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Bis(maleonitriledithiolato)Cobalt Redox Series

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The existence of Comnt$_2^{n-}$ (n = 1,2,3)* redox series can be predicted from the electronic structure of the Comnt$_2^{2-}$ complex [1] and from known theoretical principles of redox series [2]. However, only oxidation of spin-doublet square planar Co(II) complex producing dimeric [Comnt$_2$]$_2^{2-}$ species as a final product has been described up to now [3, 4]. No reduction of the Comnt$_2^{2-}$ complex has been hitherto observed.

Following our prediction concerning the existence of Comnt$_2^{n-}$ redox series, we studied both chemical and electrochemical reduction of Comnt$_2^{2-}$. Its oxidation was also re-investigated in order to examine the nature of the primary oxidation product.

Experimental

Comnt$_2^{2-}$ and [Comnt$_2$]$_2^{2-}$ complexes were used as Bu_4N^+ salts. They were prepared from Na_2mnt [5] using standard procedures [6, 7]. All experiments were performed under pure argon atmosphere in tetrahydrofuran (THF) purified by the ketyl method. Apparatus for electrochemical measurements and experimental techniques have been described elsewhere [8]. EPR spectra were obtained on a Varian E-4 instrument, visible absorption spectra were measured on a Cary 17-D spectrometer.

Results

The Comnt$_2^{2-}$ complex undergoes one oxidation and one reduction process (Fig. 1).

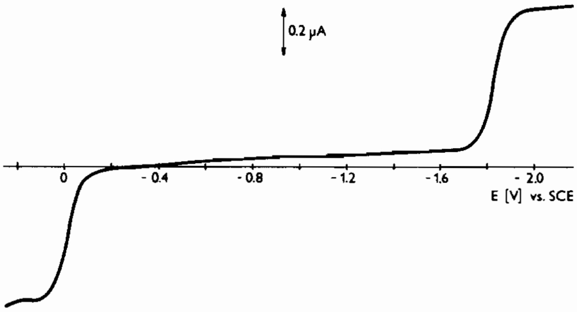

Fig. 1. Polarogram of Comnt$_2^{2-}$ complex. 10^{-3} mol l^{-1} [Bu_4N]$_2$Comnt$_2$, 10^{-1} mol l^{-1} Bu_4NPF_6 in THF, h = 81 cm, t_1 = 1.44 s.

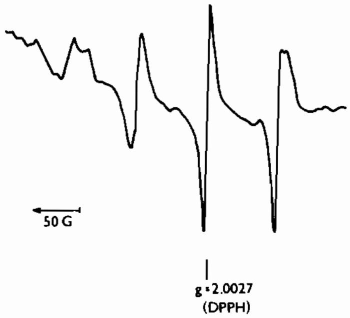

Fig. 2. EPR spectrum of Comnt$_2^-$. 6.7 × 10^{-3} mol l^{-1} [Bu_4N]$_2$[Comnt$_2$]$_2$ in DMSO.

Oxidation

Comnt$_2^{2-}$ is oxidized polarographically, both on a rotating platinum electrode and on dropping mercury electrode (DME) in a single one-electron electrochemically reversible wave at $E_{1/2}$ = –0.02 V *vs.* SCE. This oxidation was also performed chemically by I_2, O_2 (slowly), tetracyanoethylene, tetrachloro-*p*-quinone, Ph_3CCl, benzoic and all stronger protic acids. Previously, it was shown [3, 4] that the final product of the oxidation of Comnt$_2^{2-}$ is the dimeric [Comnt$_2$]$_2^{2-}$ species. Our re-investigations of the mechanism of electrochemical oxidation of Comnt$_2^{2-}$ by polarographical measurements using a Kalousek commutator at various temperatures have shown that the primary oxidation product is a monomeric complex Comnt$_2^-$, which undergoes slow follow-up dimerization [9]. Moreover, the existence of the dimer–monomer equilibrium of the oxidized species was confirmed by the mechanism of electrochemical reduction of [Comnt$_2$]$_2^{2-}$ complex [9]. This dimeric complex was found to be diamagnetic in solid state and in non-coordinating solvents, but in DMSO it is paramagnetic with a magnetic moment 2.81 B.M. due to partial dimer dissociation into spin-triplet monomer units [10]. Our measurements of the EPR spectra of [Comnt$_2$]$_2^{2-}$ in dimethylsulfoxide show a signal corresponding to the monomeric Comnt$_2^-$ species (Fig. 2). The EPR spectrum of THF solutions of [Comnt$_2$]$_2^{2-}$ is completely identical, but the concentration of EPR-active monomer is about three

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*mnt = $S_2C_3(CN)_2^{2-}$ = maleonitriledithiolate = *cis*-1,2-dicyano-1,2-dithiolato-ethylene.

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times lower than that in DMSO. Identical EPR spectra were also obtained when Comnt$_2^{2-}$ complex was electrochemically oxidized on Pt-wire electrode inside the EPR cavity in the THF solution. It may be therefore concluded that the primary oxidation product, Comnt$_2^-$, is a spin-triplet species slowly attaining the dimerization equilibrium with $[\text{Comnt}_2]_2^{2-}$.

Reduction

The Comnt$_2^{2-}$ complex is reduced in single one-electron chemically and electrochemically reversible polarographic wave at $E_{1/2} = -1.83$ V *vs.* SCE, producing the Comnt$_2^{3-}$ species [9]. This reduction may be performed chemically by dropwise addition of $LiAlH_4$ in THF to the THF solution of Comnt$_2^{2-}$ under pure argon atmosphere, until the colour turns green. These green solutions exhibit a one-electron polarographic oxidation wave at -1.83 V, thus proving the identity of the products of the chemical and electrochemical reductions.

The solutions of Comnt$_2^{3-}$ species are extremely air-sensitive, being reoxidized back to Comnt$_2^{2-}$ as was proved spectroscopically. Excess of $LiAlH_4$ decomposes Comnt$_2^{3-}$ rapidly, producing brown-yellow air-stable solutions.

Green solutions of Comnt$_2^{3-}$ in THF exhibit no EPR signal. The Comnt$_2^{3-}$ complex may be therefore regarded as a spin-singlet species. Spectroscopic characterization of Comnt$_2^{3-}$ is complicated by the opalescence of the reduced solutions and by their rather rapid decomposition. In spite of this, it may be shown that the only absorption in visible spectral region is a very broad band at 800–1000 nm with a poorly defined maximum at 950–980 nm and an extinction coefficient of 1000 ± 200. This absorption spectrum is quite different from other Mmnt$_2^{n-}$ species [10], especially that of isoelectronic Nimnt$_2^{2-}$ species. It may be concluded that molecular orbitals of Comnt$_2^{3-}$ are more close-spaced and of greater d-character in comparison with other Mmnt$_2^{n-}$ complexes.

Discussion

As Comnt$_2^{2-}$ complex may be both reduced and oxidized producing Comnt$_2^{3-}$ and Comnt$_2^-$ species respectively, The Comnt$_2^{n-}$ (n = 1, 2, 3) redox series may be formulated (Scheme I).

$$\begin{tikzcd}
\underset{(S=1)}{\text{Comnt}_2^-} \arrow[r, leftrightarrow, "-0.02V"] \arrow[d, shift left, "\text{slow}"] & \underset{(S=1/2)}{\text{Comnt}_2^{2-}} \arrow[r, leftrightarrow, "-1.83V"] & \underset{(S=0)}{\text{Comnt}_2^{3-}} \\
{[\text{Comnt}_2]_2^{2-}} \arrow[u, shift left]
\end{tikzcd}$$

Comnt$_2^{n-}$ redox series. Spin states are given in parentheses.

The ligand system in the Comnt$_2^{2-}$ complex is fully electronically saturated, *i.e.* it has no low-lying empty orbtials available for the acceptance of an electron [11]. The reduction process observed has thus to be metal-localized, producing a low-valent Co(I) complex, Comnt$_2^{3-}$. On the other hand, the oxidation of Comnt$_2^{2-}$ is mainly delocalized over the ligand system, as follows from the loss of nucleophilic reactivity of the sulphur donor atom when going from the dianion to the monoanion [11].

The measured value of the difference between $E_{1/2}$ values corresponding to successive redox processes, $\Delta E_{1/2} = 1.81$ V, is the highest one observed among all isoelectronic Mmnt$_2^{n-}$ redox series. *E.g.* in the case of M = Ni, Pd, Pt, n = 0, 1, 2, $\Delta E_{1/2}$ values fall in the range 0.8–0.9 V.

This surprisingly high value, 1.81 V, cannot be explained in the usual manner as a stepwise removal of electrons from doubly occupied orbital supposing the validity of Koopman's theorem [12]. Two factors contribute to the observed high value of $\Delta E_{1/2}$: formation of spin-triplet oxidation products and mainly great orbital relaxation concerned with highly metal-localized reduction process. Theoretical interpretation of $\Delta E_{1/2}$ values will be published elsewhere [13] together with the results of MO-calculations.

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