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Electrochemical Characteristics of Dimethyl Sulfoxide-Benzene Solutions of Cobalt, Copper, and Nickel Hemiporphyrazines Containing Oxygen

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Current-potential studies with the dropping mercury electrode and the rotating platinum electrode of 50% v/v dimethyl sulfoxide-benzene solutions of metal hemiporphyrazines containing oxygen revealed in the cases of cobalt and nickel hemiporphyrazines, superoxide-metal hemporphyrazine complex formation. Association of superoxide ion with the one-electron reduction products of cobalt and nickel hemiporphyrazines is not evident. Copper hemiporphyrazine undergoes a one-electron reduction, involving the metal, more easily than oxygen. No interaction of oxygen with hpCu or hpCu⁻, or of superoxide ion with hpCu⁻ is indicated.

Introduction

An electrochemical, electron paramagnetic resonance, and visible spectral investigation of the metal-free (hpH_2) and the cobalt, nickel and copper complexes of the macrocycle hemiporphyrazine[1] (hpM), Figure 1, in 50% v/v DMSO-benzene has been reported.[2,3]

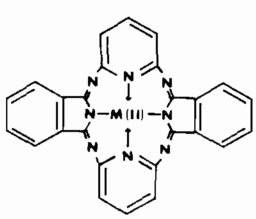

Figure 1. Metal Hemiporphyrazine.

The cobalt and nickel hemiporphyrazines both undergo ligand reductions of 1–,1–,2–, and 1–electron at –1.0, –1.6, –1.9, and –2.2 v *vs.* S.C.E., respectively, at the dropping mercury electrode (DME). No metal reductions were observed with these complexes. A one-electron oxidation wave attributed to metal oxidation was observed at +0.4 v for hpCo and +1.0 v for hpNi at the rotating platinum electrode (RPE). Unlike hpCo and hpNi, hpCu was found to undergo a one-electron metal reduction at –0.7 v, followed by a one-electron ligand reduction step then a three-electron ligand reduction step at –1.7 and –1.9 v, respectively. No oxidation step was observed for hpCu before the anodic solvent limit. Hemiporphyrazine itself undergoes 1–, 1–, 2–, and 1–electron reductions at –1.2, –1.6, –1.9, and –2.2 v, respectively, at the DME. The two acidic protons located on the *trans*-isoindolines were shown to have a dramatic effect on the electrochemical behavior of this compound.

During the course of the voltammetric investigation, it was observed that hpCo, hpNi, and hpH_2 solutions from which the residual oxygen had not been completely removed gave different electrochemical behavior from that of solutions in which oxygen was completely absent. The results of an investigation into the difference in electrochemical behavior are given in this report.

Experimental Section

The synthesis of hpCo, hpNi, hpCu, and hpH_2, the purification of the solvent, and the voltammetric and coulometric instrumentation have been previously described.[2,3] For the coulometric studies, a typical three-compartment polarographic cell was modified in such a way that a rotating platinum gauze and a rotating platinum button electrode could be placed in the center compartment. Both electrodes were rotated at 600 rpm with Sargent synchronous motors. Inlets were provided on the electrochemical cell for bubbling of either nitrogen (passed over copper turnings at *ca.* 400°) or oxygen through the solution, or for passage of nitrogen over the solution. All potentials were measured *vs.* the S.C.E. The maximum solubility of the macrocycles ranged from 1×10^{-4} *M* for hpCo to 5×10^{-4}*M* for hpH_2.

Results and Discussion

Molecular oxygen is reduced to superoxide ion in DMSO[4] and in 50% v/v DMSO-benzene (0.10 *M* Et_4NClO_4) at –0.8 to –0.9 v. The superoxide ion has been reported to decompose in DMSO at a rate

(1) J.B. Cambell, *U.S. Patent*, 2,765,308 (1956).
(2) C.G. Birch and R.T. Iwamoto, *Inorg. Chem.*, in press.
(3) C.G. Birch, Ph. D. Thesis, University of Kansas, Lawrence, Kansas, 1971.

(4) M.V. Merritt and D.T. Sawyer, *J. Org. Chem.*, 35, 2157 (1970).

less than 3%/hour.[4] The high stability of O_2^- in this solvent is also evident in the anodic to cathodic peak current ratio of unity for cyclic voltammograms obtained at the stationary gold electrode.[5]

A typical polarogram of hpCo and hpNi solutions in the absence of oxygen is shown in Figure 2-c. When a small amount of oxygen is bubbled into the solution, two new waves of equal height appear at −0.7 and −1.3 v. The sum of the diffusion currents

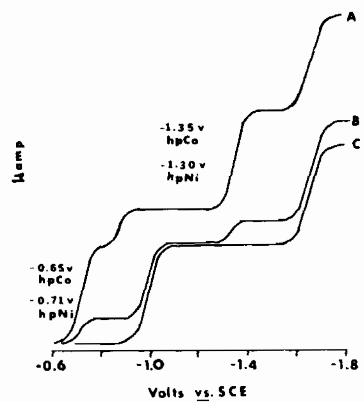

Figure 2. Effect of the presence of oxygen on the polarograms of *ca.* 1×10^{-4} *M* solutions of hpCo and of hpNi in 50% DMSO-benzene (0.10 *M* Et_4NClO_4). Curve A: excess oxygen added; curve B: partial deaeration of solution; curve C: no oxygen present.

for the −0.7 and −1.0 v waves and that for the −1.0 and −1.3 v waves are independent of the amount of oxygen added (curve 2-B). The height and position of the −1.6 v wave are unaffected by the presence of oxygen. When more oxygen is bubbled into the solution, the −0.7 and −1.3 v waves both increase in height, the same amount as the −1.0 v wave decreases in height. In the presence of a large excess of oxygen, the −0.7 and −1.3 v waves have diffusion currents equal to the −1.6 v wave and the −1.0 v wave is absent (curve 2-A). The further addition of oxygen results only in the increase of the wave for the reduction of free oxygen (−0.9 v). Regardless of the amount of oxygen added, the half-wave potential and diffusion current of the −1.6 v wave are unaffected.

The one-electron metal oxidation steps observed for hpCo and hpNi are unaffected by the presence of oxygen. In view of this fact, it can be ruled out that complexation between molecular oxygen and hpCo and hpNi occurs under the conditions of this experiment.

The appearance of two additional waves and the change in wave heights of the −1.0 v processes of hpCo and hpNi on the addition of oxygen are explained as follows. The coordination of the electrogenerated superoxide ion with hpCo and hpNi causes the reduction of oxygen to occur at a potential (−0.7 v) much more positive than in the absence of such interaction (−0.9 v). The reduction of hpCo and hpNi when complexed with superoxide ion (−1.3 v) is rendered, on the other hand, more difficult than when there is no such complex formation (−1.0 v). When there is less than 1:1 mole ratio of oxygen to hpCo and hpNi, all of the superoxide ions undergo complexation with hpCo and hpNi, but only part of the hpCo and hpNi species is complexed, causing the first three steps to occur at −0.7, −1.0, and −1.3 v. When an excess of oxygen is present, only part of the superoxide ions formed undergoes complexation with hpCo and hpNi; all the hpCo and hpNi species are complexed. This leads to the first three reduction steps occurring at −0.7, −0.9, and −1.3 v. The addition of KO_2 to solutions of hpCo and hpNi results in the same changes in the voltammograms as those caused by the *in situ* generation of O_2^-.

Since the −1.6 v wave is unaffected by the addition of oxygen, it can be concluded that no complexation occurs between O_2^- and $hpCo^-$ or $hpNi^-$.

Except for the addition of the reduction step for oxygen at −0.9 v, the introduction of oxygen to a solution of hpCu had no effect on the voltammetry of the solution. Therefore, it appears that there is also no complexation of oxygen with this metal macrocycle and of oxygen with copper(I) hemiporphyrazine (the one-electron reduction product of hpCu). Of special interest is the absence of superoxide complexation of copper(I) hemiporphyrazine.

The introduction of superoxide ion by electroreduction of the oxygen present in solution has the same effect on the voltammetry of a solution of hpH_2 as the addition of tetramethylammonium hydroxide.[2,3] Superoxide ion apparently is sufficiently basic to remove the acidic protons of hpH_2 and consequently changes the voltammograms of hpH_2 to those of hpH^-, of hp^{2-}, or of intermediate mixtures.

The stoichiometry of the O_2^-/hpCo and O_2^-/hpNi complexes was determined by introducing sufficient oxygen to solutions of hpCo and of hpNi to give waves of approximately equal heights at −1.0 and −1.3 v at the RPE. The amount of O_2 present was then determined by bulk electrolysis at −0.9 v with the rotating platinum gauze electrode. Bulk electrolysis at −1.5 v gave the millimoles of hpCo or of hpNi present. The electrochemical data and the approximation that hpCo and the hpCo-superoxide complex and hpNi and the hpNi-superoxide complex have the same diffusion coefficients gave the millimoles of O_2^- coordinated to a millimole of hpCo or hpNi by:

$$\text{millimoles of } O_2^-/\text{millimole of hpCo or hpNi} = \frac{i_{d(-1.0v)} + i_{d(-1.3v)}}{i_{d(-1.3v)}} \times \frac{\text{millimoles } O_2^-}{\text{millimoles hpCo or hpNi}}$$

The results obtained from this electrochemical analysis were 1.09 ± 0.10 molecules of O_2^- per hpNi and 1.2 ± 0.2 molecules of O_2^- per hpCo. Because of the low concentration of hpCo that had to be employed, the result of its limited solubility, the value obtained for the hpCo complex is not as reliable as that for the hpNi complex. No attempt was made to isolate the complexes.

Similar polarographic behavior was noted for systems of O_2 and Co^{II} chelates of N,N′-ethylenebis(salicyldene-iminato) dianion and its 3-methoxy derivative, N,N′-*o*-phenylenebis(salicylidene-iminato) dianion where the reduction wave for oxygen was shifted to a

(5) D.T. Sawyer and J.C. Roberts, Jr., *J. Electroanal. Chem.*, 12, 90 (1966).

more positive potential and the height of this reduction wave increased at the expense of the reduction step of the Co^{II} chelate.[6] The data in these cases were interpreted in terms of the formation of 1:1 oxygen-Co^{II} chelate complexes. The formation of 1:1 oxygen adducts of vitamin B_{12r}[7,8] and of Co^{II} mesoporphyrin IX dimethylester[8] have also been reported. On the basis of epr studies all of the above 1:1 adducts of oxygen and Co^{II} chelates have been described as superoxo-Co^{III} compounds.[7,8]

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation (GP-11313 and GP-28332), Gulf Oil Company (fellowship for C. G. B.), and the General Research Fund, University of Kansas.

(6) G. Costa, A. Puxeddu, and L.B. Stefani, *Inorg. Nucl. Chem. Letters*, *6*, 191 (1970).
(7) J.H. Bayston, N.K. King, F.D. Looney, and M.E. Winfield, *J. Am. Chem. Soc.*, *91*, 2775 (1969).
(8) S.A. Cockle, H.A.O. Hill, and R.J.P. Williams, *Inorg. Nucl. Chem. Letters*, *6*, 131 (1970).