© *1994 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *67, 3122—3124(1994)* [Vol. 67, No. 11

Voltammetric Behavior of Doubly-Bridged Dioxobis(dithiocarbamato)dimolybdenum(V) Complexes in Dichloromethane

Kei Unoura,* Yoshihiro Fukase, Yojiro Sato, Nobuyuki Chida, and Hiroshi Ogino†
Department of Chemistry, Faculty of Science, Yamagata University, Kojirakawa-machi, Yamagata 990
† Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980-77

(Received May 20, 1994)

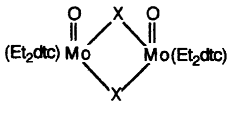
Synopsis. The electrochemical behavior of the di-μ-oxo, μ-oxo-μ-sulfido and di-μ-sulfido dinuclear molybdenum(V) complexes ligating a series of dithiocarbamates, $[Mo_2O_{4-n}S_n(R_2dtc)_2]$ ($n=0$—2; $R_2dtc^- =$ dithiocarbamate), was investigated in dichloromethane. Each complex undergoes a one-electron quasi-reversible reduction, followed by a homogeneous chemical reaction, except for the di-μ-sulfido complex $[Mo_2O_2S_2(Ph_2dtc)_2]$ which shows a complicated electrochemical process. The chemical stability of the one-electron reduction products of $[Mo_2O_{4-n}S_n(R_2dtc)_2]$ increases with increase in the number of bridging sulfides and in the electron-donating ability of the substituents on the dithiocarbamate ligands.

Electrochemical properties of the doubly-bridged dioxobis(diethyldithiocarbamato)dimolybdenum(V) complexes with the $[Mo_2O_2X_2]^{2+}$ core (Chart 1) have been investigated in dimethyl sulfoxide (DMSO),[1,2] *N*,*N*-dimethylformamide (DMF),[1] and acetonitrile (CH_3CN).[1] These studies demonstrated that the di-μ-oxo complex $[Mo_2O_4(Et_2dtc)_2]$ undergoes an irreversible two-electron reduction, and that the μ-oxo-μ-sulfido complex $[Mo_2O_3S(Et_2dtc)_2]$ and di-μ-sulfido complex $[Mo_2O_2S_2(Et_2dtc)_2]$ are reduced by two successive one-electron steps.

We found that the voltammetric behavior of $[Mo_2O_{4-n}S_n(Et_2dtc)_2]$ in dichloromethane (CH_2Cl_2) at −16 °C is different from that in DMSO, DMF, and CH_3CN.[1,2] This paper describes the voltammetric behavior of a series of dinuclear molybdenum(V)–dithiocarbamate complexes $[Mo_2O_{4-n}S_n(R_2dtc)_2]$ ($R=CH_3$ (Me), C_2H_5 (Et), *i*-C_3H_7 (*i*-Pr), *i*-C_4H_9 (*i*-Bu), C_6H_5 (Ph), $C_6H_5CH_2$ (Bz)) in CH_2Cl_2 at −16 °C. The effect of the substituents of the dithiocarbamate ligands on the voltammetric behavior will be discussed. We also report here a new method to prepare the μ-oxo-μ-sulfido and di-μ-sulfido molybdenum(V) dinuclear complexes with various dithiocarbamate ligands.

Experimental

Materials. Sodium salts of the dithiocarbamates R_2dtc^- (R = *i*-Pr, *i*-Bu, Ph, Bz) were prepared according to literature methods.[3,4] Sodium salts of dimethyldithiocarbamate and diethyldithiocarbamate were purchased from Nacalai Tesque Inc. $Na_2[Mo_2O_3S(Cys)_2]\cdot 4H_2O$ (Cys^{2-} = cystinate),[5] $Na_2[Mo_2O_2S_2(Cys)_2]\cdot 4H_2O$,[6] and $(pyH)_2[MoOCl_5]$ (pyH^+ = pyridinium)[7] were prepared by literature methods.



(X = O or S)

Chart 1.

Preparation. A series of $[Mo_2O_{4-n}S_n(R_2dtc)_2]$ (R = Me, Et, *i*-Pr, *i*-Bu, Ph, Bz) were prepared as the methods described below and characterized by elemental analysis and infrared spectroscopy.[2] Among them, however, $[Mo_2O_4(Ph_2dtc)_2]$, $[Mo_2O_3S(Ph_2dtc)_2]$, and $[Mo_2O_4(Bz_2dtc)_2]$, were not obtained in satisfactorily pure forms.

$[Mo_2O_4(R_2dtc)_2]$ (R=Me, Et, *i*-Pr, *i*-Bu). The di-μ-oxo molybdenum(V) complexes $[Mo_2O_4(R_2dtc)_2]$ were prepared by a method similar to that for the preparation of $[Mo_2O_4(Et_2dtc)_2]$[2] and were purified by recrystallization from chloroform–petroleum ether. $(pyH)_2[MoOCl_5]$ was used as the starting material instead of $MoCl_5$ which was used in the previous research,[2] because $(pyH)_2[MoOCl_5]$ can be handled more easily than $MoCl_5$.

$[Mo_2O_3S(R_2dtc)_2]$ (R=Me, Et, *i*-Pr, *i*-Bu, Bz). To a methanol solution (20 ml) of sodium salt of R_2dtc^- (6 mmol), was added $Na_2[Mo_2O_3S(Cys)_2]\cdot 4H_2O$ (0.74 g; 1.2 mmol) with stirring. A bright yellow solid which deposited was collected by filtration and washed with water until the filtrate became colorless. Then, the solid was washed with methanol and ether, and dried under vacuum. The crude product of $[Mo_2O_3S(R_2dtc)_2]$ was recrystallized from chloroform–petroleum ether.

$[Mo_2O_2S_2(R_2dtc)_2]$ (R=Me, Et, *i*-Pr, *i*-Bu, Ph, Bz). To a methanol solution (50 ml), containing sodium salt of R_2dtc^- (6 mmol), was added $Na_2[Mo_2O_2S_2(Cys)_2]\cdot 4H_2O$ (0.4 g; 0.6 mmol) with stirring. A bright yellow solid which deposited was treated in the same way as described for $[Mo_2O_3S(R_2dtc)_2]$. The crude product of $[Mo_2O_2S_2(R_2dtc)_2]$ was recrystallized from DMF–methanol.

Electrochemical Measurement. Cyclic voltammetry was performed on a HECS-312B polarographic analyzer coupled with a HECS-321B function generator (Huso Co.). A three-electrode cell consisting of a glassy-carbon-disk working electrode (diameter 0.3 cm), a Pt-coil auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE) was used for measurements. The ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as a standard of potential. Dichloromethane purchased from Wako Pure Chemicals was refluxed over CaH_2 for several hours and purified by fractional distillation before use. Tetrabutylammonium tetrafluoroborate ($(n\text{-}Bu_4N)BF_4$), obtained from Nacalai Tesque Inc., was used as a supporting electrolyte without further purification. The concentration of the supporting electrolyte was adjusted to 0.1 M (1 M = 1 mol dm^{-3}). The temperature of the cell was maintained at −16 °C. Three

Table 1. Cyclic Voltammetric Data for the First Reduction Processes of Mo(V) Dinuclear Complexes in CH_2Cl_2 Containing 0.1 M (n-Bu_4N)BF_4[a]

Complex	$E^{\circ\prime}$/V (vs. Fc/Fc$^+$)[b]	ΔE/mV	i_{pa}/i_{pc}	I_{pc}/S[c]	n[d]
(A) Dioxo-bridged complex					
[$Mo_2O_4(R_2dtc)_2$]					
R=Me	(−1.90)	Irrev.	Irrev.	450	0.9
=Et	(−1.99)	Irrev.	Irrev.	525	1.0
=i-Bu	−1.97	170	0.41	613	1.2
=i-Pr	−1.98	160	0.52	583	1.1
(B) Oxo-sulfido-bridged complex					
[$Mo_2O_3S(R_2dtc)_2$]					
R=Bz	(−1.89)	Irrev.	Irrev.	485	1.0
=Et	−1.90	150	0.53	555	1.1
=i-Bu	−1.94	160	0.93	534	1.0
=i-Pr	−1.97	160	0.99	533	1.0
(C) Disulfido-bridged complex					
[$Mo_2O_2S_2(R_2dtc)_2$]					
R=Ph[e]	(−1.86)	Irrev.	Irrev.	908	1.4
=Bz	−1.81	180	0.94	528	1.0
=Et	−1.87	190	1.04	580	1.1
=i-Bu	−1.89	170	1.04	540	1.1

a) Sweep rate is 0.5 V s^{-1}; temperature is −16 °C. b) $E^{\circ\prime}=(E_{pc}+E_{pa})/2$. If no reverse wave is observed, a reduction peak potential is given in parentheses. c) S=µA s$^{1/2}$ V$^{-1/2}$ cm^{-2} mM^{-1}. d) The value n which denotes the number of electrons involved in the electrode reactions was determined by comparison of the peak parameter with that for oxidation of ferrocene.[8] Based on the assumption that the diffusion coefficients of [$Mo_2O_{4-n}S_n(R_2dtc)_2$] (D_{Mo}) are equal to that of [$Mo_2O_3Q_4$] (Q^-=8-quinolinolate)[9] and that the ratio of diffusion coefficients D_{Fe}/D_{Mo} (D_{Fe}: the diffusion coefficient of ferrocene[8]) determined in DMSO holds in CH_2Cl_2 solvent, 2.77 was used as the value of D_{Fe}/D_{Mo}. e) Sweep rate is 0.1 V s^{-1}; At faster scan rates (>0.5 V s^{-1}), the first reduction wave splits into two peaks.

complexes, [$Mo_2O_3S(Me_2dtc)_2$], [$Mo_2O_2S_2(Me_2dtc)_2$], and [$Mo_2O_2S_2$(i-$Pr_2dtc)_2$], were found to be sparingly soluble in CH_2Cl_2, so these were not used for voltammetric measurements.

Results and Discussion

The cyclic voltammograms of [$Mo_2O_{4-n}S_n(R_2dtc)_2$] in CH_2Cl_2 exhibit well defined reduction peaks around −1.5 V (vs. SSCE) and broad and complex reduction waves from −1.6 to −2.1 V (vs. SSCE), as exemplified in Fig. 1. In this study, only the first reduction step of each complex was investigated in detail. As shown in Fig. 1, the first reduction processes of [$Mo_2O_4(Et_2dtc)_2$] and [$Mo_2O_3S(Et_2dtc)_2$] are irreversible, while that of [$Mo_2O_2S_2(Et_2dtc)_2$] is reversible. The first reduction processes of [$Mo_2O_4(Me_2dtc)_2$], [$Mo_2O_4(Et_2dtc)_2$], and [$Mo_2O_3S(Bz_2dtc)_2$] are irreversible over the entire range of scan rates (0.05—1 V s^{-1}). Those of [Mo_2O_4(i-$Pr_2dtc)_2$], [Mo_2O_4(i-$Bu_2dtc)_2$], and [$Mo_2O_3S(Et_2dtc)_2$] become reversible at faster scan rates (>0.5 V s^{-1}). The first reduction for the other μ-oxo-μ-sulfido and di-μ-sulfido complexes exhibits reversible behavior over the entire range of scan rates, except for [$Mo_2O_2S_2(Ph_2dtc)_2$] whose voltammetric behavior is complex, as will be mentioned later.

The cyclic voltammetric data of the complexes are summarized in Table 1. The values of peak current parameter (I_{pc}) for the first reduction processes of the complexes are substantially constant over the entire range of scan rates, except for [$Mo_2O_2S_2(Ph_2dtc)_2$]. From the comparison of the values of I_{pc} with that for oxidation of ferrocene,[8] the number of the electrons concerned with the first reduction step of each complex was determined to be one, except for [$Mo_2O_2S_2(Ph_2dtc)_2$]. The values of the peak current ratio i_{pa}/i_{pc} decreased with the decrease in scan rate. This indicates that the initial one-electron reduction product, which is apparently a Mo(V)–Mo(IV) mixed valence species,[6] is unstable and undergoes a homogeneous chemical reaction extensively at low scan rates. For [$Mo_2O_2S_2(Ph_2dtc)_2$], an irreversible peak with a large current parameter is observed at −1.41 V (vs. SSCE), when a scan rate is 0.1 V s^{-1}. At faster scan rate, the first reduction wave splits into two peaks. These results suggest that the electrochemical reduction process of [$Mo_2O_2S_2(Ph_2dtc)_2$] is complex.

This study indicates that the first reduction peaks of the di-μ-oxo complexes [$Mo_2O_4(R_2dtc)_2$] are attributable to one-electron reduction. This is quite different behavior from that observed in DMSO, DMF, and CH_3CN, where [$Mo_2O_4(Et_2dtc)_2$] undergoes an irreversible two-electron reduction to produce Mo(IV) species in the first step.[1,2] Two reasons were considered for this two-electron nature:[2] First, the one-electron reduction product of [$Mo_2O_4(Et_2dtc)_2$] is rapidly transformed into a species which undergoes further one-

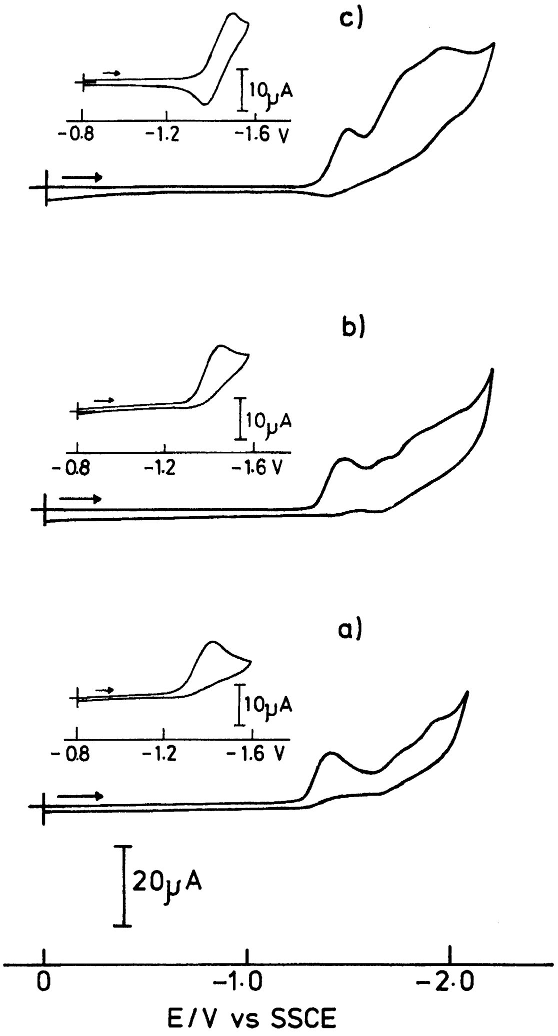


Fig. 1. Cyclic voltammograms for 1 mM $[Mo_2O_{4-n}S_n(Et_2dtc)_2]$ at a glassy carbon electrode in CH_2Cl_2 containing 0.1 M $(n\text{-}Bu_4N)BF_4$. (a) $[Mo_2O_4(Et_2dtc)_2]$, (b) $[Mo_2O_3S(Et_2dtc)_2]$, (c) $[Mo_2O_2S_2(Et_2dtc)_2]$ (scan rate; 0.1 $V\,s^{-1}$, temperature; −16 °C). Cyclic voltammograms reversed at potentials just after first reduction peaks are given in insets.

electron reduction. Another reason is that a direct irreversible two-electron reduction occurs. The results obtained in this study support the conclusion that the two-electron nature of $[Mo_2O_4(Et_2dtc)_2]$ in DMSO, DMF, and CH_3CN is due to the former reason.

The values of the peak current ratio i_{pa}/i_{pc} (Table 1) depend on the kind of the substituents of the dithiocarbamate ligands in the order R=Ph<Bz<Et<*i*-Bu<*i*-Pr. This order corresponds to that of increasing chemical stability of the one-electron reduction products and agrees with the increasing order of electron-donating ability of the substituents (Ph<Bz<Me<Et<*i*-Bu<*i*-Pr).[10] The values of i_{pa}/i_{pc} also indicates that the chemical stability of the one-electron reduction products of $[Mo_2O_{4-n}S_n(R_2dtc)_2]$ increases with increase of the number of the bridging sulfide ligand.

The values of the formal potentials ($E^{\circ\prime}$) given in Table 1 shift to more negative side in the order R=Bz>Et>*i*-Bu>*i*-Pr. This indicates that, with increase in the electron-donating ability of the substituents, the initial complexes $[Mo_2O_{4-n}S_n(R_2dtc)_2]$ are more stabilized than the one-electron reduction products. A trend similar to this was observed for the reduction processes of *cis*-dioxomolybdenum(VI) complexes $[MoO_2(R_2dtc)_2]$.[11] These results suggest that the increase of the electron-donating ability of the substituents on the dithiocarbamate ligands makes molybdenum complexes with higher oxidation states more stable.

References

1) L. J. De Hayes, H. C. Faulkner, W. H. Doub, Jr., and D. T. Sawyer, *Inorg. Chem.*, **14**, 2110 (1975).

2) F. A. Schultz, V. R. Ott, D. S. Rolison, D. C. Bravard, J. W. McDonald, and W. E. Newton, *Inorg. Chem*, **17**, 1758 (1978).

3) H. L. Klopping and G. L. M. Van Der Kerk, *Recl. Trav. Chim. Pays-Bas*, **70**, 917 (1951).

4) E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, **4**, 973 (1965).

5) T. Shibahara, H. Akashi, S. Nagahata, H. Hattori, and H. Kuroya, *Inorg. Chem.*, **28**, 362 (1989).

6) V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, **16**, 2538 (1977).

7) Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, **1975**, 396.

8) K. Unoura, T. Ooi, K. Tanaka, and A. Iwase, *J. Electroanal. Chem.*, **252**, 335 (1988).

9) A. F. Isbell, Jr., and D. T. Sawyer, *Inorg. Chem.*, **10**, 2449 (1971).

10) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **75**, 4231 (1953).

11) K. Unoura, A. Iwase, and H. Ogino, *J. Electroanal. Chem.*, **295**, 385 (1990).