Preparation and crystal structure of polymeric lithium[dioxoTc(V)–tetraazaundecane]-bis(trifluoromethanesulfonate) complex

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(Received March 20; revised May 10, 1990)

Abstract

The polymeric $\{Li[TcO_2(2,3,2\text{-tet})](CF_3SO_3)_2\}_n$ complex was obtained via ligand exchange reaction of $(n\text{-Bu})_4N[(TcNBr_4)_{0.8}/(TcOBr_4)_{0.2}]$ with 1,4,8,11-tetraazaundecane. The resulting compound is a monodimensional polymer. The crystals are monoclinic, space group $P2_1/n$ (I.T.C. No. 14), $a=10.471(3)$, $b=12.698(3)$, $c=16.455(3)$ Å, $\beta=104.00(2)°$, $Z=4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares technique up to $R=0.034$ and $R_w=0.039$. The crystallographic asymmetric unit consists of the monomer unit $Li[TcO_2(2,3,2\text{-tet})](CF_3SO_3)_2$.

Introduction

$TcOX_4^-$ is a useful starting material for the preparation of either monooxo- [1–4] or dioxo–technetium(V) complexes [5–8]. Starting from $TcNX_4-$, by ligand substitution reactions, nitrido–technetium(V) complexes are obtained [9].

Recently, we have reported the preparation, chemical characterization and X-ray structure determination of $(n\text{-Bu})_4N[(TcNBr_4)_{0.8}/(TcOBr_4)_{0.2}]$ [10]. The reaction of the latter product with 1,4,8,11-tetraazaundecane (2,3,2-tet) leads to a polymeric complex of $Tc(V)O_2^+$ and Li^+. Previously, $[TcO_2(2,3,2\text{-tet})]PF_6$ was obtained by the reaction of $(n\text{-Bu})_4N[TcOCl_4]$ with 2,3,2-tet in THF [7]. However, the chemical characterization was restricted only to elemental analysis, spectroscopy and electrophoresis. The X-ray structure determination was achieved neither for $[TcO_2(2,3,2\text{-tet})]PF_6$ nor for $[ReO_2(2,3,2\text{-tet})]A$ ($A=Cl^-$, PF_6^-) [11].

In the present paper, we report the isolation and X-ray crystal structure determination of $\{Li[TcO_2(2,3,2\text{-tet})](CF_3SO_3)_2\}_n$. The formation of this polymer is only due to the addition of $LiCF_3SO_3$, which also permits the growth of crystals.

Experimental

Materials

^{99}Tc was obtained from the Radiochemical Centre Amersham as an ammonium pertechnetate solution. The ligand 1,4,8,11-tetraazaundecane was purchased from Aldrich Chemical Co. $(n\text{-Bu})_4N[TcNBr_4/TcOBr_4]$ was prepared according to the published procedure [10]. All other chemicals were of reagent grade and were used without further purification.

Preparation of $\{Li[TcO_2(2,3,2\text{-tet})](CF_3SO_3)_2\}_n$

Forty mg of $(n\text{-Bu})_4N[(TcNBr_4)_{0.8}/(TcOBr_4)_{0.2}]$ were dissolved in 4 ml of CH_2Cl_2 and 18 μl of 2,3,2-tet in 0.5 ml ethanol were added. The resulting reddish-orange precipitate was filtered off, washed with CH_2Cl_2 and dissolved in 1.5 ml water. The aqueous solution was charged onto a Bio-Gel P2 column. Elution of the latter with water produced two bands (in order of elution): pink–orange and yellow (major).

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0020-1693/90/$3.50

The pink–orange eluted fractions with identical UV–Vis spectra were combined and concentrated under a stream of nitrogen. Electrophoresis showed a single cationic species. The pink crystals were formed upon slow evaporation following the addition of 0.1 ml of 4 M $LiCF_3SO_3$ solution.

Single pink crystals suitable for X-ray diffraction study were grown by slow evaporation (two weeks) at -5 °C of an ethanol–water (1:1 vol./vol.) solution.

The yellow band was collected and evaporated to dryness. The characterization of this product is under investigation.

Electrophoresis analysis

Electrophoresis was run in a Camag chamber on Schleicher-Schull 2043B paper in 0.1 M phosphate buffer (pH 7) at 2000 V for 30 min. The ^{99}Tc activity on the paper strips was measured with a TLC linear Analyzer LB 282 consisting of a position sensitive proportional counter tube connected to a Silena multichannel analyzer.

Spectral measurements

Infrared spectra were obtained as KBr disks using a Pye-Unicam SP 1100 spectrophotometer. UV–Vis spectra were recorded on a HP 8450 A Diode Array spectrophotometer in aqueous solution.

Elemental analysis

Determination of the lithium content was performed by Chemolab AG, Windisch, Switzerland.

Data collection and processing

Intensities data were recorded at room temperature on a Syntex R3m automatic four-circle diffractometer. Cell dimensions were refined from 21 accurately centred reflections with $15 \leqslant 2\theta \leqslant 30°$. A total of 7183 intensities was recorded in the 2θ range 4–55°, with the θ–2θ scan technique, a width of 2° and a variable scan speed between 2.0 and 10° min^{-1}. The index range of the reflections was $-3 \leqslant h \leqslant 13$, $-3 \leqslant k \leqslant 13$ and $-21 \leqslant l \leqslant 21$. The intensities of three standard reflections, monitored periodically, showed no significant variations. A ψ-scan data collection ($\Delta\psi = 15°$) 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 effects. This approximation was used to perform an empirical correction on the set of data corrected for Lorentz polarization. The internal consistency index R_i decreased to 0.015 from the initial value 0.021 for the 4347 independent intensities. A total of 3112 reflections was considered as observed for $I \geqslant 2.5\sigma(I)$, where $\sigma(I)$ represents the estimated standard deviation from counting statistics.

Crystal data

$TcS_2F_6O_8N_4C_9H_{20}Li$, molecular weight 596.24, monoclinic, space group $P2_1/n$ (I.T.C. No. 14), $a = 10.471(3)$, $b = 12.698(3)$, $c = 16.455(3)$ Å, $\beta = 104.00(2)°$, $V = 2122(1)$ Å^3, $Z = 4$, $F(000) = 1192$, $T = 295$ K, $\rho_{calc} = 1.87$ g cm^{-3}, Mo Kα graphite-monochromatized radiation ($\lambda = 0.71073$ Å), μ(Mo Kα) $= 9.43$ cm^{-1}, mean $\mu r = 0.20$, transmission coefficient range $= 0.53$–0.59.

Structure analysis and refinement

The technetium position was deduced from a sharpened three-dimensional Patterson map. The other non-hydrogen atoms were located by a combination of difference Fourier synthesis and full-matrix least-squares refinement technique. In the last cycles, with all anisotropic atoms, the difference maps unexpectedly showed one significant electron density residual (almost three electrons) bridging two equivalent TcO_2 moeities and surrounded by two sulfonate anions. Stereochemical considerations suggested it be interpreted as a small metal atom characterized by tetrahedric coordination. A chemical microanalysis pointed out the presence of lithium in the solid compound. The Li atoms are strongly involved in the crystal packing probably captured during the crystallization process in the solution of the title substance. The Li atom was introduced in the structure refinement which showed a sensitive improvement. All the hydrogens were included in the model refinement with fixed positions calculated from geometric considerations (N, C–H = 1.08 Å) and with one unique refined isotropic displacement parameter. The three fluoromethyl fragments of the two sulfonates were highly disordered, clearly due to the free rotation about the C–S single bond. Their geometry was forced to a regular arrangement constraining the C–F bond lengths and the S–C–F and F–C–F angles to be equal, with the three corresponding values attached to the refinement process. The final model reached $R = 0.034$ and $R_w = 0.039$ with a maximum shift/error $= 0.07$ and a goodness of fit $S = 1.16$ with 11 observations per parameter. The weighting scheme was $w = [\sigma^2(F) + 16.5 \times 10^{-4} F_o^2]^{-1}$. On the final weighted difference Fourier map the highest density residual peaks were of about 0.6 electron value and located around the disordered $-CF_3$ fragments.

The fractional coordinates with equivalent isotropic displacement parameters of non-hydrogen atoms are reported on Table 1. See also 'Supplementary material'.

TABLE 1. Atomic fractional coordinates and equivalent isotropic displacement parameters (Å^2) with corresponding e.s.d.s. in parentheses

Atom	x	y	z	U_{eq}[a]
Tc	0.23444(3)	0.05425(2)	0.20645(2)	0.0280(1)
O(1)	0.2088(3)	−0.0789(2)	0.1845(2)	0.0378(9)
O(2)	0.2622(3)	0.1862(2)	0.2370(2)	0.0359(9)
S(1)	0.2606(1)	−0.23377(9)	0.00378(6)	0.0441(4)
O(3)	0.2751(4)	−0.2707(3)	0.0879(2)	0.056(1)
O(4)	0.3214(6)	−0.1354(3)	−0.0014(3)	0.091(2)
O(5)	0.1304(4)	−0.2482(4)	−0.0472(3)	0.092(2)
C(8)	0.3557(3)	−0.3294(3)	−0.0393(2)	0.062(2)
F(1)	0.3074(4)	−0.4223(2)	−0.0406(2)	0.104(2)
F(2)	0.3588(5)	−0.3064(3)	−0.1146(2)	0.168(4)
F(3)	0.4752(3)	−0.3340(4)	0.0037(3)	0.197(4)
S(2)	−0.1264(1)	−0.2175(1)	0.08568(7)	0.0497(4)
O(6)	−0.1879(4)	−0.2602(3)	0.0068(2)	0.072(1)
O(7)	−0.0094(3)	−0.2677(3)	0.1318(2)	0.068(1)
O(8)	−0.1172(5)	−0.1062(3)	0.0863(4)	0.120(3)
C(9)	−0.2414(4)	−0.2444(4)	0.1475(2)	0.127(5)
F(4)	−0.3539(2)	−0.2030(5)	0.1157(3)	0.188(4)
F(5)	−0.2597(5)	−0.3435(4)	0.1539(4)	0.207(5)
F(6)	−0.2019(4)	−0.2080(6)	0.2219(2)	0.253(5)
N(1)	0.3211(4)	0.0740(3)	0.1007(2)	0.048(1)
C(1)	0.4661(6)	0.0758(5)	0.1329(4)	0.068(2)
C(2)	0.5049(5)	−0.0048(5)	0.2011(3)	0.061(2)
N(2)	0.4342(3)	0.0181(3)	0.2668(2)	0.043(1)
C(3)	0.4514(5)	−0.0651(4)	0.3320(3)	0.056(2)
C(4)	0.3750(6)	−0.0410(4)	0.3973(3)	0.057(2)
C(5)	0.2269(5)	−0.0580(3)	0.3703(3)	0.050(2)
N(3)	0.1598(4)	0.0274(3)	0.3148(2)	0.037(1)
C(6)	0.0170(5)	0.0127(4)	0.2871(3)	0.053(2)
C(7)	−0.0395(5)	0.0944(4)	0.2197(4)	0.060(2)
N(4)	0.0291(4)	0.0842(3)	0.1516(2)	0.047(1)
Li	0.1745(7)	−0.2242(5)	0.1680(4)	0.034(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Data reduction, structure refinement and drawings were performed with the aid of the SHELXTL-PLUS system (1987) from Nicolet XRD Co., while structure refinement and geometric computations were carried out by SHELX76 [12] and PARST [13] programs, respectively. Atomic scattering factors were taken from the International Tables of Crystallography [14].

Results and discussion

Chemical characterization

As expected, the reaction of (n-Bu)$_4$N[TcNBr$_4$/TcOBr$_4$] with 2,3,2-tet leads to the formation of TcO$_2$$^+$ and Tc≡N^{n+} (n = 2,3) complexes; they originate from TcOBr$_4$$^-$ and TcNBr$_4$$^-$ anions, respectively.

The structure of the yellow complex has not been determined, but it is clear that the Tc≡N group is retained as shown by the IR absorption at 1070 cm^{-1}. Also, the dissolution of this product in concentrated HBr and addition of (n-Bu)$_4$NBr solution resulted in the precipitation of (n-Bu)$_4$N[TcNBr$_4$]. This transformation is a slow process (one week). The IR absorptions at 3300–2990 cm^{-1} (attributed to N–H bonds) reflect the presence of the 2,3,2-tet ligand. Further characterization of this compound is in progress.

The electrophoresis of the solution after the dissolution of pink crystals in water showed a single cationic complex. Its migration distance was 9 cm from the starting point. The UV–Vis spectrum exhibited absorption maxima at 229, 312 and 478 nm (ϵ = 8520, 870 and 70 l M^{-1} cm^{-1}, respectively). The infrared spectrum of the solid showed a strong absorption at 830 cm^{-1} assignable to the *trans*-TcO$_2$$^+$ moiety in addition to absorptions at 3300–2990 and 1610 cm^{-1} attributed to N–H and antisymmetric NH$_2$ bending vibrations, respectively. The absorptions at 520(m), 580(w), 640(s), 760(w) and 1230–1300(sh) cm^{-1} were observed in LiCF$_3$SO$_3$ as well as in the complex. In the region of 1000–1200 cm^{-1} the absorptions at 1060(s) and 1200(s) cm^{-1} found in LiCF$_3$SO$_3$ are shifted to 1040(s) and 1180(s) cm^{-1} in the complex.

From the electrophoretic and spectrophotometric data which are comparable to those of [TcO$_2$(2,3,2-tet)]PF$_6$ [7] and [TcO$_2$(en)$_2$]Cl [6], we can assume the formula [TcO$_2$(2,3,2-tet)]$^+$ for the complex in solution. Its isolation as the CF$_3$SO$_3$$^-$ salt is expected following the addition of LiCF$_3$SO$_3$ solution. However, the IR spectrum of the solid shows the absorption band assigned to the O=Tc=O core at 830 cm^{-1} with respect to 790 cm^{-1} given in previously isolated [TcO$_2$(2,3,2-tet)]PF$_6$. Moreover, in the latter complex, two strong absorptions at 790 and 810 cm^{-1} are observed. Recently, it has been reported [11] that the IR spectra of [ReO$_2$L]$^+$ (L = 2,3,2-tet) isolated as either Cl$^-$ or PF$_6$$^-$ salts exhibited double absorption at *c.* 800 cm^{-1}. The precise reason for the appearance of two absorptions in the Tc(V)- and Re(V)-dioxo complexes with the tetramine ligand is not yet clear.

In order to better understand the structural feature of the 2,3,2-tet complex, a crystallographic analysis is required. Instead of the dioxo Tc(V) monomer, the polymeric {Li[TcO$_2$(2,3,2-tet)](CF$_3$SO$_3$)$_2$}$_n$ complex was isolated and its structure was determined by X-ray diffraction method. The lithium content was determined by single-crystal microanalysis. *Anal.* Calc. for TcS$_2$F$_6$O$_8$N$_4$C$_9$H$_{20}$Li:Li, 1.16. Found: Li, 1.8%.

Structure description

The title compound is a monodimensional polymer (Fig. 1) with the monomer Li[TcO$_2$(2,3,2-tet)](CF$_3$SO$_3$)$_2$ contained in the crystallographic

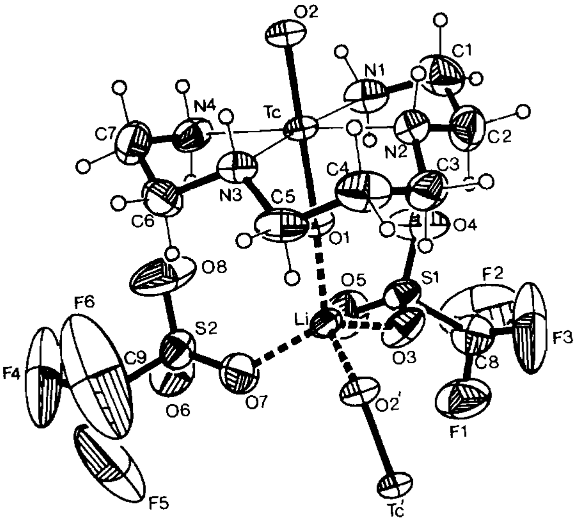

Fig. 1. View of the asymmetric unit consisting of the molecular monomer $Li[TcO_2(N_4C_7H_{20})](CF_3SO_3)_2$; O_2' and Tc' atoms represent equivalent positions of the polymeric chain. Non-hydrogen atoms are drawn with 50% probability. Hydrogen size is arbitrary.

asymmetric unit. The chains are formed by a linear alternation ••Li••Tc••Li••Tc•• of the two coordination polyhedra, each one having two opposite vertices in common with the two adjacent polyhedra of the other metal atom. These polymeric columns are directed along the screw-axis 2_1, with an approximate mean plane parallel to the crystallographic *bc* plane. In the three-dimensional structure, the interconnection between adjacent chains is performed by some hydrogen bonds, while others are involved between sequential molecular monomers in the same chain. The chemical characterization suggests the formation in solution of the dioxo–technetium complex with a net charge of +1. Unexpectedly, in the solid state, both oxygens of the TcO_2 moiety were able to coordinate the lithium atoms, the charge being balanced by one additional $CF_3SO_3^-$ anion for each molecule (Fig. 2). Relevant data on the two complex cations are reported in Tables 2 and 3, see also 'Supplementary material'. The four coordinated O atoms around Li have an approximative tetrahedric arrangement, as reported in the literature [15]. The two Li–O(sulphonate) distances are equivalent within the experimental error. Their mean value 1.960(8) Å is significantly greater than the corresponding 1.903(7) Å of the two bonds with the non-equivalent oxygens of the two adjacent TcO_2 moieties. This may be explained by the different nucleophilic character of the two O-ligand types and by the hindering effects of the

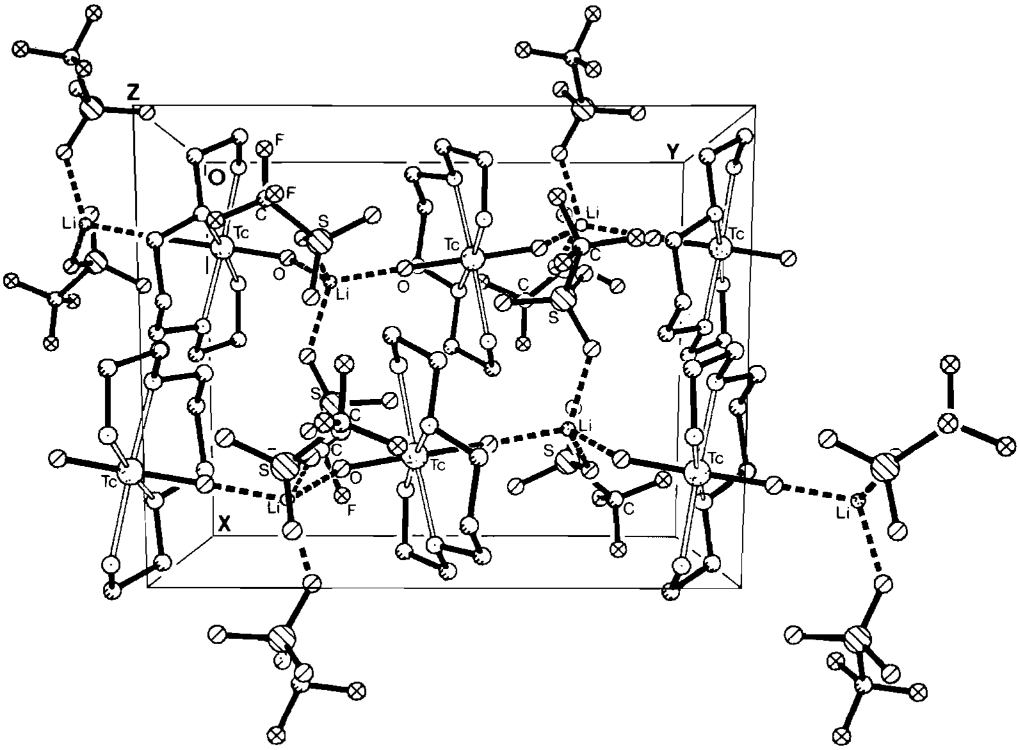

Fig. 2. Crystal packing of the molecule within unit cell. The coordination around the lithium is represented by dotted bonds, whereas that of technetium–nitrogen is drawn with shaded bonds. Atom size is arbitrary.

TABLE 2. Selected bond lengths (Å) and bond angles (°) of the Li coordination and the Tc complex[a]

Tc–O(1)	1.736(3)	Tc–O(2)	1.753(3)
Tc–N(1)	2.163(4)	Tc–N(2)	2.136(3)
Tc–N(3)	2.139(4)	Tc–N(4)	2.155(4)
O(1)–Li	1.888(7)	O(2)′–Li	1.918(7)
O(3)–Li	1.966(8)	O(7)–Li	1.953(7)
S(1)–O(3)	1.434(3)	S(2)–O(7)	1.426(3)
N(1)–C(1)	1.482(8)	C(1)–C(2)	1.500(8)
C(2)–N(2)	1.479(7)	N(2)–C(3)	1.486(6)
C(3)–C(4)	1.518(8)	C(4)–C(5)	1.521(8)
C(5)–N(3)	1.482(5)	N(3)–C(6)	1.466(6)
C(6)–C(7)	1.529(7)	C(7)–N(4)	1.475(8)
N(3)–Tc–N(4)	81.3(1)	N(2)–Tc–N(3)	95.3(1)
N(1)–Tc–N(4)	102.3(2)	N(1)–Tc–N(2)	81.0(2)
O(1)–Tc–O(2)	175.5(1)	Tc–O(1)–Li	175.4(3)
Tc′–O(2)′–Li	143.3(3)	Tc–N(1)–C(1)	107.9(3)
N(1)–C(1)–C(2)	109.0(5)	C(1)–C(2)–N(2)	108.6(5)
Tc–N(2)–C(2)	108.0(3)	C(2)–N(2)–C(3)	113.2(4)
Tc–N(2)–C(3)	115.0(3)	N(2)–C(3)–C(4)	112.1(4)
C(3)–C(4)–C(5)	116.0(4)	C(4)–C(5)–N(3)	112.0(4)
Tc–N(3)–C(5)	114.5(3)	C(5)–N(3)–C(6)	113.2(4)
Tc–N(3)–C(6)	108.2(3)	N(3)–C(6)–C(7)	109.0(4)
C(6)–C(7)–N(4)	108.5(4)	Tc–N(4)–C(7)	108.5(3)
O(3)–Li–O(7)	111.1(3)	O(1)–Li–O(7)	117.4(4)
O(1)–Li–O(3)	106.0(3)	O(1)–Li–O(2)′	116.5(4)
O(3)–Li–O(2)′	103.5(3)	O(7)–Li–O(2)′	101.6(4)
O(2)–Tc–N(4)	91.8(1)	O(2)–Tc–N(3)	89.0(1)
O(2)–Tc–N(2)	89.8(1)	O(2)–Tc–N(1)	92.7(1)
O(1)–Tc–N(4)	89.8(2)	O(1)–Tc–N(3)	87.1(1)
O(1)–Tc–N(2)	88.4(1)	O(1)–Tc–N(1)	91.1(1)

[a] The prime denotes the symmetry equivalent position $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$ of the corresponding atom. e.s.d.s. are given in parentheses.

big $CF_3SO_3^-$ ions located between two adjacent 2,3,2-tet planes as in a sandwich. This steric tension is confirmed by the angle value of O(Tc)–Li–O(Tc) which is noteworthy larger than the mean value, causing a significant deviation from a regular tetrahedric arrangement. Further, the slight difference between the two Li–O(dioxide) bonds (1.888(7) versus 1.918(7) Å) is mainly related to the different orientation of the two TcO_2 linear moieties, as clearly shown by the corresponding Li–O–Tc angles (175.4(3) versus 143.3(3)°) and O–Tc distances (1.736(3) versus 1.753(3) Å). These discrepancies in O_{Tc} surroundings might be interpreted as effects of different hybridation states of the two oxygens O(1) and O(2) (almost sp1 versus sp2). However, it is more probable that they are due to the hindering effects between the two metal fragments around each oxygen; they are larger for O(2) in the bended Li--O--Tc moiety, in agreement with the corresponding longer bond-lengths. The two sulfonates are practically equivalent. Both ions have disordered fluorine atoms due to the possible free rotation of the $-CF_3$ fragment around the S–C single bond, as indicated by their displacement parameters (see 'Supplementary material') and the residuals of the electron density surrounding it. However, as expected from stereochemical considerations, each anion configuration shows a three-fluoromethyl group staggered with respect to $-SO_3$. In the 2,3,2-tet complex the coordination geometry is almost a regular square bipyramid with the two oxygen atoms along the axis, as already observed in an analogous dioxo–technetium complex with a similar tetradentate cyclic ligand [8]. The TcO_2 central moiety is slightly bended and asymmetric, probably due to the different strength of the corresponding coordination bonds with the two adjacent lithium atoms. The four nitrogen atoms of the ligand lie perfectly on the equatorial plane from which the metal is displaced by only 0.032(1) Å, as shown by the weighted mean atom plane data reported in Table 3. The four Tc–N bond lengths are almost equivalent with the mean value 2.151(7) Å, but the distances for the two terminating atoms N(1) and N(4) are slightly longer. The difference is much more evident on observing the N–Tc–N angles the values of which are directly proportional to the N···N interatomic distances, i.e. to the lengths of the corresponding carbon chain linking the two adjacent nitrogens. The angles corresponding to the two ethyl fragments are equal within the experimental error to 80.2(2), while for the propyl chain, a larger value of 95.3(1) is observed. Consequently, the N(1)–Tc–N(4) angle of the two heads shows the largest value 102.3(2) due to the absence of a direct interconnection through any carbon chain. Thus, it is possible to conclude that the linear polydentate ligand 2,3,2-tet is folded around the technetium by the metal coordination which forces it in a plane configuration suitable to generate the four equatorial bonds. This has been observed by Thörn *et al.* in analogous cyclic tetradentate ligand complexes [16]. This capacity depends mainly on the size of the metal (covalent radius 1.36 Å) that could perfectly fit with the dimension of the folded ligand cavity, which is approximately 2.80 Å (calculated from the minimum distance between two opposite N atoms minus their covalent radii). In addition, the normal values observed for the bond geometry of the 2,3,2-tet configuration and the agreement of the Tc–N bond lengths with the usual value reported for analogous compounds confirm the absence of tensions in the alkylic bridges. One H atom of each nitrogen ligand is involved in a strong hydrogen bond with an oxygen of one $CF_3SO_3^-$ anion, as shown by the data reported on Table 4. The hydrogens of N(2) and N(3) are directed on the same side of the ligand plane and bond to two sulfonate oxygens coordinating the lithium directly connected to the TcO_2 moiety,

TABLE 3. Selected weighted least-squares planes with deviations (Å^2) and dihedral angles (°)^a

Plane 1							
N1*	0.0009	N2*	−0.0010	N3*	0.0008	N4*	−0.0010
Tc	−0.0322	O1	1.7023	O2	−1.7836	Li	3.5772
C1	−0.2806	C2	0.4331	C3	0.7776	C5	0.7897
C5	0.7897	C6	0.4222	C7	−0.2893		
Plane 2							
O2*	−0.0304	Tc*	0.0034	O1*	0.0041	Li	−0.1082
O2′*	0.0033	Tc′	0.2101	O1′	0.4524	S1	1.8618
O3	1.4951	S2	−2.6748	O7	−1.7264	N1	1.5707
N2	1.6989	N3	−1.4501	N4	−1.7804		
Plane 3							
O3*	0.0000	S1*	0.0000	C8*	0.0000	O4	−1.1865
O5	1.2388	F1	1.0588	F2	−0.0563	F3	−1.0017
Li	0.3318						
Plane 4							
O7*	0.0000	S2*	0.0000	C9*	0.0000	O6	−1.1565
O8	1.2118	F4	0.0217	F5	−1.0419	F6	1.0198
Li	1.0342						
Line 1							
O2*	0.0196	Tc*	0.0459	O1*	0.0263	Li	0.2442
N1	2.2018	N2	2.1184	N3	2.0991	N4	2.1710
Dihedral angles							
1	2		89.3(1)	1		3	46.0(1)
2	4		162.4(1)	2		3	131.6(2)
2	4		89.8(2)	3		4	138.6(2)
Angles formed by lines and normals to planes							
Line	Plane						
1	1		179.8(1)				
1	2		90.6(1)				

[a] The atoms defining the plane are characterized by *. All the deviation e.s.d.s. are in the range 0.02–0.002. Prime denotes the equivalent position $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$ for the corresponding atom.

TABLE 4. Geometric information on the hydrogen bonds between N(ligand) and O(sulfonate) atoms^a

Donor	H	Acceptor	D–H	D–A	H–A	D–H–A
N1	H(1)	O(6) a)	1.080(5)	3.078(5)	2.021(5)	139.2(3)
N2	H(7)	O(7) b)	1.080(5)	3.188(5)	2.132(5)	165.3(4)
N3	H(14)	O(3) b)	1.080(5)	3.012(5)	1.940(5)	171.3(3)
N4	H(20)	O(5) a)	1.080(5)	2.947(6)	2.053(6)	138.3(4)

[a] Symmetry operations for the equivalent positions of the acceptor atoms: a) $-x$, $-y$, $-z$; b) $-x+\frac{1}{2}$, $+y+\frac{1}{2}$, $-z+\frac{1}{2}$. The bond lengths are in Å and angles in degrees.

i.e. both H bonds are involved between Li and Tc adjacent coordination shells in the same polymeric chain. Instead, the terminating N atoms produce H interactions on the opposite side of the ligand plane with two non-coordinated sulfonate oxygens of one Li complex on an adjacent chain. In this way, they are responsible for the cohesive force between parallel polymer columns in the three-dimensional structure of the title compound.

Supplementary material

Anisotropic displacement parameters with corresponding e.s.d.s. (Table S1, 1 page), hydrogen fractional coordinates (Table S2, 1 page), full listing of bond lengths (Table S3, 1 page), full listing of bond angles (Table S4, 1 page), torsion angles (Table S5, 5 pages) and list of observed and calculated structure factors (Table S6, 22 pages) are available from the Cambridge Crystallographic Data Centre, quote full reference to this paper.

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