

$\text{HMe}_2\text{SiO}[\text{SiH}_2\text{O}]_3\text{SiMe}_2\text{H}$ (8.0). $[\text{HMe}_2\text{SiO}]_3\text{SiH}$ and $[\text{HMe}_2\text{SiO}]_2\text{Si}(\text{H})\text{OSiH}_2\text{OSiMe}_2\text{H}$ were not present.

Addition of a 1:2 mixture of H_2SiCl_2 and Me_3SiCl in Et_2O to the buffer solution at 0–10 °C gave the following products: $\text{Me}_3\text{SiOSiMe}_3$ (44), $\text{Me}_3\text{SiOSiH}_2\text{OSiMe}_3$ (28), $\text{Me}_3\text{SiO}[\text{SiH}_2\text{O}]_2\text{SiMe}_3$ (18), $\text{Me}_3\text{SiO}[\text{SiH}_2\text{O}]_3\text{SiMe}_3$ (7.5). Here also, products of Si–H hydrolysis were not present.

More such $\text{Me}_3\text{SiCl}/\text{H}_2\text{SiCl}_2$ cohydrolysis experiments are summarized in Table I. The following siloxanes were isolated and characterized.

$\text{Me}_3\text{SiOSiH}_2\text{OSiMe}_3$: $n_D^{20} = 1.3809$. Anal. Calcd for $\text{C}_6\text{H}_{20}\text{O}_2\text{Si}_3$: C, 34.57; H, 9.67. Found: C, 34.51; H, 9.69. $^1\text{H NMR}$ (CDCl_3): δ 0.14 (s, 18 H, Me_3Si), 4.50 (s, 2 H, SiH_2 , $J(^{29}\text{Si}-^1\text{H}) = 243$ Hz).

$\text{Me}_3\text{SiO}[\text{SiH}_2\text{O}]_2\text{SiMe}_3$: $n_D^{20} = 1.3828$. Anal. Calcd for $\text{C}_6\text{H}_{22}\text{O}_3\text{Si}_4$: C, 28.31; H, 8.71. Found: C, 28.38; H, 8.67. $^1\text{H NMR}$ (CDCl_3): δ 0.15 (s, 18 H, Me_3Si), 4.57 (s, 4 H, SiH_2 , $J(^{29}\text{Si}-^1\text{H}) = 248$ Hz).

$\text{Me}_3\text{SiO}[\text{SiH}_2\text{O}]_3\text{SiMe}_3$: $n_D^{20} = 1.3847$. Anal. Calcd for $\text{C}_6\text{H}_{24}\text{O}_4\text{Si}_5$: C, 23.97; H, 8.05. Found: C, 24.24; H, 8.13. $^1\text{H NMR}$ (CDCl_3): δ 0.15 (s, 18 H, Me_3Si), 4.59 (s, 4 H, $\text{Me}_3\text{SiOSiH}_2$, $J(^{29}\text{Si}-^1\text{H}) = 252$ Hz), 4.64 (s, 2 H, center SiH_2 , $J(^{29}\text{Si}-^1\text{H}) = 252$ Hz).

$[\text{Me}_3\text{SiO}]_3\text{SiH}$: $n_D^{20} = 1.3861$. Anal. Calcd for $\text{C}_9\text{H}_{28}\text{O}_3\text{Si}_4$: C, 36.44; H, 9.51. Found: C, 36.18; H, 9.57. $^1\text{H NMR}$ (CDCl_3): δ 0.12 (s, 27 H, Me_3Si), 4.20 (s, 1 H, SiH).

$[\text{Me}_3\text{SiO}]_2\text{Si}(\text{H})\text{OSiH}_2\text{OSiMe}_3$: $n_D^{20} = 1.3882$. Anal. Calcd for $\text{C}_9\text{H}_{30}\text{O}_4\text{Si}_5$: C, 31.54; H, 8.82. Found: C, 31.69; H, 8.93. $^1\text{H NMR}$ (CDCl_3): δ 0.15 (s, 27 H, Me_3Si), 4.20 (s, 1 H, O_3SiH), 4.54 (s, 2 H, SiH_2).

$\text{HMe}_2\text{SiOSiH}_2\text{OSiMe}_2\text{H}$: $n_D^{20} = 1.3756$. Anal. Calcd for $\text{C}_4\text{H}_{16}\text{O}_2\text{Si}_3$: C, 26.63; H, 8.94. Found: C, 26.85; H, 8.82. $^1\text{H NMR}$ (CDCl_3): δ 0.23 (d, 12 H, Me_2Si), 4.53 (s, 2 H, SiH_2 , $J(^{29}\text{Si}-^1\text{H})$

= 248 Hz), 4.68 (hept, 2 H, Me_2SiH).

$\text{HMe}_2\text{SiO}[\text{SiH}_2\text{O}]_2\text{SiMe}_2\text{H}$: $n_D^{20} = 1.3798$. Anal. Calcd for $\text{C}_4\text{H}_{18}\text{O}_3\text{Si}_4$: C, 21.21; H, 8.01. Found: C, 21.12; H, 7.95. $^1\text{H NMR}$ (CDCl_3): δ 0.23 (d, 12 H, Me_2Si), 4.58 (s, 4 H, SiH_2 , $J(^{29}\text{Si}-^1\text{H}) = 250$ Hz), 4.69 (hept, 2 H, Me_2SiH).

$\text{HMe}_2\text{SiO}[\text{SiH}_2\text{O}]_3\text{SiMe}_2\text{H}$: $n_D^{20} = 1.3823$. Anal. Calcd for $\text{C}_4\text{H}_{20}\text{O}_4\text{Si}_5$: C, 17.62; H, 7.39. Found: C, 17.60; H, 7.33.

$[\text{HMe}_2\text{SiO}]_3\text{SiH}$: $n_D^{20} = 1.3822$. Anal. Calcd for $\text{C}_6\text{H}_{22}\text{O}_3\text{Si}_4$: C, 28.31; H, 8.71. Found: C, 28.22; H, 8.65. $^1\text{H NMR}$ (CDCl_3): δ 0.22 (d, 18 H, Me_2Si), 4.20 (s, 1 H, O_3SiH), 4.69 (hept, 3 H, Me_2SiH).

$[\text{HMe}_2\text{SiO}]_2\text{Si}(\text{H})\text{OSiH}_2\text{OSiMe}_2\text{H}$: $n_D^{20} = 1.3845$. Anal. Calcd for $\text{C}_6\text{H}_{24}\text{O}_4\text{Si}_5$: C, 23.97; H, 8.05. Found: C, 23.95; H, 8.02. $^1\text{H NMR}$ (CDCl_3): δ 0.23 (d, 18 H, Me_2Si), 4.25 (s, 1 H, O_3SiH), 4.58 (s, 2 H, SiH_2), 4.70 (hept, 3 H, Me_2SiH).

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Registry No. SiH_2Cl_2 , 4109-96-0; CH_3Br , 74-83-9; Me_3SiOH , 1066-40-6; Et_3SiOH , 597-52-4; $\text{Me}_3\text{SiOSiMe}_3$, 107-46-0; Me_3SiCl , 75-77-4; Me_2SiHCl , 1066-35-9; $\text{Me}_3\text{SiOSiH}_2\text{OSiMe}_3$, 93254-88-7; $\text{Me}_3\text{SiO}[\text{SiH}_2\text{O}]_2\text{SiMe}_3$, 93254-89-8; $\text{Me}_3\text{SiO}[\text{SiH}_2\text{O}]_3\text{SiMe}_3$, 93254-90-1; $[\text{Me}_3\text{SiO}]_3\text{SiH}$, 1873-89-8; $[\text{Me}_3\text{SiO}]_2\text{Si}(\text{H})\text{OSiH}_2\text{OSiMe}_3$, 93254-91-2; $\text{HMe}_2\text{SiOSiH}_2\text{OSiMe}_2\text{H}$, 20363-25-1; $\text{HMe}_2\text{SiO}[\text{SiH}_2\text{O}]_2\text{SiMe}_2\text{H}$, 93254-92-3; $[\text{HMe}_2\text{SiO}]_3\text{SiH}$, 17449-78-4; $[\text{HMe}_2\text{SiO}]_2\text{Si}(\text{H})\text{OSiH}_2\text{OSiMe}_2\text{H}$, 93254-93-4; $\text{HMe}_2\text{SiO}[\text{SiH}_2\text{O}]_3\text{SiMe}_2\text{H}$, 93254-94-5.

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An Electroactive Polymer Film on a Mercury Electrode Based on a Thallium Macrocylic Polyether Complex

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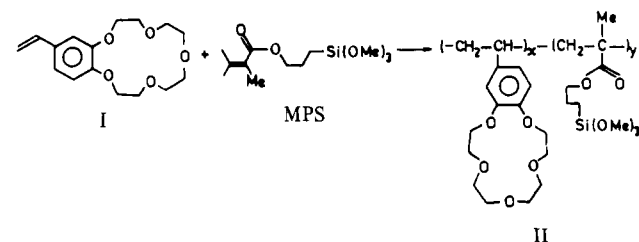
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Films of a copolymer of 4-vinylbenzo-15-crown-5 and (3-methacryloxypropyl)trimethoxysilane were formed and cross-linked on mercury electrodes by solution evaporation followed by exposure to moist HCl vapor. The films in-partition ions complexed by the polyether crown, such as thallium(I) from acetonitrile solution. After partitioning and transfer of the coated electrode to a thallium-free solution, electrochemical waves due to reduction of crown-complexed thallium to mercury amalgam, and the reverse, can be observed. In the presence of thallium in the solution, both crown-complexed and free thallium waves appear. Many monomolecular layer equivalents of crown-complexed thallium react in a cyclic voltammogram, and it is proposed that the thallium migrates to the electrode by hopping between crown sites.

Macrocylic polyethers (crown ethers) have been the focus of much research since recognition of their properties as selective complexing agents.¹ They are typically uncharged compounds with an internal oxygen-donor-rich cavity capable of cation encapsulation, with selectivity toward cations being primarily a function of the number of oxygen donors and ring size. Applications of crown ethers have been quite diverse, including phase-transfer catalysis, stabilization of Na^+ ions, and utilization in ion-selective membrane electrodes.²

An important goal in the chemical design of electrode surfaces is the transposition of known chemistry of dissolved substances to the electrode surface. This has been of interest to us and others³ in the design of monolayer films and poly-

Scheme I



meric multilayer films on electrodes. Recent work has included polyionic ion-exchanging polymer films⁴ on electrodes, capable

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(1) (a) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49. (b) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441. (c) Kolthoff, I. M. *Anal. Chem.* **1979**, *51*, 1R.

(2) Melson, G. A. "Coordination Chemistry of Macrocylic Compounds"; Plenum Press: New York, 1979.

of extracting electroactive counterions (such as metal complexes) from solutions to yield electroactive film coatings. The ion-exchange polymer films are generally easy to make and are applicable to many different electroactive ions; thus, they have been intensively researched.

Crown ethers should similarly have application to a range of electroactive metal ions and should, moreover, exhibit more coordinating selectivity between ions than do the electrostatic and other interactions of ion-exchange polymers. It would accordingly be desirable to determine how crown ethers can be incorporated into polymeric materials suitable for electrode coatings and to examine the characteristics of such films by making electroactive films of crown-coordinated metal ions. This has not heretofore been done and was the objective of the experiments that led to this report.

We chose for these experiments 4-vinylbenzo-15-crown-5 (I). This vinyl monomer has been previously polymerized.⁵ However, we chose a previously^{4m-6} used copolymerization strategy to help ensure stable electrode polymer coatings, based on the reaction shown in Scheme I. Incorporation of the (commercially available) organosilane reagent (3-methacryloxypropyl)trimethoxysilane (MPS) into copolymer II allows cross-linking of films cast from toluene solutions of II onto electrodes. Freshly cast films of II form siloxane-SiO-Si-bonds upon exposure to moist HCl, yielding a film of insoluble polymer designated as polymer III.

Thallium(I) has in noncoordinating solvents a well-characterized solution chemistry^{2,7} with crown ethers, including relatives of I, and can be reduced quasi-reversibly to $Tl^0(Hg)_x$ at a Hg electrode in acetonitrile. Experiments described here will show that cross-linked films of polymer III, when exposed to dilute solutions of thallium picrate in acetonitrile solution, incorporate Tl^+ ions, as demonstrated both by decrease of the thallium picrate concentration in the contacting solution (in partitioning experiments) and by appearance of Tl^+ -(crown)/ $Tl^0(Hg)_x$ electrochemistry (in cyclic voltammetric experiments).

Experimental Section

Chemicals. 4-Vinylbenzo-15-crown-5 (I) was synthesized according to the procedure of Kopolow et al.⁵ (3-Methacryloxypropyl)trimethoxysilane (MPS; Petrarch, Levittown, PA) was distilled before use, and azobis(isobutyronitrile) (AIBN) was recrystallized three times from methanol. Toluene used for the polymerization solvent and for dissolving the resulting polymer was distilled from benzophenone/potassium metal. Thallium picrate was prepared by addition of picric acid to an aqueous solution of thallium nitrate and recrystallizing the resulting precipitate twice from hot water. Tetraethylammonium perchlorate was recrystallized three times from water. Spectroquality

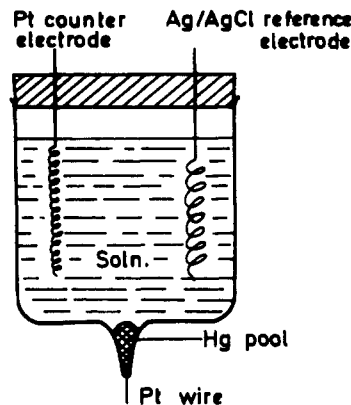


Figure 1. Cell with a minipool mercury electrode; area of pool about 0.2 cm².

acetonitrile (Burdick and Jackson) was stored over 4-Å molecular sieves. Mercury (Bethlehem Instrument) was used as received.

Equipment. A PAR 173/176 potentiostat/current follower and a PAR 175 programmer were used in electrochemical experiments with the Hg minipool electrode cell shown in Figure 1. XPS of films of polymer III on Pt electrodes was performed on a Du Pont 650 electron spectrometer with a Mg anode. A Unicam UV-vis SP1800 spectrometer was used to measure picrate concentrations in the partition experiments.

Polymerization. A 90-mg sample of the vinyl crown monomer I, 10 mg of MPS, and 1 mg of AIBN were dissolved in 0.10 mL of freshly distilled toluene in a 3-mm-diameter tube. The tube was degassed by four freeze/degas/thaw cycles and then sealed and placed in a 70 °C oil bath for 24 h. The resulting gelatinous mass was redissolved in toluene and reprecipitated three times by dropping the toluene solution into ligroin followed by centrifugation. The resultant white powder, II, was stored as a toluene solution (1.8 mg/mL of toluene) in a desiccator to minimize premature hydrolysis of the Si-OCH₃ bonds.

The copolymerization reaction was similarly carried out by using a related methylsilane monomer, (3-methacryloxypropyl)penta-methylidisiloxane (Me-MPS), which gave a toluene-soluble copolymer IV whose structure was presumed to be analogous to that of III except that siloxane cross-linking of this copolymer is not possible.

The assigned proton NMR bands of I and IV determined in CDCl₃ on a Bruker 250-MHz instrument, in δ relative to Me₄Si, are for I 3.75 (s, 8 H, CH₂), 4.0 (m, 8 H, CH₂), 5.4 (m, 2 H, C=CH₂), 6.65 (m, 1 H, CH=C), and 6.9 (m, 3 H, aromatic) and for IV broadened band, 0.064 (s, SiCH₃), 3.88 (m, CH₂), and 6.29 (m, aromatic). An infrared spectrum of a film of III showed the expected C=O stretch at 1730 cm⁻¹.

Elemental analysis of copolymer II prepared as above, after exposure to HCl for a prolonged period (20 min) to ensure hydrolysis of all of the Si-O-Me linkages (to obtain an interpretable elemental analysis): C, 57.12; H, 7.04; Si, 4.19. On the basis of the amount of silicon present, this analysis indicates that copolymer II and cross-linked copolymer III contain a molar ratio of 3.8 parts of the silane reagent MPS to 6.2 parts of the vinyl crown monomer I. The reaction preparing the copolymer used a molar feed ratio of 1 part of silane to 7 parts of crown. We did not explore other copolymer feed ratios; results reported here are all for the above polymer II preparation.

Partition Experiments. Two types of partition measurements were performed. In one, a thallium salt in aqueous medium was contacted with a methylene chloride solution containing either the (non-water-soluble) monomer polyether I or the non-cross-linking Me-MPS copolymer, polymer IV. Thallium is extracted as the crown complex into the methylene chloride phase. The amount of thallium remaining in the aqueous phase at equilibrium was measured spectrophotometrically, on the basis of the concentration of the salt's chosen anion, picrate. The thallium and polyether concentrations were such that ca. 50% of the thallium picrate remained in the aqueous phase after partitioning. The partition result is expressed as $K_{soln} = [\text{moles of } Tl(\text{crown}) \text{ complex}]/[\text{mole of total crown}]$, both in the methylene chloride phase. This partition measurement is analogous to that described by Kopolow et al.⁵ except that this work employs thallium picrate, not a metal hydroxide, in the water phase. For monomer I

- (3) (a) Murray, R. W. *Electroanal. Chem.* **1983**, *13*. (b) Murray, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 145.
 (4) (a) Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 247. (b) Oyama, N.; Shigehara, K.; Anson, F. C. *Inorg. Chem.* **1981**, *20*, 518. (c) Oyama, N.; Yamaguchi, S.; Hishiki, Y.; Tokuda, K.; Matsuda, H.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *139*, 371. (d) Anson, F. C.; Saveant, J.-M.; Shigehara, K. *J. Am. Chem. Soc.* **1983**, *105*, 1096. (e) Ohsaka, T.; Anson, F. C. *J. Phys. Chem.* **1983**, *87*, 640. (f) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685. (g) Henning, T. P.; White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 3937. (h) White, H. S.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4811. (i) Martin, C. R.; Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4817. (j) Faulkner, L. R.; Majda, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *137*, 149. (k) Oyama, N.; Sato, K.; Matsuda, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *115*, 149. (l) Kuo, K. N.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *131*, 37. (m) Facci, J.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 339. (n) Facci, J.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 2870. (o) Schneider, J. R.; Murray, R. W. *Anal. Chem.* **1982**, *54*, 1508.
 (5) Kopolow, S.; Hogen-Esch, T. E.; Smid, J. *Macromolecules* **1973**, *6*, 133.
 (6) Nakahama, S.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *158*, 303.
 (7) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

and polymer IV, K_{soln} is 0.0018 and 0.025, respectively.

Partition of thallium picrate from acetonitrile solution into the polymer phase of III was measured in a preweighed test tube onto the sides of which had been coated a film of II. This film was cross-linked with HCl to form polymer III and rinsed twice with pure acetonitrile, and the test tube was reweighed to determine the weight of polymer III present. The weight was 14 mg of III, which, given the crown/silane mole ratio from the elemental analysis, corresponds to 3.1×10^{-5} mol of crown sites in the polymer film. Two hours after adding 5 mL of 2.1×10^{-4} M thallium picrate to the test tube, the decrease in absorption in the UV-vis spectrum of the test-tube solution showed that 7.6×10^{-7} mol of thallium picrate had been partitioned into the polymer phase. This result is expressed as $K_{\text{poly}} = [\text{moles of Tl(crown) complex}]/[\text{mole of total crown}] = 0.025$, both in the polymer III phase. An analogous measurement of K_{poly} for IV in acetonitrile is not possible because of its solubility in acetonitrile. To allow comparison of K_{soln} and K_{poly} values, similar $[\text{Tl}^+]$ were employed in the water and acetonitrile phases in the partition and voltammetry experiments.

Polymer-Coated Electrode Preparation. Mercury was added to the cell shown in Figure 1 up to the top of the well, forming an electrode with an estimated 0.2-cm^2 area. To seek a relatively uniform coating of crown polymer II on the Hg electrode surface, 0.3 mL of pure toluene was added to the electrode surface followed by the desired amount (5–20 μL) of polymer solution. After the toluene had slowly evaporated, the polymer film was cross-linked by blowing HCl vapors onto it. Upon exposure to HCl, the Hg electrode surface, which was shiny and reflective when coated with II, immediately developed a faint haze, which we take to indicate that cross-linking to form III was occurring. Prior to exposure to HCl, the film of polymer II could be redissolved in toluene whereas, afterward, it was (as III) insoluble in toluene.

Results

The previously known vinyl crown ether polymers are typically soluble in aprotic, noncoordinating solvents like acetonitrile and so were not per se suitable for preparing polymer-coated electrodes. We had employed the cross-linking strategy embodied in Scheme I earlier with vinylpyridine,^{4m,n} vinylferrocene,⁶ and sulfonated styrene^{4o} to successfully insolubilize their copolymers as films on electrodes. The present application of MPS to insolubilize the vinyl crown polymer was also successful; films cast from the copolymer II from toluene could be redissolved in toluene or in acetonitrile whereas, following exposure to HCl to form the presumably cross-linked polymer III, the films were soluble in neither solvent. The 7:1 I:MPS molar feed ratio produced a polymer, II, with a molar ratio of approximately 3:2, indicating that the MPS silane is more reactive than the crown to polymerization. It is also possible that the higher amount of silane incorporated reflects some SiOSi coupling via the Si-OCH₃ groups during the polymerization reaction.

An initial, qualitative test of whether the polymer III would complex Tl^+ was conducted by exposing a film prepared on a Pt electrode (evaporate a droplet of a solution of II, cross-link with HCl vapor) to a thallium picrate/acetonitrile solution. This surface was then thoroughly rinsed with pure acetonitrile, dried, and analyzed by XPS, which showed a strong peak indicating that Tl^+ was present in the film.

The quantitative degree of coordination of crown sites in the cross-linked polymer III by Tl^+ was determined as described in the Experimental Section. Equilibrating a film of III with an acetonitrile solution of thallium picrate (of concentration similar to that employed in the voltammetric experiments) gave the result $K_{\text{poly}} = [\text{moles of Tl(crown) complex}]/[\text{mole of total crown}] = 0.025$ in polymer III. In other words, approximately 1 in 40 of the available crown sites in III coordinates to Tl^+ . In comparison, analogous partition-determined fractional degrees of Tl^+ complexation by the crown monomer I and by the soluble version of the crown copolymer, polymer IV, in methylene chloride were $K_{\text{soln}} = 0.0018$ and 0.026, respectively. The polymer film III appears

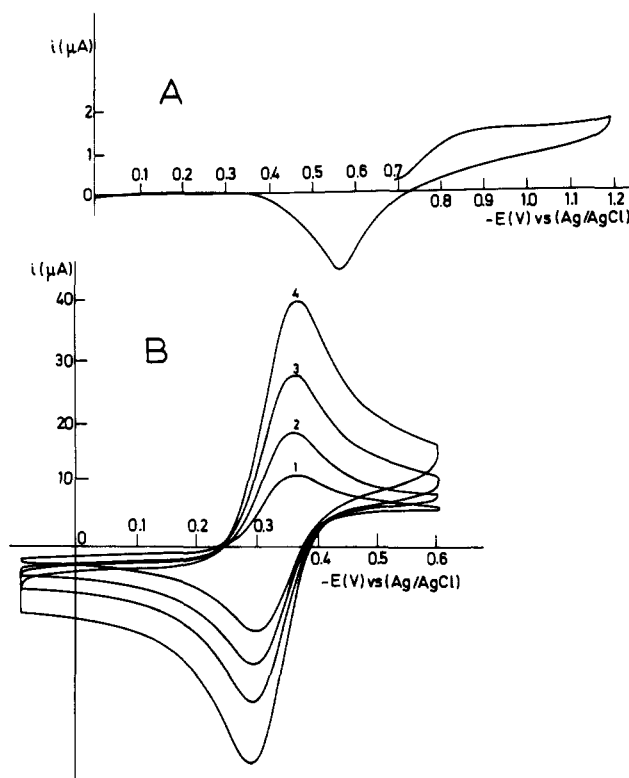


Figure 2. (A) Cyclic voltammetry of Tl^+ solution at naked Pt; scan rate 20 mV/s. (B) Cyclic voltammetry of 1.7×10^{-4} M Tl^+ at minipool Hg; scan rate 20, 50, 100, 200 mV/s for curves 1–4, respectively. All experiments were performed in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$.

to complex Tl^+ from acetonitrile solution ($K_{\text{poly}} = 0.025$) as well as does the related polymer IV from methylene chloride solution ($K_{\text{soln}} = 0.026$); the solvent effect appears to be minimal. Both the crown polymers complex Tl^+ better than does the monomer crown I in methylene chloride solution ($K_{\text{soln}} = 0.0018$), a comparison that agrees with previous results which show that crowns in close proximity (i.e., in dimers⁸ or polymers⁵) have a higher affinity for metal ions than do monomers in solution.

Tl^+ is strongly partitioned from acetonitrile into the polymer phase III as shown by reexpressing $K_{\text{poly}} = 0.025$ as a partition ratio $P = [\text{Tl(crown) complex in polymer III phase}]/[\text{Tl}^+ \text{ in acetonitrile}] \approx 10^3$. (Unit density of the III phase was assumed in this conversion.)

Having established and quantitated the affinity of films of crown ether polymer III for Tl^+ , we turn to the electrochemical behavior of the polymer film. Most of the current work with polymer-coated electrodes has relied on solid electrode substrates like Pt, SnO_2 , etc. Were metal deposition not involved in the Tl^+ electrochemistry, solid electrodes would probably have been suitable. The reduction of Tl^+ to Tl^0 at Pt from acetonitrile solvent is, however, very irreversible (Figure 2A). There have been some recent reports⁹ of polymer electrode coatings as well as older¹⁰ polymer membrane-covered electrode experiments, using Hg as the substrate electrode. Tl^+ is reduced on Hg from acetonitrile in a well-defined quasi-reversible wave (Figure 2B), and so Hg was chosen as the polymer-coating substrate in the cell of Figure 1.

- (8) Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* **1975**, *97*, 3462.
- (9) (a) DeGrand, C.; Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 283. (b) Elliott, C. M.; Redepenning, J. G. *J. Electroanal. Chem. Interfacial Electrochem.*, in press.
- (10) (a) Bowers, R. C.; Murray, R. W. *Anal. Chem.* **1966**, *38*, 461. (b) Murray, R. W. Ph.D. Thesis, Northwestern University, Evanston, IL, 1960.

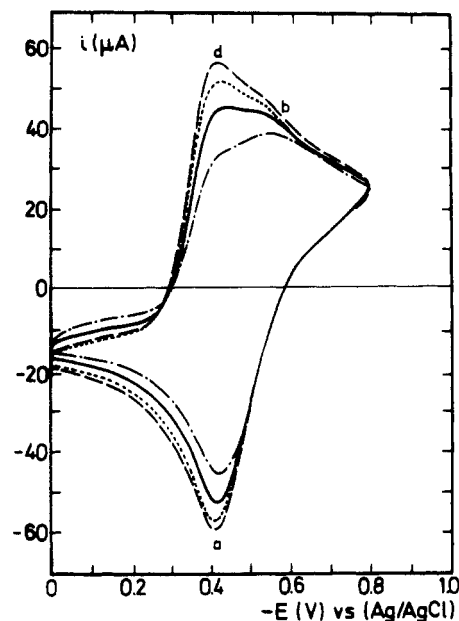


Figure 3. Cyclic voltammograms (scan rate 100 mV/s) in acetonitrile solution containing 8.7×10^{-5} M thallium picrate and 0.1 M Et_4NClO_4 . The Hg electrode has a polymer III layer ($5 \mu\text{L}$ of evaporated stock solution; $\Gamma_{\text{crown}} = 1 \times 10^{-7}$ mol/cm 2). Currents increased to a limit in 30 min ((- - - -) 5 min; (—) 10 min; (- - -) 20 min; (- - -) 30 min). Peak d is “free” Tl^+ , and peak b is $\text{Tl}^+(\text{crown})$.

The partitioning of Tl^+ into a film of III on Hg from 0.1 M Et_4NClO_4 /acetonitrile is readily evident by monitoring the cyclic voltammetry of the film after thallium picrate is added to the cell, as shown in Figure 3. Repetitively sweeping the Hg electrode potential through the region of Tl^+/Tl^0 electroactivity reveals two Tl^+ reduction peaks, one at peak d and a second ca. 100 mV more negative peak at peak b, growing up over a 30-min period. After 30 min, the original solution was removed, the electrode rinsed with pure acetonitrile, and Tl^+ -free 0.1 M Et_4NClO_4 /acetonitrile added to the cell (in essence, transferring the mercury electrode to fresh electrolyte solution). The “transferred” electrode gives the voltammogram of Figure 4, which has a somewhat broadened reduction peak at -0.58 V and a sharper, more symmetrical oxidation wave at -0.43 V. The voltammetry was reasonably stable, indicating that Tl^+ escapes only slowly from the film; scanning the potential of the Tl -crown polymer electrode for 20 min caused only a 19% drop in peak current. The voltammetry of Figure 4, where no Tl^+ is present in the contacting solution, clearly represents electroactivity of $\text{Tl}^+(\text{crown})$ complex sites in the polymer. On the basis of this, and on the basis of the similarity of the potential for peak d in Figure 3 to that for reduction of Tl^+ on naked Hg (Figure 2B), we assign reduction peak d to “free” Tl^+ and peak b to crown-complexed Tl^+ .

In the Figure 3 experiment, Tl^+ is repetitively reduced to $\text{Tl}^0(\text{Hg})_x$ and so the “transferred” thallium electrochemistry seen in Figure 4 is, possibly, thallium not transferred as $\text{Tl}^+(\text{crown})$ but instead as residual $\text{Tl}^0(\text{Hg})_x$. To evaluate this possibility, two experiments were performed. First, a fresh polymer-coated Hg electrode was exposed to a thallium picrate/0.1 M Et_4NClO_4 /acetonitrile solution for 1 h while the Hg electrode potential was swept between 0 and -0.2 V, i.e., not through the Tl^+ reduction wave. After the electrode was “transferred” to fresh electrolyte, a voltammogram very similar to that in Figure 4 was obtained. Second, an electrode was subjected to the same potential scanning procedure as in Figure 3, but then, before being “transferred” to fresh electrolyte, the electrode was potentiostated at 0.0 V (oxidizing $\text{Tl}^0(\text{Hg})_x$) until the current died away to background level. Again, after “transferring”, the same peaks were seen as in Figure 4. These

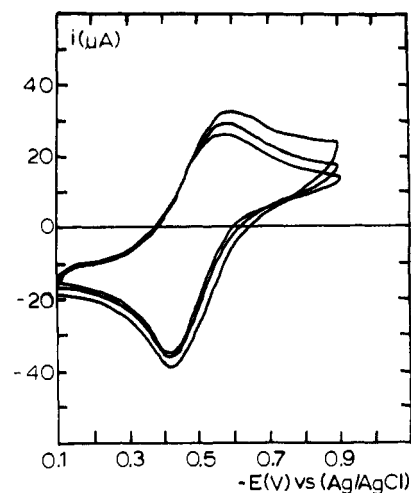


Figure 4. Cyclic voltammograms of the polymer-III-coated Hg electrode of Figure 3, after transfer to 0.1 M Et_4NClO_4 in acetonitrile, after 5, 10, and 20 min for curves from bottom to top, respectively (scan rate 100 mV/s).

results show that it is not necessary to produce a $\text{Tl}^0(\text{Hg})_x$ amalgam to “transfer” the thallium electroactivity, and so the “transferred” thallium must be $\text{Tl}^+(\text{crown})$ complex.

To eliminate the possibility that the above effects might somehow be trivially due to a polymer coating on the surface, a film of polystyrene was droplet evaporated onto the Hg electrode and its potential scanned first with Tl^+ and then with ferrocene in the cell solution. The membrane-diffusion-limited electrochemistry of ferrocene could be clearly seen, but only a very small $\text{Tl}^+/\text{Tl}^0(\text{Hg})_x$ wave at potential d and nothing at potential b. “Transfer” of the electrode from Tl^+ solution produced no thallium electrochemistry at all.

A value for extraction of Tl^+ from the solution into the film of III, [moles of $\text{Tl}^+(\text{crown})$ complex]/[mole of total crown] = $K_{\text{poly}} = 0.05$, was obtained by measuring the coulombs of Tl^+ reduced in a slow potential sweep on a “transferred” electrode like that used to obtain Figure 4. This value of K_{poly} is in rough agreement with the spectrophotometric value of 0.025. The polymer III film on the mercury electrode contained $\Gamma_{\text{crown}} = 1 \times 10^{-7}$ mol/cm 2 of crown sites and incorporated ca. 5×10^{-9} mol/cm 2 of Tl^+ . The latter quantity corresponds to 50–100 monolayers of $\text{Tl}^+(\text{crown})$ complex sites.

The number and relative magnitudes of the peaks observed in the voltammograms of Tl^+ -containing polymer-III-coated electrodes immersed in Tl^+ solution and in Tl^+ -free (“transferred”) solution are dependent on the initial bathing solution concentration of Tl^+ (C_{Tl}), the potential sweep rate, and the quantity of crown (Γ_{crown} ; i.e., film thickness) present in the film. Figures 5 and 6 show several experiments in Tl^+ -containing solutions; in Figure 5 Γ_{crown} is changed and C_{Tl} is constant, and in Figure 6 C_{Tl} is changed and Γ_{crown} is constant.

If the trace in Figure 5A, recorded at a sweep rate of 100 mV/s, is examined, four peaks are evident. Decreasing the sweep rate to 20 mV/s causes a decrease in peak a with respect to peak c. In Figure 5B, Γ_{crown} was increased 4-fold by applying 20 μL rather than 5 μL of stock polymer solution to the Hg during preparation of the film. For the same C_{Tl} and sweep rates, peak a is larger in the voltammogram at all sweep rates compared to peak c, so much so that peak c was not visible at 100 mV/s. The ratio of peaks d and b remained relatively the same.

The voltammograms in Tl^+ -containing solutions are also sensitive to changing C_{Tl} in the bathing solution, as shown in Figure 6. If C_{Tl} is decreased (from the above value of $1.7 \times$

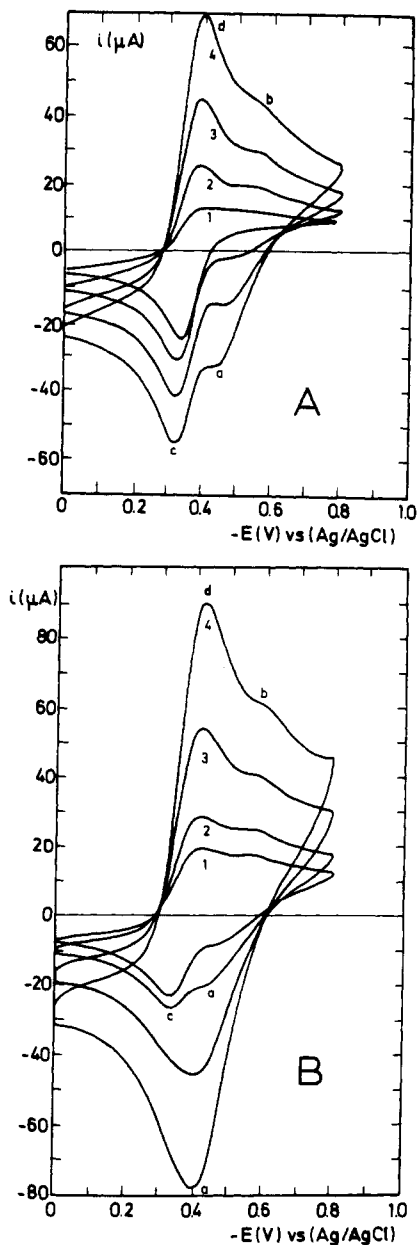


Figure 5. Cyclic voltammograms in acetonitrile solutions containing 1.7×10^{-4} M thallium picrate and 0.1 M Et_4NClO_4 . The coverage, Γ_{crown} , of polymer III is 1×10^{-7} mol/cm² of crown ($5 \mu\text{L}$ of evaporated stock solution) for panel A and 4×10^{-7} mol/cm² of crown for panel B ($20 \mu\text{L}$ of evaporated stock solution). Curves 1–4 refer to scan rates 10, 20, 50, and 100 mV/s, respectively. Peaks c and d are ascribed to “free” thallium, and peaks a and b to $\text{Tl}^+(\text{crown})$.

10^{-4} M to 8.7×10^{-5} M, with the same Γ_{crown} as Figure 5A), Figure 6A shows changes similar to those seen in Figure 5 for increasing Γ_{crown} ; i.e., peak a is enhanced compared to peak c. Additionally, peak d is smaller with respect to peak b. Finally, in Figure 6B, C_{Tl} is decreased even further, to 2.2×10^{-5} M, and now peaks d and c are absent even at the slowest sweep rate examined, 10 mV/s. In Figure 6B, the solution concentration C_{Tl} is too low for “free” Tl^+ to give an easily perceptible wave even at a naked electrode, so the disappearance of the “free” Tl^+ peaks c and d is expected, and occurs.

The electrode of Figure 6B is shown in Figure 7 after “transfer” to Tl^+ -free electrolyte. The $\text{Tl}^+(\text{crown})$ electroactivity is similar to that seen in Figure 4, but the wave is more symmetrical. After differences in sweep rate are accounted for, the peak current in Figure 4 is ~ 3 times larger than that in Figure 7, for an ~ 4 times difference in concen-

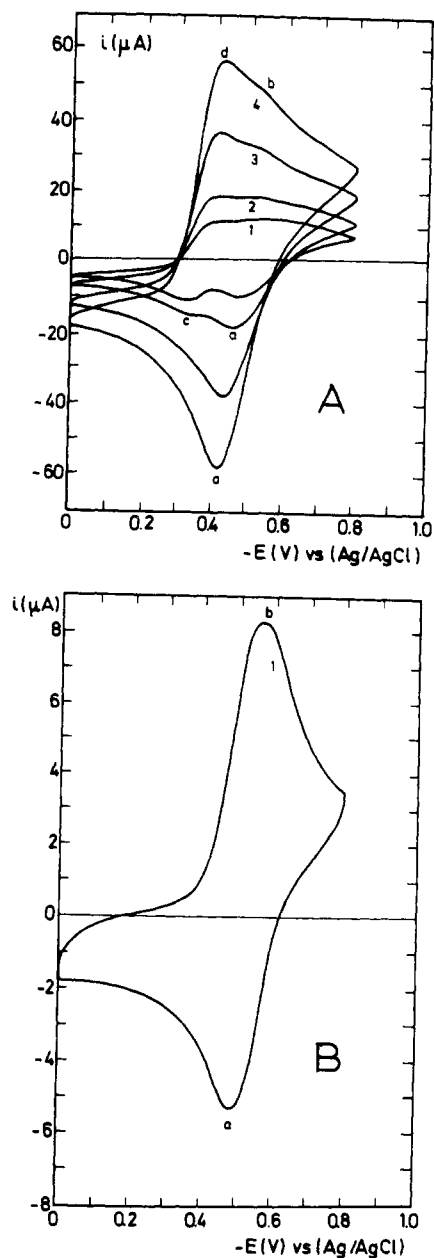


Figure 6. Cyclic voltammograms in acetonitrile solutions containing 8.7×10^{-5} (panel A) and 2.2×10^{-5} M (panel B) thallium picrate and 0.1 M Et_4NClO_4 . The coverage, Γ_{crown} , of polymer III is 1×10^{-7} mol/cm² of crown ($5 \mu\text{L}$ of evaporated stock solution). Curves 1–4 refer to scan rates 10, 20, 50, and 100 mV/s, respectively. Peaks c and d are ascribed to “free” thallium, and peaks a and b to $\text{Tl}^+(\text{crown})$.

tration. This is roughly as expected for an equilibrium partitioning process in which the quantity of crown polymer complex formed in the film is proportional to the C_{Tl} in the contacting solution. A further increase in C_{Tl} to 1.7×10^{-4} M produces, however, a much less than proportional increase in the size of the wave, indicating onset of some kind of saturation effect. The small magnitude of K_{poly} suggests that many more, uncomplexed crown sites should remain in the “saturated” film. Perhaps the crown sites that are “saturated” are those which are in closest proximity to one another and which thereby have the largest affinity for Tl^+ .

Discussion

The voltammetry in Figures 3–7 can be explained by using Scheme II. Scheme II assumes that there are four kinds of thallium, two of which are similar: (i) “free” Tl^+ , which exists in two similar forms, that in the acetonitrile ($\text{Tl}^+(\text{soln})$) and

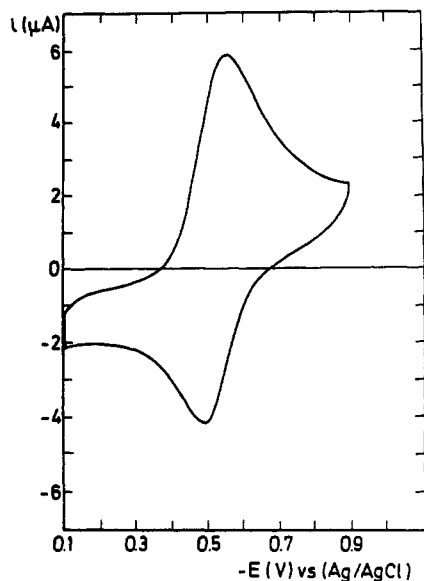
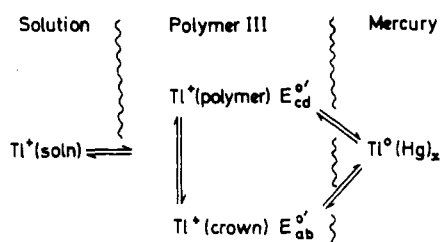


Figure 7. Cyclic voltammogram of the electrode of Figure 5B transferred to fresh 0.1 M $\text{Et}_4\text{NClO}_4/\text{acetonitrile}$, after the potential was cyclically scanned for 10 min over the indicated range at 100 mV/s.

Scheme II



that which is in the polymer III phase ($\text{Tl}^+(\text{polymer})$) in a coordination state (and $E_{cd}^{\circ'}$) little different from that of $\text{Tl}^+(\text{soln})$; (ii) Tl^+ that is complexed by the crown polymer ($\text{Tl}^+(\text{crown})$), which thereby has a more negative formal potential $E_{ab}^{\circ'}$; (iii) reduced, electrode-phase $\text{Tl}^0(\text{Hg})_x$. Scheme II further assumes that the free Tl^+ is able to enter the polymer film ($\text{Tl}^+(\text{polymer})$) and diffuse through it to the mercury electrode on the time scale of the cyclic voltammetric potential sweep. Finally, and importantly, Scheme II assumes that the kinetics of the $\text{Tl}^+(\text{crown}) \rightleftharpoons \text{Tl}^+(\text{polymer})$ equilibrium within the polymer are fast on the voltammetric time scale.

Given these assumptions, consider the cyclic voltammogram of Figure 5A through a negative and subsequent positive potential sweep. The value of C_{Tl} in the bathing solution used for Figure 5A is sufficiently high that $\text{Tl}^+(\text{polymer})$ diffusing through the polymer film gives a measurable reduction peak d. Tl^+ that has been partitioned into the film as $\text{Tl}^+(\text{crown})$ is subsequently reduced in peak b. The two forms of Tl^+ are reduced to a common, indistinguishable product, $\text{Tl}^0(\text{Hg})_x$. Upon a subsequent positive sweep of the potential, $\text{Tl}^0(\text{Hg})_x$ is oxidized first to form $\text{Tl}^+(\text{crown})$ (peak a) and then, once the crown sites near the electrode are concentration polarized (occupied) by complexation, to form $\text{Tl}^+(\text{polymer})$ (peak c).

Figures 5 and 6 illustrated the changes in relative magnitudes of peaks a–d as C_{Tl} , potential sweep rate, and Γ_{crown} were varied. The changes, mainly in the positive potential sweep in peak a vs. peak c, are explicable with Scheme II. As the negative potential sweep passes peak b, reducing $\text{Tl}^+(\text{crown})$, the resulting depletion of Tl^+ from the film allows additional $\text{Tl}^+(\text{soln})$ to enter the film, becoming $\text{Tl}^+(\text{polymer})$ and occupying vacated $\text{Tl}^+(\text{crown})$ sites. When the experiment is conducted with sufficiently slow potential sweeps, high C_{Tl} , and/or thin polymer film (low Γ_{crown}), the latter process causes

peak a to be diminished in the subsequent positive potential sweep. This is because the $\text{Tl}^+(\text{crown})$ sites have under those circumstances been reoccupied by fresh, incoming $\text{Tl}^+(\text{soln})$. Under these circumstances, peak a becomes a minor process compared to production of $\text{Tl}^+(\text{polymer})$ via peak c. Conversely, when the experiment uses fast potential sweeps or when little or no thallium is present in the solution (low C_{Tl}), wave a dominates. These qualitative rationales are amenable to simulation of theoretical voltammograms, but this has not been attempted.

Consider next the very occurrence of the $\text{Tl}^+(\text{crown})/\text{Tl}^0(\text{Hg})_x$ wave ab. How is the equivalent of many monomolecular layers of $\text{Tl}^+(\text{crown})$ complex reduced in wave b during a negative potential sweep? Electroactive polymer films on electrodes that exhibit voltammetric waves corresponding to oxidation or reduction of many monolayer equivalents of electroactive sites are now well-known phenomena.³ When the sites are molecularly fixed in the polymer, electroactivity of sites remote (more than a monolayer or two) from the electrode is thought¹¹ to occur by electron hopping (electron self-exchange) from redox site to redox site. When the sites are electroactive counterions of an ion-exchanger polymer, electroactivity is transmitted by a combination of electron hopping (electron self-exchange) and physical diffusion of the electroactive counterion.^{4f,4h,4n}

The present case, reduction of $\text{Tl}^+(\text{crown})$ in wave ab, is analogous to the diffusion of electroactive counterions in ion-exchange polymer films, by the following reasoning. First, electron self-exchange involving a $\text{Tl}^+(\text{crown})/\text{Tl}^0(\text{polymer})$ or $\text{Tl}^+(\text{polymer})/\text{Tl}^0(\text{polymer})$ couple would require Tl^0 states in the polymer, which is unlikely on the basis of both the absence of nucleating sites in the polymer upon which Tl^0 could rapidly deposit and the absence of the large change in potential that would result from loss of the mercury amalgamation energy (compare potentials in Figure 2A vs. Figure 2B). Second, the $\text{Tl}^+(\text{crown})$ sites in the polymer film III are unlikely to migrate (as such) over significant (many monolayer equivalents) distances, since the crown ligand is affixed to the polymer lattice. Consequently, it would appear that $\text{Tl}^+(\text{crown})$ most logically migrates by "ion hopping" of the Tl^+ from crown site to crown site. Since this may occur via the $\text{Tl}^+(\text{polymer}) \rightleftharpoons \text{Tl}^+(\text{crown})$ equilibrium it is not necessary to assume close proximity of crown sites for the "ion hopping".

The ion-hopping mode of electrochemical charge transport through polymer III is, formally, similar to physical diffusion of electroactive counterions in ion-exchange polymer films,^{4f} but it is different in detail. In the crown polymer, the binding sites are molecularly well-defined (the crown cavity) as compared to the diffuse and relatively undefined locations of electrostatically bound counterions. The dimensions of the ion-hopping process in the crown ether polymer may thus be eventually more amenable to quantitative understanding.

Finally, note that the polymer film III can be regarded as a membrane between two immiscible liquids, Hg and acetonitrile, where one form of thallium (Tl^+) is soluble only in acetonitrile and the other (Tl^0) only in mercury. The polymer membrane would, in fact, appear to be capable of acting to promote a buildup of thallium in the mercury phase during cyclic voltammetry to a greater extent than during naked-electrode experiments, due to the reoccupancy of $\text{Tl}^+(\text{crown})$ sites by incoming $\text{Tl}^+(\text{soln})$ discussed above. That is, the membrane may act as an "ion pump" and as such may be useful for trace-metal scavenging/accumulation experiments beyond simply static scavenging of trace metal by the polymer

(11) (a) Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1980**, *102*, 483. (b) Pickup, P. G.; Murray, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 4510 and references therein.

film itself. These and other aspects of crown polymer film electrochemistry promise interesting further investigations.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Insertion Reactions of Hexaalkoxydimolybdenum and -ditungsten Compounds with Organic Isocyanates. Syntheses and Structures of $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ and $Mo_2(O-i-Pr)_4[N(C_6H_5)C(O)O-i-Pr]$

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Dimolybdenum and ditungsten hexaalkoxides react with phenyl isocyanates (2 equiv) in nonpolar solvents to form products involving insertion of the isocyanate into the metal alkoxide bond. The new products $Mo_2(O-i-Pr)_4[N(C_6H_5)C(O)O-i-Pr]_2$ (**1**) and $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ (**2**) have both been characterized by X-ray crystallography. Compound **1** crystallizes in space group *Pnab* with $a = 18.652$ (22) Å, $b = 10.808$ (11) Å, $c = 18.912$ (24) Å, and $Z = 4$ (at -55 °C). The molecule has a twofold axis of symmetry perpendicularly bisecting the Mo-Mo bond, and it consists of two cis bridging bidentate ligands and four isopropoxy groups. Each molybdenum atom is in the +3 oxidation state, and the Mo-Mo bond length is 2.221 (5) Å. Compound **2** crystallizes in space group *P1̄* with $a = 10.48$ (1) Å, $b = 11.38$ (1) Å, $c = 11.80$ (1) Å, $\alpha = 96.96$ (3)°, $\beta = 110.02$ (3)°, $\gamma = 106.93$ (3)°, $V = 1226$ (2) Å³, and $Z = 1$. The molecule is centrosymmetric and consists of two trans bridging bidentate ligands and four *tert*-butoxy ligands. Each tungsten atom is in the +3 oxidation state, and the W-W bond length is 2.290 (1) Å. The bond distance in each compound is consistent with a bond order of 3, and the magnitude of the difference, 0.069 (5) Å, is as expected.

Introduction

The reactivity of metal-metal triple bonds of ditungsten and dimolybdenum alkoxides or amides has attracted considerable interest in recent years. Schrock and co-workers² have shown that $W_2(OCMe_3)_6$ reacts with various alkynes to give $(Me_3CO)_3W\equiv CR$, which catalytically metathesizes acetylenes. Chisholm and co-workers³ have shown that acetylenes and peroxides oxidatively add to $M_2(OR)_6$ ($M = Mo, W$; $R \neq OCMe_3$ when $M = W$). Cotton, Schwotzer, and Shamsoum⁴ have shown that under more vigorous conditions still other, new types of products are obtained.

The insertions of various unsaturated organic molecules such as CO_2 , isocyanates, and CS_2 into $M-X$ ($X = O, N$) bonds are well-known processes. With respect to isocyanates, the reactants of interest here, Davies and co-workers,⁵ and also Mehrotra and co-workers,⁶ have demonstrated the insertion of isocyanates into a titanium alkoxide bond and into a niobium alkoxide bond. Later, Cotton, Chisholm, and co-workers⁷ have also shown that CO_2 can insert into $M-X$ ($M = Mo, W$; X

$= O, N$) bonds of dinuclear species to form bridging bidentate ligands. In this report, we bring these two lines of work together and report the insertion products obtained from the reaction of phenyl isocyanate with $W_2(OCMe_3)_6$ and several $Mo_2(OR)_6$ compounds.

Experimental Section

Ditungsten hexa-*tert*-butoxide, $W_2(OCMe_3)_6$, was prepared² by Na/Hg reduction of WCl_4 in THF at -10 °C in the presence of $LiOCMe_3$, followed by recrystallization from hexane at -10 °C. Dimolybdenum hexaalkoxides were prepared³ by first reacting $MoCl_3$ with $LiNMe_2$ (3 equiv) in THF to give $Mo_2(NMe_2)_6$, which was sublimed. Excess 2-propanol or 2,2-dimethyl-1-propanol was then added to a hexane solution of $Mo_2(NMe_2)_6$, and the $Mo_2(O-i-Pr)_6$ or $Mo_2(OCH_2-t-Bu)_6$ products were recrystallized from hexane at -20 °C. All reactions were done under an argon atmosphere.

NMR spectra of the molybdenum products were recorded on a Varian HR-220 spectrometer at 16 °C in toluene- d_8 or benzene- d_6 . Chemical shifts were calculated on the basis of the residual protons in the solvent and referenced to Me_4Si . Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer in a Nujol mull between CsI plates. Elemental analysis were done by Bernhardt Microanalytical Laboratories, West Germany. ¹H NMR spectra of $W_2(OCMe_3)_4[N(C_6H_5)C(O)OCMe_3]_2$ were recorded on a Varian XL-200 PET spectrometer in $CDCl_3$. The infrared spectrum was recorded on a Perkin-Elmer 783 infrared spectrophotometer.

Preparations. $Mo_2(O-i-Pr)_4[N(Me)C(O)O-i-Pr]_2(py)_2$. $Mo_2(O-i-Pr)_6$ (0.6 g, 1.10 mmol) was suspended in hexane (10 mL) and then frozen at liquid-nitrogen temperatures. The flask was evacuated and methyl isocyanate (2.20 mmol) was vacuum distilled into the flask from a calibrated vacuum gas line. The solution was warmed to 25 °C, and pyridine (1 mL) was added. Slow cooling to -15 °C produced a homogeneous mass of dark red crystals of $Mo_2(O-i-Pr)_4[(N(Me)C(O)O-i-Pr)]_2(py)_2$. Yield: 80% based on molybdenum.

- (1) (a) Indiana University. (b) Texas A&M University.
- (2) Schrock, R. R.; Listerman, M. L.; Sturgeoiff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.
- (3) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.
- (4) (a) Cotton, F. A.; Schwotzer, W.; Shamsoum, E. *Organometallics* **1983**, *2*, 1167. (b) Cotton, F. A.; Schwotzer, W.; Shamsoum, E. *Organometallics* **1983**, *2*, 1340.
- (5) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 5238, 6858.
- (6) Bohra, R.; Mehrotra, R. C.; Rai, A. K. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1887.
- (7) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727.