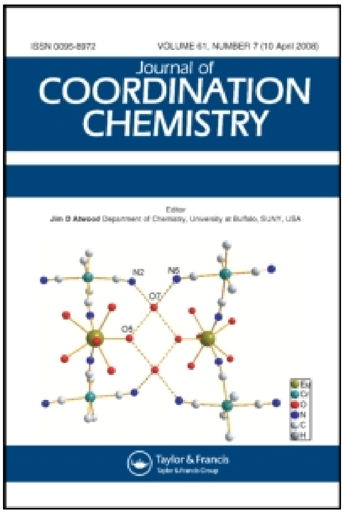

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Binuclear Complexes of Technetium. Evidence for Bis(Terdentate)Bidentate Coordination by the Bridging Ligand 2,3,5,6-Tetrakis(2-pyridyl)Pyrazine to Technetium(V)

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

To cite this Article Preez, J. G. H. Du , Gerber, T. I. A. , Gibson, M. L. and Geyser, R.(1990) 'Binuclear Complexes of Technetium. Evidence for Bis(Terdentate)Bidentate Coordination by the Bridging Ligand 2,3,5,6-Tetrakis(2-pyridyl)Pyrazine to Technetium(V)', Journal of Coordination Chemistry, 22: 3, 249 — 254

To link to this Article: DOI: 10.1080/00958979009408221

URL: http://dx.doi.org/10.1080/00958979009408221

J. Coord. Chem. 1990, Vol. 22, pp. 249–254
Reprints available directly from the publisher
Photocopying permitted by license only

NOTE

BINUCLEAR COMPLEXES OF TECHNETIUM. EVIDENCE FOR BIS(TERDENTATE)BIDENTATE COORDINATION BY THE BRIDGING LIGAND 2,3,5,6-TETRAKIS(2-PYRIDYL)PYRAZINE TO TECHNETIUM(V)

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

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

(Received May 31, 1990)

The preparation and study of polymetallic complexes bound through novel bridging ligands has generated a lot of recent interest. These investigations have concentrated mainly on bimetallic ruthenium(II) polyazine complexes[1-4] for photocatalyzed intramolecular energy transfer processes, and have focussed on nitrogen aromatic heterocyclic bridging ligands such as pyrazine,[1] 2,2′-bipyrimidine,[5,6] 2,3-bis(2-pyridyl)pyrazine[4,7,8] and 2,5-bis(2-pyridyl)pyrazine.[2]

We have used the potentially bis(terdentate) nitrogen aromatic heterocyclic ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz; Figure 1) to prepare mono- and bimetallic technetium(V) complexes bound to tppz. Homonuclear bimetallic technetium(V) complexes have previously been prepared by us using the bridging ligand 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (bptz).[9]

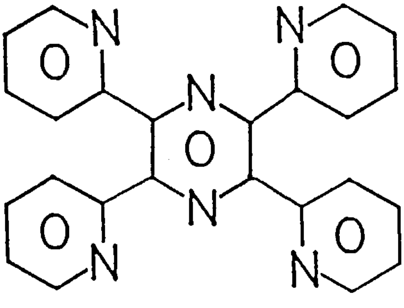

FIGURE 1 2,3,5,6-Tetrakis(2-pyridyl)pyrazine (tppz).

The stimulus for the development of the coordination chemistry of the man-made element technetium is provided by the use of complexes of this element as anatomical imaging agents in nuclear medicine.[10] Although the chemistry of technetium(V) with

---

* Author for correspondence.

nitrogen donor ligands is well understood,[11,12] no complexes have been prepared using potentially terdentate neutral nitrogen donor ligands of this metal in the +5 oxidation state.

EXPERIMENTAL

The compound (n-Bu_4N) [$TcOCl_4$] was prepared as reported.[13] The tppz ligand was prepared without difficulty according to literature procedures.[14] All solvents used were purified and dried by standard methods. Scientific instrumentation used in this study is the same as reported elsewhere.[15]

Preparation of Complexes

(μ-tppz) [TcOCl$_2$ (OEt)]$_2$

A solution of 0.2002 g of (n-Bu_4N) [$TcOCl_4$] (401 μmol) in 15 cm^3 ethanol was added with stirring to 0.0770 g of tppz (198 μmol) in 15 cm^3 ethanol. After heating under reflux conditions for 90 min, a dark green precipitate was obtained, which was filtered and washed with ethanol and acetone. The yield of (μ-tppz) [$TcOCl_2$ (OEt)]$_2$ was 0.1235 g (145 μmol), 73% based on tppz. The compound is soluble in dichloromethane, acetonitrile, DMF and nitromethane, slightly soluble in chloroform and acetone and insoluble in hydrocarbons. Anal.: Calcd. for $C_{28}H_{26}Cl_4N_6O_4Tc_2$; C, 39.55; H, 3.08; N, 9.88; Cl, 16.68%. Found: C, 39.60; H, 3.27; N, 10.19; Cl, 17.42%. Optical spectrum (CH_2Cl_2, nm, (ε) M^{-1} cm^{-1}): 720 sh, 585 sh, 334 sh (10000), 296 (10900), 248 sh (11900). Conductivity (10^{-3} M, DMF): 7.6 ohm^{-1} cm^2 mol^{-1}. IR(KBr): ν(Tc=O), 916, 938 cm^{-1}; ν(Tc-ethoxide), 561, 570 cm^{-1}.

TcOCl$_2$ (OEt) (tppz)

A solution of 0.1000 g of (n-Bu_4N) [$TcOCl_4$] (200 μmol) in 10 cm^3 of ethanol was added to 0.0774 g of tppz (199 μmol) in 20 cm^3 dichloromethane, and the mixture was stirred at 40°C for 2 h. During this time the colour of the solution turned from green to very dark blue. After evaporation of the dichloromethane, a turquoise-blue crystalline precipitate was obtained. The product was filtered and washed with ethanol and acetone. The yield of $TcOCl_2$(OEt) (tppz) was 0.0881 g (142 μmol), 71% based on Tc. The compound is soluble in acetonitrile, dichloromethane and nitromethane, slightly soluble in chloroform and acetone, and insoluble in alcohols and hydrocarbons. Anal.: Calcd. for $C_{26}H_{21}Cl_2N_6O_2Tc$: C, 50.42; H, 3.42; N, 13.57; Cl, 11.45%. Found: C, 50.21; H, 3.18; N, 13.01; Cl, 11.03%. Optical spectrum (CH_2Cl_2, nm, (ε) M^{-1} cm^{-1}): 762 sh, 590 (2200), 313 (23500), 276 sh (18300). Conductivity (10^{-3} M, DMF): 4.0 ohm^{-1} cm^2 mol^{-1}. IR(KBr): ν(Tc=O), 895 cm^{-1}; ν(Tc–Cl), 324, 333 cm^{-1}; ν(Tc-ethoxide), 556 cm^{-1}.

RESULTS AND DISCUSSION

The synthesis of the complexes reported in this communication parallels the synthetic procedures for preparations of oxotechnetium complexes with bidentate nitrogen aromatic heterocyclic ligands.[11] They were prepared from (n-Bu_4N) [$TcOCl_4$] and the ligand tppz in ethanol, and precipitated from ethanolic solution, analytically pure.

The complexes $TcOCl_2(OEt)$ (tppz) and (μ-tppz) $[TcOCl_2(OEt)]_2$ are moderately soluble in polar organic solvents. They are nonconductors in DMF solution. Some decomposition of the binuclear complex was noted in coordinating solvents over a period of several hours, and thus all necessary physical measurements were performed within 30 min of the preparation of a fresh sample solution. The mononuclear complex also undergoes decomposition, but at a rate which is much slower than that observed for the binuclear complex. No decomposition was observed, at least during several weeks, for any of the complexes in the solid state.

The infrared spectrum of the complex $TcOCl_2$ (OEt) (tppz) exhibits a single strong absorption band at 895 cm^{-1} (Figure 2a), which we ascribe to the Tc^{V}=O stretching vibration. This stretching frequency is considerably lower than that normally found for monooxotechnetium(V) complexes, which typically occurs in the 920–1020 cm^{-1} range.[16] Two strong absorption bands at 916 and 938 cm^{-1} appear in the infrared spectrum of (μ-tppz) $[TcOCl_2$ $(OEt)]_2$ (Figure 2b), and these are assigned to the stretching frequencies of two Tc^{V}=O groups in the complex. Bands at 561 and 570 cm^{-1} are in the range of metal–alkoxide stretches. A strong, broad band in the range 335–350 cm^{-1} is attributed to ν(Tc–Cl) vibrations. Owing to the broadness of this band, it was difficult to evaluate the precise number of Tc–Cl modes.

Both compounds are highly coloured. The turquoise-blue mononuclear $TcOCl_2$ (OEt) (tppz) complex has absorption bands at 762 and 590 nm in the visible region, with another strong band at 313 nm and a shoulder at 276 nm. The two bands in the visible region are ascribed to ligand-to-metal charge transfer absorptions (LMCT), possibly due to chloride-to-technetium transfer (at 762 nm) and ethoxide oxygen-to-metal transfer (at 590 nm). The absorption at 313 nm is assigned to a tppz intraligand $\pi\rightarrow\pi^*$ transition. Major changes are observed in the electronic spectrum upon coordination of the second metal centre in the green binuclear (μ-tppz) $[TcOCl_2$ $(OEt)]_2$ complex. Shoulders in the visible region appear at 720 and 585 nm, and the band of maximum intensity is found at 296 nm with intense shoulders at 334 nm and 248 nm. These bands are of considerably lower intensity than in the mononuclear case. The fine structure of the broad bands at 296 and 334 nm is observed, and this possibly suggests free rotation about one of the C–C bonds connecting the pyridine rings.

A comparison of the electronic spectra of these two complexes reveals that the intraligand tppz $\pi\rightarrow\pi^*$ transition in the binuclear complex occurs at lower energy (at 334 nm) than in the mononuclear complex, suggesting that the coordination of a second technetium results in a substantial decrease in electron density on the bridging tppz ligand. The LMCT transitions in the visible region also appear at higher energies for the binuclear complex. This indicates increased electron density donation by the chloride and ethoxide ions to "compensate" for the weaker electron transfer by the nitrogen donors of the tppz ligand caused by the coordination of a second metal centre.

Reactions of $TcOCl_4^-$ to give Tc^{V}=O complexes by ligand substitution are well known. Much less common is the reaction where the oxo oxygen in $TcOCl_4^-$ is displaced, as was recently found in the preparation of $Tc^{V}Cl(CDO)_3BC_4H_9$.[17] One of the characteristics of the complex $TcOCl_2$ (OEt) (tppz) is the extremely low stretching frequency at 895 cm^{-1} that is observed for the Tc^{V}=O bond. This value is considerably lower than is normally found for monooxotechnetium(V) complexes, and slightly out of the range of *trans*-dioxotechnetium(V) compounds (790–

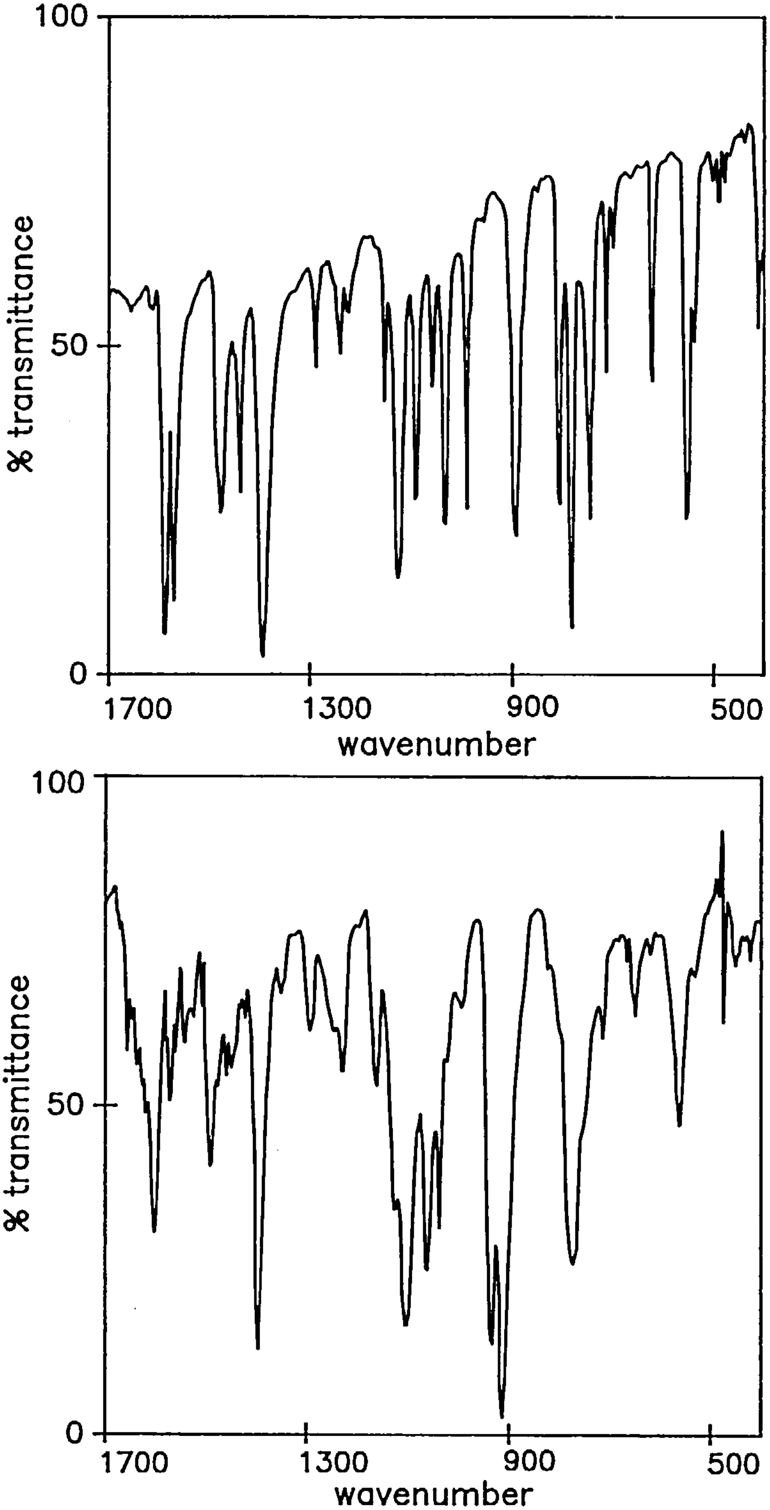

FIGURE 2 Infrared spectra of (a) $TcOCl_2$ (OEt) (tppz) and (b) (μ-tppz)$[TcOCl_2$ (OEt)$]_2$ in the range 400–1700 cm^{-1}.

880 cm^{-1}).[16] This result implies that the technetium(V)-oxo oxygen bond is considerably weaker (and longer) than previously found in monooxotechnetium(V) complexes. The mononuclear complex is non-conducting. Microanalyses and the extremely low Tc=O stretching frequency suggest that the technetium(V) ion is seven-coordinate in $TcOCl_2$ (OEt) (tppz), if it is assumed that tppz acts as a terdentate ligand. The low stretching frequency of the Tc=O bond seems to indicate that the tppz ligand indeed acts as a terdentate ligand, since the donation of electron density by five donor atoms in the plane (three nitrogens and two chloride) would weaken the Tc=O bond considerably. It is likely that the ethoxide group coordinates in a position *trans* to the oxo oxygen, as suggested and found in numerous technetium(V) complexes,[11] with a resultant Tc=O bond weakening.

If tppz were to act as a bidentate ligand, the complex $TcOCl_2$ (OEt) (tppz) would be six-coordinate, and a higher Tc=O stretching frequency could have been expected. The ν(Tc=O) stretch in the compound $TcOCl_2$ (OEt) (bipy)[11] appears at 922 cm^{-1}. Our results thus indicate that the technetium(V) ion in $TcOCl_2$ (OEt) (tppz) is indeed seven-coordinate, and that the very weak Tc=O bond is the result of increased electron donation resulting from seven-coordination. It is of course also possible that the long Tc=O bond length may be the result of steric constrictions imposed by seven-coordination.

Seven-coordinate technetium(V) centres have previously been found in the species $[Tc(DMG)_3SnCl_3(OH)]\cdot 3H_2O$[18] and $TcO(EDTA)^-$.[19] Seven-coordinate intermediates have been proposed in the reduction of oxotechnetium(V) complexes by phosphines[20] and in substitutions of $TcO_2(py)_4^+$,[21] where weakening of the Tc=O bonds by increased donation of electron density by planar ligands must facilitate oxo removal and thus reduction.

The two technetium(V) ions in the binuclear complex (μ-tppz) $[TcOCl_2$ $(OEt)]_2$ experience different coordination environments, as is indicated by the presence of two distinct Tc=O stretching vibrations at 938 and 916 cm^{-1} in the infrared spectrum. The fact that the complex is a non-conductor in acetonitrile and DMF indicates that one of the technetium(V) ions in the complex is seven-coordinate, possibly with the three nitrogen donor atoms of the tppz and two chloride ions in a distorted pentagonal plane, with the ethoxide *trans* to the oxo oxygen in apical positions. The increased donation of electron density by the five planar donor atoms will weaken the Tc=O bond considerably, and we ascribe the Tc=O stretching frequency at 916 cm^{-1} to the seven-coordinate technetium(V)–oxo bond. The strong absorption peak at 938 cm^{-1} is also ascribed to a Tc=O stretching vibration in the binuclear complex. The fact that this peak indicates a stronger Tc=O bond than the one reflected by the 916 cm^{-1} frequency illustrates that less electron density is received by the technetium(V) ion from the nitrogen donors of the tppz ligand. The existence of the stronger Tc=O bond in the complex can only be explained by the assumption that this technetium(V) ion is six-coordinate, with the tppz ligand in this instance acting in a bidentate fashion. The ligand tppz acts thus as a bis-terdentate-bidentate ligand in the complex (μ-tppz) $[TcOCl_2$ $(OEt)]_2$. We believe that this is the result of steric repulsions between the coordinating coplanar pyridine rings.

Our and other studies[22] dispel earlier speculations[14] on the ability of the potentially bis-terdentate tppz ligand to coordinate two metal centres on the same tppz ligand, on the basis of the steric repulsions of the coplanar pyridine rings. Coordination of tppz with $TcOCl_4^-$ most likely proceeds in a stepwise fashion, initially to form a seven-coordinate technetium(V) complex, followed by coordination of a second technetium(V) ion in a six-coordinate environment. Results on the coordination behaviour of tppz are scarce in the literature. Bidentate coordination of tppz has not been reported previously. However, bidentate coordination by the potentially tridentate nitrogen donor ligand terpy (terpy = 2,2':6'2"-terpyridine) has been proposed for a number of complexes[23] and has been confirmed by X-ray crystallography.[24]

ACKNOWLEDGEMENTS

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

REFERENCES

1. C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **91**, 3988 (1969).
2. W. Kaim and S. Kohlmann, *Inorg. Chem.*, **25**, 3306 (1986).
3. R.R. Ruminski and J.D. Petersen, *Inorg. Chem.*, **21**, 3706 (1982).
4. R.R. Ruminski, T. Cockroft and M. Shoup, *Inorg. Chem.*, **27**, 4026 (1988).
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. M. Shoup, B. Hall and R.R. Ruminski, *Inorg. Chem.*, **27**, 200 (1988).
8. K.J. Brewer, W.R. Murphy and J.D. Petersen, *Inorg. Chem.*, **26**, 3376 (1987).
9. J.G.H. du Preez, T.I.A. Gerber and M.L. Gibson, *J. Coord. Chem.*, in press.
10. "Technetium in Chemistry and Nuclear Medicine", E. Deutsch, M. Nicolini and H.N. Wagner, Jr., Eds, (Cortina International Verona, Verona, Italy, 1983).
11. A. Davison, A.G. Jones and M.J. Abrams, *Inorg. Chem.*, **20**, 4330 (1981).
12. P.H. Fackler, M.E. Kastner and M.J. Clarke, *Inorg. Chem.*, **23**, 3968 (1984).
13. A. Davison, H.S. Trop, B.V. DePamphilis and A.G. Jones, *Inorg. Synth.*, **21**, 160 (1982).
14. H.A. Goodwin and F. Lyons, *J. Am. Chem. Soc.*, **81**, 6415 (1959).
15. J.G.H. du Preez, T.I.A. Gerber and O. Knoesen, *J. Coord. Chem.*, **16**, 285 (1987).
16. M.J. Clarke and P.H. Fackler, *Struct. Bonding (Berlin)*, **50**, 57 (1982).
17. E.N. Treher, L.C. Francesconi, J.Z. Gougoutas, M.F. Malley and A.D. Nunn, *Inorg. Chem.*, **28**, 3411 (1989).
18. E. Deutsch, R.C. Elder, B.A. Lange, M. Vaal and D.G. Ray, *Proc. Natl. Acad. Sci. USA*, **73**, 4287 (1976).
19. E. Deutsch, K. Libson, S. Jurisson and L.F. Lindoy, *Prog. Inorg. Chem.*, **30**, 75 (1983).
20. U. Mazzi, F. Refosco, F. Tisato, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 847 (1988).
21. J. Lu and M.J. Clarke, *Inorg. Chem.*, **28**, 2315 (1989).
22. R. Ruminski, J. Kiplinger, T. Cockroft and C. Chase, *Inorg. Chem.*, **28**, 370 (1989).
23. B.E. Wilcox, D.M. Ho and E. Deutsch, *Inorg. Chem.*, **28**, 3917 (1989); D.M.W. Buck and P. Moore, *J. Chem. Soc., Dalton Trans.*, 638 (1976); G.B. Deacon and J.C. Parrott, *Aust. J. Chem.*, **27**, 2547 (1974).
24. G.B. Deacon, J.M. Patrick, B.W. Skelton, N.C. Thomas and A.J. White, *Aust. J. Chem.*, **37**, 929 (1984).