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Binuclear Copper(II) Complexes as Mimics for Type 3 Coppers in Metalloenzymes. 1. The Importance of Cooperative Interactions between Metals in the Reversible Multielectron Transfer in Bis(1,3,5-triketonato)dycopper(II) Complexes

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Abstract: The electrochemistry of several bis(1,3,5-triketonato)dycopper(II) complexes that have magnetic and spectral properties similar to type 3 coppers in metalloenzymes has been investigated. Experimentally, these complexes adhere to the usual criteria for reversibility, have diffusion constants typical of two-electron transfer, have cyclic voltammographs with 42-mV peak separations, and give polarographic $\log(i/i_d - i)$ vs. E plots with 46 ± 3 mV slopes. Also, the quantitative addition of two electrons per molecule is proven by controlled potential electrolysis. All of these facts are consistent with the two-electron reversible reduction of the Cu(II)₂Cu(I) complex to a Cu(I)₂Cu(I) product in which the electrons are added sequentially at the same potential. The net result is a single-potential, two-electron transfer. The importance of cooperative interactions between the metals, the magnetic interactions, the structural parameters, and the substituent groups is discussed. It is thought that the redox reactions of type 3 coppers involve two-electron transfer. Therefore, the observed redox properties together with the magnetic and spectral properties make the bis(1,3,5-triketonato)dycopper(II) complexes potential mimics for type 3 coppers in metalloenzymes.

Introduction

A number of multicopper proteins have been proven to contain pairs of copper atoms which in the cupric ions are strongly antiferromagnetically coupled. The better known examples include tyrosinase,¹⁻³ hemocyanin,³⁻⁶ laccase,⁶⁻⁸ ceruloplasmin,^{9,10} and ascorbate oxidase.¹¹⁻¹³ The coppers bound in this manner within the protein are commonly referred to as type 3 coppers and are characterized by lack of an EPR signal in both the oxidized and reduced states, an absorption band at about 330 nm, a relatively positive reduction potential for the process $[\text{Cu(II)}]_2 \rightarrow [\text{Cu(I)}]_2$ in which two electrons are transferred, and a large antiferromagnetic coupling constant. The chemical and physical properties of the multicopper proteins have recently been reviewed by Fee.¹⁴

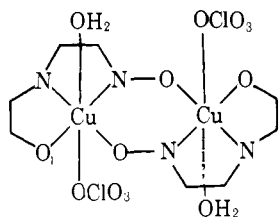
No information is yet available on the coordination geometry or the nature of the donor atoms in type 3 copper centers. However, the lack of any abnormal spectral properties asso-

ciated with the oxidized form $[\text{Cu(II)}]_2$ argues strongly against unusual coordination geometry.^{2,15} There may be a significant difference between the structural details of the type 3 coppers from one metalloenzyme to another as evidenced by differences in chemical reactivity¹⁴ and the resting oxidation state of the deoxyenzymes.^{2,6} It is not clear at this stage whether these differences are due to the detailed configuration of the enzyme or to differences in structure and bonding about the type 3 copper atoms.

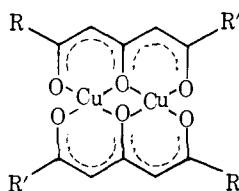
Since no structural information is available, the nature of the bridging system that gives rise to the strong antiferromagnetic interaction is not known. Several recent papers dealing mainly with EPR data for partially reduced and NO substituted systems have been concerned with structural aspects such as Cu-Cu distance.^{2,3,15-17} However, at this stage no entirely consistent understanding has emerged.

It is clear that low molecular weight copper complexes will

Chart I. Two Binuclear Cu(II) Systems That Are Diamagnetic at Room Temperature



bis[2(2-hydroxyethyl)imino 3-oximobutanato]diaquodiacopper(II) perchlorate, $\text{Cu}_2(\text{HIOB})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2$



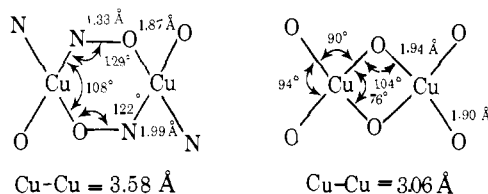
bis(1,3,5-triketonato)dacopper(II), $\text{Cu}_2(\text{TKO})_2$

not be adequate models for the reactivity and specificity of enzymes. However, as mimics for certain chemical and physical properties they may be able to furnish useful clues to the origin of the metal-based enzyme activity. In mimicking the properties of the type 3 coppers, most obviously, the low molecular weight compounds should contain two strongly antiferromagnetically coupled cupric ions, preferably exhibiting no EPR signal at or near room temperature. They should also undergo two-electron reversible reduction at relatively high potentials.

While a great many binuclear copper(II) complexes have been shown to exhibit antiferromagnetism, very few are diamagnetic at room temperature as verified by the absence of an EPR signal and/or by magnetic susceptibility measurements. These are two such diamagnetic binuclear Cu(II) systems of particular interest to this study. Interestingly, one contains a diatomic bridge and the other a monatomic bridge. The diatomic bridged complex which contains two Cu(II) ions bridged by oximes was studied by Ablov et al.¹⁸ and later by Bertrand, Smith, and Eller¹⁹ (Chart I). The monatomic bridged complexes which contain bridging ketonic oxygens in 1,3,5-triketonato have been studied in our laboratory^{20,21} (Chart I). Although there is no indication that the EPR of $\text{Cu}_2(\text{HIOB})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ was investigated, its room temperature diamagnetism would preclude an EPR absorption. A handful of $\text{Cu}_2(\text{TKO})_2$ complexes have proven to be EPR silent at room temperature and below.^{20,21}

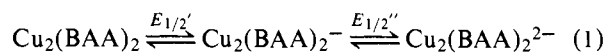
It is generally recognized that structural features play an important role in magnetic superexchange theory.²² Therefore, in recent studies on the magnetic properties of binuclear complexes, complete structural characterization has been a prerequisite. In the course of studies on varied and diverse binuclear Cu(II) complexes, it has become apparent that any or all of the following structural features affect the strength of the superexchange interaction: The relative symmetry of the exchanging electrons (orientation of the magnetic planes),²³ distortions from coplanarity,^{24,25} the magnitude of the bridging angle,²⁶⁻²⁹ the dihedral angle between the copper-donor atom planes,²³ and the hybridization of the bridging atom or atoms. Many of these structural factors have been placed into a more complete theoretical framework recently by Hay, Thibeault, and Hoffmann,³⁰ who state that the splitting energy between the two highest molecular orbitals is the dominant factor in antiferromagnetic interactions of binuclear copper complexes.

The structural features that bring about very strong antiferromagnetic exchange in binuclear complexes are not known in great detail, but whatever they are, it is reasonable to assume that similar features are present in the type 3 coppers in metalloenzymes. The two diamagnetic complexes shown in Chart I have been structurally characterized^{19,23} and the data pertinent to magnetic exchange are summarized in the schematic drawings. In both cases one is struck by the planarity of donor atoms and the copper atoms. The 0.2-Å deviation of the coppers from the plane of the six oxygens in the triketonato complex is undoubtedly due to the strong interaction with a fifth ligand (pyridine) which is apparently required for single crystal formation. Weaker or nonexistent axial interactions probably result in even a more coplanar arrangement. The similarity in magnetic properties between the two complexes is amazing in view of the tremendous structural differences.



The chemical consequences of cooperative interactions between the metals in binuclear complexes have not been well documented. It is one of our goals to investigate the chemical properties of the bis(1,3,5-triketonato)dacopper(II) complexes, in which the cooperative interaction is particularly strong. Since these complexes have magnetic properties similar to type 3 coppers which function as multielectron transfer agents in many metalloenzymes, we have chosen initially to investigate the electron transfer properties of the bis(1,3,5-triketonato)dacopper(II) complexes.

Our preliminary results, which have been communicated,³¹ showed that bis(1-phenyl-1,3,5-hexanetrionato)dacopper(II), $\text{Cu}_2(\text{BAA})_2$, undergoes two sequential, one-electron reversible reductions in which the potentials are identical, i.e., $E_{1/2}' = E_{1/2}''$.



The net result of this process is the transfer of two electrons at the same potential. In contrast, the electrochemical behavior of other binuclear Cu(II) complexes studied to date has shown either (a) one-electron reduction to a Cu(II),Cu(I) species³² or (b) two single-electron reductions occurring at different potentials.^{33,34}

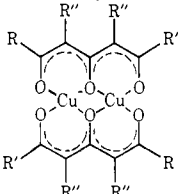
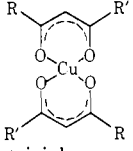
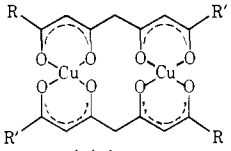
The work reported here was undertaken to obtain a more detailed understanding of the unusual electrochemical properties of $\text{Cu}_2(\text{BAA})_2$, to determine whether multielectron transfer is observed for related binuclear complexes, and to investigate the molecular properties that influence the mechanism and the potentials for electron transfer.

Experimental Section

Schematic structures of the compounds studied, trivial nomenclature, and abbreviations used are presented in Table I. Several of the compounds have been reported and completely characterized previously. These include $\text{Cu}(\text{BA})_2$,³⁵ $\text{Cu}(\text{DBM})_2$,³⁵ $\text{Cu}_2(\text{BAA})_2$,²³ $\text{Cu}_2(\text{DBA})_2$,³⁶ $\text{Cu}_2(\text{DBCP})_2$,²³ and $\text{Cu}_2(\text{HDBAA})_2$.³⁷ Elemental analysis and infrared spectra proved samples of these compounds used in this work were identical with the previously reported compounds in each case.

Synthesis of Ligands and Complexes. The previously unreported 1,3,5-triketones were prepared by the method of Miles, Harris, and Hauser.³⁸ The Cu(II) complexes were prepared by mixing a methanolic ligand solution and a methanolic cupric acetate solution in stoichiometric quantities. A precipitate forms immediately. The resulting mixture was refluxed for 1 h and the product filtered and air

Table I. Trivial Nomenclature and Abbreviations for the Mono- and Binuclear Copper(II) Complexes

A. Binuclear Triketonates				
				
R	R'	R'' R'''	trivial name	abbreviation
CH ₃	C ₆ H ₅	H H	bis(benzoylacetylacetonato)dicopper(II)	Cu ₂ (BAA) ₂
C ₆ H ₅	C ₆ H ₅	H H	bis(dibenzoylacetonato)dicopper(II)	Cu ₂ (DBA) ₂
CH ₃	<i>p</i> -CH ₃ OC ₆ H ₄	H H	bis(anisoylacetylacetonato)dicopper(II)	Cu ₂ (ANAA) ₂
<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -CH ₃ OC ₆ H ₄	H H	bis(dianisoylacetonato)dicopper(II)	Cu ₂ (DANA) ₂
C ₆ H ₅	C(CH ₃) ₃	H H	bis(benzoylpivaloylacetonato)dicopper(II)	Cu ₂ (BPA) ₂
C ₆ H ₅	CF ₃	H H	bis(benzoyltrifluoroacetylacetonato)dicopper(II)	Cu ₂ (BTFAA) ₂
C ₆ H ₅	C ₆ H ₅	H ₂ C—CH ₂ 	bis(dibenzoylcyclopentonato)dicopper(II)	Cu ₂ (DBCP) ₂
B. Mononuclear Diketonoates				
				
R	R'	trivial name		abbreviation
CH ₃	C ₆ H ₅	bis(benzoylacetonato)copper(II)		Cu(BA) ₂
C ₆ H ₅	C ₆ H ₅	bis(dibenzoylmethanato)copper(II)		Cu(DBM) ₂
C. Binuclear Tetraketonates				
				
R	R'	trivial name		abbreviation
C ₆ H ₅	C ₆ H ₅	bis(dibenzoylacetylacetonato)dicopper(II)		Cu ₂ (HDBAA) ₂

dried. The products were washed with H₂O and methanol. They are sparingly soluble in CHCl₃ and CH₂Cl₂ and can be recrystallized from these solvents. In each case the elemental analysis and infrared spectra were consistent with pure compounds as formulated in Table I.

Electrochemical Measurements. All electrochemical measurements were made in dimethylformamide (DMF) 0.1 M in tetraethylammonium perchlorate (TEAP). The DMF was purified by vacuum distillation over calcium hydride. Commercial TEAP was purified by three passes through an activated alumina column, recrystallization from diethyl ether, and vacuum drying.

All solutions were deoxygenated by bubbling with nitrogen. The nitrogen was purified by bubbling through a chromous-perchloric acid solution and passing through a calcium sulfate drying tube.

An all-glass three-electrode cell was used at ambient temperatures. The saturated calomel reference electrode was separated from the working electrode by two bridges, the first a DMF-0.1 M TEAP solution, the second a 1 M NaNO₃ aqueous solution. No adjustment has been made for junction potential effects. Blanks were run to check the purity of solvent and electrolyte and the completeness of degassing.

For both polarography and cyclic voltammetry an *iR* compensated potentiostat³⁹ was used. For all measurements the current follower type *iR* compensator was adjusted as closely as possible to the point of self-induced oscillation. Potential measurements were checked using a Data Precision Model 175 voltmeter capable of an accuracy of 0.25%.

Polarography. The dropping mercury electrode was constructed from commercially available capillary tubing. The counter electrode was platinum. The potential ramp was provided by a Sargent Model XXI polarograph. Recording was done on a standard X-Y recorder.

Cyclic Voltammetry. The hanging mercury drop electrode was a Parr Model 9323. The triangle wave for cyclic voltammetry was provided by a Wavetek 112 wave generator. Measurements were re-

corded on an X-Y recorder or a Tektronix type 549 oscilloscope.

Controlled Potential Electrolysis. Electrolysis was performed at a stirred mercury pool working electrode. The counter electrode, either copper or platinum, was separated from the working solution by a DMF-0.1 M TEAP bridge. When a platinum counter electrode was used, hydrazine was added to the anode solution. A potentiostat after a design by Schroeder⁴⁰ provided the large currents necessary. The reference voltage source was a Heath Model EU80A. The current decay curve was recorded on a Heath recorder.

EPR controlled potential electrolysis experiments were designed so that samples could be withdrawn from the operating cell and placed in a quartz flat cell in the EPR cavity without exposure to the atmosphere. The EPR spectrometer used was a Varian E-4.

Results

Several of the binuclear Cu(II) triketonates studied exhibit essentially identical, multielectron redox processes as evidenced by the polarographic and cyclic voltammetry (CV) results. These are Cu₂(BAA)₂, Cu₂(DBA)₂, Cu₂(ANAA)₂, Cu₂(DANA)₂, and Cu₂(BPA)₂. A full scan from about -0.2 to -1.6 V vs. SCE for Cu₂(BPA)₂ is shown in Figure 1 (scan A) and is typical of the other four compounds. The only significant difference between the five is the value of the redox potentials observed. The reduction at about -0.49 V is due to Cu(II) with no other reductions until about ≈ 1.4 V, at which point an irreversible reduction is observed. The potential for ligand reduction was confirmed by investigating the analogous binuclear Zn(II) chelate which exhibits no reductions at potentials more positive than -2.0 V under identical conditions, Figure 1 (scan B). At about -2.0 V, irreversible reduction of the li-

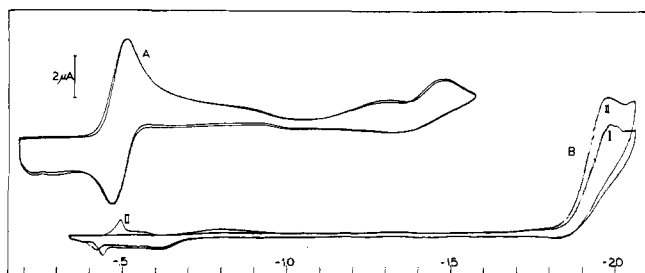


Figure 1. (A) Cyclic voltammogram of 0.5 mM $\text{Cu}_2(\text{BPA})_2$ in DMF at 97 mV/s. Two scans are represented. (B) Cyclic voltammogram of 0.5 mM $\text{Zn}_2(\text{ANAA})_2$ in DMF at 140 mV/s. Two scans (I and II) are represented.

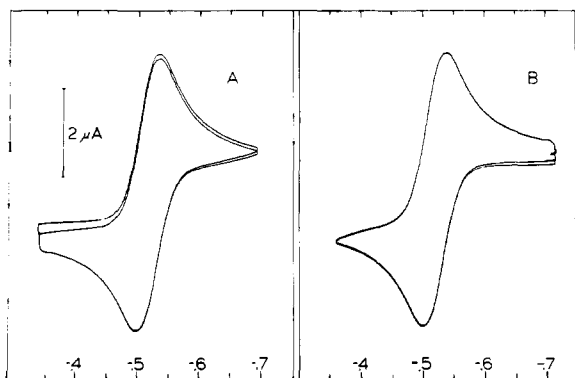


Figure 2. Cyclic voltammograms of 0.70 mM $\text{Cu}_2(\text{DANA})_2$ in DMF at 30 mV/s. Part A is two "forward" scans beginning at -0.35 V. Part B is two "reverse" scans beginning at -0.7 V.

gand takes place similarly in the $\text{Zn}(\text{II})$ and $\text{Cu}(\text{II})$ cases.

In Figure 2, the CV results, including forward and reverse scans, for $\text{Cu}_2(\text{DANA})_2$ from -0.35 to -0.7 V are presented. In this region only copper redox processes are observed. Scan A is a normal sweep starting at -0.35 V vs. SCE. Scan B was recorded by allowing the system to sit at -0.8 V for about 1 min and scanning in the positive direction and then back to the negative potential. The similarity of the waves resulting from forward and reverse scans is strong evidence for a reversible redox process. The cathodic and anodic waves in each case have equal heights and are symmetric which also indicates a reversible process. Identical behavior is observed for the other four compounds listed above. In each case the peak separation is 42 ± 1 mV.

Another standard test of reversibility in CV is to observe the peak current as a function of scan rate. The relationship for a reversible process was originally derived by Shain and Nicholson.⁴¹ A rearranged form of their equation shows that for a reversible process a straight line should result from the plot of peak current, i_p , vs. the square root of the scan rate:

$$i_p = [602n^{3/2} \sqrt{D_0 C_0} * \sqrt{\pi} \chi(at)] \sqrt{V} + [96nAC_0 * D_0 \phi(at)] \quad (2)$$

where V is scan rate and all other values in the brackets are experimental constants. In Figure 3, the plot of cathodic peak current vs. the square root of the scan rate is presented for the five compounds that appear reversible on the basis of other criteria. An extremely good straight line relationship is observed for scan rates from 10 to 300 mV/s, which represents our experimentally recordable range. Higher scan rates, to 10 V/s, were observed to cause no change in peak separation, nor any change in overall wave shapes. This result lends further strong support to the conclusion that the redox process is reversible.

In order to determine the importance of adjacent, coupled $\text{Cu}(\text{II})$ ions in the redox processes, some mononuclear 1,3-

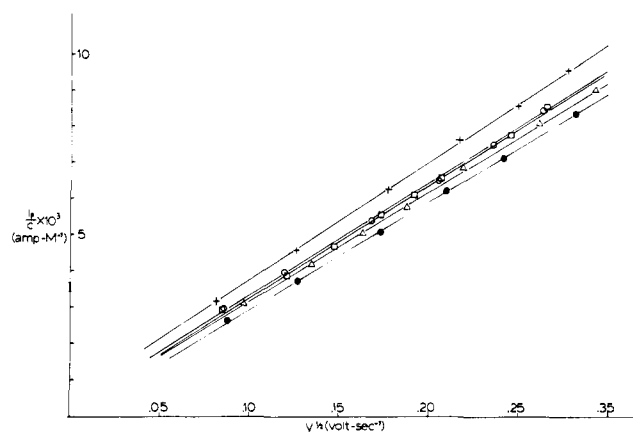


Figure 3. Peak current divided by concentration of electroactive species vs. the square root of the scan rate for the complexes: Δ , 0.50 mM $\text{Cu}_2(\text{DBA})_2$; \circ , 0.70 mM $\text{Cu}_2(\text{DANA})_2$; \square , 0.27 mM $\text{Cu}_2(\text{DBA})_2$; $+$, 0.50 mM $\text{Cu}_2(\text{ANAA})_2$; \bullet , 0.80 mM $\text{Cu}_2(\text{BAA})_2$.

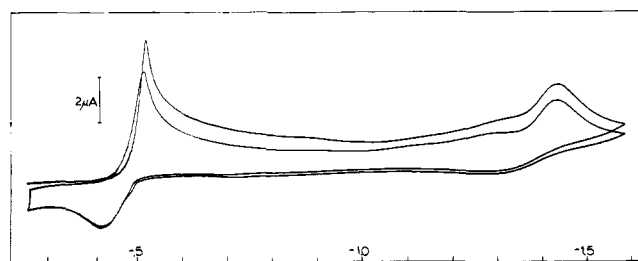


Figure 4. Cyclic voltammogram of 0.82 mM $\text{Cu}_2(\text{DBCP})_2$ in DMF at 130 mV/s. Two scans are represented.

diketonate $\text{Cu}(\text{II})$ chelates and a binuclear 1,3,5,7-tetraketonate in which the $\text{Cu}(\text{II})$ ions are separated³⁷ were investigated under identical conditions as used for the binuclear 1,3,5-triketonates. For both of these systems (mononuclear and uncoupled binuclear), the cyclic voltammograms are irreversible, and in most cases show no evidence of an anodic wave. In addition to these irreversible systems two binuclear 1,3,5-triketonates exhibit irreversible behavior. The chelate with the cyclopentane moiety in the "backbone", $\text{Cu}_2(\text{DBCP})_2$, exhibits irreversible behavior of an intermediate type; see Figure 4. There is a spiked cathodic wave, with a large peak separation dependent on scan rate. The trifluoromethyl-substituted triketonate, $\text{Cu}_2(\text{TFBA})_2$, demonstrates totally irreversible behavior, exhibiting no clear cathodic or anodic peak in the region from 0.0 to -1.6 V. The CV results for all of the reversible binuclear compounds are presented in Table II.

Table II also includes the pertinent polarographic results obtained on the identical solutions used in the CV work. In Figure 5 the standard polarographic plot of $\log(i/i_d - i)$ vs. potential is presented for $\text{Cu}_2(\text{BAA})_2$. Similar results are obtained for each of the five reversible systems. The value of i_d and results of $\log(i/i_d - i)$ vs. potential near $E_{1/2}$ are consistent with the transfer of two electrons per molecule. The logarithmic plot deviates markedly from linearity at potentials removed from $E_{1/2}$ and gives an S-shaped curve over the entire potential range. Such behavior is indicative of a complex, mechanistic control of the overall reversible redox process. Fitting of this curve on the basis of a mechanistic model will be presented in the Discussion.

The controlled potential electrolysis (CPE) of the five reversible systems was performed in order to accurately measure the number of electrons transferred. The potential used was more negative than the $\text{Cu}(\text{II})$ reduction wave by about 0.2 V, but much more positive than the ligand related reduction. Three of the compounds ($\text{Cu}_2(\text{DBA})_2$, $\text{Cu}_2(\text{DANA})_2$, and

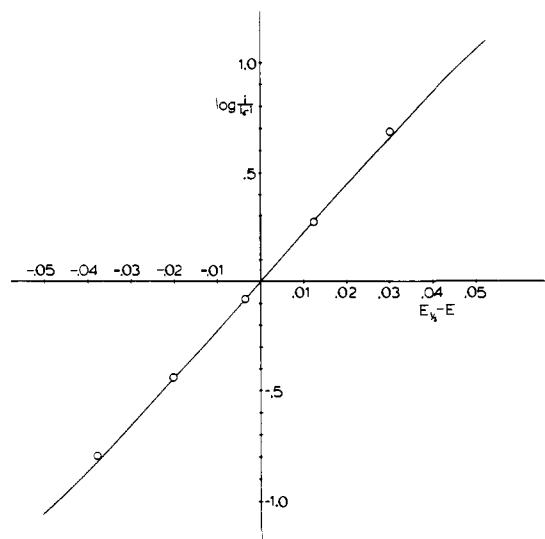


Figure 5. Plot of $\log(i/(i_d - i))$ vs. $E_{1/2} - E$ from the polarographic reduction of $\text{Cu}_2(\text{BAA})_2$. The solid line is theoretically derived using eq 10. The circles are experimental points.

Table II. Cyclic Voltammetric and Polarographic Results for the Five Bis(1,3,5-triketonato)dicopper(II) Complexes That Exhibit Reversible Reduction

compd	cyclic voltammetry			polarography	
	$E_{1/2}$, V vs. SCE	separation, mV ^a	H_c/H_a ^b	log plot ^c slope	D , cm ² /s $\times 10^6$
$\text{Cu}_2(\text{ANAA})_2$	-0.65	42	1.08	44	5.3
$\text{Cu}_2(\text{BAA})_2$	-0.48	42	1.02	46	4.5
$\text{Cu}_2(\text{BPA})_2$	-0.49	43	1.03	47	5.2
$\text{Cu}_2(\text{DANA})_2$	-0.52	42	1.03	49	6.0
$\text{Cu}_2(\text{DBA})_2$	-0.46	42	0.97	46	5.5

^a Peak separation equals the difference between the potentials of the anodic and cathodic peaks. ^b Ratio of the cathodic to anodic peak heights. ^c Slope of the potential vs. $\log i/i_d - i$ plot.

$\text{Cu}_2(\text{BPA})_2$ exhibit straightforward exponential decay characteristic of the transfer of *two* electrons per molecule, i.e., one electron per Cu(II). The other two compounds, $\text{Cu}_2(\text{BAA})_2$ and $\text{Cu}_2(\text{ANAA})_2$, behave in a more complex manner. Initial electrolysis of these two at 0.2 V more negative than the CV Cu(II) reduction results in the transfer of slightly more than 0.5 electron per molecule. The CV of the resulting solution showed none of the original electroactive Cu(II) species, but did contain a new species that reduces somewhat irreversibly at about -0.9 V. This species was not present, of course, in the original solution. Subsequent CPE of the new species at about -1.1 V yielded the transfer of slightly less than 1.5 e⁻ per molecule of the original species. Thus, the net result of the two CPE is the transfer of 2 e⁻ per molecule. These results are presented in Table III. The plot of the ratio of the current at a given time (*i*) to the initial current (*i*₀) vs. Q/FcV , which corresponds to the number of electrons transferred per molecule at -0.7 V, is given in Figure 6. The two types of behavior are readily apparent.

The CPE results for $\text{Cu}_2(\text{BAA})_2$ and $\text{Cu}_2(\text{ANAA})_2$ are consistent with the following mechanism. The net result is the transfer of 0.5 e⁻ per molecule at -0.7 V.

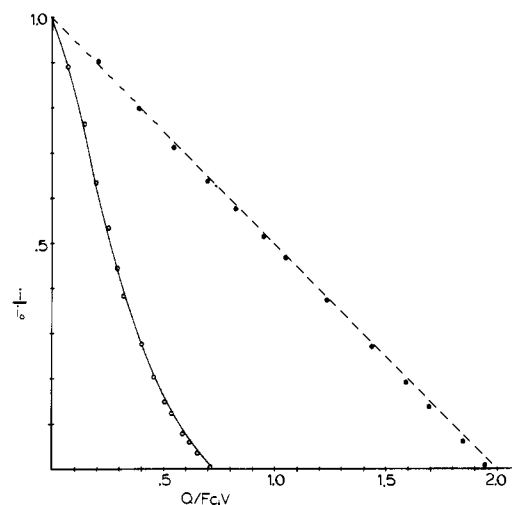
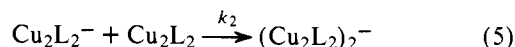
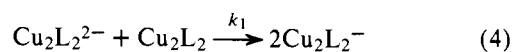
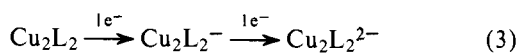


Figure 6. Current divided by initial current vs. Q/FC_1V , where Q is number of coulombs, F is Faraday's constant, C_1 is the initial concentration, and V is the volume. Q/FC_1V is a ratio equivalent to electrons per molecule. The dashed line represents the theoretically expected plot for a two-electron reduction. The solid circles are experimental from the reduction of $\text{Cu}_2(\text{BPA})_2$. The solid line is computer generated assuming formation of a dimer (see text). The open circles are experimental points from the reduction of $\text{Cu}_2(\text{BAA})_2$.

Table III. Potential and Number of Electrons Transfers per Molecule for the Controlled Potential Electrolysis of Some Bis(1,3,5-triketonato)dicopper(II) Complexes

compd	first stage		second stage	
	potential, V vs. SCE	e ⁻ /molecule	potential, V vs. SCE	e ⁻ /molecule
$\text{Cu}_2(\text{ANAA})_2$	-0.80	0.77	-1.2	1.30
$\text{Cu}_2(\text{BAA})_2$	-0.70	0.72	-1.1	1.35
$\text{Cu}_2(\text{BPA})_2$	-0.70	2.03		
$\text{Cu}_2(\text{DANA})_2$	-0.72	1.94		
$\text{Cu}_2(\text{DBA})_2$	-0.70	2.07		

The proposed reactions 3, 4, and 5 for the formation of a singly reduced dimer, $(\text{Cu}_2\text{L}_2)_2^-$, were computer simulated using the three rate expressions:

$$\Delta[\text{Cu}_2\text{L}_2] = K[\text{Cu}_2\text{L}_2] \quad (6)$$

$$\Delta[\text{Cu}_2\text{L}_2^-] = k_1[\text{Cu}_2\text{L}_2][\text{Cu}_2\text{L}_2^{2-}] \quad (7)$$

$$\Delta[(\text{Cu}_2\text{L}_2)_2^-] = k_2[\text{Cu}_2\text{L}_2][\text{Cu}_2\text{L}_2^-] \quad (8)$$

The first is a rate expression for the rate of reduction of the Cu(II), Cu(II) species at the electrode. Because the concentrations of intermediates are always very low, no other reduction need be considered as contributing to the current. Equations 7 and 8 are the simple rate expressions for the formation of the singly reduced monomer, Cu_2L_2^- , and the singly reduced dimer, $(\text{Cu}_2\text{L}_2)_2^-$. Suitable adjustments were made to the concentrations of each species after each iteration. Because the simulation iterated every second the rate constants derived are only approximate. A good fit to the experimental data plotted as i/i_0 vs. Q/FcV for the reduction of $\text{Cu}_2(\text{BAA})_2$ at -0.7 V is shown in Figure 6. To arrive at the calculated curve K was set to 0.001 s⁻¹, k_1 to 1.7×10^4 s⁻¹ mol⁻¹, and k_2 to 1.5×10^4 s⁻¹ mol⁻¹. These values indicate that the reactions are relatively fast, though the shape of the curve is somewhat insensitive to variations of k_2 . K sums up several experimental conditions including stir rate, electrode area, etc., as well as other properties such as diffusion rate.

Electrolysis of $\text{Cu}_2(\text{BAA})_2$ and $\text{Cu}_2(\text{ANAA})_2$ at -1.1 and -1.2 V, respectively, yields the expected transfer of 2 e⁻ per

molecule without any indication of an intermediate step. Thus, these two compounds behave as the others if the electrolysis potentials are about 0.6 V beyond the $E_{1/2}$.

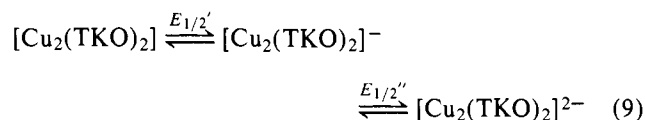
During electrolysis of $\text{Cu}_2(\text{BPA})_2$, $\text{Cu}_2(\text{BAA})_2$ and $\text{Cu}_2(\text{ANAA})_2$ samples were removed to an EPR spectrometer. The solutions initially were EPR silent. During the electrolysis a weak signal characteristic of Cu(II) was noted. After the electrolysis was complete the Cu(II) signal remained, though weak. No attempt was made to ascertain the concentrations required to produce such a signal, though it is suspected that the signal is due to minor products of decomposition of the Cu(I)-Cu(I) product.

Discussion

The principal, identifying properties¹⁴ of type 3 coppers in copper proteins follow: they are EPR silent in the oxidized state, the reduction potential for the oxidized form is quite positive, they apparently undergo reversible two-electron transfer, and they have no unusual electronic spectral properties (only a band at 330 nm tentatively assigned to ligand to metal charge transfer). Largely owing to their magnetic and spectral properties, the donor atoms and structural features of type 3 coppers remain a mystery. It is quite well accepted, however, that the site contains two copper atoms juxtaposed and involved in superexchange interactions strong enough to result in diamagnetism at room temperature. Our interest in type 3 copper grew out of the observation that some binuclear copper(II) 1,3,5-triketones are diamagnetic and EPR silent at room temperature and also appear to undergo two-electron reductions to Cu(I), Cu(I).^{20,31} In addition, these compounds do exhibit very intense absorption in the 300–360-nm region as well as a weak d-d band at about 640 nm.⁴² Because of these similarities, the copper triketones may mimic certain aspects of the enzymatic coppers. Of considerable interest to us is the possibility that they mimic the reversible, single potential two-electron transfer which can give rise to multielectron reactions. The advantage to be gained in such reactions is that two-electron transfer at a single potential avoids radical intermediates and the deleterious effects they have on products and yields. Presumably, the enzymatic reduction of O_2 to H_2O takes place by way of multielectron transfer steps.¹⁴

Since we have obtained preliminary electrochemical evidence for reversible, single-potential, two-electron transfer in bis(1,3,5-triketonato)dicopper(II) complexes, this detailed electrochemical study was undertaken to investigate more precisely the nature of the transfer and the effect of molecular variations. A major point to be determined was whether the unusual electrochemical behavior observed for $\text{Cu}_2(\text{BAA})_2$ ³¹ is typical of a class of compounds or simply a fortuitous situation restricted to one compound.

The results of this study have uncovered five bis(1,3,5-triketonato)dicopper(II) complexes that undergo reversible, two single-electron sequential transfers at the same potential as evidenced by polarographic and CV data. In each case, the cathodic and anodic peak separation of the reversible systems is 42 mV and is invariant with scan rate. We have communicated this result for $\text{Cu}_2(\text{BAA})_2$ ³¹ and noted that 42 mV is exactly the separation predicted by Polcyn and Shain⁴³ for the reversible *sequential* transfer of two electrons in which the two potentials are identical. This report was the first experimental confirmation of the Polcyn and Shain theory. The four other compounds, reported herein, that exhibit reversible two-electron reduction have essentially identical CVs except that the $E_{1/2}$'s are different. This observation argues strongly for the premise that this unique electrochemical behavior is a property of a class of compounds rather than a curiosity associated with only one compound. The sequential process may, in general, be represented as



in which $E_{1/2}' = E_{1/2}''$. The net result, of course, is the transfer of two electrons at a single potential.

Further evidence for sequential transfer of two electrons at the same potential comes from the polarographic results. First, the diffusion current corresponds to the transfer of two electrons according to the Lingane-Loveridge equation using $D = 4.5 \times 10^{-6} \text{ cm}^2/\text{s}$ as determined from the cyclic voltammograms.⁴⁴ Second, the characteristics of the $\log(i/i_d - i)$ vs. potential plots (Figure 5) are consistent with the above mechanism of sequential two-electron transfer, i.e., the slope of the plot near $E_{1/2}$ is approximately 46 mV and the plot is not linear at potentials removed from $E_{1/2}$. The experimental plot is accurately reproduced by deriving an expression from the boundary value problem used by Polcyn and Shain⁴³ for the polarography of two sequential, one-electron reversible, single-potential reductions. The result is

$$\frac{i}{i_d} = \frac{1 + \theta/2}{1 + \theta + \theta^2}, \quad \theta = 10^{16.903(E-E^0)} \quad (10)$$

where i is the observed current, i_d is the diffusion current, E is the applied potential, and E^0 is the formal half-wave potential. This equation is essentially identical with an earlier one derived by Müller.⁴⁵ From this treatment the predicted slope of $\log(i/i_d - i)$ vs. E near $E_{1/2}$ is 45 mV, extremely close to our experimental values of $46 \pm 3 \text{ mV}$.

The controlled potential electrolysis (CPE) data are also consistent with the transfer of two electrons per molecule in these binuclear complexes. Three of the five reversible systems ($\text{Cu}_2(\text{DBA})_2$, $\text{Cu}_2(\text{DANA})_2$, and $\text{Cu}_2(\text{BPA})_2$) give straightforward CPE results with no complications. However, $\text{Cu}_2(\text{BAA})_2$ and $\text{Cu}_2(\text{ANAA})_2$ exhibit unusual two-step electrolyses, the sum of which corresponds to the transfer of two electrons per molecule. The first stage of these electrolyses (at -0.7 V) transfers slightly more than 0.5 e^- /molecule and generates a new electroactive species in solution. The second stage CPE (at -1.1 V) reduces the new species by transferring slightly less than 1.5 e^- /molecule.

The transfer of about 0.5 electron per molecule (approximately 0.25 $e^-/\text{Cu(II)}$) requires the association of four or more Cu(II) ions in an electroactive unit. The simplest explanation for this curious behavior is the formation of a dimer during the -0.7 V electrolysis, the net result of which is the transfer of one electron per tetranuclear species. All of the experimental data are consistent with this interpretation and the mechanism represented by eq 3–5. In addition, there is extremely good agreement between the experimental data and the computer simulation of the proposed mechanism for reasonable values of the pseudo-rate constants. Although nothing is known of the nature of such a tetranuclear species, it is perhaps significant that we have determined the crystal structure of a bis(1,3,5-triketonato)dicopper(II) complex in which the structural unit is tetranuclear dimer.²³ Thus, at least in the solid state and with completely oxidized complexes, there is precedent for association of binuclear molecules. There appears to be a real structural control over this process inasmuch as the only two compounds that exhibit it are the only two with methyl substituents.

There is no indication that this partial reduction and association observed in the CPE of $\text{Cu}_2(\text{BAA})_2$ and $\text{Cu}_2(\text{ANAA})_2$ is taking place in the CV or polarographic experiments. This is not surprising since CPE is a bulk technique in stirred solutions while in CV and polarography the electrochemical processes take place very near the electrode in static solutions. As a result, the reduced product in CV and polarography would

not have the opportunity to react with the oxidized starting material in the bulk solution. On the other hand, the reduced product in CPE is driven into the bulk solution where it could interact with the starting material.

During our preliminary studies it became apparent that the nature of the electrochemical behavior observed for a particular binuclear triketonate depends upon the type of substituent group bonded to the ligand "backbone". For example, $\text{Cu}_2(\text{BAA})_2$ is electrochemically very well behaved while $\text{Cu}_2(\text{BTFAA})_2$ is not. The difference between them is that $\text{Cu}_2(\text{BAA})_2$ contains a $-\text{CH}_3$ in the 5 position and $\text{Cu}_2(\text{BTFAA})_2$ a $-\text{CF}_3$ group. Similar strong differences in electrochemical behavior exist between $\text{Cu}_2(\text{DBA})_2$ and $\text{Cu}_2(\text{DBCP})_2$. Here the structural difference is that there is an ethylene linkage across the 2 and 4 positions resulting in a pentane ring fused to the triketonate moiety. The reduction of $\text{Cu}_2(\text{DBA})_2$ is ideally reversible while $\text{Cu}_2(\text{DBCP})_2$ is, at best, quasi-reversible. The special function of the substituent groups in the electrochemical process is not known. However, in each of the five complexes that undergo reversible, two-electron transfer at least one substituent on the triketonate is phenyl or substituted phenyl. Substituent effects will obviously have to be kept in mind when attempting to design complexes with particular electrochemical properties.

One of our continuing interests in the polynuclear transition metal complexes of β -polyketonates is whether the cooperative interaction between the metal centers has a marked influence on their reactivity. In order to determine the importance of the cooperative interaction in the reversible, multielectron transfer described above we have also investigated (1) some mononuclear 1,3-diketonoate copper(II) complexes and (2) a binuclear 1,3,5,7-tetraketonate in which the Cu(II) ions are not adjacent, i.e., they are about 6 Å apart. In both of these cases the donor atoms and the gross coordination sphere geometries of the Cu(II) ions are similar to those of the 1,3,5-triketonoate Cu(II) ions. The electrochemistry of the mononuclear 1,3-diketonoates, however, is vastly different from that of the binuclear 1,3,5-triketonoates. One, $\text{Cu}(\text{BA})_2$, yields an unsymmetric CV with a large peak separation varying from 85 to 185 mV at scan rates of 5.5 and 228 mV/s, respectively. The other, $\text{Cu}(\text{DBM})_2$, yields a CV with no oxidation wave. This is undoubtedly due to reduction to Cu^0 and amalgam formation. In other words, both are irreversible. In addition, there is ample evidence that polarographic reduction of bis(1,3-diketonoate)-copper(II) complexes is extremely irreversible and proceeds to Cu^0 with formation of copper-mercury amalgam.³⁵

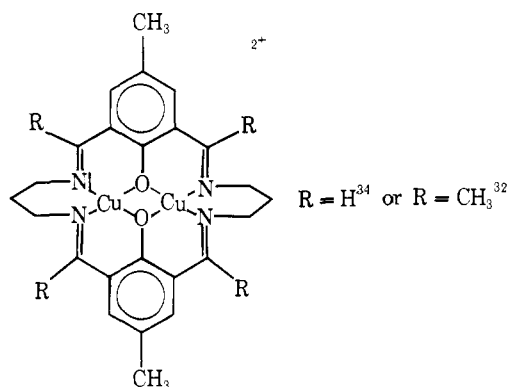
The CV of the binuclear 1,3,5,7-tetraketonate $\text{Cu}_2(\text{H}_2\text{DBAA})_2$ indicates a completely irreversible reduction in that no anodic wave is observed. The fact that the Cu(II) ions are not adjacent has been established by magnetic susceptibility measurements, i.e., the magnetic moment per Cu(II) is 1.83 μ_B down to 77 K.³⁷ Thus, although this is a binuclear Cu(II) complex, it is devoid of any significant cooperative interactions between the metal ions.

A comparison of the electrochemical results for the mononuclear diketonoates, the binuclear tetraketonate, and the binuclear triketonoates leads to a preliminary conclusion; in order to observe reversible, two-electron transfer at a single potential it is necessary to have two, adjacent and presumably strongly interacting Cu(II) ions. In the case of electron transfer, the cooperation interaction between metal ions appears to be quite important.

Since a primary experimental measurement of the strength of the interaction between paramagnetic metal ions is magnetic susceptibility, it is reasonable to ask if there is any correlation between the magnetic properties and electron transfer in binuclear complexes. No detailed correlation can be attempted at this point owing to the great paucity of data. However, a few studies pertinent to this discussion have been reported. One of

the first reported involves the pyrazine bridged complexes studied originally by Taube⁴⁶ and later by Meyer.⁴⁷ These binuclear complexes exhibit very weak magnetic interactions and undergo two single-electron transfers with widely separated potentials. In other words, it is quite easy to produce the mixed valence state complex containing pyrazine bridged Ru(II),Ru(III), for example.

The electrochemistry of a much different type of binuclear complex, a class more closely related to the 1,3,5-triketonoates, has been reported by Addison³² and Gagne.³⁴ These binuclear macrocyclic complexes which were originally characterized by Robson⁴⁸ are represented schematically below. The mag-



netic interaction between metal ions is quite strong in these complexes as indicated by room temperature magnetic moments of about 0.60 μ_B per Cu(II).⁴⁸ In this regard, they are reasonably similar to the triketonoates. The electrochemistry, however, is quite different. In the macrocyclic complex where $\text{R} = \text{CH}_3$, Addison³² observed only a one-electron reversible reduction to a Cu(II),Cu(I) mixed valence state complex. Presumably the potential for adding the second electron is very negative. For the complex where $\text{R} = \text{H}$, Gagne³⁴ observed two stepwise, one-electron reductions which are quasi-reversible. The potential separation between the two reductions is 0.39 V. Gagne was able to isolate the mixed valence state complex that results from electrolysis at a potential halfway between the two reductions.

Thus, although there are tremendous differences between the bridged pyrazine complexes and the binuclear macrocyclics, their overall redox behavior is fairly similar. In both cases the mixed valence complexes are readily prepared by electrochemical means. It is reasonable to assume that this behavior depends in some manner on cooperative interactions between the metal ions, albeit the strength of this interaction must vary between the two systems by a great deal. The electrochemical behavior of the triketonoates is all the more intriguing in light of these two systems since there is no thermodynamic preference for the mixed valence state intermediate. Then, if the nature of the cooperative interaction plays a role in the electrochemistry the differences between the triketonoate and the other systems would have to be partially attributed to the great strength of the interaction in the triketonoates. Although quantitative statements are not possible at this time, one conclusion is obvious. *An interaction between two metal ions does not in itself imply that electron transfer will take place in a stepwise, one-electron manner at two different potentials.*

It is entirely possible that a combination of factors is required to observe multielectron transfer at a given potential. One factor besides the cooperative interaction between metal ions may be associated with structural details. The triketonoates and the macrocyclics which exhibit such different electrochemical behavior have some important structural similarities and differences. The single-crystal X-ray structure determinations of two of the compounds that exhibit the reversible, sequential electron transfer, $\text{Cu}_2(\text{BAA})_2$ ²³ and Cu_2 -

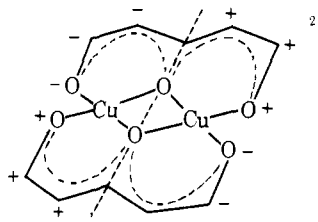
Table IV. Polarographic Reduction Potentials as a Function of Substituent Groups for Some 1,3-Diketonate Chelates

M	electrode process	$E_{1/2}$, V vs. SCE, vs. R				ref
		R = CF ₃	C ₆ H ₅	CH ₃	C(CH ₃) ₃	
Ru	III \rightleftharpoons II ^a	+0.726 ^d	-0.501	-0.728	-1.038	51
Cr	III \rightleftharpoons II ^b	-0.40	-1.26	-1.73	(-1.96) ^e	52
Cu	II \rightarrow 0 ^c	+0.038	-0.379	-0.502	-0.687	35

^a In DMF except where noted. ^b In Me₂SO and 85% dioxane-15% water. ^c In 75% dioxane-25% water. ^d In acetonitrile. ^e Calculated from data in ref 51.

(DANA)₂,⁴⁹ have been completed in our laboratories. The coordination geometries about the Cu(II) ions are essentially identical in the two compounds; the most pertinent structural features have been summarized above. It is reasonable to assume that the other bis(1,3,5-triketonato)dicopper(II) complexes would have very similar features. The structure of the macrocyclic complexes has apparently been completed, but the results have not been published.⁴⁸ The preliminary results indicate that the donor atoms are coplanar and that the Cu(II) ions are slightly out of the plane in typical square pyramidal geometry with Cl⁻ in the fifth coordination site. Thus, the similarities between the two classes of binuclear complexes are in the coordination geometry and the internal bridging system. The major structural differences between the triketonate and macrocyclic complexes are most probably due to the restriction imposed by the diamine linkages on the external Cu-donor atom bond angle (\angle O-Cu-O = 94° vs. \angle N-Cu-N \approx 90°) and on any possible distortion from planarity. For obvious reasons, the structural differences are most important in this discussion.

There has been considerable comment recently about the desirability of the copper sites in proteins being able to accommodate both Cu(II) in its preferred square planar and Cu(I) in its preferred tetrahedral environments.⁵⁰ It is thought that intermediate or flexible geometries would facilitate electron transfer in Cu(II) \rightleftharpoons Cu(I) processes. Although the Cu₂(1,3,5-triketonato)₂ complexes are rigidly planar in the solid, oxidized state, it is possible that the molecule distorts on going from Cu(II),Cu(II) to Cu(I),Cu(I). Since each triketonate moiety is conjugated, it is unlikely that it undergoes significant distortion from planarity. However, the complex as a whole may distort as shown below where the + and - signs indicate movement out of the original molecular plane. The



effect of this movement is to rotate each triketonate moiety in opposite directions about an axis through the bridging carbonyl groups. Since the external O-Cu-O angle is already 94° before the distortion, the rotation would result in significant tetrahedral character about the coppers. Such a distortion would not appear nearly as feasible for the macrocyclic complexes and may account for some of the electrochemical differences observed.

While there are some striking similarities between the type 3 coppers and the triketonates, there is a very important difference. The reduction potentials of the type 3 copper as determined by chemical redox titrations are quite positive while

binuclear Cu(II) triketonates have relatively negative reduction potentials (Table II). As a result of this difference, one cannot expect that the triketonates studied to date will model the reactivity of the enzymatic coppers. On the other hand, it is well known that the reduction potential of a given metal ion can be made to undergo very large shifts by rather subtle changes in the ligands. Therefore, by judicious molecular design it may be possible to prepare binuclear complexes with appropriate magnetic and electrochemical properties and also to more closely approach the reduction potential of the enzymatic coppers. Several metal 1,3-diketonate systems graphically illustrate how sensitive the reduction potential of the metal ion is to the substituent groups in the 1 and 3 positions. Some results are summarized in Table IV. In the cases of tris(1,3-diketonato)M(III) where M = Ru⁵¹ and Cr⁵² the III \rightleftharpoons II reduction is reversible and the $E_{1/2}$ has a linear dependence upon the substituent group electronic effect as measured by the Hammett constant. Also, the potential is quite sensitive to donor atom variation as evidenced by the fact that substitution of S atoms for the O atoms in Ru(acac)₃ to produce Ru(SacSac)₃ changes the reduction potential from -0.73 to -0.01 V.⁵¹ In addition to the diketonates, there are ample examples in nitrogen donor atom complexes in which the metal ion redox potential varies tremendously with the nature of the nitrogen, degree of unsaturation in the ligand, etc.^{53,54}

In any of the systems studied, it is not uncommon for the potential of a given redox reaction to vary by 1-2 V depending upon seemingly minor changes in the ligand. Thus, it certainly is within the realm of possibility that binuclear Cu(II) complexes related to the triketonates can be prepared that exhibit both magnetic and electrochemical properties similar to the type 3 coppers. Part of our emphasis in future studies will be to prepare complexes with more positive reduction potentials that exhibit multielectron transfer at a single potential. Obviously such complexes would be much better mimics for type 3 coppers.

At the outset of this study we were aware that these binuclear Cu(II) complexes mimic the magnetic properties of type 3 coppers in copper enzymes. At this point it seems likely that they also mimic the electron transfer properties with regard to the transfer of two electrons at a given potential. We are currently investigating the oxidase activity of the triketonates, specifically their catecholase activity, to determine if the mimicking properties will extend to reactivity. Preliminary results will be reported soon.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the National Science Foundation, Grant CHE-77-02664. Several useful discussions with Professor R. R. Schroeder contributed greatly to this paper.

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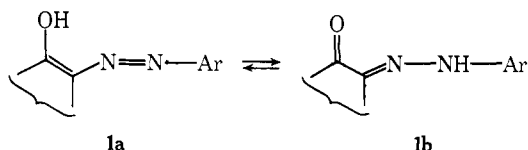
Resonance Interactions in Metal Chelates of *o*-Hydroxyazo Compounds. Crystal Growth, Structure, and Spectra of 1-(2-Pyridylazo)-2-naphtholatochlorocopper(II)

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Abstract: Single crystals of the title compound have been grown by a modified gel diffusion technique. The compound crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 15.817(3) \text{ \AA}$, $b = 8.255(1) \text{ \AA}$, $c = 10.404(3) \text{ \AA}$, $\beta = 103.46(2)^\circ$, $V = 1321.1(5) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd}} = 1.746 \text{ g cm}^{-3}$, $d_{\text{meas}} = 1.71 \text{ g cm}^{-3}$. Intensities were collected by counter methods on a card-controlled diffractometer operating in the θ - 2θ mode and employing Mo $K\alpha$ radiation. The structure, including hydrogen atoms, was solved by the heavy-atom method and refined by full-matrix least squares to $R_1 = 0.031$ and $R_2 = 0.040$. The pyridylazonaphthol ligand (PAN) coordinates to copper as a planar tridentate chelate with strong covalent bonds through the pyridyl nitrogen (1.991 (2) \AA), the azo nitrogen adjacent to the naphthol group (1.964 (2) \AA), and the naphthol oxygen (1.984 (2) \AA). In the fourth position of an approximately square planar array about copper is found a strongly bound chloride ion (2.263 (1) \AA). Pairs of these Cu(PAN)Cl units combine to form a centrosymmetric dimer through weak bridging Cu-Cl bonds (2.647 (1) \AA) in the axial or fifth coordination site. The net coordination around copper is approximately square pyramidal, with the copper displaced 0.145 \AA from the equatorial plane toward the axial chlorine atom. The possibility for delocalization of electron density in anions of *o*-hydroxyazo compounds is discussed. The bond lengths observed in the ligand in Cu(PAN)Cl agree well with those predicted for a resonance hybrid involving roughly equal contributions from 12 canonical structures. Qualitative single-crystal polarized reflectance measurements indicate possible directions for the molecular transition moments.

The tautomeric equilibria of *o*-hydroxyazo compounds involve hydroxyazo, **1a**, and quinonehydrazone, **1b**, forms. The



factors affecting these equilibria have been studied using a variety of chemical,¹ spectroscopic,²⁻⁸ and crystallographic techniques.⁹⁻¹¹ These compounds are known to act as polydentate ligands to form chelates with a large number of metal ions.^{12,13} In these chelates, however, the ligands exist in their anionic form, and the tautomeric forms **1a** and **1b** of the ligand collapse to canonical forms **2a** and **2b** of a single anion structure. There is some question as to the extent of delocalization