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Molecular Structures and Magnetic Properties of Strongly Antiferromagnetically Coupled Binuclear Copper(II) Complexes [Cu_2 REP(μ-X)(Y)$_2$]

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The molecular structures of binuclear copper(II) complexes [Cu_2REP(μ-OH)(ClO_4)$_2$] (**4**) and [Cu_2REP(μ-Cl)Cl_2] (**5**), in which REP = deprotonated 2,6-bis(1′-(4′-(2″-pyridyl)-2′-thiabutyl))-4-methylphenol, have been characterized by single-crystal X-ray diffraction. The former crystallizes in the triclinic space group $P\bar{1}$ with a = 10.156(3), b = 12.631(3), c = 25.128(10) Å, α = 92.03(3), β = 96.84(3), γ = 108.02(2)°, and Z = 2. Complex **5** crystallizes in the monoclinic space group C 2/c with a = 12.166(2), b = 11.825(2), c = 18.240(4) Å, β = 100.97(2)°, and Z = **4**. All copper ions are pentacoordinated with ligation to a sulfur, a nitrogen, and the bridging phenolato oxygen of the REP ligand, the exogenous bridge, and a counteranion. The coordination geometry of each copper of the binuclear copper sites is square pyramidal in both **4** and **5**. Magnetic susceptibility measurements in the temperature range 6-300 K reveal a strong antiferromagnetic spin exchange in **5** (exchange integral 2J = -460 cm^{-1}). A diamagnetic behavior is observed for **4** according to a similar cryomagnetic investigation. The diamagnetism of **4** is further confirmed by measurements of magnetic susceptibility through Evan's method at room temperature. Complex **4** has no EPR signal. The powder EPR spectrum of **5** shows the typical triplet state characteristics with $\Delta m = \pm 1$ transitions at g = 2.15 and a weaker $\Delta m = 2$ transition at half field with g = 4.24.

INTRODUCTION

Binuclear copper complexes containing metal ion centers in close proximity and an endogenous phenolato bridging ligand have been extensively studied in recent years.[1-5] Complexes with this structure unit are considered important in mimicking the physical properties and various biochemical processes of copper proteins. The polyphenol oxidases and tyrosinase are groups of copper proteins which contain a strongly antiferromagnetically coupled binuclear copper(II) active site. Both copper(II) ions in the active site have a relatively large (positive) redox potential, being readily reduced to copper(I) by polyphenols and reoxidized to copper(II) by dioxygen.[6] Thus, the antiferromagnetic coupling behavior and the capability of interaction with dioxygen are the most obvious features of the active site of copper oxidases.

In bioinorganic or biomimetic studies, bioinorganic chemists have endeavoured to mimic the magnetic and redox properties of the O_2-interacting active site of the copper oxidases by using complexes of small molar mass.[7-10] Recent studies have shown that binuclear copper(II) complexes with a bridging phenolato network and a soft coordination environment (with sulfur and aromatic nitrogen donors) have well succeeded in mimicking the magnetic properties of copper oxidases.[5] We report here the molecular structures and magnetic properties of binuclear copper(II) complexes [Cu_2REP(μ-OH)(ClO_4)$_2$][11] and [Cu_2REP(μ-Cl)Cl_2], in which REP is a thioether-containing binucleating ligand similar to the one reported by Latour and Rey[5] but with the benzimidazolyl group of the latter replaced by a pyridyl group. These REP ligand and binuclear copper(II) complexes were first mentioned by Urbach,[3,12] but details of their structural characterization and related studies have not been reported. The present work complements that of Urbach and other authors.[13-15]

EXPERIMENTAL SECTION

Synthesis of 2,6-Bis(chloromethyl)-4-methylphenol (1)[16]

A slurry of 2,6-bis(hydroxymethyl)-4-methylphenol (15 g, 0.096 mol) in acetone was slowly added to cold, conc. HCl (180 mL). The mixture was mechanically stirred for 15

Dedicated to Professor Sheng-Lieh Liu (劉盛烈) on the occasion of his eightieth birthday.

min and filtered under suction. The precipitate was dried and sublimed under vacuum at 85°C and 1 torr. The product **1** was obtained in white crystals in about 62% yield; *mp* 84°C.

Synthesis of 2-(2'-Mercaptoethyl)-pyridine (2)[17]

This compound was synthesized by a literature method.

Synthesis of 2,6-Bis(1'-(4'-(2"-pyridyl)-2'-thiabutyl))-4-methylphenol (REPH) (3)[12]

A solution of **1** (2.05 g, 10 mmol) in dinitrogen-saturated abcclute ethanol (25 mL) was added dropwise to a solution of **2** (2.78 g, 20 mmol) and sodium metal (0.46 g, 20 mmol) in dinitrogen-saturated absolute ethanol (35 mL). After refluxing for 2 h under dinitrogen, the solution was filtered to remove NaCl and the solvent was removed by rotary evaporation. The product **3** was obtained as a viscous yellow oil in about 64% yield.

Synthesis of the Dicopper(II) Complexes[12]

The following general procedure was used to prepare dicopper(*II*) complexes: *REPH* (2 mmol) was first ionized with a base (NaOH for **4**; triethylamine for **5**) in 95% ethanol (25 mL), and this solution was added dropwise to the appropriate copper(II) salt (4 mmol; $Cu(ClO_4)_2 \cdot 6H_2O$ for **4**; $CuCl_2.2H_2O$ for **5**) dissolved in the same solvent (25 mL). After filtration, the precipitates were washed with cold ethanol and dried under vacuum. The complexes were obtained in brown (**4**) and purple (**5**) powder.

Anal. Calcd for $[Cu_2REP(\mu\text{-}OH)(ClO_4)_2]$ (**4**),[11] $C_{47}H_{57.5}N_4O_{20}S_4Cu_4Cl_{3.5}$: C, 37.51; H, 3.85; N, 3.72. Found: C, 35.89; H, 3.67; N, 3.70.

Anal. Calcd for $[Cu_2REP(\mu\text{-}Cl)Cl_2] \cdot H_2O$ (**5**), $C_{23}H_{27}N_2O_2S_2Cu_2Cl_3$: C, 41.79; H, 4.12; N, 4.24; O, 4.82; Cl, 16.09. Found: C, 41.91; H, 4.10; N, 4.22; O, 4.97; Cl, 16.09.

Crystal Growth

Single crystals of **4** were obtained by the liquid-diffusion method using methanol as solvent and diethyl ether as precipitant. A methanol solution (5 mL) of the complex was placed in a test tube and a layer of diethyl ether (15 mL) was added onto it. The sealed tube was allowed to stand and single crystals **4** formed after 72 h. Single crystals of **5** suitable for X-ray analysis were grown by slow crystallization from an methanol/ethanol/benzene (2:1:1) solution.

X-ray Data Collection and Structure Determination

The intensity data for well defined crystals of **4** (0.30 x 0.30 x 0.50 mm) and **5** (0.30 x 0.35 x 0.40 mm) were measured at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.7107 A). Accurate cell dimensions were obtained by least-squares fitting of the setting angles of 25 reflections and are reported in Table 1 with other experimental parameters for the two complexes. The space groups $P\bar{1}$ for **4** and C 2/c for **5** were established from systematic absences. The intensities were corrected for Lorentz, polarization and absorption effects (calculated transmission range 0.84-1.00 according to experimental psi curves).

All the structural analyses were performed on a μVAX computer using the NRCVAX program. The interpretation of the Patterson synthesis enabled the location of the Cu atom and the remaining non-hydrogen atoms were located from the subsequent Fourier syntheses. All the non-hydrogen atoms were refined anisotropically whereas the hydrogen atoms were fixed at calculated positions. In the case of **4**, one of the two perchlorate ions in the asymmetric unit, CL(1C), O(1C), O(2C), O(3C) and O(1CA), was found to be disordered. The maximum shift/error ratio of the final refinement was 0.006 for **4** and 0.000 for **5**. In the last difference map the deepest hole and the highest peak for **4** and **5** were (-0.630e/Å^3, 1.350e/\Å^3) and (-0.650e/Å^3, 0.790e/Å^3), respectively. Final positional parameters of **4** are listed in Table 2 and those of **5** are listed in Table 4.

Physical Measurements

EPR spectra were measured with a Bruker ER-200D X-band spectrometer which is equipped with a variable temperature accessory and a frequency counter. The g-values were measured using a DPPH (g = 2.00374) reference which was inserted in one of the sample ports in a dual cavity. The magnetic field difference between the two sample positions in the dual cavity were carefully calibrated using a proton NMR magnetometer. Magnetic susceptibilities of the two complexes were measured in the temperature range 6-300 K with a Quantum Design MPMS SQUID Magnetometer. The amount of sample employed for magnetic susceptibility measurements was about 25-30 mg, and the data collected were corrected for the diamagnetism of the constituent atoms estimated from Pascal's parameters. Elemental analyses were carried out on a

Table 1. Crystallographic Data for Complexes **4** and **5**

Formula	$C_{47}H_{57.5}N_4O_{20}S_4Cu_4Cl_{3.5}$	$C_{23}H_{25}N_2OS_2Cu_2Cl_3$
mol wt/g	1505.00	643.03
Cryst dimens/mm	0.30 x 0.30 x 0.50	0.30 x 0.35 x 0.40
Cryst system	triclinic	monoclinic
Space group	$P\bar{1}$	C 2/c
Cell dimens		
a/Å	10.156(3)[b]	12.166(2)[c]
b/Å	12.631(3)	11.825(2)
c/Å	25.128(10)	18.240(4)
α/deg	92.03(3)	
β/deg	96.84(3)	100.97(2)
γ/deg	108.02(2)	
V/Å^3	3034.7(17)	2576.3(8)
F(000)	1534.74	1303.77
Z	2	4
d_{calcd}/g cm^{-3}	1.648	1.658
Scan method	0/20	0/20
Scan range/deg: below $K\alpha_1$, above $K\alpha_2$	0.8, 0.8	1.0, 1.0
Scan rate/deg min^{-1}	16.48/10 to 16.48/2	16.48/8 to 16.48/2
bkgd/scan time	0.25	0.25
2θ range/deg	2-45°	2-50°
No. of total reflecns	8335	2370
No. of unique reflecns	7899	2257
No. of obsd. reflecns $I_o > 2\sigma(I_o)$	5572	1810
μ/cm^{-1}	17.5	21.5
Transmission coeff: min, max	0.84, 1.00	0.86, 1.00
R, R_w[a] for obsd reflecns	0.056, 0.067	0.039, 0.044
R, R_w[a] for all reflecns	0.085, 0.086	0.052, 0.044

[a] $R = \Sigma[||F_o|-|F_c||/\Sigma|F_o|]$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

[b] cell dimensions were obtained from 25 reflections with the 2θ angle in the range of 18.28-21.26°.

[c] cell dimensions were obtained from 25 reflections with the 2θ angle in the range of 21.00-26.66°.

Heraeus CHN-O-Rapid Analyzer.

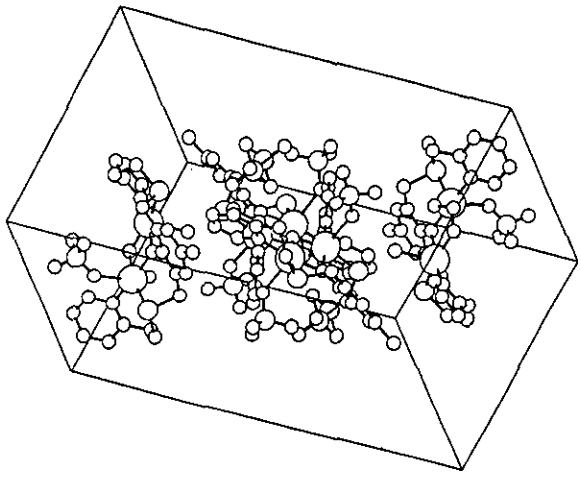

Fig. 1. Unit cell packing diagram for complex **4**.

RESULTS AND DISCUSSION

Description of the Structures

A method of comparison of the dihedral angle between trigonal faces of the coordination polyhedra developed by Muetterties and Guggenberger (M-G)[18] was used for the analysis of the copper coordination polyhedra. This approach compares the actual geometry of a metal site to ideal geometries by the way of a key shape-determining angle. For the pentacoordinate metal centers found in the present case, the two limiting geometries to be considered are the square-based pyramid and the trigonal bipyramid, for which the key angles (e_3) are 0.0 and 53.1°, respectively.

Structure of 4

The triclinic unit cell in which **4** was found to crystallize is illustrated in Fig. 1. The packing in the lattice (see Fig. 1) is composed of four copper complexes, two

Table 2. Atomic Positional Parameters for Complex 4

atom	X	Y	Z
Cu(1A)	0.11646(12)	0.21565(10)	0.35578(5)
Cu(2A)	0.35290(12)	0.43122(10)	0.36710(5)
S(1A)	0.0278(3)	0.08589(21)	0.28292(11)
S(2A)	0.5643(3)	0.48115(21)	0.33338(11)
Cl(1A)	0.2900(3)	0.01869(22)	0.38977(10)
Cl(2A)	0.0740(4)	0.5129(3)	0.28130(14)
N(1A)	-0.0507(8)	0.1652(6)	0.3929(3)
N(2A)	0.4105(8)	0.5678(6)	0.4156(3)
C(1A)	-0.0316(11)	0.1564(9)	0.4459(4)
C(3A)	-0.2726(11)	0.0937(10)	0.4491(5)
C(2A)	-0.1386(11)	0.1210(10)	0.4753(4)
C(4A)	-0.2942(10)	0.1049(9)	0.3953(4)
C(5A)	-0.1815(10)	0.1412(8)	0.3674(1)
C(6A)	-0.1998(11)	0.1512(9)	0.3082(4)
C(7A)	-0.1572(11)	0.0644(9)	0.2760(4)
C(8A)	0.0809(11)	0.1846(9)	0.2322(4)
C(9A)	0.2342(11)	0.2098(8)	0.2317(4)
C(10A)	0.2845(13)	0.1813(8)	0.1855(4)
C(11A)	0.4261(13)	0.2013(9)	0.1837(4)
C(12A)	0.4778(16)	0.1668(11)	0.1347(5)
C(13A)	0.5183(12)	0.2540(9)	0.2287(5)
C(14A)	0.4718(11)	0.2830(8)	0.2755(4)
C(15A)	0.3295(11)	0.2609(8)	0.2768(4)
C(16A)	0.5741(11)	0.3405(9)	0.3233(4)
C(17A)	0.6883(11)	0.5333(9)	0.3938(5)
C(18A)	0.6242(12)	0.5231(10)	0.4447(4)
C(19A)	0.5333(11)	0.5980(9)	0.4480(4)
C(20A)	0.5744(12)	0.6947(10)	0.4813(4)
C(21A)	0.4900(14)	0.7605(9)	0.4802(5)
C(22A)	0.3686(14)	0.7319(10)	0.4475(5)
C(23A)	0.3292(11)	0.6329(9)	0.4157(4)
O(1A)	0.2025(7)	0.3486(5)	0.4020(3)
O(2A)	0.2823(7)	0.2901(5)	0.3220(3)
O(3A)	0.2244(10)	0.0950(8)	0.4083(3)
O(4A)	0.3814(8)	-0.0006(7)	0.4323(3)
O(5A)	0.1838(10)	-0.0839(8)	0.3714(4)
O(6A)	0.3616(9)	0.0597(8)	0.3461(3)
O(7A)	0.2146(11)	0.5088(9)	0.2965(4)
O(8A)	0.0442(20)	0.5838(19)	0.3138(8)
O(9A)	-0.0181(17)	0.4166(11)	0.2713(12)
O(10A)	0.0859(17)	0.5611(18)	0.2325(6)
CU(1B)	0.50465(14)	0.57768(11)	0.15770(5)
CU(2B)	0.43056(13)	0.78958(11)	0.16424(5)
S(1B)	0.4235(3)	0.90363(22)	0.23712(11)
S(2B)	0.6936(3)	0.53784(23)	0.20423(11)
Cl(2B)	0.7636(3)	0.9412(3)	0.12249(12)
N(1B)	0.4760(10)	0.4654(7)	0.0976(3)
N(2B)	0.3166(9)	0.8511(7)	0.1133(3)
C(1B)	0.3497(13)	0.3986(11)	0.0782(5)
C(2B)	0.3251(16)	0.3242(12)	0.0327(6)
C(3B)	0.4346(17)	0.3228(12)	0.0079(5)
C(4B)	0.5633(16)	0.3893(12)	0.0268(5)
C(5B)	0.5834(13)	0.4614(9)	0.0721(4)
C(6B)	0.7265(14)	0.5370(12)	0.0954(5)
C(7B)	0.7790(13)	0.5046(11)	0.1494(5)
C(8B)	0.7996(11)	0.6828(9)	0.2227(4)
C(9B)	0.7443(10)	0.7306(8)	0.2667(4)
C(10B)	0.8235(10)	0.7661(8)	0.3165(4)
C(11B)	0.7727(11)	0.8130(8)	0.3575(4)
C(12B)	0.8609(13)	0.8512(10)	0.4115(5)
C(13B)	0.6408(12)	0.8223(8)	0.3473(4)
C(14B)	0.5579(10)	0.7882(8)	0.2979(4)
C(15B)	0.6091(10)	0.7413(8)	0.2569(4)
C(16B)	0.4169(11)	0.8012(8)	0.2871(4)
C(17B)	0.2435(12)	0.9053(10)	0.2259(5)
C(18B)	0.1529(12)	0.8302(11)	0.1775(5)
C(19B)	0.1978(11)	0.8634(10)	0.1246(5)
C(20B)	0.1200(15)	0.9044(14)	0.0867(6)
C(21B)	0.1656(17)	0.9331(16)	0.0376(6)
C(22B)	0.2833(17)	0.9165(14)	0.0267(6)
C(23B)	0.3599(13)	0.8763(11)	0.0655(5)
O(1B)	0.4125(8)	0.6645(6)	0.1165(3)
O(2B)	0.5317(7)	0.7089(5)	0.20805(25)
O(3B)	0.3275(10)	0.4736(7)	0.1981(4)
O(7B)	0.6465(10)	0.9358(11)	0.1467(5)
O(8B)	0.8103(23)	1.0288(24)	0.1009(10)
O(9B)	0.7402(18)	0.8631(23)	0.0867(10)
O(10B)	0.8709(13)	0.9426(12)	0.1608(5)
Cl(1C)	0.0238(9)	0.5410(6)	0.5022(4)
O(1C)	0.0731(16)	0.4703(13)	0.4743(7)
O(2C)	0.1492(23)	0.6034(21)	0.5331(11)
O(3C)	-0.0072(24)	0.6081(20)	0.4621(10)
O(4C)	0.0543(15)	0.5621(12)	0.0266(6)
C(1C)	0.0979(23)	0.5754(19)	0.0874(9)

methanol molecules and an uncoordinated perchlorate ion. These four copper complexes include two identical **4A**s: $[Cu_2REP(\mu\text{-}OH)(ClO_4)_2]$ and two **4B**s: $[Cu_2REP(\mu\text{-}OH)(ClO_4)(1/2OH)(1/2H_2O)](1/2ClO_4)$. The molecular structure of **4A** and **4B** are shown in Figs. 2 and 3, respectively.

$[Cu_2REP(\mu\text{-}OH)(ClO_4)_2]$ (4A)

Fig. 2. depicts the molecular structure of the hydroxo complex, **4A**, and Table 3 summarizes important bond lengths and angles. Each copper(II) ion is pentacoordinate with ligation to a nitrogen, a sulfur and three oxygens coming from the two bridging ligands and a perchlorate. The two copper ions are bridged by the hydroxo and phenolato oxygens, O1A and O2A, respectively. The Cu-Cu distance is 2.9999(19) Å, and the angles around the bridging atoms are Cu1A-O1A-Cu2A = 104.2(3)° and Cu1A-O2A-Cu2A = 99.6(3)°. The M-G approach gives e_3 values of 5.1° for Cu1A and 18.3° for Cu2A. Thus, the geometries around Cu1A and Cu2A can be described as slightly distorted square pyramid (sp) with the basal planes occupied by O1A, O2A, S1A and N1A, and O1A, O2A, S2A and N2A, respectively. Cu1A lies 0.15 Å above its basal plane toward the apical perchlorate ion, O3A, and Cu2A lies 0.20 Å above its basal plane toward the apical perchlorate ion, O7A. All metal-lioand distances are in the range observed for analogous five-coordinate copper(II) complexes with tetragonal geometries.

$[Cu_2REP(\mu\text{-}OH)(ClO_4)(1/2OH)(1/2H_2O)](1/2ClO_4)$ (4B)

The molecular structure of **4B** is shown in Fig. 3, and important bond lengths and angles are collected in Table 3.

Table 4. Atomic Positional Parameters for Complex 5

Atom	X	Y	Z
Cu	0.48133(4)	0.43477(4)	0.16063(3)
S	0.60173(11)	0.56038(10)	0.10772(6)
Cl(1)	0.29587(10)	0.48849(12)	0.11723(7)
Cl(2)	1/2	0.28862(13)	1/4
N	0.5003(3)	0.3179(3)	0.08557(18)
O	1/2	0.5269(3)	1/4
C(1)	0.4111(4)	0.2635(4)	0.04817(25)
C(2)	0.4190(5)	0.1761(4)	-0.0007(3)
C(3)	0.5235(5)	0.1447(4)	-0.0094(3)
C(4)	0.6157(5)	0.1981(4)	0.0302(3)
C(5)	0.6026(4)	0.2858(4)	0.07778(23)
C(6)	0.7007(4)	0.3464(5)	0.1206(3)
C(7)	0.7129(5)	0.4664(5)	0.0919(3)
C(8)	0.6690(4)	0.6335(4)	0.19293(24)
C(9)	0.5816(4)	0.6999(3)	0.22132(22)
C(10)	0.5791(4)	0.8179(4)	0.2202(3)
C(11)	1/2	0.8761(5)	1/4
C(12)	1/2	1.0063(6)	1/4
C(13)	1/2	0.6424(5)	1/4

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **4**

4A		**4B**	
Cu(1A)-Cu(2A)	2.9999(19)	Cu(1B)-Cu(2B)	3.0001(18)
Cu(1A)-S(1A)	2.309(3)	Cu(1B)-S(2B)	2.325(3)
Cu(1A)-N(1A)	1.976(8)	Cu(1B)-N(1B)	1.967(9)
Cu(1A)-O(1A)	1.909(6)	Cu(1B)-O(1B)	1.907(7)
Cu(1A)-O(2A)	1.965(6)	Cu(1B)-O(2B)	1.978(6)
Cu(1A)-O(3A)	2.470(8)	Cu(1B)-O(3B)	2.251(9)
Cu(2A)-S(2A)	2.315(3)	Cu(2B)-S(1B)	2.312(3)
Cu(2A)-N(2A)	1.964(8)	Cu(2B)-N(2B)	1.963(9)
Cu(2A)-O(1A)	1.894(7)	Cu(2B)-O(1B)	1.899(7)
Cu(2A)-O(2A)	1.962(6)	Cu(2B)-O(2B)	1.939(6)
Cu(2A)-O(7A)	2.541(8)	Cu(2B)-O(7B)	2.489(1)
Cu(1A)-O(1A)-Cu(2A)	104.2(3)	Cu(1B)-O(1B)-Cu(2B)	104.1(3)
Cu(1A)-O(2A)-Cu(2A)	99.6(3)	Cu(1B)-O(2B)-Cu(2B)	100.0(3)
S(1A)-Cu(1A)-N(1A)	95.4(2)	S(2B)-Cu(1B)-N(1B)	95.0(3)
S(1A)-Cu(1A)-O(1A)	165.26(2)	S(2B)-Cu(1B)-O(1B)	156.1(3)
S(1A)-Cu(1A)-O(2A)	91.25(2)	S(2B)-Cu(1B)-O(2B)	91.8(2)
S(1A)-Cu(1A)-O(3A)	94.18(2)	S(2B)-Cu(1B)-O(3B)	101.1(3)
N(1A)-Cu(1A)-O(1A)	94.7(3)	N(1B)-Cu(1B)-O(1B)	93.5(3)
N(1A)-Cu(1A)-O(2A)	170.8(3)	N(1B)-Cu(1B)-O(2B)	169.8(3)
N(1A)-Cu(1A)-O(3A)	90.2(3)	N(1B)-Cu(1B)-O(3B)	94.7(4)
O(1A)-Cu(1A)-O(2A)	77.6(3)	O(1B)-Cu(1B)-O(2B)	77.4(3)
O(1A)-Cu(1A)-O(3A)	96.5(3)	O(1B)-Cu(1B)-O(3B)	100.4(4)
O(2A)-Cu(1A)-O(3A)	95.6(3)	O(2B)-Cu(1B)-O(3B)	91.5(3)
S(2A)-Cu(2A)-N(2A)	92.22(25)	S(1B)-Cu(2B)-N(2B)	94.4(3)
S(2A)-Cu(2A)-O(1A)	159.92(23)	S(1B)-Cu(2B)-O(1B)	164.1(3)
S(2A)-Cu(2A)-O(2A)	92.40(20)	S(1B)-Cu(2B)-O(2B)	92.69(20)
S(2A)-Cu(2A)-O(7A)	98.7(3)	S(1B)-Cu(2B)-O(7B)	88.2(3)
N(2A)-Cu(2A)-O(1A)	97.3(3)	N(2B)-Cu(2B)-O(1B)	93.6(3)
N(2A)-Cu(2A)-O(2A)	175.3(3)	N(2B)-Cu(2B)-O(2B)	171.8(3)
N(2A)-Cu(2A)-O(7A)	93.8(3)	N(2B)-Cu(2B)-O(7B)	90.4(4)
O(1A)-Cu(2A)-O(2A)	78.0(3)	O(1B)-Cu(2B)-O(2B)	78.5(3)
O(1A)-Cu(2A)-O(7A)	98.3(3)	O(1B)-Cu(2B)-O(7B)	105.4(4)
O(2A)-Cu(2A)-O(7A)	86.5(3)	O(2B)-Cu(2B)-O(7B)	93.9(3)

The two copper ions are pentacoordinate in which a tridentate binucleating ligand provides each copper a nitrogen, a sulfur and a bridging phenolato oxygen donor. One bridging hydroxide and a terminal ligand (see Fig. 3: a perchlorate for Cu2B, a hydroxide or water molecule for Cu1B) complete the donor atom array. As only one uncoordinated perchlorate ion can be found in a unit cell, each complex of the two **4**Bs is assigned to have 1/2OH and 1/2 H_2O coordinated to Cu1B. The Cu-Cu separation is 3.0001(18) Å and the angles around the bridging atoms are Cu1B-O1B-Cu2B = 104.1(3)° and Cu1B-O2B-Cu2B = 100.0(3)°. The shape-determining angles e_3 have the values 16.8 and 11.1° for Cu1B and Cu2B, respectively. Therefore, the coordination sphere of each copper belongs to distorted square pyramid (sp), with the four basal atoms N1B, O1B, O2B and S2B for Cu1B and N2B, O1B, O2B and S1B for Cu2B.

Structure of complex 5

The molecular structure of the chloride complex is shown in Fig. 4, and the relevant bond lengths and angles are collected in Table 5. The two copper ions are pentacoordinated; each one is bound to a nitrogen, a sulfur, and the oxygen of the ligand and two chloride anions. The phenolato oxygen and one chloride bridge the two metal

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **5**

Cu-S	2.4128(13)	S-Cu-O	90.43(7)
Cu-Cl(1)	2.3328(14)	Cl(1)-Cu-Cl(2)	113.21(4)
Cu-Cl(2)	2.3569(13)	Cl(1)-Cu-N	100.78(11)
Cu-N	1.989(3)	Cl(1)-Cu-O	94.78(5)
Cu-O	1.9376(20)	Cl(2)-Cu-N	87.60(10)
Cu-Cu	3.205(1)	Cl(2)-Cu-O	81.37(9)
S-Cu-Cl(1)	108.56(5)	N-Cu-O	163.56(12)
S-Cu-Cl(2)	137.91(4)	Cu-Cl(2)-Cu	85.67(6)
S-Cu-N	89.63(11)	Cu-O-Cu	111.59(17)

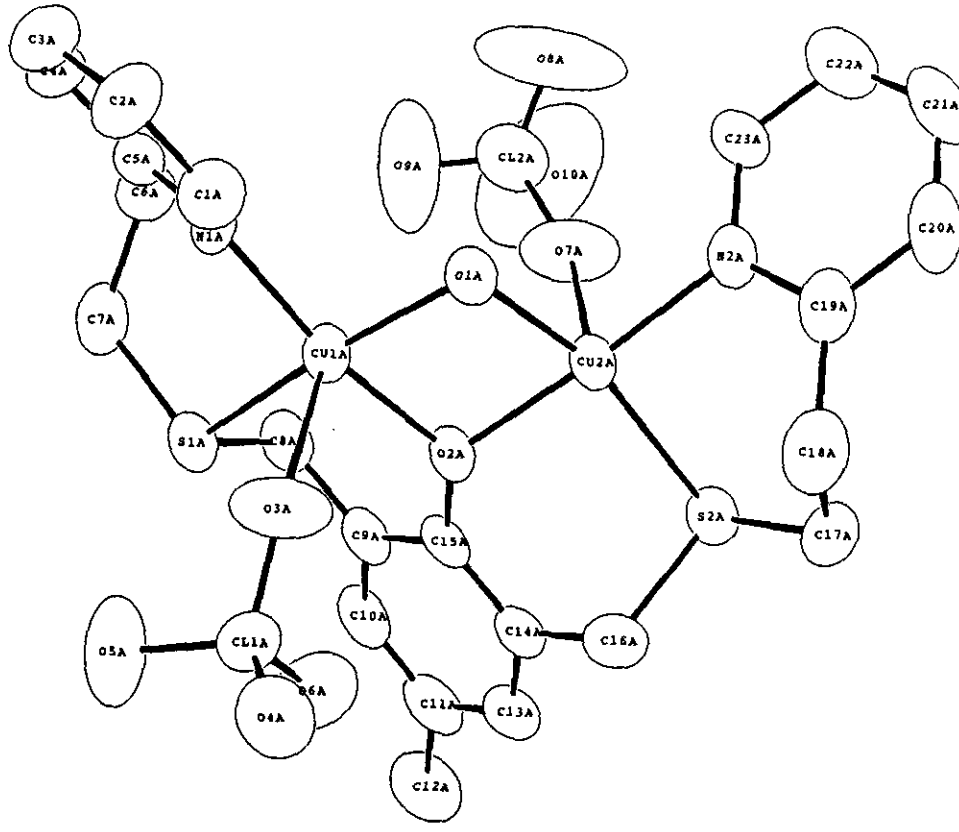

Fig. 2. ORTEP drawing of **4A** and its atom-labeling scheme.

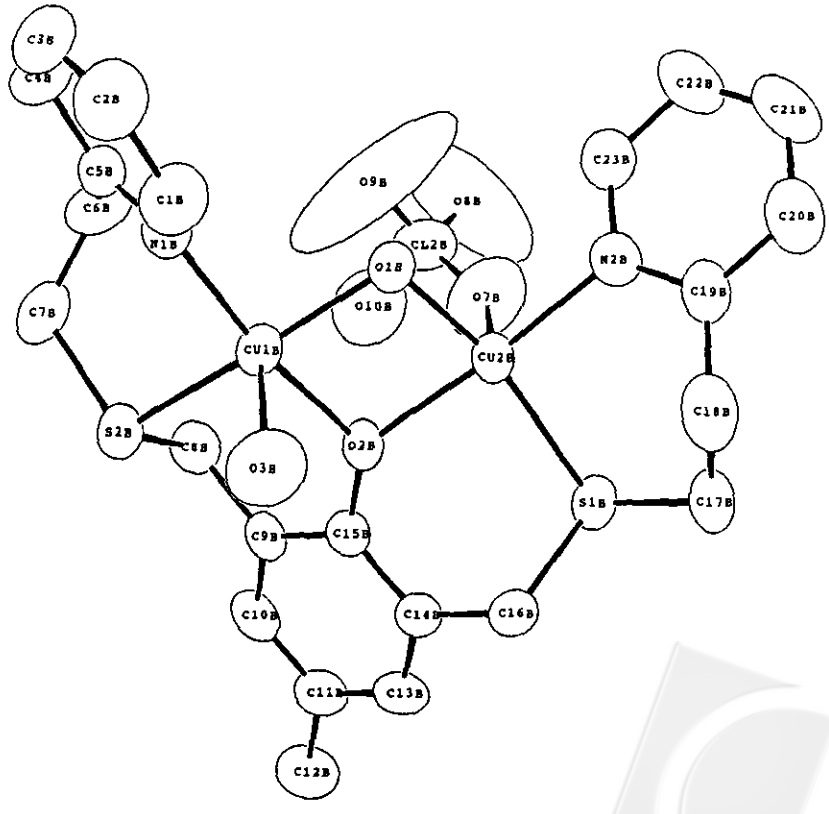

Fig. 3. ORTEP drawing of **4B** and its atom-labeling scheme.

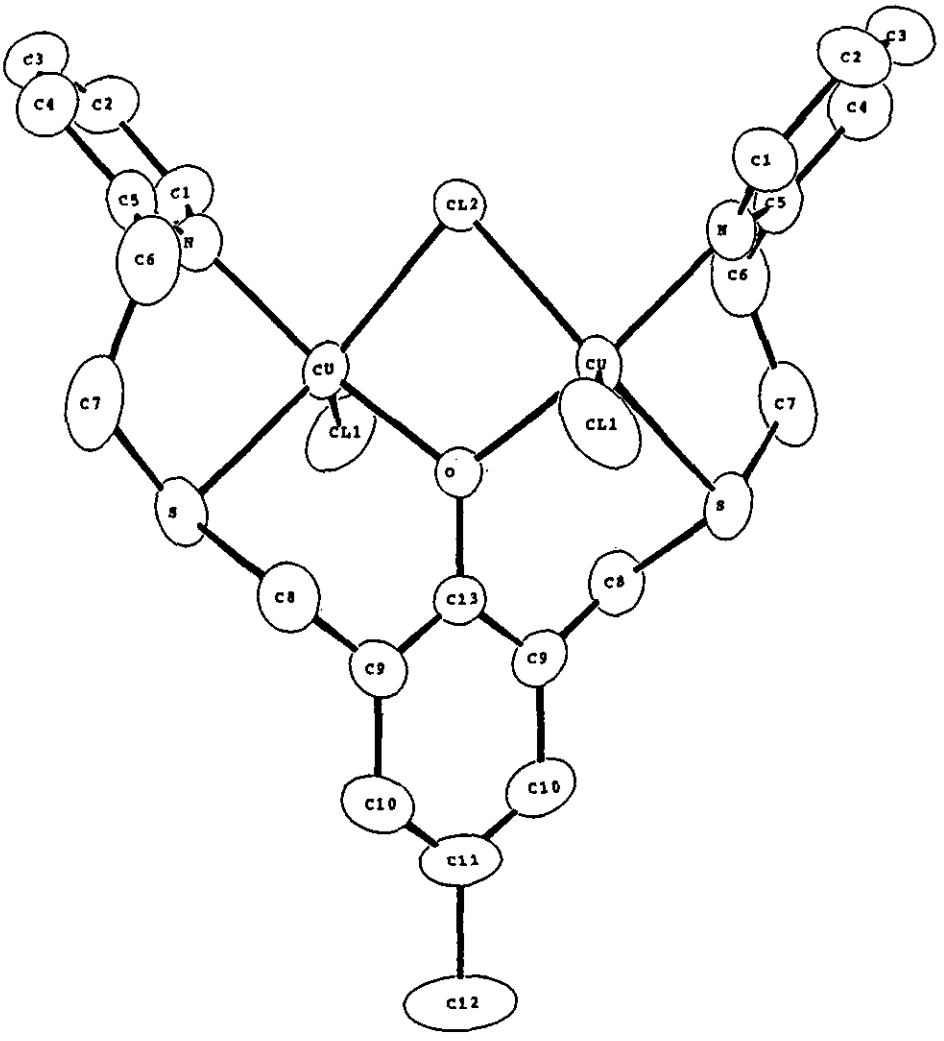

Fig. 4. ORTEP drawing of complex **5** and its atom-labeling scheme.

ions, and the Cu-Cu separation is 3.205(1) Å. The angles around the bridging atoms are Cu-O-Cu = 111.59(17)° and Cu-Cl(2)-Cu = 85.67(6)°. Moreover, the two copper ions are crystallographically related by a C_2 axis running through the phenolato atoms C11, C12, C13, and O and the chloride anion Cl(2). Therefore, the Cu-O-Cu-Cl(2) core is perfectly planar. The M-G approach gives a shape-determining angle e_3 = 33.98°, which does not permit a straightforward determination of the coordination geometry of the copper ions. However, from a close inspection of the bond lengths and angles, one can tentatively describe the copper coordination sphere as distorted square pyramid with the basal plane occupied by N, S, O, and Cl(2).

In the present two complexes with thioether-containing binucleating ligand, a distorted sp coordination is found for each Cu(II) ion in both complexes **4** and **5**. Various coordination geometries exhibited by similar binuclear copper(II) complexes with which only the exogenous bridging ligand is different has been found in Latour and Rey's complexes $[Cu_2L(\mu\text{-}OH)(ClO_4)_2]$ (**6**) and $[Cu_2L(\mu\text{-}Cl)Cl_2]$ (**7**),[5] in which L is a multidentate ligand similar to REP with the pyridyl group in REP replaced by the 2-benzimidazolyl group. For example, a distorted sp coordination is found for both Cu(II) sites in **6**, but a coordination of tbp for one Cu(II) whereas the other being distorted sp is exhibited by **7**. In contrast to the complexes mentioned above, complexes with the nitrogen analogue of the binucleating ligand

REP or L have the preference of sp coordination at their Cu(II) sites.[2,14,15] Latour and Rey attribute the observed different coordination geometries of copper ions in their system to a balance effect operating between the large sulfur atom of the binucleating ligand and the exogenous bridging ligand. Obviously, this balance effect is not observed in present system.

EPR Spectrum and Magnetic Properties

The powder EPR spectrum of **5** (Fig. 5) shows the typical triplet state characteristics with $\Delta m = \pm 1$ transitions at $g = 2.15$ and a weaker $\Delta m = 2$ transition at half field of $g = 4.24$.[19,20] These spectral features prevail up to 360 K. Further increase of temperature leads to sample decomposition. In methancl solution, only the $\Delta m = \pm 1$ transition can be observed at room temperature; the $\Delta m = 2$ transition is presumably too weak to be detected.

Magnetic susceptibility data of **5**, as measured on the SQUID magnetometer, are shown in Fig. 6. These data were analyzed according to the Bleaney-Bowers equation[21] employing a non-linear least-squares fitting procedure. After taking into account of the presence of small amount of paramagnetic impurity (2.25%), we fitted the susceptibility with $2J = -460$ cm^{-1} and $g = 2.00$ as indicated by the solid curve in Fig. 6.

When the bridging ligand is hydroxide, complex **4** lacks an EPR signal. The SQUID magnetometer measurement between 2.2 K and 310 K reveals that **4** is diamagnetic. Further measurements of susceptibility according to Evan's method confirm that complex **4** in methanol has negligible paramagnetism at room temperature. Therefore, the antiferromagnetic coupling between the two Cu(II) ions in **4** is strong enough to prevent observation of any paramagnetism up to 300 K no matter whether in solid or solution state. Based on the X_m value of 5.2×10^{-4} cm^3 mole^{-1} obtained by Evan's method at room temperature and corrected by taking the Pascal parameters into account, we estimate that $2J = -1040$ cm^{-1}. The fact that paramagnetism is observed in solution but not in the pure solid powder is not surprising because there may be intermolecular antiferromagnetic coupling which further reduces the paramagnetism. Furthermore, the structure of **4** in solution may be different from that in the solid. Therefore, the 2J value -1040 cm^{-1} is considered only a rough estimate for the coupling parameter in the solid.

Both **4** and **5** have a large value of E_{ST} ($|2J|$) compared with the corresponding (μ-OH)(μ-phenolato) and (μ-Cl)(μ-phenolato) binuclear copper(II) complexes with similar multidentate ligands in which nitrogen has replaced sulfur in REP.[2,14,15] The large value of E_{ST} has also been reported for **6** and **7**.[6] The presence of the large value of E_{ST} in the sulfur-coordinated binuclear copper(II) complexes can be explained because the s, p orbitals are more diffuse in sulfur than in nitrogen. The diffuse orbitals also render the magnetic orbital more diffuse and consequently increase the antiferromagnetic coupling because of better overlap among the magnetic orbitals. Besides, the diffuse magnetic orbitals also reduce the Coulombic repulsion between the odd electrons and lead to a reduced ferromagnetic coupling.[6,22]

It has been established that a wide angle Cu-O-Cu at the bridging ligand leads to an important antiferromagnetic

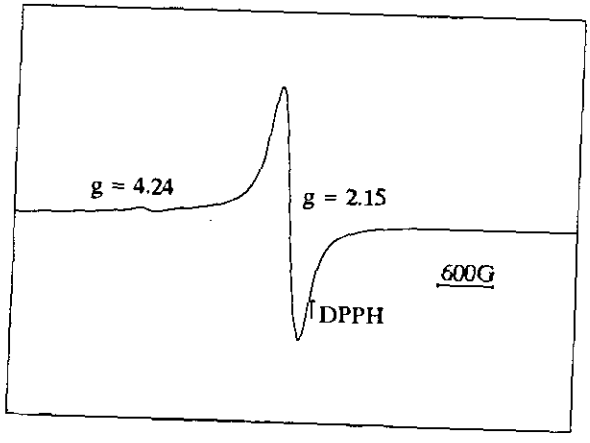

Fig. 5. The powder EPR spectrum of undoped complex **5** with microwave frequence at 9.5789 GHz at 313 K.

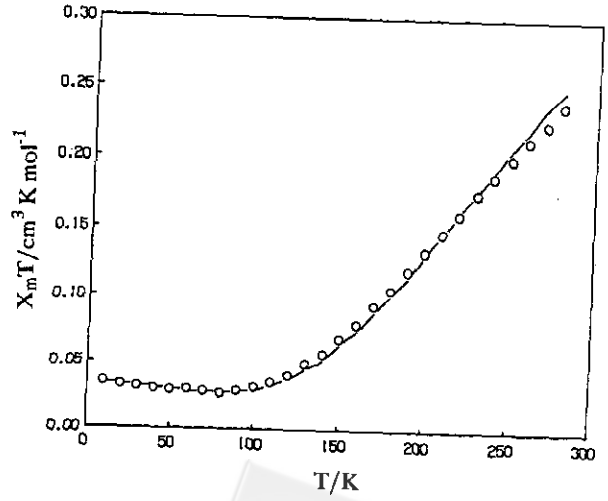

Fig. 6. The magnetic susceptibility data XmT as a function of temperature of complex **5**. The solid line is the best fit of the data according to Bleaney-Bowers equation.

coupling.[23] However, the values of E_{ST} and Cu-OPh-Cu angles of **5** (460 cm^{-1}, 111.6°) and **7** (443 cm^{-1}, 113.4°) are obviously not in accordance with the relation between E_{ST} and the Cu-O-Cu angle relation. Likewise, the values of E_{ST} and Cu-OH-Cu angles of **4** (1040 cm^{-1}, 104.2°) and **6** (809 cm^{-1}, 106.5°) do not follow the established trend. Therefore, other factors must be considered to explain the relation between the value of E_{ST} and the Cu-O-Cu angle. One possible candidate is the local coordination environments around the Cu(II) ions. For example, the coordination geometry of both Cu(II) centers in **5** are distorted square pyramid, whereas in **7** one Cu(II) is a distorted square pyramid and the other is a distorted trigonal bipyramid. These local coordination environments influence the overlap of the magnetic orbitals and consequently the antiferromagnetic coupling between the Cu(II) centers. Hence, the Cu-O-Cu angle can't be the sole determining factor.

CONCLUSION

Complexes **4** and **5** have been prepared as copper complexes of a type which contains a strongly coupled binuclear copper(II) active site. The two copper(II) ions are doubly bridged by an endogenous phenolate oxygen atom and an exogenous anion. Both cupric ions in each complex have the same coordination geometry of distorted square pyramid. These two complexes are the first to give rise to such large antiferromagnetic interactions. Especially, the hydroxide bridge analogue is completely diamagnetic in the solid state. The success in mimicking the magnetic property of the copper oxidase of these two complexes shows that the study of complexes with sulfur-containing binucleating ligand is of interest.

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Key Words

Binuclear copper(II) complex; Magnetic susceptibility.

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