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AN ELECTROCHEMICAL STUDY OF THE INCORPORATION OF COBALT MACROCYCLIC COMPLEXES INTO NAFION FILMS

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SUMMARY

Cobalt complexes of the macrocyclic ligand, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM) and its hydroxy derivatives, were incorporated in Nafion films by electrochemical cycling and by ion exchange in aqueous solution. Cyclic voltammetric studies show that the redox potentials of the Co(TIM) complexes undergo a significant anodic shift when incorporated in the films. Electrochemical studies also indicate that, while the Co(TIM) complexes reside in hydrophilic regions of the Nafion film, the metallated porphine complex, cobalt tetrakis(pentafluorophenyl)porphine, is probably immobilized in hydrophobic regions. The incorporation of the complexes was also followed by electronic absorption spectrophotometry.

INTRODUCTION

Surface modified electrodes have been intensively investigated in recent years owing to their possible applications as electrocatalytic systems for a host of electrochemical reactions, one of the most important of which is the reduction of oxygen in fuel cells [1,2,3]. Attempts have been made to exploit the electrochemistry of compounds that model biologically important substances which coordinate oxygen (heme and vitamin B_{12}). As simple models of heme, the phthalocyanines and porphyrins have received considerable attention [1,4-7] and a modified electrode having vitamin B_{12} on the surface catalyzes the reduction of oxygen [8]. Unfortunately, many modified electrodes are easily degraded under the stringent conditions of temperature and acidity in the fuel cell [1]. Nafion is an attractive material for use in electrochemical experiments involving electrocatalysis because it is soluble in alcohols, allowing films of the polymer to be cast on electrodes quite easily, and the fluorocarbon-ether structure renders the films thermally and chemically stable [9]. These films have been shown to incorporate electroactive species in a number of cases

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[3,10-14]. Since cobalt complexes of the tetraaza macrocycle, 2,3,9,11-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, (TIM), have been used as models for vitamin B_{12} [15], are very stable, and can be oxidized from the II state to the III state by oxygen [16,17], it seemed appropriate to investigate the electrochemical properties of these complexes. In this paper, we report on a study of the incorporation of the cobalt(TIM) complex and its 6-hydroxy and 6,13-dihydroxy derivatives, $[Co(TIM)(H_2O)_2]^{3+}$, $[Co(6\text{-}OH\text{-}TIM)(H_2O)_2]^{3+}$, $[Co(6,13\text{-}(OH)_2\text{-}TIM)(H_2O)_2]^{3+}$, in Nafion films. In addition, we have investigated the incorporation in Nafion of 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphine cobalt (III) by electrochemistry and electronic absorption spectrophotometry.

EXPERIMENTAL

Materials A 5% Nafion solution in an unspecified mixture of alcohols was obtained from Solutions Technology, Inc. Films were cast from this solution directly or from one prepared by dilution of the 5% solution (10:1) with 2-propanol. The supporting electrolytes were reagent grade KCl, K_2SO_4, NaCl (Fisher Scientific), tetrabutylammonium hydroxide (Aldrich), tetrabutylammonium bisulfate (Labkemi), and tetrabutylammonium tetrafluoroborate (prepared by lit. methods [18]). $TBABF_4$ was recrystallized from ethanol water. $TBAHSO_4$ was recrystallized from 2-butanone. The others were used as received. Ammonium hexafluorophosphate was obtained from Aldrich. $[Co(TIM)Cl_2]PF_6$, $[Co(TIM\text{-}6\text{-}OH)Cl_2]PF_6$, and $[Co(TIM\text{-}6,13\text{-}(OH)_2)Cl_2]PF_6$ were prepared by literature methods, and proton NMR and IR spectra (KBr pellets) were in agreement with published data [16, 17]. 5,10,15,20-tetrakis(pentafluorophenyl)-2H,23H-porphine was obtained from Aldrich and used without further purification.

Electrochemical methods Glassy carbon disc electrodes (0.07 cm^2) and a platinum disc electrode (0.06 cm^2) were employed for the electrochemical measurements. Nafion films were cast on the surface of these electrodes by dipping in 0.5% Nafion/alcohol solution three times and air-drying between dips or by adding 5% Nafion solution dropwise with a micropipet and either air-drying or curing at 70-80°C for 1.5 hr and then at 110°C for 1 hr. Cyclic voltammetry was carried out using an EG&G PARC Model 175 waveform generator driving a Model 173 potentiostat equipped with a Model 179 digital coulometer. Data were recorded on a Houston Instruments XY Recorder. In the case of the cobalt(TIM) complexes, incorporation was accomplished during repetitive cycling of the working electrode, immersed in a 1-6 X 10^{-3} mol dm^{-3}solution of the cobalt(TIM) complex, over a potential range in which the complex was electrochemically active. For the cobalt tetrakis(pentafluorophenyl)porphine complex it was necessary to use a method which had been applied earlier in the preparation of the analogous cobalt tetraphenylporphine complex [6]. The protonated porphine (9 mol dm^{-3} H_2SO_4) was incorporated by ion-exchange in a Nafion film previously cast on an electrode. The Nafion-coated electrode was then neutralized and soaked in 0.1 mol dm^{-3} $Co(NO_3)_2$ solution to introduce cobalt.

Electronic spectra were obtained with a Hewlett-Packard Model 8452 Diode Array Spectrophotometer. Film samples resulting from incorporation of Co(TIM) complexes during cycling of the applied potential were mounted on quartz plates and compared with samples prepared on quartz by evaporation of 40 microliter portions of 5% Nafion (1100 EW) in round cutouts of area 0.86 cm^{-2} which were subsequently treated with 10^{-2} or 10^{-3} mol dm^{-3} solutions of the appropriate cobalt(TIM) complex, washed 4 times with deionized water and dried. A similar method was used for the preparation of films containing the cobalt porphine complexes except that the porphine was first incorporated in the film and the metal complex formed in situ by the technique described above.

RESULTS

It was observed that Nafion cast on glassy carbon or platinum electrodes adhered better in aqueous solution than in acetonitrile. The film also appeared to adhere more strongly to platinum than to glassy carbon especially when it was cured at 110^{o} rather than air-dried. In addition, cyclic voltammograms obtained with a bare glassy carbon electrode in 3.0×10^{-3} mol dm^{-3} [Co(TIM-6, 13-$(OH)_2$)Cl_2]PF_6 with 0.1 mol dm^{-3} TBAB/CH_3CN as the supporting electrolyte showed a distinct oxidation wave at 628 mV and a faint reduction wave at 466 mV (E = 162 mV) while a platinum electrode immersed in the same solution gave prominant oxidation and reduction waves at 534 and 456 mV (E = 78 mV) indicating that the system was more reversible on platinum. Thus, most of our work was carried out using a platinum working electrode in aqueous media with Nafion films cured at 110^{o}. An indium/tin oxide glass electrode appeared to work reasonably well with uncured films and was employed in some cases.

Since the cobalt(TIM) macrocycles containing halo ligands exchange relatively rapidly with water and the extremely labile Co(TIM)(II) complex is produced during electrochemical cycling [19], it is reasonable to assume that the species near the electrode is predominantly the bis-aquo complex; the orange-pink color of the solution is consistent with this assumption. Although the cobalt-TIM macrocycles containing bromo ligands are more soluble in water than those containing chloro ligands, it was deemed advisable to use the latter because, in some cases, the cyclovoltammetric scans were taken to +1.0 V which is above the oxidation potential for Br^- (E^o Br_2/Br^-, 0.845 V; E^o Cl_2/Cl, 1.116 V). The concentration of free chloride in the resulting solution was further reduced by using the hexafluorophosphate instead of the chloride salts. The hexafluorophosphate salts of $[Co(TIM)X_2]^+$ are much less soluble in water than the halo salts, but solutions of concentration suitable for electrochemical studies could be prepared owing to the fact that exchange of chloro for aquo ligands renders the complexes more soluble. On standing, some reduction to the cobalt(II) species also takes place.

Attempts were made to incorporate the cobalt(TIM) macrocycle compounds in Nafion films in the presence of 0.1 mol dm^{-3} aqueous KCl and K_2SO_4 as supporting electrolytes, but no incorporation was observed presumably owing to competition of the relatively small K^+(150 pm [20]) ions with the relatively large $[Co(TIM)(OH_2)_2]^{3+}$ (600 pm [21]) ions for available sites in the film. Therefore , a suitable supporting electrolyte for the electrochemical observation of incorporation of the cobalt(TIM) macrocyclic compounds in Nafion films must provide a large cation which will not compete with the cobalt complex and must provide an anion which is chemically inert and difficult to oxidize. In addition, the resulting solution must be neutral, since the Nafion film is initially protonated and an acidic solution would shift the equilibrium in favor of the acid form. Tetrabutylammonium sulfate, $(TBA)_2SO_4$, was found to be an ideal supporting electrolyte for this purpose.

Incorporation of cobalt(TIM) macrocyclic complexes was observed to take place readily in 0.1 mol dm^{-3} aqueous $(TBA)_2SO_4$ typically containing 1-6 X 10^{-3} mol dm^{-3} of the cobalt macrocyclic complex (see Fig. 1). When the electrode was removed from the solution containing the cobalt(TIM) complex and placed in a 0.1 mol dm^{-3} solution of $(TBA)_2SO_4$, electrochemical responses, as shown in Fig. 1, were still observed indicating that the complexes were incorporated in the Nafion films. With repeated scanning over the potential region in Fig. 1, the current decreased slowly (about 57% after 35 scans) which indicated that the complex was leaching slowly from the film.

The electrochemical parameters for the cobalt(TIM) complexes in solution and incorporated in the film are listed in Table 1, and cyclic voltammograms for each are shown in Fig. 1. The most important features of the cyclic voltammograms are that the quasi-reversible character of the electron transfer does not change very much upon incorporation of the cobalt-TIM complex in Nafion, but the formal redox potential undergoes a pronounced anodic shift indicating that the bound species is more difficult to oxidize. Since the highly electronegative perfluoroalkylsulfonate group would be expected to withdraw electron density from the complex if it were coordinated (increasing the positive charge on cobalt), this result indicates that at least one aquo ligand in the axial position has been displaced by perfluoroalkylsulfonate groups in the Nafion film. A small feature appearing at about 220 mV in the cyclic voltammograms of 1. and 3. in Fig. 1 may be indicative of a very minor electrochemical process which is not associated with either the bound or solution phase Co(TIM) complex.

Incorporation of the cobalt(TIM) complexes was followed by UV-visible spectrophotometry of the treated Nafion films. Strong bands in the UV region

TABLE I

Electrochemical Parameters

Complex	Phase	$E_{1/2}$	E_p
$[Co(TIM)(H_2O)_2]^{3+/2+}$	solution	268	111
(6.34×10^{-3} mol dm^{-3})	film	490	143
$[Co(6\text{-}OH\text{-}TIM)(H_2O)_2]^{3+/2+}$	solution	307	133
(3.71×10^{-3} mol dm^{-3})	film	423	108
$[Co(6,13\text{-}(OH)_2\text{-}TIM)(H_2O)_2]^{3+/2+}$	solution	325	100
(6.42×10^{-3} mol dm^{-3})	film	433	115

TABLE II

Electronic Spectra

Complex	Phase	ν_E	ν_A	ν_{E+B}
$[Co(TIM)(H_2O)_2]^{3+/2+}$	soln	530	428[a]	378
	film	520		
$[Co(6\text{-}OH\text{-}TIM)(H_2O)_2]^{3+/2+}$	soln	536	420[a]	364
	film	527		
$[Co(6,13\text{-}(OH)_2\text{-}TIM)(H_2O)_2]^{3+/2+}$	soln	524	a	358
	film	518		360

[a] shoulders of low intensity on very strong UV bands.

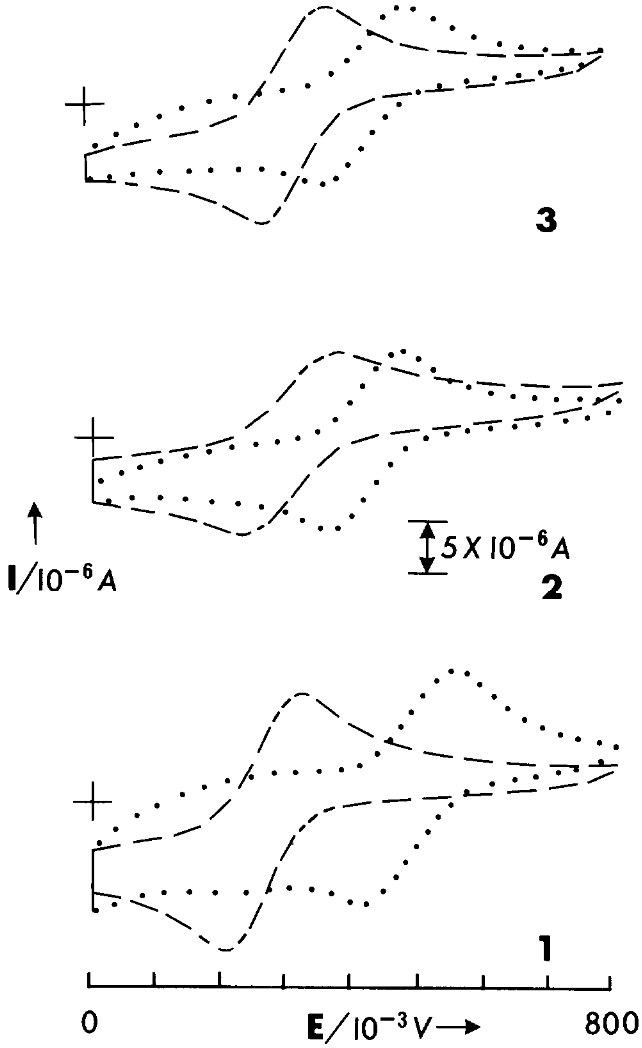

Fig. 1. Cyclic voltammograms, Pt (---) and Nafion-coated Pt(
SCE ref., v = 100 mV s^{-1}, 0.1 mol dm^{-3} $(TBA)_2SO_4$

1. $[Co(TIM)(H_2O)_2]^{3+/2+}$, 6.24 X 10^{-3} mol dm^{-3}
2. $[Co(6\text{-}OH\text{-}TIM)(H_2O)_2]^{3+/2+}$, 3.71 X 10^{-3} mol dm^{-3}
3. $[Co(6,13\text{-}(OH)_2\text{-}TIM)(H_2O)_2]^{3+/2+}$, 6.42 X 10^{-3} mol dm^{-3}

and weaker bands in the visible region were observed indicating that the complexes resided in the films (see Fig. 2). The bands associated with the ^1E_g <--- $^1A_{1g}$ transitions (ν_E) were well-resolved and similar to those found earlier for aqueous solutions of $[Co(TIM)(H_2O)_2]^{3+}$ complexes [16, 17] and to those found for authentic aqueous samples prepared in our laboratory but were shifted to higher energies. This result is consistent with the observed increase in the redox potentials. The other bands occur as shoulders on the very intense ultra-violet band and were not definitively identified in film samples and in some solutions.

The cobalt tetrakis(pentafluorophenyl)porphine was found to exhibit no electrochemical response other than a slightly enhanced background current in Nafion films prepared as described above, although the complex was shown to be incorporated in the films by electronic absorption spectrophotometry. The very prominent Soret band was observed for Nafion films containing the protonated (426 nm), neutral (408 nm), and metallated porphine (416 nm) (see Fig. 3) but was absent for a pure Nafion film. The shifts in wavelengths were similar to those observed in a study of the cobalt tetraphenylporphine earlier (412 nm for neutral porphine) [6]. The complex did not leach noticeably from the film upon prolonged soaking in deionized water.

CONCLUSIONS

Cobalt(TIM) macrocyclic complexes are incorporated in Nafion films cast on platinum and indium/tin oxide-coated glass electrodes in the presence of supporting electrolytes having large cations. The electrochemical results show that the redox potentials of the complexes are quite different on the bare electrode than when they are incorporated in the film. In a recent electrochemical study of the incorporation of $Fe(o\text{-}phen)_3^{2+}$ in Nafion films, Lu and Dong [23] observed only a slight anodic shift in going from the solution to the film-bound species. Since axial sites in the $Fe(o\text{-}phen)_3^{2+}$ complex are not readily available for substitution by sulfonate, the binding must be essentially electrostatic. The much larger anodic shift observed for the bis-aquo Co(TIM) complexes is consistent with substitution of the aquo ligands by the highly electron withdrawing perfluoroalkanesulfonate groups in the hydrophilic regions of the Nafion film. In terms of the catalysis of oxygen reduction, this is a desirable outcome since the potential of the cobalt complex is shifted towards the four-electron redox potential for oxygen [22].

The lack of electroactivity of the cobalt tetrakis(pentafluorophenyl)-porphine complex indicates that it resides in an hydrophobic region of the

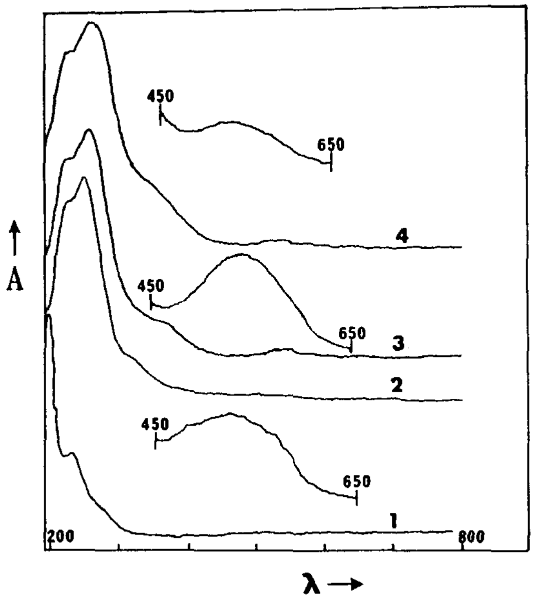

Fig.2. Ultraviolet-visible spectra: nm

1. Nafion-quartz.
2. $[Co(TIM)\ (H_2O)_2]^{3+/2+}$ - Nafion.
3. $[CO(6\text{-}OH\text{-}TIM)\ (H_2O)_2]^{3+/2+}$ - Nafion.
4. $[Co(6,13\text{-}OH\text{-}TIM)\ (H_2O)_2]^{3+/2+}$ - Nafion.

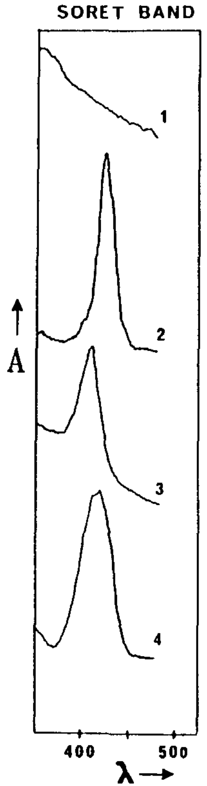

Fig.3. Visible spectra: nm

1. Nafion - glass.
2. Protonated tetrakis-(pentafluorophenyl)porphine - Nafion.
3. Neutral tetrakis(pentafluorophenyl)-porphine - Nafion.
4. Cobalt tetrakis-(pentafluorophenyl)porphine.

Nafion film in which it is relatively immobile. This interpretation is consistent with the difficulty of removing the complex from the film. This behavior contrasts with that of the cobalt(TIM) complexes, which are slowly leached from the film by voltammetric cycling in water containing supporting electrolyte. These results are similar to those reported for cobalt tetraphenylporphine [6].

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