–C(14)–C(15)	124.5(31)
C(9)–N(2)–C(10)	106.9(11)	C(10)–C(15)–C(14)	116.0(26)
Cu–N(3)–Cu	104.6(5)		

a 1:1 electrolyte, which suggests that only one axial chloride is dissociated giving two dissimilar copper centres. This interpretation is favoured (over an equilibrium between $[Cu_2LCl_3]$ and $[Cu_2LCl]^{2+}$) by the occurrence of such dissymetric dicopper complexes in which an axial ligand is a halide ion and the other a solvent molecule.[18] For the bromide the value of the conductivity is intermediate between those for 1:1 and 1:2 electrolytes, which suggests the occurrence of the anation equilibrium (1).

$$[Cu_2LBr_2]^+ \rightleftharpoons [Cu_2L(Br)]^{2+} + Br^- \qquad (1)$$

The electronic absorption spectra of all complexes exhibit three main features (Table 6) a highly intense (ε *ca.* 9000 dm^3 mol^{-1} cm^{-1}) band at 300 nm with a shoulder at lower energy (λ *ca.* 350 nm) and a prominent absorption around 545 nm with absorption coefficient in the range 1000–2000 dm^3 mol^{-1} cm^{-3}. Both the location and the intensity of the latter band depart from the values expected for usual copper d–d transitions which appear in the 600–800 nm domain with ε ≈ 50–100 dm^3 mol^{-1} cm^{-1}.[19] The origin of both the hypsochromic shift and the enhancement of these absorptions is to be found in the occurrence of sulphur ligation. This kind of enhancement has been observed[20] in copper(II)–thioether complexes and is attributed to intensity borrowing from the $S(\sigma)\rightarrow Cu(d_{x^2-y^2})$ charge-transfer band.[21] The latter band generally appears in the 320–380 nm region with a moderate intensity ε ≈ 100–5000 dm^3 mol^{-1} cm^{-1}), and is present in all spectra as a shoulder at ≈ 350 nm. The most intense band of the spectra consistently occurs at 300 nm and may be assigned to a ligand transition possibly hiding the $N(\pi)\rightarrow Cu(d_{x^2-y^2})$ charge transfer.[22] In addition to these three bands, the spectrum of the azide shows a medium-intensity absorption (ε ≈ 3300 dm^3 mol^{-1} cm^{-1}) at 385 nm; this

Table 6 Spectral and conductivity data in dimethyl sulphoxide solution

Compd.	Conductivity*/ µs cm^{-1}	λ/nm (ε/dm^3 mol^{-1} cm^{-1})			
1	35	530 (2070)		345	290 (9930)
2	52	550 (1115)	410	350	300 (10 385)
3	80	575 (1410)	410	350	303 (9120)
4	120	573 (1205)		350	303 (9660)
5	74.5	515 (1705)	385 (3210)	350	297 (8027)
6	75.5	515 (1795)	385 (3420)	355	300 (8411)

* Millimolar solutions.

Table 7 Fitting parameters for the magnetic data

Compd.	g	P	10^6 t.i.p.	E_{ST}/cm^{-1}	10^3R
1	2.086	0.35	114	−443	0.36
3	1.953	0.93	80	−809	0.03
4	1.909	6.6	397	−362	3.2
5	1.989	0.30	283	−388	0.16
6	2.099	0.15	60	−482	0.8

$P = \%$ of paramagnetic impurity. t.i.p. = Temperature-independent paramagnetism. $R = \Sigma[(\chi T_{exp})^2 - (\chi T_{calc})^2]/\Sigma(\chi T_{exp})^2$.

Table 8 Electrochemical data for millimolar solutions in dimethyl sulphoxide (potentials in V *vs.* SCE)*

Compound	E_{p_c}		E_{p_a}		ΔE/mV	
1	0.07	0.23	0.08	0.40	150	170
	(0.26)		(0.42)		(160)	
2	0.01	0.15	0.39			
3	0.02		0.46		440	
4	0.02		0.32		300	
5, **6**	0.05		0.15	0.34		
	(0.05)		(0.28)		(230)	

* Values for the two-electron reduced solution are given in parentheses.

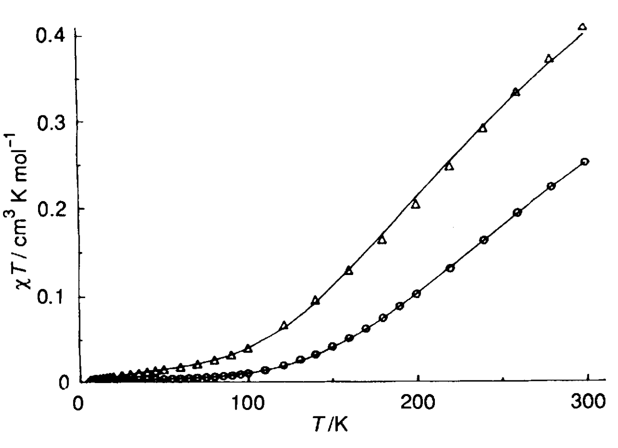


Fig. 3 Temperature dependence of the product of the temperature and the molar susceptibility for complexes **5** (△) and **6** (○). The solid line corresponds to the theoretical values (see text)

band can be safely assigned to the $N_3^- \rightarrow Cu$ charge transfer.[23] No obvious absorption can be attributed to the phenoxide to copper charge transfer which is expected[9] to occur with moderate intensity (ε ≈2500 dm^3 mol^{-1} cm^{-1}) in the 380–450 nm region. Only weak shoulders at 410 nm are seen in this spectral domain for complexes **2** and **3**. As reported by Suzuki *et al.*[24] and Karlin *et al.*,[9] the position of this band is very sensitive to the value of the Cu–O–Cu angle among other factors. It is thus likely that its location changes and that it may be hidden by other absorptions.

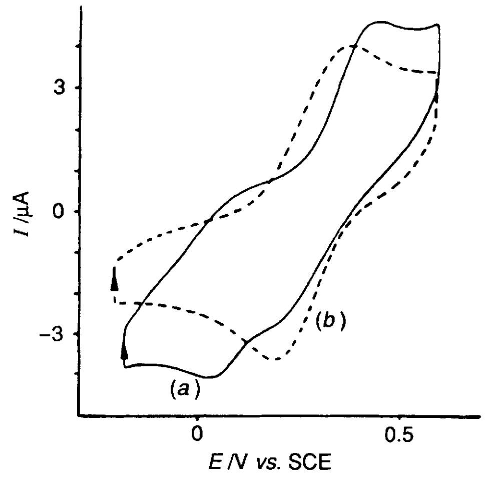


Fig. 4 Cyclic voltammetric curves of compound **1** at a sweep rate of 6 V min^{-1} in dmso solution (*a*) before (solid line) and (*b*) after (dashed line) two-electron reduction (see text)

Magnetic Susceptibility.—Fig. 3 shows the temperature dependence of the magnetic susceptibility of the two azido complexes, **5** and **6**. These data clearly demonstrate that the antiferromagnetic exchange is stronger in **6** than it is in **5** (singlet–triplet gap: $E_{ST} = -388$ cm^{-1}).[6] The value of the singlet–triplet gap in **6** is estimated at $E_{ST} = -482$ cm^{-1} through least-squares fitting of the experimental data, as is usually done for binuclear copper complexes.[6] Table 7 lists the corresponding values obtained for the whole series of complexes.

Electrochemistry.—Table 8 gives the electrochemical data obtained at a platinum electrode for millimolar solutions of complexes in dimethyl sulphoxide at sweep rates of 50 mV s^{-1}. All compounds present irreversible electron transfers at positive potentials. Reduction generally occurs in the 0–0.1 V range, while oxidation is observed between 0.25 and 0.5 V. Three main behaviours can be distinguished. First, the hydroxide **3** and the nitrate **4** exhibit a single electron transfer with cyclic voltammetric peak separations of 440 and 300 mV, respectively. Exhaustive electrolyses at potentials 200 mV more negative than E_{p_c} consume 2 F mol^{-1} as do reoxidations at potentials 200 mV more positive than E_{p_a}. Therefore, complexes **3** and **4** can exchange two electrons in a chemically reversible process, as depicted in reaction (2) for the nitrate **4**.

$$[Cu_2L(dmso)_x]^{3+} + 2e^- \rightleftharpoons [Cu_2L(dmso)_x]^+ \quad (2)$$

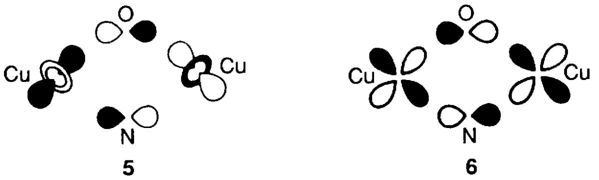
Secondly, cyclic voltammetry shows that the azide dication $[Cu_2L(N_3)]^{2+}$ is reduced in a single step at $E_{p_c} = 0.05$ V, but the reoxidation occurs in two steps at $E_{p_a} = 0.15$ and 0.34 V. Exhaustive electrolysis at −0.4 V consumes 2 F mol^{-1}. Cyclic voltammetry of the reduced solution shows a single couple at $E_{p_a} = 0.28$ V and $E_{p_c} = 0.05$ V. This suggests that a chemical process follows the reduction of the complex. This process cannot be the release of the azide ion since free azide is not detected by its oxidation wave at *ca.* 0.8 V. Reoxidation of the reduced solution at 0.5 V requires 2 F mol^{-1} and regenerates the initial solution.

Thirdly, the behaviour of the halides **1** and **2** is more complicated as detailed below for the chloride. As shown in Fig. 4(*a*) the reduction occurs in two separate one-electron transfers. Reduction at −0.2 V consumes 2 F mol^{-1}. The resulting solution exhibits a single couple in cyclic voltammetry [curve (*b*)]. Reoxidation (2 F mol^{-1}) of the solution at 0.5 V does not regenerate the starting compound, since the couple of the reduced solution is retained. The UV/VIS spectrum of this reoxidized solution is similar to those of all compounds of this series attesting that the basic structure of the complex is maintained.

Discussion

The structural analyses of derivatives **1**, **3**, **5** and **6** of the present series reveal a great plasticity of the copper co-ordination sphere. Trigonal bipyramidal (*TBPY*) as well as square pyramidal (*SPY*) geometries were found, with all three combinations possible to dinuclear sites being observed: *SPY–TBPY* in **1**, *SPY–SPY* in **3** and *TBPY–TBPY* in **5**. Therefore, the structure of **6**, which presents two square-pyramidal copper sites, more closely resembles that of **3** than that of **5**, its chemical analogue. This structural dissimilarity of the two azido complexes re-emphasizes the fact that very subtle factors (nitrate *vs.* perchlorate apical binding, crystal packing) govern the copper stereochemistry in the present compounds. The occurrence of both trigonal-bipyramidal and square-pyramidal geometries in the solid state has been described for a mononuclear complex of an imidazole thioether ligand.[25] Although plasticity of the copper co-ordination sphere is a common feature, it appears even especially enhanced when comparatively weaker and sterically more constraining thioether ligation is involved.

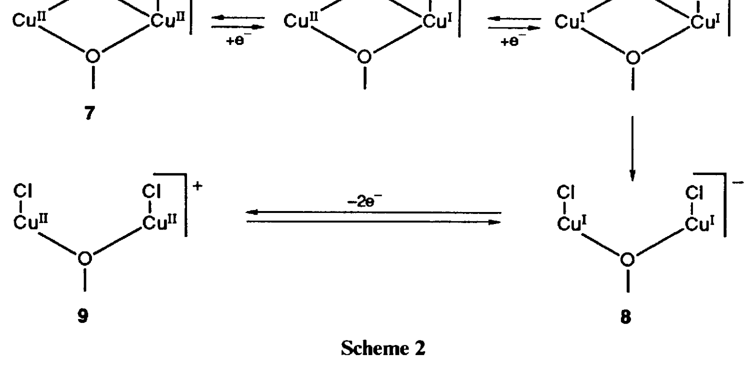
Examination of Table 7 shows that all compounds are strongly antiferromagnetically coupled. The origin of this high interaction is to be found in the co-ordination of the sulphur donor as discussed by Kahn *et al.*[8c] and by us.[6] The case of the two azido complexes **5** and **6** is worth discussing in more depth. Actually, Kahn showed experimentally that a μ-1,1-azido bridge causes a ferromagnetic[26a] coupling of the two copper ions and later proposed the spin-polarization concept[26b] to rationalize this effect. The orbital situation encountered in the present azido derivatives is illustrated in Fig. 5. In **5** the trigonal-bipyramidal geometry of the copper ions means that the magnetic orbital is d_{z^2}. It follows that the major lobe of the orbital points toward the phenolate while its torus interacts with the azide. Overlap considerations justify that the antiferromagnetic interaction mediated by the phenolate dominates the ferromagnetic one carried out by the azide. The situation is quite different in complex **6**. Owing to the tetragonal symmetry, the magnetic orbital is $d_{x^2-y^2}$ which points similarly toward both bridging ligands. Accordingly, as far as overlap is concerned, the two ligands may be similarly active. An enhanced ferromagnetic contribution is expected. Moreover, a reduced antiferromagnetic contribution is expected from the acuteness of the Cu–O(1)–Cu angle (98.4°).[2a] Both effects should combine to give a small antiferromagnetic interaction as observed in similar complexes of nitrogen ligands[9] and, at least, to give an antiferromagnetic interaction far weaker in **6** than it is in **5**. The opposite is observed. We believe that sulphur co-ordination is responsible for the enhanced antiferromagnetic coupling in **6** for two reasons linked to the specific interaction of the sulphur with the $d_{x^2-y^2}$ magnetic orbital. First, as a consequence of the electronegativity effect discussed by Hoffmann and co-workers,[2a] one expects the sulphur co-ordination to contribute strongly to increasing the energy gap between the overall magnetic orbitals and thus the anti-ferromagnetic interaction.[27] Secondly, in the same way, it contributes to increasing the gap between these orbitals and the azido π_g orbital thus lessening the spin-polarization effect.[26a]



5 **6**

Fig. 5 Magnetic orbitals of compounds **5** and **6**

Examination of Table 8 shows that whatever the exogenous ligand the complexes exchange electrons at positive potentials. These potentials are in the range of or higher than those observed for complexes of acyclic[28] and macrocyclic ligands[29] involving sulphur and nitrogen donors. This means that the negative influence of the phenoxo oxygen is counterbalanced by the soft character of the thioether and the aromatic nitrogen, and the flexibility of the ligand which can accommodate the steric requirements of the copper(I) ions. However, the flexibility of the pentadentate ligand is not sufficient freely to allow the stereochemical changes; this results in slow electron transfers as revealed by the large peak potential differences. Also, in the case of the halides **1** and **2**, the overall two-electron exchanges appear as separate one-electron processes indicating that reduction at one site induces steric influences on the other site. This is true in particular for the nitrate derivative **4** where, owing to the broadness of the cyclic voltammetry peaks, it is not possible to ascertain whether a single two-electron transfer (*vs.* two one-electron transfers) is occurring. Also in several instances chemical processes follow the electron transfer. In the case of the azide these are probably stereochemical since the overall reduction–oxidation cycle is chemically reversible. However the situation is more complicated for the chloride **1** since after a two-electron reduction a new compound is formed. This compound behaves as the nitrate **4** exchanging electrons in a chemically reversible process. As shown by UV/VIS spectroscopy the basic structure of the present complexes is retained in this new oxidized derivative. A tentative rationalization of these observations is given in Scheme 2. Upon dissolution in dmso, **1** looses one chloride ion producing **7** probably a monochloro monosolvated species. Two-electron reduction would result in **8**, a dichlorodicopper(I) species with a single phenolate bridge. Two-electron oxidation of **8** would produce **9**, the corresponding singly bridged dichlorodicopper(II) complex. In support of this mechanism it is worth noting that several dicopper(I)



Scheme 2

compounds[30] and a dichlorodicopper(II) complex[16] with a single phenoxo bridge (analogous to **8** and **9**, respectively) have been characterized.

Conclusion

The studies described in this paper together with previous ones[6] reveal that the present ligand HL is able (*i*) to accommodate the presence of various exogenous bridging anions, (*ii*) to mediate a strong interaction between the two copper ions as shown by the high antiferromagnetic coupling of all complexes, and (*iii*) to provide the copper atom with an environment soft enough to achieve moderately positive potentials of the Cu^I–Cu^{II} couple so that both oxidation states are stable in solution. However, the ligand is not flexible enough freely to accommodate the structural change associated with the redox process. This leads to slow electron transfers and, in most cases, the two-electron exchanges do not occur in one step as desired. These specific drawbacks are linked to the peculiarity of the Cu^I–Cu^{II} pair in this domain and should not play a significant role for other metal ions.

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Received 31*st May* 1991; *Paper* 1/02585F