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Bis(maleonitriledithiolato)Rhodium Redox Series

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In the course of our systematic study of relations between electronic structure and redox properties of metal–dithiolene complexes, the electrochemical behaviour of the Rhmnt$_2^{2-}$* complex was studied.

Rhmnt$_2^{2-}$ is a square planar Rh(II) complex [1]. By a single crystal EPR study it was shown [2] that the electronic structure of the Rhmnt$_2^{2-}$ complex differs considerably from that of other paramagnetic Mmnt$_2^{2-}$ complexes, especially from the isoelectronic and isostructural Comnt$_2^{2-}$ complex. Redox properties of the Rhmnt$_2^{2-}$ complex have not yet been investigated.

Experimental

$(Bu_4N)_2[Rhmnt_2]$ was synthesized according to Gray [1]. The crude product was recrystallized from acetone–isopropyl alcohol mixture. All synthetic procedures were carried out in pure argon atmosphere. Cyclic voltammetry was measured by the single sweep method at a dropping mercury electrode (DME). Each sweep started 3.1 s after the beginning of the drop. A potentiostatic Kalousek commutator [3, 4] instrument with synchronous mercury drop time was used. The number (M) of rectangular potential pulses laid on each mercury drop was held constant. 18 pulses at each mercury drop with frequency 12.5 Hz were used. For M = 18, it follows [4] that the value of commutated diffusion current ratio ($\bar{i}_c/\bar{i}_d$) should equal 2.356 for a fully chemically reversible electrode reaction without any adsorption at DME or coupled chemical reaction. Decrease of $\bar{i}_c/\bar{i}_d$ under this value indicates a follow-up inactivation of the primary product of the electrode reaction [3].

All measurements were performed in moisture and oxygen free THF obtained by the ketyl method. Freshly distilled THF was transferred into the electrochemical cell under argon atmosphere. Bu_4NPF_6 (Ozark-Mahoning Co.) was used as ground electrolyte. Potential values were measured against Ag/AgCl in 1 mol l^{-1} aqueous LiCl and corrected for SCE using $Cu(biphenyl)_2I$ standard ($E_{1/2}$ = –0.65 V) [5].

Results and Discussion

Rhmnt$_2^{2-}$ shows one electrochemical oxidation and one reduction.

Oxidation

Rhmnt$_2^{2-}$ gives at a rotating platinum electrode (RPE) a single one-electron reversible oxidation wave at $E_{1/2}$ = –0.7 V *vs.* SCE (at 837 RPM). The primary product of electrode oxidation undergoes rapid inactivation, the products of this inactivation being strongly adsorbed at the electrode surface. This indicated that the inactivation might be a polymerization process analogous to that described by Cleverty for solution oxidation [6]. This process complicated the proof of the reversibility: the log $\bar{i}/(\bar{i}_d - \bar{i})$ E-plot is linear with slope 80 mV. This slope is identical with that obtained for the reversible oxidation of ferrocene in THF, where an analogous complication arises. Cyclic voltammetry of Rhmnt$_2^{2-}$ at a platinum electrode shows one anodic peak, the corresponding cathodic peak being, however, much smaller (Fig. 1). The peak potential difference equals approximately 60 mV.

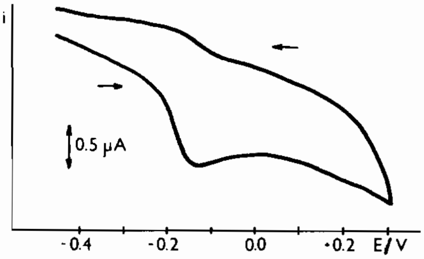

Fig. 1. Single sweep cyclic voltamogram of oxidation of Rhmnt$_2^{2-}$ on Pt electrode. Solution: 4.8 × 10^{-4} mol l^{-1} $(Bu_4N)_2[Rhmnt_2]$, 10^{-1} mol l^{-1} Bu_4NPF_6 in THF. Sweep rate 1 V s^{-1}.

Repetition of the potential sweep at the same electrode surface leads to disappearance of both anodic and cathodic peaks due to the inactivation of electrode surface by adsorption of final oxidation products.

From these facts it may be concluded that the oxidation of Rhmnt$_2^{2-}$ is an electrochemically reversible process forming Rhmnt$_2^{-}$ as primary product. This complex is rapidly inactivated most probably by polymerization.

The oxidation of Rhmnt$_2^{2-}$ by I_2 or TCNE was followed using the EPR technique. No signal attributable to spin triplet was observed. We therefore conclude that Rhmnt$_2^{-}$ is in the spin singlet state in contrast to the analogous Comnt$_2^{-}$ complex [7]. However, the homogeneous oxidation mechanism is more complicated and will be reported in detail later.

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*mnt^{2-} = $S_2C_2(CN)_2^{2-}$ = maleonitriledithiolato ligand.

Reduction

The Rhmnt$_2^{2-}$ complex is polarographically reduced at DME in a single one-electron reversible wave with $E_{1/2} = -1.37$ V (SCE). The reversibility of the electrochemical reduction was tested by the log $\bar{i}/(\bar{i}_d - \bar{i})$ *vs.* E plot (linear, slope 64 mV), the electrochemical and chemical reversibility by cyclic voltammetry (peak potential difference 60 mV, see Fig. 2) and by the Kalousek commutator method. The product formed, Rhmnt$_2^{3-}$, is fairly stable as cyclic voltammetry shows the anodic to cathodic peak current ratio 0.93 at sweep rate 10 V s^{-1} and the Kalousek commutator $\bar{i}_c/\bar{i}_d$ ratio is 2.09, only slightly less than the theoretical value, 2.356. These data point to a very slow follow-up inactivation of Rhmnt$_2^{3-}$.

The reduction of Rhmnt$_2^{2-}$ may be also performed chemically by the THF solution of $LiAlH_4$ in argon atmosphere. The colour of the solution changes from bright green to wine-red after addition of the $LiAlH_4$ solution. The reduced solution is very air-sensitive. Reaction with O_2 regenerates the original Rhmnt$_2^{2-}$ complex. The product of the chemical reduction is identical with the product of the electrode reduction as is manifested by the appearance of an oxidation wave of the reduced species at a $E_{1/2}$ identical with that of the reduction wave of Rhmnt$_2^{2-}$. An anodic–cathodic wave is observed when the original solution of Rhmnt$_2^{2-}$ is only partially reduced by $LiAlH_4$.

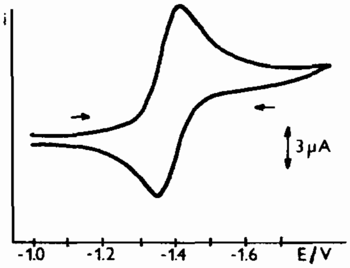

Fig. 2. Single sweep cyclic voltamogram of reduction of Rhmnt$_2^{2-}$ on DME. Solution: 7.5 × 10^{-4} mol l^{-1} $(Bu_4N)_2[Rhmnt_2]$, 10^{-1} mol l^{-1} Bu_4NPF_6 in THF. Sweep rate 10 V s^{-1}.

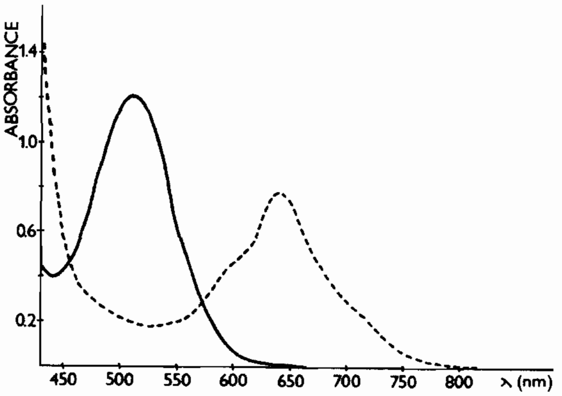

Fig. 3. Absorption spectra of Rhmnt$_2^{2-}$ and Rhmnt$_2^{3-}$. Solid line: 2.13 × 10^{-4} mol l^{-1} $(Bu_4N)_2[Rhmnt_2]$ in THF. Dashed line: after reduction by $LiAlH_4$ (Rhmnt$_2^{3-}$).

The visible absorption spectrum of the Rhmnt$_2^{3-}$ solution is presented in Fig. 3. The peak at λ_{max} = 510 nm, ϵ = 5680 is attributed to Rhmnt$_2^{3-}$. This peak decreases very slowly with time due to the slow decomposition of the Rhmnt$_2^{3-}$ trianion. The solution of Rhmnt$_2^{3-}$ shows no EPR signal.

Rhmnt$_2^{3-}$ reacts only very slowly with water as is manifested by a decrease of $\bar{i}_c/\bar{i}_d$ ratio from the original value 2.09 to 1.92 upon addition of 4.8 × 10^{-1} mol l^{-1} H_2O. This reaction is strongly accelerated by the addition of Li^+ ions to the solution [8]. When all water present in the solution of Rhmnt$_2^{2-}$ with excess of $LiClO_4$ is titrated off by $LiAlH_4$ solution*, both the $\bar{i}_c/\bar{i}_d$ ratio as well as the $E_{1/2}$ value are identical with those obtained in absence of Li^+ and water. Subsequent H_2O addition to this solution decreases the $\bar{i}_c/\bar{i}_d$ ratio to the value 0.63. At the same time the $E_{1/2}$ is strongly shifted to positive potentials and the cyclic voltammetry anodic peak is much decreased due to the fast follow-up reaction (see Fig. 4).

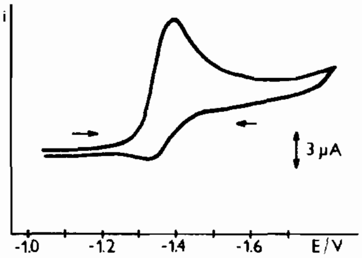

Fig. 4. Single sweep cyclic voltamogram of reduction of Rhmnt$_2^{2-}$ in presence of Li^+ and H_2O. Solution: 7.5 × 10^{-4} mol l^{-1} $(Bu_4N)_2[Rhmnt_2]$, 10^{-1} mol l^{-1} Bu_4NPF_6, 2.1 × 10^{-2} mol l^{-1} $LiClO_4$, 4.8 × 10^{-1} mol l^{-1} H_2O in THF. Sweep rate 10 V s^{-1}.

From these data it can be concluded that Li^+ ions are in THF preferentially solvated by H_2O [9], $[Li \cdot nH_2O]^+$ ions being stronger H^+ donors than free water. A similar follow-up reaction of Rhmnt$_2^{3-}$ proceeds with other weak acids, *e.g.* pivalic acid. The detailed mechanism of the reaction of Rhmnt$_2^{3+}$ with H donors is under investigation.

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*The reaction between $LiAlH_4$ and water is much faster than the reduction of Rhmnt$_2^{3-}$. The end point of the titration was indicated by the transient appearance of the red colour after the last $LiAlH_4$ addition and by simultaneous appearance of the anodic maximum of free $LiAlH_4$.

Conclusions

The Rhmnt$_2^{2-}$ complex is reversibly oxidized to Rhmnt$_2^-$ spin singlet product and reversibly reduced to spin singlet Rhmnt$_2^{3-}$ complex. Rhmnt$_2$ complexes form an hitherto not described redox series:

$$\begin{tikzcd}
\text{Rhmnt}_2^- \arrow[r, leftrightarrow, "E_1^0"] \arrow[d] & \text{Rhmnt}_2^{2-} \arrow[r, leftrightarrow, "E_2^0"] & \text{Rhmnt}_2^{3-} \\
\text{polymer} & &
\end{tikzcd}$$

The difference of successive E^0, *i.e.* $(E_1^0 - E_2^0)$ equals approximately 1.2 V and is thus much less than that of the analogous Comnt$_2^{n-}$ redox series [7]. This seems to be mainly due to the monoanions, that of the Rh series being a spin singlet in contrast to the spin triplet of the corresponding Co species.

References

1 E. Billig, S. I. Shupack, J. H. Waters, R. Williams, H. B. Gray, *J. Am. Chem. Soc., 86,* 926 (1964).

2 A. H. Maki, M. Edelstein, A. Davison, R. H. Holm, *J. Am. Chem. Soc., 86,* 4580 (1964).

3 J. Volke, O. Manoušek, *Faraday Disc. Chem. Soc., 56,* 300 (1973).

4 J. Koutecký, *Coll. Czech. Chem. Commun., 21,* 433 (1956).

5 A. Rusina, G. Gritzner, A. A. Vlček, *Proc. IVth Int. Congress Polarography, Prague,* p. 79 (1966).

6 N. G. Connelly, J. A. McCleverty, *J. Chem. Soc. A,* 1621 (1970).

7 A. Vlček, Jr., A. A. Vlček, *Proc. XIX ICCC Prague,* 127 (1978).

8 A. Vlček, Jr., A. A. Vlček, *J. Electroanal. Chem., 100* (1979), in press.

9 D. R. Cogley, J. N. Butler, E. Grunwald, *J. Phys. Chem., 75,* 1477 (1971).