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Preparation, Crystal and Molecular Structure of *trans*-Dioxo(1,4-dithia-8,11-diazacyclotetradecane)technetium(V) Hexafluorophosphate

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Abstract

The preparation and X-ray structure of *trans*-$[TcO_2(14\text{-ane-}N_2S_2)]PF_6$ are described. The complex is obtained via a ligand exchange reaction of $(n\text{-Bu})_4N[TcOBr_4]$ with 1,4-dithia-8,11-diazacyclotetradecane. The crystals are monoclinic, space group $P2_1/n$, with $a = 9.726(3)$, $b = 9.668(2)$, $c = 19.262(3)$ Å, $\beta = 95.84(2)°$ and $Z = 4$. The structure was solved by the heavy-atom method and refined using the full-matrix least-squares technique up to $R = 0.036$ and $R_w = 0.037$. The two ions are characterized by the presence of centrosymmetric dimers generated by strong intermolecular hydrogen bonds.

Introduction

The chemistry of technetium complexes with macrocyclic ligands has received little attention in comparison with that of complexes with open-chain ligands. $[TcO_2cyclam]ClO_4 \cdot H_2O$ is the first *trans*-dioxo-technetium(V) complex with a macrocyclic ligand to be structurally characterized [1]. Recently, we have reported the preparation and chemical characterization of the complexes of ^{99}Tc and ^{99m}Tc with 1,4-dithia-8,11-diazacyclotetradecane (14-ane-N_2S_2) [2]. It has been found that the same complex was formed with both radionuclides. The results suggested that the technetium complex with a 14-membered N_2S_2 macrocycle belongs to the same class of TcO_2^+ complexes as $[TcO_2cyclam]^+$, $[TcO_2(en)_2]^+$ [3] and $[TcO_2(2,3,2\text{-tet})]^+$ [4].

However, the chemical characterization of $[^{99}TcO_2(14\text{-ane-}N_2S_2]^+$ was restricted to only spectroscopy, electrophoresis and charge determination. Here, the first report dealing with the X-ray structure of a PF_6^- salt of $[TcO_2(14\text{-ane-}N_2S_2)]^+$ is presented.

Experimental

Materials

^{99}Tc was obtained from the Radiochemical Centre Amersham as an ammonium pertechnetate solution. The Tc concentrations were determined by measuring the ^{99}Tc radioactivity with a Packard Tri-Carb 460CD liquid scintillation system. The ligand 1,4-dithia-8,11-diazacyclotetradecane dihydrochloride was prepared [5] and kindly provided by the Institute of Inorganic Chemistry, Basel. $(n\text{-Bu})_4N[TcOBr_4]$ was prepared according to the method described previously [6]. All other chemicals were of reagent grade.

Preparation of trans-[$TcO_2(14\text{-ane-}N_2S_2)]PF_6$

Ligand dihydrochloride (39 mg, 1.27×10^{-1} mmol) was dissolved in 0.1 M NaOH and the free amine was extracted three times with 2 ml CH_2Cl_2. The combined organic phases were dried (Na_2SO_4), filtered and evaporated. The free base dissolved in 1 ml CH_2Cl_2 was added to a solution of $(n\text{-Bu})_4N[TcOBr_4]$ (4.23×10^{-2} mmol) in CH_2Cl_2. From the resulting mixture the yellow-brownish crude product was extracted three times with 0.5 ml water, the aqueous solution was concentrated and was charged onto a Bio-Gel P2 column. The latter was eluted with water which removed the desired complex as a yellow band. The fractions with identical UV–Visible spectra were combined and concentrated under a stream of nitrogen. The hexafluorophosphate salt precipitated as yellow crystalline blocks, upon slow evaporation, following the addition of a saturated aqueous solution of KPF_6. The crystals were washed with a cold 50:50 *v*/*v* ethanol–water mixture followed by absolute ethanol.

Electrophoretic Analysis

The electrophoreses were run in a Camag Chamber on Schleicher-Schull 2043 B paper. When not specified, the conditions were: 0.1 M phosphate buffer (pH 7), 2000 V, 30 min. The ^{99}Tc activity on the paper strips was measured with a TLC Linear

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Analyser LB 282 consisting of a position sensitive proportional counter tube connected to a Silena multichannel analyser.

Spectral Measurements

The UV–Visible spectra of solutions were obtained with a HP 8450 A Diode Array spectrophotometer. The infrared spectra in the 4000–400 cm^{-1} range were obtained with a Pye-Unicam SP 1100 spectrophotometer using KBr pellets. Those in the 1000–50 cm^{-1} range were recorded on a FTIR Brucker IFF 113 C device, using polyethylene pellets.

Data Collection and Processing

A suitable crystal was sealed in a Lindeman capillary tube and mounted on a Syntex R3*m* automatic four-circle diffractometer. Cell dimensions were refined by 23 accurately centered reflections with $14 \leqslant 2\theta \leqslant 30°$. 5705 intensities were recorded at room temperature up to $2\theta = 55°$ with the θ–2θ scan technique, a width of 2° and a variable scan speed between 2.0 and 12.0° min^{-1}. The intensities of three standard reflections, monitored periodically, showed no significant variation. The space group was uniquely determined by the systematic absences $h0l$ with h+l odd and $0k0$ with k odd.

A series of ϕ-scan ($\Delta\phi = 15°$) was performed on the 15 strongest reflections with $\chi \geqslant 70°$. From the 360 intensities six parameters defining a pseudo-ellipsoid were refined to simulate the crystal absorption effect. This approximation was used to perform an empirical correction on the set of data corrected for Lorentz-polarization. The internal consistency index R_i reduced to 0.015 as compared to the previous value 0.021 for the 3874 independent intensities. 3000 reflections were considered as observed for $I \geqslant 3\sigma(I)$, where $\sigma(I)$ represents the estimated standard deviation from counting statistics.

Crystal Data

$TcS_2PF_6O_2N_2C_{10}H_{22}$, molecular weight 510.29, monoclinic space group $P2_1/n$ (I.T.C. N. 14), a = 9.726(3), b = 9.668(2), c = 19.262(3) Å, β = 95.84(2)°, V = 1801.8(7) $Å^3$, Z = 4, $F(000)$ = 1024, T = 295 K, ρ_{calc} = 1.88 g cm^{-3}, Mo Kα graphite-monochromatized radiation (λ = 0.71073 Å), μ(Mo Kα) = 11.54 cm^{-1}, mean $\mu r \cong 0.20$ (for the empirical absorption correction), transmission coefficient range = 0.53–0.59.

Structure Analysis and Refinement

The structure was solved from a sharpened three-dimensional Patterson map. Additional Fourier synthesis and full-matrix least-squares refinement technique were used to solve the whole structure. Most of the H atoms were found with rather unexpected C–H geometry from a weighted difference-Fourier map. They were introduced in the structure refinement, with calculated positions derived from geometrical considerations and fixed parameters (N–H and C–H = 0.960 Å and U = 0.060 $Å^2$) in addition to the anisotropic non-hydrogen atoms. The final agreement was R = 0.036 and R_w = 0.037, and the corresponding goodness of fit was S = 1.68. On a final difference-Fourier only two significant electron density residuals (almost 1 e $Å^{-3}$) were observed at 1 Å from the S atoms, obviously due to their lone pairs. The weighting scheme used was $[1.0/(\sigma^2(F) + 2.89 \times 10^{-4}F^2)]$. The fractional atomic coordinates of the non-H atoms are reported in Table 1. See also 'Supplementary Material'.

Data-reduction, structure refinement and drawings were performed with the aid of SHELXTL-PLUS system (1987) from Nicolet XRD Co. on a μ-VAX II, the geometrical calculations were performed with the PARST [7] program.

TABLE 1. Atomic Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a]

Atom	x	y	z	U_{eq}
Tc	2232(1)	668(1)	869(1)	31(1)
O(1)	1866(3)	90(3)	10(1)	40(1)
O(2)	2561(3)	1342(3)	1712(1)	41(1)
S(1)	4530(1)	−241(2)	982(1)	61(1)
C(1)	4450(6)	−1089(7)	1821(3)	78(2)
C(2)	3287(7)	−2149(7)	1746(3)	82(2)
S(2)	1645(1)	−1523(1)	1344(1)	53(1)
C(3)	706(6)	−938(6)	2056(2)	68(2)
C(4)	−572(5)	−115(7)	1766(3)	68(2)
C(5)	−407(5)	1351(6)	1537(2)	58(2)
N(1)	156(3)	1445(4)	853(2)	44(1)
C(6)	148(5)	2861(5)	541(3)	64(2)
C(7)	1514(6)	3586(5)	737(3)	68(2)
N(2)	2650(4)	2734(4)	538(2)	53(1)
C(8)	4011(6)	3322(6)	799(3)	76(2)
C(9)	5252(6)	2393(8)	683(4)	95(3)
C(10)	5596(6)	1237(8)	1189(4)	95(3)
P	2414(1)	4101(1)	−1446(1)	49(1)
F(1)	2565(4)	4888(4)	−718(2)	87(1)
F(2)	850(5)	4002(6)	−1400(3)	153(3)
F(3)	2270(5)	3305(4)	−2157(2)	97(2)
F(4)	4010(4)	4213(4)	−1494(3)	117(2)
F(5)	2245(5)	5525(3)	−1817(2)	112(2)
F(6)	2597(5)	2662(3)	−1068(2)	116(2)

[a] e.s.d.s given in parentheses. Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Chemical Characterization

$[TcO_2(14\text{-ane-}N_2S_2)]^+$ could be obtained only if *cis*(14-ane-N_2S_2) free of HCl was used in the substitution reaction with (n-Bu)$[TcOBr_4]$. As the reaction takes place in organic solvents the disproportionation of $[TcOBr_4]^-$ ions is avoided. The products soluble in water were removed from the organic phase by extraction. The UV–Visible spectrum of the yellow-brownish aqueous solution exhibited absorptions at 240, 320, 365 and 488 nm. The spectral changes as a function of time, *i.e.* decrease of absorptions at 365 and 488 nm and increase at 240 and 320 nm, suggest the presence of at least two species in solution. This was confirmed by a chromatographic separation on a Bio-Gel column. A yellow band followed by pink–orange fractions and finally by TcO_4^- were removed with water. Their proportions were 85%, 3% and 12%, respectively.

The electrophoresis of the yellow fractions showed a pure cationic product. Its migrating distance was 9 cm from the starting point. The UV–Visible spectrum exhibited absorption maxima at 240, 320, 430 and a weak absorption at 570 nm ($\epsilon = 10\,200$, 858, 66 and 4 l M^{-1} cm^{-1}, respectively). The yellow cationic complex was isolated as PF_6^- and ClO_4^- salts. The infrared spectra of both salts exhibit a strong absorption at 800 cm^{-1} assignable to the $[O{=}Tc{=}O]^+$ group, in addition to N–H absorptions in the region 3100–3300 cm^{-1}. The formula $[TcO_2(14\text{-ane-}N_2S_2)]^+$ supported by these and previously [2] published results is confirmed by X-ray diffraction analysis of $[TcO_2(14\text{-ane-}N_2S_2)]PF_6$.

The electrophoresis revealed the lability of the pink–orange product in phosphate buffer at pH 7. The UV–Vis spectrum of this product in water (pH 6) exhibited absorption maxima at 368, 488 and 712 nm. The spectral changes as a function of time are fast during the first hour. At this point, the spectrum showed absorptions at 240 and 320 nm attributed to the *trans*-dioxo complex, and at 375 and 488 nm. However, only after 10 days, 100% of a cation possessing the same spectrophotometric and electrophoretic characteristics as those of $[TcO_2(14\text{-ane-}N_2S_2)]^+$ was obtained. The above results suggest the $[TcO(OH)(14\text{-ane-}N_2S_2)]^+$ formula for the pink–orange product. It may be assumed that the ligand exchange reaction in organic medium leads to a five-coordinated complex containing the TcO^{3+} core. However this complex is not stable. The UV–Vis spectrum in dichloromethane showed a gradual increase of absorptions at 244 and 287 nm, attributed to $[TcO_4]^-$. In aqueous solution, the Tc(V) complex is stabilized by attaching a water molecule to the sixth position *trans* to the oxo group. The subsequent deprotonation will produce $TcO(OH)^{2+}$ and finally the more stable TcO_2^+ group. Indeed, in solution at $pH \geqslant 6$, the $[TcO_2(14\text{-ane-}N_2S_2)]^+$ is the most stable complex.

The dissolution of $[TcO_2(14\text{-ane-}N_2S_2)]ClO_4$ in 1 M HCl resulted immediately in a pink solution. However a constant UV–Vis spectrum was obtained after 2 h. It exhibits absorption maxima at 364, 488 and 712 nm ($\epsilon = 8100$, 6230 and 690, respectively). The electrophoresis in 1 M HCl (400 V and 2 h) showed a single cationic species. Its migrating distance is 7 cm from the starting point. The results suggest that this species can be $[TcO(OH)(14\text{-ane-}N_2S_2)2^+$. Work is in progress in order to isolate and characterize this product.

Structure Description

The asymmetric unit contains one molecule in the general position. It consists of a cationic complex of *trans*-dioxo-technetium(V) with the tetradentate saturated ligand 1,4-dithia-8,11-diazacyclotetradecane $[TcO_2(S_2N_2C_{10}H_{22})]^+$ and a PF_6^- anion. The two ions are connected by two intramolecular H bonds linking two fluorine atoms and the hydrogen of the ligand nitrogen N(2) (Fig. 1). The two contacts reveal a noteworthy difference: H(16)···F(1) and H(16)···F(6) distances are 2.558(5) and 2.134(5) Å respectively. Furthermore, each molecule shows two equivalent and strong hydrogen interactions between H(11) and O(1) of the dioxide moieties of two adjacent centrosymmetric cations (1.901(4) Å). The four hydrogen bonds are oriented toward the same side of each complex mean plane. Consequently the crystal packing is formed by independent molecular dimers having almost a sandwich shape with the two anions inside (Fig. 2).

The cyclic ligand of the complex can be considered an intermediate between 1,4,8,11-tetraazacyclotetradecane (cyclam) and the four-sulfur analogue 1,4,8,11-tetrathiacyclotetradecane, both already studied with many transition metals [8–13]. No information is available about the dithia deriva-

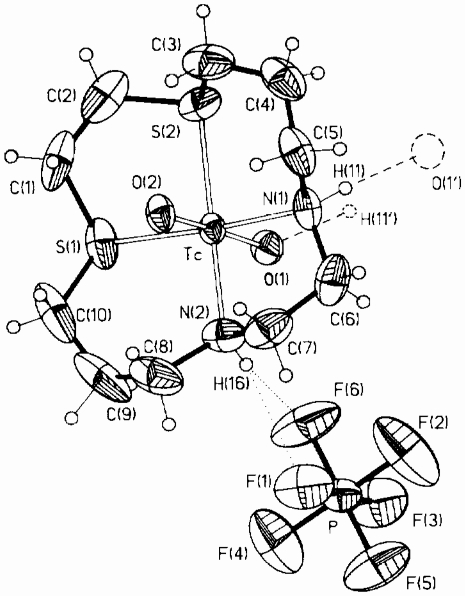

Fig. 1. View of $[TcO_2(S_2N_2C_{10}H_{22})]^+$ and PF_6^- indicating the atom-numbering scheme, the intra- and intermolecular hydrogen bonds (dotted and shaded lines, respectively). 50% Thermal ellipsoids are indicated for non-H atoms while hydrogen size is arbitrary.

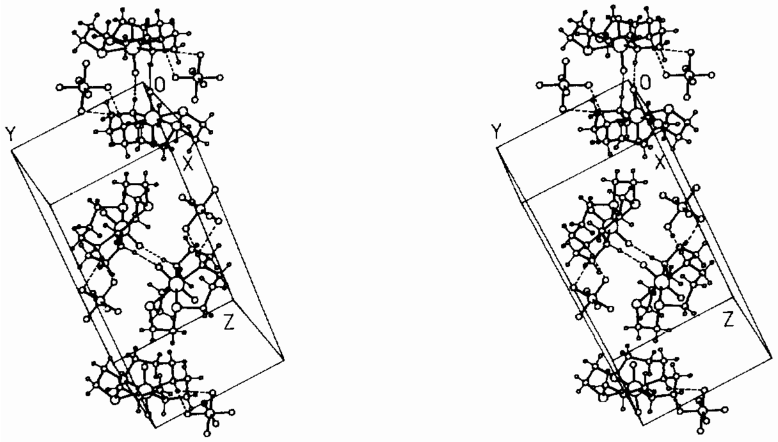

Fig. 2. Stereoscopic view of crystal packing showing the centrosymmetric bi-molecular aggregate with the hydrogen bonds in dashed-line type. Atom size is arbitrary.

tive. For the dioxo-technetium(V) only the tetraaza form is known which is analogous to the present complex. Both compounds show the cyclic ligand in *endo*-conformation with the lone pairs of the heteratoms directed toward the center of the cavity. This is usually observed in the similar transition metal complexes. Indeed such a ring disposition gives a better overlap with the d orbital of Tc atom enclosed in the middle than the *eso*-conformation found in both the uncomplexed cyclam [14] and the tetrathia analogue [15].

The coordination around technetium can be approximated by a compressed octahedron with the ligand heteratoms almost lying on the equatorial plane with a slightly displaced metal atom (*cf.* Table S3). The two oxygens are placed on the axis. The deformation is rather due to the four different bonds with the ligand than to the puckered ring conformation (Table 2). This seems to be confirmed by the almost regular arrangements of the cyclam analogues and other tetraaza- and tetrathia-hexacoordinated complexes. The two Tc–O bonds are equal and in agreement with the average 1.75 Å usually reported for the dioxo-Tc compounds, and almost 0.10 Å longer than the corresponding value in the monoxide structures. This is expected for the *trans*-influence of the two opposite oxygens. The intermolecular hydrogen interaction of O(1) is not sufficient to induce any significant effect on the TcO_2 moiety, larger than experimental error.

The 14-ane-S_2N_2 coordination shows interesting properties. The two distances for each type of Tc–X bond (X = N, S) are almost perfectly equal and show the mean value 2.150(4) and 2.395(1) Å respectively. The Tc–N mean bond is significantly shorter than the Tc–S bond as expected for the bigger radius of the sulfur atom. Despite the differences between these Tc–X lengths and the corresponding average, C–X distances in the ligand (1.479 and 1.807 Å) are 0.671 and 0.588 Å, for the N and S atom respectively. This bigger value found for the nitrogen reveals a shortening effect on the technetium–sulphur interaction which is significantly stronger than for the Tc–N bond. This was already observed by Glick *et al.* [16] in the structural study of some (14-ane-N_4) and (14-ane-S_4) complexes. The Tc–N bond lengths are slightly longer than in the corresponding cyclam compound, but in accord with the mean value found in the *trans*-$[O_2(en)_2Tc]^+$ cation. The Tc–S distances are almost 0.10 Å longer than the average length observed in some Tc monoxides [17, 18], probably due to the bigger ionic radius of the metal with a higher coordination number and to a *trans*-effect of the opposite nitrogens.

Despite the different atom size and the four almost equal values usually found in the tetrathia derivatives, the X–Tc–X angles follow the general cyclam arrangement: almost 96° for the propylene bridge arc and 84° for the ethylene one. The reason can be found in the chelating ring dimension: the six-membered configuration (generally in chair conformation as in the present) is more flexible than the strained five-atom analogue. This is confirmed by the internal angle values smaller than 85° reported for the $Tc(XCH_2CH_2X)_2$ complexes. The difference in the coordination arrangement of the (14-ane-N_4) and (14-ane-S_4) ligands discussed by Glick *et al.*, was attributed to size effect of the bigger sulfur atoms generating a stronger steric hindrance on the tetrathia ring conformation. In fact the present cyclam derivative shows torsion angles closer to the energetically favorable values (180 and 60° for the *anti* and *gauche* disposition, respectively) in the diaza fragment rather than in the dithia part.

An interesting characteristic of the (14-ane-S_2N_2) arrangement is the orientation of the nitrogen hydrogens and sulfur lone-pairs toward the same side of the heteratom mean plane. This disposition corresponds to the type I form in the conformation study performed on the tetraaza complexes by Thöm *et al.*

TABLE 2. Main Bond Lengths (Å), Bond Angles (°) and Torsion Angles (°)[a]

Tc–O(1)	1.748(2)	Tc–O(2)	1.748(2)
Tc–S(1)	2.391(1)	Tc–S(2)	2.400(1)
Tc–N(1)	2.152(3)	Tc–N(2)	2.148(4)
O(2)–Tc–O(1)	176.6(1)	N(2)–Tc–N(1)	82.9(2)
S(2)–Tc–S(1)	84.1(1)	N(1)–Tc–S(2)	93.1(1)
N(1)–Tc–S(1)	175.4(1)	N(2)–Tc–S(2)	173.6(1)
N(1)–Tc–O(1)	89.9(1)	N(2)–Tc–S(1)	99.5(1)
N(1)–Tc–O(2)	88.1(1)	N(2)–Tc–O(1)	92.5(1)
N(2)–Tc–O(2)	84.6(1)	S(1)–Tc–O(1)	93.9(1)
S(1)–Tc–O(2)	88.3(1)	S(2)–Tc–O(1)	92.6(1)
S(2)–Tc–O(2)	90.2(1)		
P–F(1)	1.589(3)	P–F(2)	1.536(4)
P–F(3)	1.564(3)	P–F(4)	1.568(4)
P–F(5)	1.552(3)	P–F(6)	1.572(3)
F(2)–P–F(1)	88.9(3)	F(3)–P–F(1)	179.1(2)
F(3)–P–F(2)	91.0(3)	F(4)–P–F(1)	91.0(2)
F(4)–P–F(2)	179.6(2)	F(4)–P–F(3)	89.1(2)
F(5)–P–F(1)	88.8(2)	F(5)–P–F(2)	91.3(3)
F(5)–P–F(3)	92.1(2)	F(5)–P–F(4)	88.3(3)
F(6)–P–F(1)	91.1(2)	F(6)–P–F(2)	89.1(3)
F(6)–P–F(3)	88.0(2)	F(6)–P–F(4)	91.3(3)
F(6)–P–F(5)	179.6(2)		

1	2	3	4	1–2	1–2–3	1–2–3–4
S(1)	C(1)	C(2)	S(2)	1.821(6)	108.5(4)	–49.8(5)
C(1)	C(2)	S(2)	C(3)	1.522(9)	115.6(4)	–91.8(5)
C(2)	S(2)	C(3)	C(4)	1.806(6)	105.8(2)	168.3(4)
S(2)	C(3)	C(4)	C(5)	1.814(6)	109.8(3)	–77.9(5)
C(3)	C(4)	C(5)	N(1)	1.532(8)	119.5(4)	76.3(6)
C(4)	C(5)	N(1)	C(6)	1.499(8)	112.4(4)	171.1(4)
C(5)	N(1)	C(6)	C(7)	1.480(6)	115.2(4)	93.4(5)
N(1)	C(6)	C(7)	N(2)	1.495(6)	110.8(4)	54.9(5)
C(6)	C(7)	N(2)	C(8)	1.516(8)	110.0(4)	–172.9(4)
C(7)	N(2)	C(8)	C(9)	1.460(7)	111.7(4)	173.2(5)
N(2)	C(8)	C(9)	C(10)	1.480(7)	114.5(5)	–80.9(7)
C(8)	C(9)	C(10)	S(1)	1.538(9)	117.9(5)	81.7(6)
C(9)	C(10)	S(1)	C(1)	1.498(10)	111.5(4)	152.1(5)
C(10)	S(1)	C(1)	C(2)	1.787(7)	103.8(3)	165.8(4)

[a] e.s.d.s given in parentheses.

[19]. According to their work, for the present average bond length of 2.30 Å it might be energetically more favorable if the ligand *cis*-form for the linear TcO_2 moiety cannot be achieved. More probably, this is due to steric effects generating from packing interactions of the two molecules interconnected by H bonds, forcing the ligand alkyl bridges outside the sandwich.

Supplementary Material Available

Calculated hydrogen positions (Table S1, 1 page), anisotropic displacement parameters (Table S2, 1 page), selected weighted least-squares planes (Table S3, 1 page) and list of the observed and calculated structure factors (Table S4, 22 pages) are available from the Cambridge Crystallographic Data Centre.

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