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A Technetium(V) Complex Resulting from Intramolecular Ring Closure of a Tridentate Schiff Base Ligand. X-ray Crystal Structure of Chlorobis(2-(2-hydroxyphenyl)benzothiazolato)oxotechnetium(V)

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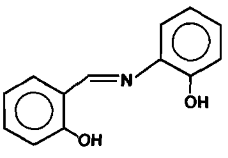
Abstract

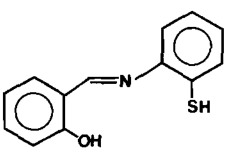
The X-ray crystal structure of a new technetium(V) complex, chlorobis(2-(2-hydroxyphenyl)benzothiazolato)oxotechnetium(V), $TcO(hbt)_2Cl$, is reported. Crystals of this complex were obtained from a dichloromethane solution containing predominately chloro[*N*-(2-mercaptophenyl)salicylideneiminato]-oxotechnetium(V), TcO(Sphsal)Cl. The new $TcO(hbt)_2Cl$ complex is presumably a minor product in the preparation of TcO(Sphsal)Cl; the bidentate hbt ligand is generated upon intramolecular ring closure of the tridentate Sphsal ligand. Single crystal X-ray structure analysis shows the $TcO(hbt)_2Cl$ complex to be six coordinate with two hbt ligands coordinating to a monooxo technetium(V) core through the phenolate oxygen atoms and the nitrogen atoms of the benzothiazole rings. One of the phenolate oxygen atoms is *trans* to the Tc=O linkage. The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.288(6)$, $b = 16.12(2)$, $c = 13.64(1)$ Å, $\beta = 94.65(6)°$, $V = 2912.05$ Å^3 and $Z = 4$. The structure has been refined to $R = 0.082$ for 1978 observed reflections.

Introduction

In a previous paper [1] we reported on the synthesis and characterization of two technetium(V) complexes with tridentate Schiff base ligands, *N*-(2-hydroxyphenyl)salicylideneimine ($H_2Ophsal$) and *N*-(2-mercaptophenyl)salicylideneimine ($H_2Sphsal$). The complexes TcO(Ophsal)Cl and TcO(Sphsal)Cl were characterized by elemental analysis, which gave a 1:1:1 Tc:Schiff base:Cl ratio, and by infrared and UV–Vis spectroscopy. Additionally, the Ophsal complex was characterized by single crystal X-ray diffraction. That structure determination showed that the complex was five coordinate with the tridentate Ophsal ligand binding through the two phenolate oxygen atoms and the imine nitrogen atom.

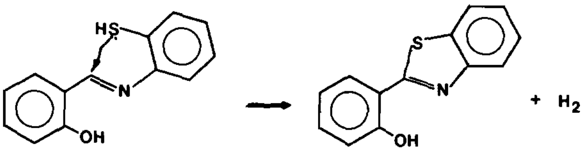


$H_2Ophsal$



$H_2Sphsal$

Subsequent to the publication of the above report, single crystals suitable for X-ray analysis were obtained from a dichloromethane/heptane solution of the TcO(Sphsal)Cl complex. X-ray structure analysis of these crystals, which we present here, shows that they are composed not of TcO(Sphsal)Cl as expected, but rather of a new complex, chlorobis(2-(2-hydroxyphenyl)benzothiazolato)-oxotechnetium(V), $TcO(hbt)_2Cl$. The new hbt ligand is formed from Sphsal by an oxidative intramolecular ring closure reaction.



$H_2Sphsal$ hbt

Experimental

Single crystals were obtained by slow evaporation of a solution of TcO(Sphsal)Cl in dichloromethane/heptane. A red–purple polyhedral crystal of approximate dimensions 0.25 × 0.30 × 0.35 mm was mounted on a glass fiber. Cu Kα radiation was used with a precession camera to obtain the *h*0*l*, *h*1*l*, 0*kl* and 1*kl* layer photographs. The systematic absences of *h*0*l* ($h + l =$ odd) and 0*k*0 ($k =$ odd) indicated the monoclinic space group $P2_1/n$, a nonconventional setting of the space group $P2_1/c$ used to obtain a β value close to 90°.

Data were collected on a Syntex P$\bar{1}$ automated diffractometer using Mo Kα radiation passed through

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a graphite monochromator. A least-squares analysis of 14 intense reflections in the region $4° < 2\theta < 16°$ yielded cell constants of $a = 13.288(6)$, $b = 16.12(2)$, $c = 13.64(1)$ Å, $\beta = 94.65(6)°$ and $V = 2912.05$ Å^3. For $Z = 4$ the calculated density (based on TcO-$(hbt)_2Cl \cdot 1.25CH_2Cl_2$ (*vide infra*)) is 1.62 g cm^{-3}, whereas the experimentally measured density is 1.71 g cm^{-3} (as determined by neutral buoyancy in a mixture of bromoform and carbon tetrachloride). Intensities were measured by using our established procedure [2] for 3814 reflections of the type $h, k \pm l$ in the region $2.5° < 2\theta < 45°$. From these, 1978 independent observed reflections ($I > 3\sigma(I)$) were obtained by averaging. To monitor crystal stability and long-term drift, four standard reflections were measured after every 36 reflections. The instability correction increased continuously from 1.00 to 1.52 indicating that the crystal was decomposing during data collection. Empirical absorption corrections were made [3] with the resulting corrections applied to I_0 varying from 1.02 to 1.16. The other details of data collection are as follows: scan method $2\theta/\theta$; scan rate 2–8°/min; scan range from 1.2° below the Kα_1 peak to 1.2° above the Kα_2 peak in 2θ; max $h = 14$, max $k = 15$, extreme $l = \pm 14$.

Structure Solution and Refinement

Zerovalent scattering curves from Cromer [4] were used for Tc, Cl, S, O, N and C. Scattering curves for hydrogen were taken from Stewart [5]. A Patterson vector map was calculated from the reduced diffraction data. From this map the positions of the Tc and coordinated Cl atoms were determined. The remaining atom positions were determined by using difference Fourier techniques. All of the non-hydrogen atoms of the complex and of a dichloromethane molecule were located. Two additional peaks were assigned as two chlorine atoms of a second dichloromethane molecule in a partially occupied site; each was assigned an occupancy coefficient of 0.25*. Refinement, based on F, of the positional parameters and the anisotropic thermal parameters of all other non-hydrogen atoms led to a final convergence at $R_1 = 0.082$ and $R_w = 0.106$. A final difference Fourier map indicated fifteen unassigned peaks that are greater than 0.5 e Å^{-3}. The five highest peaks, ranging from 0.72 to 2.3 e Å^{-3}, are located in the vicinity of the partially occupied CH_2Cl_2 molecule and probably represent an error in the estimation of the population factor and disorder of the positions of these atoms. It is likely that this situation is further complicated due to the decomposition of the crystal that occurred during data collection. The remaining ten peaks, each representing less than 0.71 e Å^{-3}, were located in close proximity to atoms of the metal complex or the other dichloromethane molecule.

Results and Discussion

The molecular structure of the complex, with associated atom numbering scheme and ellipsoids, is depicted in Fig. 1. Final atomic positional parameters are found in Table I. Selected bond lengths and angles are listed in Table II. See also 'Supplementary Material'

Crystal decomposition during data collection, as evidenced by visual inspection and by the continual decrease in the intensities of the standard reflections, most likely accounts for the partial occupancy of the second dichloromethane molecule. Using the experimentally determined value of the crystal density, a population factor of 0.73 for the second dichloromethane molecule can be obtained. Further refinement of this molecule was not attempted because all of the atoms of the metal complex and all but one Cl of the first dichloromethane molecule had converged with anisotropic refinement.

The crystallographic analysis clearly shows that the complex is six coordinate with a Tc:ligand:Cl ratio of 1:2:1, not the 1:1:1 ratio observed for the parent TcO(Sphsal)Cl complex [1]. Since the solution of TcO(Sphsal)Cl in dichloromethane/heptane yielded only a few crystals and a large amount of further uncharacterized powder, this new complex is presumably a minor product in the original TcO-(Sphsal)Cl preparation. To form this bidentate 2-(2-hydroxyphenyl)benzothiazole moiety (hbt), the tridentate *N*-(2-mercaptophenyl)salicylideneimine species undergoes an intramolecular ring closure at the thiol sulfur and an imine carbon atom. This ring closure has also been observed by Duatti and co-workers [6] who have done extensive work with tridentate sulfur-containing Schiff bases and their

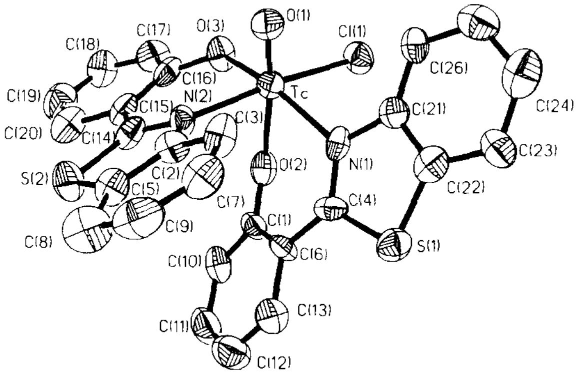

Fig. 1. ORTEP drawing of $TcO(hbt)_2Cl$ showing structure and atom numbering scheme.

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*One of these chlorine atoms (Cl(4)) was assigned an isotropic temperature parameter, B, of 4.2 Å^2. Isotropic temperature parameters are of the form $\exp(-B(\sin^2\theta/\lambda^2))$.

TABLE I. Atomic Positional Parameters ($\times 10^4$) for TcO(hbt)$_2$Cl·1.25CH$_2$Cl$_2$

Atom	*x*	*y*	*z*
Tc	5165(1)	2675(1)	5633(1)
O1	3974(10)	2886(8)	5702(10)
O2	6474(9)	2441(7)	5109(9)
O3	5862(10)	3561(8)	6408(9)
Cl1	5517(4)	1814(3)	7025(3)
N1	4787(11)	1544(8)	4779(10)
N2	5051(11)	3454(9)	4355(11)
S1	4708(4)	439(3)	3450(3)
S2	5703(4)	4484(4)	3108(4)
C1	6719(14)	2251(13)	4217(12)
C2	4493(14)	3312(12)	3482(14)
C3	3669(15)	2723(14)	3354(16)
C4	5227(15)	1329(12)	4000(13)
C5	4781(14)	3772(13)	2700(14)
C6	6069(14)	1733(12)	3622(13)
C7	3229(15)	2624(15)	2350(16)
C8	4389(18)	3710(17)	1701(18)
C9	3529(20)	3098(17)	1619(17)
C10	7576(15)	2551(12)	3865(14)
C11	7835(18)	2365(16)	2916(16)
C12	7183(19)	1870(16)	2312(17)
C13	6355(19)	1530(14)	2653(16)
C14	5691(15)	4094(11)	4273(15)
C15	6339(16)	4469(12)	5082(15)
C16	6362(16)	4194(12)	6078(16)
C17	7024(16)	4624(15)	6781(17)
C18	7560(18)	5311(15)	6561(17)
C19	7510(19)	5580(15)	5588(21)
C20	6910(16)	5159(14)	4827(18)
C21	3976(14)	1017(12)	5011(13)
C22	3849(16)	375(13)	4311(13)
C23	3122(16)	-268(13)	4387(15)
C24	2520(19)	-204(14)	5202(17)
C25	2638(17)	469(15)	5890(16)
C26	3386(15)	1075(12)	5785(14)
C27[a]	935(35)	1650(22)	3915(24)
Cl2[a]	1(7)	874(6)	4022(7)
Cl3[a]	1001(11)	2302(7)	4870(9)
Cl4[b]	8878(17)	4520(14)	3550(16)
Cl5[b]	4434(21)	1075(17)	417(14)

[a] Atom of the fully occupied dichloromethane molecule. [b] Atom of a dichloromethane molecule with a population factor set at 0.25. The carbon atom of this dichloromethane molecule was highly disordered and was not included in the final refinement.

TABLE II. Selected Bond Distances (Å) and Angles (°) for TcO(hbt)$_2$Cl·1.25CH$_2$H$_2$

Bond distances			
Tc–O1	1.63(1)	Tc–N2	2.14(1)
Tc–Cl1	2.368(6)	S1–C4	1.76(2)
Tc–O2	1.97(1)	S1–C22	1.71(2)
Tc–O3	1.96(1)	S1–C14	1.71(2)
Tc–N1	2.20(2)	S2–C5	1.74(2)
Bond angles			
O1–Tc–O2	162.1(6)	N2–Tc–O3	164.9(5)
O1–Tc–Cl1	101.9(5)	N2–Tc–O2	79.9(5)
O1–Tc–O3	103.6(6)	O3–Tc–O2	86.7(5)
O1–Tc–N1	91.2(6)	Tc–O3–C16	127(1)
O1–Tc–N2	85.4(6)	Tc–O2–C1	132(1)

derivatives. In the case we report here, it is unknown whether the hbt moiety is an impurity in the original preparation of the H$_2$Sphsal ligand or if it is formed during the reaction of the H$_2$Sphsal ligand with the technetium starting material.

Figure 1 shows that two hbt moieties each act as bidentate O, N donor ligands to the Tc atom which resides in an approximately octahedral environment. The arrangement of ligating atoms (one phenolate oxygen atom of one of the Schiff base ligands in an axial position *trans* to an 'yl' oxygen atom, two imine nitrogen atoms from the two Schiff base ligands in a *cis* configuration, with one chlorine atom and the second phenolate oxygen atom occupying the other two sites of the equatorial plane) is consistent with other structures observed for Tc(V) complexes of this type [7, 8]. The TcO^{3+} core is central to this and many other technetium(V) complexes containing anionic ligands [1, 7–15]. The Tc–O(1) bond distance of 1.63(1) Å is typical of Tc=O lengths in complexes where only one such linkage is present (1.65 Å average) [7]. The steric requirements of the 'yl' oxygen atom severely distort the geometry of the complex and result in non-orthogonal angles at technetium (Table II). As a result, the technetium atom is displaced 0.20 Å out of the mean equatorial plane towards the 'yl' oxygen. This value is similar to those reported for other six coordinate species containing the TcO^{3+} core [7, 8, 15]. The Tc–N distances of 2.14(1) and 2.20(2) Å are similar to others reported where the technetium atom is bonded to an equatorial nitrogen atom which is part of a conjugated ligand system [7, 8].

Supplementary Material

Tables of anisotropic thermal parameters (Table A), bond lengths (Table B), bond angles (Table C), root mean square displacements (Table D), and observed and calculated structure factors (Table E) (16 pages) are available. Ordering information is given on any current masthead page.

Acknowledgements

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