Crystal Structures and Magnetic Properties of Binuclear Five-co-ordinate Copper(II) Complexes with a Phenolate Bridge and their Catalytic Functions in Multielectron Redox Reactions†

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Crystal structures of the binuclear five-co-ordinate copper(II) complexes $[Cu_2(L^1)(CH_3CO_2)][PF_6]_2$ **(1)**, $[Cu_2(L^1)Cl_2]ClO_4$ **(2)**, and $[Cu_2(L^2)(OH)][ClO_4]_2$ **(3)** (HL^1 = 2,6-bis[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenol and HL^2 = 2,6-bis{bis[2-(methylthio)ethyl]aminomethyl}-4-methylphenol) have been determined by *X*-ray diffraction methods. The structures were solved by direct methods and refined by block-diagonal least squares to R = 0.071, 0.077, and 0.059 for **(1)**, **(2)**, and **(3)**, respectively. All the complexes are binuclear; the two copper atoms are bridged by acetate and phenolate, phenolate, and hydroxide and phenolate groups with Cu–Cu separations of 3.549, 4.128, and 3.020 Å, for **(1)**, **(2)**, and **(3)**, respectively. The magnitude of the antiferromagnetic interaction varies remarkably on going from **(1)** to **(3)**, *i.e.*, $-2J$ = 80, 0, and 675 cm^{-1} for **(1)**, **(2)**, and **(3)**, respectively. The variation is explained in terms of overlapping between the copper 3*d* and intervening oxygen 2*p* orbitals based on the molecular structures determined. The catalytic activities of these complexes for the O_2 oxidation of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine were measured, together with those of mononuclear complexes of similar co-ordination environments. In spite of large Cu–Cu separations (>3.5 Å), complexes **(1)** and **(2)** showed remarkably high catalytic activity compared with those of the mononuclear complexes. The result is discussed in terms of the co-ordination structures.

Binuclear transition-metal complexes are of great interest because they provide the opportunity to study (*i*) the mechanism of superexchange interaction between paramagnetic ions, and (*ii*) the roles of the metal ions in multielectron redox reactions and in the activation of small molecules such as O_2 and N_2. They also serve as models for some metalloproteins whose biological functions are associated with the metal centre in pairs.[1–3]

In order to perform the above studies, a large number of binuclear copper(II) complexes with binucleating ligands have been prepared and characterized.[4] Binuclear copper(II) complexes with phenolate bridges have been studied by many workers.[5–10] Typical complexes are those of binucleating ligands derived from 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde and various amines,[5–8] where the environments around copper(II) ions are generally square planar. For five-co-ordinate binuclear copper(II) complexes with a phenolate bridge, only a few studies have been reported so far,[9,10] although Karlin *et al.*[11] and Nishida *et al.*[12] have shown that five-co-ordinated copper(II) ions of tripodal ligands are useful to mimic the biological copper proteins.

Very recently the binuclear copper(II) complexes with tripod-like ligands, $[Cu_2(L^1)(CH_3CO_2)][PF_6]_2$ **(1)**, $[Cu_2(L^1)Cl_2]ClO_4$ **(2)**, and $[Cu_2(L^2)(OH)][ClO_4]_2$ **(3)** were prepared,[13,14] and assumed to involve five-co-ordinate copper(II) ions with phenolate bridges, where HL^1 = 2,6-bis[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenol and HL^2 = 2,6-bis{bis[2-(methylthio)ethyl]aminomethyl}-4-methylphenol. The most interesting feature of the complexes is their remarkable variation in magnetism, *i.e.*, $-2J$ = 80, 0, and 675 cm^{-1} for **(1)**, **(2)**, and **(3)**, respectively, where $-2J$ denotes the singlet–triplet energy separation. In this study we have determined the crystal structures of these complexes in order to clarify the origins of the difference in $-2J$ values. Furthermore, the catalytic activities of these complexes for the O_2 oxidation reaction of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (tmpd) were studied, since the present complexes seem to be much better models for Type III copper than the planar complexes whose catalytic behaviour was extensively studied by Nishida and co-workers.[15,16]

Experimental

Syntheses.—The copper(II) complexes **(1)**,[13] **(2)**,[13] and **(3)**[14] were prepared by published methods. Single crystals for the *X*-ray work were obtained as prisms by slow evaporation of an acetonitrile–water solution at room temperature. Compounds **(4)**[17] and **(6)**[18] were prepared according to the literature methods.

2-[*Bis*(2-*pyridylmethyl*)*aminomethyl*]-4-*nitrophenol* (Hbpnp). A tetrahydrofuran (thf) solution containing 2-chloromethyl-4-nitrophenol (0.005 mol) was added to a thf solution of bis(2-pyridylmethyl)amine (0.005 mol) at room temperature. To this solution was added triethylamine (0.005 mol) and the mixture heated under reflux for 2 h. After cooling, triethylamine hydrochloride was removed by filtration, and the filtrate was evaporated to obtain a syrup which was used for the preparation of complex **(5)** without further purification.

$[Cu(bpnp)]PF_6$ **(5)**. When the syrup (0.001 mol ligand) obtained above, copper(II) nitrate (0.001 mol), triethylamine (0.001 mol), and ammonium hexafluorophosphate (200 mg) were mixed in methanol (50 cm^3), $[Cu(bpnp)]PF_6$ was obtained as green crystals (Found: C, 40.80; H, 3.05; N, 9.80. $C_{19}H_{15}CuF_6N_4O_6$ requires C, 40.90; H, 3.05; N, 10.05%).

X-Ray Data Collection.—The crystals were mounted on a Rigaku AFC-5 four-circle automatic diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å). Automatic centring and least-squares routines were carried out on 25 reflections for each complex to obtain the cell constants given in Table 1. The θ–2θ scan technique was employed to

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† *Supplementary data available* (No. SUP 56271, 7 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Crystal data for complexes (**1**)—(**3**)

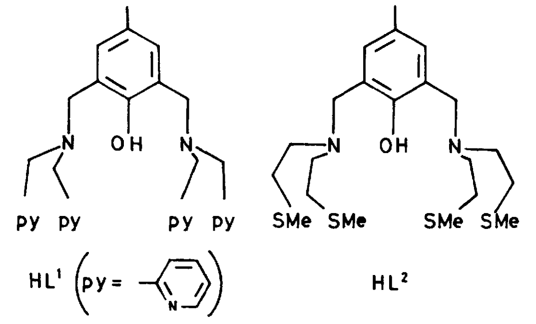
Complex	(**1**)	(**2**)	(**3**)
Formula	$C_{35}H_{36}Cu_2F_{12}N_6O_3P_2$	$C_{33}H_{33}Cl_3Cu_2N_6O_5$	$C_{21}H_{38}Cl_2Cu_2N_2O_{10}S_4$
M	993.7	827.1	804.8
Space group	$P2_1/a$	Pn	$P2_1/a$
a/Å	17.843(4)	12.065(4)	21.531(6)
b/Å	21.226(5)	12.592(5)	18.479(2)
c/Å	11.206(3)	12.006(4)	8.177(1)
β/°	105.47(2)	102.85(3)	90.47(2)
U/Å^3	4 090(1)	1 778(1)	3 253(1)
Z	4	2	4
D_c/g cm^{-3}	1.61	1.54	1.64
$F(000)$	2 032	844	1 652
Crystal dimensions/mm	0.2 × 0.3 × 0.3	0.2 × 0.15 × 0.15	0.3 × 0.2 × 0.4
Scan rate/° min^{-1}	6	6	6
Scan range (2θ)/°	3.0—55.0	3.0—55.0	3.0—55.0
Reflections collected	4 845	4 286	3 745
Independent reflections ($> 3\sigma\|F_o\|$)	3 318	2 559	2 704
μ(Mo-K_α)/cm^{-1}	12.1	14.5	17.5
R ($=\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$)	0.0708	0.0771	0.0589
R' [($=\Sigma\|\|F_o\| - \|F_c\|\|^2/\Sigma\|F_o\|^2)^{\frac{1}{2}}$]	0.0723	0.0998	0.064

Table 2. Atomic co-ordinates (× 10^4) for (**1**) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Cu(1)	3 802(1)	2 858.7(7)	1 352(1)	C(22)	3 335(8)	4 543(6)	−2 989(10)
Cu(2)	3 948(1)	4 213.9(6)	−426(1)	C(23)	2 655(8)	4 596(5)	−2 407(10)
O(1)	4 132(5)	3 216(3)	−8(6)	C(24)	1 911(9)	4 803(7)	−3 029(12)
O(2)	3 319(6)	3 641(4)	1 631(7)	C(25)	1 356(10)	4 880(7)	−2 437(13)
O(3)	3 989(5)	4 458(3)	1 260(6)	C(26)	1 524(9)	4 748(6)	−1 158(13)
N(1)	3 954(6)	4 119(4)	−2 251(6)	C(27)	2 259(9)	4 526(6)	−566(12)
N(2)	2 826(6)	4 459(5)	−1 163(8)	C(28)	4 716(8)	4 281(6)	−2 399(9)
N(3)	5 095(6)	4 237(4)	−181(8)	C(29)	5 372(8)	4 160(5)	−1 206(9)
N(4)	4 557(6)	2 106(4)	1 584(6)	C(30)	6 116(9)	4 031(6)	−1 167(12)
N(5)	3 064(6)	2 214(5)	−83(8)	C(31)	6 661(9)	3 959(6)	−46(12)
N(6)	3 560(7)	2 487(5)	2 874(8)	C(32)	6 398(8)	4 009(6)	1 033(11)
C(1)	4 513(7)	2 865(5)	−685(8)	C(33)	5 636(8)	4 147(5)	962(9)
C(2)	4 326(8)	2 977(5)	−1 986(9)	C(34)	3 623(8)	4 174(6)	1 906(9)
C(3)	4 703(8)	2 623(5)	−2 695(9)	C(35)	3 543(9)	4 505(7)	3 076(11)
C(4)	5 232(8)	2 162(6)	−2 192(10)	P(1)	5 747(3)	3 694(2)	4 526(3)
C(5)	5 615(10)	1 739(7)	−2 990(12)	P(2)	6 101(3)	262(2)	2 944(4)
C(6)	5 414(5)	2 044(6)	−910(10)	F(1)	4 991(8)	3 585(5)	5 000(10)
C(7)	5 042(8)	2 404(5)	−179(9)	F(2)	6 134(8)	3 945(4)	5 846(8)
C(8)	5 266(7)	2 278(5)	1 233(9)	F(3)	5 458(6)	4 380(4)	4 103(8)
C(9)	4 799(8)	1 961(6)	2 965(9)	F(4)	6 443(7)	3 830(6)	4 020(11)
C(10)	4 073(8)	2 017(6)	3 375(9)	F(5)	5 220(7)	3 453(5)	3 243(7)
C(11)	3 890(10)	1 623(7)	4 297(11)	F(6)	6 009(6)	3 008(4)	4 941(8)
C(12)	3 210(12)	1 758(10)	4 628(14)	F(7)	5 619(11)	441(8)	3 827(15)
C(13)	2 727(12)	2 251(9)	4 170(15)	F(8)	6 702(13)	632(10)	3 842(16)
C(14)	2 897(10)	2 632(8)	3 195(12)	F(9)	6 319(12)	952(8)	2 710(24)
C(15)	4 153(8)	1 531(6)	929(10)	F(10)	5 462(14)	621(10)	2 112(20)
C(16)	3 502(8)	1 733(5)	−209(9)	F(11)	6 505(12)	173(9)	1 965(13)
C(17)	3 372(9)	1 365(6)	−1 302(11)	F(12)	5 449(14)	19(14)	1 892(21)
C(18)	2 746(8)	1 546(7)	−2 275(10)	F(13)	6 128(15)	−322(11)	3 594(20)
C(19)	2 267(9)	2 055(6)	−2 149(11)	F(14)	6 807(13)	−8(13)	3 931(18)
C(20)	2 449(9)	2 396(6)	−1 029(11)	F(15)	5 673(14)	−424(10)	2 649(23)
C(21)	3 714(8)	3 444(5)	−2 589(9)	F(16)	6 768(12)	−5(11)	2 238(23)

record the intensities for a unique set of reflections for which $3 \leqslant 2\theta \leqslant 55°$. Three check reflections were measured every 100 reflections; they exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarization effects.

Structure Solution and Refinement.—In each case the positional parameters of the copper atoms were determined by direct methods.[19] The remaining non-hydrogen atoms were located by subsequent Fourier maps and least-squares refinement. The refinement was effected by the block-diagonal least-squares technique by using anisotropic thermal parameters. As usual, the hexafluorophosphate and perchlorate ions proved awkward. In (**1**), one of the two anions was ordered [P(1) and F(1)—F(6) in Table 2]. For the second anion [P(2) and F(7)—F(16)], 10 fluoride atoms were located in the difference-Fourier map and each given an occupancy factor of 0.5 and refined anisotropically. In (**2**), a high degree of disorder was observed for the perchlorate anion, and the four oxygen atoms observed were refined anisotropically with occupancy factors of 0.5. In (**3**), eight perchlorate oxygen atoms were refined anisotropically irrespective of their high isotropic thermal



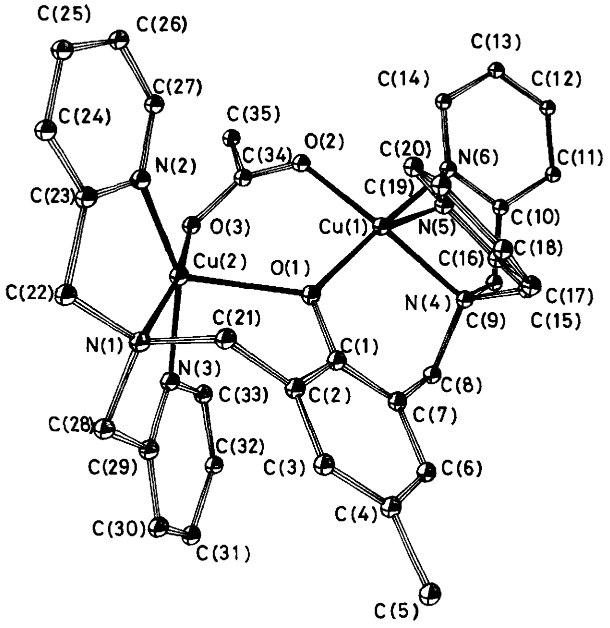


Figure 1. Perspective drawing of $[Cu_2(L^1)(CH_3CO_2)]^{2+}$

parameters ($B_{eq}/\text{Å}^2 = 9$—24). In the last stage of refinement, the difference-Fourier map showed no significant peaks and all parameter shifts were less than 0.5 σ. The crystal data and final *R* values are listed in Table 1. Programs used for the structure solution and anisotropic refinement were supplied by the local version[20] of the UNICS system.[21] Atomic scattering factors were taken from ref. 22. All calculations were performed on a Facom M-200 computer at the Computer Centre of Kyushu University.

Measurements.—Absorption spectra were obtained with a Shimadzu model UV-240 spectrophotometer at 288 K.

Results and Discussion

Molecular Structure of (**1**).—Compound (**1**) crystallizes in the monoclinic space group $P2_1/a$. The final atomic parameters are listed in Table 2, and important bond distances and angles in Table 3. As shown in Figure 1, the two copper(II) atoms are bridged by the phenolate and acetate ions.

The copper–ligand bond distances are in the range of Cu–N and Cu–O distances observed for similar complexes.[9] There is, however, a significant difference between the bond lengths Cu(1)–O(1) and Cu(2)–O(1) (*cf.* Table 3). This probably arises from the inequivalent geometry about the two copper ions. For Cu(1), the geometry is best described as a square pyramid with the basal plane consisting of O(1), O(2), N(4), and N(6). The axial position of the square pyramid is occupied by one of the pyridyl nitrogens, N(5). The geometry around Cu(2) is also described as a square pyramid, but in this case the apical position is occupied by the bridging phenolate oxygen atom, and the basal plane comprises O(3), N(1), N(2), and N(3). The two copper(II) atoms deviate considerably from the plane of the phenolate ring, the deviations being summarized in Table 4.

Table 3. Selected bond distances (Å) and angles (°) for (**1**)

Cu(1)–O(1)	1.931(7)	Cu(1)–O(2)	1.936(8)
Cu(1)–N(4)	2.066(9)	Cu(1)–N(5)	2.251(8)
Cu(1)–N(6)	2.027(10)	Cu(1)–Cu(2)	3.549(2)
Cu(2)–O(1)	2.178(6)	Cu(2)–O(3)	1.942(6)
Cu(2)–N(2)	2.020(7)	Cu(2)–N(3)	2.000(10)
Cu(2)–N(1)	2.056(7)		
O(1)–Cu(1)–O(2)	92.0(3)	O(1)–Cu(1)–N(6)	174.3(4)
O(1)–Cu(1)–N(4)	94.2(3)	O(1)–Cu(1)–N(5)	85.3(3)
O(2)–Cu(1)–N(6)	89.6(4)	O(2)–Cu(1)–N(4)	161.8(3)
O(2)–Cu(1)–N(5)	115.9(3)	N(6)–Cu(1)–N(4)	82.7(4)
N(6)–Cu(1)–N(5)	98.9(4)	Cu(1)–O(1)–Cu(2)	119.3(4)
O(1)–Cu(2)–O(3)	95.0(3)	O(1)–Cu(2)–N(2)	114.9(3)
O(1)–Cu(2)–N(1)	94.5(3)	O(1)–Cu(2)–N(3)	84.2(3)
O(3)–Cu(2)–N(2)	95.9(3)	O(3)–Cu(2)–N(1)	169.7(3)
O(3)–Cu(2)–N(3)	94.9(3)	N(1)–Cu(2)–N(2)	83.7(4)
N(1)–Cu(2)–N(3)	82.0(3)	N(2)–Cu(2)–N(3)	157.0(4)

Table 4. Deviations (Å) of copper(II) atoms from the phenolate planes *

Complex	(1)	(2)	(3)
Cu(1)	−0.99	−1.73	−0.78
Cu(2)	+1.18	+1.69	+0.17

* O(1), C(1)—C(7) for (**1**) and (**2**); O(2), C(3)—C(9) for (**3**).

Molecular Structure of (**2**).—Complex (**2**) crystallizes in the monoclinic space group *Pn*. Final atomic co-ordinates, important bond distances and angles, and deviations from the least-squares planes are listed in Tables 5—7, respectively. As shown in Figure 2, the two copper atoms are bridged by the phenolate oxygen.

The copper–ligand bond distances fall in the range of normal Cu–N and Cu–Cl distances.[9,18] The co-ordination geometries of both copper(II) ions are best described as square pyramidal, with basal planes formed from Cl(1), N(1), N(3), and N(4) for the Cu(1) chromophore and from Cl(2), N(2), N(5), and N(6) for the Cu(2) chromophore. The two square pyramids share the phenolate oxygen at the axial positions. The Cu–O(1) distances are in the range 2.16(2)—2.23(2) Å (*cf.* Table 6), and very close to that of Cu(2)–O(1) [2.178(6) Å] for complex (**1**).

Molecular Structure of (**3**).—Compound (**3**) crystallizes in the monoclinic space group $P2_1/a$. Final atomic parameters, selected bond distances and angles, and deviations from the least-squares planes are listed in Tables 8—10 respectively. As shown in Figure 3, the two copper atoms are bridged by the phenolate and hydroxide oxygen atoms.

The copper–ligand bond distances are in the range of Cu–S(thioether) and Cu–N bond lengths observed for similar complexes.[23] It should be noted that the geometries around the copper atoms are best described as trigonal bipyramidal (*cf.* Tables 9 and 10, and ref. 23). The trigonal plane for Cu(1) is formed by O(2), S(1), and S(2), and that for Cu(2) by O(2), S(3), and S(4); *i.e.*, the trigonal axes lie along the O(1)–Cu(1)–N(1) and O(1)–Cu(2)–N(2) bonds for Cu(1) and Cu(2) respectively.

Table 5. Atomic co-ordinates (× 10^4) for (**2**) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Cu(1)	1 073(2)	802(2)	3 953(2)	C(16)	575(27)	−1 869(22)	5 971(23)
Cu(2)	4 208(2)	775(2)	6 199(2)	C(21)	−460(16)	2 688(21)	3 855(20)
Cl(1)	1 856(5)	−435(5)	2 986(6)	C(22)	228(15)	2 784(15)	2 939(18)
Cl(2)	3 370(5)	−366(5)	7 204(5)	C(23)	1 683(23)	2 972(23)	1 384(22)
O(1)	2 704(23)	1 379(9)	5 054(26)	C(24)	831(23)	3 817(26)	1 494(23)
N(1)	47(14)	1 877(16)	4 591(16)	C(25)	124(20)	3 702(23)	2 260(17)
N(2)	5 186(12)	1 771(13)	5 465(13)	C(26)	1 651(16)	2 106(17)	2 081(19)
N(3)	520(13)	−213(12)	4 978(14)	C(31)	5 756(16)	2 550(16)	6 436(18)
N(4)	1 017(12)	1 952(16)	2 817(13)	C(32)	4 936(17)	2 720(22)	7 242(16)
N(5)	4 284(14)	1 969(13)	7 299(14)	C(33)	5 048(22)	2 660(19)	7 905(24)
N(6)	4 681(14)	−353(17)	5 148(14)	C(34)	4 354(24)	3 771(20)	8 682(22)
C(1)	2 692(34)	2 421(14)	5 047(26)	C(35)	3 681(22)	2 997(22)	3 725(20)
C(2)	1 706(14)	3 034(18)	5 372(17)	C(36)	3 511(22)	1 965(27)	8 065(19)
C(3)	1 733(17)	4 130(18)	5 418(19)	C(41)	6 029(19)	1 192(18)	5 057(21)
C(4)	2 517(32)	4 674(15)	5 011(39)	C(42)	5 580(16)	169(21)	4 700(17)
C(5)	3 506(16)	4 068(18)	4 815(17)	C(43)	6 061(22)	−467(23)	3 958(19)
C(6)	3 499(15)	2 988(16)	4 818(16)	C(44)	5 379(30)	−1 589(26)	3 592(25)
C(7)	2 527(35)	5 866(18)	4 930(39)	C(45)	4 604(22)	−1 895(26)	4 069(20)
C(8)	855(16)	2 400(16)	5 666(17)	C(46)	4 309(19)	−1 228(19)	4 902(19)
C(9)	4 519(16)	2 342(21)	4 425(19)	Cl(3)	1 743(4)	5 615(10)	−1 424(12)
C(11)	−790(15)	1 143(19)	5 085(18)	O(21)	1 939(34)	6 643(36)	−1 012(54)
C(12)	−254(19)	42(19)	5 515(19)	O(22)	722(41)	5 935(28)	−2 306(36)
C(13)	1 041(21)	−1 222(21)	5 250(22)	O(23)	1 388(42)	5 004(68)	−932(72)
C(14)	−611(18)	−567(18)	6 361(19)	O(24)	2 451(24)	5 509(28)	−2 042(28)
C(15)	−342(20)	−1 422(20)	6 510(18)				

Table 6. Selected bond distances (Å) and angles (°) for (**2**)

Cu(1)–O(1)	2.23(2)	Cu(1)–N(1)	2.09(2)
Cu(1)–N(3)	1.99(1)	Cu(1)–Cl(1)	2.271(7)
Cu(1)–N(4)	1.98(2)	Cu(1)–Cu(2)	4.128(3)
Cu(2)–O(1)	2.16(2)	Cu(2)–N(2)	2.05(2)
Cu(2)–N(5)	1.99(2)	Cu(2)–N(6)	2.06(2)
Cu(2)–Cl(2)	2.255(7)		
O(1)–Cu(1)–Cl(1)	96.5(6)	O(1)–Cu(1)–N(3)	102.4(8)
O(1)–Cu(1)–N(4)	93.5(7)	O(1)–Cu(1)–N(1)	95.1(7)
Cl(1)–Cu(1)–N(3)	96.4(5)	Cl(1)–Cu(1)–N(1)	168.2(5)
Cl(1)–Cu(1)–N(4)	96.0(5)	N(3)–Cu(1)–N(1)	83.2(7)
N(3)–Cu(1)–N(4)	158.6(6)	N(1)–Cu(1)–N(4)	81.2(7)
Cu(1)–O(1)–Cu(2)	140.2(5)	O(1)–Cu(2)–Cl(2)	98.8(7)
O(1)–Cu(2)–N(6)	99.2(8)	O(1)–Cu(2)–N(2)	89.6(8)
O(1)–Cu(2)–N(5)	93.7(7)	Cl(2)–Cu(2)–N(6)	96.1(5)
Cl(2)–Cu(2)–N(2)	171.5(4)	Cl(2)–Cu(2)–N(5)	95.0(5)
N(6)–Cu(2)–N(2)	83.9(7)	N(6)–Cu(2)–N(5)	161.4(7)
N(2)–Cu(2)–N(5)	82.9(7)		

Table 7. Deviations (Å) of atoms from the least-squares planes in (**2**)

Plane 1: Cu(1), Cl(1), N(1), N(3), and N(4)

Cu(1) 0.200, Cl(1) −0.003, N(1) −0.015, N(3) −0.078, N(4) −0.078, O(1) +2.430

Plane 2: Cu(2), Cl(2), N(2), N(5), and N(6)

Cu(2) −0.162, Cl(2) 0.005, N(2) −0.012, N(5) 0.085, N(6) 0.083, O(1) −2.309

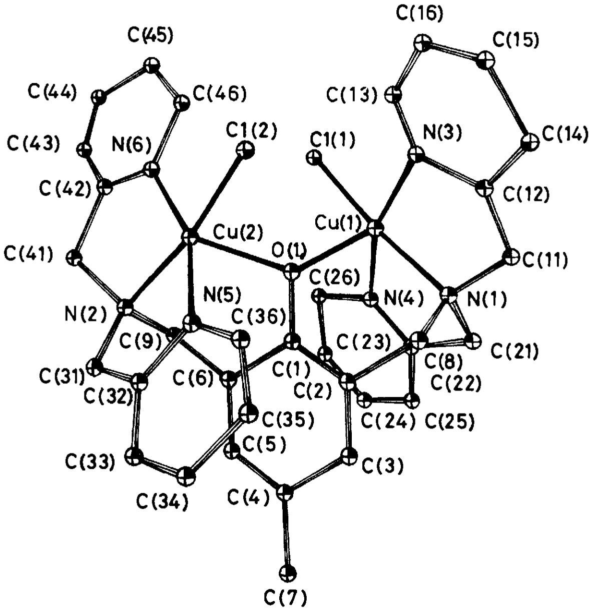


Figure 2. Perspective drawing of $[Cu_2(L^1)Cl_2]^+$

Magnetic Properties and Crystal Structure.—The magnetic properties of the binuclear copper(II) complexes have been interpreted in terms of the Bleaney–Bowers equation (i), where g, J, and N_α have their usual meanings.[24] According to the theory of superexchange,[2,25] the overlapping between the metal magnetic orbitals and the highest occupied orbital(s) of the intervening atom(s) (*i.e.*, the length of the σ-bonding pathway), is the major determining factor for antiferromagnetic interaction.

$$\chi = \frac{Ng^2\beta^2}{3kT}\left\{1 + \frac{1}{3}[\exp(-2J/kT)]\right\}^{-1} + N_\alpha \qquad \text{(i)}$$

In square-pyramidal copper(II) complexes, an unpaired electron is localized in the $d_{x^2-y^2}$ orbital whose lobes are directed to the four ligand atoms in the basal plane. Therefore, the exchange interaction between the copper(II) ions must be negligible when two square pyramids share an atom at their apexes (this corresponds to the case of zero σ-bonding pathway). This is the case for compound (**2**) ($-2J = 0$ cm^{-1}).

In (**1**), the co-ordination units are both square pyramidal and are linked by the acetate and phenolate ions. The acetate

Table 8. Atomic co-ordinates (× 10^4) for (3) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu(1)	1 426.1(7)	7 457.5(6)	7 185(1)
Cu(2)	2 473.8(7)	6 538.7(7)	8 520(1)
S(1)	1 505(2)	8 729(2)	7 325(3)
S(2)	1 108(2)	6 896(2)	4 628(3)
O(1)	2 283(3)	7 243(4)	6 888(8)
O(2)	1 594(3)	6 732(3)	8 957(7)
N(1)	523(4)	7 529(4)	7 741(8)
N(2)	2 499(4)	5 767(4)	10 240(9)
C(3)	1 172(5)	6 354(5)	9 827(9)
C(4)	589(5)	6 646(6)	10 116(9)
C(5)	146(5)	6 251(5)	10 989(10)
C(6)	301(5)	5 565(5)	11 609(10)
C(7)	1 328(5)	5 666(5)	10 435(10)
C(8)	892(5)	5 289(5)	11 344(10)
C(9)	−183(5)	5 137(6)	12 570(12)
C(10)	429(5)	7 405(5)	9 572(10)
C(11)	278(6)	8 271(6)	7 358(13)
C(12)	717(6)	8 861(6)	7 996(14)
C(13)	1 457(7)	9 033(7)	5 209(15)
C(14)	124(5)	6 984(6)	6 838(11)
C(15)	278(5)	6 966(6)	4 998(12)
C(16)	1 280(6)	5 967(6)	5 267(12)
S(3)	3 036(2)	5 757(2)	6 785(3)
S(4)	3 108(2)	7 287(2)	10 405(4)
C(17)	1 936(5)	5 297(5)	10 065(12)
C(18)	2 509(6)	6 128(6)	11 917(11)
C(19)	3 051(6)	6 657(7)	12 101(14)
C(20)	2 519(8)	7 955(8)	10 899(19)
C(21)	3 078(5)	5 315(6)	10 032(13)
C(22)	3 122(6)	5 021(6)	8 279(13)
C(23)	3 801(6)	6 167(8)	6 857(16)
Cl(1)	5 148(2)	4 048(2)	−2 337(3)
O(11)	−444(5)	8 946(7)	832(11)
O(12)	354(7)	9 451(13)	2 122(17)
O(13)	−7(12)	8 435(8)	2 980(19)
O(14)	−531(9)	9 404(8)	3 356(17)
Cl(2)	3 320(2)	8 812(2)	5 294(4)
O(21)	3 129(9)	8 130(7)	5 018(16)
O(22)	3 942(5)	8 953(7)	5 579(14)
O(23)	2 988(8)	9 070(13)	6 616(20)
O(24)	3 127(7)	9 224(9)	3 923(19)

Table 9. Selected bond distances (Å) and angles (°) in (3)

Cu(1)–Cu(2)	3.020(2)	Cu(1)–O(1)	1.906(8)
Cu(1)–O(2)	2.004(6)	Cu(1)–N(1)	2.006(8)
Cu(1)–S(1)	2.358(3)	Cu(1)–S(2)	2.428(3)
Cu(2)–O(1)	1.906(7)	Cu(2)–O(2)	1.964(7)
Cu(2)–N(2)	2.004(8)	Cu(2)–S(3)	2.365(3)
Cu(2)–S(4)	2.474(4)		
Cu(1)–O(1)–Cu(2)	104.8(3)	Cu(1)–O(2)–Cu(2)	99.1(2)
O(1)–Cu(1)–O(2)	77.6(3)	O(1)–Cu(1)–S(1)	98.3(2)
O(1)–Cu(1)–S(2)	93.9(2)	O(1)–Cu(1)–N(1)	170.1(3)
O(2)–Cu(1)–N(1)	92.8(3)	O(2)–Cu(1)–S(1)	128.2(2)
O(2)–Cu(1)–S(2)	112.6(2)	N(1)–Cu(1)–S(1)	89.6(2)
N(1)–Cu(1)–S(2)	87.5(2)	S(1)–Cu(1)–S(2)	119.1(1)
O(1)–Cu(2)–O(2)	78.5(3)	O(1)–Cu(2)–N(2)	169.1(3)
O(1)–Cu(2)–S(3)	96.1(2)	O(1)–Cu(2)–S(4)	99.7(2)
O(2)–Cu(2)–N(2)	91.3(3)	O(2)–Cu(2)–S(3)	136.0(2)
O(2)–Cu(2)–S(4)	108.2(2)	N(2)–Cu(2)–S(3)	88.6(2)
N(2)–Cu(2)–S(4)	87.1(2)	S(3)–Cu(2)–S(4)	115.7(1)

Table 10. Deviations (Å) of atoms from the least-squares planes in (3)

Plane 1: Cu(1), S(1), S(2), and O(2)

Cu(1) −0.001, S(1) 0.000, S(2) 0.000, O(2) 0.000, O(1) 1.859, N(1) −2.004

Plane 2: Cu(2), S(3), S(4), and O(2)

Cu(2) −0.025, S(3) 0.010, S(4) 0.006, O(2) 0.010, O(1) −1.878, N(2) 1.976

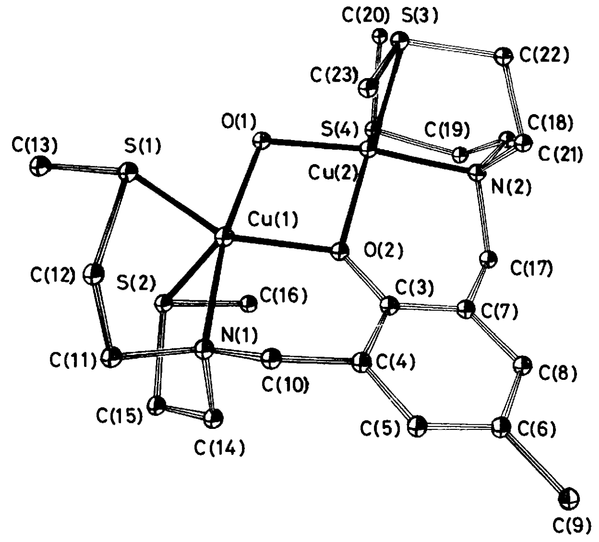
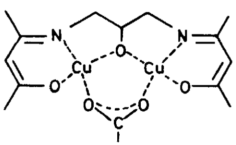


Figure 3. Perspective drawing of $[Cu_2(L^2)(OH)]^{2+}$

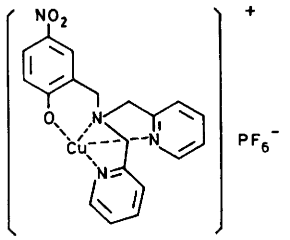
oxygens each occupy a vertex of the respective basal planes and the phenolate oxygen occupies the apex of one square pyramid and the vertex of the basal plane of the other. In this case, overlapping between the phenolate oxygen 2*p* orbital and the magnetic orbital of Cu(2) is also negligible. Therefore, superexchange *via* the phenolate oxygen is also negligible, and the antiferromagnetism observed for (1) due to a superexchange interaction through the acetate bridge. The value ($-2J = 80$ cm^{-1}) seems to be reasonable because (*i*) $-2J = 330$ cm^{-1} for copper(II) acetate in which four acetate bridges are present, and (*ii*) $-2J = 105$ cm^{-1} for binuclear copper(II) complexes with two acetate bridges.[26]

In contrast to the low antiferromagnetism of (1) and (2) a large $-2J$ value was observed for (3) ($-2J = 675$ cm^{-1}). In the case of (3), each unpaired electron is localized in the copper d_{z^2} orbital, which mainly spreads along the trigonal axis of the trigonal bipyramid. Since the two trigonal axes interact at the hydroxide oxygen, a substantial magnetic coupling is feasible through this pathway (this corresponds to the case of short σ-bonding pathway). This situation is very similar to those in $[(tren)Cu(OH)Cu(tren)]X_3$ [tren = tris(2-aminoethyl)amine, $-2J = 700$ cm^{-1} for X = PF_6; $-2J = 720$ cm^{-1} for X = ClO_4].[27,28] On the other hand, the phenolate oxygen occupies a vertex of each trigonal plane of both copper ions, hence the antiferromagnetic interaction *via* the phenolate must be negligible. The large antiferromagnetism observed for (3) should therefore arise from the superexchange interaction through the bridging hydroxide ion. The Cu(1)–O(1)–Cu(2) angle is 104.8(3)°, compatible with Hodgson's rule.[29]

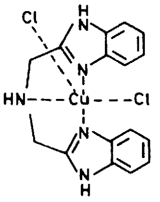
Catalytic Activity of Five-co-ordinate Complexes.—The catalytic activities of (1), (2), and (3) for the O_2 oxidation of



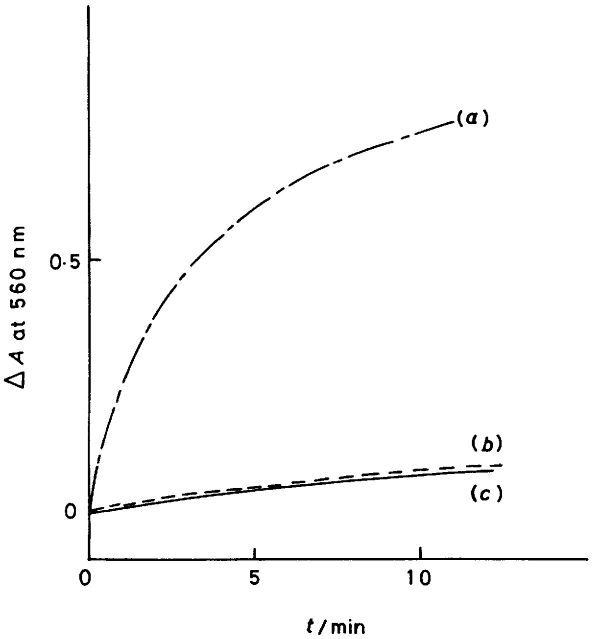
(4)



(5)



(6)



gure 4. Increase of absorbance at 560 nm (in 1 mm cell) in the reaction ixtures of tmpd and (*a*) $[Cu_2(L^1)(CH_3CO_2)][PF_6]_2$ (**1**), (*b*) complex), and (*c*) complex (**5**)

npd [equation (ii)] were determined and compared with those

$$\text{tmpd} \xrightarrow[Cu^{2+}]{O_2} \text{tmpd}^+ \qquad \text{(ii)}$$

f complexes (**4**), (**5**), and (**6**), where (**5**) and (**6**) are mononuclear ɔecies with co-ordination entities similar to (**1**) and (**2**), ɛspectively, and (**4**) is a binuclear complex resembling (**1**) in the ridging system but differing in the co-ordination geometry.

The reaction was run at 288 K in the presence of a copper(II) ɔmplex and tmpd in methanol–dimethylformamide (7:1, v/v) ith an initial [tmpd]:$[Cu^{2+}]$ molar ratio of 10:1 ($[Cu^{2+}]$ = .5 × 10^{-4} mol dm^{-3}). The catalytic activity was evaluated by ıeasuring the increase of the absorbance at 560 nm (due to npd$^+$ formed) of the reaction mixture.[16]

The mononuclear complexes (**5**) and (**6**) exhibited little ɛtivity for the reaction. Catalytic activities of the binuclear ɔmplexes (**1**)—(**3**) were very high, as shown in Figure 4 [order f activity: (**3**) > (**2**) ~ (**1**)]. However, complex (**4**), though inuclear, showed little activity. According to the crystal-structure determination,[14] the co-ordination geometries of (**4**) are square planar and both planes are coplanar. The Cu–Cu distance of (**1**) (3.549 Å) is very close to that of (**4**) (3.502 Å),[14] and thus the high catalytic activity of (**1**) is likely to be closely related to the five-co-ordinate structure.

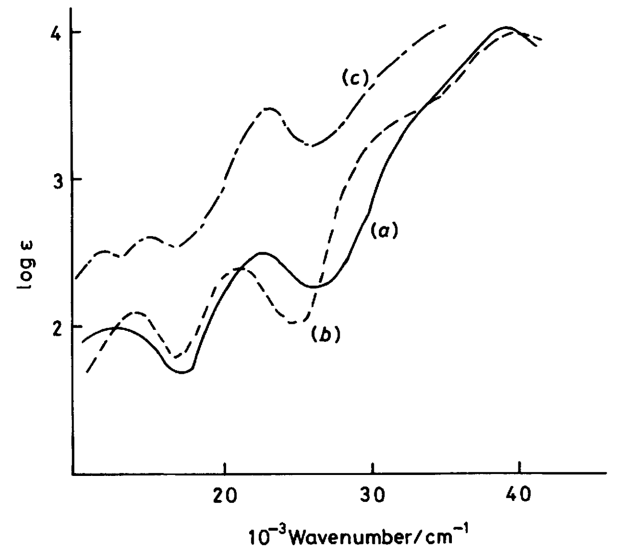
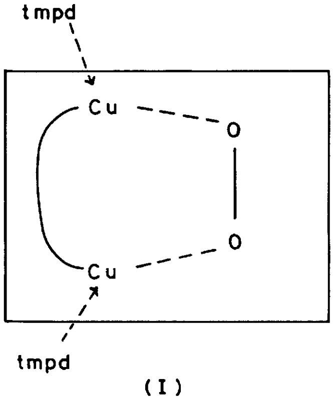


Figure 5. Absorption spectra of (*a*) $[Cu_2(L^1)(CH_3CO_2)][PF_6]_2$ (**1**), (*b*) $[Cu_2(L^1)Cl_2]ClO_4$ (**2**), and (*c*) $[Cu_2(L^2)(OH)][ClO_4]_2$ (**3**) in MeCN at 288 K

We previously reported that a number of planar binuclear copper(II) complexes exhibit high catalytic activities for the O_2 oxidation of tmpd compared with those of planar mononuclear complexes,[16] and concluded that (*i*) two electrons are transferred from tmpd to O_2 *via* the formation of an intermediate complex (**I**) as shown below, and (*ii*) the Cu–Cu distance must be in the range 3.0—3.1 Å for the facile formation of such an intermediate.[16c] Thus the low activity of (**4**) should be due to its long Cu–Cu distance.



(I)

According to Suzuki *et al.*[30] the Co–Co distance in $[Co_2(L^1)(C_6H_5CO_2)(O_2)]^{2+}$ is 3.15 Å. This implies that the binucleating ligand HL^1 allows the metal–metal distance to vary at least in the range 3.1—3.5 Å for complexes with carboxylate and phenolate bridges.

Co-ordination to an apical position of square-planar copper(II) complexes is very weak. However, a further co-ordination is likely to occur readily in five-co-ordinate complexes with tripodal ligands; in fact many six-co-ordinate copper(II) complexes have been obtained by the use of tripodal ligands.[31,32] Such a tendency to increase the co-ordination number must be preferable for the formation of the intermediate (**I**). Thus the high catalytic activities observed for (**1**) and (**2**) should originate from the elasticity of the Cu–Cu distance and the versatility of their co-ordination modes, as described above. These results indicate that the five-co-ordinate binuclear complexes used in this study are good models for Type III copper because the reaction (ii) is believed to be one of the model reactions for laccase.[16a]

Absorption Spectra.—The absorption spectra of complexes (**1**)—(**3**) (in acetonitrile) are shown in Figure 5. The band observed in the range 14×10^3—16×10^3 cm^{-1} is due to the *d*–*d* transitions. In the case of (**3**) the band is split (two bands were also observed in the reflectance spectrum), in accordance with its trigonal bipyramidal structure.[31,33] A band of high intensity was observed at 21×10^3—24×10^3 cm^{-1} for each complex [13] and may be assigned to charge transfer from the phenolate [13,34] or hydroxide groups [35] to the copper(II) ions.

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