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Preparation, Crystal and Molecular Structure of Tetraethylammonium Oxotetrabromoaquo-technetium(V)

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Abstract

The preparation, chemical characterization and the X-ray structure of $[(CH_3CH_2)_4N][TcOBr_4(H_2O)]$ are described. The crystals are orthorhombic, space group *Pnma*, with $a = 11.155(4)$, $b = 12.929(2)$, $c = 11.531(1)$ Å and $Z = 4$. The structure was solved by the automatic direct-method routine and was refined using the full-matrix least-squares cycles which gave the final R values of $R = 5.41\%$ and $R_w = 5.44\%$. The oxygen atoms are *trans* to each other. Tc=O and Tc–O bond lengths are 1.618(9) and 2.317(9) Å, respectively.

Introduction

Tc(V) complexes of the type $[TcOX_4]^-$ serve as important starting materials for the preparation of a wide variety of oxotechnetium(V) complexes. The five-coordinate $TcOX_4^-$ ion is formed when pertechnetate $(TcO_4)^-$ is treated in a concentrated HX (X = Cl, Br) solution, under the presence of large cations such as $(n\text{-}C_4H_9)_4N^+$ and $(C_6H_5)_4N^+$ [1, 2]. On the other hand, with small K^+, Rb^+, Cs^+ and NH_4^+ cations, six-coordinated species of the type $[TcOX_5]^{2-}$ are obtained [3–6]. However the role of the counterion in the differentiating formation of $[TcOX_4]^-$ from that of $[TcOX_5]^{2-}$ is not yet clear. Interestingly, we found that the addition of tetraethylammonium bromide to a concentrated HBr solution of TcO_4^- yielded $[(CH_3CH_2)_4N][TcOBr_4]$ [6], while for the related chloride system, formation of $[(CH_3CH_2)_4N]_2[TcOCl_5]$ was reported [5].

Since all attempts to grow single crystals of salts of either $[TcOBr_4]^-$ or $[TcOX_5]^{2-}$ (X = Cl, Br) were unsuccessful, $[(n\text{-}Bu)_4N][TcOBr_4]$ and $Cs_2[TcOX_5]$ (X = Cl, Br), have been structurally characterized by EXAFS [5]. However, the precise composition of the coordination sphere could not be obtained by this technique.

In the present paper, we report the isolation, chemical characterization and X-ray crystal structure determination of $[(CH_3CH_2)_4N][TcOBr_4(H_2O)]$, which is the first well characterized bromo-oxotechnetium(V) complex. A single example of the structurally well characterized tetrahalogeno-oxotechnetium is $[(Ph_3P)_2N][TcOCl_4]$ [7].

Experimental

Materials

An ammonium pertechnetate solution (^{99}Tc) was obtained from the Radiochemical Center, Amersham. All common laboratory chemicals were of reagent grade.

Preparation of $[(CH_3CH_2)_4N][TcOBr_4(H_2O)]$

This compound was obtained by reduction of NH_4TcO_4 (5.4 mg) with 0.1 ml HBr (48%) in a 2 ml beaker kept at −5 °C. The resulting mixture was stirred, and as the NH_4TcO_4 dissolved, the solution turned yellow. After 20 min, the salt was completely dissolved to give a dark yellow–brown solution. The addition of 0.1 ml of 4 M tetraethylammonium bromide produced a dichroic green orange precipitate which was filtered and washed with 3 ml aliquots, cooled at −5 °C, of 4 M HBr, isopropyl alcohol and diethylether. The compound is soluble and relatively stable in acetonitrile, chloroform, dichloromethane, methylacetate and ethylacetate; unstable in methanol, ethanol and water; insoluble in diethylether and hydrocarbons. The dark brown single crystals suitable for the X-ray diffraction study were grown by slow evaporation (6 weeks) at −15 °C of an acetonitrile–ethylacetate (1:3 vol./vol.) solution.

Spectral Measurements

Infrared spectra were recorded from 50 to 1000 cm^{-1} on an FTIR Brucker IFF 113 C, and from 400

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to 4000 cm^{-1} on a Pye-Unicam Sp 1100. The UV–Vis spectra of solutions were obtained with a Hewlett-Packard 8450 A diode array spectrophotometer.

Data Collection and Processing

A crystal with approximate dimensions 0.5 × 0.4 × 0.2 mm was sealed in a Lindeman capillary tube and was mounted on an Enraf-Nonius CAD-4 automated diffractometer. Lattice parameters were refined by least-squares on the basis of 25 well centered reflections ($0° \leqslant 2\theta \leqslant 20°$) measured with graphite Mo Kα radiation. A total of 2616 reflections having $2\theta < 50°$ were measured using the standard ω–2θ scan technique. Scanning rates of 1.6–5.5°/min were employed, and the scan of each reflection was set 1.5° above and below the calculated Kα doublet. The intensities of three standard reflections were monitored periodically, with no significant variations in intensity during the entire data collection. The reflection data were corrected for Lorentz and polarization effects, but no absorption corrections were made because the crystal dimensions were reasonably uniform. Of 1304 observed reflections with $F_o^2 > 3.0\sigma(F_o^2)$, 1298 reflections were used in the final refinement.

Crystal Data

$TcBr_4O_2NC_8H_{22}$, mol. wt. = 582.9, orthorhombic space group *Pnma* (I.T.C. No 62), a = 11.155(4), b = 12.929(2), c = 11.531(1) Å, V = 1663.1(5) Å^3, Z = 4, $F(000)$ = 1104, T = 295 K, ρ_{calc} = 283 g/cm^3, Mo Kα graphite-monochromatized radiation, (λ = 0.71073 Å), μ(Mo Kα) = 102.4 cm^{-1}.

Structure Analysis and Refinement

All crystallographic computations were performed on a VAX 780 computer with the SHELX-76 PROGRAM [8]. The atomic scattering factors and anomalous dispersion factors were taken from Cromer *et al.* [9]. According to the systematic absences, either $Pn2_1a$ (No. 33 with the b and c axes intechanged) or *Pnma* (No. 62) was possible. Simple E statistics, $|E^2 - 1|$ = 0.93–1.05, favoured the latter centrosymmetric space group, and successful refinement of the structure based on the *Pnma* group proved the choice to be correct. The structure was solved by the automatic centrosymmetric direct-method routine. The technetium and two oxygen atoms were found at sets of fourfold special positions on the mirror plane and two bromine atoms at eightfold general positions. The non-hydrogen atoms $(CH_3CH_2)_4N^+$ were located from difference Fourier synthesis. The nitrogen atom appeared at fourfold special position and two peaks assignable to the terminal carbons of the ethyl groups were found in general positions. Each methylene-bridge carbon atom was disordered between two sites in such a way that the ethyl group has two different orientations with 50% probability for each. Then in all structure factor calculations, the four methylene carbons were assigned a site occupation factor of 0.5, in order to fulfil the symmetry required by the *Pnma* space group. A similar disorder of ethyl group was found in $[(CH_3CH_2)_4N][ReOBr_4(H_2O)]$ [10]. Full-matrix least-squares refinement cycles which incorporated anisotropic thermal parameters for all non-hydrogen atoms gave R = 5.41% and R_w = 5.44% ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ with $w = 1.0(\sigma(F)^2 + 0.001 \times F_o^2)^{-1}$). A difference Fourier map after the final cycle showed two peaks of 2.4 and 2.1 e$^-$/Å^3 on the mirror plane in the vicinity of the Tc atom and all other residual peaks were below 1.4 e$^-$/Å^3. Among these last peaks, one of 0.9 e$^-$/Å^3 was located close to the nitrogen atom, but none in the vicinity of the water-oxygen atom. It was therefore impossible to determine the precise positions of hydrogen atoms of the coordinated water molecule. This is probably due to the disorder of the cation which does not allow a better refinement of the structure.

Results and Discussion

Chemical Characterization

The successful synthesis of the Tc(V) complex is achieved by controlling the relative rates of HBr reduction of Tc(VII) to Tc(V) and Tc(V) to Tc(IV), the last being thermodynamically the most stable product. At room temperature, Tc(IV) is rapidly produced and Tc(V) is only a short-life intermediate. By lowering the temperature to –5 °C, the reduction rate of Tc(V) can be sufficiently delayed to allow the isolation of the $[TcOBr_4(H_2O)]^-$ ion. The UV–Vis spectrum of $[(CH_3CH_2)_4N][TcOBr_4(H_2O)]$ in dichloromethane exhibits absorption maxima at 628, 468, 356, 300 (shoulder), 252 and 230 nm with molar extinction coefficients of 40, 180, 4200, 3200, 8500 and 10000 [l mol^{-1} cm^{-1}], respectively. The results are very similar to those given for $[(n\text{-}C_4H_9)_4N][TcOBr_4]$ [1, 2], indicating the resemblance of the coordination environment in solution. The absorptions are due to forbidden d–d transitions in the visible region and due to halogen (and/or oxygen)-to-metal charge-transfer transitions in the ultraviolet region.

The IR spectra obtained in KBr for the 400–4000 cm^{-1} range and in polyethylene for the 50–1000 cm^{-1} range, show a strong absorption at 1000 cm^{-1}, assignable to the Tc=O stretching vibration. The absorptions at 260 and 160 cm^{-1} with medium intensities are attributed to the Tc–Br stretching and bending modes, respectively and those at 3500, 1600 and 600 cm^{-1} are characteristic absorptions of a water molecule. It has been reported [5] that for five-coordinated complexes of the type $[TcOX_4]^-$, the Tc=O stretching frequencies appear at 1010–1020 cm^{-1} while for six-coordinated $[TcOX_5]^{2-}$ they are in the range 950–954 cm^{-1}. The shift to lower frequencies is due to weakening of the Tc=O bond upon coordination of an X^- ligand in the position *trans* to the oxygen atom. The absorptions at 3500, 1600 and 600 cm^{-1} suggest the presence of a water molecule in the coordination sphere of the complex studied in this work. The stretching frequency at 1000 cm^{-1}, a value rather similar to that for $[(n\text{-}C_4H_9)_4N][TcOBr_4]$ (1010 cm^{-1}), indicates a weak coordination of a water molecule in the *trans* position. The formula $[TcOBr_4(H_2O)]^-$ suggested by these spectroscopic results, is confirmed by X-ray diffraction.

Structure Description

A listing of fractional coordinates is presented in Table 1, while selected interatomic distances and angles are summarized in Table 2. The crystal structure of the title compound consists of discrete $(CH_3CH_2)_4N^+$ cations and $[TcOBr_4(H_2O)]^-$ anions. A perspective view of the anion is shown in Fig. 1, with the numbering scheme adopted. Figure 2 illustrates

Table 1. Atomic fractional coordinates

Atom	*x*	*y*	*z*
Tc	0.7287(1)	0.25(0)	0.4062(1)
Br1	0.6444(1)	0.3846(1)	0.2726(1)
Br2	0.8606(1)	0.3856(1)	0.4945(1)
O	0.6255(9)	0.25(0)	0.5048(7)
Ow	0.8823(9)	0.25(0)	0.2710(6)
N	0.2424(9)	0.25(0)	0.6156(6)
C1	0.357(2)	0.188(1)	0.623(1)
C11	0.237(2)	0.182(2)	0.506(1)
C2	0.249(2)	0.182(1)	0.726(1)
C22	0.132(2)	0.185(2)	0.609(1)
C3	0.364(1)	0.1135(9)	0.501(1)
C4	0.124(1)	0.1121(9)	0.726(1)

TABLE 2. Selected bond lengths (Å) and angles (°)

Atom–Atom	Distance	Atom–Atom	Distance
Tc–Br1	2.508(1)	N–C	1.55(2)
Tc–Br2	2.505(1)	N–C22	1.50(2)
Tc–O	1.618(9)	C1–C3	1.72(2)
Tc–Ow	2.317(9)	C11–C3	1.67(3)
N–C1	1.51(2)	C2–C4	1.66(2)
N–C11	1.54(2)	C22–C4	1.64(2)
Atoms	**Angle**	**Atoms**	**Angle**
Br2–Tc–Br1	89.1(0)	Br2–Tc–Br2′	88.9(1)
O–Tc–Br1	99.5(3)	C2–N–C11	110(1)
O–Tc–Br2	97.6(2)	C22–N–C1	114(1)
Ow–Tc–Br1	82.2(2)	C3–C1–N	107(1)
Ow–Tc–Br2	80.7(2)	C3–C11–N	108(1)
Ow–Tc–O	177.7(4)	C4–C2–N	106(1)
Br1–Tc–Br1′	87.9(1)	C4–C22–N	109(1)

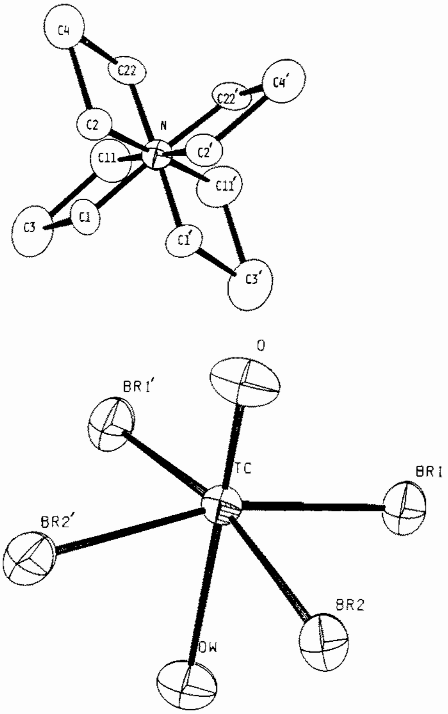

Fig. 1. An ORTEP view of $[TcOBr_4(H_2O)]^-$ and $[(CH_3CH_2)_4N]^+$. Thermal ellipsoids are drawn with 50% probability contours.

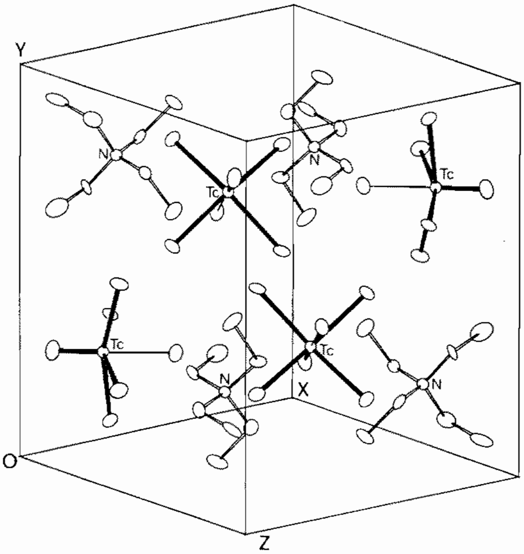

Fig. 2. Packing diagram of $[(CH_3CH_2)_4N][TcOBr_4(H_2O)]$. Thermal ellipsoids are drawn with 30% probability contours; only one of the two disordered carbons of each ethyl group has been drawn for clarity.

the unit cell where the two orientations of the disordered ethyl groups of the cation are superimposed. In the anion, Tc is coordinated to oxygen, four bromine atoms and a water molecule, the coordination geometry of which may be viewed either as a distorted octahedron or as a capped square-pyramid. The four bromine atoms define a plane ($0.7276x + 0.0000y - 0.6859z = 3.00276$), due to the crystallographically imposed symmetry, to which the O=Tc–Ow spine stands perpendicularly. The Br_4 plane is nearly square. A slight deviation from the regular square arrangement can be seen in the small difference of Br–Tc–Br angles: viz. Br1–Tc–Br1 = 87.9(1), Br2–Tc–Br2 = 88.9(1), and Br1–Tc–Br2 = 89.1(0)°. The Tc atom lies 0.37 Å above the plane toward the oxo-ligand. The very short Tc=O bond distance (1.618(9) Å) is within the range of known terminal technetium–oxygen bonds [11], while the water oxygen atom is weakly bound below the plane (2.317(9) Å). These structural features are consistent with the observed IR spectra. Interestingly, the distances between the plane and the two oxygen atoms at opposite sides are nearly the same, being 1.99 (O) and 1.94 (Ow) Å. The average Tc–Br bond length of 2.507 Å may be compared with the EXAFS-derived Tc–Br distances of 2.48 Å in $[TcOBr_4]^-$ and 2.54 Å in $[TcOBr_5]^{2-}$ (equatorial bromides). The increasing order of the Tc–Br distances, $[TcOBr_4]^- < [TcOBr_4(H_2O)]^- < [TcOBr_5]^{2-}$, is in harmony with the corresponding Tc–Br stretching frequencies of 306, 260 and 248 cm^{-1}, respectively.

The Tc–Br and Tc–Ow distances in $[TcOBr_4(H_2O)]^-$ are close to the corresponding Re–Br and Re–Ow bond lengths in $[ReOBr_4(H_2O)]^-$ [10]. A minor difference may be seen in the Re=O distance which is 0.1 Å longer than the Tc=O bond. The out-of-plane displacement of Re (0.32 Å) is also slightly less pronounced.

Supplementary Material

Lists of anisotropic displacement parameters (Table S1, 1 page) and of observed and calculated structure factors (Table S2, 13 pages) are available from the authors on request.

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