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Synthesis and structure of oxotechnetium(V) complexes of *N,N'*-ethylenebis(acetylacetone thioimine) and *N,N'*-ethylenebis(benzylacetone thioimine)

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Abstract

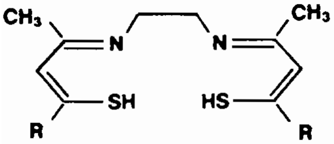
The synthesis, characterization, structural studies in solution and single-crystal X-ray analysis of two new oxotechnetium(V) complexes with *N,N'*-ethylenebis(acetylacetone thioimine) and *N,N'*-ethylenebis(benzylacetone thioimine) are reported. The crystals of the aqua [*N,N'*-ethylenebis(acetylacetone thioiminato)] oxotechnetium(V) complex, $TcO(H_2O)C_{12}H_{18}N_2S_2Cl$, are orthorhombic, space group *Pbcn* with $a = 24.609(1)$, $b = 12.4708(6)$, $c = 10.9951(5)$ Å, $V = 3374.4(1)$ Å^3 and $Z = 8$. The complex has a distorted octahedral coordination geometry containing a *trans*-oxoaquatechnetium(V) core. The UV–Vis and ^{1}H NMR spectra of the complexes in solution are solvent dependent indicating the presence of various ligands at the *trans* axial position.

Introduction

The value of ^{99m}Tc complexes in diagnostic nuclear medicine has stimulated considerable research on the coordination chemistry of technetium in the last decade. A significant portion of this work has been concentrated on the synthesis and structure determination of complexes containing oxotechnetium(V) centres [1–5].

Jurisson *et al.* studied the chemistry of N_2O_2 tetradentate Schiff base ligands with the TcO^{3+} core [6]. Such complexes can be used as precursors for the preparation of Tc(III) complexes which present interest as potential myocardial perfusion agents [7, 8].

Here we report the synthesis and structural studies of two new oxotechnetium(V) complexes with the N_2S_2 tetradentate Schiff bases I and II (Scheme 1).



Scheme 1. I: $(sacac)_2enH_2$, R = Me; II: $(phenylsacac)_2enH_2$, R = Ph

Experimental

Materials and methods

All laboratory chemicals were of reagent grade. Acetylacetone, benzoylacetone, ethylenediamine, boron fluoride etherate, epichlorhydrin and tetrabutylammonium chloride were used without further purification. Sodium hydrosulfide hydrate was ground to a powder and dried under vacuum for 24 h prior to use. Thiethyloxonium tetrafluoroborate, *N,N'*-ethylenebis(acetylacetone imine) and *N,N'*-ethylenebis(benzoylacetone imine) were prepared using literature methods [9, 10].

^{99}Tc was purchased from Amersham as ammonium pertechnetate in 0.088M NH_4OH (34 mg Tc/ml). n-Bu_4N ($TcOCl_4$) was prepared using the method of Davison *et al.* [11].

IR spectra were obtained from KBr pellets on a Perkin-Elmer 1600 FT-IR spectrophotometer. UV–Vis spectra were recorded in methanol and dichloromethane on a Beckman DU-65 spectrophotometer. The ^{1}H NMR spectra were obtained on a Varian FT-XL 100 spectrophotometer. Elemental analyses were performed by the Centre National de la Recherche Scientifique, Vernaison, France.

Ligand synthesis

The ligands $(sacac)_2enH_2$ (I) and $(phenylsacac)_2enH_2$ (II) were synthesized in a manner similar

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to that reported previously [12, 13]. The synthesis proceeds via nucleophilic substitution on *N*,*N'*-ethylenebis(acetoimine) precursors with hydrosulfide anion.

A dichloromethane solution of Et_3OBF_4 (0.1 mol to 50 ml CH_2Cl_2) was added to a dichloromethane solution of the appropriate *N*,*N'*-ethylenebis(acetoimine). After the addition was completed the reaction mixture was stirred for 30 min and 8 g NaHS in 100 ml EtOH were added. Stirring continued for a further 1 h in the case of $(sacac)_2enH_2$ and 12 h in the case of $(phenylsacac)_2enH_2$.

Crude **I** was isolated after filtration of the insoluble material and removing the solvent with a rotary evaporator at 25 °C. It was recrystallized from methanol at 25 °C. Yield 50%, m.p. 148–150 °C.

Crude **II** was isolated after evaporation of solvent under a nitrogen stream and extraction of the solid residue with dichloromethane. The dichloromethane was removed by rotary evaporation at 25 °C and hexane was added. The product was precipitated and recrystallized from benzene–ethanol at 25 °C. Yield 45%, m.p. 203–205 °C (decomposition).

Complex synthesis

TcO((sacac)$_2$en(H$_2$O))Cl (A)

n-$Bu_4N(TcOCl_4)$ (0.146 g; 0.293 mmol) was dissolved in absolute ethanol (20 ml) and ligand **I** (0.0768 g; 0.299 mmol) was added. The resulting solution was stirred until all the ligand had dissolved. The reaction mixture was rotary evaporated to dryness. The solid residue was recrystallized from acetone–methanol. Portions of ether were added and the solution allowed to stand overnight at 0 °C. Deep brown crystals were collected, washed with ether and dried over P_2O_5 *in vacuo*. Yield 59%. *Anal.* Calc. for $C_{12}H_{20}ClN_2O_2S_2Tc$: C, 34.08; H, 4.77; N, 6.62; S, 15.16. Found: C, 34.63; H, 5.38; N, 6.52; S, 14.66%.

TcO((phenylsacac)$_2$en)Cl (B)

The synthesis was carried out by a method similar to that described above. The crude product was recrystallized from acetone–dichloromethane. Brown crystals were collected, washed with ether and dried over P_2O_5 *in vacuo*. Yield 40%. *Anal.* Calc. for $C_{22}H_{22}ClN_2OS_2Tc$: C, 29.95; H, 4.19; N, 5.30; S, 12.12. Found: C, 49.61; H, 4.33; N, 5.17; S, 11.39%.

X-ray diffraction studies

Collection and reduction of intensity data

The complete crystal and intensity collection data are reported in Table 1. Space group *Pbcn* was recognized from preliminary oscillation and Weissenberg photographs. Unit cell parameters were derived from a least-squares refinement of the setting angles of 28 automatically centered intermediate 2*θ* reflections on a Syntex P2$_1$ diffractometer controlled by the Crystal Logic software. The intensities of three standards monitored after every 100 reflections were stable, with a scatter of less than 3% from their respective means. Lorentz and polarization, but no absorption, corrections were applied.

TABLE 1. Summary of crystal and intensity collection data.

Formula	$C_{12}H_{20}N_2S_2O_2ClTc$
M_r	421.89
a (Å)	24.609(1)
b (Å)	12.4708(6)
c (Å)	10.9951(5)
V (Å^3)	3374.4(1)
Z	8
D_{calc}/D_{meas} (g/cm^3)	1.661/1.66
Space group	*Pbcn*
Crystal dimensions (mm)	0.08×0.19×0.4
Radiation	Mo Kα (0.7107 Å)
μ (cm^{-1})	4.15
Scan speed (°/min)/scan range	3./1.9 plus α_1-α_2 divergence
2θ-limits (°)	51
Data collected/unique	3555/3131
Data used (observed with $F_o \geqslant 5.0\sigma(F_o)$)	2180
Data form (collected)	$h = -29 \rightarrow 0$, $k = -15 \rightarrow 0$, $l = 0 \rightarrow 13$
Weighting scheme	$1/w = ((\sigma(F_o))^2 + 0.0001xF_o^2)$
R/R_w (observed)	2.4/2.6
R/R_w (all data)	4.8/3.5
$F(000)$	1632
No. refined parameters	262
S[a]	1.29
$\Delta(\rho_{max})/\Delta(\rho_{min})$ (e/Å^3)	0.23/0.20
$\lvert\Delta/\sigma\rvert_{max}$	0.026

[a] $S = (\Sigma w(\Delta F)^2/(N-NP))^{1/2}$ (N = no. of F_{obs}, NP = no. of refined parameters.

Solution and refinement of the structure

The structure was solved by the SIR [14] and refined with the SHELX76 [15] programs using the full-matrix least-squares method. The weighting scheme applied in the final cycles is given by $1/\omega = \sigma^2(F_o) + 0.0001F_o^2$ and was chosen so that the average values of $\omega\Delta^2$ for ranges of increasing F_o were almost constant. H atoms were located from the difference Fourier map. Atomic scattering factors were taken from International Tables for X-Ray Crystallography [16].

TABLE 2. Identification of complexes

Absorption	IR (KBr) (cm^{-1})			
	Complex A		Complex B	
C=N	1512–1495		1496–1420	
C=C	1590		1586	
Tc=O	964		964	
C–H aromatic			763–690	
UV–Vis				
Color	yellow[a]	pinkish yellow[b]	yellow[a]	pinkish yellow[b]
λ_{max} (nm) $(\epsilon/\epsilon_0)^c$	414(1)	485(1)	360(1)	488(1)
	307sh(2.820)	305(3.104)	278(1.712)	340sh(3.413)
	270(3.913)	289(3.372)		270(5.151)

[a] In methanol. [b] In dichloromethane. [c] Ratio of extinction coefficients where ϵ_0 is the extinction coefficient of the absorption occurring at the highest wavelength.

TABLE 3. ^{1}H NMR chemical shifts in chloroform-d, δ (ppm)

Compound	$NCCH_3$	$SCCH_3$	NCH_2CH_2N	=CH	Aromatic			SH
					o	*m*	*p*	
Ligand **I**	2.10	2.54	3.72	6.14				14.40
TcO complex **A**	2.48	2.60	4.32	6.43				
Ni complex **A**	2.01	2.14	3.70	6.07				
Ligand **II**	2.45		3.90	6.60	7.75	7.30	7.33	14.72
TcO complex **B**	2.80		4.66	7.00	7.87	7.50	7.54	
Ni complex **B**	2.14		3.49	6.40	7.30		7.60	

Results

UV–Vis and ^{1}H NMR data obtained in solution

The position of maxima in the UV–Vis spectra of the complexes depends on the solvent used. Thus, complex **A** gives a maximum at 414 nm in methanol whereas in dichloromethane the maximum appears at 485 nm. The maximum of complex **B** in dichloromethane is at 488 nm whereas in methanol the maximum occurs at 360 nm (Table 2).

Table 3 gives the proton NMR chemical shifts of the ligands and the complexes at room temperature in chloroform-d solutions. Two *gauche* and one *trans* rotameric isomers about the ethylenic C–C bond are possible for the ligands. The *gauche* conformers are stabilized by intramolecular hydrogen bonds involving the thioiminato protons [17]. Each rotamer gives a A_2B_2 pattern for the NCH_2CH_2N protons which are equivalent in pairs. The barrier to rotation is low so that the spectrum observed at room temperature corresponds to the average of rotamers (Fig. 1). In the complexes all protons are shifted to lower field with respect to the ligands. A *trans* coupling of 0.9 Hz is observed in complex **A** between the CH proton and the methyl protons adjacent to sulfur. Each tetradentate ligand appears as completely symmetrical in the complexes: the chemically equivalent CH, $NCCH_3$ and $SCCH_3$ protons are also magnetically equivalent and the bridging ethylene protons give a simple A_2B_2 pattern. This is due to thermal motions which result in an averaged structure where the nitrogen and the sulfur atoms are effectively in one plane and the ethylenic protons are interconverting rapidly on the NMR scale [18].

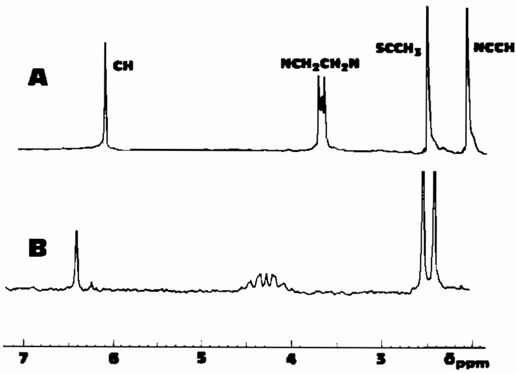

Fig. 1. ^{1}H NMR spectra at 100 MHz, room temperature, in chloroform-d. A: $(sacac)_2enH_2$, B: $(sacac)_2enTcO$.

Solid state data

Each complex exhibits a characteristic Tc=O stretching vibration at 964 cm^{-1} which is indicative of a monooxo Tc(V) species (Table 2).

X-ray diffraction analysis of complex **A** shows that the technetium is hexacoordinated. The octahedral geometry is distorted with the TcO^{3+} core lying 0.42 Å above the NNSS mean plane and a water molecule occupying the *trans* axial position (Fig. 2 and Table 4). The *trans*-oxoaqua Tc(V) core is very similar to that of the *N*,*N*′-ethylenebis(acetylacetone imine) complex ($TcO(H_2O)(acac)_2en$) [6] with a very short Tc=O bond, 1.643(3) Å, and a long Tc–Ow bond, 2.384(3) Å (Table 5). Again the strong *trans* influence of the Tc=O bond weakens the Tc–Ow bond. There is one chlorine atom per cation but it occupies two independent special positions. Two cations related by a two-fold axis are hydrogen bonded to each other via the water molecules and the chloride ions thus forming discrete 'dimers' (Fig. 3).

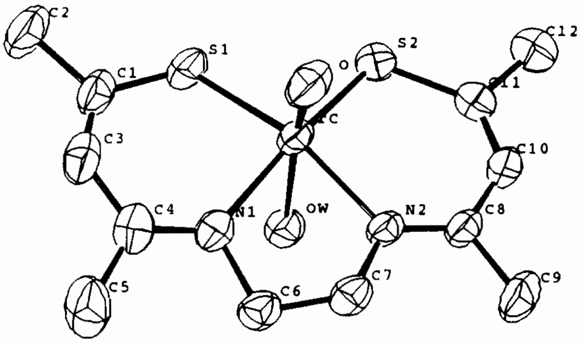

Fig. 2. ORTEP drawing of complex **A** showing the labelling scheme. 50% probability ellipsoids are shown.

TABLE 4. Positional and equivalent thermal parameters (×10⁴) of non-hydrogen atoms

Atom	*x*	*y*	*z*	*U*ᵃ
Tc	3446.2(1)	2211.5(2)	1158.0(3)	402
Cl(1)	5000	60(9)	2500	465
Cl(2)	5000	3822(1)	2500	595
S(1)	3428.9(4)	3954.9(7)	1850(1)	558
S(2)	2913.3(4)	1919.9(7)	2857(1)	598
N(1)	4154(1)	2488(2)	151(3)	425
N(2)	3709(1)	623(2)	1021(2)	390
O	2999(1)	2186(2)	49(3)	646
Ow	4148(1)	2044(2)	2640(3)	458
C(1)	3748(2)	4748(3)	766(4)	555
C(2)	3603(3)	5917(3)	890(6)	778
C(3)	4101(2)	4428(3)	−78(4)	574
C(4)	4351(2)	3398(3)	−248(3)	518
C(5)	4894(3)	3419(5)	−878(6)	819
C(6)	4474(2)	1500(3)	−8(4)	479
C(7)	4119(2)	522(3)	43(3)	475
C(8)	3515(1)	−233(2)	1549(3)	434
C(9)	3718(3)	−1321(3)	1181(6)	697
C(10)	3116(1)	−233(3)	2498(4)	495
C(11)	2863(1)	557(3)	3102(3)	481
C(12)	2474(2)	293(4)	4105(5)	661

ᵃ$U=(U_{11}+U_{22}+U_{33})/3$.

TABLE 5. Selected interatomic distances (Å) and angles (°)

Tc–S(1)	2.304(1)	N(1)–C(4)	1.310(4)
Tc–S(2)	2.311(1)	N(1)–C(6)	1.473(4)
Tc–N(1)	2.092(3)	C(6)–C(7)	1.501(5)
Tc–N(2)	2.089(2)	N(2)–C(7)	1.480(4)
Tc–O	1.643(3)	N(2)–C(8)	1.305(4)
Tc–Ow	2.384(3)	C(8)–C(9)	1.503(5)
S(1)–C(1)	1.736(4)	C(8)–C(10)	1.434(5)
C(1)–C(2)	1.507(5)	C(10)–C(11)	1.341(5)
C(1)–C(3)	1.334(6)	C(11)–C(12)	1.496(6)
C(3)–C(4)	1.436(5)	S(2)–C(11)	1.726(4)
C(4)–C(5)	1.507(6)		
S(1)–Tc–S(2)	82.6(1)	Tc–N(2)–C(8)	129.1(2)
S(1)–Tc–N(1)	92.0(1)	C(7)–N(2)–C(8)	120.2(3)
S(2)–Tc–N(1)	157.8(1)	S(1)–C(1)–C(2)	112.5(4)
S(1)–Tc–N(2)	157.6(1)	S(1)–C(1)–C(3)	127.1(3)
S(2)–Tc–N(2)	94.9(1)	C(4)–N(1)–C(6)	119.2(3)
N(1)–Tc–N(2)	82.0(1)	C(2)–C(1)–C(3)	120.4(4)
S(1)–Tc–O(1)	104.5(1)	C(1)–C(3)–C(4)	129.5(4)
S(2)–Tc–O(1)	102.5(1)	N(1)–C(4)–C(3)	125.1(4)
O(1)–Tc–N(1)	99.7(1)	N(1)–C(4)–C(5)	119.8(4)
O(1)–Tc–N(2)	97.8(1)	C(3)–C(4)–C(5)	115.1(4)
S(1)–Tc–Ow	82.5(1)	N(1)–C(6)–C(7)	111.3(3)
S(2)–Tc–Ow	81.1(1)	N(2)–C(7)–C(6)	110.8(3)
Ow–Tc–N(1)	76.9(1)	N(2)–C(8)–C(9)	119.8(4)
Ow–Tc–N(2)	75.1(1)	N(2)–C(8)–C(10)	125.1(3)
O(1)–Tc–Ow	172.3(1)	C(9)–C(8)–C(10)	115.1(3)
Tc–S(1)–C(1)	107.6(1)	C(8)–C(10)–C(11)	132.7(3)
Tc–S(2)–C(11)	108.8(1)	S(2)–C(11)–C(10)	127.8(3)
Tc–N(1)–C(4)	128.8(2)	S(2)–C(11)–C(12)	112.2(3)
Tc–N(1)–C(6)	111.8(2)	C(10)–C(11)–C(12)	120.0(4)
Tc–N(2)–C(7)	110.1(2)		

The two hydrogen bonds are Ow–HwA...Cl2 and Ow–HwB....Cl1 with Ow–Cl equal to 3.055(3) and 3.247(3) Å, and Ow–H...Cl equal to 168(4) and 167(4)°, respectively.

Complex **B** according to elemental analysis does not contain water in the solid state but chlorine is present 1:1 to technetium.

Discussion

Diamagnetic square planar complexes of Ni, Pd, Zn and Cd with ligand **I** and the complex of Ni with ligand **II** have been reported [18, 19], In all cases the ^1H NMR chemical shifts observed upon complexation were of less magnitude than in the present oxo–technetium(V) complexes and to opposite direction. In Table 2 the chemical shifts of

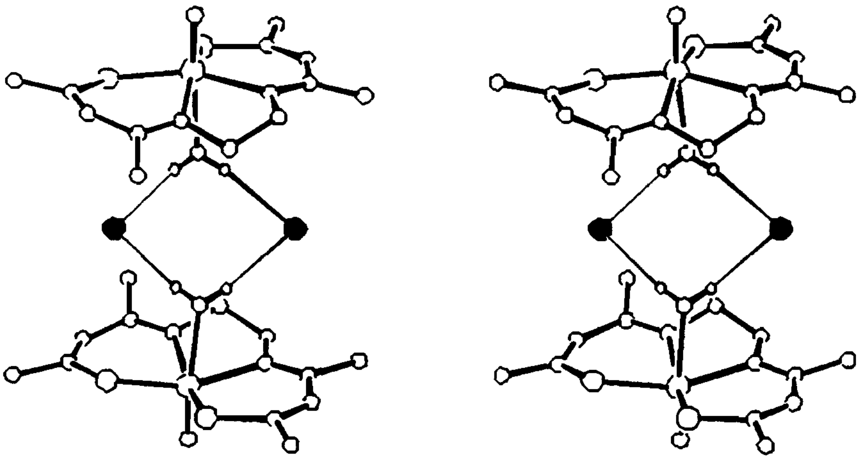

Fig. 3. ORTEP stereo drawing showing the discrete 'dimers' of complex I generated through the H bonds. Chlorine atoms are shaded.

Ni complexes with ligands I and II are listed for comparison with the oxotechnetium complexes. The largest upfield shift was observed in Ni complexes for the $SCCH_3$ protons. Accordingly, the shifts to higher field have been attributed to the increase of electron density on the ligand due to the metal to sulfur backbonding. Complexes **A** and **B** have a distorted octahedral geometry with the metal lying out of the plane defined by the nitrogen and sulfur atoms. This configuration might be unfavorable for the interaction of the pair of d_ϵ electrons with the d orbitals of sulfur. In addition the oxygen of the Tc=O group is expected to drain electron density from the ligand.

The thioiminato oxotechnetium(V) complexes **A** and **B** reported in this paper are closely related to the corresponding iminato complexes reported by Jurisson *et al.* [6]. The X-ray structure of complex **A** establishes the presence in the solid state of a water molecule at the axial site *trans* to the oxygen. Accordingly, the oxotechnetium configuration corresponds to the $(O{=}Tc{-}OH_2)^{3+}$ core. A similar core is present in methanolic solution with one solvent molecule at the *trans* axial position. This is confirmed by the presence of the UV charge transfer band at 414 nm. In dichloromethane, a non-coordinating apolar solvent, the maximum is shifted to 485 nm, a sign that the identity of the *trans* axial ligand has changed. The bathochromic shift suggests that the new ligand is a halide ion. Chloride ions are present in the solution originating from the crystal. Chloride is a better donor than the oxygen of water or methanol and thus the energy required for the transition is lower. The negative charge of the halide neutralizes the positive charge of the oxotechnetium core and thus the complex is stabilized in the non-polar medium. The presence of chloride in the first coordination sphere of the closely related *N,N'*-ethylenebis(salicylidene imine)oxotechnetium(V) complex has been established by X-ray analysis [6]. Moreover, halogen-to-technetium charge transfer bands have been reported for other Tc complexes [20]. The elemental analysis of complex **B** has not revealed the presence of water in the solid state probably because the compound was recrystallized from acetone–dichloromethane and not acetone–methanol as was the case for complex **A**. It seems that under the influence of dichloromethane the chloride ion was favored as the *trans* axial ligand.

The geometry of oxotechnetium(V) complexes is defined by the nature of the ligands [21]. We have presented here experimental evidence showing that the complexes of *N,N'*-ethylenebis(acetylacetone thioimine) and *N,N'*-ethylenebis(benzylacetone thioimine) are hexacoordinated and their structure in solution and in the solid state is similar to that reported for Tc oxotechnetium(V) acetylacetone imine complexes.

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