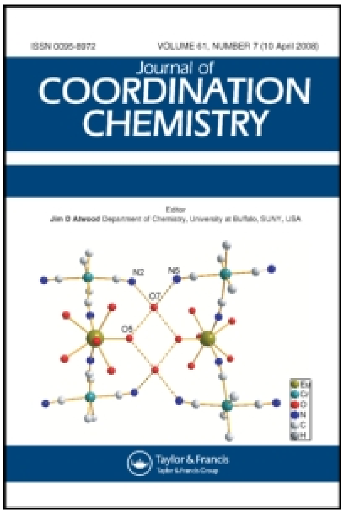


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Binuclear Complexes of Technetium. Synthesis and Characterization of Binuclear tEchnetium(V) and (VII) Complexes with 3,6-bis(2'-pyridyl)-1,2,4,5-Tetrazine

J. G. H. Du Preez[a]; T. I. A. Gerber[a]; M. L. Gibson[a]
[a] Chemistry Department, University of Port Elizabeth, Port Elizabeth, Republic of South Africa

To cite this Article Preez, J. G. H. Du , Gerber, T. I. A. and Gibson, M. L.(1990) 'Binuclear Complexes of Technetium. Synthesis and Characterization of Binuclear tEchnetium(V) and (VII) Complexes with 3,6-bis(2'-pyridyl)-1,2,4,5-Tetrazine', Journal of Coordination Chemistry, 22: 1, 33 — 42

To link to this Article: DOI: 10.1080/00958979009408205

URL: http://dx.doi.org/10.1080/00958979009408205

J. Coord. Chem. 1990, Vol. 22, pp. 33–42
Reprints available directly from the publisher
Photocopying permitted by license only

BINUCLEAR COMPLEXES OF TECHNETIUM. SYNTHESIS AND CHARACTERIZATION OF BINUCLEAR TECHNETIUM(V) AND (VII) COMPLEXES WITH 3,6-BIS(2′-PYRIDYL)-1,2,4,5-TETRAZINE

J. G. H. DU PREEZ, T. I. A. GERBER* and M. L. GIBSON

Chemistry Department, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, Republic of South Africa

(Received March 8, 1990)

Novel binuclear complexes of heptavalent and pentavalent technetium with the bridging ligand 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (bptz) have been prepared and characterized by analysis and optical and vibrational spectroscopy. The heptavalent complexes with the formulation (μ-bptz)[TcO_3X]$_2$ (X = Cl, OCH_3, OCH_2CH_3) were synthesized from pertechnetate and the ligand bptz·2HCl in the appropriate alcohol (X = OMe, OEt) or from pertechnetate and bptz in ethanolic aqueous HCl (for X = Cl). Binuclear complexes of technetium(V) with the formulation (μ-bptz)[$TcOCl_2X$]$_2$ (X = OEt, Cl) were prepared in ethanol from $TcOCl_4^-$ and bptz in the absence (X = OEt) and presence (X = Cl) of ethanolic aqueous HCl. The mononuclear technetium(V) complex [TcO_2(bptz)$_2$]Cl has also been isolated under certain experimental conditions. Mononuclear complexes of the ligand 4-phenyl-3,6-bis(2′-pyridyl)pyridazine (pppz) with formulae TcO_3(pppz)Cl and TcO(pppz)Cl_3 were prepared from pertechnetate and $TcOCl_4^-$, respectively, with pppz in ethanolic aqueous hydrochloric acid solution.

Keywords: Synthesis, binuclear, complexes, technetium, bridging ligand

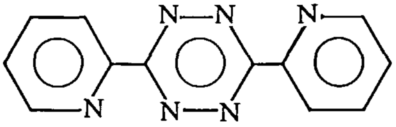
INTRODUCTION

Several nitrogenous aromatic heterocyclic ligands, such as 2,3-bis(2-pyridyl)pyrazine,[1-3] 2,5-bis(2-pyridyl)pyrazine[4] and 2,2′-bipyrimidine[5,6] have recently been used to form bidentate mono- and bimetallic complexes with a variety of transition metals. These complexes exhibit highly absorbing MLCT transitions in the visible-near UV region of the spectrum, and have found applications as multielectron storage systems for the activation of small molecules[7] and as light-capturing systems.[8]

Double coordination of metal fragments to such binucleating ligands is known to cause a particularly strong perturbation of the ligand π system.[9-11] Unfortunately, however, the dissociative stability of binuclear species is frequently diminished because of the reduced σ-donor strength of mononuclear complexes with respect to a second coordination; this effect is typically illustrated by the coordination behaviour of doubly monodentate bridging ligands such as pyrazine.[11,12] Improved binding conditions can be expected in complexes of doubly bidentate ligand bridges, where the chelate effect contributes to dissociative stability.

Author for correspondence.

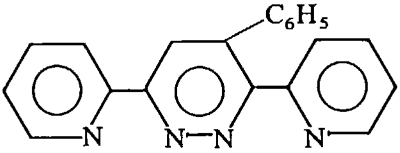
Coordination compounds of the ligand 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine (bptz) are few; only some 3d transition metal halide and pseudohalide complexes have been reported.[13,14] Also, to our knowledge, only one bimetallic complex of technetium containing a multidentate bridging ligand has been reported, *i.e.*, the metalloporphyrin (μ-tpp)$[Tc(CO)_3]_2$ [tpp = tetraphenylporphyrin].[15] Complexes containing technetium as one of the metals in a heterobinuclear system have not yet been prepared. For this particular purpose, the ligand bptz emerges as being ideally suited.



bptz

The coordination chemistry of technetium has expanded dramatically over the past few years due to its application for possible anatomical imaging agents in nuclear medicine.[16,17] The chemistry of technetium(V) with nitrogen donor ligands is well understood;[18,19] however, technetium does not, as yet, have a well-developed chemistry in the heptavalent oxidation state.

In this account we wish to report the preparation and characterization of the first bimetallic technetium(V) and (VII) complexes bound with bptz. We have also extended this work to include similar complexes of the ligand 4-phenyl-3,6-bis(2'-pyridyl)pyridazine (pppz).



pppz

EXPERIMENTAL

Ammonium pertechnetate ($NH_4{}^{99}TcO_4$) was purchased from the Oakridge National Laboratories, Tennessee. Due to the radioactivity of technetium some health precautions have been taken. All preparations have been carried out in a fume cupboard with gloves. Since ^{99}Tc is only a weak β^--emitter (specific activity 17 μCi/mg), no further precautions are necessary provided some elementary steps are taken and no volatile compounds are formed during the reaction. Normal glassware gives adequate protection against the weak β^--emission. Secondary X-rays (bremsstrahlung) become important only if ^{99}Tc is handled on a larger scale.

All common laboratory chemicals were of reagent grade. (n-$Bu_4N)TcOCl_4$ was prepared as reported.[20] The ligands bptz and pppz were synthesized according to literature procedures,[21] and their purity was checked by NMR and melting point. All the solvents used were purified and dried by standard methods.

The salt bptz·2HCl was prepared by treating the ligand bptz with an excess of a 6M aqueous HCl solution in ethanol. The bptz·2HCl salt precipitates as an orange-pink solid. [Analysis: Calcd: C, 46.62; H, 3.26; N, 27.18; Cl, 22.94%. Found: C, 46.57; H, 3.21: N, 26.98; Cl, 22.43%. M.pt., 247°C].

Infrared spectra were recorded on a Beckman IR 4250 grating spectrophotometer in the range 4000–250 cm^{-1} in KBr pellets. Optical spectra were obtained with a Perkin-Elmer 330 spectrophotometer. Conductivity measurements were performed in *N,N*-dimethylformamide using a Metrohm E518 conductometer. Elemental analyses were performed using a Heraeus Rapid Analyser. Chloride was determined by potentiometric titration with standard silver nitrate solution of solutions of the compounds decomposed by the Shoeniger method.

Preparation of the Complexes

(μ-bptz)[$TcO_3(OCH_3)$]$_2$

To a solution of 0.2230 g bptz·2HCl (7.2×10^{-4} mol) in 60 cm^3 methanol was added 1 cm^3 of a 0.36 mol dm^{-3} aqueous NH_4TcO_4 solution with stirring. This solution was heated under reflux for one hour, during which time the colour of the solution changed from pink-red to dark red to violet. After refluxing, the solution was cooled at room temperature, and the dark indigo precipitate was filtered, washed with methanol (3×3 cm^3) and dried under vacuum at 60°C. The yield of (μ-bptz)[$TcO_3(OCH_3)$]$_2$ was 0.0821 g (0.14 mmol), 77% based on Tc. This material is soluble in a variety of solvents including chloroform, dichloromethane, THF, acetonitrile and acetone. It is insoluble in methanol and ethanol. Anal.: Calcd. for $C_{14}H_{14}N_6O_8Tc_2$: C, 28.58; H, 2.40; N, 14.29%. Found: C, 28.87; H, 2.93; N, 14.15%. Optical spectrum in DMF: 295 nm (ε = 10850 M^{-1} cm^{-1}), 572(3200). IR spectrum (KBr): ν(Tc=O), 906(s), 896(s), 857(m) cm^{-1}. Conductivity (DMF, 10^{-3}M): Λ_M = 16.8 ohm^{-1} cm^2 mol^{-1}.

(μ-bptz)[$TcO_3(OCH_2CH_3)$]$_2$

This complex was prepared as a dark indigo solid in 71% yield by the above procedure using ethanol as solvent under the same experimental conditions as for that of (μ-bptz)[$TcO_3(OCH_3)$]$_2$. Its solubility is similar to that of (μ-bptz)[$TcO_3(OCH_3)$]$_2$. Anal.: Calcd. for $C_{16}H_{18}N_6O_8Tc_2$: C, 30.98; H, 2.93; N, 13.52%. Found: C, 30.84; H, 2.86; N, 14.12%. Optical spectrum in DMF: 295 nm (ε = 12100 M^{-1} cm^{-1}), 514 sh, 572 (3600). IR spectrum (KBr): ν(Tc=O), 907(s), 894(s), 856(m) cm^{-1}. Conductivity (DMF, 10^{-3} M): Λ_M = 16.1 ohm^{-1} cm^2 mol^{-1}.

(μ-bptz)[TcO_3Cl]$_2$

To a solution of 85 mg bptz (3.60×10^{-4} mol) in 20 cm^3 ethanol was added 1 cm^3 of a 0.36 M aqueous NH_4TcO_4 solution with stirring, followed by the dropwise addition of 12N HCl (2 cm^3). After heating under reflux for 15 min the dark purple precipitate was isolated by suction filtration after cooling at room temperature. The material was washed with ethanol (3×5 cm^3) and dried *in vacuo*. The yield of (μ-bptz)[TcO_3Cl]$_2$ was 0.0793 g (0.13 mmol), 73% based on Tc. This material is insoluble in methanol and ethanol, but slightly soluble in acetone, dichloromethane, THF and acetonitrile. Anal.: Calcd. for $C_{12}H_8N_6Cl_2O_6Tc_2$: C, 23.98; H, 1.34; N, 13.98%; Cl, 11.80%. Found: C, 24.03; H, 1.33; N, 14.05; Cl, 12.58%. Optical spectrum in DMF: 293 nm (ε = 37800 M^{-1} cm^{-1}), 512 sh, 558 (3100). IR spectrum (KBr): ν(Tc=O), 900(s), 892(s), 852(m) cm^{-1}. Conductivity (DMF, 10^{-3} M): Λ_M = 12.7 ohm^{-1} cm^2 mol^{-1}.

[$TcO_2(bptz)_2$]$Cl{\cdot}CH_3CH_2OH$

To a solution of 0.2800 g bptz (1.2 mmol) in 25 cm^3 ethanol was added an ethanolic solution (20 cm^3) of 0.100 g (Bu_4N)[$TcOCl_4$] (0.2 mmol). The mixture was stirred at room temperature for an hour, with the colour of the solution changing from red to a very dark indigo. An indigo coloured precipitate was isolated by suction filtration, and the material was washed with ethanol (4 x 10 cm^3) and acetone. The compound was dried *in vacuo*. The yield of [TcO_2(bptz)$_2$]Cl·EtOH was 0.0773 g (0.113 mmol), 56% based on Tc. The attempted recrystallization from hot ethanol led to the decomposition of the compound, with the isolation of the ligand bptz. The compound is insoluble in alcohol, acetone and benzene, and slightly soluble in chloroform, dichloromethane, THF and acetonitrile. Anal.: Calcd. for $C_{26}H_{22}ClN_{12}O_3Tc$: C, 45.59; H, 3.24; N, 24.54; Cl, 5.18%. Found: C, 46.08; H, 3.30; N, 24.74; Cl, 4.97%. Optical spectrum in DMF: 286 nm ($\varepsilon = 45600\ M^{-1}\ cm^{-1}$), 376(1870), 482 sh, 530(2170). IR spectrum (KBr): $\nu(TcO_2)$, 798(s) cm^{-1}; ν(Tc–N), 397, 401 cm^{-1}. Conductivity (DMF, 10^{-3} M): $\Lambda_M = 64.0\ ohm^{-1}\ cm^2\ mol^{-1}$. M.pt., 200°C.

[$TcO_2(bptz{\cdot}HCl)_2$]$Cl{\cdot}2H_2O$

A suspension of 0.3710 g bptz·2HCl (1.2 mmol) in 40 cm^3 ethanol was added with stirring to 0.100 g (n-Bu_4N)[$TcOCl_4$] in 30 cm^3 ethanol. The mixture was heated under reflux for 30 min, giving a dark blue solution from which an indigo coloured precipitate formed. The material was filtered with suction, washed with methanol (5 x 5 cm^3), and dried *in vacuo*. The yield of [TcO_2(bptz·HCl)$_2$]Cl·2H_2O was 0.1001 g (0.13 mmol), 67% based on Tc. The compound is slightly soluble in chloroform, water, dichloromethane, THF and acetonitrile, and insoluble in benzene, ethanol, methanol and acetone. Anal.: Calcd. for $C_{24}H_{22}Cl_3N_{12}O_4Tc$: C, 38.54; H, 2.97; N, 22.48; Cl, 14.22%. Found: C, 38.57; H, 3.14; N, 22.19; Cl, 14.44%. Optical spectrum in DMF: 297 nm ($\varepsilon = 18800\ M^{-1}\ cm^{-1}$), 378(1200), 485 sh, 535(1640). IR spectrum (KBr): $\nu(TcO_2)$, 800(s) cm^{-1}; ν(Tc–N),399,401 cm^{-1}. M.pt., 208°C.

(μ-bptz)[$TcOCl_2(OCH_2CH_3)$]$_2$

To a solution of 0.0472 g bptz (0.2 mmol) in 15 cm^3 ethanol was added 0.200 g (n-Bu_4N)[$TcOCl_4$] (0.4 mmol) in 40 cm^3 ethanol under nitrogen. A very dark blue precipitate formed immediately on addition, and the solution was stirred for 30 min under nitrogen. The material was separated and washed with ethanol (3 x 5 cm^3), and dried *in vacuo*. The yield of (μ-bptz) [$TcOCl_2(OCH_2CH_3)$]$_2$ was 0.0973 g (0.14 mmol), 68% based on Tc. The compound is slightly soluble in acetone, acetonitrile, dichloromethane and chloroform, and insoluble in alcohol and benzene. Anal.: Calcd. for $C_{16}H_{18}Cl_4N_6O_4Tc_2$: C, 27.52; H, 2.60; N, 12.04; Cl, 20.31%. Found: C, 27.22; H, 2.60; N, 12.09; Cl, 20.36%. Optical spectrum in DMF: 290 nm ($\varepsilon = 12200\ M^{-1}\ cm^{-1}$), 380(3580), 522 sh, 578(2860). IR spectrum (KBr): ν(Tc=O), 919 cm^{-1}.

(μ-bptz)[$TcOCl_3$]$_2$

This complex was prepared as a dark violet solid in 63% yield by the same procedure as for (μ-bptz)[$TcOCl_2(OCH_2CH_3)$]$_2$, with the only difference being the dropwise addition of 2 cm^3 12N HCl. The compound is slightly soluble in acetone, acetonitrile and dichloromethane. Anal.: Calcd. for $C_{12}H_8Cl_6N_6O_2T_2$: C, 21.23; H, 1.19; N, 12.38; Cl, 31.33%. Found: C, 21.52; H, 1.42; N, 13.05; Cl, 30.76%. Optical spectrum in DMF: 294 nm ($\varepsilon = 18500\ M^{-1}\ cm^{-1}$), 382(6800), 518 sh, 608(3400). IR spectrum (KBr): ν(Tc=O), 986(s), 982 sh, cm^{-1}. Conductivity (DMF, 10^{-3}M) = 12.3 $ohm^{-1}\ cm^2\ mol^{-1}$.

TcO_3(pppz)Cl

To a solution of 0.4520 g pppz (1.46×10^{-3} mol) in 20 cm^3 ethanol was added 1 cm^3 of a 0.36 mol dm^{-3} aqueous NH_4TcO_4 solution with stirring. The dropwise addition of 2 cm^3 concentrated hydrochloric acid changed the colour of the solution to yellow. Within 10 min a bright yellow precipitate formed, which was filtered, washed with ethanol ($3 \times 5\ cm^3$) and dried *in vacuo*. The yield was 0.1443 g (0.29 mmol), 81% based on Tc. This material is slightly soluble in acetone, acetonitrile and dichloromethane. Anal.: Calcd. for $C_{20}H_{14}ClN_4O_3Tc$: C, 48.74; H, 2.86; N, 11.37; Cl = 7.19%. Found: C, 49.01; H, 2.67; N, 11.68; Cl, 6.98%. Optical spectrum in DMF: 324 nm ($\varepsilon = 34200\ M^{-1}\ cm^{-1}$), 428(2900), 458(sh). IR spectrum (KBr): ν(Tc=O), 904(s), 889(s), 860(m) cm^{-1}. Conductivity (DMF, 10^{-3} M): $\Lambda_M = 5.8$ $ohm^{-1}\ cm^2\ mol^{-1}$.

TcO(pppz)Cl_3

A mixture of 0.1240 g of pppz and 0.100 g $(Bu_4N)[TcOCl_4]$ in 20 cm^3 ethanol was stirred at room temperature with the dropwise addition of 1 cm^3 of concentrated hydrochloric acid. Within 5 min a mustard yellow solid had precipitated. After 30 min this solid was isolated by suction filtration, washed with ethanol ($3 \times 5\ cm^3$) and dried *in vacuo*. The yield was 0.0935 g (0.176 mmol), 88% based on Tc, m.pt, 230°C. This material is slightly soluble in polar organic solvents. Anal.: Calcd. for $C_{20}H_{14}Cl_3N_4OTc$: C, 45.18; H, 2.65; N, 10.54; Cl, 20.00%. Found: C, 45.27; H, 3.10; N, 10.48; Cl, 19.83%. Optical spectrum in DMF: 287 nm ($\varepsilon = 38150\ M^{-1}\ cm^{-1}$), 380(3700), 418(2000). IR spectrum (KBr): ν(Tc=O), 982 cm^{-1}. Conductivity (DMF, 10^{-3} M): $\Lambda_M = 6.2\ ohm^{-1}\ cm^2\ mol^{-1}$.

RESULTS

The behaviour of technetium(V) and (VII) complexes containing nitrogen donor ligands has been well-studied.[18] Compounds of the general formula TcO_3XL (where L = 1,10-phenanthroline or 2,2′-bipyridine; X = Cl, Br) were obtained from the reaction of NH_4TcO_4 with L in an aqueous ethanolic solution of HX at room temperature. On heating in ethanolic aqueous HX solution, these technetium(VII) complexes are reduced to the pentavalent species $TcOX_3L$. The technetium(V) complex $TcOX_3$(bipy) could also be synthesized from $TcOCl_4^-$ and bipy in aqueous ethanolic HX. If HCl is omitted from the reaction of $TcOCl_4^-$ with bipy, then the ethoxy complex can be converted to $TcOCl_3$(bipy) by reaction with HCl in acetone.

Binuclear technetium(VII) complexes

In our study, binuclear complexes of technetium(VII) with the formulation (μ-bptz)$[TcO_3X]_2$ (X = OCH_3, OCH_2CH_3) have been prepared by the reaction of NH_4TcO_4 with the salt bptz·2HCl in methanol and ethanol respectively. These complexes are unusual since they are the first examples of technetium(VII) complexes containing an alcoholate as a ligand. The compound (μ-bptz)$[TcO_3Cl]_2$ was prepared by reacting the ligand bptz with NH_4TcO_4 in an ethanolic hydrochloric acid solution. The reaction of pertechnetate with bptz in the absence of hydrochloric acid led to the formation of unidentifiable impure products. Efforts to synthesize the mononuclear TcO_3(bptz)X complexes in these solvents were unsuccessful, and the binuclear species were isolated in each case.

These synthetic reactions occur very slowly at room temperature, and required considerable thermal activation. No reduction of technetium(VII) was observed under these reaction conditions. The complexes are only very slightly soluble in a variety of organic solvents, which precludes their recrystallization. However, they precipitated from solution in an analytically pure state.

The complexes (μ-bptz)$[TcO_3X]_2$ (X = OMe, OEt) could be converted to (μ-bptz)-$[TcO_3Cl]_2$ by careful treatment with an acetone/12 M HCl (2:1 v/v) mixture. The addition of a larger ratio of acid in acetone led to the decomposition of the compounds. In addition to the IR bands from the coordinated bptz ligand, the (μ-bptz)$[TcO_3X]_2$ complexes exhibit three bands in the range 910–850 cm^{-1}, which are ascribed to the TcO_3^+ function.

The electronic spectra of the (μ-bptz)$[TcO_3X]_2$ complexes are dominated by an intense absorption band around 295 nm, which is characteristic of all complexes containing the bptz ligand, and which also appears in the electronic spectrum of bptz itself. This band has been ascribed in the intraligand $\pi \rightarrow \pi^*$ transitions in bptz.[22] Due to the their high intensity, the lower energy bands in the 558–572 nm range are possibly due to ligand-to-metal charge transfer transitions. Conductivity measurements show the products to be non-conducting in dimethylformamide.

Mononuclear dioxotechnetium(V) complexes

The technetium(V) compounds prepared in this study follow the general trends expected for complexes of this type.[23,24] Mononuclear $[TcO_2(bptz)_2]Cl$ and $[TcO_2(bptz\cdot HCl)_2]Cl$ complexes have been prepared by the reaction of (n-Bu_4N)-$[TcOCl_4]$ with an excess of the ligands bptz and bptz·2HCl, respectively, in ethanolic solution. The formation of the complex $[TcO_2(bptz\cdot HCl)_2]Cl$ required considerable thermal activation. The complexes are only slightly soluble in a variety of organic solvents, and insoluble in acetone, benzene and alcohols. Efforts to recrystallize these two compounds led to the decomposition of the material. However, they precipitate from solution in an analytically pure state. The *trans*-dioxotechnetium(V) group has previously also been obtained with π-acceptor ligands or ligands that do not form π-bonds. Some well-characterized compounds in this class are $[TcO_2(pyridine)_4]Cl$[25] and $[TcO_2(en)_2]Cl$.[23]

The dioxotechnetium(V) complexes prepared in this study are unstable in solution, and considerable decomposition occurs over a period of 24 h in DMF. They exhibit a strong absorption band around 800 cm^{-1} in the infrared spectrum, which is ascribed to the *trans*-TcO_2 stretching vibration. Two infrared peaks around 400 cm^{-1} indicate the presence of Tc–N stretching vibrations.

The dioxo complexes exhibit the $\pi \rightarrow \pi^*$ transition of the ligand bptz around 290 nm in the electronic spectrum, with the charge transfer bands for both compounds very similar in position around 377 nm and 530 nm in the visible region. The high intensity of the band around 290 nm may be the result of overlap of the oxo-to-technetium(V) charge transfer transitions, which were previously found in this region for essentially all *trans*-dioxotechnetium complexes.[23,24]

Binuclear technetium(V) complexes

Binuclear complexes of technetium(V) with the formulation (μ-bptz)[$TcOCl_2X]_2$ ($X = OCH_2CH_3$, Cl) have been prepared in good yields by the reaction of (*n*-Bu_4N)[$TcOCl_4$] with the ligand bptz (two-fold molar excess of $TcOCl_4^-$) in ethanol. In the absence of hydrochloric acid the complex (μ-bptz)[$TcOCl_2(OEt)]_2$ was formed, and in the presence of ethanolic aqueous HCl the compound (μ-bptz)[$TcOCl_3]_2$ was isolated. Efforts to prepare and isolate the monomeric [$TcOCl_3$(bptz)] complex was unsuccessful. The formation of the binuclear ethoxymonooxotechnetium(V) compound is in accordance with similar complexes containing π-donor ligands in the equatorial plane. It has previously been suggested that solvent substitution in the position opposite the *trans* labilizing oxo ligand, followed by metal ion induced deprotonation results in alkoxo complexes similar to those reported here.[19,26,27]

In addition to the infrared bands from the coordinated bptz ligand, the (μ-bptz)[$TcOCl_3]_2$ complex has a single strong band at 986 cm^{-1}, with a shoulder at 982 cm^{-1}. These are ascribed to the Tc=O stretching vibrations. The ethoxy complex has a strong band at 919 cm^{-1} [ν(Tc=O)], as well as a band from the ethoxy ligand at 575 cm^{-1}. Both these technetium(V) complexes exhibit an intense absorption band around 290 nm in the electronic spectrum, with bands tailing into the visible region.

Mononuclear technetium complexes with ligand pppz

The technetium(VII) complex TcO_3(pppz)Cl has been prepared in good yield by the reaction of pertechnetate with an excess of the ligand pppz in an ethanolic hydrochloric acid solution at room temperature. Heating of the reaction mixture led to the reduction of the Tc(VII) and the formation of the complex TcO(pppz)Cl_3. The latter compound could also be prepared by the reaction of $TcOCl_4^-$ and the ligand pppz in ethanolic aqueous hydrochloric acid at room temperature.

In addition to the infrared bands from the coordination pppz ligand, the TcO(pppz)Cl_3 complex has a single strong band at 982 cm^{-1}, while the TcO_3(pppz)Cl complex exhibits three bands in the range 860–905 cm^{-1}. These bands are ascribed to the Tc=O stretching vibrations. Both the complexes TcO_3(pppz)Cl and TcO(pppz)Cl_3 are diamagnetic, and they are non-electrolytes in DMF solution.

DISCUSSION

Binuclear technetium(VII) complexes

The direct combination of bptz·2HCl with pertechnetate in ethanol and methanol led to the isolation of the binuclear complexes (μ-bptz)[$TcO_3(OEt)]_2$ and (μ-bptz)[$TcO_3(OMe)]_2$, respectively. The formation of these products is independent of the molar stoichiometric ratio, and the same complexes are obtained in good yield for even a 2:1 bptz·2HCl:TcO_4^- molar ratio. However, these reactions require considerable thermal activation, making it impossible to isolate a possible mononuclear species (of formulation $TcO_3(bptz)(OEt)$) in ethanol. In fact, all efforts to synthesize this mononuclear complex proved unsuccessful.

These binuclear alcoholate technetium(VII) complexes were readily isolated due to their insolubility in the reaction medium. They are hydrolytically unstable giving TcO_4^- upon reaction with water, and are sparingly soluble in organic solvents. Their formulation is based on elemental analyses and vibrational spectroscopy.

The reaction of pertechnetate with bptz, with the addition of cold ethanolic hydrochloric acid, led to the formation of the complex $(\mu\text{-bptz})[TcO_3Cl]_2$, even at equimolar quantities of ligand and metal. This compound is also hydrolytically unstable, and is only sparingly soluble in polar organic solvents. Heating of the reaction mixture causes the reduction to the technetium(V) species $(\mu\text{-bptz})[TcOCl_3]_2$.

Stirring a mixture of the ligand bptz with pertechnetate in alcohol at room temperature in the absence of acid gave no detectable reaction. It is obvious that the reaction requires the addition of acid, presumably in order to doubly protonate one oxo ligand of pertechnetate, thereby labilizing it towards replacement by a chloride ion, as in our case.

The formation of the technetium(VII) complexes containing alcoholate as a ligand is quite remarkable. It would appear as if the salt bptz·2HCl provides the protons for the protonation (and resultant labilization) of the oxo ligands. Both methanol and ethanol are known to replace oxo groups as the species RO^-, since the highly electrophilic TcO_3^+ ion is clearly making the coordinating alcohols very acidic.[27]

Mononuclear dioxotechnetium(V) complexes

The complex $[TcO_2(bptz)_2]Cl$ was prepared in good yield by the reaction of $TcOCl_4^-$ with a six-fold molar excess of the ligand bptz in ethanol. The same product was isolated when the reaction was performed in tetrahydrofuran as solvent. The attempted recrystallization of this product led to its decomposition in solution, from which the ligand bptz could be isolated. The *trans* Tc^VO_2 stretching bands of the complexes prepared in this study are somewhat lower than that observed in other *trans*-dioxotechnetium(V) complexes,[23] which normally occur in the range 810–880 cm^{-1}. In general, the dioxotechnetium(V) core is present in complexes containing π-acceptor ligands, while the monooxotechnetium(V) group is obtained in complexes with π-donor ligands in the equatorial plane. The rather lower absolute stretching frequency of the TcO_2 function in our complexes indicates rather weak σ-bonding between the ligand and technetium(V), despite the presence of pyridine "supporting" groups in bptz. Strong π interaction may compensate to some extent for the poor ligand nucleophilicity, and the unusually low N=N stretching frequencies at 1390 cm^{-1} illustrate a considerable π-back donation. In comparison to other neutral binucleating ligands of this kind,[28,29] bptz represents a rather compact system with eighteen π centers. However, the extraordinary feature of this system is its extremely low-lying LUMO level, which undergoes even further stabilization by metal coordination.

The electronic spectrum of the complex $[TcO_2(bptz)_2]Cl$ is similar to those of other *trans*-dioxotechnetium(V) complexes with imidazole and bidentate amine ligands.[19,30] Ligand field transitions are expected around 800, 600 and 500 nm, but the former two are of such low intensity as to not be easily observable, especially in unstable compounds.[31] The transition centred at 530 nm probably involves an $^1A_1 \rightarrow {}^1B_2$ ligand field transition with some increase in intensity owing to loss of inversion symmetry by random twisting of the pyridine rings in solution, or intensification by "stealing" from the charge-transfer band at 376 nm.

Binuclear technetium(V) complexes

The technetium(V) complex (μ-bptz)[$TcOCl_3$]$_2$ was prepared from (n-Bu_4N)[$TcOCl_4$] and bptz in a two-fold molar excess of the metal in ethanolic aqueous HCl. If HCl is omitted in this reaction, the ethoxy complex (μ-bptz)[$TcOCl_2(OEt)$]$_2$ is precipitated. The Tc=O stretching band in the (μ-bptz)[$TcOCl_3$]$_2$ complex occurs at 986 cm^{-1}, with a shoulder at 982 cm^{-1}, which is typical for monooxotechnetium(V) complexes (normally occurs in the range 930–1020 cm^{-1}). The ν(Tc=O) band at 919 cm^{-1} in our ethoxy complex occurs at the low end of the expected range, and the complex presumably contains the alcoholate in the position *trans* to the oxo ligand with the halides in *cis* positions. This relatively low infrared stretching frequency for the Tc=O group may suggest that significant π-bonding exists between the ethoxy oxygen and Tc(V), and thereby decreasing the Tc(V)-oxo bond order.

Technetium(V) complexes containing ethoxide or methoxide as ligands are known, with a variety of examples present in the literature.[18,19,27] It has been suggested[32] that solvent substitution in the open position opposite the *trans* labilizing oxo ligand followed by metal ion induced deprotonation results in alkoxo complexes similar to those reported there. All efforts to isolate the mononuclear species $TcO(bptz)Cl_3$ were unsuccessful, with the binuclear complexes reported here as the only products, even at an equimolar bptz/metal ratio.

An important property of binucleating ligands is their ability to keep two metals at a well-defined distance. The metal–metal distance in a ligand-bridged binuclear complex depends on the distance between the metals and the coordinating atoms; however, contributions from the ligand (size and conformation) are more important. From the model of Richardson and Taube,[33] with a standard metal–nitrogen distance of 200 pm, the calculated metal–metal distance in these technetium(V) complexes is 690 pm.

Complexes with the ligand pppz

The results obtained for the complexes $TcO_3(pppz)Cl$ and $TcO(pppz)Cl_3$ follow the general trends observed for similar and analogous 2,2'-bipyridine technetium complexes.[18] Efforts to synthesize the analogous ethoxy complex $TcO(pppz)(OEt)Cl_2$ by the reaction of $TcOCl_4^-$ with the ligand pppz in the absence of hydrochloric acid in ethanol led to the isolation of impure products, likely to be the result of the instability of such a complex. A dioxotechnetium(V) complex of formula [$TcO_2(pppz)_2$]Cl could neither be prepared, and at even a 6:1 pppz/$TcOCl_4^-$ molar ratio only the $TcO(pppz)Cl_3$ complex could be isolated.

ACKNOWLEDGEMENTS

The authors wish to thank the Medical Research Council of South Africa and the University of Port Elizabeth for financial support.

REFERENCES

1. R.R. Ruminski, T. Cockroft and M. Shoup, *Inorg. Chem.*, **27**, 4026 (1988).

2. M. Shoup, B. Hall and R.R. Ruminski, *Inorg. Chem.*, **27**, 200 (1988).
3. K.J. Brewer, W.R. Murphy and J.D. Petersen, *Inorg. Chem.*, **26**, 3376 (1987).
4. W. Kaim and S. Kohlmann, *Inorg. Chem.*, **25**, 3306 (1986).
5. E.V. Dose and R.J. Wilson, *Inorg. Chem.*, **17**, 2660 (1978).
6. C. Overton and J.A. Connor, *Polyhedron*, **1**, 53 (1982).
7. Y. Nishida, H. Shimo, H. Maehara and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1945 (1985).
8. S. Kohlmann, S. Ernst and W. Kaim, *Angew. Chem. Int. Ed. Engl.*, **24**, 684 (1985).
9. W. Kaim and S. Kohlmann, *Inorg. Chim. Acta*, **101**, L21 (1985).
10. M. Hunziker and A. Ludi, *J. Am. Chem. Soc.*, **99**, 7370 (1977).
11. A.J. Lees, J.M. Fobare and E.F. Mattimore, *Inorg. Chem.*, **23**, 2709 (1984).
12. W. Kaim, *Angew. Chem. Int. Ed. Engl.*, **22**, 171 (1983).
13. K. Gustav and C.J. Schmitt, *Z. Chem.*, **9**, 32 (1969).
14. A.A. Schilt, W.E. Dunbar, B.W. Gandrud and S.E. Warren, *Talanta*, **17**, 649 (1970).
15. M. Tsutsui, C.P. Hrung, D. Ostfeld, T.S. Srivastava, D.L. Cullen and E.F. Meyer, Jr., *J. Am. Chem. Soc.*, **97**, 3952 (1975).
16. E. Deutsch, K. Libson, S. Jurisson and L.F. Lindoy, *Prog. Inorg. Chem.*, **30**, 75 (1983).
17. T.C. Pinkerton, C.P. Desilets, D.J. Hoch, M.V. Mikelsons and G.M. Wilson, *J. Chem. Educ.*, **62**, 965 (1985).
18. A. Davidson, A.G. Jones and M.J. Abrams, *Inorg. Chem.*, **20**, 4300 (1981).
19. P.H. Fackler, M.E. Kastner and M.J. Clarke, *Inorg. Chem.*, **23**, 3968 (1984).
20. A. Davison, H.S. Trop, B.V. DePamphilis and A.G. Jones, *Inorg. Synth.*, **21**, 160 (1982).
21. J.F. Geldard and F. Lions, *J. Org. Chem.*, **30**, 318 (1965).
22. W. Kaim and S. Kohlmann, *Inorg. Chem.*, **26**, 68 (1987).
23. M.E. Kastner, M.J. Lindsay and M.J. Clarke, *Inorg. Chem.*, **21**, 2037 (1982).
24. S.A. Zuckman, G.M. Freeman, D.E. Troutner, W.A. Volkert, R.A. Holmes, D.G. van Derveer and E.K. Barefield, *Inorg. Chem.*, **20**, 2386 (1981).
25. V.G. Kuznetsov, G.N. Novitskaya, P.A. Koz'min and A.S. Kotel'nikova, *Russ. J. Inorg. Chem.*, **18**, 559 (1973).
26. J. Lu and M.J. Clarke, *Inorg. Chem.*, **27**, 4761 (1988).
27. R.M. Pearlstein, C.J.L. Lock, R. Faggiani, C.E. Costello, C.H. Zeng, A.G. Jones and A. Davison, *Inorg. Chem.*, **27**, 2409 (1988).
28. D.P. Rillema, R.W. Callahan and K.B. Mack, *Inorg. Chem.*, **21**, 2589 (1982).
29. M.A. Haga and R. Koizumi, *Inorg. Chim. Acta*, **104**, 47 (1985).
30. M.E. Kastner, P.H. Fackler, M.J. Clarke and E. Deutsch, *Inorg. Chem.*, **23**, 4683 (1984).
31. M. Baluka, J. Hanuza and B. Jezowska-Trzebiatowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **20**, 217 (1972).
32. A. Davison and A.G. Jones, *Int. J. Appl. Radiat. Isot.*, **33**, 875 (1982).
33. D.E. Richardson and H. Taube, *J. Am. Chem. Soc.*, **105**, 40 (1983).