Contribution from the Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia,
and Division of Applied Organic Chemistry, CSIRO, Lorimer Street, Fishermans Bend, Victoria 3207, Australia

Exogenous Bridging and Nonbridging in Copper(II) Complexes of a Binucleating 2,6-Bis((*N*-methylpiperazino)methyl)-4-chlorophenolate Ligand. Crystal Structures and Magnetic Properties of Bis(μ-acetato), Dinitrito, and Bis(azido) Complexes. Possible Relevance to the Type 3 Depleted Laccase Active Site

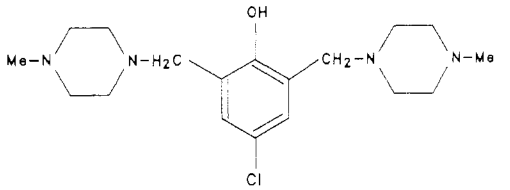
Karen Bertoncello,[†] Gary D. Fallon,[†] Jonathan H. Hodgkin,[‡] and Keith S. Murray*,[†]

Received May 12, 1988

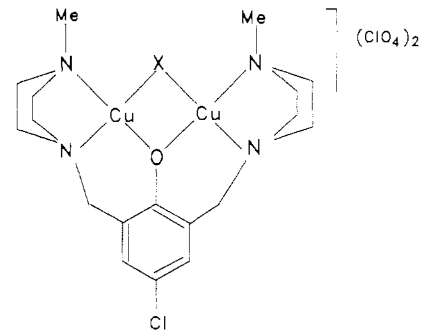
The syntheses and structural, spectral, magnetic, and redox properties of a range of binuclear copper(II) complexes of a binucleating ligand, LH, are described where LH = 2,6-bis((*N*-methylpiperazino)methyl)-4-chlorophenol. The following exogenous ligands were incorporated into the complexes: hydroxo, $[Cu_2L(OH)(H_2O)_2](ClO_4)_2\cdot H_2O$ (**1a**); pyrazolate, $[Cu_2L(pz)](ClO_4)_2$ (**1b**); acetate, $[Cu_2L(OAc)_2](ClO_4)\cdot 3H_2O$ (**1c**); nitrite, $[Cu_2L(NO_2)_2(H_2O)_2](ClO_4)\cdot H_2O$ (**1d**); azide, $[Cu_2L(N_3)_3][Cu_2L(N_3)_2](ClO_4)\cdot 2H_2O$ (**1e**). Complexes **1a–c** contain bridging exogenous groups while **1d** and **1e**, which, like **1c**, contain at least two exogenous ligands, do not. Thus **1d** and **1e** possess "open" μ-phenolate-only structures. The azide complex **1e** shows the novel feature of crystallizing into a form that contains two different binuclear molecules in the asymmetric unit, each molecule having different numbers of azide groups as indicated in the molecular formula above. Infinite "strings" of binuclear molecules are formed via weak copper–azide intermolecular contacts. **1a** also contains two structurally different, but stoichiometrically identical, molecules (see ref 6). Crystal structure data at 20 °C: **1c**, monoclinic space group $P2_1/n$ with $a = 20.127$ (7) Å, $b = 14.480$ (4) Å, $c = 11.263$ (2) Å, $\beta = 92.88$ (3)°, and $Z = 4$; **1d**, orthorhombic space group *Pbca* with $a = 20.654$ (1) Å, $b = 20.087$ (2) Å, $c = 13.873$ (3) Å, and $Z = 8$; **1e**, triclinic space group $P\bar{1}$ with $a = 91.250$ (4) Å, $b = 13.405$ (3) Å, $c = 12.873$ (3) Å, $\alpha = 121.77$ (1)°, $\beta = 98.88$ (1)°, $\gamma = 95.86$ (1)°, and $Z = 2$. **1c** contains two μ-acetate and one μ-phenolate bridging groups and thus provides another example of this rapidly growing class of compounds showing such a core unit. Like all of the other present complexes, it contains a distorted square-pyramidal geometry around each Cu. However, in contrast to **1a** (and presumably **1b**), which displays approximate coplanarity of the two basal planes, there is a large dihedral angle between the basal planes of **1c** (91.5°), **1d** (83.7°), and **1e** (83.6°, molecule 1; 71.4°, molecule 2). The μ-phenolate (endogenous) oxygen atom "hinges" these basal planes together in all of the complexes, and despite the lack of coplanarity of the Cu_{xy} planes in **1c–e**, it is still capable of providing a superexchange pathway leading to medium-strength antiferromagnetic exchange coupling. Correlations of this and of other geometric features with J values and with some features of the phenolate O $\rightarrow$ Cu(II) charge-transfer visible bands are described. Brief comments on possible relevance to recent findings on Cu–Cu biosites in the type 2 depleted (T2D) laccase enzyme are also included.

Introduction

As part of a wide study of the structure/magnetism/redox relations[1-5] in binuclear copper(II) complexes, we have employed a binucleating ligand, LH, obtained by a Mannich reaction between a para-substituted phenol, formaldehyde, and *N*-methylpiperazine.[6,7] Molecular models showed that simultaneous coordination of the phenol oxygen and the four piperazine nitrogen atoms to two Cu(II) ions, in the presence or absence of an exogenous bridging ligand, would be difficult in view of the sterically constrained ligand conformation. Nevertheless, a hydroxo-bridged complex, **1a**, was obtained and characterized by X-ray crystallographic, spectral and magnetic measurements.[1,6] **1a** was found to have one of the shortest Cu–Cu distances in μ-hydroxo complexes of this general type (viz. 2.87 Å). This and other structural features of the bridging moiety were generally compatible with the weak ferromagnetic coupling observed via variable-temperature susceptibility studies.[1,6] In attempting to insert other exogenous X groups, particularly those containing two or more atoms, we have obtained some unexpected and unusual results. With X = pyrazolate the expected μ-pyrazolate complex, **1b**, was obtained. However, in the case of X = acetate, a triply bridged (μ-phenoxo)bis(μ-acetato) complex $[Cu_2L(OAc)_2](ClO_4)\cdot 3H_2O$ (**1c**) was obtained. This contrasts with the more usual type of mono(μ-acetato)copper(II) derivatives obtained with other related binucleating ligand systems.[1,3] Interestingly, similar bis(μ-acetato)-bridged complexes of Fe(III)[8] and Mn(III)[9] have been reported since completion of the present syntheses, and this bridging unit has been proposed by Que et al.[10a] to be a thermodynamically favored core structure.[10b] Crystal structure data,



LH

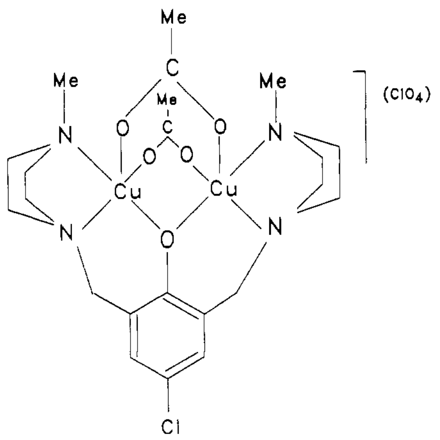


X = OH^- (**1a**)
X = pyrazolate (**1b**)

[†] Monash University.
[‡] CSIRO.

(1) Murray, K. S. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine: New York, 1986; Vol. 2, p 161.
(2) Mazurek, W.; Berry, K. J.; Murray, K. S.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1982**, *21*, 3071.
(3) Mazurek, W.; Kennedy, B. J.; Murray, K. S.; O'Connor, M. J.; Rodgers, M. J.; Snow, M. R.; Wedd, A. G.; Zwack, P. R. *Inorg. Chem.* **1985**, *24*, 3258.
(4) Mazurek, W.; Bond, A. M.; Murray, K. S.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1985**, *24*, 2484.
(5) Iliopoulos, P.; Fallon, G. D.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **1986**, 437.
(6) Fallon, G. D.; Murray, K. S.; Spethmann, B.; Yandell, J. K.; Hodgkin, J. H.; Loft, B. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1561.
(7) Hodgkin, J. H. *Aust. J. Chem.* **1984**, *37*, 2371.
(8) Murch, B. P.; Bradley, F. C.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5027.
(9) (a) Diril, H.; Chang, H.-R.; Zhang, X.; Larsen, S. K.; Potenza, J. A.; Pierpont, C. G.; Schugar, H. J.; Isied, S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6207. (b) Buchanan, R. B.; Oberhausen, K. J.; Richardson, J. F. *Inorg. Chem.* **1988**, *27*, 971.
(10) (a) Borovik, A. S.; Que, L., Jr.; Papaefthymiou, V.; Münck, E.; Taylor, L. F.; Anderson, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 1986. (b) A Bis(μ-benzoato)-bridged Cu(II) complex of a type related to **1c** has just been reported: Nishida, Y.; Tokii, T.; Mori, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 675.

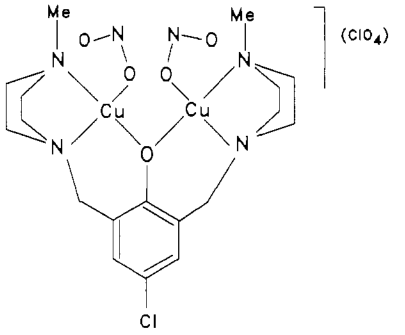
0020-1669/88/1327-4750$01.50/0



1c

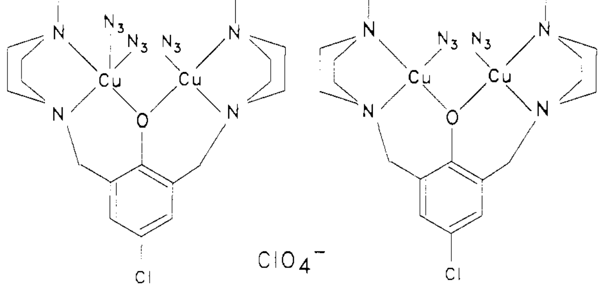
described below, show that the acetate groups in **1c** are not symmetrically bridging but, rather, adopt a semibridging mode.

Use of nitrite, NO_2^-, as a potential exogenous bridge also led to the formation of a dinitrite complex, **1d**, but in this case X-ray crystallography shows that there is no exogenous bridging between the two Cu(II) ions. This lack of nitrite bridging contrasts with the anticipated mono(μ-nitrito-*O*,*N*) bridging recently reported by Reed et al. in a related system.[11] Complex **1d** provides another addition to the small group of binucleated compounds that are now known to possess only an endogenous phenolate (or alcoholate) bridging oxygen atom.[12-16] Suzuki et al.[12] and Urbach et al.[16] have recently used the term "open" structure to describe this bridging mode and have attributed it to a less strained, more relaxed conformation of the binucleating ligand.



1d

Attempts to incorporate azide as the X group led to a number of products being formed, depending upon the precise reaction conditions used. Structural characterization of one such product, $[Cu_2L(N_3)_3][Cu_2L(N_3)_2](ClO_4)\cdot 2H_2O$ (**1e**), showed, as in the nitrite case, a lack of exogenous μ-azido bridging. Surprisingly, the crystals contain two different binuclear entities in the asymmetric unit, one containing three azides (per Cu_2), the other containing two, with a perchlorate ion shared between them. Once more, the lack of 1,1- or 1,3-(μ-azido) bridging contrasts with that recently observed in other binuclear μ-azido systems.[17-20] However, the present observations may well be relevant to a recent report by Spira-Solomon and Solomon, who have ascribed spectroscopic differences between azidohemocyanin (or azidotyrosinase) and azido T2D-laccase (type 2 depleted laccase) to the presence, or absence, of exogenous azido bridging.[21] Comments on the possible relevance to the type 3 protein sites, together with full preparative, structural, and magnetic characterization of complexes **1a–e** are now described.



1e

Experimental Section

Synthesis of Complexes. Compound 1a was synthesized as described previously by reacting an ethanolic solution of copper(II) perchlorate hexahydrate and ligand, LH, in the presence of sodium hydroxide.[1,6]

Compound 1b was obtained by mixing methanolic solutions of **1a** (0.65 g, 0.87 mmol) and pyrazole (0.062 g, 0.87 mmol). The product, obtained as green crystals on evaporation of the solution, was recrystallized from methanol. Yield: 0.31 g, 48%. Anal. Calcd for $C_{21}H_{31}Cl_3Cu_2N_6O_9$: C, 33.85; H, 4.16; N, 11.28; Cl, 14.3; Cu, 17.0. Found: C, 33.73; H, 4.19; N, 11.58; Cl, 14.4; Cu, 16.9.

Compound 1c. Copper(II) acetate monohydrate (0.4 g, 2 mmol) was dissolved in warm aqueous ethanol (75 mL). Addition of ethanolic solutions of the ligand, LH (0.35 g, 1 mmol), and of sodium perchlorate (0.7 g, 5 mmol) led to the formation of a dark green solution. When concentrated, this solution yielded needle-shaped green crystals, which were recrystallized from aqueous ethanol. Yield: 0.57 g, 76%. Anal. Calcd for a monohydrate $C_{22}H_{36}Cl_2Cu_2N_4O_{10}$: C, 36.98; H, 5.04; N, 7.84; Cl, 9.9. Found: C, 37.01; H, 5.03; N, 7.64; Cl, 10.0.

Compound 1d. To an ethanolic solution containing ligand, LH (0.05 g, 0.144 mol), and copper (II) perchlorate hexahydrate (0.107 g, 0.288 mmol) was added a solution of sodium nitrite (0.023 g, 0.333 mmol) dissolved in ethanol. The resulting green powder was recrystallized from aqueous ethanol to yield green-black crystals of **1d**. Yield: 0.05 g, 53%. Anal. Calcd for $C_{18}H_{34}Cl_2Cu_2N_6O_{12}$: C, 29.84; H, 4.72; N, 11.60; Cl, 9.8; Cu, 17.5. Found: C, 29.78; H, 4.98; N, 11.47; Cl, 10.2; Cu, 18.0.

Compound 1e. Method a. Sodium azide (0.02 g, 0.3 mmol) in water (2 mL) was added to a solution of **1a** (0.1 g, 0.134 mmol) in methanol (20 mL). After addition of 2-propanol (50 mL) and slow evaporation for several days, dark green-black crystals were obtained. They had the formula $[\{Cu_2L(N_3)_2\}\{Cu_2L(N_3)_3\}(ClO_4)\cdot 2H_2O]$ as determined by microanalysis and by the X-ray crystal structure determination. Yield: 0.013 g, 15%. Anal. Calcd for $C_{36}H_{60}Cl_3Cu_4N_{23}O_8$: C, 33.17; H, 4.63; N, 24.71; Cl, 8.2. Found: C, 33.90; H, 4.20; N, 25.0; Cl, 8.3. It was found that if the product was precipitated from methanol, without addition of 2-propanol, and then recrystallized from methanol/chloroform, crystals of $[Cu_2L(N_3)_2]ClO_4$ only were obtained. Anal. Calcd for $C_{18}H_{28}Cl_2CuN_{10}O_5$: C, 32.63; H, 4.23; N, 21.15. Found: C, 32.81; H, 4.86; N, 21.43.

Method b. An aqueous solution of sodium azide (0.022 g, 0.34 mmol) was added to an aqueous ethanolic solution containing copper(II) perchlorate hexahydrate (0.17 g, 0.29 mmol) and ligand, LH (0.051g, 0.145 mmol), whereupon a brown solid of uncertain composition was deposited. After filtration and slow evaporation of the solution, dark green-black oblong-shaped crystals of $[Cu_2L(N_3)_2](ClO_4)$ were formed as judged by the similarity of the IR spectrum to that of the analyzed sample, described above.

A number of other reactions of sodium azide with mixtures of the ligand and copper(II) salts, such as $Cu(NO_3)_2\cdot 3H_2O$ or $Cu(ClO_4)_2\cdot 6H_2O$, were attempted in the presence or absence of bases such as LiOH or KOH. Solid azido copper(II) complexes could be obtained, but because

---

(11) McKee, V.; Zvagulis, M.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 2914.

(12) Suzuki, M.; Kanatomi, H.; Demura, Y.; Murase, I. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1003.

(13) Nishida, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 2633.

(14) Nishida, Y.; Shimo, H.; Maehara, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1985**, 1945.

(15) McKee, V.; Smith, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1465.

(16) Maloney, J. J.; Glogowski, M.; Rohrbach, D. F.; Urbach, F. L. *Inorg. Chim. Acta* **1987**, *127*, L33.

(17) (a) McKee, V.; Dagdigian, J. V.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 7000. (b) McKee, V.; Zvagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765.

(18) (a) Boillot, M.-L.; Kahn, O.; O'Connor, C. J.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 178. (b) Mallah, T.; Boillot, M.-L.; Kahn, O.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 3058.

(19) Sorrell, T. N.; O'Connor, C. J.; Anderson, O. P.; Riebenspies, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 4199.

(20) Karlin, K. D.; Cohen, B. I.; Hayes, J. C.; Farooq, A.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 147.

(21) Spira-Solomon, D. J.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 6421.

Table I. Crystallographic Data

	1c	1d	1e
formula	$Cu_2C_{22}H_{34}N_4Cl_2O_9 \cdot 3H_2O$	$Cu_2C_{18}H_{32}N_6Cl_2O_{11} \cdot H_2O$	$Cu_4C_{36}H_{56}N_{23}Cl_3O_6 \cdot 2H_2O$
fw	750.7	724.5	1303.7
cryst syst	monoclinic	orthorhombic	triclinic
cryst habit	acicular	equant	acicular
cryst size, mm	0.21 × 0.10 × 0.04	0.11 × 0.11 × 0.19	0.27 × 0.11 × 0.06
space group	$P2_1/n$	*Pbca*	$P\bar{1}$ (by successful refinement)
syst abs	$h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$	$0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h \neq 2n$	
temp, °C	20	20	20
a, Å	20.127 (7)	20.654 (1)	19.250 (4)
b, Å	14.480 (4)	20.087 (2)	13.405 (3)
c, Å	11.263 (2)	13.873 (3)	12.873 (3)
α, deg	90	90	121.77 (1)
β, deg	92.88 (3)	90	98.88 (1)
γ, deg	90	90	95.86 (1)
Z	4	8	2
V, Å^3	3278	5756	2723
D_{calcd}, g cm^{-3}	1.52	1.67	1.59
D_{measd}, g cm^{-3}	1.52 (1)	1.67 (1)	1.59 (1)
radiation; λ, Å	Cu Kα; 1.5418[a]	Mo Kα; 0.7107	Mo Kα; 0.7107
μ, cm^{-1}	35.9[b]	17.3	17.3
transmissn factors: max, min[c]	0.879, 0.586	0.852, 0.823	0.900, 0.815
data colln instrum	Philips PW1100	Philips PW1100	Philips PW1100
scan speed, deg s^{-1}	0.04	0.05	0.05
scan width, deg	$\pm(0.75 + 0.2 \tan \theta)$	$\pm(0.75 + 0.3 \tan \theta)$	$\pm(0.65 + 0.2 \tan \theta)$
scan method	ω	ω	ω
colln range, deg	$6 < 2\theta < 120$	$6 < 2\theta < 60$	$6 < 2\theta < 60$
data collcd	$\pm h,k,l$	h,k,l	$\pm h,\pm k,l$
total no. of unique data	4869	8374	15865
no. of data used for refinement ($I \geq 3\sigma(I)$)[d]	3031	1324	4011
no. of params refined	240	211	372
R	0.072	0.068	0.066
R_w[c,d]	0.076	0.058	0.060
largest peak, e/Å^3	0.96	0.60	0.76

[a] Graphite monochromator. [b] Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. [c] $R_w = \sum w^{1/2}(||F_o| - |F_c||)/\sum w^{1/2}|F_o|$, where $w = [\sigma^2(F_o)]^{-1}$. [d] Sheldrick, G. M. "Shelx-76 Program System"; University of Cambridge: Cambridge, England, 1976.

of their general lability, it was usually not possible to recrystallize these various azido complexes without conversion to another species as judged by IR spectral changes.

Physical Measurements. Spectral, magnetic, and electrochemical measurements were made as described previously.[2-4]

X-ray Crystallography and Structure Solutions. Data were collected at 20 °C on a Philips PW1100 diffractometer. Full details of the diffractometry and computational procedures employed are available elsewhere.[22] Data collection parameters are summarized in Table I. The structures were solved by conventional Patterson and Fourier methods (**1c**) or by direct methods (**1d** and **1e** (the four Cu atoms)). Full-matrix least-squares refinement employing thermal parameters as described below for **1c–e** reduced R and R_w to the values given in Table I: anisotropic thermal parameters for Cu, Cl, and O of the ClO_4 ion and H_2O molecules and isotropic thermal parameters for all other non-hydrogen atoms with a single isotropic thermal parameter for hydrogen (hydrogen is geometrically idealized positions: C–H = 0.97 Å). In **1e** the solvated water molecules were disordered over several sites, the three sites with maximum density being chosen for refinement, and their occupancies were adjusted so that there were two molecules of water per asymmetric unit.

Final atomic parameters are given in Tables II–IV. Hydrogen atom coordinates, isotropic and anisotropic thermal parameters, all bond lengths and angles, and observed and calculated structure factors are given in the supplementary material (Tables S1–S15).

Results and Discussion

Synthesis and Characterization. Complex **1a** was obtained by reaction of copper(II) perchlorate and LH in a 2:1 mole ratio in the presence of sodium hydroxide.[1,6] The μ-hydroxo group in **1a** could be replaced by other exogenous groups such as pyrazolate or azide to form complexes **1b** and **1e**, respectively. The dinitrito complex **1d** was prepared in essentially the same way except that the μ-hydroxo precursor was prepared in situ prior to addition of sodium nitrite. Complex **1c** was obtained by use of copper acetate with subsequent addition of sodium perchlorate as the source of the counteranion. The azide system proved to be a rather labile and complex one. It can be seen in the Experimental Section that minor changes in reaction conditions can lead to the isolation of different crystalline species. Thus, compound **1e** was found from X-ray crystallography and microanalytical data to contain two structurally different binuclear molecules with one ClO_4^- ion shared between them in order to balance the charge, i.e. $\{Cu_2L(N_3)_3\}\{Cu_2L(N_3)_2\}(ClO_4)$. This particular phase was obtained by slow crystallization from a methanol/2-propanol solution. More rapid crystallization, in the absence of 2-propanol, yielded "half" of this structure, viz. $[Cu_2L(N_3)_2](ClO_4)$, which, in view of the similarity of its IR spectrum to that of **1e**, presumably has the same structural features. Chaudhuri and Wieghardt have recently observed a somewhat related set of products in (triazacyclononane)copper(II) azide species.[23]

Spectroscopic and analytical methods were of some use in the structural elucidation of the present complexes, but X-ray crystallographic determinations were required in order to show the full details. The acetato complex, **1c**, showed strong $\nu(CO_2)$ bands[24] at 1580 and 1460 cm^{-1}. IR bands due to the nitrite groups were observed for **1d** at 1400 and 1220 cm^{-1}, which, by comparison to recently published structural correlations, would suggest a μ-N,O bridging or a monodentate O-bonded mode for the nitrite groups.[25] The latter situation is shown (below) to be correct. Neither the symmetric nor asymmetric N_3 stretching frequencies in the spectra of the various azido products were of much diagnostic value in deciphering the mode of azido coordination.

The visible spectral bands of aqueous solutions of the complexes are given in Table V. Band A is the d–d envelope and band B

---

(22) Fallon, G. D.; Gatehouse, B. M. *J. Solid State Chem.* **1980**, *34*, 193.

(23) Chaudhuri, P.; Oder, K.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2818.

(24) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(25) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55.

Table II. Atomic Parameters for $[Cu_2L(OAc)_2]ClO_4\cdot3H_2O$ (**1c**) with Esd Values in Parentheses

atom	x	y	z
Cu(1)	0.57233 (6)	0.34675 (8)	0.07122 (12)
Cu(2)	0.49895 (6)	0.15793 (9)	0.15326 (12)
Cl(1)	0.3571 (2)	0.2276 (3)	−0.4271 (3)
Cl(2)[a]	0.7595 (2)	0.1001 (3)	0.7791 (4)
O(6)[a]	0.8193 (5)	0.1290 (9)	0.7786 (16)
O(7)[a]	0.7267 (7)	0.1291 (9)	0.8658 (13)
O(8)[a]	0.7603 (9)	0.0109 (7)	0.7790 (22)
O(9)[a]	0.728 (1)	0.127 (2)	0.681 (1)
O(10)[b]	0.198 (1)	0.153 (2)	0.890 (4)
O(11)[b]	0.590 (2)	0.181 (2)	0.506 (2)
O(12)[b]	0.159 (1)	0.214 (4)	0.990 (3)
C(1)	0.4726 (4)	0.2469 (6)	−0.0737 (8)
C(2)	0.4043 (4)	0.2241 (6)	−0.0780 (8)
C(3)	0.3699 (5)	0.2184 (6)	−0.1862 (8)
C(4)	0.4014 (5)	0.2343 (7)	−0.2929 (9)
C(5)	0.4690 (5)	0.2549 (6)	−0.2878 (9)
C(6)	0.5050 (4)	0.2591 (6)	−0.1802 (8)
C(7)	0.5798 (4)	0.2736 (6)	−0.1760 (9)
C(8)	0.5803 (5)	0.4418 (6)	−0.1412 (8)
C(9)	0.5986 (5)	0.5109 (7)	−0.0400 (9)
C(10)	0.6769 (4)	0.3514 (7)	−0.0806 (9)
C(11)	0.6944 (5)	0.4196 (7)	0.0161 (9)
C(12)	0.6456 (6)	0.5210 (8)	0.1611 (10)
C(13)	0.3675 (5)	0.2149 (7)	0.0338 (8)
C(14)	0.3717 (5)	0.1464 (7)	0.2366 (9)
C(15)	0.4145 (5)	0.0852 (8)	0.3187 (10)
C(16)	0.3942 (5)	0.0488 (7)	0.0672 (9)
C(17)	0.4374 (5)	−0.0114 (8)	0.1522 (9)
C(18)	0.5177 (6)	−0.0049 (9)	0.3260 (11)
C(19)	0.6412 (5)	0.1628 (7)	0.1543 (9)
C(20)	0.7055 (6)	0.1107 (9)	0.1734 (12)
C(21)	0.5049 (4)	0.3463 (7)	0.2914 (9)
C(22)	0.4810 (6)	0.4001 (8)	0.3944 (11)
N(1)	0.6031 (3)	0.3499 (5)	−0.0973 (6)
N(2)	0.6320 (4)	0.4604 (5)	0.0588 (7)
N(3)	0.3996 (3)	0.1450 (5)	0.1173 (6)
N(4)	0.4685 (4)	0.0465 (5)	0.2466 (7)
O(1)	0.5061 (3)	0.2515 (4)	0.0310 (5)
O(2)	0.5895 (3)	0.1137 (4)	0.1474 (6)
O(3)	0.6434 (3)	0.2493 (4)	0.1504 (6)
O(4)	0.5025 (3)	0.2591 (5)	0.2955 (6)
O(5)	0.5286 (3)	0.3927 (4)	0.2072 (6)

[a] ClO_4^- atoms. [b] H_2O atoms.

Table III. Atomic Parameters for $[Cu_2L(NO_2)_2(H_2O)_2]ClO_4\cdot H_2O$ (**1d**) with Esd Values in Parentheses

atom	x	y	z
Cu(1)	0.3724 (1)	0.0313 (1)	0.3508 (2)
Cu(2)	0.4388 (1)	0.1161 (1)	0.1444 (2)
Cl(1)	0.6608 (3)	−0.1319 (2)	0.2604 (4)
Cl(2)[a]	0.8003 (3)	−0.2444 (4)	0.4055 (6)
O(8)[a]	0.7486 (9)	−0.2667 (13)	0.3670 (23)
O(9)[a]	0.8487 (12)	−0.2549 (13)	0.3486 (23)
O(10)[a]	0.8110 (19)	−0.2744 (12)	0.4860 (15)
O(11)[a]	0.7959 (11)	−0.1814 (7)	0.4216 (17)
C(1)	0.4904 (9)	0.0079 (9)	0.2486 (16)
C(2)	0.5523 (8)	0.0336 (9)	0.2498 (13)
C(3)	0.6051 (9)	−0.0090 (9)	0.2512 (15)
C(4)	0.5951 (9)	−0.0781 (9)	0.2509 (16)
C(5)	0.5342 (9)	−0.1037 (9)	0.2498 (14)
C(6)	0.4806 (8)	−0.0621 (8)	0.2487 (14)
C(7)	0.4117 (8)	−0.0902 (9)	0.2414 (15)
C(8)	0.4000 (9)	−0.0936 (9)	0.4211 (13)
C(9)	0.3649 (9)	−0.0570 (9)	0.5008 (13)
C(10)	0.3044 (8)	−0.0874 (9)	0.3183 (12)
C(11)	0.2701 (9)	−0.0523 (10)	0.4030 (14)
C(12)	0.2859 (9)	0.0335 (11)	0.5299 (14)
C(13)	0.5630 (9)	0.1080 (8)	0.2556 (13)
C(14)	0.5643 (9)	0.1246 (9)	0.0770 (12)
C(15)	0.5206 (10)	0.1480 (11)	−0.0031 (15)
C(16)	0.5288 (10)	0.2154 (9)	0.1799 (14)
C(17)	0.4902 (8)	0.2417 (10)	0.0943 (14)
C(18)	0.4170 (9)	0.2020 (10)	−0.0317 (14)
O(1)	0.4383 (6)	0.0491 (5)	0.2486 (9)
O(2)	0.2838 (6)	0.0645 (6)	0.2583 (11)
O(3)	0.3798 (6)	0.1953 (7)	0.2303 (10)
O(4)	0.3561 (7)	0.0823 (7)	0.0892 (10)
O(5)	0.4271 (8)	0.0213 (8)	0.0251 (11)
O(6)	0.3810 (6)	0.1241 (7)	0.4032 (10)
O(7)	0.4582 (8)	0.0722 (9)	0.4734 (12)
O(12)[b]	0.2292 (8)	0.1788 (9)	0.3394 (14)
N(1)	0.3746 (7)	−0.0682 (7)	0.3269 (10)
N(2)	0.3164 (7)	−0.0112 (8)	0.4577 (12)
N(3)	0.5320 (7)	0.1403 (7)	0.1707 (10)
N(4)	0.4642 (8)	0.1833 (8)	0.0398 (11)
N(5)	0.3693 (10)	0.0326 (10)	0.0335 (14)
N(6)	0.4320 (10)	0.1247 (10)	0.4618 (14)

[a] ClO_4^- atoms [b] Hydrated H_2O.

is the phenolato-to-Cu(II) charge-transfer band. The shoulders, C, are probably charge-transfer bands involving other ligand atoms. Interestingly, the intensity of band B is much lower in **1a** than it is in **1b**, **1d**, and **1e** and in bridged phenolate–Cu(II) species in general. This, as also noted recently by Urbach et al.[16] and Sorrell et al.[19] in related systems, is probably a result of the pyramidal geometry around the phenolate oxygen atom in **1a** giving rise to poor ligand–metal orbital overlap. The intensities for **1b** and **1d** are more normal and are in line with the trigonal-planar geometry around oxygen. If this interpretation is correct, the results for the acetate complex, **1c**, suggest that the bridging phenolate oxygen adopts the more strained pyramidal geometry in solution compared to that in the solid state, which is perhaps surprising.

The spectrum of the azide complex, **1e**, is of interest for comparison with the spectra of met-azide copper(II) proteins and with those of other binuclear (μ-phenolato)copper(II) azide derivatives. In recent studies of binuclear μ-1,1-azido complexes of their 2,6-bis((2-(2-pyridyl)ethyl)amine)-substituted phenol ligand system, Karlin et al.[18] have identified a phenolate-to-Cu(II) CT band at 460 nm (ϵ = 3300 M^{-1} cm^{-1}) and a $N_3^- \rightarrow$ Cu(II) CT band at 370 nm (ϵ = 2600 M^{-1} cm^{-1}). In nonbridged monomeric Cu(II) azido complexes they observed $N_3^- \rightarrow$ Cu(II) bands in positions closer to 400 nm, which, on comparison with other data, gives a general range of 360–405 nm for $N_3^- \rightarrow$ Cu(II) LMCT. The well-defined band B at 385 nm in the spectrum of **1e** must enclose the $N_3^- \rightarrow$ Cu(II) and phenolate-to-Cu(II) LMCT bands. Suzuki et al.[12] obtained a similar band for the azido complex of a tripodal ligand system rather similar to that used by Karlin et al.[20]

We had hoped to be able to unambiguously identify the spectral bands of terminal versus μ-1,1- or μ-1,3-bridged azide groups in model binuclear Cu(II) complexes in order to make comparisons with the spectra of the T2D laccase (terminal $N_3^- \rightarrow$ Cu(II) and met-hemocyanins (μ-1,3-$N_3^- \rightarrow$ Cu(II)) reported by Solomon et al.[21] However, the significant differences in λ_{max} positions observed for various met-azidohemocyanins[26] together with the ranges observed for model complexes make this difficult at the present stage of refinement. In the T2D laccase spectrum, for instance, a band at 455 nm has been assigned to $N_3^- \rightarrow$ Cu(II) CT compatible with an equatorial nonbridging N_3^- coordination mode.[21] This coordination mode is observed in crystal of **1e** (see Figure 4) and presumably persists in solution in which the band at 380 nm is observed. Interestingly, a band was also observed at 390 nm in the azido T2D laccase system but it could not be unambiguously identified.[21]

Description of Crystal Structures. The structure of **1a** has been described earlier.[1,6] Each Cu(II) ion is five-coordinate and square-pyramidal, the apical ligands being two water molecules coordinated on the same side of the binuclear unit to each copper ion (Figure 1). The most pertinent features of the bridging moiety includes a short Cu–Cu distance (2.87 Å), small bridging Cu–O–Cu angles close to 90°, and a pyramidally coordinated endogenous phenolate–oxygen bridging atom. Comparisons with other selected mono(μ-hydroxo)-bridged complexes have been given earlier,[6] and a more extensive list of μ-hydroxo structures

---

(26) See ref 20 and 21 for summaries of these differences.

Table IV. Atomic Parameters for $[(Cu_2L(N_3)_3)(Cu_2L(N_3)_2)]ClO_4 \cdot 2H_2O$ (**1e**) with Esd Values in Parentheses

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu(11)	0.2438 (1)	0.4262 (1)	0.5579 (1)	C(210)	0.4971 (6)	0.3950 (10)	0.1086 (10)
Cu(12)	0.2969 (1)	0.6735 (1)	0.5214 (1)	C(211)	0.5053 (7)	0.3591 (10)	−0.0210 (11)
Cu(21)	0.3958 (1)	0.1807 (1)	−0.0680 (1)	C(212)	0.4973 (8)	0.1826 (13)	−0.2291 (13)
Cu(22)	0.2195 (1)	0.2003 (1)	−0.0071 (1)	C(213)	0.2248 (6)	−0.0345 (11)	−0.0348 (12)
Cl(11)	−0.0421 (2)	0.7029 (3)	0.6357 (3)	C(214)	0.1193 (7)	−0.0149 (11)	−0.1499 (12)
Cl(21)	0.3908 (2)	0.0295 (4)	0.3679 (4)	C(215)	0.0812 (7)	0.0786 (12)	−0.1485 (13)
Cl(3)[a]	0.8678 (3)	0.2369 (6)	0.8894 (6)	C(216)	0.1360 (7)	0.0819 (11)	0.0716 (12)
O(3)[a]	0.8953 (7)	0.2130 (13)	0.9735 (13)	C(217)	0.0948 (7)	0.1700 (12)	0.0678 (12)
O(4)[a]	0.7968 (6)	0.2425 (15)	0.8798 (16)	C(218)	0.0837 (7)	0.2930 (12)	−0.0178 (14)
O(5)[a]	0.9039 (9)	0.3196 (23)	0.8865 (29)	N(11)	0.2188 (5)	0.5028 (8)	0.7264 (8)
O(6)[a]	0.8711 (18)	0.1464 (39)	0.7854 (22)	N(12)	0.2462 (5)	0.3060 (9)	0.6083 (10)
C(11)	0.1705 (6)	0.5996 (9)	0.5697 (10)	N(13)	0.2151 (4)	0.6565 (8)	0.3881 (8)
C(12)	0.1250 (6)	0.6081 (9)	0.4812 (10)	N(14)	0.3383 (5)	0.7721 (8)	0.4581 (9)
C(13)	0.0603 (6)	0.6416 (9)	0.5025 (10)	N(15)	0.2276 (5)	0.3108 (9)	0.3781 (10)
C(14)	0.0402 (6)	0.6641 (10)	0.6109 (11)	N(16)	0.2429 (5)	0.3303 (8)	0.3047 (9)
C(15)	0.0862 (6)	0.6571 (9)	0.7013 (11)	N(17)	0.2541 (5)	0.3405 (9)	0.2248 (10)
C(16)	0.1523 (6)	0.6273 (9)	0.6809 (10)	N(18)	0.3129 (6)	0.8187 (10)	0.7151 (10)
C(17)	0.2038 (6)	0.6247 (10)	0.7773 (10)	N(19)	0.3612 (5)	0.9020 (9)	0.7860 (9)
C(18)	0.1562 (7)	0.4120 (11)	0.7033 (13)	N(110)	0.4067 (5)	0.9848 (9)	0.8582 (10)
C(19)	0.1747 (6)	0.2885 (11)	0.6236 (12)	N(111)	0.3875 (5)	0.6067 (9)	0.5314 (10)
C(110)	0.2807 (6)	0.5007 (11)	0.8088 (12)	N(112)	0.3802 (5)	0.5406 (10)	0.5652 (10)
C(111)	0.2961 (6)	0.3736 (10)	0.7334 (11)	N(113)	0.3710 (6)	0.4774 (10)	0.6005 (11)
C(112)	0.2646 (8)	0.1912 (12)	0.5199 (14)	N(21)	0.4671 (5)	0.2864 (8)	0.1034 (8)
C(113)	0.1448 (6)	0.5793 (10)	0.3622 (10)	N(22)	0.4928 (5)	0.2248 (9)	−0.0995 (10)
C(114)	0.2447 (6)	0.6141 (10)	0.2757 (11)	N(23)	0.1749 (5)	0.0432 (8)	−0.0315 (9)
C(115)	0.3223 (6)	0.6810 (11)	0.3219 (11)	N(24)	0.1110 (5)	0.1927 (9)	−0.0259 (10)
C(116)	0.2128 (6)	0.7839 10)	0.4426 (11)	N(25)	0.3353 (5)	0.1456 (9)	−0.2245 (9)
C(117)	0.2894 (6)	0.8543 (11)	0.4782 (12)	N(26)	0.2740 (6)	0.1040 (8)	−0.2556 (9)
C(118)	0.4139 (7)	0.8365 (12)	0.5120 (13)	N(27)	0.2122 (6)	0.0640 (10)	−0.2914 (11)
C(21)	0.3338 (6)	0.1364 (10)	0.0921 (10)	N(28)	0.2402 (5)	0.3317 (8)	−0.0292 (9)
C(22)	0.2899 (6)	0.0354 (10)	0.0751 (11)	N(29)	0.2954 (5)	0.4002 (8)	0.0109 (9)
C(23)	0.3075 (7)	0.0036 (11)	0.1615 (12)	N(210)	0.3482 (6)	0.4702 (10)	0.0489 (10)
C(24)	0.3673 (7)	0.0689 (12)	0.2582 (12)	O(11)	0.2338 (4)	0.5667 (6)	0.5482 (6)
C(25)	0.4127 (7)	0.1692 (11)	0.2781 (12)	O(21)	0.3171 (3)	0.1676 (6)	0.0079 (6)
C(26)	0.3938 (6)	0.2010 (10)	0.1914 (11)	O(7)[b]	0.0130 (12)	0.4390 (20)	0.8324 (22)
C(27)	0.4402 (6)	0.3120 (10)	0.2126 (11)	O(8)[b]	0.9821 (13)	0.0875 (20)	0.5411 (24)
C(28)	0.5252 (7)	0.2154 (11)	0.0857 (12)	O(9)[b]	0.9484 (20)	−0.0101 (35)	0.5933 (37)
C(29)	0.5429 (7)	0.1868 (12)	−0.0377 (12)				

[a] ClO_4^- atoms. [b] H_2O atoms.

Table V. Visible Spectral Data

	λ, nm (ε, M^{-1} cm^{-1}/dimer)				
band	**1a**[a]	**1b**[b]	**1c**[b]	**1d**[a]	**1e**[a]
A	615 (376)	678 (511)	635 (213)	610 (442)	650 (578)
B	400 sh (570)	418 (1749)	408 (475)	400 sh (1986)	385 (5278)
C	350 sh (1208)	350 sh (3139)	350 sh (656)	340 sh (2787)	

[a] Solvent = methanol. [b] Solvent = water.

has just been published by Thompson et al.[27]

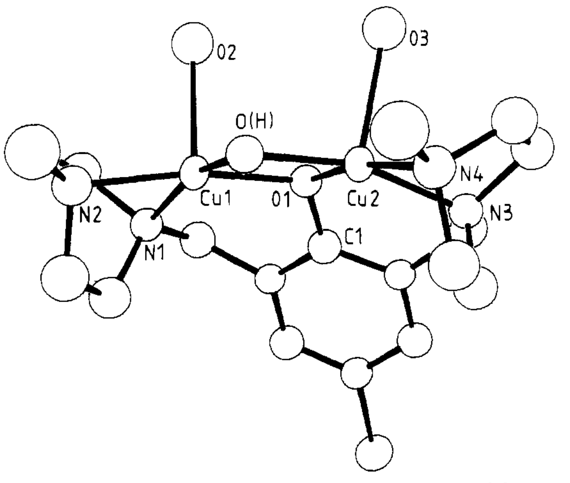


Figure 1. Molecular structure and numbering scheme of $[Cu_2L(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (**1a**). See ref 6 for details; only one of the crystallographically distinct binuclear molecules is shown, but the other is very similar. Thermal ellipsoids are drawn at the 50% probability level.

The molecular structure of the bis(acetato) complex, $[Cu_2L(CH_3CO_2)_2]ClO_4 \cdot 3H_2O$ (**1c**), is shown in Figure 2 with the relevant interatomic distances and angles being given in Tables VI and VII. In comparison to the rather symmetrical conformation of the ligand, L, found in **1a**, considerable twisting has occurred in **1c** such that the piperazine rings are now disposed approximately at right angles to each other while the phenolate ring is tilted such that the O(1) bridging atom now adopts the more usual pseudotrigonal bonding to C(1), Cu(1), and Cu(2) (solid angle = 359.8°). The five-donor atoms around each Cu, while not disposed symmetrically in either a square-pyramidal or trigonal-bipyramidal array, adopt a distorted square-pyramidal arrangement such that O(1)O(5)N(1)N(2) is the basal plane around Cu(1) while O(1)O(2)N(3)N(4) is that around Cu(2). In each case the metal is positioned out of this plane toward the apical oxygens O(3) and O(4), respectively. In contrast to complex **1a**, where the basal planes are approximately coplanar, in **1c** they are at a dihedral angle of 91.5° to each other. The bridging acetate groups are not equally bonded to each Cu. This leads, for instance, to Cu(1)–O(3) being an apical bond (2.169 (6) Å) while Cu(2)–O(2) is a basal plane bond (1.935 (7) Å). In other reported mono(μ-acetato) species, the Cu–O(acetate) bonds are usually equivalent.[28] Presumably the present semibridging mode is

---

(27) Thompson, L. K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1988**, *27*, 39.

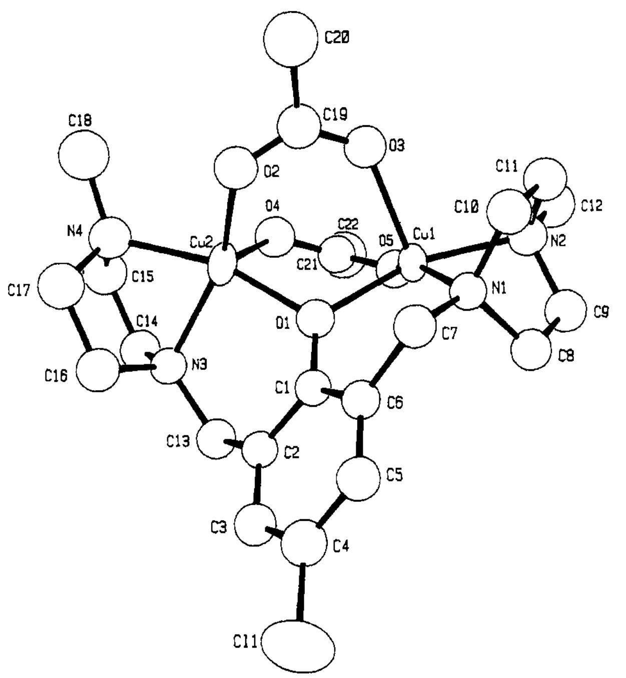


Figure 2. Molecular structure and numbering scheme of [$Cu_2L(OAc)_2$](ClO_4)·$3H_2O$ (**1c**). Thermal ellipsoids are drawn at the 50% probability level.

Table VI. Selected Bond Lengths (Å) about the Copper Atoms with Esd Values in Parentheses

	1a[a]	**1c**	**1d**	**1e** molecule 1	**1e** molecule 2
		Copper–Ligand			
Cu(1)–N(1)	1.980 (8)	2.026 (7)	2.03 (1)	2.02 (1)	2.03 (1)
Cu(1)–N(2)	2.033 (9)	2.046 (8)	2.07 (2)	2.03 (1)	2.06 (1)
Cu(1)–O(1)	2.001 (7)	1.955 (6)	2.00 (1)	1.98 (1)	1.97 (1)
Cu(2)–N(3)	1.980 (8)	2.029 (7)	2.02 (1)	2.04 (1)	2.03 (1)
Cu(2)–N(4)	2.033 (9)	2.037 (8)	2.05 (2)	2.04 (1)	2.05 (1)
Cu(2)–O(1)	2.081 (7)	1.942 (6)	1.98 (1)	1.98 (1)	1.98 (1)
Cu(1)–Cu(2)	2.872 (2)	3.263 (2)	3.603 (4)	3.655 (3)	3.605 (2)
		Copper–Exogenous Ligands			
Cu(1)–O(3)		2.169 (6)			
Cu(1)–O(5)		1.923 (6)			
Cu(2)–O(2)		1.935 (7)			
Cu(2)–O(4)		2.169 (7)			
Cu(1)–O(2)	2.323 (8)		2.33 (1)		
Cu(1)–O(6)			2.01 (1)		
Cu(2)–O(3)	2.323 (8)		2.33 (1)		
Cu(2)–O(4)			1.99 (1)		
Cu(1)–O(7)			2.59 (2)		
Cu(2)–O(5)			2.54 (2)		
Cu(11)–N(15)				1.94 (1)	
Cu(12)–N(18)				2.15 (1)	
Cu(12)–N(111)				2.06 (1)	
Cu(21)–N(25)					1.95 (1)
Cu(22)–N(28)					1.94 (1)
Cu(1)–O(H)	1.924 (6)				
Cu(2)–O(H)	1.924 (6)				
		Intermolecular Contacts			
Cu(11)–N(113)				2.37 (1)	
Cu(21)–N(110)					2.32 (1)
Cu(22)–N(17)					2.47 (1)

[a] Data given for one of the binuclear molecules in the asymmetric unit.[6]

primarily a result of the overall steric strain induced by the ligand, L, perhaps combined with the presence of two bridging acetate groups, rather than one. The Cu–Cu distance and Cu(1)O(1)-Cu(2) bridge angle in **1c**, given in Tables VI and VII, are of similar magnitude to the related dimensions found in Fe–Fe,[8] Mn–Mn[9] and Fe–Zn[10] analogues.

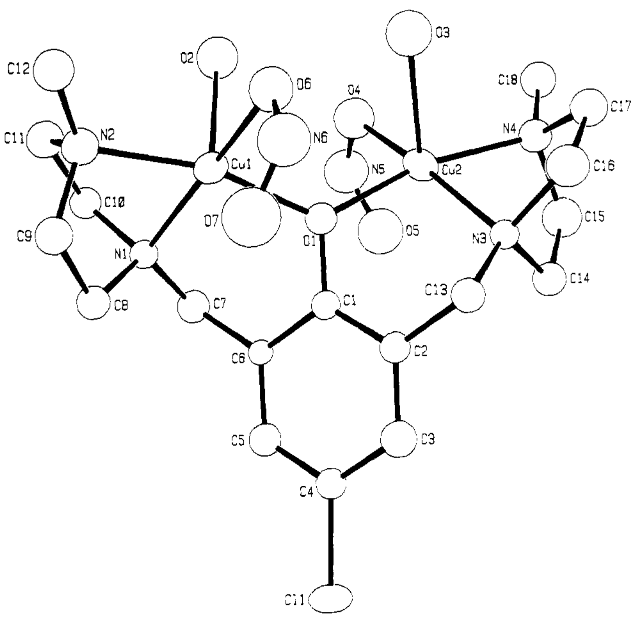


Figure 3. Molecular structure and numbering scheme of [$Cu_2L(NO_2)_2(H_2O)_2$](ClO_4)-H_2O (**1d**). Thermal ellipsoids are drawn at the 50% probability level.

The molecular structure of the nitrite complex, [$Cu_2L(NO_2)_2(H_2O)_2$]ClO_4·H_2O (**1d**), is shown in Figure 3 and the bond distances, bond angles, and basal plane data are tabulated in Tables VI–VIII. The most notable feature of the structure is that neither of the nitrite groups are bridging between the Cu ions but are bonded in an O-bonded, nonlinear arrangement to each Cu. In fact the Cu(1)–O(7) and Cu(2)–O(5) distances of ≈2.54 Å are indicative of weak chelation to the Cu ions, a situation previously observed in mononuclear metal nitrites.[25] The nitrite groups are disposed on opposite sides of the Cu(1)O(1)Cu(2) bridge. This is a result of the overall conformation of the ligand, L, which is generally similar to that adopted in **1c**. Again, we can see that the basal planes N(1)N(2)O(6)O(1) and N(3)N-(4)O(4)O(1) are not coplanar (dihedral angle 83.7°) and consequently, in contrast to the situation in **1a**, the Cu–OH_2 apical bonds are not parallel. The Cu–O(phenolate) bridging distances are longer than in **1c** and the Cu–Cu distance and Cu(1)O(1)-Cu(2) angles are correspondingly larger (Tables VI and VII). The geometry around O(1) is pseudotrigonal with a solid angle of 359.9°. In the only other reported structure of a μ-phenolate (only) complex, the Cu–Cu and Cu–O(phenolate) distances are even longer than in **1d**, but this is because the phenolate O atom is in an apical position in relation to each Cu.[14]

As indicated in the Introduction, the azide complex, **1e**, contains two different binuclear molecules in the asymmetric unit and these are shown in Figure 4. Bond distances, bond angles,and basal plane data are given in Tables VI–VIII. The conformations of the ligand, L, in each molecule are very similar and are also similar to those in **1c** and **1d**, leading to a dihedral angle of 83.6° between the adjacent basal planes such as N(13)N(14)N(111)O(11) and N(11)N((12)N(15)O(11). The molecule [$Cu_2L(N_3)_3$] possesses a square-pyramidal geometry around Cu(12), with N(18) as the apical azide donor atom, and a square-planar geometry around Cu(11). Molecule [$Cu_2L(N_3)_2$]$^+$ displays a distorted planar geometry around both Cu atoms. However, there are weak intra- and intermolecular interactions involving the "nonbonded" end of some of the coordinated azide groups. Thus, for instance, the contact Cu(11)–N(113) = 2.37 (1) Å is indicative of weak apical coordination to Cu(11) via a semibridging μ-1,3-azido group. Other intermolecular contact distances of less than 2.5 Å include Cu(21)–N(110) and Cu(22)–N(17) (Table VI), which are indicative of weak apical coordination to these, and, therefore, all Cu atoms in the unit cell. A crystal packing diagram (Figure 5) shows that these intermolecular contacts lead to infinite "strings" of the binuclear molecules in which there are no interactions

---

[28] There are many such examples known. Typical examples are found in ref 1, 13, and 19.

Table VII. Selected Bond Angles (deg) about the Bridging Atoms and Exogenous Ligands

	1a				**1e**	
	molecule 1	molecule 2	**1c**	**1d**	molecule 1	molecule 2
Cu(1)-O(1)-Cu(2)	91.7 (4)	91.4 (4)	113.7 (3)	130.1 (6)	134.5 (4)	132.3 (5)
sum of angles around O(1)	329.5	333.2	359.8	359.9	359.9	359.9
Cu(1)-O(H)-Cu(2)	96.5 (4)	96.4 (5)				
Cu(1)-O(6)-N(6)				107.3 (12)		
O(6)-N(6)-O(7)				115.7 (18)		
Cu(2)-O(4)-N(5)				108.2 (13)		
O(4)-N(5)-O(5)				114.1 (18)		
Cu(11)-N(15)-N16)					126.5 (8)	
N(15)-N(16)-N(17)					174.3 (9)	
Cu(12)-N(18)-N(19)					132.2 (11)	
N(18)-N(19)-N(110)					177.5 (14)	
Cu(12)-N(111)-N(112)					111.8 (9)	
N(111)-N(112)-N(113)					177.4 (13)	
Cu(21)-N(25)-N(26)						121.7 (11)
N(25)-N(26)-N(27)						176.3 (17)
Cu(22)-N(28)-N(29)						126.2 (11)
N(28)-N(29)-N(210)						177.4 (16)

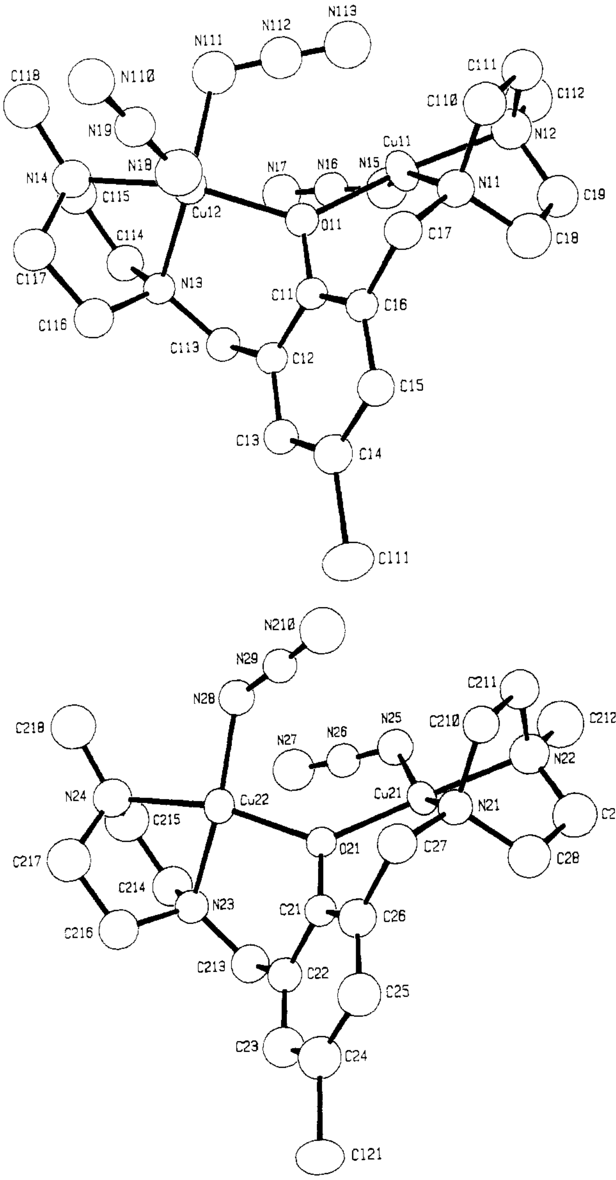


Figure 4. Molecular structure and numbering scheme of the two binuclear molecules in the asymmetric unit of $[Cu_2L(N_3)_3][Cu_2L(N_3)_2](ClO_4)\cdot 2H_2O$ (**1e**). Thermal ellipsoids are drawn at the 50% probability level.

between strings. Chaudhuri et al. have recently discussed similar weak bridging in related azido derivatives of various cyclic and open-chain amine–copper(II) chelates.[23]

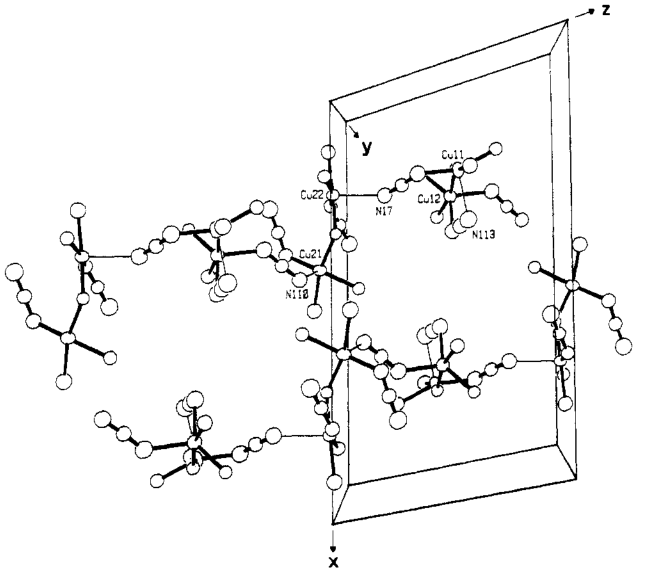


Figure 5. Packing diagram showing weak intra- and intermolecular copper–azide interactions in complex **1e**. Only the metal atoms and donor atoms from the ligand and azide groups have been included for clarity. Thermal ellipsoids are drawn at the 50% probability level.

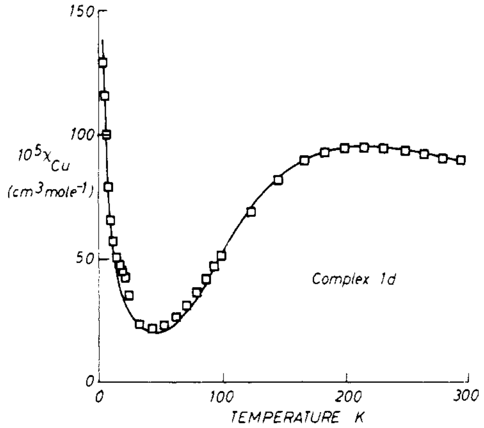


Figure 6. Observed and calculated susceptibilities (per Cu) versus temperature for complex **1d**.

Magnetic Properties. Magnetic susceptibilities of powdered samples of the complexes were measured over the temperature range 4.2–300 K by using a Faraday balance that employed a main field of 1 T and gradient field of 0.1 T cm^{-1}. A typical plot is given in Figure 6. Except for the μ-hydroxo complex, the susceptibility plots are all indicative of antiferromagnetic exchange occurring between the Cu(II) ions in the binuclear units. Thus,

Table VIII. Basal Planes around Copper

compd	plane	plane consts *A*–*D*[a]	displaced atom	displacement from plane, Å
1c	O(1),N(1),N(2),O(5)	–0.6695, 0.5994, –0.4388, –4.7183	Cu(1)	–0.309 (1)
	O(1),N(3),N(4),O(2)	–0.0114, –0.6269, –0.7790, –2.5628	Cu(2)	–0.327 (1)
1d	O(1),N(1),N(2),O(6)	–0.7797, 0.1920, –0.5961, –8.9586	Cu(1)	0.181 (2)
	O(1),N(3),N(4),O(4)	0.4099, –0.7050, –0.5788, 1.0780	Cu(2)	–0.167 (2)
1e	O(11),N(11),N(12),O(15)	–0.9494, –0.1540, –0.2738, –4.5149	Cu(11)	–0.227 (2)
	O(11),N(13),N(14),N(111)	0.2055, –0.3866, –0.8991, –5.8567	Cu(12)	–0.401 (2)
	O(21),N(21),N(22),N(25)	0.3107, –0.9106, –0.2724, –0.3327	Cu(21)	0.234 (2)
	O(21),N(23),N(24),N(28)	0.0921, –0.0207, –0.9955, 0.5084	Cu(22)	–0.125 (2)

[a] Plane is of the form $Ax + By + Cz - D = 0$.

Table IX. Magnetic Exchange Parameters

complex	μ_{Cu}(295 K),[a] μ_B (±0.01)	g (±0.02)	J,[b] cm^{-1} (±1)	% monomer (±0.1)
$[Cu_2L(OH)(H_2O)_2](ClO_4)_2\cdot H_2O$ (**1a**)	1.94	2.13	*c*	
$[Cu_2L(pz)](ClO_4)_2$ (**1b**)	1.47	2.18	–145	3.3
$[Cu_2L(OAc)_2](ClO_4)\cdot 3H_2O$ (**1c**)	1.66	2.00	–36	2.7
$[Cu_2L(NO_2)_2(H_2O)_2](ClO_4)\cdot H_2O$ (**1d**)	1.43	2.05	–122	2.4
$[Cu_2L(N_3)_{2.5}](ClO_4)_{0.5}\cdot H_2O$ (**1e**)	1.44	~2.00	~–140	~5.0

[a] The magnetic moment should strictly be given for the binuclear molecule but it is given per Cu atom ($\mu_{Cu} = 2.83(\chi_{Cu}T)^{1/2}$), to allow comparison with typical uncoupled μ_{Cu} values. [b] Singlet–triplet splitting = $2J$. [c] Weak ferromagnetic coupling. See ref 1 and 6.

in the case of the dinitrito complex, **1d**, the maximum in χ_{Cu} at ca. 220 K (Figure 6) is indicative of medium-strength intramolecular antiferromagnetic coupling. The corresponding μ_{Cu} values decrease from 1.43 μ_B at 300 K to 0.2 μ_B at 4.2 K. The increase in χ_{Cu} with decreasing temperatures at very low temperatures is due to the presence of traces of monomer impurity. The position of the maximum in χ_{Cu} for the bis(μ-acetato) complex occurs at much lower temperatures than in **1d** because of weak exchange coupling in this case.

The data for the various complexes were fitted to the Bleaney-Bowers equation[29] calculated for two $S = {}^1/_2$ centers coupled under a $-2J\hat{S}_1\cdot\hat{S}_2$ spin Hamiltonian. A nonlinear least-squares fitting program was employed, and the best-fit values for g, J, and the percent of monomer are given in Table IX. The variations in g values are not significant and result from the fitting method. The g value for **1a** was obtained from the ESR spectrum. Its magnitude suggests that the best-fit values for **1c** and **1d** are a little lower than they should be.[2,3] As discussed previously,[1,6] the χ_{Cu} (and μ_{Cu}) versus temperature behavior for **1a** shows a slight increase in μ_{Cu} with decreasing temperature, which is compatible with weak overall ferromagnetic coupling. In other words, the J_{ferro} contribution to the overall J value is slightly larger than the $J_{antiferro}$ component. In such situations it is notoriously difficult to estimate J with any degree of accuracy. The problem is further exacerbated in **1a** since there are two structurally slightly different binuclear molecules in the asymmetric unit, both of which will contribute to the average susceptibility.

From recent studies by ourselves[1–3] and others,[11,13,18,23,27] a number of qualitative correlations are beginning to emerge between structure and magnetism in systems of the present general type, i.e. asymmetrically bridged systems containing an endogenous bridging pathway and a (different) exogenous pathway. It is, therefore, interesting to relate the exchange parameters given for complexes **1a**–**e** in Table IX, to structural and other features. We have the added advantage, in the "endogenous-only" examples, **1d** and **1e**, of knowing the J value appropriate to the phenolate oxygen pathway. Furthermore, as we have seen in the structural descriptions, the conformation of ligand L$^-$ and the relative dispositions of basal planes around each Cu are rather similar in **1d**, **1e**, and **1c** but are quite different in **1a**. It is interesting to note that even though these basal planes have large dihedral angles between them, there is sufficient overlap of each Cu($d_{x^2-y^2}$) orbital with the phenolate oxygen p orbital to generate negative J values of intermediate magnitude, i.e. –120 to –140 cm^{-1} in **1d** and **1e**. Undoubtedly, the J values would have been more negative if the basal planes had been coplanar.[1–3]

The pyrazolate exogenous bridge in **1b** leads to a more negative net J value than does the diacetate bridge in **1c**. This is not surprising since pyrazolate is well-known to be a better mediator of exchange than acetate.[3] Also, the fact that the acetate groups in **1c** connect basal plane ($d_{x^2-y^2}$) positions on one Cu with apical (d_{z^2}) positions on the other will lead to a low overall J value, probably because of J_{ferro} contributions from these pathways. Any contributions from the counter complementary effects of phenolate vs acetate bridging orbitals, recently proposed by Reed et al.[11] and Nishida et al.,[13] will be small in **1c** because of the relative disposition of the Cu($d_{x^2-y^2}$) orbitals.

The weak intra- and intermolecular μ-azido bridging interactions in **1e**, described in the structural section, do not appear to significantly modify the size of the J value. This is because the azido groups involved link together basal and axial positions of the appropriate Cu atoms, which leads to poor exchange pathways. Chaudhuri et al.[23] observed J values close to zero for complexes containing azide bridging of this type but without any μ-phenolate bridge.

A final comment on the structure/magnetism correlations in this small series of complexes concerns the dependence of J on the Cu–Cu distance and Cu–O(phenolate)–Cu angle. A quick perusal of Tables VI, VII, and IX shows that, in general, as the Cu–Cu distance and Cu–O–Cu angles increase, so does J become more negative. However, it must be noted that **1a** has a bridging geometry different from the others, and the weak overall ferromagnetism has been ascribed largely to the effect of the pyramidal geometry around the phenolate oxygen atom.[30] Also, as described above, the small negative J value in the bis(μ-acetato) complex reflects the combined effects of the acetate and phenolate superexchange pathways.

Redox Properties. One of the most important properties of binuclear complexes of the present type, especially in relation to their use as credible models for type 3 copper biosites, is their redox property in solution. It is desirable that model systems show reversible $Cu^{II}–Cu^{II} \rightleftharpoons Cu^{II}–Cu^{I} \rightleftharpoons Cu^{I}–Cu^{I}$ couples, at positive redox potentials, either in two sequential one-electron steps or, preferably, in a simultaneous two-electron step. A number of models studied by electrochemical methods have exhibited properties compatible with these prerequisites.[31–33] Many other

---

(29) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451.

(30) This interpretation, while receiving support,[13,16] has also been questioned: Bailey, N. A.; Fenton, D. E.; Lay, J.; Roberts, P. B.; Latour, J.-M.; Limosin, D. *J. Chem. Soc., Dalton Trans.* **1986**, 2681.

(31) Some recent examples of Thompson et al. using pyridazine or phthalazine ligands (see also references therein): (a) Mandal, S. K.; Woon, T. C.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J. *Aust. J. Chem.* **1986**, *39*, 1007. (b) Woon, T. C.; McDonald, R.; Mandal, S. K.; Thompson, L. K.; Connors, S. P.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1986**, 2381.

(32) Tikkanen, W. R.; Krujer, C.; Bomben, K. D.; Jolly, W. L.; Kaska, W. C.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 3633.

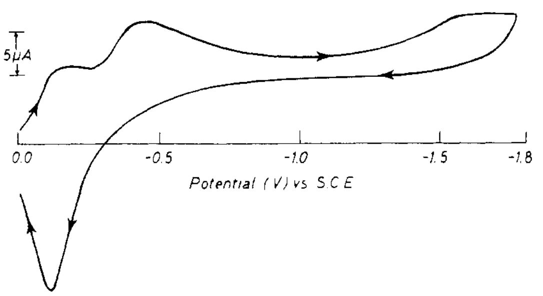


Figure 7. Cyclic voltammogram of complex **1b** in CH_3CN/TBAP/Pt versus SCE at 20 °C. Scan rate = 200 mV s^{-1}.

Table X. Cyclic Voltammetric Data[a]

complex	cathodic peaks, V				anodic peak, V
1a		−0.56	−1.15	−1.43	−0.17
1b	−0.22	−0.42	−1.52	−0.18	
1d		−0.50	−1.0	*b*	−0.17

[a] In CH_3CN/TBAP/Pt-button relative to SCE, recorded on a BAS 100 instrument. Scan rate = 100 mV s^{-1}. [b] Scanned only to −1.5 V.

studies have reported quasi-reversible or irreversible cyclic voltammetric reduction waves occurring at negative potentials, especially in asymmetrically bridged complexes of the present type.[4,34–37] The irreversibility presumably arises because of factors such as dissociation of exogenous and/or terminal ligand atoms prior to, or subsequent to, electron transfer, with associated stereochemical changes around Cu. The size of the $E_{1/2}$ values are largely determined by the nature of the atoms bonded to the Cu atoms with pyridyl N and various S donors, in particular, capable of yielding positive $E_{1/2}$ values.[31–33,38,39]

What of the present complexes? Unfortunately they fall into the irreversible/negative potential camp, at least at room temperature. Cyclic voltammetric studies in acetonitrile/tetrabutylammonium perchlorate electrolyte with a Pt-button working electrode and SCE reference electrode, were made on complexes **1a**, **1b**, and **1d**. These were chosen for study because of their apparent stability in solution as judged by conductance and UV–visible spectra. There are some similarities in the CV behavior of the three complexes studied. As can be seen in Figure 7 and Table X, complex **1b** shows three cathodic peaks and one strong anodic peak in the range +0.2 to −1.8 V. The anodic peak diminishes as the voltage range is limited to +0.2 to −0.9 V and disappears when the range is limited to +0.2 to −0.3 V, indicating that it is not the reoxidation wave of the cathodic peak at −0.22 V. In fact, the constancy of the position and shape of the anodic peak in all three complexes suggest that a common species may well be formed in solution after reduction to −1.8 V. Since complex **1d** does not have an exogenous-bridging ligand in the Cu^{II}–Cu^{II} state, it is tempting to suggest that such a common species may well be a Cu^{I}–Cu^{I} complex containing only the μ-phenolate endogenous-bridging oxygen and (at least one of) the piperazine nitrogen atoms bonded to each Cu^{I} ion, with consequent loss of exogenous ligands and possible changes in stereochemistry compared to that of the Cu^{II}–Cu^{II} parent.

Scans of the cathodic peaks measured over limited voltage ranges and at different scan rates showed that all were irreversible. Comparison to the $E_{1/2}$ values of related systems[4,34,37,40] would suggest that the first two cathodic peaks listed in Table X are due to the couples Cu^{II}–Cu^{II} → Cu^{II}–Cu^{I} and Cu^{II}–Cu^{I} → Cu^{I}–Cu^{I}, respectively. Further coulometric and variable-temperature CV studies would help to make definitive assignments, but it was decided, in view of the electrochemical irreversibility, not to proceed further.

Relevance to TD2 Laccase. As indicated in the Introduction, Spira-Solomon and Solomon[21] have recently proposed, from analyses of chemical and spectroscopic data, that there is only one exchangeable coordination position at the type 3 site of T2D laccase and that an exogenous ligand, such as N_3^-, can not bridge the binuclear copper site. This contrasts with the μ-1,3-azido bridging mode found in hemocyanins and tyrosinases. Other differences of T2D laccase compared to these latter proteins include a lack of O_2 binding of the deoxy form and a one-electron reduction only to the half-met form from the met form.[41] It was proposed that, despite these differences in the exogenous binding mode, the endogenous bridging mode remained geometrically and electronically similar in all three protein types except perhaps for small differences in the Cu–O–Cu bridge angle.[21] Bearing in mind the various structural, magnetic, and redox features of complexes such as **1d** and **1e**, which are not too dissimilar to those of T2D laccase, while at the same time being very much aware of the risks and limitations inherent in comparing simple models to complex proteins (the detailed properties of which are only partially understood), we nevertheless offer the following comments. Complexes of types **1d** and **1e** and of related ligand systems that incorporate nonbridging exogenous ligands[12–16] have the common feature of a sterically strained μ-phenolate (or μ-alcoholate) backbone ligand. In the present examples this strain is relaxed by allowing adjacent Cu–ligand basal planes to be disposed at angles of almost 90° relative to each other. Consequently, exogenous bridging becomes very difficult. The μ-phenolate ligand backbone is, of course, the analogue of the peptide chain bonded to the two Cu ions in the type 3 biosite. We suggest that the geometric features of the peptide chain binding fragment in the endogenous-bridging regions of T2D laccase and of hemocyanins (or tyrosinases) are not as similar as has been proposed but may well be significantly different. Finally, we also note in the specific case of azide binding that, apart from the subtle geometric arguments just given, there is the chemical fact that reactions of azide ions with Cu(II) complexes can lead to complicated stoichiometries and binding modes. This may also be the case with proteins.

Acknowledgment. This work was supported by grants from the Australian Research Grants Scheme and Monash University Special Research Grants. We thank B. Spethmann, S. Neate, D. Duckworth, and Dr. B. C. Loft for their contributions to this work. K.S.M. and J.H.H. acknowledge, with sincere gratitude, the scientific input and warm companionship of (the late) Dr. John Yandell. His friends and collaborators here and overseas will miss his excellent contributions to the chemistry and redox properties of copper compounds and proteins.

Registry No. **1a**, 95381-19-4; **1b**, 117469-62-2; **1c**, 117469-65-5; **1d**, 117469-68-8; $[Cu_2L(N_3)_2]ClO_4$, 117469-70-2; T2D-laccase, 80498-15-3.

Supplementary Material Available: Tables S1–S3, listing the hydrogen atom coordinates for **1c–e**, Tables S4–S6, listing the thermal parameters, Tables S7–S9, listing the complete bond lengths, and Tables S10–S12, listing the complete bond angles (22 pages); Tables S13–S15, listing the observed and calculated structure factors (48 pages). Ordering information is given on any current masthead page.

---

(33) Agnus, Y.; Louis, R.; Gisselbrecht, J.-P.; Weiss, R. *J. Am. Chem. Soc.* **1984**, *106*, 93.

(34) See paper by Bailey et al. in ref 30.

(35) Grzybowski, J. J.; Merrell, P. H.; Urbach, F. L. *Inorg. Chem.* **1978**, *17*, 3078.

(36) Gagne, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917.

(37) Mandal, S. K.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1984**, 2141.

(38) Benzekri, A.; Dubourdeaux, P.; Latour, J.-M.; Langier, J.; Rey, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1564.

(39) Mandal, S. K.; Thompson, L. K.; Gabe, E. J.; Lee, F. L.; Charland, J.-P. *Inorg. Chem.* **1987**, *26*, 2384.

(40) Mandal, S. K.; Thompson, L. K.; Nag, K.; Charland, J.-P.; Gabe, E. J. *Inorg. Chem.* **1987**, *26*, 1391 and references therein.

(41) Makino, N.; McMahill, P.; Mason, H. S.; Moss, T. H. *J. Biol. Chem.* **1974**, *249*, 6062.