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SHORT COMMUNICATION

On the electrochemically induced release of dioxygen from cobalt(II) complexes

JAMES H. CAMERON, STEVEN TURNER
Chemistry Department, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK
PETER C. MORGAN
Sowerby Research Centre, British Aerospace plc, PO Box 5, Filton, Bristol BS12 7QW, UK

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1. Introduction

Cobalt(II) chelates with Schiff's Base ligands have attracted considerable interest due to their ability to bind dioxygen reversibly [1, 2]. Complexes with this property have potential in the separation of dioxygen from gas mixtures. A recent study [3] has claimed that dioxygen is bound when air is bubbled through a non-aqueous solution containing Co(salen) (salen = *N,N'*-ethylenebis(salicylideneiminato)) and that the dioxygen is released upon electrochemical oxidation of the Co(II) to Co(III). Since we have an interest in complexes which display electrochemical release of O_2 we have re-examined the literature work and found that the results do not support the original interpretation. In this communication we report further results on the system and propose a new interpretation that is consistent with all of the experimental evidence.

2. Experimental details

Salen was prepared by the condensation reaction between two equivalents of salicylaldehyde and one equivalent of ethylenediamine [4]. Co(salen) was prepared by the literature procedure [5].

Cyclic voltammetry experiments were carried out using PAR 273 or Thompson E-series potentiostats with platinum working and counter electrodes. *N*-methylpyrrolidone (NMP) (BDH, Gold Label) was used as solvent with Bu_4NBF_4 (Aldrich, Reagent Grade) as the supporting electrolyte. The cell was designed to allow air or argon to be bubbled through the solution as required. In a typical run, cyclic voltammetry was carried out on a 50 ml solution containing Bu_4NBF_4 (0.5 g; 1.518×10^{-3} moles) and Co(salen) (0.2 g; 6.149×10^{-4} moles) at a sweep rate of $50\,mV\,s^{-1}$. All potentials were measured with respect to an SCE reference.

3. Results and discussion

The CV scan of a solution of Bu_4NBF_4 in NMP displays an anodic peak at + 1.0 V and this is ascribed to oxidation of the solvent.

When Co(salen) is added to the solution, in the absence of dioxygen, and the CV scan repeated, an anodic peak corresponding to oxidation of Co(II) to Co(III) is observed at + 0.28 V and a cathodic peak corresponding to the reduction of Co(III) to Co(II) is observed at + 0.04 V. These values are consistent with the literature data.

When air is bubbled through a solution of the complex for 15 min a new peak is observed the appearance of which is dependent upon the conditions of the scan. When the scan is reversed at potentials more positive than that required for the Co(II) → Co(III) oxidation, a cathodic peak is observed at − 0.5 V which grows in intensity as the anodic potential limit is made increasingly more positive (Fig. 1). At potentials less positive than that required for Co(II) oxidation there is no evidence for this peak.

Earlier work ascribed this peak to the reduction of dissolved molecular oxygen [3]. Its appearance was rationalized as follows: when the Co–O_2 adduct is oxidized the complex dissociates, producing Co(III)(salen) and dissolved oxygen in the solution and it is this electrochemically released O_2 that is detected at − 0.5 V. However in the present work two observations have been made which are not readily explained by this interpretation.

(1) When Co(salen) binds O_2 there is a transfer of electron density from the cobalt ion to the π^* orbitals of oxygen [2]. The reduction in the electron density located on the cobalt ion ought to render the complex less readily oxidized and this should manifest itself as a move in the peak for the oxidation of Co(II) to Co(III) to more positive potentials [6]. However the oxidation and reduction potentials of Co(salen) and the supposed oxygen adduct of Co(salen) are identical.

(2) The cathodic peak which grows in at − 0.5 V seems more to be associated with the peak due to the oxidation of the solvent at + 1.0 V than with the oxidation of the complex at + 0.28 V.

The CV scans of the electrolyte solution were run in the presence of dioxygen (Fig. 2). Although O_2 is present in both cases the peak at − 0.5 V is apparent only when the solvent is partially oxidized by first scanning to + 1.2 V. Another cathodic peak is observed at *ca* − 1.0 V and this appears to be due to dioxygen reduction. This is consistent with literature values (− 0.73 to − 0.87 V depending on solvent) [7]. The peak at − 0.5 V is associated with the presence of dioxygen in the solution because it disappears when the solution is flushed with argon. This process is reversible as is demonstrated by sequential O_2/Ar bubbling.

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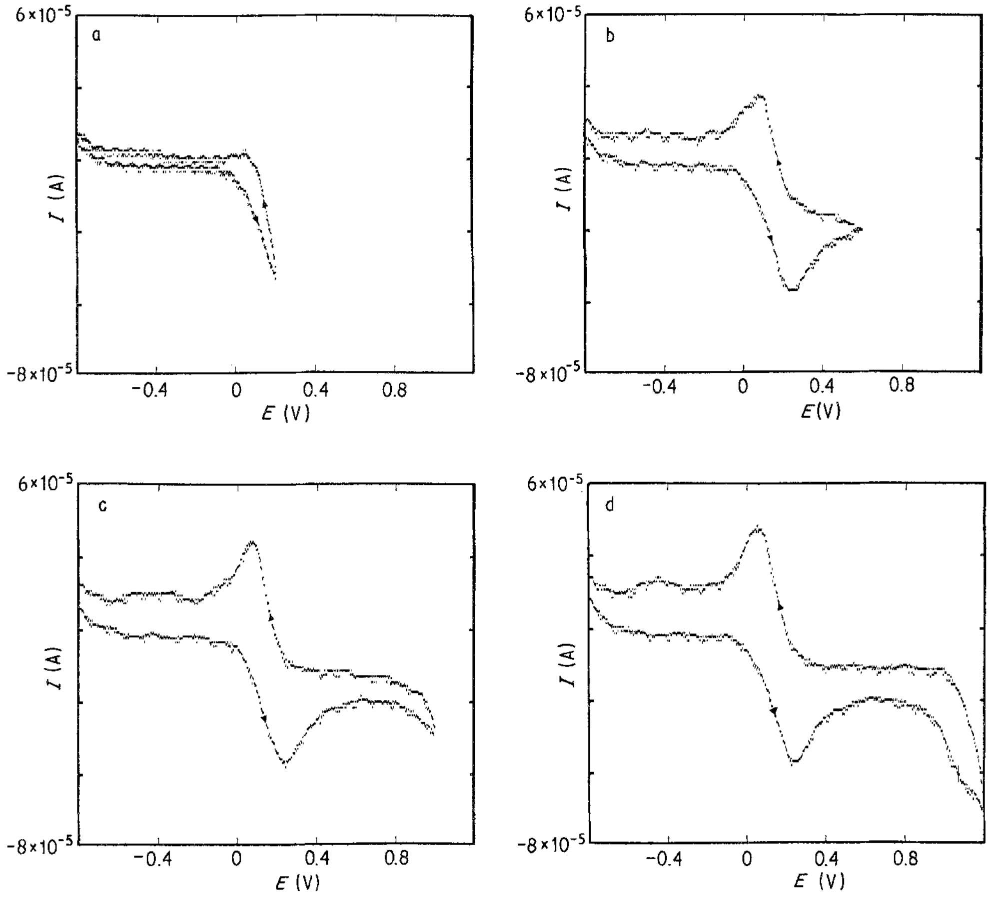

Fig. 1. CV scans recorded after bubbling air through an NMP solution containing Co(salen) (0.0123 M) and Bu_4NBF_4 (0.0304 M). The anodic potential limits are: (a) +0.2 V; (b) +0.6 V; (c) +1.0 V; (d) +1.2 V. The arrows indicate the direction of the scan.

Clearly the peak at −0.5 V is not due to direct reduction of O_2 but is due to the product of a chemical reaction between the electrochemically oxidized solvent and dioxygen and it is the product of this reaction that is being reduced. The nature of this reaction is unclear but we speculate that it involves the addition of O_2 to the radical cation of NMP, probably at the 5 position of the solvent. This is analogous to the known oxidation of NMP to *N*-methyl succinimide by peracids in the presence of an Mn(III) catalyst which is postulated to proceed via a 5-ester intermediate [8]. In the present work the intermediate displays irreversible electrochemistry, there being no evidence for an oxidation wave coupled to the reduction peak at −0.5 V.

The Co(salen) is not involved in this process and hence this system is *not* an example of the electrochemical release of O_2 from a coordination complex as was originally claimed. Further, although Co(salen) reacts with O_2 at room temperature in coordinating solvents such as pyridine to form a 2:1 Co:O_2 'peroxo' complex [2], there is no evidence to suggest

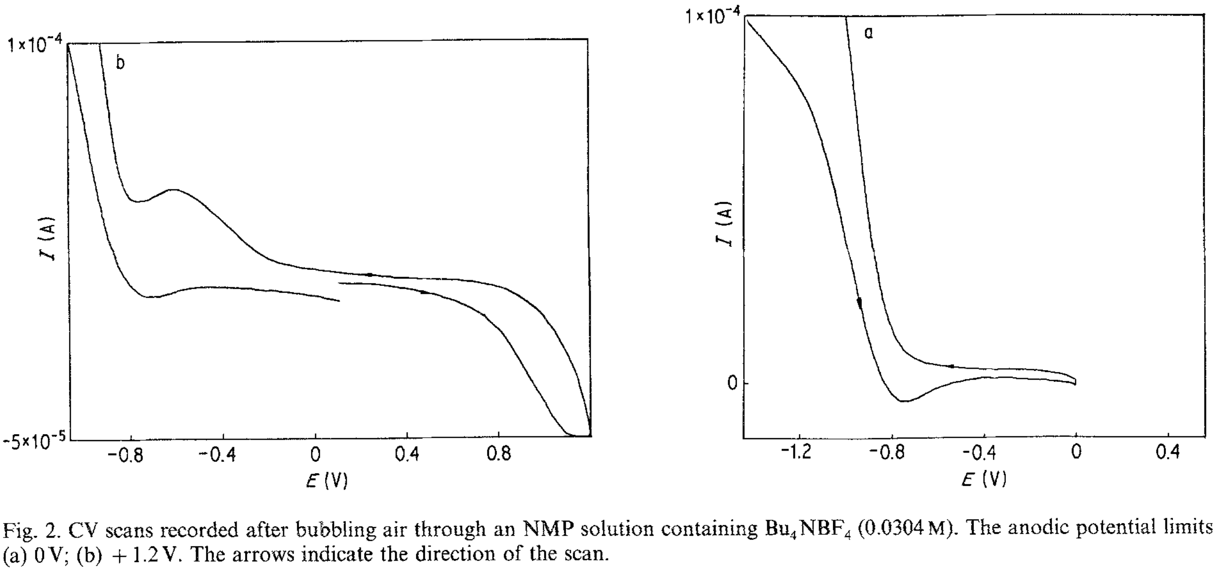

Fig. 2. CV scans recorded after bubbling air through an NMP solution containing Bu_4NBF_4 (0.0304 M). The anodic potential limits are: (a) 0 V; (b) +1.2 V. The arrows indicate the direction of the scan.

that Co(salen) forms such a complex in *N*-methylpyrrolidone solution since there is no observable change in the electrochemistry of the complex upon the addition of dioxygen. The study of complexes capable of displaying electrochemical release of dioxygen is continuing.

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References

[1] R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.* **69** (1947) 1886.

[2] R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.* **79** (1979) 139.

[3] D. L. Roberts and R. M. Laine, PCT Int. Appl. WO 86 04,363 (Cl.C25B/02), 31 Jul. (1986), US Appl. 695,440 28 Jan. (1985).

[4] D. Chen and A. E. Martell, *Inorg. Chem.* **26** (1987) 1026.

[5] G. Marcu, A. Botar and A. Nanmescu, *Rev. Roum. Chim.* **31** (1986) 981.

[6] P. Zanello, R. Cini, A. Cinquantini and P. L. Orioli, *J. Chem. Soc., Dalton Trans.* (1983) 2159.

[7] In 'Electrochemical Methods' (edited by A. J. Bard and L. R. Faulkener), Wiley, New York (1980).

[8] A. R. Doumaux, Jr and D. J. Trecker, *J. Org. Chem.* **35** (1970) 2121.