

Effect of Solvent on Sequential Two-Electron Transfer in Bis(1,3,5-triketonato)dicopper(II) Complexes

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The cyclic voltammetry of bis(1-phenyl-1,3,5-hexanetrionato)dicopper(II) has been investigated in different solvents over a scan range of 10^3 V/s. Comparisons of the behavior of this complex in DMF, DMSO, and pyridine in the presence and absence of sodium ion show that the electron-transfer properties are strongly solvent dependent. In DMSO, the complex undergoes a reversible one-electron transfer at $E_{1/2} = 0.85$ V vs SSCE. However, upon the addition of a 10-fold excess of simple cations such as Na^+ , the electron transfer is a nearly reversible, sequential two-electron transfer. In addition, the cation shifts the reduction potential to $E_{1/2} = 0.55$ V. These results are very similar to those recorded in DMF. In pyridine a quasi-reversible sequential two-electron process is observed at $E_{1/2} = 0.80$ V without the addition of simple cations. This two-electron process, upon the addition of Na^+ , is split into two one-electron processes, both of which are shifted to more positive potentials. The first is irreversible at $E_{pc} = -0.40$ V, and the second is quasi-reversible, occurring at $E_{1/2} = -0.71$ V. The potential differences, $E_1 - E_2$, for the sequential two-electron transfers observed in pyridine, DMF, and DMSO are 90, 30, and -180 mV, respectively.

Introduction

It has been observed that binuclear copper(II) 1,3,5-triketones and their diamine Schiff base derivatives in DMF and in the presence of simple cations undergo nearly reversible, sequential transfer of two electrons at very similar potentials.¹⁻³ The difference in potential between the two electron transfers is less than 50 mV. Such systems are of interest as electrocatalysts in the reactions of small molecules since virtually all useful reactions of small molecules involve multielectron transfer.⁴

Inasmuch as sequential two-electron transfer has been observed for binuclear Cu(II) complexes, it is interesting to study related complexes with more than two copper ions. The hope, of course, is to design polynuclear complexes capable of transferring more than two electrons all at similar potentials. Our initial approach has been to employ ligands, closely related to the 1,3,5-triketones, that are capable of binding four Cu(II) ions. Similarity to the 1,3,5-triketones will facilitate a direct electrochemical comparison of the tetranuclear complexes to the well-studied binuclear systems. One of the first ligands used in this work is 1,3-bis(2-methyl-3,5,7-heptanetrion-7-yl)benzene. This molecule has two 1,3,5-triketone moieties substituted at the meta positions of a benzene ring. Two ligand molecules do indeed form a discrete, neutral tetranuclear Cu(II) complex containing two binuclear Cu(II) moieties.⁵ However, low solubility in DMF prevents a direct electrochemical comparison between the structurally related bi- and tetranuclear complexes. Solubilities of high molecular weight complexes are generally sufficiently high, however, in DMSO and pyridine that comparative studies can be conducted in these solvents. DMSO and pyridine are acceptable electrochemical solvents⁶ and are well suited for such comparisons.

Since no electrochemical studies on the binuclear copper(II) 1,3,5-triketones have been carried out in DMSO or pyridine, this work was undertaken to determine the effect of solvent on the reversible, sequential two-electron transfer observed in DMF. The results in DMSO and pyridine will lay the necessary foundation for comparisons to the more complex molecules containing more than two metal ions and form the basis for comparative electrochemical studies of related polynuclear metal complexes in the same solvent media.

Experimental Section

I. Synthesis. The general synthesis of the 1,3,5-triketones has been reported.^{7,8} The synthesis of bis(1-phenyl-1,3,5-hexanetrionato)dicopper(II), $\text{Cu}_2(\text{BAA})_2$, has also been reported.⁷

II. 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 was accomplished with a Nicolet digital oscilloscope, Model 2090-3C with binary digital I/O. The data was passed to a Data General Eclipse S-130 computer where the curves were plotted and measured, after which the applicable calculations were performed. Electrochemical measurements were made in B & J Brand high-purity (Burdick & Jackson Laboratories Inc.) dimethyl sulfoxide (DMSO) and Aldrich Gold Label anhydrous pyridine without further purification. Solutions were deoxygenated with ultrahigh-purity N_2 that had been passed through a pair of chromous-perchloric acid scrubbers and a CaSO_4 drying column. Blanks indicated that no electroactive impurities were present in the scan range from 0.0 to -2.1 V.

Cyclic voltammograms were obtained by using a three-electrode glass cell with a saturated NaCl calomel (SSCE) reference electrode, a Pt-wire counter electrode, and a Brinkmann Model EA 290 hanging-mercury-drop electrode (HMDE). 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 tetraethylammonium perchlorate (TEAP) aqueous solution, and the one adjacent to the sample chamber contained a 0.1 M TEAP solvent solution. Chronoamperometry was carried out under the same conditions described for cyclic voltammetry.

Results

The cyclic voltammogram (CV) of $\text{Cu}_2(\text{BAA})_2$ in DMSO with TEAP as supporting electrolyte consists of one nearly reversible wave with $E_{1/2} = -0.85$ V vs SSCE and irreversible waves at about -1.35 and -1.60 V. The characteristic information about the reversible wave is given in Table I at various scan rates from 10 mV/s to 100 V/s. Addition of NaNO_3 (1×10^{-2} M) to the DMSO solution of $\text{Cu}_2(\text{BAA})_2$ and TEAP shifts the most positive wave by +300 mV, sharpens the wave considerably, and greatly increases the peak currents (Table I).

Chronoamperometric (CA) data for $\text{Cu}_2(\text{BAA})_2$ in DMSO with TEAP supporting electrolyte in the absence and presence of Na^+ is given in Table II. The slope of the current vs the reciprocal of the square root of time yields a straight line whose slope is proportional to the number of electrons transferred, n . This follows from the Cottrell equation⁹ modified for spherical electrodes

$$i_d(t) = nFA D_0 C_0^* [1/(\pi D_0 t)^{1/2} + 1/r_0]$$

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Table I. Cyclic Voltammetry Data for $\text{Cu}_2(\text{BAA})_2$ in DMSO and Pyridine^a

scan rate, V/s	$E_{1/2}$, V	E_{pc} , V	ΔE_p , mV	$E_{pc} - E_{pc/2}$, mV	i_{pc} , μA	i_{pa}/i_{pc}	$i_{pc}/v^{1/2}$, $\mu\text{A}/\text{s}^{1/2}$
A. DMSO							
(1) $\text{Cu}_2(\text{BAA})_2$, 5×10^{-3} M; TEAP, 0.1 M							
0.01	-0.85	-0.88	74	62	-4.59	0.90	45.84
0.02	-0.84	-0.88	78	50	-6.99	0.81	48.78
0.05	-0.86	-0.88	59	50	-10.26	0.87	45.38
0.10	-0.85	-0.87	59	47	-14.99	0.85	47.00
0.20	-0.85	-0.87	60	47	-21.22	0.88	46.84
0.50	-0.83	-0.86	49	29	-33.85	0.87	47.31
1.00	-0.84	-0.86	51	29	-47.82	0.87	47.35
2.00	-0.84	-0.86	57	29	-67.71	0.89	47.72
5.00	-0.83	-0.87	76	29	-107.23	0.89	47.64
10.00	-0.83	-0.88	84	35	-139.94	0.91	43.92
20.00	-0.83	-0.88	95	34	-213.77	0.80	47.62
50.00	-0.84	-0.90	124	39	-347.84	0.71	34.44
100.00	-0.85	-0.94	187	63	-428.96	0.74	31.62
(2) $\text{Cu}_2(\text{BAA})_2$, 5×10^{-3} M; NaNO_3 , 1×10^{-2} M; TEAP, 0.1 M							
0.01	-0.56	-0.57	28	20	-11.97	0.93	120.93
0.02	-0.55	-0.57	36	30	-15.31	1.01	109.34
0.05	-0.55	-0.57	34	24	-24.84	1.02	110.12
0.10	-0.55	-0.57	35	23	-32.62	1.06	102.14
0.20	-0.55	-0.57	37	28	-44.12	1.07	97.96
0.50	-0.55	-0.57	38	22	-73.93	1.04	102.97
1.00	-0.55	-0.57	35	20	-111.03	1.04	109.93
2.00	-0.54	-0.56	40	16	-171.97	0.85	120.60
5.00	-0.53	-0.55	55	17	-275.67	0.74	124.12
10.00	-0.52	-0.56	71	18	-373.63	0.74	118.68
20.00	-0.53	-0.56	74	16	-599.08	0.78	134.90
50.00	-0.53	-0.59	119	26	-869.31	0.82	67.57
100.00	-0.55	-0.64	195	47	-1087.90	0.77	64.10
B. Pyridine							
(1) $\text{Cu}_2(\text{BAA})_2$, 5×10^{-3} M; TEAP, 0.1 M							
0.02	-0.79	-0.85	125	47	-20.32	0.90	143.71
0.05	-0.79	-0.86	137	48	-30.17	0.69	137.48
0.10	-0.79	-0.86	144	50	-42.23	0.69	133.54
0.20	-0.79	-0.87	172	50	-59.10	0.68	132.09
0.50	-0.79	-0.87	178	58	-92.08	0.66	130.07
1.00	-0.79	-0.88	188	57	-117.00	0.67	117.12
2.00	-0.76	-0.89	246	81	-148.39	0.66	105.75
5.00	-0.80	-0.95	291	95	-213.73	0.68	95.59
10.00	-0.82	-0.99	343	124	-288.15	0.67	91.12
20.00	-0.82	-1.03	410	141	-317.69	0.67	71.28
50.00	-0.82	-1.06	469	148	-540.48	0.69	76.45
100.00	-0.80	-1.07	547	162	-664.12	0.75	66.60
(2) $\text{Cu}_2(\text{BAA})_2$, 5×10^{-3} M; NaNO_3 , 1×10^{-2} M; TEAP, 0.1 M							
0.01	-0.72	-0.75	66	61	-7.79	1.33	75.62
0.02	-0.71	-0.75	69	61	-11.78	1.10	81.23
0.05	-0.72	-0.76	84	61	-21.30	0.68	93.24
0.10	-0.71	-0.76	97	66	-42.59	0.54	131.48
0.20	-0.72	-0.79	138	73	-79.04	0.42	172.02
0.50	-0.72	-0.78	128	84	-69.90	0.56	96.52
1.00	-0.72	-0.81	174	70	-140.08	0.49	138.25
2.00	-0.72	-0.82	195	84	-151.12	0.60	105.75
5.00	-0.72	-0.84	235	99	-166.78	0.78	73.64
10.00	-0.70	-0.83	264	89	-192.95	0.87	60.20
20.00	-0.69	-0.84	305	92	-246.03	0.81	54.25
50.00	-0.67	-0.86	373	94	-355.20	0.88	49.56
100.00	-0.67	-0.87	416	100	-479.97	0.79	47.42

^aAll potentials are versus SSCE.

where the variables have their usual significance. The slope in the presence of Na^+ is twice the slope in the absence of Na^+ . Assuming the diffusion constant is the same with and without Na^+ , one can conclude that twice as many electrons are transferred with Na^+ as without Na^+ . Estimating the diffusion constant to be $6.5 \times 10^{-6} \text{ cm}^2/\text{s}$ allows one to calculate values of $n = 1$ (without Na^+) and $n = 2$ (with Na^+).²

The CV of $\text{Cu}_2(\text{BAA})_2$ in pyridine with TEAP as supporting electrolyte consists of a quasi-reversible wave at $E_{1/2} = -0.80$ V vs SSCE and an irreversible wave at -1.4 V. The characteristics of the quasi-reversible wave over a broad scan rate range are given

Table II. Chronamperometry Data for 5 mM Solutions of $\text{Cu}_2(\text{BAA})_2$ in DMSO and Pyridine

solvent	E_p , V	slope, ^a $\mu\text{A s}^{1/2}$	y-intercept, μA	r^2	n
DMSO	-0.88	9.04 (1)	2.37 (4)	0.9999	1
DMSO/ Na^+	-0.57	17.7 (1)	0.6 (3)	0.9985	2
pyridine	-0.86	24.64 (5)	3.1 (1)	0.9998	2
pyridine/ Na^+	-0.72	12.68 (3)	5.50 (9)	0.9998	1

^aWhere the slope is proportional to n .

in Table I. A trace of the wave at 20 mV/s is shown in Figure 1. Addition of NaNO_3 (1×10^{-2} M) to the pyridine solution of $\text{Cu}_2(\text{BAA})_2$ and TEAP results in three distinct waves. The

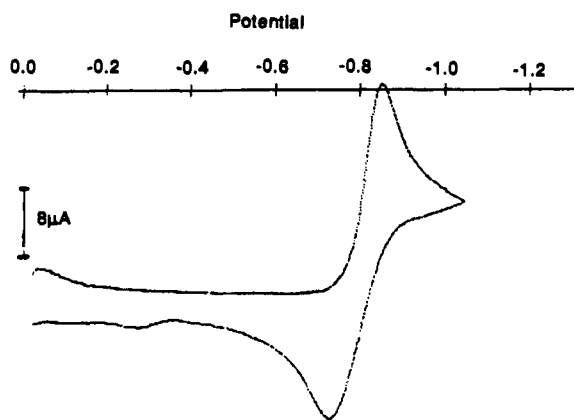


Figure 1. Cyclic voltammogram of 5.0 mM $\text{Cu}_2(\text{BAA})_2$ in pyridine at a HMDE vs SSCE. Supporting electrolyte is 0.1 M TEAP. Scan rate = 20 mV/s.

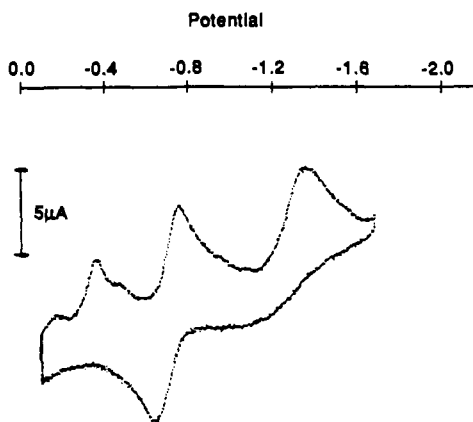


Figure 2. Cyclic voltammogram of 0.5 mM $\text{Cu}_2(\text{BAA})_2$ in pyridine with 0.01 M NaClO_4 and 0.1 M TEAP at a HMDE vs SSCE. Scan rate = 500 mV/s.

most positive is irreversible and appears at -0.4 V vs SSCE. The next is a quasi-reversible wave at about -0.7 V. The most negative occurs at -1.4 V and is irreversible. The entire CV from 0.0 to -1.6 V is shown in Figure 2 at a scan rate of 500 mV/s. The characteristics of the quasi-reversible wave at -0.7 V are given in Table I over a broad scan rate range.

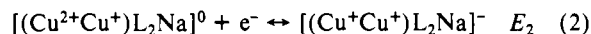
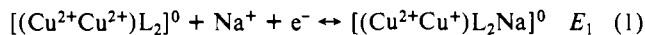
The CA results in pyridine in the absence and presence of Na^+ are reported in Table II. Of primary interest are the quasi-reversible waves at about -0.8 V (without Na^+) and -0.7 V (with Na^+). The CA potentials applied (E_p) were -0.86 and -0.80 V, respectively. The slopes of the straight lines that result from plotting the CA current vs $1/s^{1/2}$ are 24.6 and 12.7 $\mu\text{A s}^{1/2}$, respectively, indicating the transfer of twice as many electrons without Na^+ as with Na^+ . Assuming a diffusion constant of 6.5×10^{-6} cm^2/s , the value of n is 2 without Na^+ and 1 with Na^+ . On this same basis, the irreversible wave at -0.4 V in the presence of Na^+ is a one-electron-transfer wave.

Discussion

In recent years much of the research from this laboratory has dealt with multielectron-transfer electrochemistry of polynuclear metal complexes. The binuclear Cu(II) complexes of 1,3,5-triketones and their Schiff-base derivatives have been of particular interest.¹⁻³ A series of investigations has shown that these binuclear complexes in DMF and in the presence of simple cations undergo the nearly reversible, sequential transfer of two electrons at very similar potentials ($E_1 - E_2 \cong 30$ mV).²

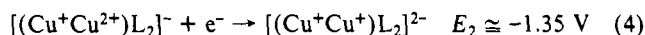
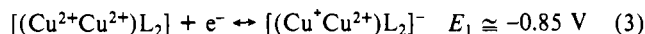
Addition of simple cations such as Na^+ or K^+ to the DMF solution containing binuclear complex and tetraethylammonium perchlorate (TEAP) supporting electrolyte results in a shift of about +300 mV in the reduction potential and in the conversion from a one-electron to a two-electron CV wave.² The magnitude of the positive shift and the details of the two-electron wave are

determined by size and charge of the added cation.³ It has been shown that the cations bind strongly to the terminal triketonate oxygens in the reduced complexes. The effect of this binding is to neutralize the negative charge on the one-electron-reduced species. The sequential transfer of two electrons can be represented by eqs 1 and 2. When $[(\text{Cu}^{2+}\text{Cu}^{2+})\text{L}_2]$ is $\text{Cu}_2(\text{BAA})_2$ the potential



for (1) is -0.52 V and the potential for (2) is -0.55 . Thus, $E_1 - E_2 = 30$ mV.² The two-electron nature of these CV waves has been confirmed by simulation² and chronoamperometry.³

In the absence of a simple cation such as Na^+ or K^+ , a one-electron reversible transfer is observed at about -0.9 V vs SSCE. Additional irreversible CV waves are observed at about -1.4 and -1.6 V. These results are reasonably represented by eqs 3 and 4.



While the electrochemistry of the binuclear copper(II) 1,3,5-triketones and their Schiff-base derivatives has been well documented in DMF, no studies have been undertaken to examine the effect of solvent changes. The solvent study takes on an additional significance since related systems with more complex ligands and more metal ions per molecule have low solubility in DMF. Since bis(1-phenyl-1,3,5-hexanetrionato)dicopper(II), $\text{Cu}_2(\text{BAA})_2$, is well characterized and electrochemically well-behaved in DMF, we chose to investigate this molecule in DMSO and pyridine so that comparisons with more complex molecules would be facilitated. DMSO and pyridine were selected as solvents because of their solvating properties for polynuclear metal complexes, in general, and because they are reasonable electrochemical solvents.

Electrochemistry in DMSO. The CV results obtained for $\text{Cu}_2(\text{BAA})_2$ in DMSO and in DMF are qualitatively very similar.¹⁻³ DMSO solutions containing only $\text{Cu}_2(\text{BAA})_2$ and TEAP exhibit a quasi-reversible one-electron wave at -0.85 V vs SSCE and irreversible waves at -1.35 and $+1.60$ V. As in DMF, eqs 3 and 4 are reasonable explanations for the behavior in DMSO under these conditions. Chronoamperometry results in both DMF³ and DMSO (Table II) under these conditions are consistent with a one-electron-transfer process for the quasi-reversible wave at about -0.94 V.

The effect of simple cations such as Na^+ on the electrochemistry of $\text{Cu}_2(\text{BAA})_2$ in DMSO is also very similar to that in DMF. DMSO solutions containing $\text{Cu}_2(\text{BAA})_2$, TEAP, and NaNO_3 exhibit a CV wave at about -0.55 V vs SSCE. When the concentration of Na^+ is 5 or more times the concentration of $\text{Cu}_2(\text{BAA})_2$, this wave is beautifully formed with peak current and wave shape that obviously indicate the transfer of more than one electron. (Figure 4 in ref 2 illustrates this effect clearly in DMF solution.) In DMSO at slow scans, this process is quite reversible as evidenced by the value of i_{pa}/i_{pc} . The values of the peak separations, ΔE_p , and the half-width of the cathodic peak, $E_{pc} - E_{pc/2}$, are about 35 and 24 mV, respectively. These values are consistent with a multielectron-transfer process.^{10,11} Both are close to the expected value (29.5 mV) for the simultaneous transfer of two electrons in which E_1 is appreciably more negative than E_2 . Chronoamperometric data also prove that this CV wave is due to a $2e^-$ transfer. Computer simulation of the type described in ref 2 (using the modified program of Sokal et al.¹²) for the wave obtained at slow scans showed that the experimental wave could

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be reproduced quite well with E_1 at least 180 mV more negative than E_2 . These are the conditions that give rise to a CV wave with ΔE_p and cathodic peak half-width of 29.5 mV. Such conditions fulfill the criteria for the simultaneous transfer of two electrons.

Although the electrochemical results in DMF and DMSO are qualitatively very similar there is an important difference between the two when simple cations are present and two-electron CV waves are observed. In DMF, the potential for the transfer of the second electron is about 30 mV more negative than the potential for the first. In DMSO, the CV wave is consistent with the potential of the second electron being about 180 mV more positive than the first. The effect of the added cation is extremely interesting in view of its profound effect on the number of electrons transferred, on the overall potential, and on the relative potentials of E_1 and E_2 . Obviously, the solvent is also a critical factor in determining these relative potentials.

Electrochemistry in Pyridine. The CV behavior of $\text{Cu}_2(\text{BAA})_2$ in pyridine is entirely different than in DMF or DMSO. In pyridine containing only $\text{Cu}_2(\text{BAA})_2$ and TEAP as supporting electrolyte, a quasi-reversible wave is observed which on the basis of cathodic peak half-width ($E_{pc} - E_{pc/2}$) involves more than one electron. That is, at slow scans $E_{pc} - E_{pc/2}$ is 50 mV or less and the cathodic peak currents (i_{pc}) are much larger than one would expect for a one-electron transfer. The values of i_{pc} for $\text{Cu}_2(\text{BAA})_2$ in DMSO + Na^+ and in pyridine at the same scan rates are comparable. The values in pyridine are approximately 33% greater than in DMSO + Na^+ . The difference may be attributable to a slightly larger diffusion constant in pyridine than in DMSO. At slow scans the wave is very well formed and fits the criteria for a quasi-reversible two-electron-transfer process (Figure 1). Thus, while it is necessary in DMF and DMSO to add a simple cation in order to induce the sequential, two-electron transfer in $\text{Cu}_2(\text{BAA})_2$, in pyridine a similar process is observed with only the supporting electrolyte present.

Nicholson and Shain¹⁰ have described various experimental criteria that may be used to characterize coupled electron transfer and chemical reactions (or transformations). In this regard, it is instructive to plot i_{pa}/i_{pc} vs $\log V$, $i_p v^{1/2}$ vs $\log V$, and $\Delta E_p/2 \Delta \log V$ vs $\log V$. These data for $\text{Cu}_2(\text{BAA})_2$ in pyridine clearly

indicate an EC_RE mechanism by the Nicholson and Shain criteria. While nothing is known for certain about the C_R step, it does seem likely that it is associated with a change in coordination number and coordination geometry about the copper atoms.

Computer simulation of the nearly reversible wave obtained at very slow scans (~ 20 mV/s) of the type described above^{2,12} yields excellent agreement with experimental results for $E_1 - E_2 \cong 90$ mV. In other words, in pyridine in the absence of simple cations, the second $\text{Cu}(\text{II})$ in $\text{Cu}_2(\text{BAA})_2$ reduces about 90 mV more negative than the first. The two-electron nature of this wave in pyridine is further substantiated by chronoamperometry. Under identical experimental conditions, the slopes of the current vs (time)^{1/2} for $\text{Cu}_2(\text{BAA})_2$ in DMSO + Na^+ and in pyridine are similar (Table II). Both can be assigned to two-electron-transfer processes and the difference attributed to a slightly greater diffusion constant in pyridine.

Addition of excess Na^+ to the pyridine solution of $\text{Cu}_2(\text{BAA})_2$ greatly complicates the resulting CV. A very positive reduction at about -0.4 V arises upon addition of Na^+ , but it is poorly formed and irreversible. No serious attempt was made to characterize it. A second, quasi-reversible wave appears at about -0.7 V. Unlike the beneficial affects in DMF and DMSO, cations added to pyridine resulted in considerable complexities and no advantages vis-à-vis multielectron-transfer processes. For this reason, the pyridine plus simple-cation solvent environment for electrochemical study of polynuclear copper complexes was not investigated further.

In summary, a single CV wave due to the transfer of two electrons has been observed for a representative binuclear $\text{Cu}(\text{II})$ 1,3,5-triketone in DMF, DMSO, and pyridine, albeit under different conditions. The two-electron nature of the process has also been confirmed by chronoamperometry. The conditions and the potential differences in each case are given below.

solvent	supporting electrolyte	other cation	$E_1 - E_2$, mV
pyridine	TEAP	none	90
DMF	TEAP	Na^+	30
DMSO	TEAP	Na^+	-180

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Tetranuclear Complexes of 1,3,5,9,11,13-Hexaketones. 1. Synthesis and Structure of Bis[1,3-bis(2-methyl-4,6,8-octanetrien-8-yl)benzenato(4-)]tetrakis(pyridine)tetracopper(II), $\text{Cu}_4(\text{MOB})_2(\text{py})_4$. Observation of Four-Electron-Transfer Electrochemistry

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A new hexaketone ligand has been prepared, 1,3-bis(2-methyl-4,6,8-octanetrien-8-yl)benzene, abbreviated H_4MOB , that is capable of binding four metal ions. Two deprotonated ligand molecules and four divalent metal ions form neutral, molecular complexes. A crystal structure is reported for the tetranuclear copper(II) complex. Recrystallization from pyridine yields single crystals of $\text{Cu}_4(\text{MOB})_2(\text{py})_4 \cdot 2\text{py}$. Crystal data: $P2_1/c$, $a = 19.33$ (2) Å, $b = 19.831$ (6) Å, $c = 9.809$ (8) Å, $\beta = 97.64$ (8)°, $Z = 2$, $V = 3727$ (5) Å³, $R_1 = 0.078$, $R_2 = 0.090$. The $\text{Cu}_4(\text{MOB})_2(\text{py})_4$ molecules consist of two binuclear copper(II) triketonate type moieties linked through 1,3-substitutions on phenyl rings. The Cu-Cu separation within a binuclear unit is 3.021 (1) Å. The closest Cu-Cu distance between the binuclear units is 6.9 Å. Each copper is bound to four ketonate oxygens and one pyridine nitrogen in typical square-pyramidal geometry. Strong magnetic superexchange between $\text{Cu}(\text{II})$'s in the binuclear units renders the molecule diamagnetic at room temperature. Cyclic voltammetry in pyridine in the range 0 to -1.2 V yields one quasi-reversible wave with $E_{1/2} \cong -0.8$ V. Chronoamperometric results show that this wave is due to a four-electron-transfer process.

Introduction

The design and synthesis of polynuclear metal complexes capable of transferring two or more electrons at similar potentials has been a goal of our research program for some time. Several studies have been reported from our laboratories dealing with the electrochemical electron transfer properties of binuclear copper

complexes derived from 1,3,5-triketones and their diamine Schiff bases.¹⁻⁴ These studies showed that the binuclear copper com-

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