are equivalent. The ^2H NMR spectrum of this complex with deuteron-substituted pyridines shows three resonance signals with relative integration values of 2:1:2 (Table I).[14] The observation of only one set of resonances for the three types of deuterons indicates the equivalence of the two pyridines, supporting the assignment based on the malonate deuteron NMR spectrum.

In the [Cr(edda)X$_2$] system (X$_2$ = two monodentates or one bidentate ligand), both the sym-cis and uns-cis isomers have been reported.[7,15] With the assumption that [Cr(edda)-(mal-d_2)]$^-$ has the sym-cis configuration as proposed on the basis of visible spectra by Radanovic et al.,[7] one resonance is predicted due to the equivalent malonate deuterons, which are related by the 2-fold axis through the malonate ring. In the sym-cis geometry the glycinate rings are also equivalent but the geminal hydrogens are inequivalent. Thus for *sym-cis*-[Cr(edda-α-d_4)(mal)]$^-$ two resonance signals with equal integration should be observed. These expectations are borne out as shown in Figure 1A,B and summarized in Table I. The corresponding Co(III) isomer behaves in an analogous manner as demonstrated by the ^1H NMR spectra obtained for the sym-cis and uns-cis isomers.[13b] Thus, [Cr(edda)(mal)]$^-$ can be assigned unambiguously as the sym-cis isomer.

We have demonstrated that deuteron nuclear magnetic resonance is a potentially valuable technique for studying Cr(III) complexes in solution. The simple zero-order spectra obtained show that even inequivalent geminal deuterons are strongly affected to different extents by paramagnetic Cr(III). It should now be possible to determine directly, and in many cases unambiguously, stereochemistries of Cr(III) complexes in solution whenever deuterated ligands can be included in the coordination sphere of the complex.

(15) Fujii, Y.; Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3451. Weyh, J. A.; Pierce, R. L. *Inorg. Chem.* **1971**, *10*, 858. Srdanov, G.; Herak, R.; Radanovic, D. J.; Veselinovic, D. S. *Inorg. Chim. Acta* **1980**, *38*, 37.
(16) On leave from the Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan.

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Synthesis, Structure, and Reactivity of a Binuclear Three-Coordinate Copper(I) Complex

Sir:

Corequisite with pursuing the goal to model the binuclear copper proteins hemocyanin[1] and tyrosinase[2] is the need to study and understand the coordination chemistry of Cu(I)

(1) McKee, V.; Dagdigian, J. V.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 7000–7001 and references therein.
(2) Winkler, M. E.; Lerch, K.; Solomon, E. I. *J. Am. Chem. Soc.* **1981**, *103*, 7001–7003 and references therein.
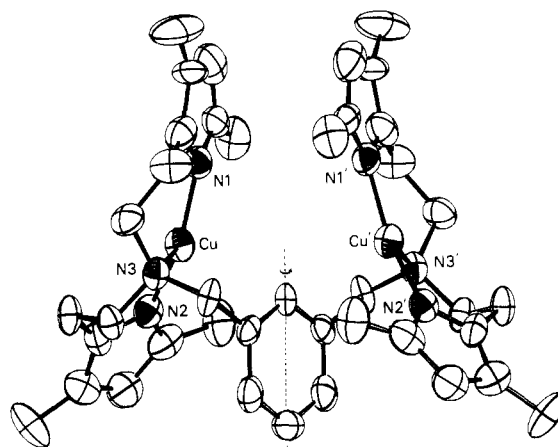
Figure 1. Full structure of the [Cu$_2$(mxyN$_6$)]$^{2+}$ cation showing 40% probability thermal elipsoids. The Cu···Cu distance is 5.100 (1) Å and the molecule sits on a 2-fold axis as indicated by the dashed lines.
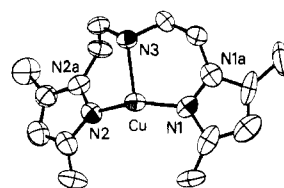

Figure 2. Coordination sphere about copper. Selected distances (Å): Cu–N1 = 1.916 (4); Cu–N2 = 1.895 (4); Cu–N3 = 2.195 (3). Bond angles (deg): N1–Cu–N2 = 156.0 (2); N1–Cu–N3 = 99.2 (2); N2–Cu–N3 = 100.0 (2).

ligated by nitrogenous donors.[3] Historically, such complexes have resisted careful scrutiny because of the absence of spectroscopic "handles" for the spin-paired d^{10} Cu(I) ion as well as their tendency to disproportionate (especially in aqueous solution)[4] and to undergo facile autoxidation in the presence of air.[5] As part of a project aimed at a systematic study of coordinatively unsaturated (two- and three-coordinate) mono- and binuclear Cu(I) complexes,[6] we report here the preparation, structural characterization, and reactions of a binuclear Cu(I) complex having the rare (N)$_3$ donor set.[7] Furthermore, we show that because small differences in structure can create significant yet unpredictable changes in reactivity, the relationship between a biological system and its alledged "model" may be obscured.

The reaction of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine[8] with α,α'-dibromo-*m*-xylene in 1:1 tetrahydrofuran–benzene gave the binucleating ligand **1** as a colorless oil after flash chromatography.[9] Slow evaporation of a solution of **1** and [Cu(CH$_3$CN)$_4$]BF$_4$[6a] in ethanol–benzene under an inert at-

(3) Osterberg, R. *Coord. Chem. Rev.* **1974**, *12*, 309–347.
(4) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115–163.
(5) Zuberbuhler, A. D. *Met. Ions Biol. Syst.* **1976**, *5*, 325–368.
(6) (a) Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 1014–1019. (b) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 2053–2054.
(7) To our knowledge, only one monomeric Cu(N)$_3$ complex has been structurally characterized: Levin, A. H.; Michl, R. J. *J. Chem. Soc., Chem. Commun.* **1972**, 661–662. A binuclear Cu(N)$_3$ complex was recently reported; however, a copper–copper bond exists, making each metal four-coordinate: Gagne, R. R.; Kreh, R. P.; Dodge, J. A.; Marsh, R. E.; McCool, M. *Inorg. Chem.* **1982**, *21*, 254–261.
(8) Prepared from bis(chloroethyl)amine hydrochloride and the anion of 3,5-dimethylpyrazole in DMF followed by crystallization from methanol–water.
(9) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
(10) Anal. Calcd for Cu$_2$(C$_{36}$H$_{52}$N$_{10}$)(BF$_4$)$_2$: C, 46.7; H, 5.67; N, 15.1; Cu, 13.7. Found: C, 46.6; H, 5.63; N, 15.1; Cu, 13.6.
(11) Crystal data for **2**: monoclinic; a = 23.788 (11), b = 13.901 (3), c = 16.688 (4) Å; β = 129.22 (3)°; Z = 4; space group *C2/c*; Mo Kα radiation; 1973 independent nonzero [$I > 3\sigma(I)$] reflections with 2θ between 2 and 50°; R = 5.4%; R_w = 6.0%. The copper atom position was located by the Patterson function, and all non-hydrogen atoms were located on difference Fourier maps. Full details will be presented in a future paper.

Table I. Selected Geometric Features of the $[Cu_2(N_6O)]^{2+}$ Cation

atoms	dist, Å	atoms	angle, deg	atoms	angle, deg
Cu1–O1	1.964 (8)	Cu1–O1–Cu2	102.3 (4)	O1–Cu1–O2	76.7 (4)
Cu1–O2	2.007 (10)	Cu1–O2–Cu2	101.8 (5)	O1–Cu2–O2	78.8 (4)
Cu1–N1	2.022 (15)	N1–Cu1–O1	88.0 (6)	N4–Cu2–O1	87.9 (5)
Cu1–N2	2.047 (12)	N1–Cu1–O2	140.4 (6)	N4–Cu2–O2	153.8 (5)
Cu1–N3	2.120 (15)	N1–Cu1–N2	96.9 (7)	N4–Cu2–N5	102.9 (6)
Cu2–O1	1.958 (8)	N1–Cu1–N3	113.6 (6)	N4–Cu2–N6	97.7 (6)
Cu2–O2	1.926 (11)	N2–Cu1–O1	170.5 (4)	N5–Cu2–O1	93.3 (5)
Cu2–N4	1.983 (15)	N2–Cu1–O2	94.4 (5)	N5–Cu2–O2	100.4 (5)
Cu2–N5	2.154 (15)	N2–Cu1–N3	95.1 (6)	N5–Cu2–N6	95.1 (6)
Cu2–N6	2.065 (13)	N2–Cu1–O1	90.2 (6)	N6–Cu2–O1	168.5 (5)
Cu1–Cu2	3.054 (4)	N3–Cu1–O2	103.0 (5)	N6–Cu2–O2	92.0 (5)

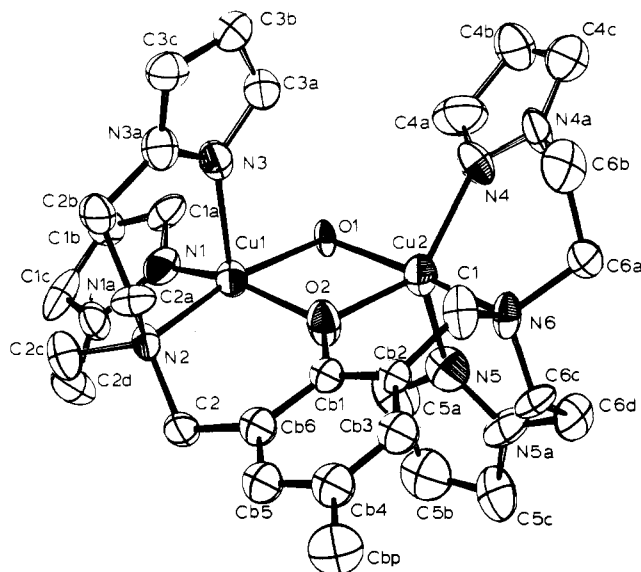**Figure 3.** Structure of the $[Cu_2(N_6O)]^{2+}$ cation showing 40% probability thermal elipsoids. Distances and angles are given in Table I.

mosphere yielded colorless $[Cu_2(mxyN_6)][BF_4]_2$ (**2**),[10] which was subsequently characterized by X-ray crystallography.[11]

The full structure of the cation portion of **2** is shown in Figure 1, and the more immediate coordination unit about the copper is shown in Figure 2. While the molecule as a whole lies on a crystallographic 2-fold axis, the copper atom sits 0.206 (1) Å from the plane formed by N1, N2, and N3 in a T-shaped coordination sphere reminiscent of the bis(benzimidazolylethyl) sulfide–copper(I) complex characterized recently by Reed.[12] The Cu–N(pyrazole) distances of 1.895 and 1.916 Å are also nearly identical with those found for the $Cu(N_2S)^+$ complex (1.91 Å)[12] and possibly reflect some π back-bonding from Cu(I) to pyrazole. Copper(I)–N(heterocycle)[13] bond lengths appear to increase with increasing coordination number; and the values of 1.87 Å for two-coordination,[6b,14] 1.89–1.92 Å for three-coordination,[15] and 1.98–2.04 Å for four-coordination[6a] may be intrinsic structural properties for $[CuL]^+$ complexes. The Cu–N(amine) bond length (2.19 Å) is much longer than the Cu–pyrazole distances and is even longer than the corresponding bond in the Cu(I) complex of our previously characterized tripod ligand (2.11 Å).[6a] The distance reported here is probably a more accurate value for Cu(I)–N(amine) co-

ordination since the increased rigidity of the tripod system[6a] would produce a shorter Cu–N bond.

Complex **2** undergoes a normal reaction with carbon monoxide, giving a carbonyl derivative in CH_3CN solution ($\nu(CO)$ = 2080 cm^{-1}) similar to previously characterized $Cu(N)_3CO^+$ complexes.[16,17] This result corroborates our earlier contention[6b] that at least three donors are necessary to promote CO binding to Cu(I).

The reaction of **2** with dioxygen offers a distinct contrast to previous results,[18,19] however, and a methanol solution of **2** and O_2 gives, after crystallization at −20 °C, the blue-green complex $[Cu_2(OH)_2(mxyN_6)][BF_4]_2\cdot 2CH_3OH$ (**3**)[20] (eq 1).

$$\tag{1}$$
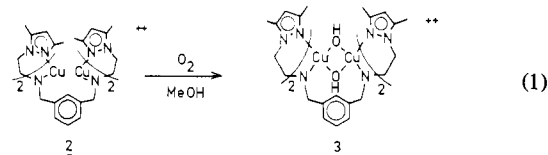
While the transformation of **2** to **3** is not unexpected, it contrasts with the reaction between the pyridine analogue **4** and O_2, which results in hydroxylation of the benzene ring (eq 2).[18]

$$\tag{2}$$
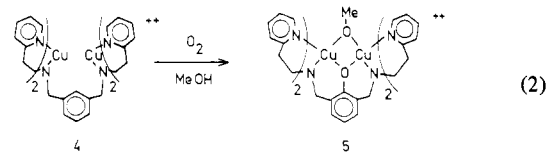
That **3** is different from **5** can be seen by comparison of the electronic spectra of **3**, **5**, and **6**, a complex which we have prepared independently (eq 3) and have characterized by

$$\tag{3}$$
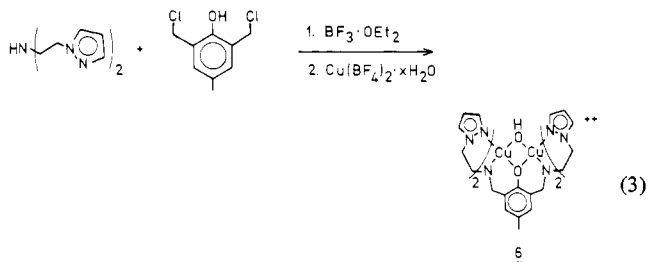
X-ray crystallography.[22] The structure of the cation portion of **6** is shown in Figure 3. There is no crystallographic symmetry imposed as is the case for **5**,[18] but the overall structure is essentially the same, showing no unusual bond distances or angles. Both **5** and **6** absorb strongly at 390 nm (ϵ 5610 M^{-1} cm^{-1} for **5** and 2250 M^{-1} cm^{-1} for **6**), and we assign that transition to a phenoxide → Cu(II) charge transfer band. While **3** lacks that feature, it instead displays two strong absorptions at 3620 and 3550 cm^{-1} in the IR region, indicative

(12) Dagdigian, J. V.; McKee, V.; Reed, C. A. *Inorg. Chem.* **1982**, *21*, 1332–1342.
(13) We consider here only the heterocycles imidazole, benzimidazole, and pyrazole as well as their derivatives.
(14) Birker, J. J. M. W. L.; Hendricks, H. J. J., Reedijk, J. *Inorg. Chim. Acta* **1981**, *55*, L17–L18.
(15) We have recently determined the structure of the bis[2-(3,5-di-methyl-1-pyrazolyl)ethyl] ether–copper(I) cation and its Cu–N distances also fall in this range: Sorrell T. N.; Malachowski, M. R., submitted for publication in *Inorg. Chem.*
(16) The isolation of this carbonyl adduct is currently in progress.
(17) Pasquali, M.; Marini, G.; Floriani, F.; Gaetani-Manfredotti, A.; Guastini, C. *Inorg. Chem.* **1980**, *19*, 2525–2531 and references therein.

(18) Karlin, K. D.; Dahlstrom, P. L.; Cozzette, S. N.; Scensny, P. M.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1981**, 881–882.
(19) Nishida, Y.; Takahashi, K.; Kuramoto, H.; Kida, S. *Inorg. Chim. Acta* **1981**, *54*, L103–L104.
(20) Anal. Calcd for **3**: C, 44.6; H, 6.12; N, 13.7. Found: C, 44.9; H, 5.28; N, 13.6. IR (KBr): ν(OH) 3620 (5), 3550 (5) cm^{-1}.[19]
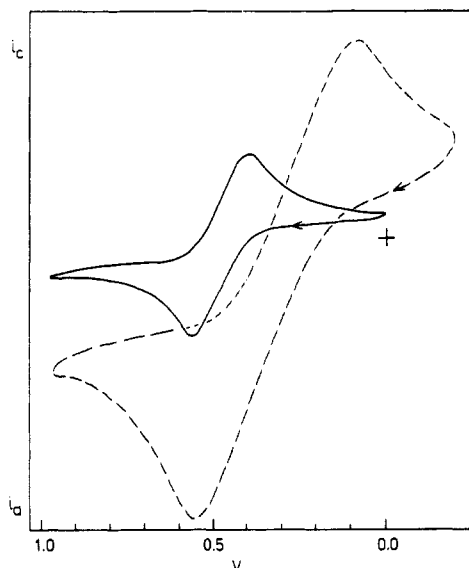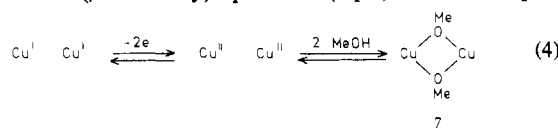(21) Cf.: McWhinnie, W. R. *J. Chem. Soc.* **1964**, 2959–2969.

Figure 4. Steady-state cyclic voltammetry for **2** (—) and for **4** (- - -). Conditions are specified in ref 21. The ordinate is an arbitrary scale of current.

of a bis(hydroxy)-bridged Cu(II) species.[21]

The reason for the difference in reactivity between **2** and **4** is not readily apparent. One speculation is that electronic effects of the ligands mediate the redox properties of each complex, and for that reason we examined briefly the electrochemistry of these systems. The results of cyclic voltammetric scans for **2** and **4** are shown in Figure 4. $E_{1/2}$ for the chemically reversible wave is +0.48 V for **2** and +0.33 V for **4**, with peak separations of 170 and 490 mV, respectively.[23] Constant-potential coulometry on **2** shows the loss of two electrons during the oxidation process,[24] and we believe one possibility is that an EC mechanism operates, wherein the two-electron oxidation is followed by reaction with methanol to give the bis(μ-methoxy) species **7** (eq 4). Another pos-

$$Cu^I \quad Cu^I \xrightarrow{-2e} Cu^{II} \quad Cu^{II} \xrightarrow{2\ MeOH} Cu \underset{O}{\overset{O}{\diagup\diagdown}} Cu \quad (4)$$

$$\text{Me} \qquad \text{Me}$$

7

sibility, which cannot be overlooked, is that the reaction follows an ECEC mechanism wherein a one-electron transfer occurs in a rate-determining step, followed by a chemical reaction, most likely with the solvent, and then sequentially a second, fast electron transfer and a second reaction with methanol to give **7**. The fact that the peaks of each cyclic scan show no splitting is noteworthy since it is unlikely that the two coppers react independently of one another. The magnitudes of the

peak separation observed during the cyclic scans on **2** and **4** suggest that, during the oxidation process, the kinetic barriers for chemical reaction with the solvent are probably different. In relating the electrochemical results to the oxidation reactions of **2** and **4** with O_2, we speculate that one or more of the following processes is slowed considerably, leading to the different observed chemistry: (1) initial reaction of the binuclear cuprous complex with O_2,[25] (2) rate of proton transfer from methanol to bound dioxygen, and/or (3) dissociation of peroxide ion from a dicopper(II) peroxide intermediate.[26] The details of those mechanistic steps will require further investigation.[27]

Biases built into a synthetic scheme provide one of the main problems associated with modeling biological systems. For example, in our model studies on copper proteins, we have elected to use pyrazole derivatives as histidyl imidazole analogues while others have chosen pyridine,[18,28] benzimidazole,[12,14] aliphatic amines,[29] and Schiff bases[30] to accomplish that goal. The drawback is that the results obtained from a particular system may obscure potentially interesting chemistry because the properties of the proposed "model" do not correspond to those displayed by the enzyme under investigation; hence, that model is eliminated from further consideration. Such a case is presented here. On the basis of the reaction of **2** with dioxygen, which gives the stable bis(μ-hydroxy)dicopper(II) complex **3**, we might have concluded that complexes like **2** would not successfully model the enzyme tyrosinase. However, just the change from pyrazole in **2** to pyridine in **4** drastically alters the outcome of the oxidation reaction.[31] We conclude instead that, with proper cultivation, binuclear Cu(N)₃ complexes, with **4** serving as a prototype, have the potential to be developed into a functional tyrosinase model.

(22) Crystal data for **6**: monoclinic; a = 22.329 (1), b = 9.552 (1), c = 16.715 (1) Å; β = 95.70 (2)°; Z = 4; space group $P2_1/c$; Mo Kα radiation; 2939 independent nonzero [$I > 3\sigma(I)$] reflections with 2θ between 2 and 55°; R = 10.2%; R_w = 10.1%. The copper atom positions were located by the Patterson function, and all non-hydrogen atoms were located on difference Fourier maps. All atoms in the cation with the exception of the phenyl ring carbons were refined anisotropically, and the remaining atoms were refined isotropically. The final difference Fourier shows no significant peaks except around one of the BF₄ groups, which is obviously disordered.

(23) Electrochemical experiments were carried out in an N₂-filled inert-atmosphere box with a PAR Model 175 Universal Programmer and a PAR Model 173 potentiostat. For display purposes, a Hewlett-Packard 7015B X-Y recorder was used. Cyclic voltammetric work was conducted either in three-compartment "H-cells" or in one-compartment cells. Coulometric experiments were carried out in three-compartment "H-cells". The experiments were conducted in methanol solution, which was 0.1 M in (TBA)BF₄ and about 5 × 10⁻³ M in metal complex. A silver wire was used as the pseudo reference electrode, a platinum bead for the working electrode, and a platinum wire for the auxiliary electrode. Potentials are reported vs. the silver pseudo reference electrode and are reproducible to within ±10 mV. The scan rates for each experiment were 200 mV s⁻¹. Because of the air sensitivity of both **2** and **4**, it was difficult to weigh each complex accurately; hence, different concentrations were used for the cyclic scans shown in Figure 3.

(24) Coulometry showed the loss of 1.86 e/molecule of complex at a constant potential of 0.575 V. Cyclic voltammetry of the resulting bis(methoxy)dicopper(II) complex (**7**) was identical with that for **2**.

(25) A methanol solution of complex **4** turns green within a matter of hours even in an inert-atmosphere box containing <1 ppm of O₂. Complex **2** on the other hand is stable indefinitely under identical conditions. Thus, there is clearly a difference in the reactivity of each of those complexes with dioxygen.

(26) We speculate that the reason hemocyanin and tyrosinase form stable dioxygen adducts while simple coordination compounds do not is the stabilization of the dicopper(II) peroxide intermediate. Once dissociation of peroxide has occurred, the reversibility of O₂ binding is lost.

(27) Further electrochemical studies, including solvent effects, are in progress.

(28) Karlin, K. D.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1979**, 465–467.

(29) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228–3229.

(30) Gagne, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917–6927.

(31) It is possible that in some cases, pyridine is a *better* mimic for a histidyl imidazole because environmental effects of a protein influence the latter in a way not easily duplicated by solution species.

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