Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Magnetic and Electrochemical Properties of Transition Metal Complexes with Multiple Metal-to-Metal Bonds. IV.

$[Mo_2Cl_8]^{n-}$ with $n = 3$ and 4 and $[Mo_2(C_3H_7COO)_4]^{n+}$ with $n = 0$ and 1

F. ALBERT COTTON* and ERIK PEDERSEN

Received June 25, 1974 AIC40409B

Rotating-disk polarography and cyclic voltammetry have been used to study the electrochemical properties of $[Mo_2Cl_8]^{4-}$ and $[Mo_2(O_2CC_3H_7)_4]$ in various solvents. The chloro species in 6 *M* hydrochloric acid is oxidized at about 0.5 V *vs.* sce but the product, presumably $[Mo_2Cl_8]^{3-}$, was short-lived and could not be observed by esr spectroscopy. The butyrate showed quasireversible oxidation in CH_3CN ($E_{1/2} = 0.39$ V *vs.* sce), CH_2Cl_2 ($E_{1/2} = 0.45$ V), and ethanol ($E_{1/2} = 0.30$ V). The rate constant for decomposition of the product $[Mo_2(O_2CC_3H_7)_4]^+$ was about 10^{-2} sec^{-1}. An esr study of the latter indicates that it has one unpaired electron delocalized over both Mo atoms, and a spin Hamiltonian with $g_\parallel = g_\perp = 1.941$, $|A_\parallel{}^{Mo}| = 35.6 \times 10^{-4}$ cm^{-1}, and $|A_\perp{}^{Mo}| = 17.8 \times 10^{-4}$ cm^{-1} satisfactorily accounts for the observed spectrum.

Introduction

This paper extends our program[1-3] to characterize binuclear complexes with quadruple bonds with respect to their electrochemical behavior and, simultaneously, to study the magnetic properties of all species with unpaired electrons. We have previously[3] reported on the $[Mo_2(SO_4)_4]^{3-}$ and $[Mo_2(SO_4)_4]^{4-}$ ions, the first of which is paramagnetic, lacking one electron in the δ-bonding orbital. In order to determine whether the observations made there are general for such systems we have now studied the pairs $[Mo_2Cl_8]^{n-}$, $n = 3, 4$, and $[Mo_2(O_2CC_3H_7)_4]^{n+}$, $n = 0, 1$.

Experimental Section

The instruments used in the investigations reported here have been described in part I of this series.[1]

$[Mo_2(C_3H_7COO)_4]$ was prepared according to the literature procedure[4] and recrystallized from butyric acid.

Thanks are due to Dr. T. R. Webb for the preparations of $K_4[Mo_2Cl_8]$ and $(NH_4)_4[Mo_2Cl_8]$ according to the procedure earlier described.[5]

Results and Interpretation

Electrochemistry of $[Mo_2(C_3H_7COO)_4]$. The butyrate complex was chosen as a representative of the tetracarboxylatodimolybdenum complexes. The tetraacetate was so insoluble that possible difficulties were anticipated in the eventual characterization of possible oxidation products by esr techniques. The results of cyclic voltammetry on the acetate were very similar to those obtained for the butyrate complex as described in the following. Cyclic voltammetry at 25 ± 1° on dimolybdenumtetrabutyrate was performed employing a platinum electrode in the following solvents: acetonitrile, dichloromethane, and ethanol. All solutions were 0.1 *M* in tetrabutylammonium perchlorate. The potential range covered was −2 to +2 V *vs.* sce in acetonitrile and −1 to +1 V *vs.* sce in the other solvents. At approximately +0.4 V *vs.* sce an oxidation reaction was observed in all solvents. At potential sweep rates $\nu > 50$ mV sec^{-1} the ratio between the cathodic and anodic peak currents, $i_p{}^c/i_p{}^a$, was unity in all solvents. In dichloromethane and ethanol solutions the voltammograms showed that the electron-transfer process was very slow. At values of $\nu = 100$ mV sec^{-1} the potential separations between the anodic and cathodic peaks, ΔE_p, were 380 and 290 mV, respectively. ΔE_p decreased with decreasing values of ν, but so did $i_p{}^c/i_p{}^a$. Thus at $\nu = 5$ mV sec^{-1} in ethanol it was found that $i_p{}^c/i_p{}^a \approx 0$. Simultaneously, the anodic peak was shifted cathodically. For all sweep rates $i_p{}^a\nu^{-1/2}$ was virtually independent of υ. These observations indicate an almost irreversible charge-transfer mechanism and a lifetime of the oxidized product of the order of 1 min.

Table I. Parameters of Eq 1 for Different Solvents

Solvent	$E_{1/2}$, V *vs.* sce	k, sec^{-1}	$\Psi\nu^{1/2}$, V$^{1/2}$ sec$^{-1/2}$
Acetonitrile	0.39	⩽3 × 10^{-3}	0.03
Dichloromethane	0.45	10^{-2}	Very slow electron transfer
Ethanol	0.30	2 × 10^{-2}	

Table II. Spin Hamiltonian Parameters for $[Mo_2(C_3H_7COO)_4]^+$

$g_\parallel$	$g_\perp$	$10^4|A_\parallel|$, cm^{-1}	$10^4|A_\perp|$, cm^{-1}
1.941	1.941	35.6	17.8

In acetonitrile solution the ratio $i_p{}^a/i_p{}^c$ was unity for all values of ν between 100 and 1 mV sec^{-1}. ΔE_p varied with ν as expected for a quasireversible reaction,[6] giving values of $\Psi\nu^{1/2} = 0.03$ V$^{1/2}$ sec$^{-1/2}$, independent of ν. Rotating-disk electrode polarography indicated that the oxidation process involves transfer of one electron. The shapes of the polarograms varied with the rate of rotation, *N*. For *N* between 30 and 1 sec^{-1} we found $i_LN^{-1/2}$ independent of *N*, where i_L is the limiting current. For values of $\nu = 0.5$ mV sec^{-1} and $N = 1$ sec^{-1} a plot of *E vs.* log $(i_L - i)/i$ had a slope of 62 ± 1 mV, very close to the value expected for transfer of a single electron.

We interpret these results in terms of reaction 1 with the

$$\begin{tikzcd} {[Mo_2(C_3H_7COO)_4]^+ + e^-} \arrow[r, shift left, "E_{1/2}"] \arrow[d, "k"] & {[Mo_2(C_3H_7COO)_4]} \arrow[l, shift left] \\ \text{decompn} \end{tikzcd} \tag{1}$$

parameters tabulated in Table I. Since one of the species in eq 1 is uncharged, it is not surprising that the value of $E_{1/2}$ varies with the solvent.

The products formed by oxidation of $[Mo_2(C_3H_7COO)_4]$ at a rotating platinum disk electrode at 0.5 V *vs.* sce in the three solvents had identical esr spectra.

Electrochemistry of the $[Mo_2Cl_8]^{4-}$ Ion. Cyclic voltammetry at 25 ± 1° on approximately 10^{-2} *M* solutions of the potassium salt in 6 *M* hydrochloric acid (the only suitable solvent) showed a single oxidation peak at 0.5 V *vs.* sce with a shape very close to that expected for a reversible reaction. The corresponding reduction peak could be observed at a sweep rate of 0.5 V sec^{-1} but was completely absent for lower sweep rates. This may indicate formation of very short-lived $[Mo_2Cl_8]^{3-}$, but since our main concern was to obtain frozen-solution esr spectra, a technique which requires somewhat longer lifetimes, we did not pursue this any further.

Cyclic voltammetry on approximately 10^{-2} *M* solutions of the ammonium salt in methanol containing 0.1 *M* tetrabutylammonium perchlorate also showed an irreversible oxidation reaction with a peak at 0.5 V *vs.* sce. No corresponding

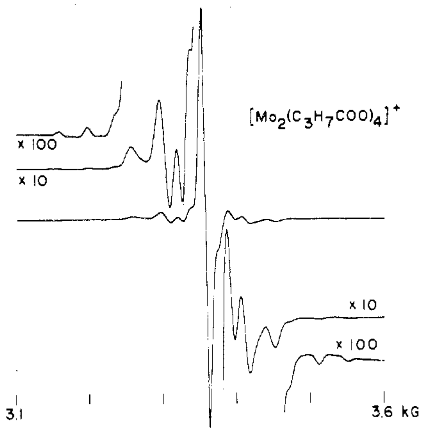

Figure 1. Frozen solution esr spectrum of [$Mo_2(C_3H_7COO)_4$]$^+$ in dichloromethane at 77 K. Microwave frequency 9.11 GHz.

reduction peak could be observed at ν = 0.5 V sec^{-1}, the fastest sweep rate available on our instrument.

Esr Spectra of [$Mo_2(C_3H_7COO)_4$]$^+$. The frozen-solution X-band esr spectrum of [$Mo_2(C_3H_7COO)_4$]$^+$, generated electrolytically in solution as discussed above, is shown in Figure 1. This spectrum resembles that of [$Mo_2(SO_4)_4$]$^{3-}$ discussed earlier,[3] and it is easily interpreted in terms of the spin Hamiltonian (2), with $S = {}^1/_2$ and including species with

$$\mathcal{H} = \mu[g_{\|}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + A_{\|}S_z(I^1{}_z + I^2{}_z) + A_{\perp}[S_x(I^1{}_x + I^2{}_x) + S_y(I^1{}_y + I^2{}_y)] \qquad (2)$$

$I^1 + I^2 = J = 0, {}^5/_2$, and 5 with the abundances 56%, 37.7%, and 6.3%, respectively. These abundances are expected for a dinuclear complex with naturally occurring molybdenum isotopes.[3] The spin Hamiltonian parameters obtained are shown in Table II. The small difference in magnetic moment of ^{95}Mo and ^{97}Mo (approximately 2%) does not give rise to observable splittings in the spectrum.

A computer simulation of the esr spectrum was performed according to the procedure earlier described[1] and including the parameters in Table II and the three nuclear isomers. The result is shown in Figure 2.

The esr spectra thus show that [$Mo_2(C_3H_7COO)_4$]$^+$ has a spin doublet ground state, and the hyperfine pattern reveals coupling to two equivalent molybdenum nuclei. The spin Hamiltonian parameters are very similar to those obtained[3] for [$Mo_2(SO_4)_4$]$^{3-}$. A correlation between the *g* factors and calculations of the energies of the excited states in similar molecules will be the subject of a future publication.

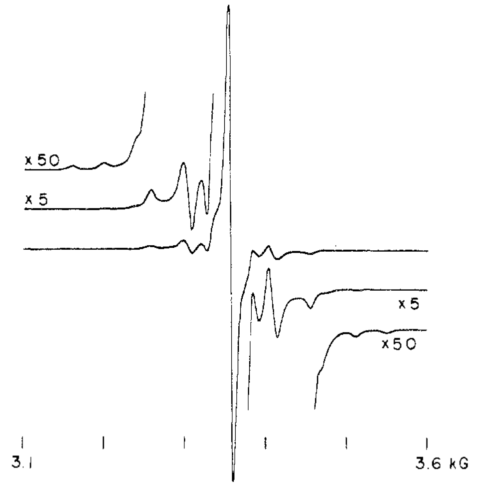

Figure 2. Computer-simulated esr spectrum using the parameters in Table II and the isotope distribution described in the text and in ref 3. First-derivative lorentzian lines having widths of 12 G were added for every step of 1° in polar angle θ.

Acknowledgment. This work was supported in part by the National Science Foundation under Grant No. 33142X, and we are grateful to The Robert A. Welch Foundation for funds to purchase the Beckman Electroscan 30. E. P. thanks Chemistry Laboratory I, The H. C. Orsted Institute, University of Copenhagen, for a leave of absence, 1973–1974.

Registry No. [$Mo_2(C_3H_7COO)_4$], 41772-56-9; [Mo_2Cl_8]$^{4-}$, 34767-26-5; [$Mo_2(C_3H_7COO)_4$]$^+$, 53260-23-4.

References and Notes

(1) F. A. Cotton and E. Pedersen, *Inorg. Chem.*, **14**, 383 (1975).
(2) F. A. Cotton and E. Pedersen, *Inorg. Chem.*, **14**, 388 (1975).
(3) F. A. Cotton, B. A. Frenz, E. Pedersen, and T. R. Webb, *Inorg. Chem.*, **14**, 391 (1975).
(4) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
(5) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 351 (1970).
(6) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).