Acknowledgment. We thank the University of Tasmania for a Special Research Project Grant, the Australian Research Grants Committee for financial support, the Australian Development Assistance Plan (N.C.), Mr. A. P. Arnold for assistance with measurement of log K_H values, and Mr. C. V. Lee for synthesis of $(py)_3COH$ an $(py)_2(N\text{-MeIm})COH$.

Registry No. $[MeHg((py)CHPh_2)]NO_3$, 79043-58-6; $[MeHg((py)_2CHPh)]NO_3$, 79043-60-0; $[MeHg((py)_3COH)]NO_3$, 79043-62-2; $[MeHg((py)_2(N\text{-MeIm})COH)]NO_3$, 79043-64-4; $(py)_2CHPh$, 79057-57-1; 2-benzylpyridine, 101-82-6; 2-bromopyridine, 109-04-6; $MeHgNO_3$, 2374-27-8.

Supplementary Material Available: Calculated hydrogen atom positions and thermal parameters (Tables VII and VIII), mean planes data (Tables IX and X), packing diagrams (Figures 4 and 5), and a list of observed and calculated structure factors for $[MeHgL]NO_3$ [L = $(py)_3COH$ and $(py)_2(N\text{-MeIm})COH$] (33 pages). Ordering information is given on any current masthead page.

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New 2,2′-Bipyridine and 1,10-Phenanthroline Oxohalide Complexes of Technetium(VII) and -(V)

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Novel complexes of heptavalent technetium with the formualtion TcO_3XL (L = 2,2′-bipyridine, X = Cl, Br; L = 1,10-phenanthroline, X = Cl) have been prepared and characterized by elemental analysis and optical and vibrational spectroscopy. These complexes can be reduced to the pentavalent species, $TcOX_3L$, by heating in ethanolic aqueous HX. $TcOX_3$(2,2′-bipyridine) (X = Cl, Br) can be synthesized independently from $n\text{-}Bu_4NTcOX_4$ and 2,2′-bipyridine in ethanolic aqueous HX.

Introduction

One of the basic differences between the chemistry of technetium and that of rhenium is that, under similar conditions, technetium is easier to reduce than rhenium.[2,3] For example, the interaction of ReO_4^- with phosphines in ethanolic HCl yields complexes of stoichiometry $ReOCl_3(PR_3)_2$. Under similar conditions, TcO_4^- reacts to give the complexes *trans*-$TcCl_4(PR_3)_2$ and *mer*-$TcCl_3(PR_3)_3$.[4] Also, in contrast to rhenium, technetium does not, as yet, have a well-developed chemistry in the heptavalent oxidation state.

We now report the preparation of 2,2′-bipyridine and 1,10-phenanthroline oxohalide technetium(VII) complexes from NH_4TcO_4 and the respective ligands in ethanolic aqueous haloacids. These complexes, unlike the known rhenium analogue $ReO_3Cl(bpy)$, are readily reduced to oxohalide technetium(V) species.

Experimental Section

Technetium as $NH_4{}^{99}TcO_4$ was obtained as a gift from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity (^{99}Tc is a weak β emitter with a half-life of 2.12×10^5 years and particle energy of 0.292 MeV). All precautions followed have been detailed elsewhere.[5,6] Rhenium, as $NaReO_4$, was obtained from Cleveland Refractory Metals, Solon, OH.

Infrared spectra were recorded in the range 4000–300 cm^{-1} on a Perkin-Elmer PE180 grating infrared spectrophotometer as KBr pellets. Optical spectra, in solution, were measured with a Cary 17 spectrophotometer. Raman spectra were obtained as solid samples using a Spex Ramalog with the 5145-Å line of an Ar laser. ^1H NMR measurements were made on a Jeol FX-90Q 90-MHz spectrometer with acetone-d_6 as solvent and Me_4Si as the internal calibrant. Conductivity measurements were performed in acetonitrile with use of a Yellow Springs Model 3403 conductivity cell and a Beckman RC-16C conductivity bridge. Melting points were obtained with a Mel-Temp apparatus and are uncorrected.

Prior to use, distilled water was passed through a Barnstead Ultrapure D8902 cartridge, followed by redistillation in a Corning AG-1 water still. The ligands, 2,2′-bipyridine (bpy) and 1,10-phenanthroline hydrate (phen) were obtained from the J. T. Baker Chemical Co., Phillipsburg, NJ. $n\text{-}Bu_4NTcOCl_4$ and $n\text{-}Bu_4NTcOBr_4$ were prepared by literature methods.[6,7] Absolute ethanol was used throughout. All other chemicals were used without further purification unless otherwise specified. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Preparation of the Complexes. Trioxochloro(2,2′-bipyridine)technetium(VII). To a 50-mL round-bottom flask were added a stirbar, EtOH (10 mL), and 0.70 mL of 0.379 M NH_4TcO_4 (0.26 mmol). To the stirred solution was added 0.30 g of bpy (1.97 mmol) dissolved in EtOH (10 mL), followed by the dropwise addition of 12 N HCl (2 mL). Within 10 min a bright yellow solid precipitated. This solid was isolated by suction filtration, washed with acetone (3 × 15 mL), and dried in vacuo. The yield of $TcO_3Cl(bpy)$ was 0.07 g (0.21 mmol), 81% based on Tc; mp 162 °C dec. This material is insoluble in toluene, ethanol, methanol, and slightly soluble in acetone, methylene chloride, and acetonitrile. In water, the complex hydrolyzes back to TcO_4^-.

Anal. Calcd for $C_{10}H_8ClN_2O_3Tc$: C, 35.46; H, 2.39; Cl, 10.47; N, 8.27. Found: C, 35.61; H, 2.11; Cl, 10.49; N, 8.29. Optical spectrum in (CH_3CN: 298 nm (ϵ 1.9×10^4 L mol^{-1} cm^{-1}), 310 (sh). IR spectrum (KBr): $\nu_{Tc=O}$, 905 (s), 885 (s), 865 (m) cm^{-1}. Raman spectrum: $\nu_{Tc=O}$, 882 (m), 902 (s) cm^{-1}.

Trioxochloro(1,10-phenanthroline)technetium(VII). This complex was prepared as a yellow solid in 75% yield by the above procedure using phen (6:1 excess over TcO_4^-). It solubility is similar to $TcO_3Cl(bpy)$; mp 205 °C dec. Anal. Calcd for $C_{12}H_8ClN_2O_3Tc$: C, 39.74; H, 2.23; Cl, 9.77; N, 7.73. Found: C, 40.14; H, 2.26; Cl, 9.81; N, 7.74. Optical spectrum in CH_3CN: 269 (3.7×10^4). IR (KBr): $\nu_{Tc=O}$ 895 (s), 885 (s), 870 (m) cm^{-1}. Raman spectrum: $\nu_{Tc=O}$, 898 (vs) cm^{-1}.

Trioxobromo(2,2′-bipyridine)technetium(VII). This complex was prepared similarly to $TcO_3Cl(bpy)$ by using HBr (48%) instead of 12 N HCl. It was washed with 4 N HBr after filtration, followed by acetone and dried in vacuo. The yellow orange solid was obtained

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in 70% yield and has similar properties to those of $TcO_3Cl(bpy)$; mp 134 °C dec.

Anal. Calcd for $C_{13}H_8BrN_2O_3Tc$: C, 31.35; H, 2.11; Br, 20.86; N, 7.31. Found: C, 32.31; H, 2.22; Br, 21.28; N, 7.39. Optical spectrum in CH_3CN: 301 (1.7×10^4). IR (KBr): $\nu_{Tc=O}$ 902 (s), 881 (s), 856 (m). Raman: $\nu_{Tc=O}$ 902 (m), 881 (m) cm^{-1}.

Trioxochloro(2,2′-bipyridine)rhenium(VII). To a 50-mL round-bottom flask were added a stirbar, 0.20 g of $NaReO_4$ (0.73 mmol), EtOH (8 mL), and 12 N HCl (2 mL). This mixture was refluxed with stirring. When all the $NaReO_4$ had dissolved, 0.50 g of bpy (3.2 mmol) in EtOH (10 mL) was added.

After 20 min of refluxing, a very pale yellow solid had precipitated. This solid was isolated by suction filtration, washed with 12 N HCl (5 mL) in EtOH (10 mL) and dried in vacuo. The yield of $ReO_3Cl(bpy)$ was 0.09 g (0.21 mmol), 29% based on Re; mp 283 °C dec. This material has an infrared spectrum identical with that reported by Guest and Lock[8] for $ReO_3Cl(bpy)$ prepared by the reaction of ReO_3Cl and bpy in dry carbon tetrachloride.

Anal. Calcd for $C_{10}H_8ClN_2O_3Re$: C, 28.20; H, 1.90; Cl, 8.32; N, 6.58. Found: C, 28.31; H, 1.73; Cl, 8.30; N, 6.62. IR (KBr): $\nu_{Re=O}$ 945 (s), 925 (s), 910 (s), 885 (m) cm^{-1}. The material was too insoluble in CH_3CN for an accurate determination of its optical spectrum.

Oxotrichloro(2,2′-bipyridine)technetium(V). To a 50-mL round-bottom flask were added a stirbar, 0.21 g of $n\text{-}Bu_4NTcOCl_4$ (0.42 mmol), and EtOH (15 mL). Upon addition of 12 N HCl (3 mL), the stirred green-yellow solution turned pale green. To this solution was added dropwise 0.39 g of bpy (2.5 mmol) dissolved in EtOH (10 mL). Within 5 min a yellow-orange solid had precipitated. After 10 min this solid was isolated by suction filtration and washed with EtOH (5 mL) and dried in vacuo. The yield of $TcOCl_3(bpy)$ was 0.16 g (0.41 mmol), 98% based on Tc, mp 240 °C dec. This material is very slightly soluble in CH_2Cl_2 and moderately soluble in CH_3CN and acetone. The material was recrystallized by slow evaporation of an acetone/12 N HCl (4:1 v/v) solution. The material is stable to oxygen both in the solid state and in solution but is very water sensitive.

Anal. Calcd for $C_{10}H_8Cl_3N_2OTc$: C, 31.81; H, 2.14; Cl, 28.17; N, 7.42. Found: C, 31.73; H, 2.42; Cl, 28.12, N, 7.41. Optical spectrum in CH_3CN nm (ϵ L mol^{-1} cm^{-1}), 920 (28), 285 (2.2×10^4), 298, 310 (sh). Conductivity (CH_3CN, 10^{-3} M): $\Lambda_M = 3.3\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (KBr): $\nu_{Tc=O}$ 980 (s).

Oxotribromo(2,2′-bipyridine)technetium(V). To a 50-mL round-bottom flask were added a stirbar, EtOH (25 mL), and 0.15 g of $n\text{-}Bu_4NTcOBr_4$ (0.22 mmol). When all the $n\text{-}Bu_4NTcBr_4$ dissolved, 48% HBr was added (5 mL). To this stirred solution was added dropwise 0.34 g of bpy (2.2 mmol) dissolved in EtOH (10 mL). Within 5 min, an orange solid had precipitated. After 10 min, the solid was isolated by suction filtration, washed with EtOH (2 × 10 mL), and dried in vacuo. The yield of $TcOBr_3(bpy)$ was 0.04 g (0.078 mmol), 35% based on Tc; mp 265 °C dec. This material is moderately soluble in CH_3CN and acetone and was recrystallized by slow evaporation of an acetone/toluene (5:1 v/v) solution yielding red crystals.

Anal. Calcd for $C_{10}H_8Br_3N_2OTc$: C, 23.51; H, 1.58; Br, 46.92; N, 5.48. Found: C, 23.58; H, 1.57; Br, 46.88; N, 5.48. Optical spectrum in CH_3CN: 365 (5.1×10^3), 289 (1.4×10^4), 300, 310 (sh). Conductivity (CH_3CN 10^{-3} M). $\Lambda = 8.6\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (KBr): $\nu_{Tc=O}$ 969 (s). ^1H NMR (acetone-d_6): a complex multiplet between 9.2 and 7.4 ppm, characteristic of bpy. A ^{13}C NMR spectrum could not be obtained because of the limited solubility of the complex.

Oxotrichloro(1,10-phenanthroline)technetium(V) Hydrate. To a 50-mL round-bottom flask were added to a stirbar, EtOH (10 mL), and 1.00 mL of 0.379 M NH_4TcO_4 (0.3 mmol). To the stirred solution was added 0.55 g of phen·H_2O (2.8 mmol) dissolved in EtOH (15 mL). To this solution was added dropwise 12 N HCl (2 mL). The reaction mixture was refluxed with stirring for 1.5 h. After filtration, 12 N HCl (10 mL) was added to the yellow- orange filtrate. During a 24-h period, the EtOH evaporated, yielding a yellow-orange microcrystalline product which was isolated by suction filtration and dried in vacuo. The yield of $TcOCl_3(phen)\cdot H_2O$ was 0.07 g (0.16 mmol), 57% based on Tc; mp 196 °C dec. The material was recrystallized by slow evaporation of an acetone/12 N HCl (4:1 v/v) solution. The solubility of $TcOCl_3(phen)\cdot H_2O$ is similar to the analogous bipyridyl complex. This procedure was used for the synthesis of $TcOCl_3(bpy)$ and $TcOBr_3(bpy)$, but $TcOCl_3(phen)\cdot H_2O$ could not be prepared from $n\text{-}Bu_4NTcOCl_4$ and phen in ethanolic HCl.

Anal. Calcd for $C_{12}H_{10}Cl_3N_2O_2Tc$: C, 34.35; H, 2.41; Cl, 25.38; N, 6.68. Found: C, 34.63; H, 1.97; Cl, 25.47; N, 6.72. Optical spectrum in CH_3CN: 269 (2.7×10^4), 320 (sh). Conductivity (CH_3CN, 10^{-3} M) $\Lambda_M = 18.7\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (KBr): $\nu_{Tc=O}$ 977 (s).

Oxodichloroethoxy(2,2′-bipyridine)technetium(V). To a 50-mL round-bottom flask with side arm were added a stirbar and 0.11 g of $n\text{-}Bu_4TcOCl_4$ (0.22 mmol). To another 50-mL round-bottom flask with side arm were added a stirbar and 0.42 g of bpy (2.69 mmol). Both flasks were evacuated and filled with N_2 three times. To each flask was added 15 mL of EtOH (dried by distillation from $Mg(OEt)_2$) with the use of a cannula. After both the bpy and $n\text{-}Bu_4NTcOCl_4$ had dissolved, the bpy solution was transferred via a cannula into the stirred $n\text{-}Bu_4NTcOCl_4$ solution. The solution turned green, and a green precipitate formed within 1 min. After 10 min, the product was isolated by suction filtration, washed with cold acetone (2 × 5 mL), and dried in vacuo. The yield of $TcOCl_2(OEt)(bpy)$ was 0.05 g (0.12 mmol), 55% based on Tc; mp 146 °C dec. This material is unstable in the organic solvents in which it dissolves (CH_2Cl_2, acetone, CH_3CN, DMF).

Anal. Calcd for $C_{12}H_{13}Cl_2N_2O_2Tc$: C, 37.23; H, 3.39; Cl, 18.32, N. 7.24. Found: C, 37.15; H, 3.39; Cl, 18.34; N, 7.20. IR (KBr): 2970 (w), 2920 (w), 2840 (w), 575 (m), and $\nu_{Tc=O}$ 922 (s) (shoulders at 930 and 900).

Results

Complexes of technetium(VII) with the formulation TcO_3XL (for L = bpy, X = Cl, Br; for L = phen, X = Cl) have been prepared by the reaction of NH_4TcO_4 with the ligands L in the corresponding ethanolic aqueous haloacids at room temperature. These complexes are only sparingly soluble in organic solvents, are readily reduced (vide infra), and therefore could not be recrystallized. The known rhenium complex $ReO_3Cl(bpy)$, originally prepared from ReO_3Cl, can be prepared similarly from $NaReO_4$ except the reaction must be performed under reflux.

In refluxing ethanolic HX, either NH_4TcO_4 or TcO_3XL was reduced to the technetium(V) state, allowing the isolation of the neutral complexes $TcOX_3L$. The rhenium analogue, $ReO_3Cl(bpy)$, cannot be reduced to the known complex $ReOCl_3(bpy)$ under these conditions. It requires a more powerful reducing agent such as H_3PO_2 to be present in the reaction mixture.[9]

The technetium(V) complexes $TcOX_3(bpy)$ (X = Cl, Br) were prepared independently from $n\text{-}BuN_4TcOX_4$ and bpy in ethanolic aqueous HX. The phen complex could not be prepared in this manner. These new technetium(V) complexes are moderately soluble in polar organic solvents and can be readily recrystallized. They are nonconductors in acetonitrile. If HCl is omitted in the reaction of $n\text{-}Bu_4NTcOCl_4$ with bpy, the ethoxy complex, $TcOCl_2(OEt)(bpy)$, is precipitated. The instability of this complex in solution precluded its recrystallization but it precipitated out of solution analytically pure. It can be converted to $TcOCl_3(bpy)$ by treatment with an acetone/12 N HCl (1:1 v/v) mixture.

In addition to the IR bands from the coordinated amine ligands, the $TcOX_3L$ complexes have a single strong band in the range 1000–950 cm^{21} while the TcO_3XL complexes exhibit three bands in the range 910–850 cm^{-1}. The ethoxy complex has a strong band at 922 cm^{-1} as well as bands from the ethoxy ligand. The Raman spectra of the $TcO_3X(bpy)$ complexes exhibit two bands between 905 and 880 cm^{-1} while $TcO_3Cl(phen)$ has a single intense band at 898 cm^{-1}.

Discussion

Perrhenate is a weaker oxidant than pertechnetate. A number of oxygen-containing rhenium(VII) species have been

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obtained.[10,11] These can be considered to be derivatives of the perrhenate ion, ReO_4^-. The reaction of perrhenic acid in concentrated hydrochloric acid produces a yellow solution from which the hydrolytically unstable *fac*-$Cs_2ReO_3Cl_3$ was isolated.[10] The cold concentrated hydrohalic acids HCl and HBr react with TcO_4^- to produce the Tc(V) species, $TcOX_4^-$ that have been conveniently isolated as tetrabutylammonium salts in high yield.[6,7] In some preparations of the chloro complex, a transient yellow species was observed that rapidly reacts to give the green $TcOCl_4^-$. The yellow species is thought to be $TcO_3Cl_3^{2-}$ by analogy to the known rhenium chemistry.

In an attempt to characterize such a species, the reaction of TcO_4^- with cold, ethanolic hydrohalic acids in the presence of bpy and phen was undertaken. This led to the formation of the technetium(VII) complexes, TcO_3XL. These complexes were readily isolated due to their insolubility in the reaction medium. They are hydrolytically unstable, giving TcO_4^- upon reaction with H_2O, and are sparingly soluble in polar organic solvents. Their formulation is based on elemental analyses and vibrational spectroscopy.

Heating the reaction mixture causes reduction to the technetium(V) species, $TcOX_3L$. Alternatively, when L = bpy, these complexes can be prepared from *n*-Bu_4NTcOX_4 and ethanolic HX containing excess bpy. It is important that HCl is present in this preparation of $TcOCl_3$(bpy), otherwise the unstable ethoxy compound $TcOCl_2$(OEt)(bpy) is produced. The latter can be converted to $TcOCl_3$(bpy) by treatment with acetone/HCl.

The oxo-technetium(V) complexes are nonelectrolytes in CH_3CN and show a single strong Tc=O stretch in their infrared spectra. The band assigned to the Tc=O stretch in $TcOCl_3$(bpy) occurs at lower energy (ca. 10 cm^{-1}) than that found in the analogous rhenium complex.[9] This difference can be explained by the greater orbital overlap of 5d orbitals (Re) with the 2p orbitals of oxygen contrasted with that of 4d orbitals (Tc).[5] The 575-cm^{-1} band in $TcOCl_2$(OEt)(bpy) is in the range of metal-alkoxide stretches.[12]

The geometry of the MO_3XL species is likely to be a facial arrangement in keeping with the known tendency of d^0 metals to have mutually cis oxo ligands.[11,13] This is supported by the fact that the TcO_3X(bpy) complexes show two bands in the Tc=O region of the Raman spectra which is consistent with an idealized C_{3v} symmetry of the oxo ligands.

The isolation of these technetium(VII) complexes with poorly reducing ligands shows that such complexes are capable of existence, and, therefore, there may be similar heptavalent intermediates in the reactions of MO_4^- (M = Re, Tc) under acidic conditions that lead to the preparation of complexes in lower oxidation states with other ligands.

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Registry No. Trioxochloro(2,2′-bipyridine)technetium(VII), 78939-76-1; trioxochloro(1,10-phenanthroline)technetium(VII), 78939-77-2; trioxobromo(2,2′-bipyridine)technetium(VII), 78939-78-3; trioxochloro(2,2′-bipyridine)rhenium(VII), 57526-16-6; oxotrichloro(2,2′-bipyridine)technetium(V), 78939-79-4; oxotribromo-(2,2′-bipyridine)technetium(V), 78939-80-7; oxotrichloro(1,10-phenanthroline)technetium(V), 78939-81-8; oxodichloroethoxy-(2,2′-bipyridine)technetium(V), 78939-82-9.

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Infrared Spectroscopic Characterization of Metal Cluster Complexes. Hydrohalogenation Products of $Ru_5C(CO)_{15}$

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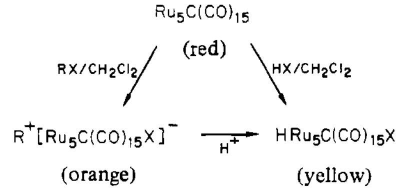
The hydrohalogenation products of the semiinterstitial carbido metal clusters $Ru_5C(CO)_{15}$, $HRu_5C(CO)_{15}Cl$, and $HRu_5C(CO)_{15}Br$ have been examined by infrared spectroscopy in the solid state. The presence of μ-bridging hydride and terminal halide was inferred. The infrared absorptions due to the carbido ligands in the spectra of the two halide complexes differ considerably from those observed in the spectrum of $Ru_5C(CO)_{15}$. A structural rearrangement of the Ru_5C skeleton on hydrohalogenation, to a bridged butterfly configuration, similar to that found in an analogous osmium cluster, is postulated.

Introduction

This paper deals with the infrared spectroscopic characterization of the metal cluster species which were recently reported to result from the hydrohalogenation of the semiinterstitial carbido cluster $Ru_5C(CO)_{15}$.[1] Considerable interest is attached to the reactions of carbido species of this type in view of their potential catalytic value (see, for example, ref 2). The carbido complexes $M_5C(CO)_{15}$, M = Fe, Ru, and Os, are isostructural, each such cluster unit being composed of a square pyramid of metal atoms with the carbido atom located slightly (ca. 0.1 Å) below the basal plane.[3-5] Despite the presence of the four *axial* carbonyl groups which are disposed around it, the carbido atom is thus somewhat exposed.

Scheme I



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