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Cyclic Voltammetric Wave Symmetry and Peak Current Calculations as Confirmation of the Reversible, Sequential Transfer of Two Electrons at Very Similar Potentials in Bis(1,3,5-triketonato)dicopper(II) Complexes and Their Diamine Schiff Bases. Comparison between Mono- and Binuclear Complexes and a Study of the Effect of Na^+ and Li^+ on the Electron-Transfer Process

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The cyclic voltammetry of a series of related mono- and binuclear Cu(II) complexes of 1,3,5-triketonates and their diamine Schiff-base derivatives has been investigated in a scan range of greater than 10^3 V/s in both the presence and absence of simple cations such as Na^+ and Li^+. In all cases the mononuclear complexes exhibit irreversible electron transfer while the binuclear complexes in both the presence and absence of simple cations exhibit reversible electron transfer over a wide scan rate range. In the absence of Na^+ or Li^+ there is one CV wave in the 0- to −1.7-V region for each of the binuclear complexes, which occurs between about −0.8 and −1.1 V vs. SSCE. On the basis of wave symmetry and peak current calculations, this wave is attributed to a reversible, one-electron transfer. Addition of an excess of Na^+ or Li^+ results in a +300-mV shift of the wave, a large increase in the peak currents, a decrease in ΔE_p, and a decrease in $E_{pc} - E_{pc/2}$. Peak current calculations together with ΔE_p and $E_{pc} - E_{pc/2}$ values confirm that the electron-transfer process is the reversible, sequential transfer of two electrons at very nearly the same potentials. The single wave in the 0- to −1.7-V region occurs from about −0.4 to −0.8 V vs. SSCE, depending upon the ligand. In each case the shapes of the CV waves for the simple binuclear triketonates and the diamine Schiff-base derivatives are virtually the same under identical experimental conditions. The only significant difference between the CV properties of the two classes is that the Schiff-base complexes have reduction potentials about 150 mV more negative than the parent triketonate complex.

Introduction

Identification and design of species capable of reversibly transferring two or more electrons at the same or very nearly the same potential is important in the reaction chemistry of small molecules since virtually all of the useful reactions of small molecules whether stoichiometric, catalytic, or enzymatic involve the transfer of two or more electrons. Therefore, it is essential that the electron-transfer reagents, catalysts, or enzymes be capable of transferring two or more electrons at very similar potentials so as to avoid the deleterious effects of radical intermediates that result from single-electron transfer. This is presumably the reason that enzymes associated with the electron-transfer reactions of small molecules contain two or more metal ions at or near the reaction site.[1] Although it is not known what effect the juxtaposition of the metal ions and resulting interactions have upon electron-transfer mechanisms in multimetal enzymes, it does seem eminently reasonable to assume that such structural and electronic factors are critical in determining the binding and electron-transfer characteristics. It seems especially reasonable in the enzymes containing the so-called type 3 copper centers since two copper(II) ions are known to be close enough to be completely antiferromagnetically coupled at room temperature[2] and such enzymes are typically involved in the four-electron reduction of O_2 to H_2O.[1] Solomon and co-workers[3] have argued convincingly that an endogenous protein bridge between the Cu atoms in the binuclear type 3 site is phenolate or carboxylate oxygen yielding a Cu–Cu distance of about 3.6 Å. The mixed-valence state $Cu^{II}Cu^{I}$ resulting from a one-electron reduction seems to be accessible in hemocyanin, implying a considerable redox potential difference between the two coppers although the site is physiologically involved in the two-electron reduction of $O_2 \rightarrow O_2^{2-}$.[3]

A fundamental reason for studying polynuclear complexes is to determine whether the presence of two or more metal ions held in juxtaposition by the ligands results in useful chemical properties not observed in mononuclear analogues. Since redox behavior is so important in the chemical properties of transition-metal complexes, we have chosen to investigate the electrochemical properties of poly-vs. mononuclear complexes as an experimental means of assessing the chemical significance of multimetal centers. There are several advantages of employing ligands based on the β-polyketones in this regard. These include the fact that homologous series containing one, two, three, etc. metal ions per molecule can be designed from homologous ligands, the complexing ability of these ligands is such that many different metal ions systems can be envisioned, and one can easily change substituent groups and donor atoms as a means of controlling chemical and physical properties. For these reasons, we have concentrated our attention on systems closely related to the β-polyketonates.

The question of what role is played by structural and electronic factors in determining the nature of multielectron transfer in polynuclear complexes is one that has not received much attention. The situation in which the redox centers are identical and totally noninteracting in polynuclear systems has been treated by Ammar and Saveant[4] and by Anson and co-workers.[5] In this case, statistical factors give rise to cyclic voltammetric waves that have peak separations and half-widths reminiscent of one-electron waves but with current values indicative of the number of electrons transferred per molecule. When the metal ions are close enough to interact magnetically and/or contain bridging ligands capable of transmitting a magnetic interaction, the usual observation is two separated redox processes for binuclear complexes. As a result, it is often possible to isolate mixed-valence complexes in these cases. Mixed-valence species have been isolated in such widely varying complexes as the pyrazine-bridged ruthenium compounds[6] where the metal–metal interaction is very weak to the

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(4) Ammar, B.; Saveant, J. M. *J. Electroanal. Chem.*

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binuclear macrocyclic phenol-based copper complexes[7] in which the magnetic interaction is quite strong.

The fact that even a strong magnetic interaction between metal ions in a binuclear complex is not a prerequisite for observing stepwise, one-electron transfers at two different potentials is illustrated by the electrochemical properties of the bis(1,3,5-triketonato)dicopper(II) complexes.[8] These complexes exhibit strong antiferromagnetic coupling ($-J \geq 800\ \mathrm{cm}^{-1}$) and undergo two reversible, sequential one-electron transfers at a single potential ($E_1 \cong E_2$).[9,10] The basis for this interpretation of the electrochemistry was the excellent agreement between the experimental data and the theory for overlapping CV waves developed by Shain and co-workers.[11,12] The cyclic voltammetry predicted for the reversible, sequential transfer of two electrons at the same potentials is characterized by a symmetric wave with $I_{pa}/I_{pc} = 1.0$, $I_{pc}/v^{1/2}$ constant, $\Delta E_p \cong 42$ mV, and $E_{pc} - E_{pc/2} \cong 42$ mV. These conditions were met quite well for bis(1,3,5-triketonato)dicopper(II) complexes, especially at relatively slow scans. It was determined that this electron-transfer process was extremely sensitive to the presence of Na^+ or similar simple cations and that, in the original work, Na^+ was introduced into the cell from an aqueous $NaNO_3$ salt bridge. Once this was realized, a detailed and controlled study of the effect of Na^+ was carried out.[10] A major conclusion was that Na^+ (or other simple cations) is complexed to Cu_2L_2, $Cu_2L_2^-$, and $Cu_2L_2^{2-}$, which accounts for a +300-mV shift in the CV wave upon addition of Na^+. An interpretation for the effect of Na^+ was presented as a set of complexation equilibria involving all three redox species. Interestingly, the only other binuclear molecule of which we are aware that exhibits $E_1 \cong E_2$ is a Pt^{II}_2 complex containing a formal Pt–Pt bond.[13] Hence, there are at least two systems, both with strong metal–metal interactions, that have very similar redox potentials for the two metal ions involved. At this point, the structural, electronic, and mechanistic factors that induce concerted two-electron transfer in binuclear complexes are essentially unknown. Before it is possible to systematically design molecules or moieties capable of multielectron transfer, it is necessary to gain an understanding of these factors. The current study using a series of closely related mono- and binuclear Cu(II) complexes was undertaken to investigate certain of these factors.

Experimental Section

I. Synthesis. A. Ligands. The general syntheses of the 1,3,5-triketones and the ethylenediamine Schiff-base derivatives have been reported.[14,15] The 1,3-propanediamine derivatives were prepared straightforwardly by substituting 1,3-propanediamine for ethylenediamine and using the same procedure. However, for the case of $H_4(BAA)_2$-1,3-pn, complete evaporation of the solvent followed by two recrystallizations from acetone is suggested in order to obtain a pure product.

B. Complexes. Bis[2,2-dimethyl-3,5,7-octanetrionato(2–)]dicopper, $Cu_2(PAA)_2$.[16] Equimolar quantities of the ligand, H_2PAA, and $Cu(C_2H_3O_2)_2{\cdot}H_2O$ were dissolved in methanol in separate beakers, and the resultant mixture was heated to boiling. The solutions were mixed, heated for several minutes, and cooled. The product forms as small dark green crystals that crumble to a powder upon air-drying on a filter. The product may be recrystallized from $CHCl_3$; it sublimes at about 230 °C and decomposes at about 270 °C. Anal. Calcd for $Cu_2C_{20}H_{28}O_6$: C, 48.88; H, 5.70. Found: C, 48.73; H, 5.84. Mass spectrum: parent ion 490 *m/e*.

[7,7′-(1,2-Ethanediyldinitrilo)bis(2,2-dimethyl-3,5-octanedionato)(4–)]dicopper, $Cu_2(PAA)_2en$. The ligand, $H_4(PAA)_2en$ (0.503 g, 1.28×10^{-3} mol), was dissolved in 100 mL of $CHCl_3$, and the resultant mixture was added dropwise to a solution of 0.520 g (2.60×10^{-3} mol) of $Cu(C_2H_3O_2)_2{\cdot}H_2O$ in 100 mL of CH_3OH. A lime green powder formed upon addition of 0.71 mL of triethylamine dissolved in 30 mL of CH_3OH. The reaction mixture was stirred for about 1 h after which the solid was isolated, washed well with CH_3OH, and air-dried. The solid can be recrystallized from benzene; mp 249–51 °C. Anal. Calcd for $Cu_2C_{22}H_{32}N_2O_4$: C, 51.25; H, 6.26; N, 5.43; Cu, 24.65. Found: C, 51.14; H, 6.22; N, 5.35; Cu, 24.41.

[7,7′-(1,3-Propanediyldinitrilo)bis(2,2-dimethyl-3,5-octanedionato)(4–)]dicopper–0.5-Benzene, $Cu_2(PAA)_2$-1,3-pn·C_6H_6. The same procedure used to prepare $Cu_2(PAA)_2en$ was used to prepare $Cu_2(PAA)_2$-1,3-pn. The product was isolated as dark green crystals. The product was recrystallized from benzene. Anal. Calcd for $Cu_2C_{26}H_{37}H_2O_4$: C, 54.91; H, 5.56; N, 4.93; Cu, 22.35. Found: C, 55.56; H, 6.94; N, 4.80; Cu, 22.24.

[7,7′-(1,2-Ethanediyldinitrilo)bis(2,2-dimethyl-3,5-octanedionato)(2–)-$N^7,N^{7'},O^5,O^{5'}$]copper, $CuH_2(PAA)_2en$-N_2O_2. Triethylamine, 0.7 mL, in 10 mL of $CHCl_3$ was added to 0.494 g (1.26×10^{-3} mol) of the ligand, $H_4(PAA)_2en$, dissolved in 20 mL of $CHCl_3$. A solution of $Cu(C_2H_3O_2)_2{\cdot}H_2O$, 0.250 g ($1.26 \times 10^{-3}$ mol), in 50 mL of CH_3OH was added dropwise to the ligand solution and the mixture stirred for about 1 h at room temperature. At least half of the solvent was removed at reduced pressure. A purple-brown solid was isolated, washed well with H_2O, and air-dried; mp 122–25 °C. Anal. Calcd for $CuC_{22}H_{34}N_2O_4$: C, 58.19; H, 7.55; N, 6.17; Cu, 13.99. Found: C, 58.09; H, 7.70; N, 6.15; Cu, 13.60.

[7,7′-(1,3-Propanediyldinitrilo)bis(2,2-dimethyl-3,5-octanedionato)(2–)-$O^3,O^{3'},O^5,O^{5'}$]copper, $CuH_2(PAA)_2$-1,3-pn-O_2O_2. A solution of 0.247 g (1.24×10^{-3} mol) of $Cu(C_2H_3O_2)_2{\cdot}H_2O$ in 100 mL of CH_3OH was added to a solution of $H_4(PAA)_2$-1,3-pn (0.502 g, 1.24×10^{-3} mol) in 50 mL of $CHCl_3$ at room temperature. This solution was stirred for about 30 min and the volume reduced to 30–40 mL under reduced pressure. During evaporation a gray-olive precipitate formed. The product was isolated, washed with H_2O, and dried under vacuum; mp 193–95 °C. Anal. Calcd for $CuC_{23}H_{36}N_2O_4$: C, 58.02; H, 7.75; N, 5.98; Cu, 13.58. Found: C, 59.23; H, 7.75; N, 5.88; Cu, 13.76.

[5,5′-(1,3-Propanediyldinitrilo)bis(1-phenyl-1,3-hexanedionato)-(2–)-$O^1,O^{1'},O^3,O^{3'}$]copper, $CuH_2(BAA)_2$-1,3-pn-O_2O_2. Solutions of 1.14 g (2.54×10^{-3} mol) of $H_4(BAA)_2$-1,3-pn plus 0.7 mL of $(C_2H_5)_3N$ in 100 mL of $CHCl_3$ and 0.500 g (2.51×10^{-3} mol) of $Cu(C_2H_3O_2)_2{\cdot}H_2O$ in 100 mL of CH_3OH were mixed and stirred for 30 min. A green crystalline solid was recovered, washed with H_2O, and air-dried; mp 233–36 °C. Anal. Calcd for $CuC_{27}H_{30}N_2O_4{\cdot}2H_2O$: C, 59.60; H, 5.93; N, 5.15; Cu, 11.68. Found: C, 59.73; H, 5.23; N, 5.05; Cu, 11.75.

[5,5′-(1,3-Propanediyldinitrilo)bis(1-phenyl-1,3-hexanedionato)-(4–)]dicopper, $Cu_2(BAA)_2$-1,3-pn. A solution of 0.502 g of $H_4(BAA)_2$-1,3-pn (1.12×10^{-3} mol) plus 0.243 g of $NaOCH_3$ (4.40×10^{-3} mol) was prepared with 50 mL of CH_3OH and 80 mL of $CHCl_3$. This solution was added dropwise to a refluxing solution of 0.480 g (2.40×10^{-3} mol) of $Cu(C_2H_3O_2)_2{\cdot}H_2O$ in 100 mL of CH_3OH. Reflux was maintained overnight. A lime green solid was recovered, washed with CH_3OH, and air-dried; mp 277–79 °C. Anal. Calcd for $Cu_2C_{27}H_{26}N_2O_4$: C, 56.94; H, 4.78; N, 4.92; Cu, 22.31. Found: C, 56.63; H, 4.69; N, 4.88; Cu, 22.32.

Bis[2,2-dimethyl-3,5,7-octanetrionato(2–)]dizinc, $Zn_2(PAA)_2$. The ligand, H_2PAA (5.53 g, 0.030 mol), and $NaOCH_3$ (3.25 g, 0.060 mol) were dissolved in 100 mL of MeOH. To this solution was added $Zn(C_2H_3O_2)_2{\cdot}2H_2O$ (6.78 g, 0.031 mol) dissolved in MeOH dropwise

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(16) Abbreviations are based on the trivial nomenclature described in ref 12 and 13.

with stirring. After about 0.5 h, 500 mL of H_2O was added and the precipitate collected and air-dried. The product may be recrystallized from pyridine or MeOH both of which yield pale yellow crystals. Analysis of the pyridine-recrystallized product, $Zn_2(PAA)_2$·3py, follows. Anal. Calcd for $Zn_2C_{35}H_{43}N_3O_6$: C, 57.39; H, 5.92; N, 5.74; Zn, 17.85. Found: C, 57.46; H, 5.95; N, 5.69; Zn, 17.84.

Three compounds used in this study have been prepared and characterized previously: $Cu_2(BAA)_2$,[14] $CuH_2(BAA)_2$en-O_2O_2,[14] and $Cu_2(BAA)_2$en.[15]

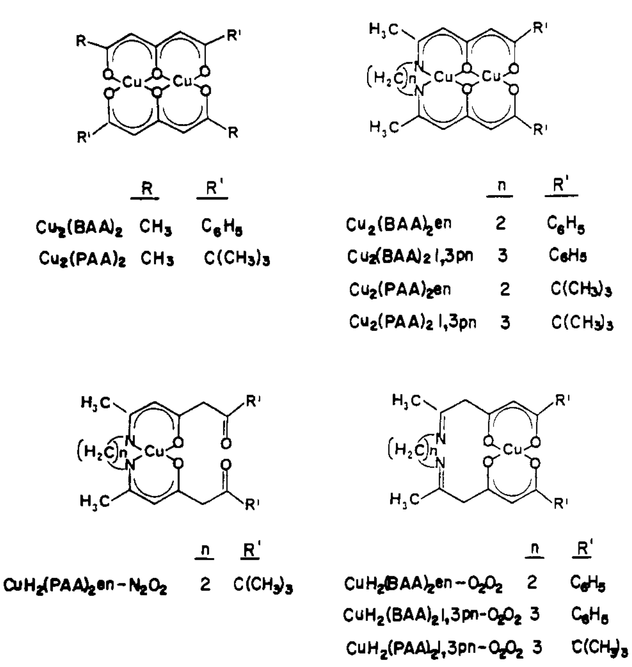
II. Infrared and Magnetic Susceptibility Measurements. Infrared spectra were recorded as neat liquids or as KBr pellets on a Perkin-Elmer 283B spectrophotometer. Magnetic susceptibility was measured with standard Faraday balance techniques using $Hg[Co(SCN)_4]$ as the calibrant.[17] Pascal's constants were used for the diamagnetic corrections.[18]

III. Electrochemical Measurements. Electrochemical results were obtained with a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a PAR Model 179 digital coulometer and Model 175 universal programmer. Data collection and output for scan rates greater than 100 mV/s was accomplished with a Nicolet digital oscilloscope, Model 2090-3C, with pen output, disk recorder, and binary digital I/O. Electrochemical measurements were made in OmniSolv grade (MCB Reagents) *N,N*-dimethylformamide (DMF), which was used without further purification. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte and was purified by a chromatographic procedure developed in our laboratory.[10,19] Solutions were deoxygenated with ultrahigh-purity N_2 that had been passed through a chromous-perchloric acid scrubber, a $CaSO_4$ drying column, and a DMF-TEAP solution. Blanks indicated that no electroactive impurities were present in the scan range from 0 to −2.0 V.

Cyclic voltammograms were obtained with use of a three-electrode glass cell with a saturated NaCl calomel reference electrode, a Pt-wire counterelectrode, and a Brinkmann Model EA 290 hanging-mercury-drop electrode (HMDE) or a Pt-disk working electrode. The reference electrode was separated from the sample chamber by two salt bridges. The bridge adjacent to the reference electrode contained a 0.13 M TEAP aqueous solution, and the one adjacent to the sample chamber contained a 0.1 M TEAP in DMF solution. Coulometry was carried out at a stirred-Hg pool or a Pt-gauze working electrode with a counterelectrode consisting of a Cu coil in a 0.10 M NaCl aqueous solution, separated by a salt bridge containing 0.10 M TEAP in DMF solution.

Results

Several mono- and binuclear Cu(II) complexes of 1-phenyl- and 1-(*t*-C_4H_9)-substituted 1,3,5-hexanetrione and their diamine Schiff-base derivatives have been prepared. Characterization of the binuclear complexes is straightforward on the basis of analytical results and the fact that they all exhibit very low room-temperature magnetic moments due to strong antiferromagnetic exchange between the Cu(II) ions that are bridged by the central carbonyl oxygens. The effective magnetic moments of $Cu_2(BAA)_2$, $Cu_2(PAA)_2$, $Cu_2(BAA)_2$en, $Cu_2(BAA)_2$-1,3-pn, $Cu_2(PAA)_2$en, and $Cu_2(PAA)_2$-1,3-pn are all 0.7 μ_B/Cu or lower at room temperature. For the mononuclear Schiff-base complexes, analytical and magnetic moment results (ca. 1.8 μ_B/molecule) do not allow identification of the positional isomer present, of which there are two possibilities, i.e., the Cu(II) bound to two nitrogen and two oxygen donor atoms or to four oxygen donors atoms. The infrared spectrum in the carbonyl region is, however, diagnostic. The infrared spectrum of $CuH_2(PAA)_2$en contains a strong "free carbonyl" band at 1712 cm^{-1} and is virtually identical with the 1712-cm^{-1} band in $NiH_2(BAA)_2$en, which has been previously shown to contain Ni(II) bound to the N_2O_2 donors.[20,21]



	R	R'
$Cu_2(BAA)_2$	CH_3	C_6H_5
$Cu_2(PAA)_2$	CH_3	$C(CH_3)_3$

	n	R'
$Cu_2(BAA)_2$en	2	C_6H_5
$Cu_2(BAA)_2$ 1,3pn	3	C_6H_5
$Cu_2(PAA)_2$en	2	$C(CH_3)_3$
$Cu_2(PAA)_2$ 1,3pn	3	$C(CH_3)_3$

	n	R'
$CuH_2(PAA)_2$en-N_2O_2	2	$C(CH_3)_3$

	n	R'
$CuH_2(BAA)_2$en-O_2O_2	2	C_6H_5
$CuH_2(BAA)_2$1,3pn-O_2O_2	3	C_6H_5
$CuH_2(PAA)_2$1,3pn-O_2O_2	3	$C(CH_3)_3$

Figure 1. Structural representations and abbreviations for the mono- and binuclear complexes studied.

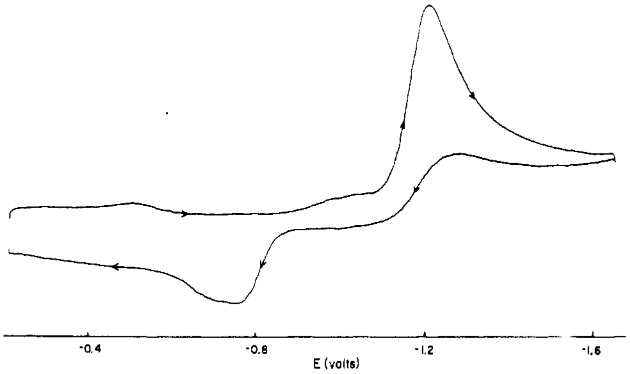


Figure 2. CV of $CuH_2(PAA)_2$en-N_2O_2 in DMF with 0.1 M TEAP at 0.100 V/s (1.27×10^{-3} M).

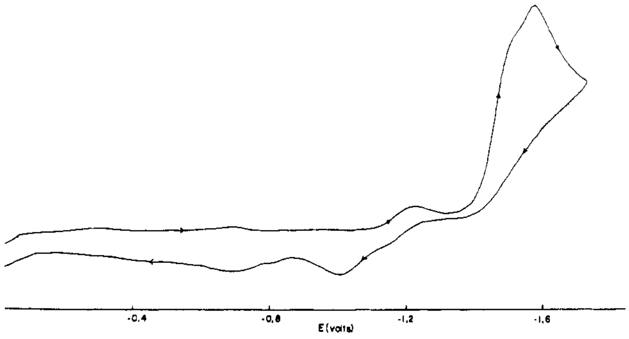


Figure 3. CV of $CuH_2(PAA)_2$-1,3-pn-O_2O_2 in DMF with 0.1 M TEAP at 2.00 V/s (0.83×10^{-3} M).

For $CuH_2(PAA)_2$-1,3-pn, however, a strong band at 1622 cm^{-1} is the highest energy absorption in this region. This is similar to the band found in $CuH_2(BAA)_2$en, which has been proven by X-ray structure determination to contain the Cu(II) ion bound to the four ketonic oxygens.[14] Structural representations along with the abbreviations used are given in Figure 1 for the mono- and binuclear complexes.

The cyclic voltammograms (CV) of the mononuclear complexes are typical of almost totally irreversible electron-transfer processes. Typical cyclic voltammograms for $CuH_2(PAA)_2$en-N_2O_2 and $CuH_2(PAA)_2$-1,3-pn-O_2O_2 in di-

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Table I. Cyclic Voltammetry of $Cu_2(PAA)_2$ (0.969×10^{-3} M, 0.1 M TEAP in DMF)[a]

scan rate, V/s	$E_{1/2}$, V	E_{pc}, V	I_{pc}, μA	I_{pa}/I_{pc}	$I_{pc}/v^{1/2}$ [b]	ΔE_p, mV	$E_{pc} - E_{pc/2}$, mV
0.020	−0.86	−0.90	2.21	0.88	0.49	73	69
0.050	−0.87	−0.90	3.50	0.87	0.49	72	61
0.100	−0.87	−0.90	4.88	0.88	0.49	70	61
0.500	−0.87	−0.90	10.36	0.95	0.46	65	64
1.000	−0.86	−0.90	13.28	0.99	0.42	61	66
2.000	−0.85	−0.88	19.91	0.99	0.44	63	63
5.000	−0.85	−0.88	32.82	0.97	0.46	68	65
10.000	−0.84	−0.87	47.86	0.94	0.48	61	63
20.000	−0.84	−0.87	70.95	0.96	0.50	57	62
50.000	−0.83	−0.86	119.38	0.92	0.53	70	71

[a] Hanging-mercury-drop electrode. [b] $\mu A/(mV\ s^{-1})^{1/2}$.

Table II. Cyclic Voltammetry of $Cu_2(BAA)_2$-1,3-pn (1.23×10^{-4} M, 0.1 M TEAP in DMF)[a]

scan rate, V/s	$E_{1/2}$, V	E_{pc}, V	I_{pc}, μA	I_{pa}/I_{pc}	$I_{pc}/v^{1/2}$ [b]	ΔE_p, mV	$E_{pc} - E_{pc/2}$, mV
0.050	−1.10	−1.14	0.46	0.83	0.06	73	68
0.100	−1.10	−1.13	0.64	0.86	0.06	66	65
0.500	−1.08	−1.12	1.62	0.86	0.07	58	65
1.000	−1.08	−1.11	2.45	0.87	0.08	59	66
2.000	−1.08	−1.11	3.92	0.91	0.09	51	72
5.000	−1.08	−1.10	8.05	0.88	0.11	47	
10.000	−1.08	−1.10	14.46	0.84	0.14	40	
20.000	−1.07	−1.09	26.29	0.81	0.19	44	
50.000	−1.06	−1.08	62.71	0.77	0.28	40	

[a] Hanging-mercury-drop electrode. [b] $\mu A/(mV\ s^{-1})$.

methylformamide are shown in Figures 2 and 3. The peak potentials are −1.6 V for $CuH_2(PAA)_2en\text{-}N_2O_2$, −1.2 V for $CuH_2(PAA)_2\text{-}1,3\text{-}pn\text{-}O_2O_2$, −1.2 V for $CuH_2(BAA)_2en\text{-}O_2O_2$, and −1.1 V for $CuH_2(BAA)_2\text{-}1,3\text{-}pn\text{-}O_2O_2$, all vs. the saturated NaCl calomel electrode. Addition of $NaNO_3$ to the electrochemical cell so that $[Na^+]/[\text{complex}] = 10$ results in a positive shift of the peak potentials for $CuH_2(BAA)_2en\text{-}O_2O_2$ and $CuH_2(BAA)_2\text{-}1,3\text{-}pn\text{-}O_2O_2$ of about 300 mV to −0.85 and −0.88, respectively. Addition of like amounts of $NaNO_3$ to the $CuH_2(PAA)_2en\text{-}N_2O_2$ and $CuH_2(PAA)_2\text{-}1,3\text{-}pn\text{-}O_2O_2$ solutions did not appreciably change the peak potentials of these compounds. The cyclic voltammograms for the binuclear complexes $Cu_2(PAA)_2$, $Cu_2(PAA)_2en$, $Cu_2(PAA)_2$-1,3-pn, $Cu_2(BAA)$, and $Cu_2(BAA)_2$-1,3-pn, on the other hand, show one quite reversible wave in the 0- to −1.6-V region. The data for $Cu_2(PAA)_2$ and $Cu_2(BAA)_2$-1,3-pn are presented in Tables I and II. The analogous data for $Cu_2(PAA)_2en$, $Cu_2(PAA)_2$-1,3-pn, and $Cu_2(BAA)_2$ are very similar except for the values of $E_{1/2}$ and have been deposited as supplementary material. The values of $E_{1/2}$ for $Cu_2(PAA)_2en$, $Cu_2(PAA)_2$-1,3-pn, and $Cu_2(BAA)_2$ are −1.02, −1.16, and −0.82 V, respectively. Also, $Cu_2(BAA)_2$ is more irreversible than the others as evidenced by the fact that the value of ΔE_p increases to 115 mV at 20.00 V/s. Comparable data could not be obtained for $Cu_2(BAA)_2en$ due to adsorption problems. The last four columns in each table give values for functions commonly used to test reversibility, i.e. I_{pa}/I_{pc}, $I_{pc}/v^{1/2}$, ΔE_p, and $E_{pc} - E_{pc/2}$, at all scan rates. It is clear from the similarities in the numerical values of these functions, obtained under nearly identical conditions, that the electron-transfer processes are similar for all the compounds. Indeed, the only significant difference between the CV's of these binuclear compounds is the value of $E_{1/2}$.

Table III. Cyclic Voltammetry of $Cu_2(PAA)_2en$ in the Presence of a 10-fold Excess of Na^+ [a]

scan rate, V/s	$E_{1/2}$, V	E_{pc}, V	I_{pc}, μA	I_{pa}/I_{pc}	$I_{pc}/v^{1/2}$ [b]	ΔE_p, mV	$E_{pc} - E_{pc/2}$, mV
0.020	−0.69	−0.72	5.08	1.03	1.14	49	54
0.050	−0.70	−0.72	7.91	0.96	1.12	49	58
0.100	−0.69	−0.72	11.03	0.94	1.10	51	57
0.500	−0.68	−0.71	23.42	0.94	1.05	52	48
1.000	−0.68	−0.70	35.46	0.86	1.12	52	45
2.000	−0.68	−0.71	49.85	0.81	1.12	58	45
5.000	−0.68	−0.71	84.77	0.77	1.20	63	50
10.000	−0.68	−0.71	131.30	0.67	1.31	69	48
20.000	−0.68	−0.71	203.30	0.56	1.44	74	47
50.000	−0.68	−0.72	400.60	0.43	1.79	86	43

[a] 1.018×10^{-3} M $Cu_2(PAA)_2en$, 1.018×10^{-2} M $NaNO_3$, 0.1 M TEAP in DMF with a hanging-mercury-drop electrode.
[b] $\mu A/(mV\ s^{-1})^{-1/2}$.

Table IV. Cyclic Voltammetry of $Cu_2(BAA)_2$ in the Presence of a 20-fold Excess of Na^+ [a]

scan rate, V/s	$E_{1/2}$, V	E_{pc}, V	I_{pc}, μA	I_{pa}/I_{pc}	$I_{pc}/v^{1/2}$ [b]	ΔE_p, mV	$E_{pc} - E_{pc/2}$, mV
0.005	−0.54	−0.55	2.56	1.06	1.14	31	54
0.010	−0.53	−0.55	3.42	1.02	1.08	36	53
0.020	−0.54	−0.56	4.67	0.94	1.04	41	59
0.050	−0.54	−0.56	7.21	0.92	1.02	47	65
0.100	−0.54	−0.56	10.00	0.89	1.00	57	58
0.500	−0.52	−0.55	22.36	0.86	1.00	60	44
1.000	−0.51	−0.54	31.00	0.86	0.98	62	42
2.000	−0.51	−0.55	43.00	0.86	0.96	75	44
5.000	−0.51	−0.55	67.45	0.82	0.95	78	47
10.000	−0.51	−0.56	92.20	0.80	0.92	79	55
20.000	−0.51	−0.55	138.10	0.77	0.98	78	55
50.000	−0.51	−0.56	214.80	0.69	0.96	108	80

[a] 1.017×10^{-3} M $Cu_2(BAA)_2$, 2.034×10^{-2} M $NaNO_3$, 0.1 M TEAP in DMF with a hanging-mercury-drop electrode.
[b] $\mu A/(mV\ s^{-1})^{1/2}$.

Table V. Cyclic Voltammetry of $Cu_2(BAA)_2$ in the Presence of a 20-fold Excess of Li^+ [a]

scan rate, V/s	$E_{1/2}$, V	E_{pc}, V	I_{pc}, μA	I_{pa}/I_{pc}	$I_{pc}/v^{1/2}$ [b]	ΔE_p, mV	$E_{pc} - E_{pc/2}$, mV
0.020	−0.45	−0.47	4.57	1.03	1.02	50	51
0.050	−0.46	−0.49	6.99	0.97	0.99	61	50
0.100	−0.45	−0.48	9.74	0.94	0.97	66	52
0.500	−0.44	−0.48	21.43	0.82	0.96	81	46
1.000	−0.41	−0.45	30.12	0.81	0.95	86	50
2.000	−0.42	−0.46	42.75	0.79	0.96	93	54
5.000	−0.41	−0.47	69.25	0.76	0.98	109	53
10.000	−0.41	−0.41	100.30	0.72	1.00	128	55
20.000	−0.41	−0.49	147.90	0.65	1.05	160	65
50.000	−0.40	−0.49	259.20	0.60	1.16	180	74

[a] 1.023×10^{-3} M $Cu_2(BAA)_2$, 2.046×10^{-2} M $LiNO_3$, 0.1 M TEAP in DMF with a hanging-mercury-drop electrode.
[b] $\mu A/(mV\ s^{-1})^{1/2}$.

Addition of simple cations such as Na^+ or Li^+ (as nitrates) to the electrochemical cell has a substantive effect on the cyclic voltammograms.[10] The CV results for $Cu_2(PAA)_2en$ and $Cu_2(BAA)_2$ in the presence of excess Na^+ or Li^+ are presented in Tables III–V. Analogous data for $Cu_2(PAA)_2$, $Cu_2(BAA)_2en$, and $Cu_2(BAA)_2$-1,3-pn were similar except for $E_{1/2}$ values and were deposited as supplementary material. The $E_{1/2}$ values for $Cu_2(PAA)_2$, $Cu_2(BAA)_2en$, and $Cu_2(BAA)_2$-1,3-pn with excess Na^+ are −0.57, −0.64, and −0.74 V, respectively. Both $Cu_2(PAA)_2$ and $Cu_2(BAA)_2$-1,3-pn are quasi-reversible on the basis of increasing ΔE_p as a function of scan rate. Except for the presence of Na^+ or Li^+, the experimental conditions are the same as in the previous experiments. The changes that take place upon addition of these simple cations are (1) a potential shift of +300–+400 mV, (2) a sharpening of the wave as evidenced by a decrease in ΔE_p and $E_{pc} - E_{pc/2}$, and (3) a large increase in the peak currents, I_{pa} and I_{pc}. As a means of investigating the effect of cations

Table VI. Comparison between Experimental and Calculated Cathodic Peak Currents in the Absence of Na^+

	I_{pc}, μA (exptl (calcd))[a]				
scan rate, V/s	$Cu_2(PAA)_2$[b]	$Cu_2(PAA)_2en$[b]	$Cu_2(PAA)_2$-1,3-pn	$Cu_2(BAA)_2$	$Cu_2(BAA)_2$-1,3-pn[c]
0.020	2.21 (2.48)	2.44 (2.48)	2.19 (2.18)		
0.050	3.50 (3.53)	3.86 (3.77)	3.67 (3.44)		0.46 (0.38)
0.100	4.88 (4.89)	5.29 (5.22)	5.08 (4.87)	4.90 (5.15)	0.64 (0.56)
0.500	10.36 (10.64)	10.94 (11.35)	10.91 (10.88)	10.58 (11.51)	1.62 (1.53)
1.000	13.28 (14.95)	14.95 (15.94)	14.85 (15.39)	14.47 (16.29)	2.45 (2.45)
2.000	19.91 (21.04)	21.74 (22.43)	21.41 (21.76)	20.08 (23.04)	3.92 (4.04)
5.000	32.82 (33.13)	36.14 (35.31)	34.44 (34.41)	31.58 (36.43)	8.05 (28.19)
10.000	47.86 (46.76)	53.20 (49.82)	50.80 (48.67)	44.97 (51.51)	14.46 (14.45)
20.000	70.95 (66.02)	81.65 (70.35)	76.30 (68.82)	68.64 (72.85)	26.29 (26.17)
50.000	119.38 (104.25)	143.40 (111.08)	132.80 (108.8)		62.71 (59.39)

[a] Calculations are based on eq 1 with $D = 6.50 \times 10^{-6}$ cm²/s, $A = 2.22 \times 10^{-2}$ cm² and $\pi^{1/2}\chi(at) = 0.446$. The value of C_0^* for each compound is given in Tables I–IV. [b] A spherical correction was included. [c] Weak reactant adsorption included; $a = 1.47$, $b = 0.98$ (eq 2).

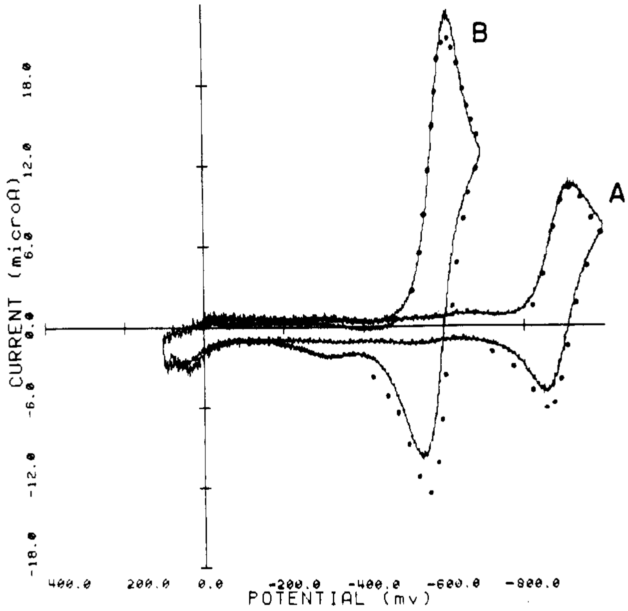

Figure 4. Experimental (solid lines) and simulated (dots) CV waves for 1.00×10^{-3} M $Cu_2(PAA)_2$ in DMF with 0.1 M TEAP at 0.500 V/s: (A) no Na^+ present, (B) 1.00×10^{-2} M Na^+ present. Values of the diffusion constant, D, and electrode area, A, used in the simulation were determined experimentally to be 6.0 (±5) × 10^{-6} cm²/s[26] and 2.21×10^{-2} cm², respectively. Wave A (no Na^+) was reproduced with current functions corresponding to a one-electron, reversible transfer. Curve B (×10 Na^+) was simulated with current functions corresponding to the transfer of two electrons with a potential separation, $E_2 - E_1$, of −30 mV.

on the electron-transfer process, the CV waves have been simulated by using the relationship in eq 1. The experimental

$$I = 602AD^{1/2}C_0{}^*v^{1/2}\pi^{1/2}\chi(\mathrm{at}) \qquad (1)$$

and calculated CV's for $Cu_2(PAA)_2$ in the absence and presence of Na^+ are presented in Figure 4. The experimental conditions for the two CV's are identical except for the presence of Na^+. Indeed, the same solution was used to record both waves. The CV of $Cu_2(PAA)_2$ in the absence of Na^+, which occurs at the more negative potential, is very well simulated with current functions appropriate for the reversible transfer of one electron. The more positive wave (resulting from the addition of Na^+) with its much larger currents is well simulated with current function values appropriate for the sequential, reversible transfer of two electrons in which $E_2 - E_1 = -30$ mV.[22]

A comparison of the experimental and calculated values of I_{pc} for all of the compounds obtained in the absence of Na^+ or Li^+ at the various scan rates is shown in Table VI. In these calculations the value of the peak current function, $\pi^{1/2}\chi(\mathrm{at})$, was held constant at 0.446, which is appropriate for a one-electron process, $n = 1$.[23] The agreement between experimental and calculated values is very good especially at the slower scan rates. At fast scans the experimental I_{pc} values are somewhat larger than the calculated values, which can be attributed to weak reactant absorption.[24] In the case of $Cu_2(BAA)_2$-1,3-pn, adsorption is quite pronounced and a reasonable fit of the data requires inclusion of the adsorption contribution to the total current. This contribution is not diffusion controlled and is proportional to v. The appropriate equation (2) contains a diffusion-controlled term, $av^{1/2}$ and a diffusion-independent adsorption term, bv. For $Cu_2(BAA)_2$-1,3-pn a good fit of the experimental data is achieved with $a = 1.47$ and $b = 0.98$.

$$I_{pc} = av^{1/2} + bv \qquad (2)$$

The cathodic peak currents in the presence of excess Na^+ are much larger under comparable conditions than those recorded in the absence of Na^+, which is indicative of a change from one-electron- to a two-electron-transfer process upon addition of Na^+(Figure 4). The peak currents (I_{pc}) in the presence of Na^+ were calculated by first determining the appropriate value of the current function for two overlapping CV waves with small separation between the $E°$ values.[22] These were estimated from the experimental values of ΔE_p and $E_{pc} - E_{pc/2}$ as discussed by Shain and co-workers.[11,12] Alternatively they may be determined by simulation calculations. The estimations were made with use of the slow-to-medium rate data since the adsorption effects are small at slow scan rates. The cathodic peak currents for the diamine complexes increased more rapidly than $v^{1/2}$ increases, which is attributed to weak adsorption of the reactant.[24] Therefore, the calculated peak currents have been obtained by application of eq 2 in which $a = 602D^{1/2}AC_0{}^*\pi^{1/2}\chi(\mathrm{at})$ and b is an adjustable parameter. The results of the calculations and the values of the current functions used are presented in Table VII.

As a means of ascertaining the nature of the two-electron-reduction product, experiments were performed in which $Cu(CH_3CN)_4{}^+$ (as the $PF_6{}^-$ salt)[25] and $Na_2(PAA)$ were added to DMF and 0.1 M TEAP in the electrochemical cell. Sweeping in the positive direction from about −1.6 to 0 V yielded only one well-formed wave with peak potentials of $E_{pa} = -0.51$ V and $E_{pc} = -0.60$ V. These values are virtually

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[22] We are indebted to Prof. Dennis Evans for supplying us with the program. See: Sokol, W. F.; Evans, D. H.; Niki, K.; Yagi, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *108*, 108.

[23] Nicolson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706; **1965**, *37*, 178, and 191.

[24] Wopschall, K. H.; Shain, T. *Anal. Chem.* **1967**, *39*, 1514.

[25] Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.

Table VII. Comparison between the Experimental and Calculated Cathodic Peak Currents in the Presence of Excess Na^+

	I_{pc}, µA (exptl (calcd))[a]				
scan rate, V/s	$Cu_2(PAA)_2$[b]	$Cu_2(PAA)_2en$[c]	$Cu_2(BAA)_2$[d]	$Cu_2(BAA)_2en$[e]	$Cu_2(BAA)_2$-1,3-pn[f]
0.005			2.56 (2.34)		
0.010			3.42 (3.17)		
0.020	3.78 (3.50)	5.08 (4.70)	4.67 (4.48)		
0.050	5.68 (5.54)	7.91 (7.48)	7.21 (7.08)	1.67 (1.75)	1.05 (1.15)
0.100	7.96 (7.83)	11.03 (10.66)	10.00 (10.01)	2.40 (2.53)	1.63 (1.79)
0.500	16.44 (17.51)	23.42 (24.54)	22.36 (22.39)	5.79 (6.15)	5.26 (5.52)
1.000	22.74 (24.76)	35.46 (35.46)	31.00 (31.66)	8.69 (9.22)	9.30 (9.42)
2.000	31.14 (35.01)	49.85 (51.65)	43.00 (44.77)	13.68 (14.09)	16.91 (16.54)
5.000	45.55 (55.37)	84.77 (86.39)	67.45 (70.79)	24.65 (25.59)	37.93 (36.26)
10.000	65.25 (78.30)	131.30 (129.70)	92.20 (100.0)	46.25 (41.46)	70.25 (67.40)
20.000		203.30 (198.50)	138.10 (141.60)	73.55 (69.18)	133.40 (127.50)
50.000		400.60 (361.10)	214.80 (223.80)		312.90 (302.70)

[a] Calculations are based on eq 1 with $D = 6.50 \times 10^{-6}$ cm²/s and $A = 2.22 \times 10^{-2}$ cm². Where weak reactant adsorption is evident, $I_{pc} = a\nu^{1/2} + b\nu$ with $a = 602D^{1/2}AC_0{}^* \pi^{1/2}\pi^{1/2}\chi(at)$ and b treated as an adjustable parameter. The spherical correction term has been ignored. [b] $\pi^{1/2}\pi^{1/2}\chi(at) = 0.910$, $C_0{}^* = 0.800 \times 10^{-3}$ M, $b = 0$ (no adsorption). [c] $\pi^{1/2}\pi^{1/2}\chi(at) = 0.950$, $C_0{}^* = 1.018 \times 10^{-3}$ M, $a = 32.89$, $b = 2.67$. [d] $\pi^{1/2}\pi^{1/2}\chi(at) = 0.910$, $C_0{}^* = 1.017 \times 10^{-3}$ M, $b = 0$ (no adsorption). [e] $\pi^{1/2}\pi^{1/2}\chi(at) = 0.977$, $C_0{}^* = 2.232 \times 10^{-4}$ M, $a = 7.42$, $b = 1.80$. [f] $\pi^{1/2}\pi^{1/2}\chi(at) = 1.000$, $C_0{}^* = 1.152 \times 10^{-4}$ M, $a = 3.92$, $b = 5.50$.

identical with those obtained for $Cu_2(PAA)_2$ when the potential is swept in the opposite direction. Simple $Cu(CH_3CN)_4^+$ with no ligand present is oxidized at about +0.30 V and then reduced at −0.21 V in DMF with 0.1 M TEAP.

In order to be certain that the ligand was not actively involved in the redox process of the binuclear Cu(II) complexes, the CV of the complex $Zn_2(PAA)_2$ was examined. Since Zn(II) is not electroactive in the region of interest, the redox properties of the complexed ligand can be investigated. Under the same experimental conditions employed for the Cu(II) complexes, no reduction occurs for $Zn_2(PAA)_2$ before −2.2 V. An irreversible oxidation wave is present at about +0.66 V.

Controlled-potential electrolysis (CPE) carried out at about 60 mV more negative than E_{pc} resulted in the transfer of 2.0 electrons/molecule for $Cu_2(PAA)_2$, $Cu_2(PAA)_2en$, $Cu_2(BAA)_2$, and $Cu_2(BAA)_2en$. No further reduction takes place before at least −1.6 V. The reduced solutions can be reoxidized with the transfer of approximately 2.0 electrons/molecule at about −0.3 V. However, if the Hg pool is removed after the initial reduction and replaced by a fresh Hg pool, reoxidation does not occur, indicating that reduced copper has been removed as an amalgam with the Hg. The solution after the 2.0-electron reduction is still distinctly green consistent with the presence of Cu(II). Further reduction occurs at about −1.7 V with the transfer of approximately 2 electrons/molecule, yielding a yellow solution. Controlled-potential electrolyses were carried out at concentrations of 0.84×10^{-4}, 2.0×10^{-4}, 2.5×10^{-4}, and 1.0×10^{-3} M with no change in the results; i.e., the current vs. time curves and the number of electrons transferred indicate the same process occurring in each case. In the case of $Cu_2(PAA)_2$-1,3-pn, the initial CPE 60 mV negative of E_{pc} results in the transfer of 4.0 electrons/molecule and, therefore, decomposition. At no time did the presence or absence of Na^+ change in CPE results. Only the potentials were affected.

Discussion

The simplest members of the homologous series of copper(II) β-polyketonates are the bis(1,3-diketonato)copper(II) complexes. The cyclic voltammetry of three copper(II) diketonates has been investigated in DMF with TEAP as the supporting electrolyte under the same conditions used for the binuclear complexes.[26] In each case, the electron transfer is irreversible or, at best, only slightly quasi-reversible. Bis(2,4-pentanedionato)copper(II), $Cu(acac)_2$, has no anodic wave and is, therefore, completely irreversible. The approximate value of E_{pc} for $Cu(acac)_2$ is −0.85 V vs. SSCE. The CV's of both bis(1,3-diphenyl-1,3-propanedionato)copper(II), $Cu(DBM)_2$, and Bis(1-phenyl-1,3-butanedionato)copper(II), $Cu(BA)_2$, exhibit anodic waves, but I_{pa} is significantly smaller than I_{pc}. In addition, the peak separations are very scan rate dependent. Both of these factors indicate considerable irreversibility. The approximate values of E_{pc} for $Cu(DBM)_2$ and Cu(BA) are −0.67 and −0.58 V vs. SSCE, respectively.

Mononuclear Cu(II) complexes of the 1,3,5-triketonates have not been prepared, and attempts to prepare them have led only to the isolation of the binuclear product and uncomplexed ligand. The diamine Schiff-base derivatives of 1,3,5-triketones, on the other hand, do form mononuclear Cu(II) complexes without difficulty. Indeed, it is possible to isolate the nitrogen-bound isomer in certain cases and the oxygen-bound isomer in others. The control of the Cu(II) position appears to be determined by ligand substituent effects and/or the number of methylene groups in the diamine. The CV's of these compounds (Figures 2 and 3) show that the electron-transfer processes are irreversible. The lack of an anodic wave indicates that the reduced species decompose rapidly.

The CV behavior of the binuclear Cu(II) complexes is in marked contrast to that of the mononuclear complexes. The most obvious difference that takes place upon the addition of the second Cu(II) is that the electron-transfer process becomes quite reversible. This is true both in the presence and absence of Na^+. A second dramatic change takes place with the addition of simple cations such as Na^+ or Li^+. In the presence of sufficient concentrations of these cations, the electron-transfer process in the binuclear complexes is best described as two sequential, one-electron, reversible electron transfers occurring essentially at the same potential. A further elucidation of this two-electron transfer is a major concern of this work. A comparison of the data in Tables IV and V shows the effect of Na^+ vs. Li^+ on the CV wave of $Cu_2(BAA)_2$. Except for the substitution of Li^+ for Na^+, the experimental conditions are constant. When Na^+ is replaced by Li^+, an additional +100-mV shift is observed. With the exception of this positive potential shift and a slightly different dependence of ΔE_p on the scan rate, the waves are virtually identical at all scan rates. The more positive potential in the presence of Li^+ is indicative of a stronger complexation between Li^+ and the electroactive species than between Na^+ and those same species. This is expected due to the smaller size of Li^+ and strengthens the conclusion that there is association between simple cations and Cu_2L_2, $Cu_2L_2^-$, and $Cu_2L_2^{2-}$.

Another conclusion reached in the previous paper[10] was that the electron-transfer process was not altered when the tri-

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(26) Fenton, D. E. Ph.D. Thesis, Wayne State University, 1978.

ketonate ligand was converted to a diamine Schiff base resulting in two different coordination enviroments for the two Cu(II) ions. In the presence of Na^+, both the simple, symmetric binuclear triketonato complexes and their unsymmetric diamine Schiff bases undergo two sequential, reversible one-electron transfers at virtually the same potential. The value of $E_{1/2}$ is, however, 100–200 mV more negative for the diamine Schiff bases than the triketonates. For example, in the presence of excess Na^+, the values of $E_{1/2}$ for $Cu_2(PAA)_2$ and $Cu_2(PAA)_2en$ are −0.58 and −0.69 V vs. saturated NaCl calomel, respectively. Such a shift is also observed in the diamine-substituted mononuclear complexes.[27] In essentially all other characteristics, the CV waves of the two compounds are nearly identical.

A principal characteristic of the CV wave for the binuclear complexes, in both the absence and presence of Na^+, that has not been investigated up to this point is the magnitude of the current function. Principal reasons for carrying out the current study were to obtain detailed information about the CV wave in the absence of small cations and to determine the current functions, $\pi^{1/2}\chi(at)$, for electron transfer in both the presence and absence of Na^+. This was prompted by the observation that the addition of Na^+ not only shifted the potential about +300 mV but also substantially increased the cathodic and anodic peak currents. The lower peak currents in the absence of Na^+ could mean either that one electron is transferred or that two are transferred, and the difference in the two potentials is such that E_2 is more negative than E_1, i.e., $E_2 - E_1 < 0$. Cathodic peak current calculations and wave simulations for CV's without Na^+ were done to distinguish between these possibilities. Similar calculations for CV's obtained in the presence of Na^+ were carried out to further substantiate the two-electron nature of the wave with excess Na^+.

The CV results for five of the binuclear complexes in the absence of any small cations are quite similar. On the basis of $I_{pa}/I_{pc} \cong 1.0$ (especially at scan rates faster than 0.100 V/s) and $I_{pc}/v^{1/2}$ being constant through scan rate changes of about 10^3, these appear to be highly reversible processes. In addition, for the most part ΔE_p and $E_{pc} - E_{pc/2}$ are constant as a function of scan rate. These latter parameters are close to those associated with one-electron, reversible systems. However, the fact that they are generally greater than 59 mV leaves open the possibility that the wave is due to the sequential transfer of two electrons with $E_2 - E_1 \cong -40$ mV.[11] For $E_2 - E_1 = -40$ mV, the CV wave due to the reversible sequential transfer of two electrons would yield $\Delta E_p \cong 59$ mV and $E_{pc} - E_{pc/2} \cong 59$ mV and, therefore, would be indistinguishable on the basis of these parameters from a one-electron reversible wave. The peak currents for the two cases would be considerably different, however. For a simple one-electron reversible transfer, the current function, $\pi^{1/2}\chi(at)$, at 25 °C for the maximum cathodic current, I_{pc}, is 0.4463,[23] while it is 0.8768 for the two-electron case in which $E_2 - E_1 = -40$ mV.[22] Therefore, at a given scan rate, I_{pc} for the two-electron transfer is, in fact, almost exactly twice that of the one-electron case under these conditions. The results of the I_{pc} calculations with $\pi^{1/2}\chi(at) = 0.446$ are presented in Table VI. The agreement between experimental and calculated values is excellent over the entire scan rate range of about 10^3 V/s. In addition, the excellent agreement between the experimental and simulated CV waves in the absence of Na^+ (Figure 4) with one-electron current functions leaves little doubt that *in the absence of* Na^+ the CV wave is due to the reversible transfer of *one* electron. There is no indication of any additional redox process in the CV before −1.7 V in either the reasonably symmetric triketonates or their diamine Schiff bases.

Unfortunately, the CPE results are not helpful in confirming the one-electron behavior in the absence of Na^+. Electrolysis carried out 60 mV more negative than E_{pc} results in the transfer of 2 electrons/molecule. Thus, apparently the time interval and the stirring conditions used in CPE result in additional reaction, electron transfer, and/or decomposition. The fact that CPE results are not dependent upon concentration in the 0.8×10^{-4} to 1.0×10^{-3} M range supports an intramolecular reaction. This, together with the apparent loss of copper as Cu^0, is consistent with the following sequence taking place during CPE:

$$Cu^{II}Cu^{II}L_2 \xrightarrow{e^-} Cu^{II}Cu^{I}L_2^-$$

$$Cu^{II}Cu^{I}L_2^- \rightarrow Cu^{II}L_2^{2-} + Cu^+(solv)$$

$$Cu^{I}(solv) \xrightarrow{e^-} Cu^0(Hg)$$

Under CV conditions, there is no indication that the second and third reactions take place. Thus, there is not straightforward correspondence between the CV and CPE results.

The results of the calculations of I_{pc} as a function of scan rate in the presence of excess Na^+ are given in Table VII. The agreement between experimental and calculated values is excellent for each of the five complexes. The current function at I_{pc} clearly indicates a two-electron-transfer process with small separations in the individual reduction potentials, E_1 and E_2. This result is confirmed by simulations of the entire wave of the type shown in Figure 4. For the diamine derivatives, it is obvious, especially at fast scans, that I_{pc} increases more rapidly than $v^{1/2}$. At the same time, there is no distortion of the wave as evidenced by a nearly constant value of $E_{pc} - E_{pc/2}$ at all scan rates. Such behavior is characteristic of weak reactant adsorption,[24] which gives rise to a portion of the current that is not diffusion controlled. This is taken into account by adding a term, bv, that is directly proportional to v. It is interesting to note that adsorption is more important for the diamine derivatives than for the simple triketonates (in both the absence and presence of Na^+) and that an excess of Na^+ increases the contribution of reactant adsorption to the I_{pc} values. This conclusion is apparent from comparisons for the same compound with and without Na^+. Inclusion of the adsorption term in the I_{pc} calculation for the diamine derivatives yields excellent results throughout the entire scan range.

The values of the current functions for I_{pc} in the presence of excess Na^+ for the binuclear complexes are all indicative of the sequential transfer of two electrons in which E_1 and E_2 are very nearly equal.[11,12,22] For $Cu_2(PAA)_2$ and $Cu_2(BAA)_2$, the current function that best reproduces the experimental I_{pc} values is 0.910, which is consistent with $\Delta E_p = E_{pc} - E_{pc/2} = 55$ mV and $E_2 - E_1 = -30$ mV. Similarly, a current function of 0.950 for $Cu_2(PAA)_2en$ indicates that $\Delta E_p = E_{pc} - E_{pc/2}) = 49$ mV and $E_2 - E_1 = -20$ mV while a value of 0.977 for $Cu_2(BAA)_2en$ yields $\Delta E_p = E_{pc} - E_{pc/2} = 45$ mV and $E_2 - E_1 = -12$ mV. Finally, a current function of 1.00 for $Cu_2(BAA)_2$-1,3-pn predicts $\Delta E_p = E_{pc} - E_{pc/2} = 43$ mV and $E_2 - E_1 = -5$ mV. Thus, on the basis of experimental current values, it seems apparent that the processes involve the sequential transfer of two electrons in which the difference in potentials varies from 30 to 5 mV with E_2 slightly more negative than E_1. The predicted values of the cathodic peak half-width based on these current functions are in reasonable agreement with the experimental results.

The experimental evidence argues strongly that the reduced species produced in the presence of Na^+ is a binuclear Cu^I_2 complex. Certainly the potential region in which the CV wave is observed is a common one for Cu(II) → Cu(I) reductions. In addition, it is clear from the results with $Zn_2(PAA)_2$ that there are no ligand redox processes at all close to −0.5 V where

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[27] Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.

the CV process being considered occurs. This is as one would expect for such ligands. Strong evidence for the binuclear Cu^{I}_2 complex as the product comes from the CV results obtained when $Cu(CH_3CN)_4^+$ and $Na_2(PAA)$ are allowed to react in the electrochemical cell. Sweeping the potential in the positive direction starting from −1.6 V yields a CV wave very similar to the one recorded when sweeping negatively with $Cu_2(PAA)_2$. Thus, the species involved in both cases appear to be the same.

Several conclusions may be drawn from the current study. One is that there are major differences between the redox behavior of the mono- and binuclear complexes and, hence, that the presence of the second metal ion significantly alters the chemical properties. Another is that the electron-transfer properties of these compounds in the absence of simple ions is a reversible, one-electron transfer. However, in the presence of excess simple ions the electron-transfer process consists of two reversible, sequential one-electron transfers with very similar potentials. Finally, there is no significant difference in CV behavior between the bis(1,3,5-triketonato)dicopper(II) complexes and their diamine Schiff-base derivatives except for the absolute value of the redox potentials. In all other aspects the CV waves are superimposable.

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Registry No. $Cu_2(PAA)_2$, 84130-49-4; $Cu_2(PAA)_2$en, 60116-99-6; $Cu_2(PAA)_2$-1,3-pn, 88476-09-9; $CuH_2(PAA)_2$en-N_2O_2, 66745-47-9; $CuH_2(PAA)_2$-1,3-pn-O_2O_2, 88476-10-2; $CuH_2(BAA)_2$-1,3-pn-O_2O_2, 66745-40-2; $Cu_2(BAA)_2$-1,3-pn, 66745-65-1; $Zn_2(PAA)_2$, 88476-11-3; $Cu_2(BAA)_2$, 29745-70-8; $Cu_2(BAA)_2$en, 56550-34-6; Na, 7440-23-5; Li, 7439-93-2.

Supplementary Material Available: Listings of cyclic voltammetric data (6 pages). Ordering information is given on any current masthead page.

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Parametrization of Static Magnetic Susceptibility of a "Linear" Tetranuclear Chromium(III) Complex by Isotropic Heisenberg–Dirac–Van Vleck Hamiltonians and Correlation with Structural Data

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The static magnetic susceptibility of the tetranuclear chromium(III) complex $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]^{6+}$ as a bromide salt, the preparation and X-ray structure of which have been previously reported, has been measured and subjected to interpretation within several different models based on isotropic Heisenberg–Dirac–Van Vleck Hamiltonians with or without biquadratic exchange terms. This has been accomplished with use of new programs that are based on computer diagonalization of such operators because no explicit eigenvalue formulas are known for the linear configuration. The simplest description emerging exhibits two antiferromagnetic couplings, $J_{12} = J_{34} \approx 19$ cm^{-1} and $J_{23} \approx 14$ cm^{-1}, where chromiums 1 and 4 are the terminal ones, and the Hamiltonian is $\sum_{k<l}^{4} J_{kl}\hat{S}_k\cdot\hat{S}_l$. The energy levels corresponding to the various parameter sets obtained are presented; the lowest spin multiplets are, in all cases, a ground-state singlet, a triplet at approximately 10 cm^{-1}, and a quintet at approximately 32 cm^{-1}. The parameters of the simplest model are correlated with the structural data by using a generalization of a model recently proposed for corresponding dinuclear complexes.

Introduction

Oligonuclear oxo-, hydroxo- and alkoxo-bridged chromium(III) complexes have become the subject of extensive research in recent years,[1–12] the main effort in work from this laboratory being put into the investigation of correlations between magnetic and structural data for these systems. A model has recently been proposed[9] for such correlations in the dinuclear complexes, and the present work and a related one[4] now give opportunities to investigate extensions of the model to systems with more than two centers. We discuss here the static magnetic susceptibility for the bromide salt $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]Br_6\cdot 2H_2O$, of the particular stereoisomer of a tetrameric cation for which the preparation and structure were reported previously.[10]

Susceptibility data are normally interpreted in terms of just a single model, and the estimated standard deviations for the resultant parameters often seem underestimated. Here we have used two independent data sets and five coupling models and have thereby obtained a broader illustration of the uncertainties involved in deriving the coupling constants and the energies of the spin multiplets.

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