Inorganica Chimica Acta, *128* (1987) L17–L18

Cyclic Voltammetry of $[CpMo(CO)_3]_2$, $[CpMo(CO)_2]_2$ and Chalcogenato-bridged Dimolybdenum Complexes $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ (E = S, Se, Te)*

PETER JAITNER** and WOLFGANG WINDER

Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, 6020 Innsbruck, Austria

(Received November 10, 1986)

Recently we described the syntheses of chalcogenato-bridged compounds $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ (E = S, Se, Te) [1]. The X-ray structure of $[CpMo(CO)_2(\mu\text{-}TePh)]_2$ revealed a structure which is analogous with the homologous sulphur compound. The asymmetric molecule contains a convoluted Mo_2Te_2 four membered ring with Mo–Te distances of 2.785–2.865 Å without a metal–metal bond. The Te···Te distance of 3.24 Å is unexpectedly short compared to the S···S distance of 2.98 Å in $[CpMo(CO)_2(\mu\text{-}SR)]_2$ [2].

Our synthetic studies of this low valent type of complexes are focussed on their electrochemistry. Herein we report electrochemical studies of the bridged thiolato, selenolato and tellurolato complexes $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ as well as of the starting materials $[CpMo(CO)_3]_2$ and $[CpMo(CO)_2]_2$ obtained by cyclic voltammetry.

The presence of Mo–S bonding in a variety of redox enzymes has prompted electrochemical investigations of dimeric Mo–sulfur bonds containing complexes [3]. But no comparative studies of the electrochemical behaviour of the homologous bridged selenolato and tellurolato compounds are reported.

Whilst manganese–carbonyl–thiolate systems exhibit only reversible one-electron oxidation waves [4], molybdenum–carbonyl–thiolate systems as well as phosphido-bridged iron–carbonyl species show two-electron transfers [5].

Figure 1 presents the cyclic voltammogram of the oxidation of the dimeric $[CpMo(CO)_2(\mu\text{-}TePh)]_2$ in CH_3CN. The data listed in Table I show that the obtained voltammogramms for the thiolato, selenolato and tellurolato compounds are very similar showing a moderate scan rate dependence and $[CpMo(CO)_2(\mu\text{-}TePh)]_2$ seems to be harder to oxidise than the homologous selenium or sulphur compounds. The first oxidation (a_1) step is assigned to a reversible two-electron process as derived from cyclic voltammetry and rotating disk electrode measurements (Pt, 1000 rpm). The second oxidation (a_2) also proceeds by loss of two electrons but exhibits no reversibility.

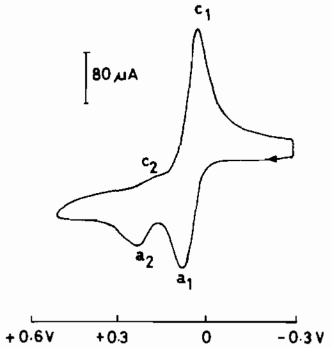

Fig. 1. Cyclic voltammogram of $[CpMo(CO)_2(\mu\text{-}TePh)]_2$ (5×10^{-4} M; 0.1 M TBHA; $V = 200$ mV/s, $T = 21$ °C; reference electrode Ag/AgCl).

TABLE I. Peak Potentials for the Oxidation of $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ (E = S, Se, Te)

Metal	E	Solvent	E_{pa_1} (mV)	E_{pc_1} (mV)	E_{pa_2} (mV)
Mo	S	CH_3CN	28	−15	263
		CH_2Cl_2	42	−5	252
Mo	Se	CH_3CN	38	−13	273
		CH_2Cl_2	169	44	477
Mo	Te	CH_3CN	82	29	291
		CH_2Cl_2	183	77	414

All values were obtained at a scan rate of 200 mV/s; supporting electrolyte = 0.1 M TBHA; electroactive species $c = 5 \times 10^{-4}$ M.

Electrochemical studies of Mo_2S_2 systems like $Mo_2(CO)_8(SR)_2$ have been reported recently and show similar behaviour to our title compounds [6]. We attribute the observed electron processes to a CO substitution by CH_3CN of $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ and assign the cathodic peaks a_1 and a_2 to the oxidation of $[CpMo(CO)(CH_3CN)(\mu\text{-}EPh)]_2$ and $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ respectively. $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ seems to be harder to oxidise than the CH_3CN substituted product $[CpMo(CO)(CH_3CN)(\mu\text{-}EPh)]_2$ ($\Delta E = 300$ mV). McDonald observed a similar value of $\Delta E = 400$ mV in his electrochemical studies of $Mo_2(CO)_8(SR)_2$ [6].

CV experiments run in CH_2Cl_2 show similar results to those in the more strongly bonding CH_3CN.

---

*Presented at the Meeting of the Gesellschaft Deutscher Chemiker and Gesellschaft Österreichischer Chemiker in Innsbruck, May 1986.

**Author to whom correspondence should be addressed.

0020-1693/87/$3.50

Even here a substitution of CO by CH_2Cl_2 takes place. Coordination of CH_2Cl_2 is confirmed by the electrochemical studies of Pickett and Fletcher of $[Mn(CO)_5CH_2Cl_2]^+$ which is obtained by electrochemical oxidation of $Mn_2(CO)_{10}$ in CH_2Cl_2 [7].

Earlier synthetic studies of our group proved that $[CpMo(CO)_2(\mu\text{-}EPh)]_2$ readily undergo partial decarbonylation by heating the solids mildly *in vacuo* (80 °C, 10^{-2} mmHg) [1]. The decarbonylated $[CpMo(CO)(\mu\text{-}EPh)]_2$ achieve 18 electron configurations by forming a formal double Mo=Mo bond [1, 2]. In agreement with the reported flexibility of the Mo···Mo distance in dimeric organometallic compounds [2], our CV results can be interpreted in terms of a creation of a single metal–metal–bond and structural rearrangement within the binuclear unit upon forming the oxidized products.

The cyclic voltammograms of the single bonded $[CpMo(CO)_3]_2$ (Mo–Mo) and of the triply bonded $[CpMo(CO)_2]_2$ (Mo≡Mo) which were used for synthesis of the chalcogenato-bridged dimolybdenum compounds are nearly identical. Cathodic and anodic values of the recently published studies of $[CpMo(CO)_3]_2$ by Kadish [8] show good agreement with our measurements (Table II). Reductive cleavage of the Mo≡Mo triple bond (c_2) is surprisingly easier to obtain than of the single bonded $[CpMo(CO)_3]_2$. The reduction of the cationic species $[CpMo(CO)_n(CH_3CN)]^+$ ($n = 2, 3$)(c_2) to regenerate $[CpMo(CO)_3]_2$ or $[CpMo(CO)_2]_2$ occurs for the triply bonded Mo≡Mo at a more negative potential than the single bonded $[CpMo(CO)_3]_2$. Coordinated CH_3CN seems to be responsible for this shift.

TABLE II. Peak Potentials (mV) for $[CpMo(CO)_3]_2$ and $[CpMo(CO)_2]_2$ in CH_3CN

	E_{pc_1}	E_{pa_1}	E_{pc_2}	E_{pa_2}
Mo–Mo	−574	975	−1171	−58
Mo≡Mo	−631	1020[a]	−1152	−74

[a] Broad peak. The corresponding electrode reactions are as follows. a_1: oxidative cleavage $Mo_2 \rightarrow 2Mo^+ + 2e^-$, c_1: reduction $2Mo^+ + 2e^- \rightarrow Mo_2$, c_2: reductive cleavage $Mo_2 + 2e^- \rightarrow 2Mo^-$, a_2: oxidation $2Mo^- \rightarrow Mo_2 + 2e^-$. Mo_2 represents the dimeric Mo-compounds (scan rate $\nu = 200$ mV/s; 0.1 M TBHA; $c = 10^{-3}$ M).

Experimental

$[CpMo(CO)_2(\mu\text{-}EPh)]_2$ were synthesized by our published method [1]. The triply bonded $[CpMo(CO)_2]_2$ was prepared by a literature method [9]. All measurements were carried out under dry argon (oxisorb, Messer-Griesheim). Solvents were dried and distilled under N_2. Tetrabutylammonium hexafluorophosphate (TBAH) was purified by double recrystallization from purified methanol and dried under vacuum with P_2O_5.

Instrumentation

All electrochemical measurements were performed with a potentiostat (Bank-Wenking LT-78), a function generator (Voltage Scan Generator VSG 72), a voltage integrator (Wenking EVI 80) and a *xy* recorder (Hewlett-Packard 7015 B). The rotating disk electrode was a Metrohm RDE 628. We utilized a three electrode system. This consisted of a Pt-ring working electrode (Ingold), a glassy carbon counter electrode (Metrohm) and a Ag/AgCl (3 M KCl, Metrohm) reference electrode.

Acknowledgement

Thanks are due to the Fonds zur Förderung der wissenschaftlichen Forschung Vienna, for generous financial support (project 4576, 5159 and 5493).

References

1 P. Jaitner, *J. Organomet. Chem., 233,* 333 (1982); P. Jaitner and W. Wohlgenannt, *Inorg. Chim. Acta, 101,* L43 (1985); P. Jaitner, W. Wohlgenannt, A. Gieren, H. Betz and T. Hübner, *J. Organomet. Chem., 297,* 281 (1985).

2 I. B. Benson, S. D. Killops, S. A. R. Knox and A. Welch, *J. Chem. Soc., Chem. Commun.,* 1137 (1980).

3 L. D. Rosenhein, J. W. McDonald and W. E. Newton, *Inorg. Chim. Acta, 87,* L33 (1984); L. D. Rosenhein, W. E. Newton and J. W. McDonald, *J. Organomet. Chem., 288,* C17 (1985); J. Courtot-Coupez, M. Guegen, J. J. E. Guerchais, F. Y. Petillon, J. Talarmin and R. Mercier, *J. Organomet. Chem., 312,* 81 (1986).

4 J. W. McDonald, *Inorg. Chem., 24,* 1734 (1985).

5 J. P. Collmann, R. K. Rothrock, R. G. Finke, E. J. Moore and F. Rose-Munch, *Inorg. Chem., 21,* 146 (1982).

6 B. Zhuang, J. W. McDonald, F. A. Schultz and W. E. Newton, *Organometallics, 3,* 943 (1984).

7 C. J. Pickett and D. J. Fletcher, *J. Chem. Soc., Dalton Trans.,* 879 (1975).

8 K. M. Kadish, D. A. Lacombe and J. E. Anderson, *Inorg. Chem., 25,* 2246 (1986).

9 G. Brauer, 'Handbuch der Anorg. Präp. Chemie', Bd. III, Enke Verlag, Stuttgart, p. 1864.