Photoelectrochemical Oxidation of Tris(dimethyldithiocarbamato-*S,S'*)cobalt(III)

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The electro-oxidation of tris(dimethyldithiocarbamato-*S,S'*)cobalt(III), $[Co(S_2CNMe_2)_3]$, at platinum electrodes in acetonitrile solution in the presence of light of wavelengths between 300 and 600 nm gave rise to appreciable photocurrents. These are suggested to arise from an absorption of light by the one-electron oxidation product $[Co(S_2CNMe_2)_3]^+$ which is followed by an internal redox reaction which leads to the fragmentation of the cation and the probable formation of $[Co(S_2CNMe_2)_2]$ and oxidised ligand. Kinetic parameters have been obtained for the decomposition of $[Co(S_2CNMe_2)_3]^+$ in the presence of light. In the absence of light the cation undergoes a rate-determining dimerisation reaction which is followed by an internal redox reaction which leads to the formation of $[Co_2(S_2CNMe_2)_5]^+$; at light intensities of *ca.* 10 mW cm^{-2} both pathways are kinetically significant and the electrode reaction consists of parallel electrodimerisation and photofragmentation pathways.

It has been previously predicted[1,2] that both inorganic complexes and organometallic compounds have the potential to display a rich photoelectrochemistry on account of the ready accessibility of both differing oxidation states and low-lying excited electronic states for the following reasons: (*a*) ligand-loss processes are promoted by both photolysis and electron transfer, (*b*) unusual oxidation states can be attained by heterogeneous electron transfer with an electrode resulting in redox products which may have radically differing reactivities to their parent compounds, and (*c*) excited electronic states achieved by photochemical stimulation may also have differing properties from those of the parent, resulting in fragmentation pathways of low-lying excited states which can lead to new species which possess voltammetric activity.

In this paper we illustrate these predictions with reference to the oxidation of tris(dimethyldithiocarbamato-*S,S'*)cobalt(III), $[CoL_3]$, in the presence of light of wavelengths between 300 and 600 nm. It is known[3] that in the dark the electro-oxidation of $[CoL_3]$ proceeds *via* an electrodimerisation mechanism [equations (1) and (2)]. The kinetics of the

$$[CoL_3] - e \longrightarrow [CoL_3]^+ \quad (1)$$

$$[CoL_3]^+ + [CoL_3]^+ \longrightarrow [Co_2L_6]^{2+} \longrightarrow [Co_2L_5]^+ + \text{oxidised ligand} \quad (2)$$

dimerisation step has been measured to be *ca.* 1.9×10^7 cm^3 mol^{-1} s^{-1} at 25 °C by means of both cyclic voltammetry and steady-state channel-electrode voltammetry as independent techniques.[3] It will be shown that the presence of light opens up the viability of a parallel route for the loss of $[CoL_3]^+$ in conjunction with its dimerisation which gives rise to further heterogeneous electron transfer thus providing an example of a photoelectrochemical process in which dual activation (oxidation followed by photolysis) induces new chemical reactivity.

Experimental

All standard electrochemical and photoelectrochemical experiments were conducted using a channel electrode made of silica of standard construction and dimensions[2] capable of delivering flow rates in the range 10^{-4}–10^{-1} cm^3 s^{-1}. Platinum foils of size *ca.* 4 × 4 mm were used as working electrodes. Precise dimensions were determined using a travelling microscope. A saturated calomel reference electrode (SCE) (Radiometer, Denmark) was positioned in the flow system upstream of the channel electrode, and a platinum gauze counter electrode was located downstream to prevent counter electrode products contaminating the channel cell. Electrochemical measurements were made using an Oxford Electrodes potentiostat modified to boost the counter voltage up to *ca.* 200 V. Methodological details were as described previously.[2,4] Irradiation was provided by a high-pressure (1000 W) xenon-arc lamp (Speirs Robertson and Co., Bedford) *via* a high-intensity grating monochromator, using silica lenses to focus light onto the electrode (incident power 10 mW cm^{-2}). The UV/VIS measurements were made with a Perkin-Elmer Lambda-5 spectrometer. Rotating-disc measurements were conducted using Oxford Electrodes equipment. Platinum microdisc electrodes of diameter 5.0 μm were supplied by Bioanalytical Systems (West Lafayette).

Experiments were performed using solutions of $[CoL_3]$ (*ca.* 10^{-4}–10^{-3} mol dm^{-3}) in dried,[5] distilled acetonitrile (Fisons) containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (Fluka, purum) as supporting electrolyte. The complex $[CoL_3]$ was prepared using methods based on standard literature procedures.[6] Stoichiometric amounts of sodium hydroxide, methylamine and carbon disulfide were reacted in cold aqueous solution to produce the sodium dithiocarbamate, NaL. Solid cobalt(II) nitrate was then added to this mixture in the presence of air to form $[CoL_3]$. Purification was carried out *via* Soxhlet extraction using chloroform or dichloromethane as the solvent. The compound was extracted as a green solid after solvent evaporation. The complex $[Co_2L_5]^+$ was prepared using literature methods.[3] Solutions were purged of oxygen by outgassing with argon that had been previously dried with calcium chloride and then pre-saturated with acetonitrile prior to electrolysis. All measurements were made under thermostatted conditions at 25 °C.

Results and Discussion

Channel-electrode voltammetry on the oxidation of $[CoL_3]$ was conducted at platinum electrodes using solutions containing concentrations of the electroactive species between

0.025 and 0.5 mmol dm^{-3} in acetonitrile solution containing 0.1 mol dm^{-3} NBu_4ClO_4. Analysis of the flow-rate dependence of the transport-limited currents revealed a cube root dependence, as illustrated in Fig. 1, and as predicted from the Levich[7] equation for a one-electron oxidation [equation (3), where a_{bulk}

$$I_{lim} = 0.925FD^{\frac{2}{3}}a_{bulk}wx_e^{\frac{2}{3}}(V_f/h^2d)^{\frac{1}{3}} \qquad (3)$$

is the bulk concentration of the electroactive species, V_f is the volume flow rate, F is the Faraday constant, h the half-height of the cell, d the channel width, w is the electrode width, D the diffusion coefficient and x_e the electrode length]. A diffusion coefficient of (2.1 ± 0.3) × 10^{-5} cm^2 s^{-1} was deduced. Current–voltage curves were next recorded using a platinum microdisc electrode of radius 5 μm and a low concentration (< 0.1 mmol dm^{-3}) of electroactive species so as to obtain a value of $E_{\frac{1}{2}}$ under conditions of ultra-fast mass transport where the kinetic effect of $[CoL_3]^+$ dimerisation may be shown to be negligible[3] so providing a true estimate of the formal oxidation potential of +883 ± 5 mV (*vs.* SCE). Under channel-flow conditions the halfwave potential was found to vary systematically in a cathodic direction with decreasing electrolyte flow rate in a manner consistent with a following second-order reaction as in reaction (2). The use of this variation of $E_{\frac{1}{2}}$ in conjunction with Tafel analysis of the voltammetric waveshapes to provide a value of 1.9 × 10^7 cm^3 mol^{-1} s^{-1} for the rate constant of step (2) is described elsewhere.[3]

We next examine the behaviour of $[CoL_3]$ in the presence of light of wavelengths greater than 300 nm. Fig. 2 shows hydrodynamic voltammograms measured at a channel electrode in the presence of monochromated light (480 nm) from a xenon-arc lamp; a significant increase in the magnitude of the transport-limited current is apparent. That no photocurrent is seen except under conditions where $[CoL_3]$ is oxidised suggests that light is absorbed not by the parent compound but by an oxidation product. In particular $[CoL_3]^+$ or $[Co_2L_5]^+$ might be thought likely candidates. Accordingly an action spectrum was measured by potentiostatting the channel electrode at +1.10 V (*vs.* SCE) corresponding to the transport-limited oxidation of $[CoL_3]$ and recording the photocurrent as a function of excitation wavelength at a fixed electrolyte flow rate of 2.3 × 10^{-3} cm^3 s^{-1}. The result is shown in Fig. 3 which reveals that a wavelength of 480 nm corresponds to maximum photocurrent. Since the power output of the xenon-arc lamp is approximately constant over the range 300–600 nm[2,4] the action spectrum should approximate to the absorption band responsible for inducing the photoelectrochemical activity. Accordingly UV/VIS absorption spectra were recorded of samples of both the parent $[CoL_3]$ and a sample of $[Co_2L_5]PF_6$ dissolved in acetonitrile. The former showed a visible band at 318 (ε = 26 000), a shoulder at 380 (12 200 dm^3 mol^{-1} cm^{-1}) and negligible absorption at 480 nm. The latter showed a band at 242 (ε = 46 700), a shoulder at 260 (38 400) a further band at 310 (31 500 dm^3 mol^{-1} cm^{-1}) and negligible absorption at 480 nm. The absorption spectra are given in Fig. 4. It may be concluded that the species responsible for the photoelectrochemical activity is neither $[CoL_3]$ nor $[Co_2L_5]^+$. Rather it is very likely $[CoL_3]^+$ which is known to absorb near 500 nm in dichloromethane solution.[8]

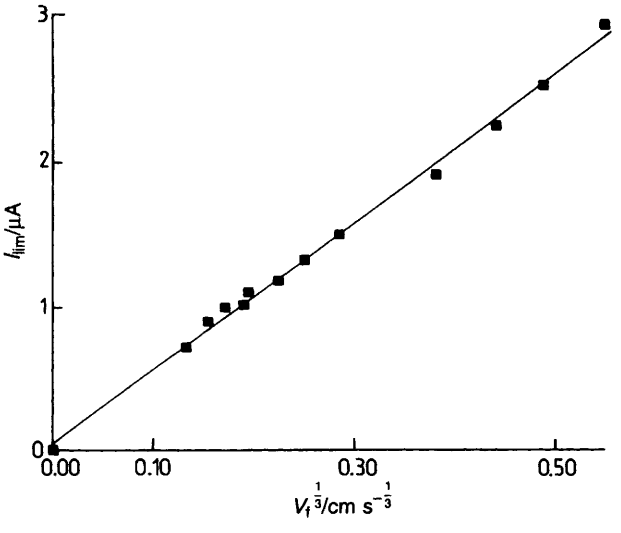

Fig. 1 The transport-limited current for the reduction of $[CoL_3]$ (0.025 mmol dm^{-3}) in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN at a platinum channel electrode (see text)

Next steady-state measurements of the photocurrent as a function of electrolyte flow rate were made using concentrations of $[CoL_3]$ in the range 0.05–0.5 mmol dm^{-3}. The ratio of the current flowing in the light to that flowing in the dark gave the effective number of electrons transferred in the electrolysis, N_{eff}, under conditions of illumination. Typical results are shown in Fig. 5. For all concentrations of $[CoL_3]$ a steady decrease of N_{eff} with flow rate was observed. This is again indicative[2,4] of light being absorbed by a post-electrolysis product and this observation together with the inferences made from the action spectra data given above led to the following model being proposed [equations (4)–(7)] for the photo-oxidation in which the $[CoL_3]^+$ cation undergoes parallel dimerisation and photofragmentation.

$$[CoL_3] - e \longrightarrow [CoL_3]^+ \qquad (4)$$

$$2[CoL_3]^+ \longrightarrow [Co_2L_6]^{2+} \longrightarrow [Co_2L_5]^+ + \text{oxidised ligand} \qquad (5)$$

$$[CoL_3]^+ + h\nu \longrightarrow X + Y \qquad (6)$$

$$X - e \longrightarrow \text{products} \qquad (7)$$

Note that the photofragment X, but not Y, is electroactive. The above mechanism was modelled using the known[3] value for the rate constant of step (5) treating the first-order rate constant, $k_{(6)}$, for the light induced step (6) and the diffusion coefficient of X, D_x, as adjustable parameters. The necessary theory for computing the theoretical behaviour for the proposed model, or any other chemical scheme, is well established and the interested reader is directed towards the literature for the necessary details.[9] No new computational or conceptual problems emerge in their application to the present work. The experimental data, as shown in Fig. 5, were found to be consistent with the choice of mechanism for the values of $k_{(6)}$ and D_x given in Table 1. The

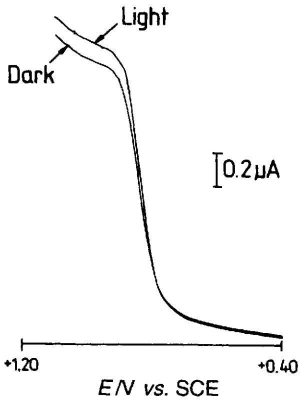

Fig. 2 Steady-state hydrodynamic voltammograms measured at a channel electrode (flow rate 2.3 × 10^{-3} cm^3 s^{-1}) for the oxidation of $[CoL_3]$ (0.025 mmol dm^{-3}) in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN for dark conditions and for the electrode uniformly irradiated by light of wavelength 480 nm and intensity 10 mW cm^{-2}

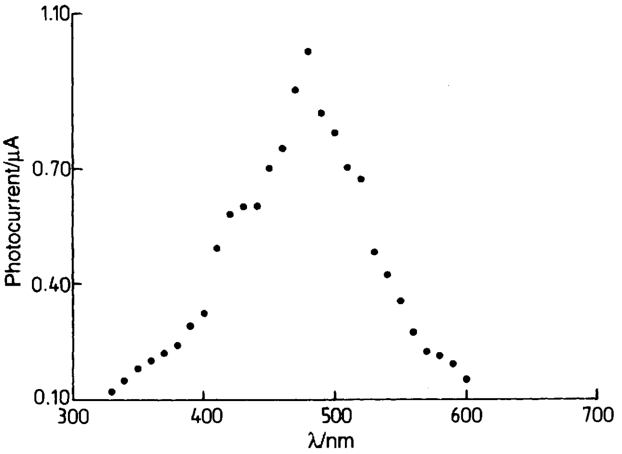

Fig. 3 An action spectrum showing the photocurrent obtained as a function of excitation wavelength for the oxidation of [CoL_3] (1.0 mmol dm^{-3}) in 0.1 mol dm^{-3} NBu_4ClO_4-MeCN at a platinum channel electrode

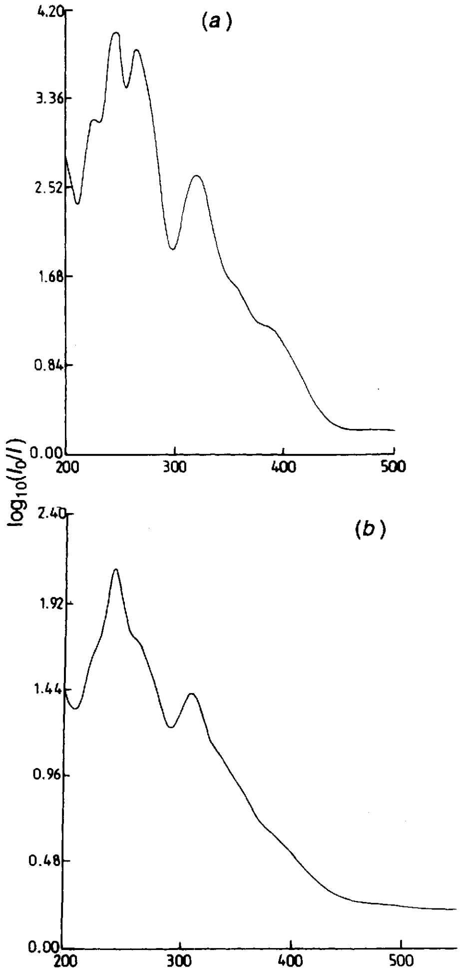

Fig. 4 The UV/VIS spectrum of (*a*) [CoL_3] and (*b*) [Co_2L_5]$^+$ in MeCN solution

good agreement between each data set together with the essential independence of either parameter on concentration suggests the veracity of the mechanism proposed and that the mean values are $D_x = (1.7 \pm 0.2) \times 10^{-5}$ cm^2 s^{-1} and $k_{(6)} = 0.08 \pm 0.02$ s^{-1}. These inferences were independently verified by means of phototransient experiments[10] in which the transport-limited current for the oxidation of [CoL_3] was established in the dark and then the evolution of the photocurrent in time monitored after the pulsewise application of light to the system. It is possible to compute the expected transient response as a function of flow rate using the chemical model and the values for D_x and $k_{(6)}$ deduced from the steady-state experiments. A typical result is shown in Fig. 6 together with the experimentally recorded phototransient. The excellent agreement between theory and experiment serves to confirm the mechanism proposed and the values of the parameters D_x and $k_{(6)}$ inferred from the steady-state experiments.

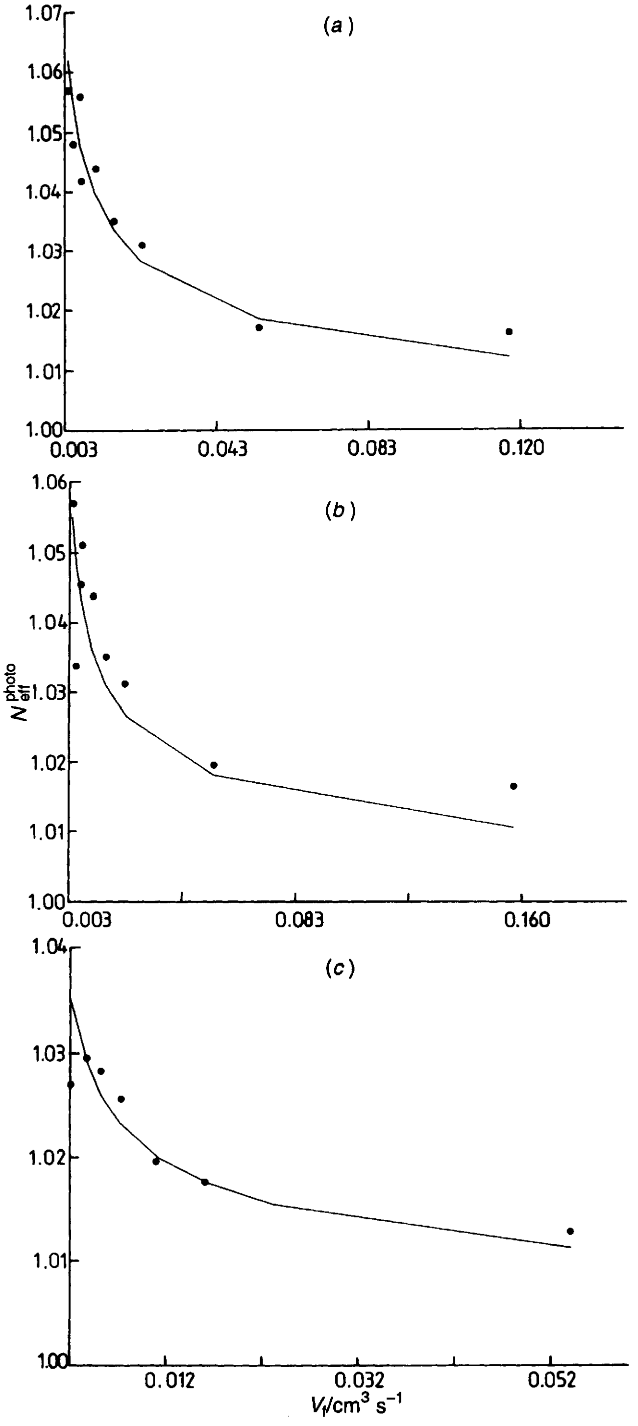

Fig. 5 The dependence of N_{eff} on the electrolyte flow rate for different concentrations of [CoL_3] recorded using a light intensity of 10 mW cm^{-2}: (*a*) 0.05, (*b*) 0.1 and (*c*) 0.5 mmol dm^{-3}

Experiments were then conducted using two further light intensities of 4.5 and 2.0 mW cm^{-2} respectively so as to change

Table 1 Rate constants and diffusion coefficients for $[CoL_3]^+$ at different concentrations

$[CoL_3]$/mmol dm^{-3}	$k_{(6)}$/s^{-1}	D_x/cm^2 s^{-1}
0.5	0.09 ± 0.01	(1.7 ± 0.2) × 10^{-5}
0.1	0.08 ± 0.02	(1.8 ± 0.3) × 10^{-5}
0.05	0.07 ± 0.01	(1.5 ± 0.3) × 10^{-5}

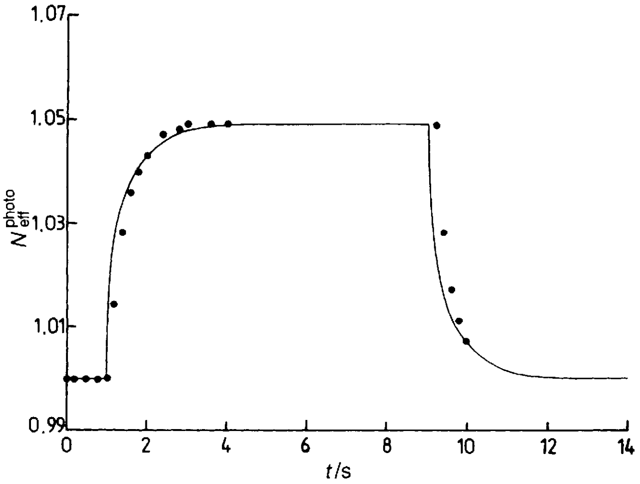

Fig. 6 Experimental phototransients (●) recorded at a light intensity of 10 mW cm^{-2} for the oxidation of $[CoL_3]$ at a flow rate of 6.9 × 10^{-3} cm^3 s^{-1}. Computed theoretical transients are shown (——) deduced using the model proposed in the text with D_x = 1.8 × 10^{-5} cm^2 s^{-1} and $k_{(6)}$ = 0.09 s^{-1}

the competition between steps (5) and (6). It was found that the same mechanism could be used to describe the photocurrent behaviour for values of $k_{(6)}$ = 0.035 and 0.011 s^{-1} respectively at the two different intensities. These values, together with that reported above for an intensity of 10 mW cm^{-2}, indicate a linear relation between $k_{(6)}$ and the light intensity as would be expected on the basis of the proposed chemistry. This further confirms the postulated mechanism.

Last we address the issue as to the identity of the species X. The likely effect of the absorption of light by $[CoL_3]^+$ [step (6)] is the loss of ligand, L, *via* an internal redox reaction, which would mimic the effect of oxidation of $[CoL_3]$ [steps (4) and (5)]. The non-co-ordinated $S_2CNMe_2^-$ ligand is known to be readily oxidised.[6] Stabilisation against oxidation is achieved by co-ordination to cobalt(III). However, an internal redox reaction associated with a formally cobalt(IV) species is likely to be energetically favourable. In the presence of light to form $[CoL_3]^{+*}$ this is even more likely. For example, photochemical work[11] on $[Cu(S_2CNR_2)_2]$ has shown intramolecular electron transfer between an equatorially bonded sulfur atom of the ligand to copper(II) with the corresponding reduction of Cu^{II} to Cu^{I} *via* an internal redox reaction and analogous observations have been made in the case of $[Ni^{IV}(S_2CNR_2)_3]^+$.[11] Thus the likely fragmentation in step (7) is the possible formation of a neutral cobalt species (X = $[CoL_2]$) together with an oxidised dithiocarbamate ligand (Y). This is further consistent with the analogy between light- and electro-induced oxidation[12] and might therefore be expected in the light of the known step (5). These inferences are supported by the value obtained for the diffusion coefficient of the electroactive photofragment X. The magnitude of diffusion coefficients may be estimated to within 10% by means of the empirical correlation of Wilke and Chang.[13] The results of this exercise would lead to a value of D = 2.0 × 10^{-5} cm^2 s^{-1} for $[Co(S_2CNMe_2)_2(MeCN)_2]$ and 2.3 × 10^{-5} for S_2CNMe_2 regardless of the charge on the two species. Accordingly we suggest that the photofragmentation leads to the formation of a neutral cobalt complex as the electroactive species X which gives rise to the photocurrents observed [equation (8)], where the oxidised ligand could be thiuram disulfide, $(R_2NCS)_2S_2$.[7]

$$[CoL_3]^+ + h\nu \longrightarrow [CoL_2] + \text{oxidised ligand} \quad (8)$$

Conclusion

The electrolysis of $[CoL_3]$ in the presence of light leads to a change of product: in the dark the dimer $[Co_2L_5]^+$ is formed whereas in the light photofragmentation of the simple cation $[CoL_3]^+$ competes with this process. The ability of light to influence markedly the nature of electrode reactions of inorganic complexes for the reasons anticipated in the introduction is clearly demonstrated.

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