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 $Cu_2(BAA)_2$ in pyridine is entirely different than in DMF or DMSO. In pyridine containing only $Cu_2(BAA)_2$ 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 $Cu_2(BAA)_2$ 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 $Cu_2(BAA)_2$, in pyridine a similar process is observed with only the supporting electrolyte present.

Nicholson and Shain[10] 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 $\Delta E_{p/2}$ Δ log V vs log V. These data for $Cu_2(BAA)_2$ 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 Cu(II) an $Cu_2(BAA)_2$ 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 $(\text{time})^{1/2}$ for $Cu_2(BAA)_2$ 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 $Cu_2(BAA)_2$ 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 Cu(II) 1,3,5-triketonate 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-Hexaketonates. 1. Synthesis and Structure of Bis[1,3-bis(2-methyl-4,6,8-octanetrion-8-yl)benzenato(4−)]tetrakis(pyridine)tetracopper(II), $Cu_4(MOB)_2(py)_4$. 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-octanetrion-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 $Cu_4(MOB)_2(py)_4\cdot 2py$. 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) Å^3, $R_1 = 0.078$, $R_2 = 0.090$. The $Cu_4(MOB)_2(py)_4$ 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 Cu(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-triketonates and their diamine Schiff bases.[1-4] These studies showed that the binuclear copper com-

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plexes in DMF and in DMSO undergo two reversible, sequential electron transfers at very similar potentials provided the solutions contain simple cations. The results are consistent with

$$\mathrm{Cu_2}^{\mathrm{II}}\mathrm{L_2}+\mathrm{M}^+ \underset{E_1}{\overset{1e^-}{\rightleftharpoons}} [\mathrm{Cu^{II}Cu^{I}L_2M}] \underset{E_2}{\overset{1e^-}{\rightleftharpoons}} [\mathrm{Cu^{I}Cu^{I}L_2M}]^-$$

where $E_1 - E_2 \sim 50$ to -180mV and $\mathrm{M}^+ = \mathrm{Li}^+, \mathrm{Na}^+, \mathrm{K}^+, \mathrm{Rb}^+$, and Cs^+. As a result of the ability of these compounds to transfer two electrons at virtually the same potential, it is reasonable to think of them as possible two-electron reagents/catalysts in multielectron-transfer reactions.

The strategy we have used to design systems capable of transferring more than two electrons has been to extend the basic 1,3,5-triketonate ligand system to higher homologues capable of binding more than two metal ions.[5-7] An approach used in this work is to synthesize a ligand with two separate 1,3,5-triketone moieties substituted at the 1- and 3-positions of a phenyl ring. The resulting hexaketone is capable of binding four metals ions in a manner analogous to the simple 1,3,5-triketonates. It has the advantage of forming complexes with separate binuclear sections, which have been shown to be capable of two-electron transfer. A primary purpose of this work is to report the properties of this new ligand system and to begin to investigate the electrochemical behavior of the complexes it forms.

Experimental Section

1. Ligand Synthesis. The ligand 1,3-bis(2-methyl-4,6,8-octanetrion-8-yl)benzene, $\mathrm{H_4MOB}$, was prepared by the condensation of 2-methyl-4-pentanone (0.2 mol) and dimethyl isophthalate (0.1 mol) in 500 mL of dry THF with NaH (0.6 mol). The mixture was refluxed for about 24 h after which the solvent was removed under vacuum. The remaining solid was slurried in about 300 mL of diethyl ether, and excess NaH was reacted carefully with water added dropwise. The solid was dissolved in water and the ether/water mixture filtered. Solid remaining was washed with water and then discarded. The aqueous layers were combined and washed with three aliquots of ether. The aqueous layer was separated, placed in an ice bath, and neutralized to pH 7 with cold 6 N HCl. The crude yellow product was filtered, dried, and recrystallized from acetone (or acetone/methanol). The yellow platelike crystals melt at 121 °C. Anal. Calcd for $\mathrm{C_{24}H_{30}O_6}$: C, 69.53; H, 7.31. Found: C, 68.46; H, 6.98.

2. Synthesis of Bis[1,3-bis(2-methyl-4,6,8-octanetrion-8-yl)benzenato(4−)]tetrakis(pyridine)tetracopper(II)−2-pyridine, $\mathrm{Cu_4(MOB)_2(py)_4{\cdot}2py}$. Reagent grade $\mathrm{Cu(C_2H_3O_2)_2{\cdot}H_2O}$ (0.015 mol) was refluxed in 400 mL of methanol. After 10 min, the ligand $\mathrm{H_4MOB}$ (0.003 mL) was added. The resulting solution was refluxed for 2 h. The volume was reduced to 100 mL and the crude green product was collected on a filter. The product was washed with water and acetone and then washed in a Soxhlet extractor for 2–3 days with THF. The solid remaining in the thimble was recrystallized from pyridine. The resulting violet crystals turn green at 120 °C and decompose at about 350 °C. Anal. Calcd for $\mathrm{Cu_4C_{78}H_{82}N_6O_{12}}$: C, 60.44; H, 5.34; N, 5.42; Cu, 16.40. Found: C, 61.09, H, 5.49; N, 5.61; Cu, 15.93.

3. Synthesis of Bis[1,3-bis(2-methyl-4,6,8-octanetrion-8-yl)benzenato(4−)]hexakis(pyridine)diuranyldizinc(II), $\mathrm{Zn_2(UO_2)_2(MOB)_2(py)_6}$. The ligand $\mathrm{H_4MOB}$ (0.0026 mol) was refluxed for 15 min in 250 mL of $\mathrm{CH_3OH}$. This solution was cooled to room temperature, and finely powdered reagent grade $\mathrm{(UO_2)(CH_3CO_2)_2{\cdot}2H_2O}$ (0.0026 mol) was added. The solution was stirred until it became a translucent red color (10–20 min). Reagent grade $\mathrm{Zn(CH_3CO_2){\cdot}H_2O}$ (0.0026 mol) was added and the resulting solution stirred at room temperature for about 12 h. The volume was reduced to 100 mL, and a brown solid with metallic luster was collected on a filter. Recrystallization from pyridine yielded metallic microcrystals. Anal. Calcd for $\mathrm{Zn_2U_2C_{78}H_{82}H_6O_{16}}$: C, 47.64; H, 4.21; N, 4.27; U, 24.21; Zn, 6.65. Found: C, 46.56; H, 4.18; N, 3.95; U, 24.69; Zn, 6.82.

4. Magnetic Susceptibility. The magnetic susceptibility was measured by using standard Faraday balance techniques with $\mathrm{Hg[Co(SCN)_4]}$ as the calibrant.[8] Pascal's constants were used for the diamagnetic correction.[9]

Table I. Experimental Crystallographic Data for $\mathrm{Cu_4(MOB)_2(py)_4{\cdot}2py}$

formula: $\mathrm{C_{78}H_{82}N_6O_{12}Cu_4}$
mol wt: 1549.70
cryst dimens: 0.56 × 0.41 × 0.15 mm
cryst syst: monoclinic
space group: $P2_1/c$
cell dimens: $a = 19.33$ (2) Å, $b = 19.831$ (6) Å,
$c = 9.809$ (8) Å, $\beta = 97.64$ (8)°,
$V = 3727$ (5) Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.402$
radiation: Mo Kα ($\lambda = 0.71069$ Å)
monochromator: graphite cryst
2θ range: 4.0–45°
max scan time: 2–5°/min
scan angle: ±1° of Kα
monitor reflcns: 3 measd for intensity check every 100 reflcns
total no. of data collcd: 5602
no. of unique data: 4900
no. of obsd data with $I_0 \geq 2\sigma(I)$: 2525
μ(Mo Kα): 11.99 cm^{-1}
transm coeff: 1.378–1.842
F(000): 1607.89
R_1: 0.078
R_2: 0.090
w: $(\sigma_F)^{-2}$

5. Electrochemical Measurements. The electrochemical instrumentation and experimental details have been described in the preceding paper in this issue.[4]

6. Atomic Absorption Measurements. Solutions for AA measurements of copper were withdrawn directly from the electrochemical cell. The concentration was adjusted to 1–5 μM. Analyses were obtained on an Instrument Laboratory Inc. IL 353 Spectrometer.

7. Crystal Measurements.[10] A violet crystal of $\mathrm{Cu_4(MOB)_2(py)_4{\cdot}2py}$ was sealed in a capillary with some mother liquor to maintain crystal stability. Preliminary examination of the crystal and the data collection were performed on a Syntex P2$_1$ four-circle automatic diffractometer. All the information concerning crystallographic data collection and results are summarized in Table I. Absorption corrections were applied with the program ABSORB.[11-13] The structure was solved by heavy-atom methods and refined as blocked matrices in least-squares calculations.[14] Hydrogen atoms were placed in calculated positions and held invariant. Isotropic temperature factors for the hydrogen atoms were all tied to a single variable; lattice solvent molecules showed large thermal parameters and oscillated between two positions leading to the conclusion that disorder existed in that area. They were treated as rigid bodies, in two half-occupied orientations without hydrogens. The remaining atoms were refined anisotropically. In a final cycle of least-squares refinement, all non-solvent atoms converged to within 0.1σ. No systematic correction for secondary extinction was made; however, one reflection (200) that obviously was affected was removed. The highest peak on a difference map represents 0.47 e Å^{-3} near the lattice solvent molecules. The number of observations was 2525, and the number of variable parameters was 251. Neutral atom scattering factors and corrections for anomalous dispersion were from ref 15. Other details of the crystallographic experiment are given in Table I. Positional coordinates are given in Table II, whereas bond distances and angles are given in Table III. Observed and calculated structure factors as well as thermal parameters are deposited as supplementary material.

Results

1. Structure of $\mathrm{Cu_4(MOB)_2(py)_4{\cdot}2py}$. The complex $\mathrm{Cu_4(MOB)_2(py)_4{\cdot}2py}$ contains the tetraanion of the ligand 1,3-bis(2-methyl-4,6,8-octanetrion-8-yl)benzene. The four copper ions

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Table II. Atomic Positional Parameters for $Cu_4(MOB)_2(py)_4 \cdot 2py$

atom	x	y	z
Cu1	0.18634 (7)	0.51083 (8)	0.6550 (2)
Cu2	0.32489 (7)	0.47724 (8)	0.5608 (1)
O1	0.1473 (4)	0.4832 (5)	0.814 (1)
O2	0.2756 (4)	0.4702 (4)	0.7188 (9)
O3	0.4118 (4)	0.4570 (4)	0.6659 (9)
O4	0.0998 (4)	0.5352 (4)	0.5497 (9)
O5	0.2349 (4)	0.5167 (4)	0.4953 (9)
O6	0.3652 (4)	0.5094 (4)	0.4086 (8)
C1	0.0377 (9)	0.418 (1)	1.146 (2)
C2	0.099 (1)	0.346 (1)	0.963 (3)
C3	0.0776 (7)	0.4157 (9)	1.012 (2)
C4	0.1427 (7)	0.4575 (7)	1.045 (1)
C5	0.1827 (7)	0.4642 (7)	0.929 (2)
C6	0.2530 (6)	0.4504 (6)	0.945 (1)
C7	0.3010 (7)	0.4499 (6)	0.847 (1)
C8	0.3715 (6)	0.4363 (6)	0.880 (1)
C9	0.4218 (6)	0.4415 (6)	0.794 (1)
C10	0.4991 (6)	0.4311 (6)	0.848 (1)
C11	0.5246 (7)	0.4061 (7)	0.978 (1)
C12	0.5924 (6)	0.3954 (7)	1.015 (1)
C13	0.6400 (6)	0.4126 (6)	0.929 (1)
C14	0.6165 (6)	0.4363 (6)	0.797 (1)
C15	0.5463 (6)	0.4454 (5)	0.758 (1)
C16	0.0349 (8)	0.6929 (8)	0.549 (2)
C17	−0.0849 (6)	0.6525 (7)	0.444 (2)
C18	−0.0089 (7)	0.6342 (8)	0.497 (2)
C19	0.0213 (6)	0.5926 (7)	0.386 (1)
C20	0.0946 (7)	0.5671 (6)	0.434 (1)
C21	0.1474 (6)	0.5790 (6)	0.355 (1)
C22	0.2158 (6)	0.5532 (6)	0.379 (1)
C23	0.2653 (6)	0.5645 (6)	0.290 (1)
C24	0.3340 (6)	0.5540 (6)	0.307 (1)
N1	0.2970 (6)	0.3705 (6)	0.484 (1)
C25	0.328 (1)	0.314 (1)	0.539 (2)
C26	0.315 (2)	0.252 (1)	0.485 (3)
C27	0.267 (1)	0.243 (1)	0.377 (3)
C28	0.238 (1)	0.297 (1)	0.318 (3)
C29	0.252 (1)	0.358 (1)	0.378 (2)
N2	0.2132 (6)	0.6179 (6)	0.743 (1)
C30	0.1777 (8)	0.6410 (9)	0.839 (2)
C31	0.184 (1)	0.703 (1)	0.898 (3)
C32	0.766 (1)	0.254 (1)	1.147 (3)
C33	0.731 (1)	0.277 (1)	1.243 (3)
C34	0.7404 (8)	0.3405 (8)	1.297 (2)
N9	0.452 (2)	0.367 (2)	0.304 (4)
C91	0.444 (2)	0.302 (2)	0.247 (4)
C92	0.493 (2)	0.252 (2)	0.290 (4)
C93	0.549 (2)	0.267 (2)	0.389 (4)
C94	0.557 (2)	0.331 (2)	0.446 (4)
C95	0.508 (2)	0.381 (2)	0.404 (4)
N9′	0.479 (3)	0.376 (2)	0.360 (6)
C91′	0.443 (3)	0.328 (2)	0.272 (6)
C92′	0.477 (3)	0.269 (2)	0.241 (6)
C93′	0.545 (3)	0.256 (2)	0.299 (6)
C94′	0.581 (3)	0.304 (2)	0.388 (6)
C95′	0.548 (3)	0.363 (2)	0.418 (6)

are grouped into two sets of two, with a metal–metal distance of 6.9 Å across the plane of the phenyl groups and an intragroup metal–metal distance of 3.021 (1) Å. The coordination sphere of the copper ions is comprised of four ketonate oxygens in the ligand plane and an axial nitrogen from a solvent pyridine molecule. The M–O bond lengths are quite normal for a d^9 metal ion of the first-row transition series as is the M–N bond length, which is elongated due to Jahn–Teller distortion. As a result, the geometry is a distorted tetragonal pyramid. Within the molecule the pyridines alternate above and below the plane of the ligand. The M–O–M bond angles are within a degree of typical polyketonate complexes of this sort.[16–18] The O–M–N angles deviate from 90° due to the copper ions residing out of the ligand plane an average of 0.21 Å in the direction of the pyridines. An average value is given since the ligand backbone is bowed, forming what could be described as a bowllike structure. The outer two pyridine molecules are tilted in toward the center of the complex forming an angle of 63.49° with the overall ligand plane. Figure 1 gives a view of the molecular plane with the atom-numbering scheme. Solvent molecules are omitted for clarity (solvent on Cu1, N2, C30–C34; solvent on Cu2, N1, C25–C29). A stereo packing diagram is given in Figure 2.

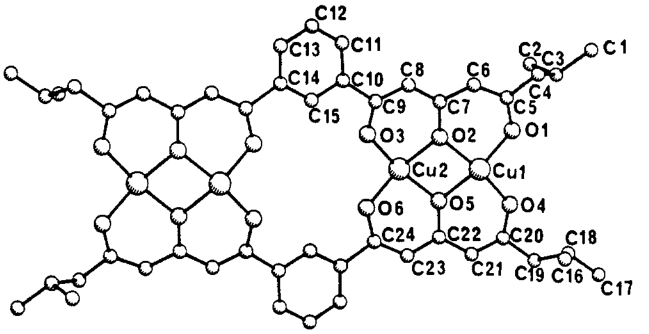

Figure 1. PLUTO drawing of $Cu_4(MOB)_2$ with atom assignments.

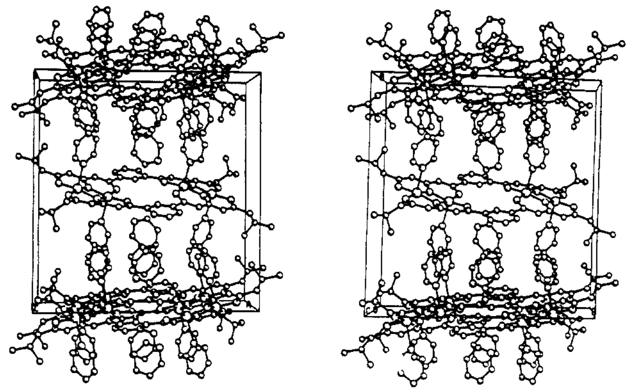

Figure 2. Stereo packing diagram for the complex $Cu_4(MOB)_2(py)_4 \cdot 2py$. The view is down the c axis.

2. Magnetic Properties. The molar susceptibility of $Cu_4(MOB)_2(py)_4$ corrected for diamagnetism at 23 °C was found to be -6.344×10^{-4} cgsu. This clearly demonstrates that this complex is diamagnetic at 23 °C. Thus, the two metal ions in each binuclear unit are antiferomagnetically coupled with a coupling constant, $|J|$, of at least 800 cm^{-1}.

3. Electrochemistry. The solubility of $Cu_4(MOB)_2(py)_4$ is low in common electrochemical solvents; therefore, the electrochemical properties were investigated only in pyridine. The complex $Cu_4(MOB)_2(py)_4$ exhibits a quasi-reversible CV wave in the scan rate range of about 0.5–50.0 V/s. The pertinent characteristics of this wave are summarized in Table IV. The CV at 500 mV/s is shown in Figure 3. There is evidence of complex behavior on both the cathodic and anodic sides, which may be due to two separate and overlapping electron transfer processes.

Chronoamperometry (CA) was used to determine the number of electrons transferred in the electron-transfer process responsible for the CV wave. The potential was pulsed from the foot of the CV wave to 150 mV beyond the cathodic peak potential. The current decay was plotted as i_d vs $1/t^{1/2}$ (t = time). The plots follow a modification of the Cottrell equation[19] for spherical electrodes

$$i_d(t) = n\mathcal{F}AD_0C_0^*[1/(\pi D_0 t)^{1/2} + 1/r_0]$$

where i_d = diffusion current, n = number of electrons transferred, $\mathcal{F}$ = Faraday constant, A = electrode area, D_0 = diffusion coefficient, C_0^* = initial concentration, t = time, and r_0 = electrode

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Table III. Bond Distances (Å) and Bond Angles (deg) for $Cu_4(MOB)_2(py)_4{\cdot}2py$

Cu1–O1	1.902 (9)	C3–C4	1.51 (2)
Cu1–O2	1.932 (8)	C4–C5	1.47 (2)
Cu1–O4	1.907 (8)	C5–C6	1.37 (2)
Cu1–O5	1.934 (8)	C6–C7	1.42 (2)
Cu1–Cu2	3.021 (2)	C7–C8	1.39 (2)
C2–C3	1.53 (3)	C8–C9	1.38 (2)
C26–C27	1.32 (4)	C9–C10	1.53 (2)
C1–C3	1.61 (2)	C10–C11	1.40 (2)
Cu1–N2	2.32 (1)	C10–C15	1.37 (2)
Cu2–O2	1.929 (8)	C11–C12	1.33 (2)
Cu2–O3	1.894 (8)	C12–C13	1.37 (2)
Cu2–O5	1.936 (7)	C13–C14	1.40 (2)
Cu2–O6	1.885 (7)	C14–C15	1.37 (2)
C25–C26	1.34 (3)	C14–C24′	1.54 (2)
O6–C24	1.29 (1)	C16–C18	1.49 (2)
N1–C25	1.35 (2)	C17–C18	1.53 (2)
C33–C34	1.38 (3)	C18–C19	1.54 (2)
Cu2–N1	2.29 (1)	C19–C20	1.52 (2)
O1–C5	1.29 (2)	C20–C21	1.38 (2)
O2–C7	1.35 (1)	C21–C22	1.41 (2)
O3–C9	1.28 (1)	C22–C23	1.39 (2)
O4–C20	1.29 (2)	C23–C24	1.38 (2)
O5–C22	1.36 (1)	N1–C29	1.29 (2)
C27–C28	1.32 (4)	C30–C31	1.36 (3)
C28–C29	1.35 (3)	C32–C33	1.31 (3)
N2–C30	1.32 (2)		

Cu1–O1–C5	125.3 (8)	Cu2–N1–C25	124 (1)
Cu1–O2–Cu2	103.0 (4)	Cu2–N1–C29	123 (1)
Cu1–O2–C7	128.7 (7)	O1–Cu1–O2	92.8 (3)
Cu1–O4–C20	124.0 (8)	O1–Cu1–O4	95.9 (3)
Cu1–O5–Cu2	102.6 (4)	O1–Cu1–O5	165.9 (4)
Cu1–O5–C22	127.1 (7)	O12–Cu1–N2	193.0 (4)
Cu–O5–C22	128.7 (7)	O1–C5–C4	116 (1)
Cu1–N2–C30	118 (1)	O1–C5–C6	124 (1)
Cu2–O2–C7	127.8 (7)	O2–Cu1–O4	164.2 (3)
Cu2–O3–C9	126.2 (7)	O2–Cu1–O5	77.2 (3)
O2–Cu1–N2	96.6 (4)	O4–C20–C21	127 (1)
O2–Cu2–O3	92.6 (3)	Cu2–O6–C24	126.1 (7)
O2–Cu2–O5	77.2 (3)	O5–Cu1–N2	97.9 (4)
O2–Cu2–O6	164.0 (3)	O5–Cu2–O6	92.8 (3)
O2–Cu2–N1	94.5 (4)	C1–C3–C2	117 (2)
O2–C7–C6	116 (1)	C1–C3–C4	107 (1)
O2–C7–C8	120 (1)	C2–C3–C4	108 (1)
O3–Cu2–O5	163.5 (4)	O5–Cu2–N1	95.9 (4)
O3–Cu2–O6	94.1 (3)	O5–C22–C21	118.7 (9)
C14–C24′–C23′	121 (1)	O5–C22–C23	119 (1)
O3–Cu2–N1	97.8 (4)	C15–C14–C24′	118 (1)
O3–C9–C8	127 (1)	O6–Cu2–N1	98.9 (4)
O3–C9–C10	113 (1)	O6–C24–C23	127 (1)
O4–Cu1–O5	91.8 (3)	O6′–C24′–C14	112 (1)
O4–Cu1–N2	96.1 (4)	C3–C4–C5	113 (1)
O4–C20–C19	113 (1)	C4–C5–C6	121 (1)
C7–C8–C9	126 (1)	C16–C18–C17	114 (1)
C5–Cu1–N2	88.8 (4)	C16–C18–C19	114 (1)
C5–C6–C7	131 (1)	C17–C18–C19	109 (1)
C6–C7–C8	124 (1)	C18–C19–C20	113 (1)
C7–Cu1–C20	169.1 (4)	C19–C20–C21	120 (1)
C7–Cu2–C22	118.2 (3)	C21–C22–C23	123 (1)
C8–C9–C10	121 (1)	C22–C23–C24	127 (1)
N1–C25–C26	123 (2)	N1–C29–C28	126 (2)
C9–C10–C11	125 (1)	C25–N1–C29	112 (1)
C9–C10–C15	117 (1)	C25–C26–C27	121 (2)
C10–C11–C12	121 (1)	C26–C27–C28	117 (2)
C10–C15–C14	121 (1)	C27–C28–C29	119 (2)
C11–C10–C15	118 (1)	N2–C30–C31	127 (2)
C11–C12–C13	121 (1)	C32–C33–C34	122 (2)
C12–C13–C14	120 (1)	C13–C14–C24′	123 (1)
C13–C14–C15	119 (1)		

radius. A straight line results with a slope proportional to the number of electrons transferred, *n*. That is, the slope is equal to $n\mathcal{F}AD_0C_0{}^*(1/(\pi D_0)^{1/2})$. Since the diffusion constant, D_0, for $Cu_4(MOB)_4$ is not known, CA experiments on a complex of the same ligand in which *n* is known were carried out. The complex, $Zn_2(UO_2)(MOB)_2(py)_6$, exhibits only the reversible U(VI) ⇌ U(V) electron transfer in the potential range 0 V to −2.0 V. Both the CV and CPE results are consistent with the transfer of 2.0 electrons at $E_{1/2} = -1.06$ V vs SSCE. The assumption is that the diffusion constants for $Cu_4(MOB)_2(py)_2$ and $Zn_2(UO_2)(MOB)_2(py)_4$ are nearly equal and, therefore, that the CA plots of i_d vs $1/s^{1/2}$ are directly comparable. In this way, the relative slopes can be used to determine *n* for $Cu_4(MOB)_2$. The results for CA experiments run under identical conditions for $Zn_2(UO_2)(MOB)_2$ and $Cu_4(MOB)_2$ are given below (r^2 is a least-squares fitting coefficient).

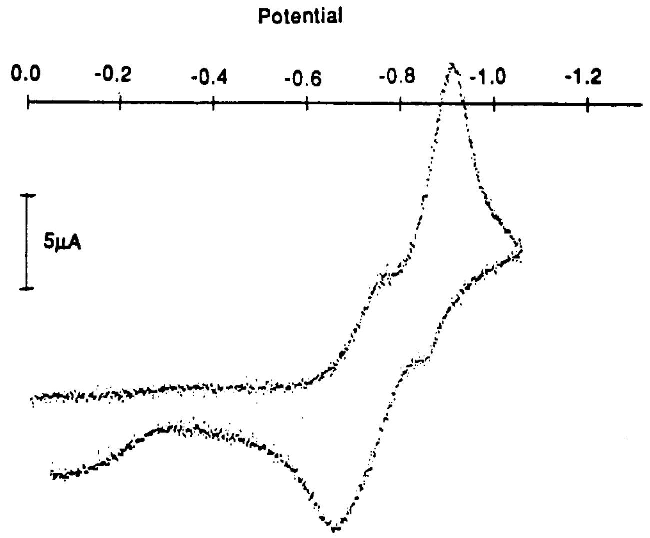

Figure 3. Cyclic voltammogram of 0.5 mM $Cu_4(MOB)_2$ in pyridine. Scan rate is 500 mV/s, and potentials are versus SSCE.

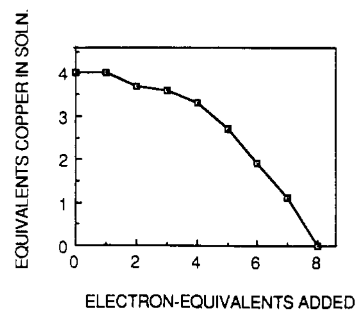

Figure 4. Plot of the equivalents of copper remaining in solution as a function of electron equivalents added during the CPE of $Cu_4(MOB)_2$.

	slope, $\mu A/s^{1/2}$	r^2	*n*
$Zn_2(UO_2)_2(MOB)_2$	4.668 (5)	0.9999	2
$Cu_4(MOB)_2$	9.063 (5)	0.9994	4

These results show clearly that the CV wave observed for $Cu_4(MOB)_2$ is due to the transfer of 4 electrons.

Controlled-potential electrolysis (CPE) of $Cu_4(MOB)_2$ in pyridine at −1.10 V resulted in the transfer of $8e^-$ and the loss of copper from solution. It is clear that under the CPE conditions (long time and vigorously stirred solution) the reduced complex undergoes secondary reactions that result in the formation of Cu(Hg) amalgam. The loss of copper from the complex during CPE was investigated by analyzing the solution for copper after the addition of each electron equivalent. The analysis was done by atomic absorption spectrometry. A plot of the equivalents of copper remaining in solution as a function of equivalents of electrons added is shown in Figure 4. While these results indicate some loss of copper after the addition of $2e^-$, less than 1 equiv of copper is lost after $4e^-$ were added. Beyond $4e^-$, one copper is lost from solution for each electron equivalent added.

Discussion

The synergistic effect of two closely spaced metal ions on electron-transfer properties is apparent in the electrochemistry of binuclear bis(1,3,5-triketonato)dicopper(II) complexes as

Table IV. Cyclic Voltammetric Data for $Cu_4(MOB)_2(py)_4$[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}	$i_{pc}/v^{1/2}$, $\mu A/s^{1/2}$
1.00	-0.80	-0.93	262	59	-82.8	0.62	82.8
2.00	-0.81	-0.94	255	72	-97.7	0.63	70.3
5.00	-0.82	-0.95	267	68	-142.4	0.62	63.7
10.00	-0.84	-1.02	360	103	-184.5	0.65	59.2
20.00	-0.84	-1.04	392	116	-239.0	0.61	54.3
50.00	-0.85	-1.07	430	133	-315.7	0.61	44.9

[a] Pyridine solution contains 5 mM $Cu_4(MOB)_2(py)_4$ and 0.1 M tetraethylammonium perchlorate as supporting electrolyte. Potentials are versus SSCE.

compared to related mononuclear Cu(II) complexes (see for example refs 20 and 21). The extremely well-behaved reversible, sequential transfer of two electrons at very similar potentials in the binuclear triketonates is qualitatively and quantitatively unlike the electrochemistry observed in structurally similar mononuclear complexes. This furnishes significant impetus for interest in the design of new molecules containing more than two interacting metal centers. Clearly, one goal is to discover molecules capable of transferring several electrons at similar potentials.

Observation of the reversible, sequential transfer of two electrons in the binuclear copper(II) triketonates and their diamine Schiff-bases has depended upon adding simple cations to the solution.[1,2,3,20,21] There is significant experimental data to support the fact that these cations bind strongly to the terminal oxygens of the first reduction product, $[Cu^{II}Cu^{I}L_2]^-$. As a result, this initial one-electron-reduced product has the same charge as the starting complex, Cu_2L_2.[3] The charge similarity undoubtedly contributes to the fact that the potential for adding the second electron is very similar to the potential for adding the first. A recent study dealing with the effect of solvent on the multielectron-transfer process showed that the presence of simple cations was not an absolute requirement.[4] In pyridine, bis(1,3,5-triketonato)dicopper(II) exhibits the two-electron CV wave without adding simple cations. In DMF and DMSO *without* simple cations, a reversible one-electron CV wave is observed in the potential range 0 to −2.6 V. The reduction of the second Cu(II) under these conditions takes place irreversibly at about −1.7 V.

Results in pyridine are particularly useful from two points of view. First, the multielectron transfer process can be investigated in reasonably simple solutions; i.e., no salts of simple cations are needed. Second, the solvating ability of pyridine makes it possible to study multielectron transfer in a variety of related polynuclear metal complexes in the same solvent environment. This second advantage is particularly important in this work since the tetranuclear Cu(II) complex of interest, $Cu_4(MOB)_2$ is not soluble enough in DMF or DMSO to conveniently use these solvents in electrochemical studies.

From the crystal structure of $Cu_4(MOB)_2(py)_4 \cdot 2py$ it is clear that the ligand has little difficulty binding four metals (Figure 1). One structurally interesting feature is the cavity between the halves of the molecule. This cavity measures approximately 6.9 Å horizontally and 5.8 Å vertically as viewed in Figure 1. Measuring from the four central oxygen atoms nearest the benzene rings and allowing 1.03 Å for C–H bond and 0.37 Å[22] for the covalent radius of hydrogen yield a cavity of approximately 6.9 × 3.0 Å. There is undoubtedly some strain in the structure as evidenced by the bowl-shaped distortion of the molecule. The structural features in each of the binuclear triketonate moieties are very similar to those in the simple bis(1,3,5-triketonato)dicopper(II) complexes.[16,18] Also, since the two d^9 Cu(II) ions are strongly antiferromagnetically coupled in the 1,3,5-triketonates, it is not surprising that the same is true in $Cu_4(MOB)_2$. Indeed, in both cases the molecules are diamagnetic at room temperature. It is clear that the physical properties of two binuclear moieties in $Cu_4(MOB)_2$ are virtually identical with the molecular species bis(1,3,5-triketonato)dicopper(II). This being the case, it is interesting to compare the electrochemical properties of the bi- and tetranuclear complexes.

Previous electrochemical results for bis(1-phenyl-1,3,5-hexanetrionato)dicopper(II), $Cu_2(BAA)_2$ in pyridine[4] allow a direct comparison between $Cu_2(BAA)_2$ and $Cu_4(MOB)_2$ to be made. The general characteristics of the CV's for $Cu_2(BAA)_2$ and $Cu_4(MOB)_2$ in pyridine are quite similar at the same scan rates. This includes reduction potentials, peak separations, cathodic peak half-widths, and peak ratios. Both are quasi-reversible. An obvious difference between the two is the appearance of inflections on the cathodic and anodic portions of the $Cu_4(MOB)_2$ CV waves (Figure 3). A logical explanation of this is that the wave consists of two overlapping waves due to the two noninteracting binuclear units. Another problem with the CV comparison is that the electron-transfer process for $Cu_2(BAA)_2$ is much more reversible at very slow scans while for $Cu_4(MOB)_2$ it is much better behaved at fast scan rates. These factors prevent one from making very detailed comparisons.

It is most interesting to compare the chromoamperometric results for $Cu_2(BAA)_2$ and $Cu_4(MOB)_2$. For $Cu_2(BAA)_2$ in pyridine, the CA results prove that the CV wave centered at about −0.80 V is due to the transfer of two electrons.[4] At slow scans (0.020 V/s), this is a very nearly reversible CV process with a potential separation for the two transfers ($E_1 - E_2$) of about 90 mV. Under the same conditions, the CA results for $Cu_4(MOB)_2$ prove that the CV wave centered at about −0.80 V is due to the transfer of four electrons. Since the interpretation of the CA results depends upon knowing either the value of n, the number of electrons transferred, or D_0, the diffusion constant, one must have some independent measure of one of these unknowns. We have addressed this problem by investigating a complex of MOB^{4-} in which the value of n is known with some certainty. Inasmuch as the values of D_0 for $Cu_4(MOB)_2(py)_4$ and another tetranuclear complex of MOB^{4-} can be expected to be very similar, the value of n for $Cu_4(MOB)_2(py)_4$ can be deduced by comparing the CA results. The complex synthesized for this purpose is $Zn_2(UO_2)_2(MOB)_2(py)_6$. Previous experience with binuclear UO_2^{2+} complexes of 1,3,5,7-tetraketonates has shown that they exhibit reversible $U(VI) \rightleftharpoons U(V)$ electrochemistry.[6] For $Zn_2(UO_2)_2(MOB)_2(py)_6$ in pyridine, one reversible CV wave is observed with $E_{1/2} = -1.06$ V vs SSCE. In the scan range 0.01–20.00 V/s the $\Delta E_p = 70 \pm 4$ mV, $i_{pa}/i_{pc} = 0.95 \pm 0.1$ and $i_{pc}/v^{1/2}$ is essentially constant. CPE at −1.35 V results in the transfer of 2.0 electrons. From CA, the slope of an i_d vs $1/s^{1/2}$ plot for $Zn_2(UO_2)_2(MOB)_2(py)_6$ is 4.67 $\mu A/s^{1/2}$. Under identical conditions, the slope of i_d vs $1/s^{1/2}$ for $Cu_4(MOB)_2(py)_4$ is 9.06 $\mu A/s^{1/2}$. Since the diffusion constants, D_0, for the two are assumed to be nearly the same, the value of n for $Cu_4(MOB)_2(py)_4$ must be twice the value of n for $Zn_2(UO_2)_2(MOB)_2(py)_6$. Hence, n must equal 4 for $Cu_4(MOB)_2(py)_4$.

There is additional support for the conclusion that the CV wave for $Cu_4(MOB)_2$ is the result of four-electron transfer. A comparison of CA results for $Cu_2(BAA)_2$ and $Cu_4(MOB)_2$ in pyridine shows that two and four electrons, respectively are transferred. In this case the comparison is somewhat more ambiguous since the diffusion constants for the two complexes can be expected to be somewhat different. The values of the slopes of i_d vs $1/s^{1/2}$ for 1 mM $Cu_2(BAA)_2$ and 1 mM $Cu_4(MOB)_2$ in pyridine are 4.93 and 9.06 $\mu A/s^{1/2}$, respectively. There is little question that these

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values are due to two and four electrons. Deviation from a 2:4 ratio is easily explainable on the basis of diffusion constant differences—D_0 for $Cu_2(BAA)_2$ would be expected to be slightly greater than that for $Cu_4(MOB)_2$. A reasonable interpretation of the CV shown in Figure 3 is that each binuclear unit undergoes the quasi-reversible, sequential transfer of two electrons at similar potentials and that the potential difference between the two units is on the order of 100–150 mV.

Unfortunately, CPE performed in the normal, preparative sense in pyridine is not very useful for studying this four-electron-transfer process. CPE at −1.10 V results in the addition of eight electrons and, obviously, the loss of all four Cu(II)'s from solution as Cu(Hg) amalgam. Similarly, CPE of $Cu_2(BAA)_2$ in pyridine at −1.20 V resulted in the addition of four electrons, whereas, in DMF/Na^+ 2 electrons were added at potentials corresponding to the two-electron CV wave.[4] Thus, although the CV and CA results for $Cu_2(BAA)_2$ in all three solvent environments are consistent with a two-electron-transfer process, the CPE results differ greatly. In pyridine two electrons per Cu(II) are added during CPE for both $Cu_2(BAA)_2$ and $Cu_4(MOB)_2$ in contrast to CV and CA results, which indicate only one electron per Cu(II). Thus, in pyridine, the conditions for bulk electrolysis (rapid stirring and greatly changing concentrations) cause a reaction or transformation that yields a species reducible at potentials more positive than −1.10 V. The simplest and, perhaps, most logical explanation is that the Cu(I) initially produced during CPE is lost from the complex and is present as $Cu(py)_x^+$. Further reduction of this species at the same potential yields (Cu(Hg) amalgam.

The loss of copper ions from $Cu_4(MOB)_2$ during CPE was monitored by analyzing the solution after the addition of each electron equivalent. The results are shown in Figure 4. If there were no secondary reactions during CPE, the plot should show 4 equiv of copper remaining in solution for each of 1, 2, 3, and 4 electron equiv added. Of course, after 4 electron equiv the current would be expected to drop to nearly 0 at the CPE potential applied. The fact that it does not is evidence for the importance of reactions that take place subsequent to the initial reduction of the Cu(II)'s to Cu(I)'s. The copper-containing product(s) of this reaction reduce at potentials more positive than −1.10 V. Thus, then they are formed, they are immediately reduced.

The results shown in Figure 4 indicate that even though there is decomposition under CPE conditions, a fair amount of the four-electron-reduced complex does exist after the addition of 4 equiv of electrons. After four electrons are added, less than one copper, on the average, has been lost from solution. If direct reduction to Cu^0 were occurring, then two coppers would be lost after four electrons were added. The simplest interpretation of these results is that when four electrons per molecule of $Cu_4(MOB)_2$ have been added the solution contains a mixture of species including the expected Cu(I) product, species with less then four copper's, and partially reduced Cu(II), Cu(I) species. Such a mixture would explain the facts that (1) four electrons per molecule have been transferred and (2) only about 3.2 equiv of the original 4.0 equiv of copper remain in solution. Subsequent addition of electrons beyond four result in the loss of 1 equiv of copper/equiv of electrons added.

Summary

In unstirred solutions at a HMDE, the tetranuclear hexaketonate $Cu_4(MOB)_2$ exhibits electrochemical properties consistent with the transfer of four electrons at very similar potentials. This molecule contains two binuclear Cu(II) moieties separated by about 7 Å, each of which is structurally similar to the binuclear arrangement in bis(1,3,5-triketonato)dicopper(II) complexes. Since this binuclear unit is known to undergo sequential two-electron transfer in the triketonates, the four-electron transfer in $Cu_4(MOB)_2$ can be viewed as two two-electron transfers in noninteracting binuclear centers.

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Supplementary Material Available: A table of anisotropic thermal parameters and a table of hydrogen atomic parameters (5 pages); a table of structure factors (32 pages). Ordering information is given on any current masthead page.

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Phosphorus Ylides as Hard Donor Ligands: Synthesis and Characterization of MCl_4(ylide-*O*)(THF) (M = Ti, Zr, Hf; Ylide = (Acetylmethylene)triphenylphosphorane, (Benzoylmethylene)triphenylphosphorane). Molecular Structure of *trans*-((Acetylmethylene)triphenylphosphorane-*O*)(tetrahydrofuran)tetrachlorotitanium(IV)–Tetrahydrofuran

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The reactions between oxophilic group 4 metal chlorides and the ambidentate α-keto ylides (acetylmethylene)triphenylphosphorane (APPY) and (benzoylmethylene)triphenylphosphorane (BPPY), in THF, lead to the formation of O-bound transition-metal–ylide complexes. The compounds were characterized by proton, carbon-13, and phosphorus-31 NMR spectroscopy and by infrared spectroscopy. Crystallographic characterization of *trans*-[$TiCl_4$(APPY-*O*)(THF)]·THF (**4**) revealed that the ylide adopts the cisoid conformation in the solid state. **4** crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions a = 15.735 (5) Å, b = 9.818 (3) Å, c = 19.992 (5) Å, β = 105.17 (2)°, and V = 2981 (1) Å^3, with R_F = 0.0554 (R_{wF} = 0.0554) for 286 parameters and 2251 observed reflections having $F_o > 5\sigma(F_o)$. The potential of these complexes for forming O-bound, orthometalated species is discussed.

Introduction

Our laboratory has long been interested in the coordination chemistry of ambidentate ligands.[1] One of our goals was to find an ambidentate ligand wherein control of the bonding mode (C vs O) would reside, at least in part, in variables that were found within the ligand itself.[2] The ease of systematic variation of the R, R′ and/or R″ groups in the phosphorus ylides of the type $R_3PCR'C(O)R''$ (**1**) suggested that these are ideal candidates.

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