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Reversible Sequential Transfer of Two Electrons at the Same Potential in Bis(1,3,5-triketonato)dicopper(II) Complexes and Their Diamine Schiff Bases. Effect of Na^+ and Similar Ions on the Cyclic Voltammetry

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The cyclic voltammetry of four binuclear Cu(II) 1,3,5-triketonates and their diamine Schiff-base derivatives has been investigated in DMF with $(C_2H_5)_4NClO_4$ as the supporting electrolyte. Addition of simple cations such as Na^+ to these solutions has a profound effect on the reduction potentials of the Cu(II) ions and on the stability of the reduced product. In the presence of a sufficient concentration of Na^+ ions, the complexes exhibit one CV wave due to the coppers with peak separations of 42–44 mV and cathodic half-peak widths of 42–44 mV also. These results may be obtained with no instrumental *iR* compensation, providing a high concentration of the supporting electrolyte is present. The process is reversible with use of the criteria of scan rate dependence of the cathodic peak current and width and the equivalence of the cathodic and anodic peak heights. Controlled-potential electrolysis results prove that the process involves the transfer of two electrons. All of the experimental facts may be explained by the reversible, sequential transfer of two electrons at the same potential. Although the two Cu(II) ions in the diamine Schiff bases are in much different coordination environments within the same molecule, they give rise to the same CV wave shapes as the triketonates; i.e., ΔE_p and $E_{pc} - E_{p/2}$ both are very nearly 42 mV. Thus, they also undergo two-electron transfer at the same potential. The only significant difference between the simpler binuclear Cu(II) triketonates and the diamine Schiff-base derivatives is that $E_{1/2}$ values for the Schiff bases are about 0.1 V more negative than for their triketonate analogues. These observations are consistent with treating the coppers as one electroactive center capable of accepting two electrons at a single potential. The effect of changing the donor atoms or the ligand substituents is simply to change the value of the apparent $E_{1/2}$.

Introduction

An intriguing reason for studying polynuclear transition-metal complexes is the possibility that the chemical reactivity associated with the metal center is significantly altered due to the presence of two or more metal ions per molecule. Such a possibility becomes especially interesting if reactivity changes are not simply additive.

It is logical to examine the electrochemical behavior of polynuclear complexes as one means of determining reactivity differences between polynuclear and simple mononuclear complexes, since electron transfer is an important reactivity mode for transition-metal compounds. In addition, there is considerable interest in designing compounds that can function as multielectron-transfer agents, in which two or more electrons are transferred at the same or very nearly the same potential. Such reagents used in reactions requiring two or more electrons in going from reactants to products may prevent the formation of radical intermediates that would be produced by a one-electron transfer. From this point of view, multielectron-transfer reagents might be particularly advantageous in the reactions of small molecules. For these reasons, many of our initial studies dealing with the reactivity of polynuclear complexes have centered on electrochemistry.

Initial electrochemical results from our laboratory reported the cyclic voltammetric, polarographic, and coulometric properties of several bis(1,3,5-triketonato)dicopper(II) complexes that have magnetic and certain spectral properties similar to those of the type 3 copper centers in metalloenzymes.[1,2] These complexes were shown to undergo sequential, one-electron, reversible reductions that are represented by eq 1. This interpretation of the experimental results

$$\mathrm{Cu_2(TKO)_2} \xrightleftharpoons{E_{1/2}'} \mathrm{Cu_2(TKO)_2}^- \xrightleftharpoons{E_{1/2}''} \mathrm{Cu_2(TKO)_2}^{2-} \qquad E_{1/2}' = E_{1/2}'' \tag{1}$$

is based upon the theory of multielectron cyclic voltammetry (CV) developed by Shain and co-workers[3,4] and a related treatment for polarography presented by Muller.[5] In both cases there is excellent agreement between theory and experiment. Regardless of the mechanism involved, it is clear from CV, polarographic, and electrolysis results that the binuclear Cu(II) complexes discussed can undergo two-electron transfer at a single potential. This result is quite unexpected since by magnetic criteria the Cu(II) ions are strongly interacting as evidenced by the fact that they are diamagnetic or very nearly so at room temperature. Indeed, if one were dealing with "normal" binuclear redox behavior, one would expect to see some significant separation of the potentials.

As a means of investigating the influence of the ligand environment on the two-electron-transfer behavior of binuclear complexes, the electrochemical study has been extended to the ethylenediamine Schiff-base derivatives of the binuclear Cu(II) 1,3,5-triketonates. In contrast to the situation fo the triketonates, in which the Cu(II) ions are in the same coordination environment, in the Schiff-base derivatives one Cu(II) is bound to two nitrogen and two oxygen donors while the other is bound to four oxygen donors. A detailed comparison of the electrochemical behavior of the two classes is presented below.

In all of the bis(1,3,5-triketonato)dicopper(II) and the diamine Schiff-base complexes studied to date, there is a quasi-reversible CV wave at about 0.3 V more negative than the two-electron wave of interest. In our initial studies, this wave was thought to be due to O_2 since it disappears on extended degassing with nitrogen and its reduction potential is similar to reported values for O_2 in DMF. Results presented herein prove that this wave is not due to O_2 but to the binuclear complex. Its disappearance in the initial studies was caused by the introduction of Na^+ ions (from an aqueous salt bridge), which form ion-paired species with the complex. As the Na^+ ion concentration increased, the complex was quantitatively converted to the ion-paired species, resulting in the total disappearance of the more negative wave. Thus, the wave that exhibits essentially reversible, sequential two-electron transfer at a single potential is due to a Na^+ ion-paired complex.

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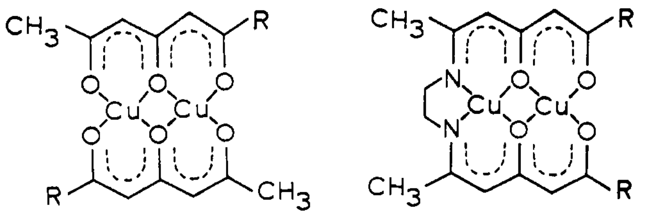
Chart I



R	ABBR	ABBR
C_6H_5	$Cu_2(BAA)_2$	$Cu_2(BAA)_2en$
t-C_4H_9	$Cu_2(PAA)_2$	$Cu_2(PAA)_2en$

Somewhat similar results have been observed in ion-paired organic molecules, some of which undergo two-electron reduction in the presence of small cations and one-electron reduction otherwise.[6-8] The influence of small cations on the electrochemical properties of these binuclear Cu(II) complexes is carefully investigated in this study.

Experimental Section

The abbreviations are based on nomenclature discussed elsewhere[9] and summarized in Chart I.

Synthetic procedures for the ligands and the complexes have been reported.[2,9] OmniSolv grade DMF and Kryptofix 221 were obtained from MCB Reagents.

Electrochemical Measurements. Unless otherwise stated, electrochemical measurements were made in *N*,*N*-dimethylformamide (DMF), which was used without further purification (OmniSolv grade, MCB). In order to ensure that the electrochemical behavior of the compounds was not affected by commercial DMF, we also recorded cyclic voltammograms using freshly distilled DMF that was refluxed for 4 h over calcium hydride and vacuum distilled at a temperature not exceeding 25 °C. The second third of the DMF collected was used. Base lines were run for both types of DMF to ensure electrochemical purity. Cyclic voltammograms obtained in OmniSolv and in freshly distilled DMF were not appreciably different. Reagent grade dimethyl sulfoxide (Me_2SO) and dichloromethane were used without purification. Tetraethylammonium perchlorate was used as the supporting electrolyte and was purified by a method developed by Handy.[10] A 50–100-g quantity of TEAP was dissolved in 300 mL of acetonitrile and passed through from one to three activated alumina columns, depending upon the initial purity of the TEAP. The TEAP was then precipitated by adding ca. 800 mL of ether. The mixture was cooled in a freezer to maximize the yield, and then the precipitate was collected by filtration. The pure white TEAP was air dried and then heated at ca. 60 °C overnight.

Solutions were deoxygenated by bubbling with ultra-high-purity N_2 that had previously been passed through a chromous-acid–perchloric acid scrubber, a calcium sulfate drying column, and a solution of solvent and TEAP. After deoxygenation, a slow stream of N_2 was passed over the solution throughout the experiment.

Cyclic Voltammetry. A Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a PAR Model 179 digital coulometer was used to obtain the cyclic voltammograms. The potential was controlled by a PAR Model 175 universal programmer. Scans of 50 mV/s and below were recorded on a PAR Model RE0074 X-Y recorder. Faster scans were photographed on a Tetronix Type 564B storage oscilloscope with two Type 2A63 differential amplifier (voltage recording) plug-in modules.

Cyclic voltammograms were obtained with use of three-electrode glass cell. The saturated NaCl calomel 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, while the second bridge contained a 0.1 M TEAP solution of the appropriate solvent. The usual salt bridge solutions such as 1.0 M $NaNO_3$ were not used (vide infra). A platinum wire served as the counterelectrode. The working electrode was a Brinkmann Model EA 290 hanging-mercury-drop electrode. Data were taken at temperatures between 22 and 25 °C. No correction was made for junction potentials. All potentials are quoted vs. the saturated NaCl calomel electrode.

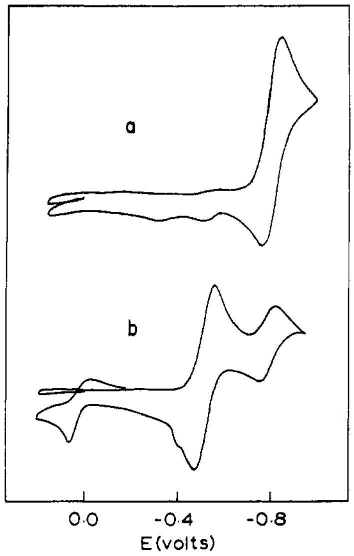


Figure 1. CV of 0.001 M $Cu_2(PAA)_2$ in DMF with 0.1 M TEAP at 50 mV/s: (a) no Na^+ added; (b) 0.0004 M $NaNO_3$ added.

Electrolysis was performed at a stirred Hg pool working electrode with use of PAR Model 173 potentiostat/galvanostat and a Model 175 universal programmer. The current–time curve was recorded with a Hewlett-Packard Model 7123A strip chart recorder. The counterelectrode consisted of a copper coil in a 0.13 M TEAP aqueous solution.

Results

As stated in the Introduction, the cyclic voltammograms of all the binuclear Cu(II) complexes initially contain two waves separated by about 0.3 V when run in the normal cell arrangement as described in ref 2. Our original observation was that the more negative of these waves (at about –0.9 V) disappears after extensive degassing with N_2. Therefore, we concluded that it was due to O_2 although it was inexplicably difficult to remove. Questions about whether it could be due to O_2 led to experiments in which the solutions containing the complex and TEAP were rigorously degassed with O_2-free nitrogen. The CV's obtained were identical in the presence or absence of O_2. On the basis of these results, it is possible to conclude that the second wave is not due to O_2 but to the complex. In addition, the relative concentrations of the two electroactive species vary from compound to compound, which also suggests that both waves are due to the complex. There is no apparent simple relationship between the currents of the two.

Observation of the two waves as a function of time in the electrochemical cell revealed that the more negative wave shrinks and the less negative wave grows, so that eventually only the less negative wave is present in the range 0 to –1.5 V. A time study outside of the cell in which some solution was periodically transferred to the cell and the CV recorded showed that the transformation is not simply a function of time. One conclusion from these initial experiments was that the transformation is caused by something in the cell. Inasmuch as the calomel electrode was separated from the working electrode by an aqueous 1 M $NaNO_3$ solution, the most likely possibilities appeared to be H_2O, Na^+, or NO_3^-. By the addition of H_2O to the solution and then $[(C_2H_5)N_4]NO_3$ it was determined that neither H_2O nor NO_3^- is responsible for the

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Table I. Cyclic Voltammetric Data for the "More Negative" Wave[a]

compd	E_{pc}, V[b]	$E_{1/2}$, V[b]	ΔE_p, mV	$E_{pc} - E_{p/2}$, mV	i_{pc}, μA	ν, V/s	[compd], M
$Cu_2(PAA)_2$	−0.83	−0.79	74	60	4.1	0.05	0.0010
	−0.81	−0.78	65	62	18	1	
	−0.81	−0.78	54	58	59	10	
$Cu_2(BAA)_2$	−0.76	−0.73	73	60	3.6	0.05	0.0010
$Cu_2(PAA)_2en$	−1.01	−0.97	64	57	2.6	0.02	0.0010
	−1.01	−0.98	66	57	4.2	0.05	
	−1.01	−0.98	62	56	17	1	
	−1.00	−0.98	48	54	58	10	
$Cu_2(BAA)_2en$	−0.92			60	0.74	0.05	0.00011[c]

[a] Average values for cyclic voltammograms in DMF with 0.10 M tetraethylammonium perchlorate supporting electrolyte. [b] Vs. the saturated NaCl calomel electrode. [c] A lower concentration is necessary due to limited solubility.

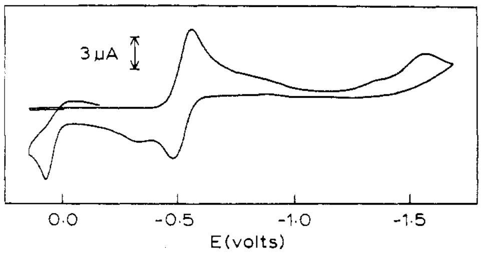

Figure 2. CV of 0.001 M $Cu_2(PAA)_2$ in DMF with 0.1 M TEAP and 0.001 M $NaNO_3$ at 50 mV/s.

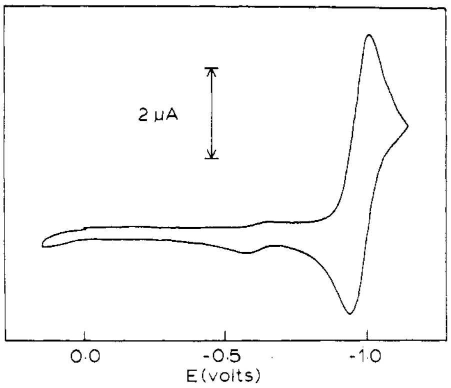

Figure 3. CV of 0.001 M $Cu_2(PAA)_2en$ in DMF with 0.1 M TEAP at 50 mV/s. No Na^+ has been added.

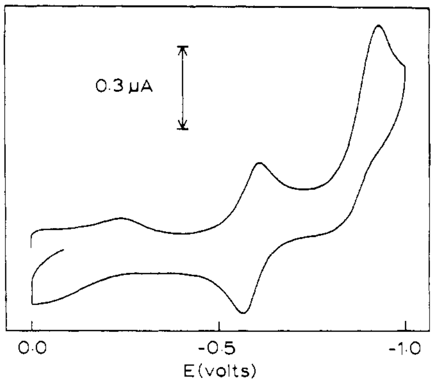

Figure 4. CV of 0.00011 M $Cu_2(BAA)_2en$ in DMF with 0.1 M TEAP at 50 mV/s. No Na^+ has been added.

transformation. At this stage the bridge was filled with an aqueous solution of TEAP so that no Na^+ ions could be introduced into the solution by the system itself. Under these conditions, only the more negative wave occurs and no transformation is observed after many hours of N_2 bubbling. Indeed, even after 3 weeks the CV is unchanged. A typical CV recorded under these conditions is shown in Figure 1a.

As small amounts of $NaNO_3$ are added, the less negative wave grows and the more negative wave shrinks (Figure 1b). In every case, the more negative wave has completely disappeared when a 1:1 molar ratio of Na^+ to complex is attained (Figure 2). The same transformation can be carried out by the addition of NaCl, NaCNS, $NaClO_4{\cdot}H_2O$, $LiClO_4{\cdot}3H_2O$, or $BaClO_4$. Thus, it appears likely that any simple cation will have the same effect. The same phenomenon has been observed for all of the bis(1,3,5-triketonato)dicopper(II) complexes and their Schiff-base diamine derivatives surveyed in DMF under the conditions described above. In addition, it has been observed for $Cu_2(PAA)_2en$ in dimethyl sulfoxide and for $Cu_2(PAA)_2$ in CH_2Cl_2. When the Na^+ ions are complexed with a cryptand-type ligand such as Kryptofix 221,[11] the transformation from the "more negative" to the "less negative" wave does not take place. Also, in solutions in which the transformation has been completed, it can be reversed by the addition of the cryptand ligand. These results are consistent with a specific interaction between Na^+ and the complex, which can be prevented by complexing the Na^+ with a large ligand. It is interesting that, in electrochemically pure DMF, one normally observes both waves with the "more negative" wave height about 20 times as great as the "less negative" height. The occurrence of a small "less negative" wave is apparently caused by trace cation impurities in the DMF since addition of the cryptand ligand completely eliminates it. In addition, increasing the concentration of the complex does not increase the height of the "less negative" wave, proving that its height is determined by a solvent constituent.

Attempts made to determine the effect of H^+ by the addition of phenol or NH_4NO_3 were not successful since each reacts with the complex and/or the reduced species. In each case, the CV waves were malformed and irreversible.

Cyclic voltammograms continued past the "less negative" wave in solutions containing $NaNO_3$, or past the ligand waves in solutions containing no $NaNO_3$, show an oxidation wave between 0 and +0.1 V on the return anodic scan (Figures 1b and 2). This wave is identical with the one obtained when $Cu(NO_3)_2{\cdot}3H_2O$ is added to the solution. Apparently the reduced triketonate slowly decomposes, resulting in the formation of some Cu/Hg amalgam. The amount of the dissociation is very small, since the anodic to cathodic peak ratios for the "less negative" wave are always very close to 1.0. The wave completely disappears at scan rates above about 100 mV/s.

Properties of the "More Negative" Wave. The cyclic voltammograms for $Cu_2(PAA)_2en$ and $Cu_2(BAA)_2en$ in DMF with TEAP but no Na^+ added are shown in Figures 3 and 4. In Figure 4 the presence of the "less negative" wave, which we attribute to a cation impurity in the DMF, is readily apparent due to the lower concentration (10^{-4} M) of $Cu_2(BAA)_2en$ required by the limited solubility.

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Table II. Cyclic Voltammetric Data for $Cu_2(PAA)_2$ for Increasing $[NaNO_3]:[Cu_2(PAA)_2]^{a,b}$

$[NaNO_3]:[Cu_2(PAA)_2]$	v, V/s	ΔE_p, mV	$E_{pc} - E_{p/2}$, mV	$E_{1/2}$, V^c	E_{pc}, V^c	i_{pc}, μA	$i_{pc}/v^{1/2}$, μA/(mV/s)$^{1/2}$
0.40	0.05	77	54	−0.51	−0.55		
1.0	0.02	65	56	−0.52	−0.55		
	0.05	71	56	−0.52	−0.55	7.2	1.0
2.0	0.02	55	48	−0.50	−0.52		
	0.05	60	48	−0.49	−0.52	8.0	1.1
	0.1	68	50	−0.51	−0.54		
	1	90	53	−0.50	−0.55	33	1.1
	10	153	60	−0.50	−0.58	100	1.0
3.0	0.02	50	46	−0.49	−0.52		
	0.05	57	47	−0.49	−0.52		
4.0	0.05	55	46	−0.49	−0.51		
5.0	0.05	53	44	−0.48	−0.50		
	10	119	48	−0.49	−0.55	110	1.1
10	0.02	42	43	−0.47	−0.49		
	0.05	49	43	−0.47	−0.50		
20.0	0.02	44	44	−0.47	−0.49		
	0.05	49	44	−0.46	−0.49		
	10	96	44	−0.47	−0.52		

[a] Average values for cyclic voltammograms in DMF with 0.10 M tetraethylammonium perchlorate. [b] The concentration of $Cu_2(PAA)_2$ is 0.0010 M throughout. [c] Vs. the saturated NaCl calomel electrode.

Table III. Cyclic Voltammetric Data for $Cu_2(BAA)_2$ for Increasing $[NaNO_3]:[Cu_2(BAA)_2]^{a,b}$

$[NaNO_3]:[Cu_2(BAA)_2]$	v, V/s	ΔE_p, mV	$E_{pc} - E_{p/2}$, mV	$E_{1/2}$, V^c	E_{pc}, V^c	i_{pc}, μA	i_{pa}/i_{pc}	$i_{pc}/v^{1/2}$, μA/(mV/s)$^{1/2}$
0.5	0.02	52	54	−0.47	−0.50			
	0.05	55	52	−0.48	−0.51	5.6		0.79
	10	114	50	−0.47	−0.53	72		0.72
1.0	0.02	52	53	−0.47	−0.49	5.1		1.1
	0.05	54	52	−0.47	−0.50	8.0		1.1
	10	107	49	−0.47	−0.52	...		...
2.0	0.02	44	48	−0.45	−0.48	5.2	0.96	1.2
	0.05	48	46	−0.45	−0.47	8.3		1.2
	10	92	44	−0.46	−0.51	110		1.1
3.0	0.05	44	44	−0.44	−0.46	...		...
4.0	0.05	44	44	−0.44	−0.46	8.2		1.2
5.0	0.02	39	44	−0.44	−0.46	...	0.95	...
	0.05	43	44	−0.44	−0.46	8.2		1.2
	10	74	42	−0.44	−0.48	110		1.1

[a] Average values for cyclic voltammograms in DMF with 0.10 M tetraethylammonium perchlorate. [b] The concentration of $Cu_2(BAA)_2$ is 0.0010 M throughout. [c] Vs. the saturated NaCl calomel electrode.

Table IV. Cyclic Voltammetric Data for $Cu_2(PAA)_2en$ for Increasing $[NaNO_3]:[Cu_2(PAA)_2en]^{a,b}$

$[NaNO_3]:[Cu_2(PAA)_2en]$	v, V/s	ΔE_p, mV	$E_{pc} - E_{p/2}$, mV	$E_{1/2}$, V^c	E_{pc}, V^c	i_{pc}, μA	i_{pa}/i_{pc}	$i_{pc}/v^{1/2}$, μA/(mV/s)$^{1/2}$
1.0	0.05	60	54	−0.66	−0.69	8.2		1.2
2.0	0.02	46	47	−0.64	−0.67	5.7	1.1	1.3
	0.05	50	46	−0.64	−0.67	8.9	1.0	1.3
	1	70	48	−0.64	−0.67	42		1.3
	10	94	48	−0.66	−0.70	160		1.6
5.0	0.02	42	44	−0.63	−0.65			
	0.05	46	44	−0.63	−0.66			
	10	76	43	−0.65	−0.68	170		1.7
10	0.02	45	43	−0.61	−0.63			
	0.05	46	43	−0.61	−0.63			
30	0.02	45	44	−0.61	−0.63		1.0	
	0.05	48	43	−0.60	−0.63			

[a] Average values for cyclic voltammograms in DMF with 0.1 M tetraethylammonium perchlorate. [b] The concentration of $Cu_2(PAA)_2en$ is 0.001 M throughout. [b] Vs. the saturated NaCl calomel electrode.

The electrochemical data for the "more negative" wave are given in Table I. These data represent scans extending about 150 mV beyond the cathodic wave. The values reported are averages from several scans. Irreversible waves found negative of −1.0 V are due to ligand reduction[2] while those positive of −1.0 V are attributable to the Cu(II) ions. The "more negative" wave is quasi-reversible with a well-formed cathodic peak whose peak half-width is about 60 mV, peak separation is about 70 mV, and anodic to cathodic current ratio is less than 1 at scan rates of 50 mV. At faster scan rates the process becomes more reversible as evidenced by a significant decrease in the peak separation and more equal anodic and cathodic currents. The shape of the cathodic peak is relatively unaffected by scan rate changes in the 50 mV/s to 10 V/s range.

Properties of the "Less Negative" Wave. The cyclic voltammograms for $Cu_2(BAA)_2$, $Cu_2(PAA)_2$, $Cu_2(BAA)_2en$, and $Cu_2(PAA)_2en$ in DMF with TEAP and at least 1 mol of Na^+/mol of complex exhibit one wave associated with the copper ions. A full scan for $Cu_2(PAA)_2$ is shown in Figure 2 and is reasonably typical of all the complexes. Figure 5 shows the wave for the two Schiff-base derivatives $Cu_2(BAA)_2en$ and $Cu_2(PAA)_2en$. Under these conditions, there

Table V. Cyclic Voltammetric Data for $Cu_2(BAA)_2en$ for Increasing $[NaNO_3]:[Cu_2(BAA)_2en]$[a,b]

$[NaNO_3]$: $[Cu_2(BAA)_2en]$	ν, V/s	ΔE_p, mV	$E_{pc} - E_{p/2}$, mV[c]	$E_{1/2}$, V[c]	E_{pc}, V[c]	i_{pc}, μA
2.0	0.02	46	46	−0.58	−0.61	
	0.05	50	47	−0.59	−0.61	1.0
10	0.05	43	44	−0.56	−0.59	
30	0.05	41	42	−0.55	−0.57	

[a] Average values for cyclic voltammograms in DMF with 0.1 M tetraethylammonium perchlorate. [b] The concentration of $Cu_2(BAA)_2en$ is 0.0001 M. The lower concentration is necessary due to limited solubility. [c] Vs. the saturated NaCl calomel electrode.

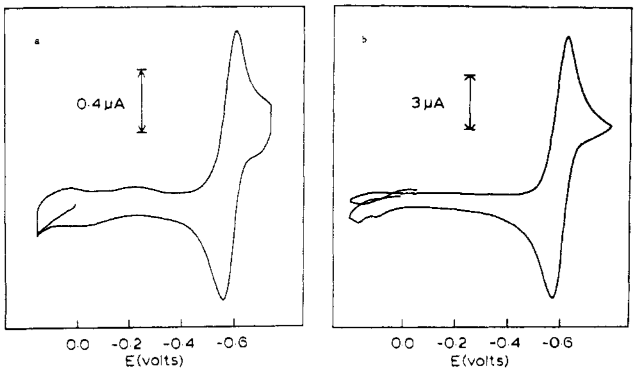


Figure 5. CV of (a) 0.00011 M $Cu_2(BAA)_2en$ in DMF with 0.1 M TEAP and 0.00022 M $NaNO_3$ at 50 mV/s and (b) 0.001 M $Cu_2(PAA)_2en$ in DMF with 0.1 TEAP and 0.002 M $NaNO_3$ at 50 mV/s.

is no remnant of the "more negative" wave. The cyclic voltammetric data for varying concentrations of Na^+ and scan rate are presented in Tables II–V. At a scan rate of 50 mV/s with a 5–10-fold molar excess of Na^+ the $E_{pc} - E_{p/2}$ and the ΔE_p values are very close to 42 mV. It should be noted that there is a significant peak separation (ΔE_p) increase, but not a great peak width increase, at rapid scans. For each of the compounds $i_{pc}/v^{1/2}$ is constant (i_{pc} is the cathodic peak current and v is the scan rate), except for $Cu_2(PAA)_2en$, for which there is a small deviation at 10 V/s.

The peak currents for each of the complexes were measured in solutions with no added Na^+ (thereby containing only the "more negative" wave) and in solutions in which sufficient Na^+ had been added so that only the "less negative" wave was present. In each case, the ratio of the peak current of the "less negative" wave to the peak current of the "more negative" wave is very close to 2. It should be noted that while both waves have been shown by CPE to be two-electron transfers (see below), they differ in shape in that the cathodic $E_{pc} - E_{p/2}$ values are approximately 45 and 60 mV for the "less negative" and "more negative" waves, respectively.

In order to ensure that the unusual peak separation and $E_{pc} - E_{p/2}$ values are not an artifact of the *iR compensation*, we conducted experiments at high electrolyte concentrations without any instrumental *iR* compensation applied. Under these conditions, the peak separation at moderate scan rates was still close to 42 mV and $E_{pc} - E_{p/2}$ is also very nearly 42 mV. For example, the cyclic voltammogram of a solution containing 1×10^{-3} M $Cu_2(PAA)_2$, 0.43 M TEAP, and 0.017 M $NaNO_3$ recorded at 50 mV/s without instrumental *iR* compensation is well formed with $\Delta E_p = 46$ mV and $E_{pc} - E_{p/2} = 42$ mV. Thus, the unusual shape and symmetry of the waves are not due to improper *iR* compensation but to the nature of the complexes themselves.

Controlled-Potential Electrolysis. Controlled-potential electrolysis (CPE) on the "more negative" wave, i.e. without Na^+ added, at a potential about 0.2 V more negative than the cathodic peak potential yields a value of 2 faradays/mol of complex. Cyclic voltammograms recorded after partial electrolysis showed an irreversible anodic wave at about −0.1 V. During the reduction, a yellowish brown precipitate forms as a scum on the surface of the Hg pool. The precipitate does not dissolve when the solution is reoxidized at 0.0 V, nor is it dissolved by adding $NaNO_3$.

Electrolysis of the "less negative" wave, i.e. with Na^+ added, at about 0.2 V more negative than the cathodic peak potential also yields a value of 2 faradays/mol of complex. The originally green solution turns yellowish or greenish brown during the reduction. A light scum forms on the Hg surface, but no precipitate forms, implying that Na^+ ions solubilize the reduced product. Cyclic voltammograms on the reduced solutions of $Cu_2(PAA)_2$ and $Cu_2(PAA)_2en$ showed a small irreversible oxidation wave at about −0.1 V. Electrolysis at 0.0 V of these solutions regenerated the original "less negative" wave essentially quantitatively.

Discussion

As described above, the cyclic voltammograms of binuclear Cu(II) complexes and their diamine Schiff-base derivatives obtained in DMF in the presence of Na^+ contain two-electron waves with peak separation (at moderate scan rates) and cathodic peak half-widths very close to 42 mV. The fact that these CV waves are due to copper redox and not the ligand has been established by investigating the cyclic voltammetric behavior of analogous binuclear Zn(II) complexes.[2] On the basis of these studies, it is clear that ligand reduction does not take place until at least −1.5 V, which is about 1.0 V more negative than the copper redox processes. The four related compounds studies, $Cu_2(BAA)_2$, $Cu_2(BAA)_2en$, $Cu_2(PAA)_2$, and $Cu_2(PAA)_2en$, show a high degree of electrochemical reversibility on the basis of $i_{pc}/v^{1/2}$ values, i_{pc}/i_{pa} ratios, cathodic peak half-widths, and peak separation as a function of scan rate. At very high scan rates, quasi-reversibility is evidenced by increased values of ΔE_p. It is also significant that these results may be obtained without instrumental *iR* compensation by operating at high concentrations of supporting electrolyte. Therefore, the unusual nature of the CV waves is not due to an instrumental artifact.

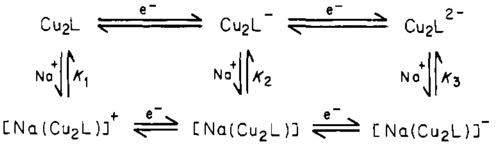
Shain and co-workers,[3,4] in developing the theory of multielectron cyclic voltammetry, have derived the theoretical CV wave for a process they describe as the reversible, sequential transfer of two electrons in which the formal potentials for the two steps are equal (eq 1). This reversible wave is characterized by a peak separation (ΔE_p) of 42 mV and a cathodic peak half-width ($E_{pc} - E_{p/2}$) of 42 mV. In this treatment, if the potential for the transfer of the second electron, E_2, were more positive than the potential for the first, E_1, the values of both ΔE_p and $E_{pc} - E_{p/2}$ would be less than 42 mV. Analogously, if E_2 were more negative than E_1, both ΔE_p and $E_{pc} - E_{p/2}$ would be greater than 42 mV. A working curve relating $E_2 - E_1$ to the cathodic peak half-width is presented in ref 4. On the basis of this treatment and on the fact that for $Cu_2(BAA)_2$, $Cu_2(PAA)_2$, $Cu_2(BAA)_2en$, and $Cu_2(PAA)_2en$ the copper electrochemistry is a nearly reversible two-electron process, we have interpreted the CV results as proving that each of these compounds undergoes sequential, two-electron transfer in which E_1 and E_2 are very nearly equal.

The fact that the potentials, E_1 and E_2, are essentially equal is quite surprising since intuitively one would expect a significant separation. For two totally noninteracting Cu(II) ions reducing sequentially, one expects a 35.6-mV separation in the potentials from statistical considerations.[12,13] However, the compounds studied herein must be considered to have relatively strong Cu(II)–Cu(II) interactions, judging from the fact that they are diamagnetic, or very nearly so, at room temperature corresponding to an antiferromagnetic exchange constant, $-J$, of at least 850 cm^{-1}.[9,14] As a result, one might have expected a significantly larger separation between E_1 and E_2 than 35.6 mV. A large separation has been observed in macrocyclic binuclear Cu(II) complexes containing bridging phenoxide-type oxygens and moderately strong antiferromagnetic exchange.[15,16] In contrast, a binuclear Cu(II) cryptate with very weak Cu(II)–Cu(II) interactions has been reported to have a potential separation of about 30 mV based on cathodic peak half-widths.[17]

It is surprising that the binuclear Cu(II) triketonates (in which the Cu(II) ions reside in equivalent coordination environments) undergo sequential two-electron redox at the same potential and that the diamine Schiff-base derivatives undergo the same electrochemistry. Inasmuch as the two Cu(II) ions in the Schiff-base complexes are in dramatically different coordination environments, one might have expected the reduction potentials to be widely separated. This is not the case, however, since only one reversible, sequential two-electron CV wave is observed for $Cu_2(BAA)_2en$ and $Cu_2(PAA)_2en$. The only significant difference between the CV waves of the triketonates vs. those of the Schiff-base derivatives is in the value of the potentials; i.e., for $Cu(BAA)_2$ and $Cu_2(BAA)_2en$, the $E_{1/2}$ values are −0.44 and −0.56 V, respectively, while the $E_{1/2}$ values for $Cu_2(PAA)_2$ and $Cu_2(PAA)_2en$ are −0.47 and −0.61 V, respectively.[18] The more negative potentials for the Cu(II) reductions in the binuclear Schiff-base derivatives is in keeping with the observation that, in *mononuclear* Cu(II) complexes, imine coordinated Cu(II) reduction potentials are more negative than those of analogous ketonate oxygen coordinated Cu(II).[19] On the basis of this general observation for mononuclear Cu(II) complexes, the potentials for $Cu_2(BAA)_2en$ and $Cu_2(PAA)_2en$ are expected to be more negative than for $Cu_2(BAA)_2$ and $Cu_2(PAA)_2$. The potential shifts for $Cu_2(BAA)_2en$ and $Cu_2(PAA)_2en$ and the fact that they reduce by the addition of two electrons at a single potential make it appear that the effect of nitrogen coordination is to change the *average* environment of both metal centers rather than to change the potential of only one Cu(II). One way to look at these results is that all of the compounds studied appear to have *only one electroactive center* (in the range 0 to −1.5 V), which undergoes two-electron transfer, rather than two centers each capable of one-electron transfer. With this view, modifications of the ligand result in a perturbation of this electroactive center but not in a separation into two centers.

As the results show, the presence of small cations such as Na^+ has a profound effect on the nonaqueous electrochemistry of all of the binuclear Cu(II) 1,3,5-triketonates and their Schiff-base derivatives. Two related effects have been observed that are dependent upon the concentrations of Na^+: First, there is a shift in the redox potentials of about +0.30 V when Na^+ is present. When the concentration of Na^+ is equal to or greater than the complex concentration, only the more positive CV wave is observed. Second, at high concentrations of Na^+, the potentials for the transfer of the two electrons become more nearly equal as evidenced by the approach of ΔE_p and $E_{pc} - E_{p/2}$ to 42 mV, as the Na^+ concentration increases relative to that of the complex (Tables II–V). Thus, in the absence of Na^+ or similar ions a quasi-reversible CV wave is observed at about −0.9 V. The introduction of Na^+ causes the growth of the wave at about −0.5 to −0.6 V. The conversion of the "more negative" wave to the "more positive" wave is complete at a 1:1 Na^+:complex ratio.[20] Addition of more Na^+ gives the final wave in which ΔE_p and $E_{pc} - E_{p/2}$ are very nearly 42 mV.

Scheme I



Similar shifts to more positive potentials have been observed for organic compounds in the presence of Na^+ ions,[6-8] which are attributed to ion pairing. A model based on ion-pair formation between the neutral binuclear Cu(II) complex and its reduction products that may be useful in explaining the results is shown in the Scheme I.[21] Strong binding between Na^+ and the ionic reduction products such that $K_3 > K_2 > K_1$ would result in a positive shift of the potential.[8]

In the absence of Na^+ or other small cations only the quasi-reversible "more negative" wave at about −0.9 V is observed in the range 0 to −1.5 V (Figures 1a and 3). Controlled-potential electrolysis (CPE) at about 0.2 V more negative than this wave results in the transfer of 2.0 electrons. On the basis of $i_{pc}/v^{1/2}$ data (Table I) the wave appears reversible; however, at slow scans the cathodic peak current is considerably greater than the anodic peak current. At very rapid scans the peak currents are equal, and the process appears quite reversible by standard criteria. The cathodic peak half-width, $E_{pc} - E_{p/2}$, is nearly constant over a large range of scan rates and has a value of about 60 mV for all of the compounds. ΔE_p is somewhat scan rate dependent and decreases to about 50 mV at very rapid scans. At moderate scan rates ΔE_p is typically about 65 mV. The other significant characteristic of this wave is that the peak current, i_{pc}, is considerably less than observed for the "less negative" wave. The values of ΔE_p and $E_{pc} - E_{p/2}$ as well as the reduced peak current are consistent with the sequential transfer of two electrons in which the potential for the addition of the second is more negative than that for the first.[4] Since the process is not completely reversible, it is not possible to rigorously apply the Myers and Shain[4] treatment to determine the values of $E_2 - E_1$ from the values of $E_{pc} - E_{p/2}$. However, the degree of reversibility is perhaps high enough to justify stating that $E_2 - E_1$ is on the order of 40 mV. If this interpretation of the

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(20) In an earlier paper,[2] we reported that the CPE of the more positive wave for certain compounds resulted in the transfer of fractional numbers of electrons and that this must be due to the formation of a partially reduced dimer. A mechanism for dimer formation was proposed. In actual fact, the CPE in these cases was unknowingly carried out in solutions containing both the Na^+ ion paired species and the Na^+-free species. Both waves were present because of a small amount of Na^+ introduced from the salt bridge, the significance of which was not suspected at the time. The CPE potential was such that only the "more positive" wave was reduced, leaving the Na^+-free species unreduced. Thus, the number of electrons transferred corresponded to a fraction of the total Cu(II) ion present.

(21) We thank a reviewer for suggesting this scheme and pointing out the similarity of this system to that for the electrochemical properties of organic molecules that form Na^+ ion pairs.

"Na^+-free" wave is correct, then operationally the processes responsible for it are not all that different from those responsible for the Na^+ ion paired wave.

Conclusions

1. In the presence of simple cations such as Na^+, the binuclear Cu(II) 1,3,5-triketonates and their diamine Schiff-base derivatives undergo reversible, sequential, two-electron reduction (in the range −0.5 to −0.65 V) in which the potentials for the transfer of the two electrons are nearly equal.

2. The only significant difference between the electrochemical results for $Cu_2(BAA)_2$ and $Cu_2(PAA)_2$ vs. those for $Cu_2(BAA)_2en$ and $Cu_2(PAA)_2en$ is a difference in the potential. The perturbation of the electroactive center by the diamine nitrogen donor atoms results in a more negative value of $E_{1/2}$ but does not cause E_1 and E_2 to separate. In this regard, the complexes behave as if they have one electroactive center that is sensitive to the average ligand environment rather than two.

3. Na^+ ions form ion pairs with reduced complexes and in doing so significantly stabilize the Cu^I, Cu^I state as evidenced by the potential shift of about +0.3 V from that for the Na^+-free system. In addition, the equivalence of E_1 and E_2 is dependent upon the Na^+ concentration.

4. In the absence of simple cations such as Na^+ (with Et_4NClO_4 as supporting electrolyte) a quasi-reversible, two-electron CV wave is observed in the range −0.8 to −1.0 V. This Na^+-free species appears to have a potential separation, $E_2 - E_1$, of approximately −40 mV for the transfer of the two electrons. Addition of 1 equiv of Na^+ causes the disappearance of this wave and the appearance of the −0.5 to −0.65 V wave.

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Registry No. $Cu_2(PAA)_2en$, 60116-99-6; $Cu_2(PAA)_2$, 84130-49-4; $Cu_2(BAA)_2en$, 56550-34-6; $Cu_2(BAA)_2$, 29745-70-8; Na, 7440-23-5; TEAP, 2567-83-1.

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Mechanism of Nucleophilic Displacement of the Bromide Ion by Thioethers in the Bromo(1,5-diamino-3-azapentane)platinum(II) Cation

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The kinetics of the displacement of bromide from $Pt(dien)Br^+$ (dien = 1,5-diamino-3-azapentane) by the thioethers $(CH_3)_2S$, $(C_2H_5)(CH_3)S$, $(C_2H_5)_2S$, $(\beta\text{-}ClC_2H_4)(CH_3)S$, $(i\text{-}C_3H_7)_2S$, $(n\text{-}C_4H_9)_2S$, $(sec\text{-}C_4H_9)_2S$, $(CH_2)_4S$, and thioxane have been studied in 95/5 vol % methanol/water solution at 25.0 °C. The second-order rate constants are insensitive to the changes in the inductive effect of the organic groups attached to the sulfur but decrease as their bulkiness is increased.

Introduction

Systematic studies of the way in which the nucleophilicities with respect to platinum(II) of a series of ligands with a constant donor atom depend upon the nature of the substituents have so far been confined to N donors (amines and heterocyclic nitrogen bases) and S donors (thioethers) reacting with neutral substrates.[3] It has been possible, unambiguously, to separate electronic and steric effects in heterocyclic nitrogen bases by choosing the 4-position for the variation of the electronic effect and the 2- and 6-positions for the variation of the steric effect, and the conclusion from studies of this sort could be used to assess hindrance of less obvious molecules; i.e., it was shown that diethylamine had a steric hindrance similar to that of 2-methylpyridine.[4] Early observations suggested significant retardation by steric hindrance and the absence of any marked inductive effects (as measured by the proton basicity of the amine) on the reactivity. Recently we have shown that this is not always true for substitutions at platinum(II) but depends upon the nature of the intimate mechanism.[5]

In the case of thioethers, the systematic studies involve the reaction of the neutral substrates[6-8]

$$trans\text{-}[Pt(py)_2Cl_2] + RSR' \rightarrow trans\text{-}[Pt(py)_2(RSR')Cl]^+ + Cl^- \quad (1)^{6,7}$$

$$[Pt(bpy)(C)X] + RSR' \rightarrow [Pt(bpy)(C)RSR']^+ + X^- \quad (2)^{8}$$

(py = pyridine; bpy = 2,2′-bipyridyl; C and X are anionic ligands, X being the one which is displaced). In the reactions of the bpy complexes the plots of log k_2 against $-\sum\sigma^*$, where k_2 is the second-order rate constant for the entry of thioether and σ^* the Taft polar parameter for a substituent, are linear, with no significant deviations that might be ascribed to steric hindrance, while the reactions of *trans*-$[Pt(py)_2Cl_2]$ with aliphatic thioethers show both effects.[6] In the systematic study of Gaylor and Senoff[7] the steric effect is held constant by using 4,4′-substituted diphenyl sulfides as nucleophiles. Here there is a marked dependence of nucleophilicity upon the inductive effect.

However, a study of the reaction between the palladium(II) substrate $[Pd(dien)H_2O]^{2+}$ and thioethers in methanol/water has revealed the importance of steric effects and very little

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