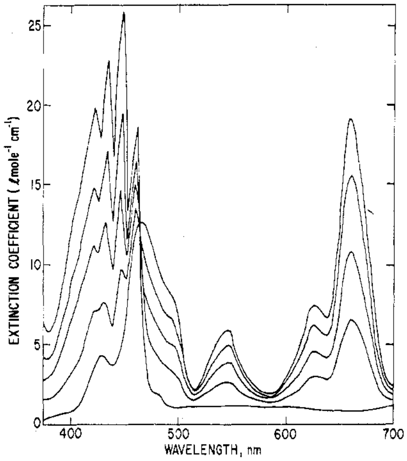

Figure 4. Oxidation by air of U(IV) (0.02 M) in $NaHCO_3$ (1 M) as followed in the visible spectrum. An isosbestic point occurs at 465 nm. Absorbance less than 465 nm increases as the oxidation proceeds, while absorbance greater than 465 nm decreases.

scan rates. The U(IV) peak current is greater than that for U(V) since the disproportionation reaction is completed. As the scan rate is increased, the anodic scan is completed before the disproportionation reaction proceeds to any great extent. Thus, an anodic peak at ca. −0.47 V corresponding to oxidation of U(V) is the only feature at the fastest scan rates. The anodic peak at ca. −0.30 V, which occurs between the two major peaks, is ascribed to the oxidation of an intermediate species. From studies in carbonate media, the anodic wave corresponding to oxidation of U(V) is known to occur at ca. −0.50 V, i.e., the wave seen at the fastest scan rates. At slower scan rates, disproportionation has produced some intermediate, the oxidation wave of which is postulated to occur at ca. −0.30 V. However, at the same scan rates at which the intermediate is first observed, the oxidation wave of U(IV) also appears. Thus, the intermediate that is produced quickly undergoes disproportionation while U(V) may exist for a time that is relatively long compared to the lifetime of the intermediate.

Controlled-potential reduction at −1.25 V of 0.01 M UO_2^{2+} in 1 M $NaHCO_3$ solution gives an average value of 2.00 ± 0.03 electrons for each uranium. Reduction of the solution is accompanied by a color change from yellow to pale brownish yellow. Cyclic voltammograms of the reduced solution show a cathodic wave at ca. −1.05 V and an anodic wave at ca. 0.12 V. It is interesting to note that repetitive scans of the reduced solution indicate a buildup of both U(VI) and U(V) in the diffusion layer.

The visible spectrum of the reduced solution is similar to that of U(IV) in carbonate.[4] Comparison with previously reported spectra of $U(CO_3)_x^{(4-2x)+}$ complexes,[10] U(IV) polymeric solutions,[11] and a $U(OH)^{3+}$ spectrum[12] shows a remarkable degree of similarity in view of the widely differing systems. The major peaks (with extinction coefficients in parentheses) are located at 430 (4.45), 466 (12.8), 495 (sh, 8.25), 547 (5.85), 625 (7.45), and 660 (19.1) nm. The solution follows Beer's law over the concentration range 0.02–0.001 M.

Figure 4 shows the changes in the visible spectrum as U(IV) in bicarbonate is oxidized by air. The initial U(IV) spectrum gradually changes to that of $UO_2(CO_3)_3^{4-}$. An isosbestic point occurs at 465 nm. The occurrence of the isosbestic point is consistent with the oxidation proceeding to only one product. Therefore, the U(IV) species may prove to be an excellent 2-equiv reductant in basic solution.

Chemical synthesis of the U(IV)–bicarbonate species is readily accomplished by dissolving UCl_4 in 1 M $NaHCO_3$. Addition of solid UCl_4 to 1 M $NaHCO_3$ leads initially to a greenish precipitate which readily dissolves on gentle heating. Cyclic voltammograms and visible spectra of this solution are identical with those of solutions produced by electrochemical reduction of UO_2^{2+} in 1 M $NaHCO_3$.

Registry No. $UO_2(ClO_4)_2$, 13093-00-0; U, 7440-61-1.

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Technetium Radiopharmaceutical Development. 2. Preparation, Characterization, and Synthetic Utility of the Oxotetrahalotechnetate(V) Species $TcOX_4^-$

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Received February 13, 1980

The preeminence of ^{99m}Tc in diagnostic nuclear medicine has led to considerable interest in developing the nascent inorganic chemistry of technetium.[3] To this end our research groups have recently prepared and characterized the complexes $TcOCl_4^-$[4] and $TcHBPz_3Cl_2O$[5] ($HBPz_3^-$ = hydrotris(1-pyrazolyl)borate anion) utilizing the long-lived ^{99}Tc isotope. We have now extended this work to include the bromo analogues $TcOBr_4^-$ and $TcHBPz_3Br_2O$. It appears that $TcOX_4^-$ anions are probable intermediates in the preparation of the poly(1-pyrazolyl)borate complexes, and we have thus focused our attention on these oxotetrahalotechnetate(V) anions as valuable synthetic starting materials for the development of technetium radiopharmaceuticals.

Experimental Section

General Data. All common laboratory chemicals were of reagent grade. The $NH_4{}^{99}TcO_4$, containing technetium-99 of >99% radiochemical purity, was obtained from Oak Ridge National Laboratories, Oak Ridge, TN. $K^{99}TcO_4$ was made from NH_4TcO_4 by metathesis with KOH and was twice recrystallized from water. Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, TN. Hexane and dichloromethane were dried over 3-Å molecular sieves for 1 week prior to use. Visible–UV spectra were recorded on a Varian 634 spectrophotometer at ambient temperature in dichloromethane. Mass spectra were obtained by using a RMU-7 instrument at 50 eV and 50 °C. ^1H NMR spectra were obtained with a Varian T-60 instrument in acetone-d_6 (internal Me_4Si reference). IR spectra were recorded on a Perkin-Elmer 599 in Nujol mulls and KBr pellets. The laser Raman spectrum was obtained in the solid state through the courtesy of Dr. J. E. Smith, Union Carbide Corp., Tarrytown, NY.

Tetrabutylammonium Oxotetrabromotechnetate(V), $[(n\text{-}Bu)_4N]TcOBr_4$. To 43.0 mg of $KTcO_4$ held at 0 °C in a 10-mL beaker was added 2.0 mL of 48% HBr at ambient temperature. The resulting mixture was stirred at 0 °C, and as the $KTcO_4$ dissolved, the mixture

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0020-1669/80/1319-2840$01.00/0

turned yellow. After 40 min, the $KTcO_4$ had dissolved, and the solution was dark yellow-brown. To this solution was added 4.0 mL of 0.38 M aqueous tetra-*n*-butylammonium bromide at 0 °C. The resultant light green precipitate was removed by filtration and successively washed with three 4.0-mL aliquots of 4.0 M HBr and two 4.0-mL aliquots of a 1:3 mixture of isopropyl alcohol and isopropyl ether. This precipitate was recrystallized from dry CH_2Cl_2/hexane to yield large green-yellow plates. The yield of recrystallized product (on the basis $KTcO_4$) after being dried for 2 days at 25 °C, ca. 0.1 torr, was 60%. Anal. Calcd for $[C_{16}H_{36}N]TcOBr_4$: C, 28.38; H, 5.36; N, 2.07; Br, 47.20. Found: C, 28.45; H, 5.35; N, 2.16; Br, 47.03.

Dibromo[hydrotris(1-pyrazolyl)borato]oxotechnetium(V), $TcHBPz_3Br_2O$. This complex was prepared by first generating $TcOBr_4^-$ in situ. To 100 mg of $KTcO_4$ was added 6.0 mL of 48% HBr as above. After 40 min, 1.0 g of $KHBPz_3$ dissolved in 10 mL of 0 °C water was added; the reaction mixture became cloudy and was stirred for an additional 20 min before the volume was adjusted to 40 mL with 0 °C water. After 30 min, the crude yellow-brown product was removed by filtration and washed with seven 5.0-mL aliquots of cold water. This crude product was dissolved in CH_2Cl_2 and purified by chromatography on silica gel (CH_2Cl_2 matrix). After removal of the solvent and drying of the product for 8 h at 25 °C, ca. 1.0 torr, the yield was 40%. Anal. Calcd for $C_9H_{10}N_6BTcOBr_2$: C, 22.16; H, 2.06; N, 17.23; B, 2.21; Br, 32.76; mol wt 487. Found:[6] C, 22.33; H, 2.06; N, 17.47; B, 2.00; Br, 33.05; mol wt 477.

Dichloro[hydrotris(1-pyrazolyl)borato]oxotechnetium(V), $TcHBPz_3Cl_2O$. This complex was prepared by initially generating $TcOCl_4^-$ in situ. A solution of 41.2 mg of $KTcO_4$ in 2.5 mL of 12 M HCl at 25 °C was stirred for 20 min. To this stirred solution was added 2.5 mL of 0.40 M aqueous $KHBPz_3$, and the solution was stirred for an additional 10 min. As the reaction proceeded, the solution turned bright green and became slightly cloudy; 4.5 mL of 0 °C water was then added. After 2.5 h, the light green product was removed by filtration, washed with three 10-mL aliquots of water, and vacuum dried (yield 21.0 mg (26%)). To the bright green filtrate were added 15 mL of dichloromethane and then an additional 4.0 mL of water. The green product was rapidly extracted, and evaporation of the dichloromethane layer yielded a green crystalline product. The yield after drying under vacuum for 24 h was 49.2 mg (60%), giving an overall yield of 86%. The visible–UV, IR, and ^1H NMR spectra of this material are in good agreement with previously published[5] spectral data for $TcHBPz_3Cl_2O$.

Results

$[(n\text{-}Bu)_4N]TcOBr_4$ is soluble in dichloromethane and acetone but appears to react with donor solvents such as *N*,*N*-dimethylformamide, dimethyl sulfoxide, and acetonitrile. The complex is sensitive to the presence of water, decomposing to yield $TcO_2 \cdot xH_2O$ and TcO_4^-. The visible–UV spectrum in dichloromethane exhibits absorption maxima at 615, 478, 353, and 248 nm (ϵ = 22, 113, 3750, and 10 400 m^{-1} cm^{-1}, respectively). The IR spectrum obtained in Nujol (Figure 1B) exhibits strong absorptions at 1011 and 306 cm^{-1} which are assigned as the $Tc{=}O$ and Tc–Br stretches, respectively. The IR spectra of $[(n\text{-}Bu)_4N]TcOBr_4$ and $[(n\text{-}Bu)_4N]TcOCl_4$ are compared in Figure 1. Grinding the chloro analogue in KBr yields the bromo derivative via a solid-state reaction (Figure 1C). Likewise, grinding $[(n\text{-}Bu)_4N]TcOCl_4$ in KI yields a material that has an IR spectrum consistent with that expected for $[(n\text{-}Bu)_4N]TcOI_4$ ($Tc{=}O$ stretch at 993 cm^{-1}, vide infra).

$TcHBPz_3Br_2O$ is insoluble in water and soluble in most polar organic solvents. The visible–UV spectrum exhibits maxima at 792 and 333 nm (ϵ = 78 and 5900 m^{-1} cm^{-1}, respectively) and a shoulder at ca. 375 nm. The IR spectrum (Table I) exhibits absorptions at 2520 and 288 cm^{-1} which are assigned as the B–H and Tc–Br stretches, respectively; the absorption at 970 cm^{-1} is tentatively assigned to the $Tc{=}O$ stretch. The Raman spectrum exhibits analogous absorptions at 283 and 967 cm^{-1}. $TcHBPz_3Br_2O$ exhibits a normal diamagnetic ^1H NMR spectrum; the assignments made in Table I are in accordance with those previously published for the chloro analogue.[5] The mass spectrum of $TcHBPz_3Br_2O$ shows intense

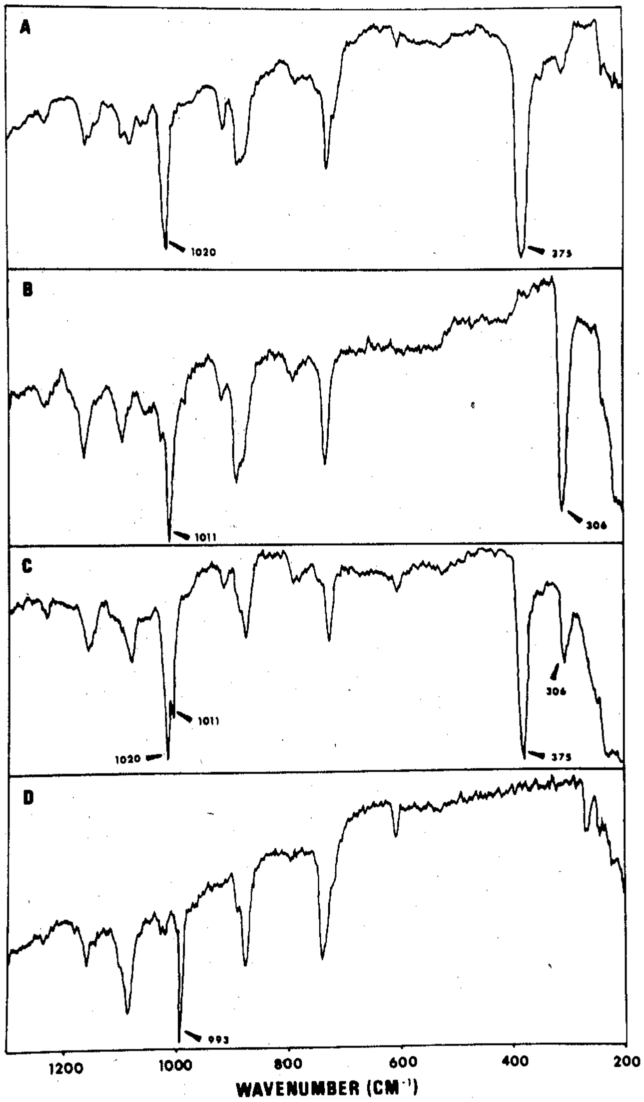

Figure 1. IR spectra: (A) $[(n\text{-}Bu)_4N]TcOCl_4$ in Nujol using CsI windows; (B) $[(n\text{-}Bu)_4N]TcOBr_4$ in KBr (spectrum obtained in a KBr pellet); (C) a mixture of $[(n\text{-}Bu)_4N]TcOCl_4$ and $[(n\text{-}Bu)_4B]TcOBr_4$ produced by grinding $[(n\text{-}Bu)_4N]TcOCl_4$ in KBr (spectrum obtained in a KBr pellet); (D) $[(n\text{-}Bu)_4N]TcOI_4$ in Nujol using CsI windows.

Table I. Spectral Parameters for $TcHBPz_3Br_2O$

A. ^1H NMR[a,b] Data

	position			
pyrazolyl ring	5	4	3	integratn ratio
trans to O	7.2 d	5.9 t	7.55 d	1
trans to Br	8.3 d	6.8 t	8.65 d	2

B. IR[c,d] Data

3120 m, 2510 m, 1495 m, 1435 m, 1400 vs, 1385 s, 1305 vs, 1205 vs, 1180 m, 1110 s, 1055 vs, 1020 w, 970 vs, 960 w, 915 m, 850 s, 825 w, 805 m, 790 s, 760 vs, 705 m, 660 w, 645 w, 610 s, 460 w, 400 w, 370 w, 345 vw, 285 s

C. Raman[c,e] Data

1380 w, 1310 vw, 1210 vw, 1180 w, 967 vs, 925 w, 705 vw, 310 w, 282 s, 235 vw, 220 vw, 165 m

[a] Spectrum determined in acetone-d_6. Chemical shifts (δ) are given relative to internal Me_4Si. [b] t = triplet, d = doublet. [c] ν values in cm^{-1}; v = very, s = strong, m = medium, w = weak. [d] Spectrum obtained as a KBr pellet. [e] Spectrum obtained in the solid state.

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[6] Analyses performed on the crude product.

peaks in the molecular ion region with a typical isotopic abundance pattern for a molecule containing two bromine atoms: m/e peaks at 486, 488, and 490 in a 1:3:1 ratio.

$TcHBPz_3Cl_2O$ was characterized by comparison of spectral data to that previously published.[5] The mass spectrum of this complex shows the appropriate isotopic distribution pattern in the molecular ion region: m/e peaks at 398, 400, and 402 in a 10:6.5:1 ratio.

Discussion

Synthesis and Characterization. Synthesis of the $TcOX_4^-$ complexes is based on control of the relative rates of HX reduction of Tc(VII) to Tc(V) and of Tc(V) to Tc(IV). In all cases (X = Cl, Br, I) the Tc(IV) complex TcX_6^{2-} is the thermodynamically stable product. When concentrated HCl at 25 °C is used as the reductant, Tc(V) is rapidly produced, but subsequent reduction to Tc(IV) is very slow. Thus the simple addition of TcO_4^- to concentrated HCl at ambient temperature provides a ready route to $TcOCl_4^-$.[4] However, when concentrated HBr at 25 °C is used as the reductant, Tc(IV) is rapidly produced, and Tc(V) is only transiently observed. By the simple expedient of lowering the reaction temperature to 0 °C, the rate of HBr reduction of $TcOBr_4^-$ can be sufficiently retarded to allow the preparation and isolation of this species. This approach can be further extended to the iodo derivative; a material with the IR spectrum expected for $[(n\text{-}Bu)_4N]TcOI_4$ (Tc=O stretch at 993 cm^{-1}, Figure 1D) can be prepared from TcO_4^- and concentrated HI at very low temperature (isopropyl alcohol/dry ice bath).

The $TcOBr_4^-$ anion is characterized by elemental analysis of an isolated salt and by comparison of IR and visible–UV spectral parameters with those reported for the established[4] (by single-crystal X-ray structure analysis) $TcOCl_4^-$ analogue. The $TcOI_4^-$ anion is characterized by comparison of its IR spectrum with those of the chloro and bromo analogues; for X = Cl, Br, and I the Tc=O stretching frequency in $TcOX_4^-$ occurs at 1020, 1011, and 993 cm^{-1}, respectively. The iodo derivative is the least stable of the three analogues and suffers considerable decomposition (presumably via internal redox reactions) during isolation.

The tris(1-pyrazolyl)borate derivatives $TcHBPz_3Cl_2O$ (X = Cl, Br) are readily prepared from the $TcOX_4^-$ anions generated in situ (eq 1). This direct substitution reaction provides

$$HBPz_3^- + TcOX_4^- \rightarrow TcHBPz_3X_2O + 2X^- \qquad (1)$$

a much more facile synthesis of $TcHBPz_3Cl_2O$ than that which was previously reported.[5] Even in the earlier synthesis, based on the reduction of TcO_4^- in the presence of $HBPz_3^-$ in 3 M HCl, $TcOCl_4^-$ is a likely reaction intermediate. The lability of the chloro ligands in $TcOCl_4^-$ is further demonstrated by the ready conversion of this species to $TcOBr_4^-$ and $TcOI_4^-$ through simple grinding in KBr or KI.

$TcHBPz_3Br_2O$ is characterized by elemental analysis, by comparison of IR, ^1H NMR and visible–UV spectral parameters with those reported for the established[5] (by single-crystal X-ray structure analysis) $TcHBPz_3Cl_2O$ analogue, and by mass spectral analysis. In the visible spectrum the low-intensity band at 798 nm is presumably a d–d transition; the corresponding transition for the chloro analogue occurs at 784 nm, indicating that bromide provides a weaker ligand field than does chloride in these spin-paired, d^2, Tc(V) complexes. In the UV spectrum the high-intensity band at 333 nm is presumably a halide-to-metal charge-transfer transition; the corresponding transition for the chloro complex occurs at 311 nm, consistent with the greater reducing power of bromide relative to chloride.

Radiopharmaceutical Development. The successful preparation of $TcHBPz_3X_2O$ (X = Cl, Br) from $TcOX_4^-$ indicates that the $TcOX_4^-$ anions are effective synthetic starting materials for the preparation of complexes containing the $Tc^{V}{=}O$ core. Some useful aspects of the $TcOX_4^-$ starting materials relevant to the preparation of potential ^{99m}Tc radiopharmaceuticals are as follows: they may be rapidly prepared and modified under conditions relevant to clinical applications; they do not have to be isolated and may be modified in situ to other more chemically stable species; the tightly bonded $Tc^{V}{=}O$ core should serve as a useful template about which to construct radiopharmaceuticals that will retain their integrity in vivo.

Acknowledgment. Financial support for this work was provided by the National Institutes of Health, Grant HL-21276 (E.D.) and Grant GM-23270 (A.D.).

Registry No. $[(n\text{-}Bu)_4N]TcOBr_4$, 73953-03-4; $[(n\text{-}Bu)_4N]TcOCl_4$, 71341-65-6; $[(n\text{-}Bu)_4N]TcOI_4$, 73940-66-6; $TcHBPz_3Br_2O$, 73940-67-7; $TcHBPz_3Cl_2O$, 71835-95-5; $KTcO_4$, 13718-33-7.

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A Binuclear Ruthenium(III) Histidine Complex: Selective Binding of the Metal Ions at the Two Nitrogens of the Imidazole Ring

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Received May 18, 1979

The presence of histidine in the active sites of a large number of metalloenzymes[1] has led to numerous studies involving the binding of imidazole and histidine to metal ions.[2] More recently structural evidence for the involvement of the deprotonated imidazole of histidine as a bridge between copper and zinc in bovine erythrocyte superoxide dismutase has been forwarded as a result of crystallographic studies on the enzyme.[3] The possibility of deprotonated imidazole bridging between copper and iron in cytochrome oxidase has also been suggested by Palmer et al.[4] The above results have increased the interest in studying the properties of bridged binuclear complexes with deprotonated imidazole as a bridging ligand.[5–8]

The possible role of imidazole as a bridging ligand led us to investigate the properties of binuclear metal complexes with deprotonated imidazole as a bridging ligand when bound to kinetically inert transition-metal ions.[7] We have previously reported on the synthesis, characterization, and electrochemical properties as well as the electron-mediating properties of the deprotonated imidazolate anion in binuclear cobalt and ruthenium complexes.[7] In this paper we have extended our studies to the synthesis of a binuclear histidine complex where the two metal ions are selectively bound to the two nitrogens of the deprotonated imidazolate anion. The synthesis, characterization, and some properties of this first binuclear histidine complex are reported and compared to the previously syn-

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