Inorganica Chimica Acta, *82* (1984) 201–205

The Chemistry of Rhenium and Technetium. Part 1. Syntheses and Characterisation of New Dioxo Technetium(V) Complexes with Schiff Base Type Ligands

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Received June 2, 1983

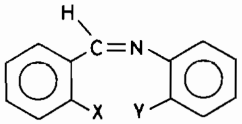
The syntheses and characterisation of several new anionic dioxo technetium(V) complexes containing dianionic tridentate and monoanionic bidentate Schiff base ligands are described. Complexes containing a sulphur donor atom as a functional group in these systems have a much lower O=T=O stretching frequency that is generally found for the trans-TcO_2 moiety. The complexes have been characterised on the basis of elemental analyses, infrared and electronic spectra, conductance and magnetic susceptibility measurements.

Introduction

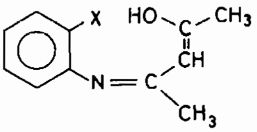
The main interest in the chemistry of the very rare and scarce element technetium centres around its applications in nuclear medicine. Although it is presently widely applied, there are some areas where its applicability is limited. The aim of this research is to obtain a closer correlation between the coordination chemistry of technetium and its application, specifically in those areas where its present application is unsatisfactory.

In our opinion, one of the main pre-requisites of nuclear medicinal systems should be their particular kinetic stability in which cases suitable chelate ligands will be preferable. Of special interest are those chelate systems in which donor atoms can readily be exchanged for other types of donor atoms as to vary significantly the electronic milieu in the coordination sphere of technetium, for example, exchanging a phenolic oxygen atom for a thiophenolic sulphur atom. Schiff-base types of ligands appear to be one of the better systems to fulfil these requirements, and although they have been well studied with the first row transition metals [1], relatively few complexes of the early heavy transition metals (including technetium) are known with Schiff bases.

In this account, we now report the formation and characterisation of potentially bi- and tridentate Schiff base complexes of technetium(V). Structural formulae for the Schiff base ligands used in this study are given in Fig. 1.



X	*Y*	*Abbreviation*
OH	OH	H_2SAL
OH	SH	H_2SAM
H	SH	HBEM
OH	H	HSAP



X	*Y*	*Abbreviation*
SH		H_2AMA
OH		H_2AHA

Fig. 1. Schiff base ligands used in this study.

In addition to the Schiff base ligands mentioned above, complexes were also prepared using part of the structural unit of the Schiff bases, namely 2-aminophenol (HAP) and 2-aminothiophenol (HATP).

Experimental

Materials

Technetium (as NH_4TcO_4) was obtained from the Oak Ridge National Laboratory. ^{99}Tc is a weak β-emitter (0.292 keV) and so all manipulations were carried out in a radiation laboratory with a monitored fume hood. Radioactive wastes, both liquid and solid, were disposed in special receptacles.

All the solvents used were purified and dried by standard methods. Tetra-n-butylammonium chloride (Fluka) was dried in vacuo at 85 °C for 24 hours prior to use. Salicylaldehyde (Riedel-de-Haën) was vacuum distilled before use; benzaldehyde, aniline (Merck), 2-aminophenol, acetylacetone (Hopkins and Williams), and 2-aminothiophenol (Fluka) were used without any further purification.

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0020-1693/84/$3.00

The ligands 2′-hydroxybenzylidine-2-hydroxyaniline (H_2SAL) [2], 2′-hydroxybenzylidine-2-thiolaniline (H_2SAM) [3], benzylidine-2-thiolaniline (HBEM) [2], 2′-hydroxybenzylidine-aniline (HSAP) [2], 4′-oxypentyl-2′-idine-2-thiolaniline(H_2AMA) [4] and 4′-oxypentyl-2′-idine-2-hydroxy aniline (H_2AHA) [4] were prepared by methods published in the literature.

Physical Measurements

Infrared spectra were recorded on a Beckman IR 4250 grating spectrophotometer in the range 4000–250 cm^{-1} as KBr pellets. Optical spectra were obtained with a Perkin-Elmer 330 UV–vis spectrophotometer. Melting points were measured on a Mettler FP1 apparatus and are uncorrected. Thermal studies were made using a Perkin-Elmer thermogravimetric balance and a System 4 Microprocessor controller. Conductivity measurements were performed in nitromethane using a Metrohm E518 conductometer. Magnetic moments were measured with a Gouy balance using a Newport Instruments electromagnet and a Sartorius balance. Elemental analyses were performed using a Heraeus Rapid Analyser.

Preparation of Complexes

$(Bu_4N)^+[TcO_2(SAL)(H_2O)]^-$

2.5×10^{-3} Mol of ligand H_2SAL (0.5331 g) was dissolved in 50 ml of a 1:1 0.6 mol dm^{-3} aqueous NaOH solution and acetone. To this solution was added 2.2 ml of a 0.362 mol dm^{-3} aqueous NH_4TcO_4 solution. A freshly prepared solution of 0.555 g $Na_2S_2O_4$ (3.2×10^{-3} mol) in 10 ml of a 0.6 mol dm^{-3} NaOH solution was added rapidly to the reaction mixture, followed shortly by the addition of 2 ml of a 30% aqueous Bu_4NCl solution. After evaporation of the acetone, the formed suspension was filtered and washed with a few ml of the hydroxide solution and distilled water. The red precipitate was dried *in vacuo* overnight. Recrystallisation from acetone/water afforded red-orange needles, yield = 68%.

$(Bu_4N)^+[TcO_2(SAM)(H_2O)]^-$; $(Bu_4N)^+[TcO_2(SAP)_2]^- \cdot 3/2H_2O$; $(Bu_4N)^+[TcO_2(AMA)(H_2O)]^- \cdot 1/2H_2O$ and $(Bu_4N)^+[TcO_2(AHA)(H_2O)]^- \cdot H_2O$

2.5×10^{-3} Mol of ligands H_2SAM, HSAP, H_2AMA and H_2AHA was dissolved in 50 ml of a 0.6 mol dm^{-3} NaOH solution, and 2.2 ml of a 0.362 mol dm^{-3} NH_4TcO_4 solution (8.15×10^{-4} mol) added. A freshly prepared solution of 0.555 g $Na_2S_2O_4$ in 10 ml of a 0.6 mol dm^{-3} NaOH solution was added to the reaction mixture rapidly, followed by the addition of 2 ml of 30% Bu_4NCl in water. After five minutes of stirring the suspension was filtered, and the solids washed with a few ml of the hydroxide solution and distilled water.

The crude precipitate was extracted three times with 5 ml portions of acetone. The combined filtered extracts were mixed with 5 ml of water and stored for 24 hours at −15 °C. The resulting dark-red crystals were filtered, washed with water, and dried overnight on a vacuum line.

$(Bu_4N)^+[TcO_2(BEM)_2]^- \cdot 3/2H_2O$

0.5332 g of HBEM (2.5×10^{-3} mol) was dissolved in 50 ml of methanol with the addition of 2.5 ml of a 1 mol dm^{-3} MeO^-Na^+ solution (23 g Na dissolved in 1000 ml methanol). To this was added 2.2 ml of a 0.362 mol dm^{-3} aqueous NH_4TcO_4 solution, followed by a freshly prepared aqueous solution of 0.555 g $Na_2S_2O_4$. One minute later 2 ml of a 40% aqueous Bu_4NCl solution was added, giving a red precipitate. After stirring for 5 minutes the precipitate was filtered, washed with water and methanol and dried under vacuum. Recrystallisation from acetone gives red crystals, yield = 72%.

$(Bu_4N)^+[TcO_2(AP)_2]^-$ and $(Bu_4N)^+[TcO_2(ATP)_2]^-$

16 Mmol of 2-aminophenol or 2-aminothiophenol was added to 10 ml of methanol with the addition of 2.5 ml of a 1 mol dm^{-3} $CH_3O^-Na^+$ solution. 2 Ml of a 0.362 mol dm^{-3} aqueous solution of NH_4TcO_4 was added, followed by a freshly prepared solution of 0.555 g $Na_2S_2O_4$ in 10 ml of a 0.6 mol dm^{-3} NaOH solution. The addition of Bu_4NCl precipitates a dark red suspension, which was filtered and washed with water and methanol.

The crude precipitate was extracted three times with 5 ml of ethyl acetate. The combined filtered extracts were left to evaporate over a period of 2 days with the formation of red pyramidal crystals, which were dried under vacuum overnight.

Results and Discussion

Pertechnetate reacts with the potentially tridentate Schiff bases in water, using sodium dithionite as reducing agent, with the formation and isolation of complexes with the general formula $(Bu_4N)[TcO_2$ (Schiff base) $(H_2O)]$. These complexes do not lose mass or decompose at 120 °C, and this suggests that the water molecule is coordinated. The potentially bidentate anionic Schiff base ligands BEM^- and SAP^- form complexes of the formula $(Bu_4N)[TcO_2$ (Schiff base$)_2] \cdot 3/2H_2O$. All these complexes are six-coordinated and contain technetium in the oxidation state +5. The physico-chemical properties and elemental analyses of these complexes are given in Table I.

All the complexes are crystalline red solids and appear to be indefinitely stable in the solid state. Although the ligands themselves are somewhat susceptible to hydrolysis, these metal chelates are quite stable towards hydrolysis. The complexes are soluble in almost all of the non-polar and low-polarity solvents tried.

TABLE I. Physico-Chemical Properties and Elemental Analyses.

Complex	%C		%H		%N		M. pt. (°C)	Colour
	Calc.	Found	Calc.	Found	Calc.	Found		
$(Bu_4N)[TcO_2(SAL)(H_2O)]$	57.8	57.6	7.9	7.8	4.7	4.7	143	red
$(Bu_4N)[TcO_2(SAM)(H_2O)]$	56.3	56.2	7.7	7.6	4.5	4.5	153	red
$(Bu_4N)[TcO_2(BEM)_2]\cdot 3/2H_2O$	60.5	60.2	7.3	7.3	5.0	5.1	113	red
$(Bu_4N)[TcO_2(SAP)_2]\cdot 3/2H_2O$	64.2	63.8	7.4	7.5	5.3	5.5	166	red
$(Bu_4N)[TcO_2(AMA)(H_2O)]\cdot 1/2H_2O$	53.5	53.8	8.3	8.2	4.6	4.6	186	orange
$(Bu_4N)[TcO_2(AHA)(H_2O)]\cdot H_2O$	54.1	54.0	8.6	8.4	4.7	4.5	172	red
$(Bu_4N)[TcO_2(AP)_2]$	57.0	57.0	8.2	8.0	7.1	7.2	141	red
$(Bu_4N)[TcO_2(ATP)_2]$	54.3	54.1	7.8	7.7	6.8	6.6	149	red

Infrared data are given in Table II. The infrared spectra of all the complexes are closely related, suggesting similar configurations of the coordinated ligands. The ν(C=N) stretching frequencies (1635–1585 cm^{-1} in the free ligands) are shifted to 1623–1562 cm^{-1} in the corresponding complexes. The ν(O–H) bands observed in the free ligands disappear upon coordination, and the ν(C–O) phenolic stretch at 1490–1540 cm^{-1} in the free ligands shift to higher energy (1535–1570 cm^{-1}) in the complexes, indicating deprotonation and coordination at the oxygen site. It is of interest that the C–O stretching frequencies are significantly increased when a thiophenolic S atom replaces a phenolic oxygen atom (Table II, compounds I, II and III, IV). The ν(C–S) band in the Schiff bases occurs at 650–680 cm^{-1}. This band shifts to higher energy (670–700 cm^{-1}) in the complexes, indicating coordination at the sulphur site. These results are fully consistent with the conclusion that the ligands H_2SAL, H_2SAM, H_2AMA and H_2AHA coordinate to Tc(V) as dianionic terdentate Schiff bases; the coordinating sites being the imino nitrogen and the oxygen and/or sulphur atoms. Ligands HBEM, HSAP, HAP and HATP coordinate to Tc(V) as mono- anionic bidentate ligands. The $\nu_{as}(TcO_2)$ stretch of the complexes containing no sulphur atoms occurs within the range observed for dioxo technetium(V) compounds, *viz.* 790–880 cm^{-1} [5, 6]. However, the TcO_2 stretching frequencies for the complexes containing sulphur as a donor atom are found between 740 and 750 cm^{-1}.

These values are of particular interest since they are lower than for any dioxo technetium(V) compound reported thus far. Replacement of an oxygen atom [for example $TcO(SCH_2CH_2O)_2^-$, $\nu(Tc{=}O) = 948$ cm^{-1}] [7] with a sulphur donor atom [as in $TcO(SCH_2CH_2S)_2^-$, $\nu(Tc{=}O) = 935$ cm^{-1}] [8] leads, without exception, to a reduction of the Tc=O stretching frequency in anionic as well as neutral technetium(V) complexes. The extent of the reduction of the technetium bond order (stretching frequency) could be expected to be lower in this type of complex, although hardly as much as that found for the dioxo complexes containing SAM$^=$, AMA$^=$ and ATP$^-$ as multidentate ligands. This phenomenon should in our view be interpreted in terms of the fact that the thiophenolic sulphur donor atom, for example in $TcO_2(SAM)(H_2O)^-$, is part of a conjugated system which could increase the Tc–S bond order significantly, resulting in a surprisingly large axial O=Tc=O bond weakening.

The nature of the donor atoms in the planar delocalized chelate system could also be expected to be a significant factor. In the case where a O_3N planar chromophore, as in $TcO_2(SAL)(H_2O)^-$, is replaced by a O_2NS chromophore, as in $TcO_2(SAM)(H_2O)^-$, the influence of the sulphur donor atom, and resultant significant increase in covalence of the Tc–S bond, is underlined by the presence of the two or three electronegative oxygen atoms which will have much greater polarity in their interactions with the technetium(V) in these systems.

Although Tc(V) has a d^2 configuration, all the complexes studied are diamagnetic. Such diamagnetism has been explained in terms of the strong π-bonding between the metals d_{xz} and d_{yz} orbitals and the p orbitals of the oxo ligands [9]. This cannot readily be visualised in the case of the complexes reported herein, as a result of the exceptionally low O=Tc=O stretching frequencies of the sulphur-containing complexes. This could only be interpreted as to indicate that the extent of the π-bonding, supplemented by extensive delocalisation in all the complexes reported here, also plays an important role in pairing the electrons of the d^2 system. Results obtained by Davison *et al.* [8] for monoxo dithiolic ligands are in agreement with this statement even though the Tc=O stretching frequencies obtained by them did not indicate such weak Tc=O bonding.

Conductivity measurements (Table III) of 10^{-3} mol dm^{-3} nitromethane solutions of these complexes at 25 °C indicate that they are 1:1 electrolytes.

Details of the optical spectra are summarised in Table IV. In general, there is at least one band in the range 320–350 nm ($\epsilon \sim 3400$–$21\,000$ dm^3 mol^{-1} cm^{-1}) and only one band in the range 285–310 nm

TABLE II. Selected Infrared Spectral Data of the Dioxo Complexes (cm^{-1})*.

Compound		ν_{as}(Tc=O)	ν(C=N)	ν(C–S)	ν(C–O)
(I)	$(Bu_4N)([TcO_2(SAL)(H_2O)]$	798	1585		1562
(II)	$(Bu_4N)(TcO_2(SAM)(H_2O)]$	748	1614	700	1568
	$(Bu_4N)[TcO_2(BEM)_2]\cdot 3/2H_2O$	743	1575 1562	695	
	$(Bu_4N)[TcO_2(SAP)_2]\cdot 3/2H_2O$	808	1623 1608		1545
(IV)	$(Bu_4N)[TcO_2(AMA)(H_2O)]\cdot 1/2H_2O$	747	1573	694	1546
(III)	$(Bu_4N)[TcO_2(AHA)(H_2O)]\cdot H_2O$	781	1623		1535
	$(Bu_4N)[TcO_2(AP)_2]$	798			1546
	$(Bu_4N)[TcO_2(ATP)_2]$	743		658	

*KBr discs.

TABLE III. Conductivities of 10^{-3} mol dm^{-3} Nitromethane Solutions of the Complexes at 25 °C.

Compounds	Λ(μS cm^{-1})
$(Bu_4N)[TcO_2(SAL)(H_2O)]$	52
$(Bu_4N)[TcO_2(SAM)(H_2O)]$	54
$(Bu_4N)[TcO_2(BEM)_2]\cdot 3/2H_2O$	47
$(Bu_4N)[TcO_2(SAP)_2]\cdot 3/2H_2O$	87
$(Bu_4N)[TcO_2(AMA)(H_2O)]\cdot 1/2H_2O$	57
$(Bu_4N)[TcO_2(AHA)(H_2O)]\cdot H_2O$	61
$(Bu_4N)[TcO_2(AP)_2]$	66
$(Bu_4N)[TcO_2(ATP)_2]$	58

TABLE IV. Electronic Absorption Spectra of the Complexes in Chloroform at 20 °C.

$(Bu_4N)[TcO_2(SAL)(H_2O)]$	324(7400), 289(9000)
$(Bu_4N)[TcO_2(SAM)(H_2O)]$	345(15100), 306(10900)
$(Bu_4N)[TcO_2(BEM)_2]\cdot 3/2H_2O$	343(21700), 327(21300) 308(23000)
$(Bu_4N)[TcO_2(SAP)_2]\cdot 3/2H_2O$	329(3400), 288(7200)
$(Bu_4N)[TcO_2(AMA)(H_2O)]\cdot 1/2H_2O$	344(14900), 304(9200)
$(Bu_4N)[TcO_2(AHA)(H_2O)]\cdot H_2O$	322(11400), 307(13400)
$(Bu_4N)[TcO_2(AP)_2]$	317(13800), 287(14600)
$(Bu_4N)[TcO_2(ATP)_2]$	344(21000), 309(14600)

($\epsilon \sim 7200$–$23\,000$ dm^3 mol^{-1} cm^{-1}). Due to the intensity of these bands, they are therefore likely to be charge-transfer transitions. The transitions at 343–345 nm are only present in the sulphur-containing complexes, and can therefore be associated with a charge transfer mainly between the sulphur donor atom and the technetium(V) ion. It can similarly be visualised that the low-wavelength peaks (highest energy) can essentially be correlated with the O=Tc=O charge transfer. It is now of interest that the low-wavelength peak is increased in each case where an oxygen atom is replaced by a sulphur atom in the planar chelate system. This is in agreement with the infrared stretching frequency of the TcO_2 moiety, which decreases correspondingly.

On the basis of information presently available, it appears that cationic dioxo complexes of Tc(V) are formed when the ancillary ligands are neutral and serve as poor π-donors, *e.g.* $[TcO_2(cyclam)]^+$ [5] and $[TcO_2(py)_4]^+$ [10]. When the ligands are negatively charged and function as good π-donors, only five-coordinate anionic monooxo complexes are formed, *e.g.* $[TcO(SCH_2CH_2S)_2]^-$ [11] and $TcOCl_4^-$ [8].

The anionic dioxo technetium(V) complexes prepared in this study contain negatively charged ancillary ligands that should donate significant negative charge to the technetium(V) centre. In terms of this one would thus rather expect the formation of cationic monoxo species. In our opinion the main contributing factors to the selective formation of these *dioxo* technetium(V) species are the overall *effective* Lewis basicity of the planar ligand systems in collaboration with the stereochemical limitations of these systems, and not so much the formal charge of the planar ancillary ligands, *i.e.* neutral or anionic. In the title complexes the dianionic Schiff bases will, in the light of their conjugated nature, be strongly covalently bonded to the technetium (σ and π), but at the same time the 'overall effective Lewis basicity', meaning the net resulting electron transfer into the technetium, will be reserved in view of the conjugated character of the total system. This will result in the residual Lewis acidity necessary for the bonding of a second oxo ligand. The unexpected stability of these anionic dioxo technetium(V) compounds corresponds to these arguments.

This study emphasises the marked influence of the extent of delocalisation in the planar system on the properties of the axial ligands, especially in anionic dioxo technetium(V) complexes, and the dramatic effect which the replacement of relatively electronegative donor atoms by only one significantly less electronegative atom in a delocalized system has on the TcO_2 moiety.

Acknowledgements

We thank the Nuclear Corporation, Council for Scientific and Industrial Research and the University of Port Elizabeth for financial assistance.

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