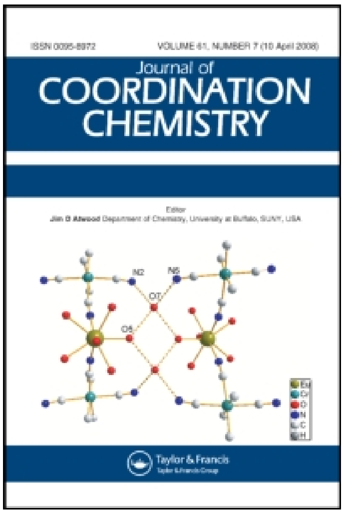

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Technetium(V) Complexes of Substituted Benzimidazolylalcohols and Thiols. Influence of the Donor Atom Type on the Configuration

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To cite this Article Preez, J. G. H. Du , Gerber, T. I. A. , Gibson, M. and Kemp, H. J.(1992) 'Technetium(V) Complexes of Substituted Benzimidazolylalcohols and Thiols. Influence of the Donor Atom Type on the Configuration', Journal of Coordination Chemistry, 25: 1, 53 — 61

To link to this Article: DOI: 10.1080/00958979209407902

URL: http://dx.doi.org/10.1080/00958979209407902

J. Coord. Chem. 1992, Vol. 25, pp. 53–61
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TECHNETIUM(V) COMPLEXES OF SUBSTITUTED BENZIMIDAZOLYLALCOHOLS AND THIOLS. INFLUENCE OF THE DONOR ATOM TYPE ON THE CONFIGURATION

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(Received February 11, 1991)

Cationic square-pyramidal complexes of general formula $[TcO(L)_2^+]Cl^-$ were prepared by the reaction of (n-Bu_4N)$TcOCl_4$ with the potentially bidentate *N,S*-donor benzimidazolylthiols (HL) as ligands in the presence of triethylamine. The corresponding reaction with the *N,O*-donor benzimidazolylalcohols led to the formation and isolation of the neutral six-coordinate complexes $TcOCl(L)_2$. These compounds were characterized by elemental analysis, vibrational and optical spectroscopy. Mechanisms for the formation reactions and probable configurations of the complexes are proposed on the basis of qualitative studies and spectroscopic results.

Keywords: Technetium(V), benzimidazolylthiols, complexes, mechanism, configuration

INTRODUCTION

The recent interest in the coordination chemistry of technetium is partially due to the potential application of coordination compounds of the short-lived isotope ^{99m}Tc ($t_{\frac{1}{2}}$ = 6h) as imaging agents in the field of nuclear medicine.[1,2] It became obvious that the oxidation state of technetium, together with the ligands coordinated around it and the total charge of the resulting complexes, plays a crucial role in the eventual localization of the agent in the body.[1,2] It was found that cationic technetium(I) complexes accumulate in myocardial tissue,[3,4] while neutral complexes have found application as brain imaging agents.[5]

Coordination compounds of technetium of which the lipophilic and polar properties can be varied by substitutions in the molecular framework of the ligands to optimize the biodistribution of such preparations are of particular importance in the development of new diagnostic imaging agents. We have used this principle in preparing a series of neutral and cationic complexes of technetium(V) by the reaction of (n-Bu_4N) [$TcOCl_4$] with substituted benzimidazolylalcohols and -thiols as ligands. In an earlier communication[6] we have reported the synthesis of cationic technetium(V) complexes by the reduction of pertechnetate in the presence of these ligands.

EXPERIMENTAL

The compound (n-Bu_4N)[$TcOCl_4$] was prepared from ammonium pertechnetate (Oakridge National Laboratory) according to literature procedures.[7] The benzimi-

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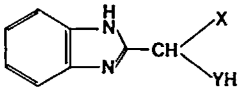
dazolylalcoholate and —thiolate ligands (Figure 1) were prepared as reported,[8] and their purity was checked by elemental analyses and melting points. The ligand 2-(2-hydroxyphenyl)benzothiazole was obtained commercially (Aldrich).

Scientific instrumentation used in this study is the same as was reported elsewhere.[9]



X	Y	Abbvn
H	S	HBMT
CH_3	S	HBET
H	O	HBMA
CH_3	O	HBEA
C_6H_5	O	HBPA

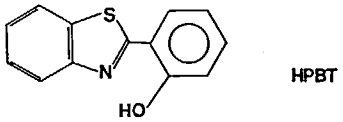


FIGURE 1 Ligands used in this study: HBMT = 2-benzimidazol-2'-yl-methanethiol; HBET = 2-benzimidazol-2'-ylethanethiol; HBMA = 2-benzimidazol-2'-ylmethanol; HBEA = 2-benzimidazol-2'-ylethanol; HBPA = 2-benzimidazol-2'-ylbenzylalcohol; HPBT = 2-(2-hydroxyphenyl)benzothiazole.

Preparation of Complexes

[TcO(BMT)$_2$]Cl·H$_2$O

To a solution of 99 mg (600 μmol) of the ligand HBMT in 5 cm^3 ethanol was added 100 mg (200 μmol) of (n-Bu_4N)[$TcOCl_4$] in 10 cm^3 ethanol, with stirring. This was immediately followed by the addition of 3 drops of triethylamine, and the reaction mixture was heated under reflux for 30 min. The dark brown solution was cooled to room temperature, then filtered to give an orange-brown precipitate, which was washed with water, 2-propanol, diethylether and acetone, and dried under vacuum. Recrystallization was from $CHCl_3$/2-propanol. The yield was 67%; mp > 300°C. *Anal.* Calcd. for $C_{16}H_{16}ClN_4O_2S_2Tc$: C, 38.83; H, 3.26; N, 11.32; Cl, 7.16%. Found: C, 39.01; H, 3.34; N, 11.10; Cl, 7.32%. Electronic spectrum (DMF, nm, ε/dm^3 mol^{-1} cm^{-1}): 588(240), 412(3500), 338(9300), 290sh, 275(28100). Conductivity (10^{-3} M DMF): 65 ohm^{-1} cm^2 mol^{-1}.

[TcO(BET)$_2$]Cl·H$_2$O

To a solution of 107 mg (600 μmol) of the ligand HBET in 5 cm^3 ethanol was added 100 mg of (n-Bu_4N)[$TcOCl_4$] in 10 cm^3 ethanol, followed by 3 drops of triethylamine.

This mixture was heated under reflux for 30 min, during which time the colour of the solution turned to dark brown, and a dark orange-brown precipitate formed. After cooling to room temperature, the brown precipitate was removed by filtration, washed with water, 2-propanol, and diethylether, and dried under vacuum at room temperature. Recrystallization was from $CHCl_3$/2-propanol. The yield was 68%; mp > 300°C. *Anal.* Calcd. for $C_{18}H_{20}ClN_4O_2S_2Tc$: C, 41.34; H, 3.85; N, 10.71; Cl, 6.78%. Found: C, 41.01; H, 3.64; N, 10.79; Cl, 6.83%. Electronic spectrum (DMF, nm, $\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$): 591(350), 408(3100), 330sh, 292sh, 269(18700). Conductivity (10^{-3} M, DMF): 63 $ohm^{-1}\,cm^2\,mol^{-1}$.

TcOCl(BMA)$_2$

A solution of 60 mg (400 µmol) of the ligand HBMA in 10 cm^3 acetonitrile was added to 100 mg (200 µmol) of (n-Bu_4N)[$TcOCl_4$] in 10 cm^3 acetonitrile. After the addition of 3 drops of triethylamine, the mixture was heated under reflux for 30 min. After cooling and reduction of the volume under vacuum, the green product was filtered, washed with methanol, 2-propanol, and diethylether, and dried under vacuum. The yield was 66%; mp, 168°C (decomp). *Anal.* Calcd. for $C_{16}H_{14}ClN_4O_3Tc$: C, 43.21; H, 3.17; N, 12.60; Cl, 7.97%. Found: C, 43.21; H, 3.12; N, 12.80; Cl, 8.20%. Electronic spectrum (CH_3CN, nm, $\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$): 548(180), 355(2300), 295(6200), 276(16800). Conductivity (10^{-3} M, DMF): 8.2 $ohm^{-1}\,cm^2\,mol^{-1}$.

TcOCl(BEA)$_2$

Some 65 mg (400 µmol) of the ligand HBEA in 10 cm^3 acetonitrile was added to 100 mg of (n-Bu_4N)[$TcOCl_4$] in 10 cm^3 acetonitrile, followed by 3 drops of triethylamine. After heating the reaction mixture under reflux for 30 min, it was cooled to room temperature, and the volume was reduced under vacuum to give a green precipitate. The product was filtered, washed with methanol, 2-propanol, and diethylether, and dried under vacuum. The yield was 62%; mp, 158°C (decomp). *Anal.* Calcd. for $C_{18}H_{18}ClN_4O_3Tc$: C, 45.72; H, 3.84; N, 11.85; Cl, 7.50%. Found: C, 45.71; H, 3.48; N, 11.84; Cl, 7.02%. Electronic spectrum (CH_3CN, nm, $\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$): 551(280), 350(3600), 299(6000), 269(14600). Conductivity (10^{-3} M, DMF): 8.1 $ohm^{-1}\,cm^2\,mol^{-1}$.

TcOCl(BPA)$_2$

To a solution of 100 mg (n-Bu_4N)[$TcOCl_4$] in 3 cm^3 methanol was added 179 mg of the ligand HBPA (800 µmol) in 5 cm^3 methanol and 3 drops of triethylamine. An immediate colour change to very dark green occurred, and after stirring for 1 h at room temperature a fine microcrystalline precipitate was collected by filtration. It was washed with water, methanol, 2-propanol, and diethylether, and dried under vacuum. The yield was 77%; mp, 169°C. *Anal.* Calcd. for $C_{28}H_{22}ClN_4O_3Tc$: C, 56.34; H, 3.71; N, 9.39; Cl, 5.94%. Found: C, 56.71; H, 4.04; N, 9.81; Cl, 5.87%. Electronic spectrum (CH_3CN, nm, $\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$): 592(1240), 370sh, 327(9600), 274(17200). Conductivity (10^{-3} M, CH_3CN): 11.2 $ohm^{-1}\,cm^2\,mol^{-1}$.

TcOCl(PBT)$_2$

To a solution of 100 mg (n-Bu_4N)[$TcOCl_4$] in 5 cm^3 methanol was added 136 mg

(600 µmol) of the ligand HPBT and 3 drops of Et_3N in 10 cm^3 methanol. After stirring the reaction solution for 1 h at room temperature the dark red precipitate was removed by filtration, and it was washed with water, methanol and diethylether, and dried under vacuum at room temperature. The yield was 73%; mp, 126°C. *Anal.* Calcd. for $C_{26}H_{16}ClN_2O_3S_2Tc$: C, 51.79; H, 2.67; N, 4.65; Cl, 5.88%. Found: C, 51.48; H, 2.81; N, 4.47; Cl, 5.73%. Electronic spectrum (DMF, nm, $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 532(1200), 332(21800), 298sh, 288(20300). Conductivity (10^{-3} M, DMF): 14.7 $ohm^{-1}\ cm^2\ mol^{-1}$.

RESULTS AND DISCUSSION

Neutral Complexes [TcOCl(L)$_2$]

The neutral complexes with the formulation $TcOCl(L)_2$ (L = BMA, BEA, PBT, BPA) have been prepared by the simple substitution of chloride in the $TcOCl_4^-$ anion by the *N,O*-donor ligands HL in refluxing acetonitrile (L = BMA, BEA) and methanol (L = BPA, PBT) in the presence of triethylamine. Both solvents, as well as ethanol, could be used for the preparation of any of these complexes, but the choice of solvent as reaction medium was important in the easy synthesis and attainment of pure products.

All the $TcOCl(L)_2$ complexes, except $TcOCl(PBT)_2$ which is red, are green in colour, and are non-electrolytes in DMF and CH_3CN. They are slightly soluble in acetone, chloroform and acetonitrile, and are indefinitely stable in the solid state and in solution.

TABLE I
Selected infrared spectral data for the complexes (cm^{-1}).*

Complex	ν(Tc=O)	ν(Tc–N)	ν(C–O)	ν(Tc–Cl)
$TcOCl(BEA)_2$	943	432, 441	1278; 1297	322
$TcOCl(BMA)_2$	945	434, 442	1273; 1295	325
$TcOCl(BPA)_2$	942	436, 445	1260; 1279	321
$TcOCl(PBT)_2$	946	431, 442	1273; 1296	318
$[TcO(BMT)_2]Cl{\cdot}H_2O$	965	442	1017†	
$[TcO(BET)_2]Cl{\cdot}H_2O$	970	440	1011†	

* In KBr discs. † ν(C–S).

The most important infrared frequencies for the complexes are given in Table I. The band due to the Tc=O bond stretch was found in the range 942–946 cm^{-1}. The values are in agreement with those found for neutral six-coordinate oxotechnetium(V) complexes,[10,11] which normally occur in the region 930–945 cm^{-1}. There are no peaks in the infrared spectrum which could be ascribed to ν(O–H) vibrations, and a band around 3200 cm^{-1} is assigned to ν(N–H) (absent in $TcOCl(PBT)_2$). These data indicate that the ligands L^- are coordinated to the technetium(V) through the deprotonated alcoholate/phenolate oxygen and the neutral imidazole/thiazole imine nitrogen. A single peak around 320 cm^{-1} in the far-infrared region of the complexes $TcOCl(L)_2$ is indicative of a Tc–Cl stretching vibration, with the chloride coordinated in a *cis* position relative to the oxo oxygen. All the complexes exhibit two strong peaks in the region 1260–1330 cm^{-1}, which are assigned to ν(C–O), and thereby indicating the presence of two molecules of the ligands L$^-$ in asymmetric positions in all complexes. Two peaks of medium intensity in the range 430–445 cm^{-1} are assigned to the Tc–N stretching vibrations, and are indicative of the two coordinating nitrogen atoms in *cis* positions, relative to each other.

The electronic spectra of the TcOCl(L)$_2$ complexes are of a complex nature, and quite a number of absorption bands appear in the 260–600 nm range. The peak around 295 nm is ascribed to an intraligand $\pi \rightarrow \pi^*$ transition, with the high energy peak around 270 nm due to oxo oxygen-to-technetium(V) charge transfer. The intensity of the peak around 350 nm suggests it is due to a ligand-to-metal charge transfer, with the peak at longer wavelengths (540–600 nm) due to a d–d transition with possible "stealing" from the adjacent LMCT band.

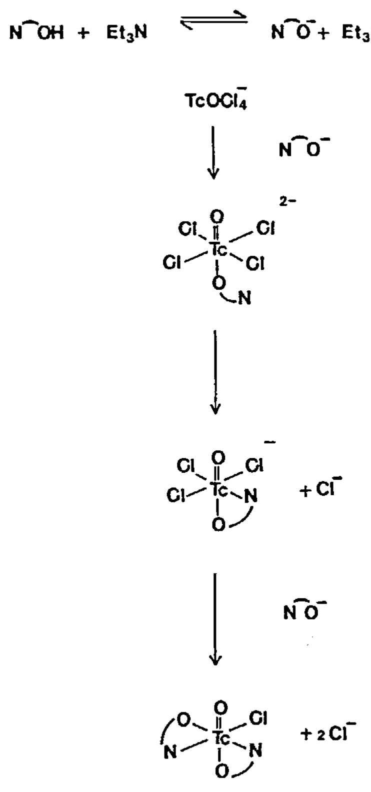
Information on the mechanism of the formation reaction of the complexes TcOCl(L)$_2$ was obtained by carrying out the reaction of a twofold excess of the ligand HBPA and (n-Bu$_4$N)[TcOCl$_4$] in the presence of triethylamine and a tenfold excess of LiCl in methanol. The excess chloride has no effect on the reaction rate, and the previously isolated product TcOCl(BPA)$_2$ was obtained in good yield. On this basis, the first step in the complex formation cannot be the substitution of a chloride from the TcOCl$_4^-$ anion, but must be the coordination of the anionic alcoholate/phenolate oxygen atom of the ligand in the vacant coordination site *trans* to the technetyl oxo oxygen in the square-pyramidal TcOCl$_4^-$ ion. It is of course also possible that the neutral OH group of the ligands HL can coordinate in this position as a first step, followed by deprotonation of the oxygen atom. The reaction then proceeds by chelation, coordination of a second chelate ligand and substitution of chloride in TcOCl$_4^-$. A probable mechanism is presented in Scheme 1.

Spectroscopic evidence indicates that the configuration of the complexes TcOCl(L)$_2$ will be as given in Scheme 1, *i.e.*, with the deprotonated anionic oxygen donor atom of one of the L$^-$ ligands coordinated *trans* to the oxo oxygen. The fact that two peaks are observed for ν(C–O) supports this assumption. Infrared spectral data also indicate that the two nitrogen donor atoms of the two L$^-$ ligands will be *cis* (to each other).

The complex TcOCl(PBT)$_2$ has been isolated previously[12] as a byproduct in the reaction of TcOCl$_4^-$ with the Schiff base *N*-(2-mercaptophenyl)salicylideneimine in dichloromethane, but no spectroscopic data were reported. A crystal structure determination revealed that one phenolate oxygen atom of the ligand PBT$^-$ is coordinated in an axial position *trans* to the "yl" oxygen atom, with the two imine nitrogen atoms from two L$^-$ ligands in a *cis* configuration, and one chloride and the second phenolate oxygen occupying the other two sites of the equatorial plane.

The reaction of TcOCl$_4^-$ with the bidentate *N,O*-donor Schiff base *N*-phenylsalicylideneimine (NOH) led to the isolation of the six-coordinate complex TcOCl(NO)$_2$.[13] The crystal structure of this complex reveals the coordination of an anionic phenolate oxygen of one Schiff base ligand in the axial position *trans* to the oxo oxygen, and with the two imine nitrogen donor atoms *cis* (to each other). The same configuration has also been observed in the complex *cis*-TcOCl(oxMe)$_2$ (HoxMe = 2-methyl-8-quinoline).[14]

In the complex TcOCl(salpd), where H$_2$salpd represents the tetradentate *ONNO* Schiff base *N,N′*-propane-1,3-diylbis(salicylideneimine), the tetradentate is coordinated in the equatorial plane, with the chloride *trans* to the oxo oxygen.[15] Our results support the suggestion that bidentate *N,O*-donor ligands will coordinate to the TcO^{3+} core with the anionic oxygen always *trans* to the oxo oxygen.



Scheme 1

Efforts to prepare complexes of the type $TcOCl_2(L)$ from (n-Bu_4N)[$TcOCl_4$] and the ligands HL in an equimolar stoichiometry in alcohol or acetonitrile in the presence of triethylamine proved unsuccessful, and no pure products with sensible analyses could be isolated.

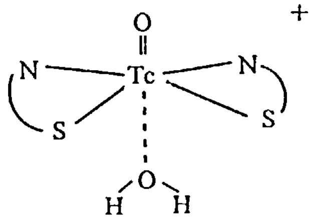
Cationic Complexes [$TcO(L)_2$]$Cl{\cdot}H_2O$ (L = BMT, BET)

The reaction of the *N*,*S*-donor benzimidazolylthiols HBMT and HBET with (n-Bu_4N)[$TcOCl_4$] in the presence of triethylamine in ethanol led to the isolation of the products [$TcO(L)_2$]$Cl{\cdot}H_2O$ in reasonable yields. These complexes are red-brown in colour, and they are 1:1 electrolytes in DMF. They are poorly soluble in polar organic solvents, and are indefinitely stable in the solid state and in solution.

Table I lists the infrared spectral parameters for the two cationic complexes. The presence of the TcO^{3+} group in both complexes is indicated by a very strong band in the range 965–970 cm^{-1}, which is typical for ν(Tc=O) of cationic square-pyramidal oxotechnetium(V) complexes.[16] The ν(S–H) vibration in the neutral free ligands disappear upon coordination, and a band around 3200 cm^{-1} is indicative of ν(N–H). These data indicate that the ligands L^- are coordinated to the technetium(V) ion through the deprotonated thiolate sulphur and the neutral imine nitrogen atoms of the chelate ligand. There are no peaks in the region 280–330 cm^{-1} which could be assigned to a Tc–Cl stretching frequency, but a single peak of medium intensity around 440 cm^{-1} indicates the presence of equivalent Tc–N bonds. The ν(Tc–S) mode could not be assigned with certainty.

The red-brown complexes $[TcO(L)_2]Cl \cdot H_2O$ give rise to green solutions in a variety of solvents and their electronic spectra display intense absorbances in the range 265–595 nm. The peak around 270 nm in both complexes is ascribed to the overlapping of an intraligand $\pi \rightarrow \pi^*$ transition with the oxo oxygen-to-technetium(V) charge transfer transition. The magnitude of the extinction coefficients of the peak around 590 nm suggests that it is due to a spin-forbidden d–d transition, with possible "stealing" from the adjacent charge transfer band around 410 nm. The intensities of all other peaks indicate that they are due to ligand-to-metal charge transfer transitions.

All examples in the literature of five-coordinate oxotechnetium(V) complexes display square-pyramidal configuration.[1] Spectral evidence obtained in this study indicate that the complexes $[TcO(L)_2]Cl \cdot H_2O$, where $L^- =$ *N*,*S*-donor ligands BMT^- and BET^-, are also of square-pyramidal configuration, rather than trigonal bipyramidal conformation with a thiolate sulphur *trans* to the oxo oxygen. In fact, it has never been found previously that an anionic sulphur coordinates in this *trans* position in oxotechnetium(V) complexes. It is however possible that the water molecule in the complexes $[TcO(L)_2]Cl \cdot H_2O$ is positioned *trans* to the oxo oxygen, and that it undergoes a weak interaction with the technetium(V) centre. We thus propose the following configuration for the complexes $[TcO(L)_2]Cl \cdot H_2O$.



The weak interaction of the water molecule with the technetium(V) centre is supported by the thermogravimetric analysis of both complexes, which showed a mass loss in the temperature range 145–152°C, equal to one molecule of water per molecule of complex.

Technetium(V) complexes of the form $[TcO(tcb)_2]Cl$, with $tcb^- =$ *N*-thiocarbamoylbenzamidinato, have been synthesized.[16] A crystal structure analysis of one of the complexes, $[TcO(Et_2tcb)_2]Cl$ [$Et_2tcb^- =$ *N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato], demonstrates a square pyramidal configuration around Tc(V), with the N_2S_2 donor atoms of the two Et_2tcb^- ligands coordinating in the equatorial plane perpendicular to the oxo oxygen.[16] The chelating ligands coordinate in such a fashion that the two nitrogen donor atoms, and the two thiolic sulphurs, are *cis* to each other.

The results obtained in this study again illustrate the influence of the nature of the coordinating donor atoms on the configuration of the complexes. It was found in this study that the reaction of $TcOCl_4^-$ with the bidentate *N*,*O*-donor ligands leads to the formation of neutral six-coordinate complexes $TcOCl(L)_2$. The similar reaction with *N*,*S*-donor ligands forms the species $[TcO(L)_2^+]Cl^-$ in which the complex has a square pyramidal configuration. This dependence of the configuration of the products on the donor atom types may be the direct result of the bulkiness of the ligands used and due to the repulsion that is exerted by the oxo oxygen on the equatorial ligands. This repulsion originates from the π electron density associated with the multiple Tc=O bond, and is greater for ligands connected by formally covalent $L^{-}:\rightarrow M^{+}$ bonds than for donor–acceptor $L:\rightarrow M$ bonds.[17] It is thus clear that this repulsion by the oxo oxygen on the equatorial ligands increases in the order N(imino) $< S^{-} < Cl^{-} < O^{-}$, which is also the order of increasing hardness of the donor atoms as bases.[18] The increasing hardness of the base leads to increasing ionic character of its bond with the hard acid technetium(V), with the result that the harder basic ligands are repelled more as a consequence of the higher population of their orbitals. This effect will mean that the affinity of above donor atoms to occupy the coordination site *trans* to the oxo group will decrease in the order $O^{-} > Cl^{-} > S^{-} > N$.

This order predicts that the complexes prepared in this study with the *N*,*S*-donor ligands would be the neutral six-coordinate species $TcOCl(L)_2$, with the chloride coordinated *trans* to the oxo oxygen. Due to the repulsion of the oxo oxygen, the equatorial N_2S_2 donor atoms will "crowd" the coordination site in the *trans* position to such an extent that the chloride cannot coordinate in this position.

The *N*,*O*- and *N*,*S*-donor ligands used in this study are examples of coordinating molecules that may contain different substituents on the ligand backbone. Substituents in the molecular structure of the ligands are possible on the protonated imidazole nitrogen, on the benzene ring, and in the X group (Figure 1). A large number of stepwise varied ligands can thus be prepared, of which ^{99m}Tc complexes of the type $TcO(L)_2^{+}$ and $TcOCl(L)_2$ should show a stepwise variation in their radiopharmaceutical properties.

ACKNOWLEDGEMENTS

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

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