CYCLIC VOLTAMMETRIC STUDY OF THE TRINUCLEAR COMPLEX [Cr$_2$MnO(CH$_3$COO)$_6$(H$_2$O)$_3$]

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Abstract: The cyclic voltammetric measurements on the heterotrinuclear μ_3-oxo-bridged complex [Cr$_2$MnO(CH$_3$COO)$_6$(H$_2$O)$_3$] were carried out at a stationary platinum electrode in dimethylsulfoxide (DMSO) with 0,1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The cyclic voltammograms exhibit two successive reduction waves in the potential range from + 0.1 V to – 2.0 V, indicating the change in the oxidation state of the two Cr^{III} ions.

Introduction

In the present paper the electrochemical behavior of the mixed valence neutral compound [Cr$_2$MnO(CH$_3$COO)$_6$(H$_2$O)$_3$] was investigated. The compound was synthesised for the first time at the Inorganic Chemistry Department, University of Bucharest.

The cluster contains a central oxide ion in a triangular arrangement of metal ions held together by six acetate groups according to the structural formula presented in Figure 1.
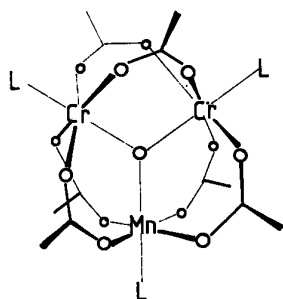

Fig. 1. *The structural formula of the complex [Cr$_2$MnO(CH$_3$COO)$_6$(H$_2$O)$_3$].*
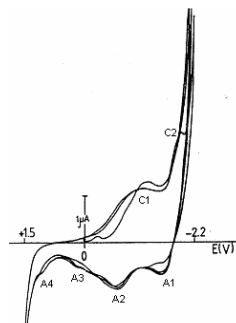.

Fig. 2. *Cyclic voltammogram over the whole investigated potential range. C$_1$, C$_2$ – cathodic peaks on direct scan; A$_1$, A$_2$, A$_3$, A$_4$ – anodic peaks on reverse scan, v = 50 mV/s.*

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Electrochemical studies concerning this complex have never been reported to our knowledge up to the present time. Similar investigations were carried out on homotrinuclear iron μ_3-oxo-bridged compounds with different carboxylate ions [1-3]. or aminoacids [4] as bridging ligands.

Experimental

The electrochemical measurements were performed with a Princeton Applied Research model 173 potentiostat, a universal programmer model 175 and an X-Y recorder, model RE 0074. The one compartment electrochemical cell was equipped with a platinum disc working electrode, a platinum plate as counter electrode and a reference electrode of an Ag wire. All measurements were carried out in dimethylsulfoxide (DMSO) with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The solutions were carefully degassed and argon bubbling was stopped during measurements to ensure semiinfinite linear diffusion conditions.

Results and Discussion

The cyclic voltammogram recorded in the potential range + 0.1 ÷ -2.2 V exhibits two reduction peaks located at – 1.3 V (C_1) and – 2.0 V (C_2) respectively (Figure 2).

Another peak observed at – 0.1 V does not appear on the following cycles. It may be generated by an adsorption process and has not been further investigated.

The first reduction wave (C_1) is extended in shape, well profiled and reproducible. It can be correlated to an anodic wave (A_1) located at – 0.3 V, which does not appear if the switching potential is more positive than – 1 V. The large potential difference (1 V) between the anodic and cathodic wave, as well as the extended shape of C_1 shows the irreversible nature of the electrochemical process [5]. This fact is supported by the high slope value (about 210 mV/decade) obtained from the linear dependence $E_p^0 = f(\lg v)$. [6]. The first reduction wave was also recorded in a restrained potential range at several sweep rates (Fig. 3). The voltammetric data are given in Table 1. The current function $i_p^c / v^{1/2}$ increases with sweep rate. It can be presumed that there is a slow chemical process competing with the first charge transfer step (C_1) revealed at low sweep rates (e.g. 20 mV/s).

Table 1 Variation of peak parameters with the sweep rate for the first cathodic wave.

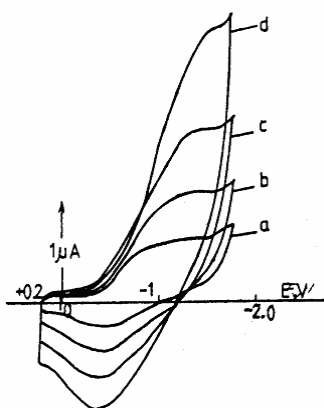| v V/s	E_P V	i_p^{C1} A	$(i_p^{C1}/v^{1/2}).10^6$	E_p^{A1} V	$i_p^{A1}.10^6$ A
0.020	-1.43	0.3	4.46	-0.44	0.27
0.050	-1.36	1.11	4.96	-0.40	0.51
0.100	-1.45	1.73	5.74	-0.39	0.78.
0.200	-1.58	2.72	6.08	-0.37	1.07
0.500	-1.60	4.30	6.08	-0.36	1.52

Fig. 3. *Cyclic voltammogram recorded on a restrained potential range showing the cathodic peak C_1 and his anodic counterpart; scan rates: 20 mV/s (a); 50 mV/s (b); 100mV/s (c); 200 mV/s (d) and 500 mV/s (e)*
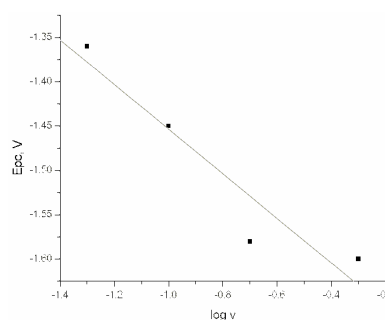
Fig. 4. *Plot of E_p^{C1} as a function of scan rate logarithm.*

The second cathodic wave corresponding to -2.0 V is less extended than the first one and shows an anodic counterpart -1.6 V. The large peak potential separation (400 mV) does not permit the evaluation of the electrochemical standard rate constant k_s, using Nicholson's [7] correlation between the peak potential separation, ΔE_P, and the function ψ.

**Table 2 Variation of peak parameters with the sweep rate for the second cathodic wave.**

v	$E_p^{C2}.10^{-6}$	$i_p^{C2}.10^{-6}$	$(i_p^{C1}/v^{1/2}).10^6$	E_p^{A1}
V/s	V	A		V
0.050	-1.84	1.98	8.85	-1.48
0.100	-1.88	3.25	10.28	-1.28
0.200	-1.88	4.50	10.06	-.07

The third anodic peak (A_3) located at 0.39 V on the reverse scan does not appear on the direct anodic scan (Fig. 5). This reverse wave becomes higher by cycling. It may be ascribed to the oxidation of the product of a chemical process:
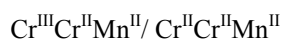
Red2 = Red2'
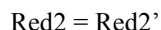
following the second reduction step.

The two cathodic waves can be ascribed to the successive monoelectronic charge transfer steps according to the formal scheme:

$Cr^{III}Cr^{III}Mn^{II}/ Cr^{III}Cr^{II}Mn^{II}$ $E_p^{C1} = -1.3$ V
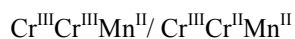
$Cr^{III}Cr^{II}Mn^{II}/ Cr^{II}Cr^{II}Mn^{II}$ $E_p^{C2} = -2.0$ V

The difference between the redox potentials of 700 mV shows an important effect of the electrochemical behavior of the neighbouring ions generated by the change in the oxidation state of the chromium ions.
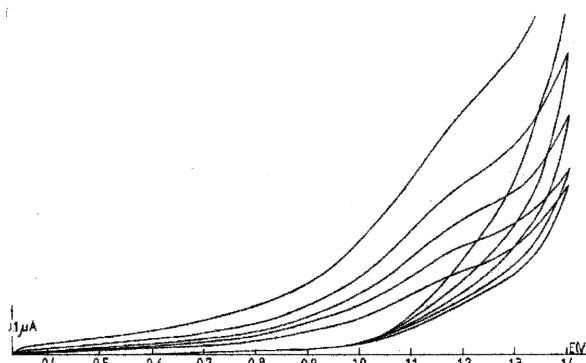

Fig. 5. *Anodic wave A_4; sweep rates: 20 mV/s (a); 50 mV/s (b); 100 mV/s (c); 200 mV/s (d); 500 mV/s (e)*

The last anodic peak in Figure 2, located at 1.2 V (A_4) was found on the direct anodic scan (Fig. 5) and may be ascribed to the change in oxidation state of the manganese ion.

Table 3. Variation of peak parameters with sweep rate for the anodic peak A_4 (direct scan).

v V/s	$E_p^{A4}.10^{-6}$ V	$i_p^{A4}.10^{-6}$ A	$(i_p^{A4}/v^{1/2}).10^6$
0.20	1.170	0.158	1.117
0.50	1.187	0.215	0.961
0.100	1.197	0.275	0.869
0.200	1.198	0.350	0.782
0.500	1.207	0.505	0.714

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