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EVIDENCE FOR BIDENTATE AND TERDENTATE COORDINATION OF THE LIGAND 2,2':6',2''-TERPYRIDINE IN OXOTECHNETIUM(V) COMPLEXES

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Complexes formed by the ligand exchange reactions of $[\text{TcOCl}_4]^-$ with the potentially terdentate nitrogen-donor ligand 2,2':6',2''-terpyridine (terpy) under different reaction conditions have been investigated. Both bidentate and terdentate coordination of terpy have been established in the complexes prepared. In dichloromethane as reaction medium the six-coordinate complex $\text{TcOCl}_3(\text{terpy-}N,N')$ has been isolated, in which terpy acts as a bidentate ligand. The reaction of terpy with a twofold molar excess of $[\text{TcOCl}_4]^-$ in boiling ethanol led to the formation of the cationic six-coordinate complex $[\text{TcOCl}_2(\text{terpy-}N,N',N'')]^+$, which precipitated from solution as the pertechnetate salt. With terpy in excess to $[\text{TcOCl}_4]^-$ the cationic dimeric complex $\mu\text{-O}[\text{TcOCl}(\text{terpy-}N,N',N'')]_2\text{Cl}_2$, was isolated in ethanol. The reaction of TcO_4^- with terpy in an ethanolic/HCl solution led to the precipitation of the neutral six-coordinate complex $\text{TcOCl}_3(\text{terpy}\cdot\text{HCl})$, which could also be prepared from $[\text{TcOCl}_4]^-$. These compounds were characterized by elemental analysis, vibrational, optical and proton nuclear magnetic resonance spectroscopy.

Keywords: Technetium(V), terpyridyl, complexes, bidentate, spectroscopy.

INTRODUCTION

The current interest in the chemistry of technetium centres around the application of Tc-99m (γ -emitter, half-life=6 h) in diagnostic nuclear medicine.¹ Although the chemistry of this element with nitrogen donor ligands is well understood,^{2,3} no technetium(V) complexes have been prepared with potentially terdentate nitrogen donor ligands.

We have used the potentially terdentate aromatic nitrogen-donor ligand 2,2':6',2''-terpyridine (terpy; Figure 1) to prepare oxotechnetium(V) complexes. Transition metal complexes have been reported⁴ in which the terpy ligand acts as a terdentate chelate, but examples where terpy acts as a bidentate (with one pyridine ring uncoordinated) have also appeared in the literature.⁵ We in fact found both coordination modes of terpy in the complexes prepared in this study.

EXPERIMENTAL

Health Precautions

All references to technetium in this paper are to the isotope ⁹⁹Tc, which is a β -emitter

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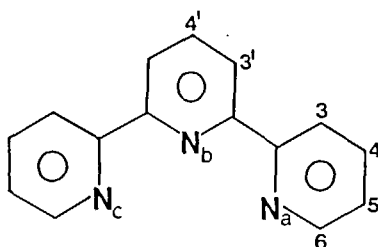


FIGURE 1 The ligand 2,2':6',2''-terpyridine in a *cis-cis* configuration.

(0.292 MeV) with a half-life of 2.12×10^5 years. Precautions have been detailed elsewhere.⁶

Materials

The compound $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ was prepared according to literature procedures.⁷ The ligand 2,2':6',2''-terpyridine was obtained commercially (Fluka AG), and was purified by sublimation. All solvents were of analytical grade, and were purified and dried by standard methods.⁸

Apparatus

Scientific instrumentation used in this study is the same as reported elsewhere.⁶

Synthesis of the Complexes

$[\text{TcOCl}_3(\text{terpy-N,N'})]$ (1)

A solution of 47 mg (201 μmol) of terpy in 5 cm^3 dichloromethane was added with stirring to 100 mg of $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ (200 μmol) in 5 cm^3 dichloromethane. The colour of the solution changed to orange-red immediately on addition, with the concomitant formation of an orange-brown precipitate. The solution was stirred for a further 20 min at room temperature, and the precipitate was removed by filtration. It was washed with ethanol and dichloromethane, and dried under vacuum. The yield was 82 mg, 76% based on Tc; mp 165°C (decomp.). The complex is moderately soluble in DMF, DMSO and nitromethane, weakly soluble in acetonitrile, poorly soluble in THF and acetone, and insoluble in alcohols and chloroform. Anal.: Calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_3\text{OCl}_5\text{Tc}$: C, 39.63; H, 2.44; N, 9.24; Cl, 23.39%. Found: C, 39.42; H, 2.68; N, 9.56; Cl, 23.61%. Conductivity (10^{-3} M, CH_3NO_2): 43 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

$[\text{TcOCl}_2(\text{terpy-N,N',N''})][\text{TcO}_4]$ (2)

To 200 mg (400 μmol) of $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ in 5 cm^3 ethanol was added 47 mg (201 μmol) of terpy in 5 cm^3 ethanol, and the reaction mixture was heated under reflux for 20 min. After cooling to room temperature, the orange precipitate was removed by filtration, washed with ethanol and acetone, and dried under vacuum. The yield was 84 mg, 72% based on Tc; mp > 300°C. The compound is moderately soluble in DMF, DMSO and nitromethane, and insoluble in chloroform, acetonitrile,

alcohols, acetone and dichloromethane. Anal.: Calcd. for $C_{15}H_{11}N_3Cl_2O_5Tc_2$: C, 30.95; H, 1.90; N, 7.22; Cl, 12.18%. Found: C, 30.76; H, 2.18; N, 7.03; Cl, 12.38%. Conductivity (10^{-3} M, CH_3NO_2): $83 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

$\mu\text{-O}[\text{TcOCl}(\text{terpy-}N,N',N'')_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (3)

A twofold excess (95 mg; $407 \mu\text{mol}$) of terpy in 10 cm^3 ethanol was mixed with 100 mg of $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ in 5 cm^3 ethanol. The reaction mixture was heated under reflux for 20 min, and after cooling to room temperature a fine, microcrystalline, dark, blue-violet precipitate was collected by filtration. This solid was washed with ethanol and dried under vacuum. The yield was 61 mg, 66% based on Tc; mp $> 300^\circ\text{C}$. The complex is soluble in DMF and DMSO, poorly soluble in acetonitrile and insoluble in dichloromethane, acetone and chloroform. Anal.: Calcd. for $C_{30}H_{30}N_6Cl_4O_7Tc_2$: C, 38.89; H, 3.26; N, 9.07; Cl, 15.31; H_2O , 7.78%. Found: C, 38.74; H, 3.13; N, 9.66; Cl, 15.31; H_2O , 7.87%. Conductivity (10^{-3} M, DMF): $122 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

$[\text{TcOCl}_3(\text{terpy.HCl})]$ (4)

A solution of 145 mg ($622 \mu\text{mol}$) terpy in 10 cm^3 ethanol was added to 0.65 cm^3 of a 0.34 M aqueous NH_4TcO_4 ($221 \mu\text{mol}$) solution in 10 cm^3 ethanol. The dropwise addition of 2 cm^3 concentrated HCl solution to this mixture resulted in the formation of a white precipitate (possibly $\text{terpy} \cdot 2\text{HCl}$). The reaction mixture was heated under reflux for 10 min, and a clear yellow solution was obtained, which was filtered whilst hot. The solution was cooled to room temperature, and after an hour a green precipitate was collected by filtration. This material was washed with ethanol and acetone, and dried under vacuum. The yield was 77 mg, 71% based on Tc; mp 139°C (decomp). It is insoluble in acetone, toluene, dichloromethane, acetonitrile and chloroform. Anal.: Calcd. for $C_{15}H_{12}N_3Cl_4OTc$: C, 36.69; H, 2.46; N, 8.56; Cl, 28.88%. Found: C, 36.98; H, 2.67; N, 8.36; Cl, 28.44%. Conductivity (10^{-3} M, DMF): $107 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

This complex could also be obtained by the reaction of $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ with a twofold molar excess of terpy in the presence of hydrochloric acid in ethanol. This method of preparation led to a slightly better yield (78%), and the melting point, colour, infrared and NMR spectra of this product were identical to that obtained with NH_4TcO_4 as one of the starting materials.

RESULTS

Syntheses

The room temperature reaction of $[\text{TcOCl}_4]^-$ with an equimolar quantity of terpy in anhydrous dichloromethane led to the isolation of the product $[\text{TcOCl}_3(\text{terpy-}N,N')]$ in good yield. The reaction of terpy with a twofold molar excess of $[\text{TcOCl}_4]^-$ in boiling ethanol led to the formation of the cationic six-coordinate complex $[\text{TcOCl}_2(\text{terpy-}N,N',N'')]^+$, which precipitated from solution as the pertechnetate salt. With terpy in excess to $[\text{TcOCl}_4]^-$, the cationic dimeric compound $\mu\text{-O}[\text{TcOCl}(\text{terpy-}N,N',N'')_2\text{Cl}_2$ was isolated in ethanol under aerobic conditions. The reaction of TcO_4^- with terpy in an ethanolic/HCl solution led to the precipitation of the neutral six-coordinate complex $[\text{TcOCl}_3(\text{terpy.HCl})]$. The same product was also prepared independently from $[\text{TcOCl}_4]^-$ and terpy in ethanolic aqueous hydrochloric acid solution at room temperature. The latter method of synthesis led

to an increased yield, and the identical character of the product obtained by these two preparative methods was established by melting point, electronic, infrared and ^1H NMR spectroscopy.

The complexes are poorly soluble in common organic solvents, but they are reasonably soluble in DMF and DMSO. In the latter solvents complexes (1), (2) and (4) dissolve to give yellow solutions, but (1) assumes an orange colour on standing for 5 minutes. The dark purple complex (3) dissolves in DMF to give purple solutions, which turn green on standing in air. The complexes are stable in the solid state for weeks.

Conductivity measurements performed on complex (4) in DMF showed a value of $107 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (Λ_M in DMF for 1:1 electrolyte = $65\text{--}90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; 1:2 electrolyte = $130\text{--}170 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$), indicating dissociation of the pyridinium chloride and possibly also partial dissociation of a technetyl chloride.

All other physico-chemical properties of the complexes are given in the Experimental Section.

Characterization

In the infrared spectra of the complexes in the solid state the $\nu(\text{Tc}=\text{O})$ of complex (1) was found at 974 cm^{-1} , and in the cationic complex (2) this frequency shifted to 979 cm^{-1} (see Table 1). The $\nu(\text{Tc}=\text{O})$ in the complex $\text{TcOCl}_3(\text{bipy})$ was reported² to occur at 980 cm^{-1} . The presence of the TcO_4^- entity in compound (2) was indicated by two strong bands at 911 and 899 cm^{-1} , which are assigned to $\nu(\text{Tc}^{\text{VII}}=\text{O})$. In complex (3) there is only one peak of medium intensity at 936 cm^{-1} , which is assigned to $\nu(\text{Tc}=\text{O})$. An intense band at 679 cm^{-1} , which is absent in the spectra of complexes (1) and (2), is ascribed to $\nu_{\text{asym}}(\text{Tc}-\text{O}-\text{Tc})$, as was reported previously for similar dimeric $[\text{M}_2\text{O}_3]^{4+}$ species.⁹ Complex (4) displays the $\nu(\text{Tc}=\text{O})$ at 941 cm^{-1} , which occurs in the range expected for neutral six-coordinate monooxotechnetium(V) complexes.

TABLE I
Principal infrared spectral parameters (in cm^{-1}) of the complexes.

Compound	$\nu(\text{Tc}=\text{O})$	$\nu(\text{Tc}-\text{Cl})$	$\nu(\text{pyridine})^*$ deform
$\text{TcOCl}_3(\text{terpy}-N,N')$	974	315	1618 1605 1589
$[\text{TcOCl}_2(\text{terpy}-N,N',N'')][\text{TcO}_4]$	979 911 899	310 297	1617 1603
$\mu\text{-O}[\text{TcOCl}(\text{terpy}-N,N',N'')]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	936 679*	315	1611 1591
$\text{TcOCl}_3(\text{terpy} \cdot \text{HCl})$	941	319 315 284	1618 1607 1588

* Frequencies of pyridine ring deformations, * $\nu(\text{Tc}-\text{O}-\text{Tc})$.

The three distinct bands that are displayed by complexes (1) and (4) in the range $1588\text{--}1618\text{ cm}^{-1}$ are assigned to deformation vibrations of the three pyridine rings, and are indicative of bidentate coordination of terpy to Tc(V). A similar infrared criterion has been used to detect free 2-pyridyl groups in complexes of (2-pyridylmethyl)amines.¹⁰ Terdentate coordination of terpy in complexes (2) and (3) are indicated by the appearance of only two bands in the range $1591\text{--}1617\text{ cm}^{-1}$.

All the complexes display a band of medium intensity in the near-infrared region around 315 cm^{-1} , which is ascribed to the Tc-Cl stretching vibrations of chlorine atoms *cis* to the technetyl oxo oxygen. An additional band in the range $284\text{--}297\text{ cm}^{-1}$ for complexes (2) and (4) is indicative of $\nu(\text{Tc-Cl})$, with the chloride *trans* to the Tc=O bond.

Proton nuclear magnetic resonance spectral data for the complexes are summarized in Table II. The labelling scheme for the protons is shown in Figure 1. The aromatic regions of the proton NMR spectra of terpy and the complexes are shown in Figure 2. Assignments follow those previously published.¹¹

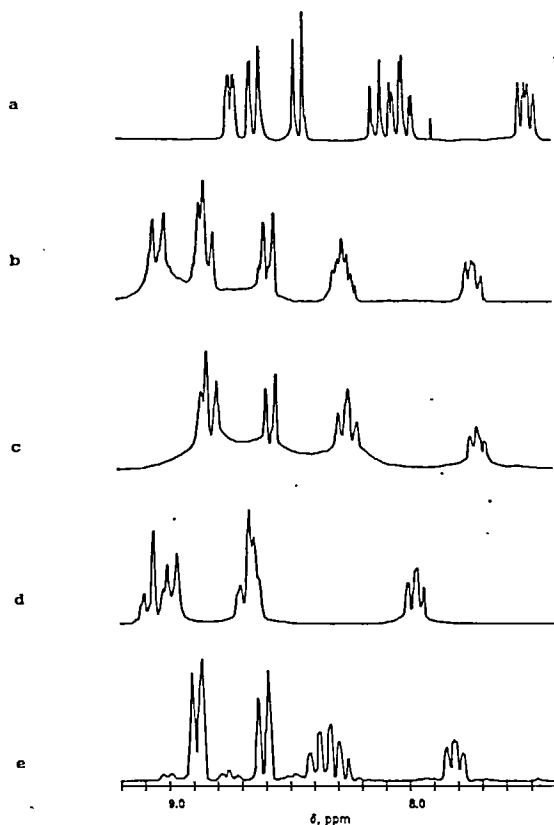


FIGURE 2 The 200 MHz proton magnetic resonance spectra of (a) terpy, (b) $\text{TcOCl}_3(\text{terpy-}N,N')$, (c) $[\text{TcOCl}_2(\text{terpy-}N,N',N'')]_2^+$, (d) $\mu\text{-O}[\text{TcOCl}(\text{terpy-}N,N',N'')]_2^+$ and (e) $\text{TcOCl}_3(\text{terpy.HCl})$ in $(\text{CD}_3)_2\text{SO}$ in parts per million from internal Me_4Si at 22°C .

TABLE II
Proton nuclear magnetic resonance shifts (δ ppm) and coupling constants (Hz).

	H ₄	H ₄ '	H ₅	H ₅ '	H ₃	H ₃ '	H ₃ '	H ₃ '	H ₄	H ₄ '	H ₄ '	J _{H5-H6}	J _{H4-H3}
terpy	8.73	8.73	7.50	7.50	8.45	8.63	8.45	8.63	8.02	8.02	8.10	4.7	7.6
TcOCl ₃ (terpy- <i>N,N'</i>)	9.04	8.68	7.72	7.72	8.85	8.57	8.85	8.57	8.25	8.23	8.28	6.3	6.6
[TcOCl ₂ (terpy- <i>N,N',N''</i>)]TcO ₄	8.56	8.56	7.71	7.71	8.81	8.81	8.81	8.81	8.24	8.24	8.24	6.1	7.3
μ -O[TcOCl(terpy- <i>N,N',N''</i>)] ₂ Cl ₂ ·4H ₂ O	9.00	9.00	7.97	7.97	9.07	9.07	9.07	9.07	8.69	8.69	8.69	6.1	7.5
TcOCl ₃ (terpy·HCl)	8.63	8.63	7.82	7.82	8.90	8.90	8.90	8.90	8.37	8.37	8.30	6.4	7.0

The spectrum of complex (1) in d_6 -(CD₃)₂SO shows complex patterns in the aromatic region as can be expected for the unsymmetrical coordination of the terpy ligand, and the region integrates for 11 protons as required for one terpy ligand. The doublet that appears the farthest downfield at δ 9.04 ppm is assigned to proton 6 of a coordinated pyridine ring, and the additional small splittings of this peak indicate long range coupling to protons 3 and 4. It is also the small splittings (\sim 1–2 Hz) in the doublet at δ 8.68 ppm that makes it assignable to proton 6 of the uncoordinated pyridine ring. The two overlapping triplets at \sim δ 7.72 ppm integrate for two protons, and are assigned to protons 5. The two multiplets in the regions δ 8.57–8.85 ppm and δ 8.23–8.28 ppm are assigned to the four protons 3 and 3' and protons 4 and 4', respectively.

A particularly interesting feature of the ¹H NMR spectrum of complex (2) is the switch of the resonances of the four protons 3 and 3' (which occur as a doublet the farthest downfield at δ 8.81 ppm and that integrates for 4 protons) and protons 6 (which occur as a doublet at δ 8.56 ppm and that integrates for two protons). It is assumed, *mutata mutandis*, that the presence of the counterion does not change the chemical shifts of the protons in the cation. With reference to the shifts assigned to the protons of the complex TcOCl₃(terpy-*N,N'*), the chemical shifts of protons 4 and 4' and 5 and 5' remain basically unchanged. The magnetic equivalence and identical chemical shifts of the corresponding protons of the two terminal pyridine rings suggest that terpy acts as a terdentate ligand in the complex, *i.e.*, with a planar *cis-cis* configuration. In such a planar arrangement of the three pyridine rings, protons 3 and 3' will lie very close to each other, and van der Waals forces are expected to contribute significantly, together with the anisotropic effect of the ring current, to the observed deshielding of these protons. The triplet at δ 8.24 ppm is assigned to protons 4 and 4' and the equivalence of the two protons 5 is illustrated by the triplet that appears at δ 7.71 ppm.

The relative simplicity of the ¹H NMR spectrum of the complex μ -O[TcOCl(terpy-*N,N',N''*)]₂Cl₂·4H₂O in d_6 -(CD₃)₂SO illustrates that the corresponding protons in the two terpy ligands are magnetically equivalent. The whole spectrum is shifted further downfield than that of [TcOCl₂(terpy-*N,N',N''*)]⁺. The presence of four moles of water is illustrated by the peak at δ 2.53 ppm, which integrates for 8 protons. The well-defined triplet that appears at δ 7.97 ppm integrates for 4 protons, and are assigned to protons 5 of two terpy ligands. The resonances of protons 3 and 3' (a doublet at δ 9.07 ppm) again appear further downfield than the resonances of protons 6 (a doublet at δ 9.00 ppm). These results imply that both the terminal pyridine rings of the terpy ligands are coordinated.

The ¹H NMR spectrum of complex (4) in (CD₃)₂SO is inconclusive with regard to the coordination mode of terpy and the structure of the complex in solution. The

TABLE III
Electronic absorption bands for the complexes in acetonitrile.

	$\lambda_{\max}(\text{nm})$	$\epsilon(\text{M}^{-1} \text{cm}^{-1})$
TcOCl ₃ (terpy- <i>N,N'</i>)	668	125
	526	590
	370sh	
	316	12500
	280	13400
[TcOCl ₂ (terpy- <i>N,N',N''</i>)] [TcO ₄]	642sh	
	552	1850
	437	3570
	330sh	
	311	9230
$\mu\text{-O}[\text{TcOCl}(\text{terpy-}N,N',N'')]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	282sh	
	271	13700
	627sh	
	559	2430
	328sh	
TcOCl ₃ (terpy·HCl)	310	10050
	302sh	
	275	12550
	659	170
	531	490
	368sh	
	333sh	
	319	13200
	283	13700

complex decomposes in DMSO, in which it dissolves to give a pink solution, which turns to red on standing for a few minutes. The aromatic region of the spectrum of this red solution integrates nevertheless for 11 protons. The resonance of the NH⁺ proton could not be established.

Ultraviolet spectra of the complexes are dominated by absorptions due to electronic transitions centred on the terpy ligand (see Table III). It has previously been suggested¹² that a considerable amount of structural information can be obtained from these spectra. It has been reported¹² that terpy exists in the *trans-trans* configuration in basic solution with two absorption maxima at 227 and 290 nm, and that three maxima are discernible at intermediate pH at 232, 279 and 320 nm. A blurring of the fine structure in the 279 nm band was ascribed to rotation about the C–C bond. In acidic solution it was suggested that terpy exists in the *cis-cis* configuration since fine structure in the 279 nm band is evident, indicating a coplanar structure. It was found¹³ that the complex Cu(terpy)₂⁺ exhibits three absorption maxima at 227, 275 and 308 nm, with a blurred fine structure in the absorption maxima at 275 nm, which suggests free rotation about one of the C–C bonds connecting the pyridine rings. These results were interpreted in terms of bidentate coordination of the two terpy ligands in the compound Cu(terpy)₂⁺.

TcOCl₃(terpy-*N,N'*) exhibits two dominant absorptions in the ultraviolet region at 280 and 316 nm (Table III). A blurring of the fine structure in the 280 nm peak

suggests rotation about the C–C bond, and the most likely structure for the complex appears to be one in which terpy acts as a bidentate ligand, with one pyridine ring free to rotate in solution.

Ultraviolet spectra of complexes (2) and (3) in acetonitrile are characterized by intense absorption maxima around 273 and 310 nm. Fine structure is clearly discernible in the absorption band around 273 nm, which suggests terdentate coordination of the ligand terpy. Evidence of fine structure in the intense band in the range 270–285 nm for numerous metal complexes having terpy as one of the ligands has been interpreted in terms of terdentate coordination of terpy¹², and independent evidence has indicated that this interpretation was indeed correct.¹³

DISCUSSION

[TcOCl₃(terpy-*N,N'*)]

Our results suggest that TcOCl₃(terpy) is a neutral six-coordinate complex with terpy functioning as a bidentate ligand, both in solution and in the solid state. The $\nu(\text{Tc}=\text{O})$ band at 974 cm⁻¹ is very similar to that in the complex TcOCl₃(bipy)², in which a nitrogen atom *trans* to the oxo oxygen was suggested. A crystal structure determination³ of the complex TcOCl(eg)(phen) (eg = 1,2-ethanediolate) indicated coordination of a 1,10-phenanthroline nitrogen *trans* to the technetyl oxo oxygen.

[TcOCl₂(terpy-*N,N',N''*)] [TcO₄]

Six-coordinate cationic monooxotechnetium(V) complexes are few in the literature, and only one example, the complex [TcO(L)](ClO₄) (L = pentadentate chelate with N₃O₂²⁻ donor atoms) could be found.¹⁴ Square-pyramidal cationic monooxotechnetium(V) complexes are better known, and whose central Tc=O unit is illustrated by strong infrared absorptions in the 965–990 cm⁻¹ region.¹⁵ Several neutral chelating and monodentate nitrogen ligands, including ethylenediamine, cyclam, 1,2-diaminocyclohexane, imidazole and some pyridine derivatives, have led to the preparation of six-coordinate cationic *trans*-dioxotechnetium(V) complexes.¹⁶

Formation of the counterion TcO₄⁻ from TcOCl₄⁻ for the complex [TcOCl₂(terpy-*N,N',N''*)]⁺ in the reaction solution is unusual. However, it has previously been observed¹⁷ that nitropyridine complexes of technetium(V) in alcohol undergo aerial oxidation to yield TcO₄⁻, and the difficulties encountered in the recrystallization of some dioxotechnetium complexes containing pyridine derivatives have also been ascribed¹⁸ to oxidation of technetium(V) to TcO₄⁻ by aerial oxygen. It was also found¹⁹ that the compounds [TcO(L)₄]⁻ (L = 2,3,5,6-tetramethylbenzenethiolate or 2,4,6-triisopropylbenzenethiolate), prepared from TcOCl₄⁻ and the ligands HL, are oxidized by air in alkaline methanolic solutions to TcO₄⁻. In dichloromethane solutions the complex²⁰ [TcO(14-ane-N₂S₂)]⁺ is also oxidized to TcO₄⁻.

$\mu\text{-O}[\text{TcOCl}(\text{terpy-}N,N',N'')\text{]}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

Neutral μ -oxo complexes containing the [O=M–O–M=O]⁴⁺ core are well known for technetium(V)^{21,22} and rhenium(V)²³ with dianionic tetradentate diamine-diol ligands. The existence of the *quasi*-linear [O=M–O–M=O]⁴⁺ core has been established by X-ray diffraction for the complexes $\mu\text{-O}[\text{TcO}(\text{HL})\text{]}_2$ {H₃L = *N,N'*-2-hydroxypropane-1,3-bis(salicylideneimine)}⁹, $\mu\text{-O}[\text{TcO}(\text{sal}_2\text{pn})\text{]}_2$ ²⁴ and $\mu\text{-O}[\text{ReO}(\text{Et}_2\text{dtc})\text{]}_2$ (Et₂dtc = diethyldithiocarbamate).²⁵ The Tc₂O₃⁴⁺ arrange-

ment can be considered as an intermediate between the *trans*- TcO_2^+ and TcO^{3+} cores, which are the most common cores in technetium(V) chemistry.

The linear $\text{M}_2\text{O}_3^{4+}$ core has also been found for a variety of rhenium(V) complexes containing neutral mono- and bidentate nitrogen donor ligands. The neutral dinuclear $\mu\text{-O}[\text{ReOCl}_2(\text{dipy})]_2$ was prepared by heating $\text{ReOCl}_3(\text{dipy})$ under reflux conditions in ethanol.²⁶ The treatment of a suspension of *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$ with wet pyridine in benzene²⁷ led to the isolation of $\mu\text{-O}[\text{ReOCl}_2(\text{py})_2]_2$. The μ -oxo bridged dimer $\text{Re}_2\text{O}_3\text{Cl}_2(\text{Me}_2\text{pzH})_4$ (pzH = pyrazole) has also been characterized by X-ray crystallography.²⁸

The complex prepared in this study, $\mu\text{-O}[\text{TcOCl}(\text{terpy-}N,N',N'')]_2\text{Cl}_2$, extends examples of the $\text{Tc}_2\text{O}_3^{4+}$ core to also include neutral terdentate nitrogen donor ligands, and the complex can be considered as the result of the hydrolysis of the *trans* chloride ligands (to the oxo oxygen) in the complex $[\text{TcOCl}_2(\text{terpy-}N,N',N'')]^+$. Although no cationic compounds of the type $\text{Tc}_2\text{O}_3^{4+}$ is known in the literature, the cationic oxo bridged trimer $[\{\text{ORe}(\text{OC}_6\text{H}_4\text{-2-CMe=NCH}_2)_2(\mu\text{-O})\}_2\text{Re}(\text{OC}_6\text{H}_4\text{-2-CMe=NCH}_2)_2]^+$ has been structurally characterized.²⁹

[TcOCl}_3(\text{terpy.HCl})]

Spectroscopic and analytical results suggest that $\text{TcOCl}_3(\text{terpy.HCl})$ is a neutral six-coordinate complex, with bidentate coordination of the ligand terpy. The nitrogen atom of the uncoordinated pyridine ring is protonated, and terpy coordinates, together with two chloride atoms, in the equatorial plane *cis* to the axial oxo oxygen. The position *trans* to the oxo oxygen is occupied by a chloride.

The large difference in $\nu(\text{Tc}=\text{O})$ for the two complexes $\text{TcOCl}_3(\text{terpy-}N,N')$ (at 974 cm^{-1}) and $\text{TcOCl}_3(\text{terpy.HCl})$ (at 941 cm^{-1}) is ascribed to the difference in the nature of the coordinating atom in the position *trans* to the oxo group, with a pyridine nitrogen in this position in the complex $\text{TcOCl}_3(\text{terpy-}N,N')$. A contributing factor to the lower $\text{Tc}=\text{O}$ stretching frequency in the compound $\text{TcOCl}_3(\text{terpy.HCl})$ may be weak hydrogen bonding between the oxo oxygen and the NH^+ group of the uncoordinated pyridine ring.

The difference in the nature of the coordinating atom in the position *trans* to the oxo group in the complexes $\text{TcOCl}_3(\text{terpy-}N,N')$ and $\text{TcOCl}_3(\text{terpy.HCl})$ deserves some comment. In dichloromethane the equatorial chloride ions in the square-pyramidal $[\text{TcOCl}_4]^-$ ion would be difficult to replace, since solvation of the displaced chloride ions by the low polar solvent will be very weak. The only available site for attack by the terpy ligand on $[\text{TcOCl}_4]^-$ will be the position *trans* to the oxo oxygen, and a chloride can then be displaced by chelation of a second nitrogen of the terpy ligand. In the presence of hydrochloric acid in the highly polar solvent ethanol the displaced chloride ions can be sufficiently solvated. The *trans* position in the complex $\text{TcOCl}_3(\text{terpy.HCl})$ is occupied by chloride.

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