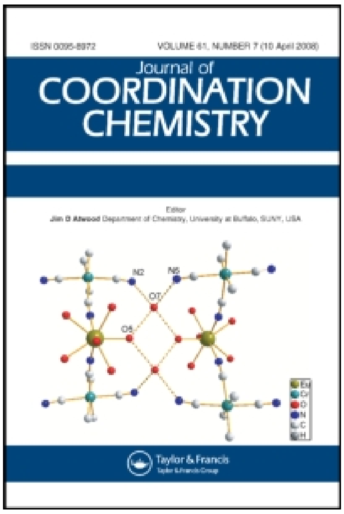

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE MIXED TER- AND BIDENTATE SCHIFF BASE TECHNETIUM(V) COMPLEX $TcO\{(o\text{-}O\text{-}C_6H_4)(CH_3)C{=}NN{=}C(S)(SCH_3)\}\{(CH_3)_2C{=}NN{=}C(S)(SCH_3)\}$[‡]

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(Received May 17, 1993)

The complex $TcO\{(o\text{-}O\text{-}C_6H_4)(CH_3)C{=}NN{=}C(S)(SCH_3)\}\{(CH_3)_2C{=}NN{=}C(S)(SCH_3)\}$ was prepared by the reaction of $(n\text{-}Bu_4N)[TcOCl_4]$ in methanol with the Schiff base *S*-methyl-*β*-*N*-(2-hydroxyphenylethylidene)dithiocarbazate in acetone. The compound was characterized by elemental analysis, vibrational and optical spectroscopy, and X-ray crystallography. Crystal data: $C_{15}H_{19}N_4O_2S_4Tc$, monoclinic, space group $P2_1/c$, $a = 14.799(5)$, $b = 7.470(2)$, $c = 19.272(5)$Å, $U = 2064.4(1.8)$Å^3, $Z = 4$, $D_{calc} = 1.65$ g cm^{-3}. The structure was refined by least-squares methods to $R = 0.102$. The complex has a Tc=O bond distance of 1.633(8)Å, and the deprotonated phenolic oxygen of the terdentate ONS-donor ligand is coordinated *trans* to the oxo oxygen.

KEYWORDS: Technetium(V), ter- and bidentate Schiff bases, crystal structure

INTRODUCTION

Oxotechnetium(V) complexes with polydentate Schiff base ligands have been extensively studied during the last few years. These ligands were mainly derivatives of *N*-phenylsalicylideneimine[1–3] and *S*-methyldithiocarbazate,[4–7] and generally contained the coordinating donor atom sets ON, SN, ONO, ONS, ONN, ONNO and SNNS.

It was established that the coordination mode of the Schiff bases depends on the number and nature of their donor atoms. Focusing on the site *trans* to the Tc=O linkage, ON donor ligands yield distorted octahedral complexes of the type $[TcOCl(ON)_2]$, with a phenolate oxygen *trans* to Tc=O.[1] Terdentate dianionic

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[‡] 1-Oxo-2,3,6-[*S*-methyl-*β*-*N*-(2-hydroxyphenylethylidene)dithiocarbazato-*N*,*S*,*O*]-4.5-[*S*-methyl-*β*-*N*-(isopropylidene)dithiocarbazato-*N*,*S*]technetium(V); a preliminary account of this work has been presented to the Topical Symposium on the Behaviour and Utilization of Technetium '93, Sendai (Japan), March 1993.

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ligands have been found to always coordinate in the equatorial plane *cis* to the oxo oxygen in distorted square pyramidal complexes of the type [TcOCl(ONX)] (X=O or S).[3,7,8] In a similar way, tetradentate ligands with the XNNX donor atom set coordinate in the equatorial plane.[2]

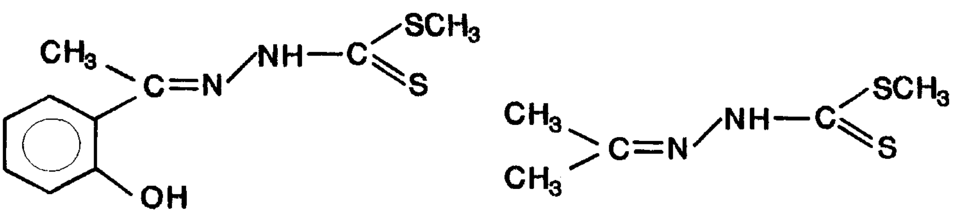
Examples of oxotechnetium(V) complexes containing both bi- and terdentate Schiff base ligands are rare in the literature. Tisato and coworkers[3] have found that the square pyramidal [TcOCl(ONS)] (ONS^{2-} = *N*-(2-mercaptophenyl) salicylideneiminate) does not react with bidentate Schiff bases containing NS^- donor atoms, but with ON^- donors the "mixed" complex [TcO(ONS)(ON)] were isolated, with the nitrogen atom occupying an equatorial position and the oxygen in the apical site *trans* to the oxo oxygen. These results imply that complexes of the type [TcO(ONS)(NS)] could not be formed, since the terdentate ligand would always coordinate in the equatorial plane, and the hard base O^-(of the bidentate ligand) is required to occupy the site *trans* to the oxo oxygen.

In this paper we report the synthesis and structural characterization of the distorted octahedral complex TcO(HAF)(PAC) containing the terdentate Schiff base ligand *S*-methyl-*β*-*N*-(2-hydroxyphenylethylidene)dithiocarbazate(HAF^{2-}), with an ONS^{2-} donor atom set, and the bidentate NS^- donor ligand *S*-methyl-*β*-*N*-(isopropylidene)dithiocarbazate (HPAC) (see Figure 1). The oxygen donor atom of the terdentate HAF^{2-} ligand occupies the axial site *trans* to the Tc=O bond, with the S_2N_2 donors in the equatorial plane.

EXPERIMENTAL

Materials

The compound (*n*-Bu_4N)[$TcOCl_4$][9] and the ligand H_2HAF[10] were prepared according to literature procedures. All solvents were of analytical grade and were purified and dried by standard methods.[11] All common laboratory chemicals were of analytical grade and were used without further purification.



H_2HAF **HPAC**

Figure 1 Ligands used in the study (H_2HAF = *S*-methyl-*β*-*N*-(2-hydroxyphenylethylidene) dithiocarbazate; HPAC = *S*-methyl-*β*-*N*-(isopropylidene)dithiocarbazate).

Apparatus

Scientific instrumentation used in this study is the same as reported elsewhere.[12]

Synthesis of [TcO(HAF)(PAC)]

To 50 mg (100 μmol) of (n-Bu_4N) [$TcOCl_4$] in 10 cm^3 methanol was added a solution of 96 mg (400 μmol) of H_2HAF in 10 cm^3 acetone with stirring. A brown precipitate immediately formed from the dark red solution. Stirring was continued for 30 min., after which the solution was filtered, and the filtrate was left to evaporate at room temperature for 48 h, with the concomitant formation of dark red crystals. The crystals were filtered off, washed with cold methanol and dried *in vacuo*. Crystals suitable for structure analysis were selected from this batch. Anal.: Calcd. for $C_{15}H_{19}N_4O_2S_4Tc$: C, 35.01; H, 3.72; N, 10.89%. Found: C, 35.43; H, 3.70; N, 10.74%. Conductivity (10^{-3}M, DMF): 18.0 $ohm^{-1}cm^2mol^{-1}$. IR spectrum (KBr): ν(Tc=O), 926; ν(C–O), 1253; ν(C=N), 1597, 1616: ν(Tc–S), 362,374 cm^{-1}. Electronic spectrum ($CHCl_3$, $cm^{-1}(\varepsilon/M^{-1}cm^{-1})$): 35800(17500), 29800(9300), 21600(3200).

Crystal data, structure determination and refinement

Details of crystal data, measurements of intensity, and processing are summarized in Table 1. Final atomic positional parameters are listed in Table 2. Selected

Table 1 Crystallographic data, collection, and refinement details for TcO(HAF)(PAC).

Molecular formula	$C_{15}H_{19}N_4O_2S_4Tc$
Molecular weight	514.5
Crystal dimensions/mm	0.20x0.15x0.08
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants (at 22°C); Mo-K_α radiation, λ = 0.71073Å)	a = 14.799(5) b = 7.470(2) c = 19.272(5)Å β = 104.31(10)° U = 2064.4(1.8)$Å^3$
Z	4
Density (calc.)	1.65 gcm^{-3}
F(000)	1040
μ/cm^{-1}	10.11
Diffractometer	Philips PW 1100
Scanning range for 2Θ	3–25°
Scan type	ω-2Θ
Scan speed	0.03° sec^{-1}
Scan range (ω)	1.25° plus K_α-separation
Independent reflections	3291
Reflections, $I > 2\sigma(I)$	2930
System used	SHELX 76
Solution	Heavy-atom methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Weighing scheme	$w^{-1} = \sigma^2(F)$
Number of parameters refined	256
Final R index (observed data)	R = 0.102

Table 2 Atomic coordinates (X 10^4) and equivalent isotropic displacement coefficients ($\text{Å}^2 \text{x} 10^3$).

Atom	*x/a*	*y/b*	*z/c*	*U**
Tc	2472(1)	1995(2)	1605(1)	61(1)
S(1)	1643(3)	-273(6)	2004(2)	105(4)
S(2)	3856(3)	666(6)	2199(2)	101(3)
S(3)	-225(3)	-18(7)	2158(2)	112(4)
S(4)	5685(3)	828(6)	1915(2)	75(3)
O(2)	2687(5)	840(9)	725(4)	51(5)
O(1)	2342(6)	3647(12)	2133(5)	68(6)
N(1)	340(6)	1921(17)	1192(6)	31(6)
N(2)	1140(8)	2281(15)	892(6)	75(9)
N(3)	4386(6)	3140(14)	1352(5)	44(6)
N(4)	3471(6)	3828(13)	1258(5)	46(6)
C(1)	713(12)	724(17)	1716(6)	141(15)
C(2)	943(8)	2576(15)	215(8)	36(8)
C(3)	-49(8)	2667(19)	-261(8)	35(8)
C(4)	4577(8)	1785(17)	1752(6)	54(9)
C(5)	3390(9)	5435(18)	1000(6)	60(9)
C(6)	2442(9)	6356(16)	879(8)	45(9)
C(7)	-1112(8)	1210(15)	1588(6)	60(9)
C(8)	6279(9)	2261(20)	1417(8)	72(11)
C(9)	4178(9)	6488(17)	838(7)	58(9)
C(10)	2538(8)	1695(14)	104(5)	61(8)
C(11)	3239(9)	1557(18)	-266(7)	74(10)
C(12)	3099(12)	2499(23)	-927(8)	119(15)
C(13)	2264(16)	3462(24)	-1179(9)	188(24)
C(14)	1608(12)	3517(22)	-832(8)	110(15)
C(15)	1701(9)	2640(16)	-181(6)	70(10)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

calculated bond lengths and angles are given in Table 3. The atom numbering scheme is shown in Figure 2. Additional data, including non-essential bond lengths and angles, anisotropic thermal parameters and a listing of the observed and calculated structure factors, are available as supplementary material from the authors, upon request.

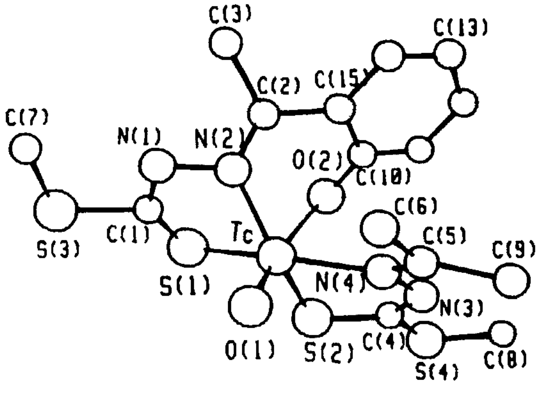


Figure 2 The structure of the TcO(HAF)(PAC) complex showing the atom labelling scheme.

Table 3 Bond lengths (Å) and angles (°) in the inner coordination sphere.

Tc–O(1)	1.633(8)		
Tc–O(2)	1.991(7)		
Tc–S(1)	2.327(4)		
Tc–S(2)	2.307(4)		
Tc–N(2)	2.114(11)		
Tc–N(4)	2.234(9)		
C(1)–N(1)	1.359(14)		
C(4)–N(3)	1.265(13)		
C(1)–S(1)	1.542(15)		
C(4)–S(2)	1.742(13)		
O(1)–Tc–O(2)	157.0(4)	N(4)–Tc–O(2)	76.1(3)
S(1)–Tc–S(2)	89.7(2)	N(4)–Tc–O(1)	84.7(4)
O(2)–Tc–S(1)	99.7(2)	N(4)–Tc–N(2)	108.7(4)
O(2)–Tc–S(2)	86.0(2)	C(1)–S(1)–Tc	91.6(5)
O(1)–Tc–S(1)	101.2(3)	S(1)–C(1)–N(1)	138.3(11)
O(1)–Tc–S(2)	103.4(3)	C(1)–N(1)–N(2)	101.1(10)
N(2)–Tc–S(1)	78.9(3)	N(1)–N(2)–Tc	115.9(7)
N(2)–Tc–S(2)	159.1(3)	Tc–S(2)–C(4)	97.2(4)
N(2)–Tc–O(2)	78.8(3)	S(2)–C(4)–N(3)	128.0(10)
N(2)–Tc–O(1)	96.0(4)	C(4)–N(3)–N(4)	115.5(10)
N(4)–Tc–S(1)	170.0(3)	N(3)–N(4)–Tc	114.8(7)
N(4)–Tc–S(2)	81.0(3)	N(3)–N(4)–C(5)	112.2(10)

RESULTS

The neutral six-coordinate technetium(V) complex TcO(HAF)(PAC) (HPAC = bidentate ligand *S*-methyl-*β*-*N*-(isopropylidene)dithiocarbazate) was prepared by the reaction of (*n*-Bu_4N)[$TcOCl_4$] in methanol with a fourfold molar excess of the potentially terdentate ligand *S*-methyl-*β*-*N*-(2-hydroxyphenylethylidene)dithiocarbazate (H_2HAF) in acetone under aerobic conditions at room temperature. The complex is dark red-brown in colour, and it dissolves in a variety of solvents to give orange-red solutions. The diamagnetic compound is a non-electrolyte in DMF and acetonitrile solution.

The infrared spectrum of the complex displays a very intense band at 926 cm^{-1}, which we attribute to the stretching frequency of the Tc=O group. This frequency occurs in the range 920–947 cm^{-1} in other neutral six-coordinate oxotechnetium(V) complexes containing terdentate and bidentate Schiff bases as ligands.[13,14] Two peaks at 1597 and 1616 cm^{-1} are assigned to ν(C=N), with the former value being associated with the coordinating aldimine nitrogens. The C=N vibrations of each ligand are not distinguishable. A doublet of peaks at 362 and 374 cm^{-1} is indicative of Tc-S stretching frequencies, and the ν(C—0) value of 1253 cm^{-1} suggests the coordination of the phenolic oxygen.

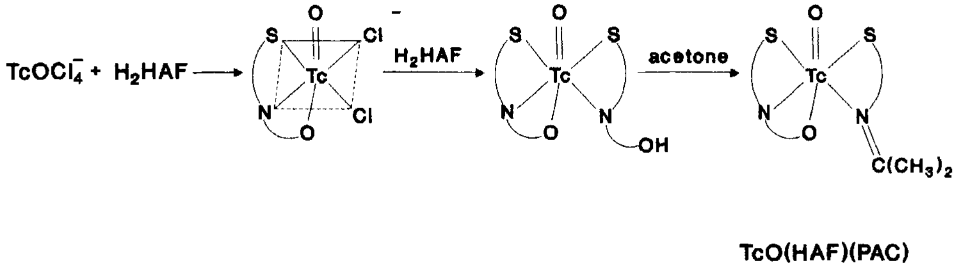
The crystal structure of TcO(HAF)(PAC) contains discrete, monomeric, neutral monooxotechnetium(V) complex units. Figure 2 illustrates the geometry and atom-numbering scheme. The HAF^{2-} moiety acts as a dinegative, terdentate O^-,N,S^--donor ligand to the technetium(V) ion, which resides in an approximately distorted octahedral coordination environment with the phenolic oxygen O(2) occupying the site *trans* to the oxo oxygen atom O(1). The PAC^- moiety acts as an uninegative bidentate N,S^--donor ligand, occupying the other two coordination sites in the equatorial square plane *cis* to the O(1) oxo ligand. The S and N atoms of the two ligating ligands form a *cis* arrangement in the equatorial plane. Distortions from an ideal Tc-centered octahedron are primarily due to the steric requirements of the oxo ligand and to the acute bite angles of the HAF^{2-} and PAC^{-} ligands: 78.9(3)° for N(2)—Tc—S(1) and 81.0(3)° for N(4)—Tc—S(2).

The Tc—O(1) distance of 1.633(8)Å indicates multiple bond character and is shorter than Tc=O lengths in complexes where only one such linkage is present (1.65Å average).[14] The steric requirements of this short bond profoundly distort the stereochemistry of the molecule. Particularly significant here is the repulsion between O(1) and the sulfur donor atoms, as evidenced by nonorthogonal angles at Tc of 101.2(3)° and 103.4(3)°. Consequently, the Tc atom is displaced by 0.20Å from the mean equatorial plane toward atom O(1). The distortion also results in a non-linear O(1)—Tc—O(2) axis of 157.0(4)°, accomplished by N(4)—Tc—S(1) and N(2)—Tc—S(2) angles of 170.0(3) and 159.1(3)°, respectively. The angle subtended at Tc by N(2) and O(2), involving a more rigid six-membered chelate containing an aromatic bond and a C=N double bond, also deviates considerably from the ideal value (N(2)—Tc—O(2) = 78.8°).

The bond lengths in the 'inner core' [Tc—O(2) 1.991(7), Tc—N(2) 2.114(11), Tc—N(4) 2.234(9), Tc—S(1) 2.327(4), Tc—S(2) 2.307(4)], apart from the somewhat long Tc—N(4) distance, do not merit any comment, since they do not differ significantly from expected values.[14–16] There is, however, a discrepancy in the bond lengths of the two non- coordinating C=N moieties [C(1)=N(1) 1.359(14), C(4)=N(3) 1.265(13)Å]. The shorter C=N bond is accompanied by a surprising lengthening of the adjacent C(4)—S(2) bond (1.742(13)Å),with the longer C=N bond accompanied by a shorter C(1)—S(1) bond of 1.542(15)Å. This phenomenon has previously been found for technetium complexes containing Schiff base type ligands,[7,17] and may contribute to the relatively high final discrepancy factor.

DISCUSSION

The formation of the ligand PAC^{-} from H_2HAF and its coordination to technetium are unexpected and surprising. Its formation is the result of ketone exchange between the solvent acetone and the 2-hydroxyacetophenone group of a H_2HAF molecule. We believe that this exchange occurs after the coordination of a second HAF^{2-} ligand, since such a substitution would be facilitated by the protons that are dissociated from the coordination of two H_2HAF molecules. A suggested reaction mechanism for the ketone exchange is presented in Scheme 1.



Scheme 1 Suggested reaction mechanism for the formation of TcO(HAF)(PAC).

No evidence could be found in this study, or in the literature, for the existence of an intermediate of the form $[TcOCl_2(HAF)]^-$ (see Scheme 1). Previous studies[7] of terdentate ligands of this type have only indicated the formation of the square pyramidal complex TcOCl(HAF), with no suggestion of an anionic intermediate. However, it was shown that the reaction of $(n\text{-}Bu_4N)[ReOCl_4]$ with H_2L (H_2L = potentially terdentate ligand *N*-(2-mercaptophenyl)salicylideneimine) in acetone, acetonitrile or dichloromethane led to the formation of the anion $[ReOCl_2(L)]^-$, which was isolated as the $n\text{-}Bu_4N^+$ salt.[3] It was suggested[3] that the terdentate ligand L^{2-} coordinates to rhenium(V) in the equatorial plane *cis* to the oxo oxygen, with a chloride in the *trans* position. If this configuration is also true for the suggested intermediate $[TcOCl_2(HAF)]^-$, the result would be that the bidentate ligand PAC^- must bridge an equatorial site and the position *trans* to the oxo group in the complex TcO(HAF)(PAC). The crystal structure determination of the complex clearly indicates that this is not the case.

Anionic intermediates are not without precedent in the literature. A six-coordinate anionic complex of the form $[TcOCl_3(L)]^-$ (HL = potentially bidentate NO- donor *N*-phenylsalicylideneimine) was isolated as the tetraphenylarsonium salt by the reaction of $[AsPh_4][TcOCl_4]$ with excess HL in ethanol under mild conditions, but no configuration for the compound was suggested.[2] Five-coordinate technetium(V) complexes of the type $TcOCl_2(L)$ have not been reported in the literature.

An anionic complex $[TcOCl_3(HL)]^-$ [L^{2-} = potentially quadridentate ONNO-donor *N,N'*-propane-1,3-diylbis(salicylideneiminate)], in which the ligand HL^- coordinates bidentately through one deprotonated phenolic oxygen and one imine nitrogen, has been isolated by the reaction of $TcOCl_4^-$ with excess H_2L in ethanol.[2] The reaction of $TcOCl_4^-$ with the potentially terdentate ONN-donor ligand 1-(8'-quinolyliminomethyl)-2-naphthol (HL) in anhydrous dichloromethane was reported to produce the intermediate complex $[TcOCl_3(L)]^-$, in which it was suggested that the ligand L^- acts in a bidentate manner, with the phenolate oxygen *trans* to the oxo group.[18]

While it was found that TcOCl(ONS) (ONS^{2-} = *N*-(2-mercaptophenyl)salicylideneiminate) does not react with bidentate Schiff bases with an NS-donor atom set,[3] the complex ReOCl(MeOH)(ONS) does react with *N*-(2-mercaptophenyl)-*p*-nitrobenzylideneimine (NS^-) to form the six-coordinate complex ReO(ONS)(NS). It was suggested that the mercapto sulfur of the bidentate ligand occupies the site *trans* to the Re=O bond.[3]

We believe that the relatively shorter Tc=O(1) bond length (1.633(8)Å) in TcO(HAF)(PAC) can be rationalized in terms of the considerable deviation of the O(1)—Tc—O(2) angle from linearity, which reduces π-bonding between the metal and O(2) and is responsible for the weakening of the *trans* influence of O(2). Table 4 shows that an increase in the $O{=}Tc{-}O_{trans}$ bond angle leads to an increase in the Tc=O bond length in complexes containing a phenolic oxygen in the *trans* position.

Acknowledgements

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Table 4 Relationship between the $O{=}Tc{-}O_{trans}$ bond angle and the Tc=O bond length in complexes containing a phenolic oxygen in the *trans* position.

Complex	$O{=}Tc{-}O_{trans}$ angle(°)	Tc=O bond length (Å)
TcO(HAF)(PAC)	157.0	1.633(8)
$TcO(oxMe)_2Cl$[a]	161.8	1.649(3)
$TcO(OPhsal)_2Cl$[b]	167.1	1.67(1)

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