Technetium(V)–Nitrido Complexes of Dithiocarbazic Acid Derivatives. Reactivity of $[Tc{\equiv}N]^{2+}$ Core towards Schiff Bases derived from *S*-Methyl Dithiocarbazate. Crystal Structures of [*S*-Methyl 3-(2-hydroxyphenylmethylene)dithiocarbazato]nitrido(triphenylphosphine)technetium(V) and Bis(*S*-methyl 3-isopropylidenedithiocarbazato)nitridotechnetium(V) †

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New technetium(V)–nitrido complexes with bi- and tri-dentate Schiff bases, derived from the condensation of various aldehydes and acetone with the methyl ester of dithiocarbazic acid, $NH_2NHC(=S)SCH_3$, were prepared by substitution or substitution–reduction reactions on the square-pyramidal complexes $[Tc^{V}NCl_2(PPh_3)_2]$ and $[Tc^{VI}NCl_4]^-$. The final complexes all maintain the square-pyramidal geometry of the starting compounds with the Tc≡N group in an apical position. The bidentate ligands give rise to mono- and di-substituted complexes, in which they are co-ordinated to the metal through the β-nitrogen atom and the thiol sulphur atom; in monosubstituted complexes, the remaining two positions in the plane of the square pyramid are occupied by triphenylphosphine (PPh_3) and Cl^- groups. The tridentate Schiff bases co-ordinate to the metal, in the basal plane, as doubly negatively charged ligands through the phenolic oxygen atom, the β-nitrogen atom, and the thiol sulphur atom, the fourth position being occupied by the phosphorus atom of a PPh_3 group. The crystal structures of $[TcNL^1(PPh_3)]$ (**1**) [H_2L^1 = *S*-methyl 3-(2-hydroxyphenylmethylene)dithiocarbazate] and $[TcN(L^{12})_2]$ (**2**) (HL^{12} = *S*-methyl 3-isopropylidenedithiocarbazate) have been determined. Relevant crystal data for (**1**) are: refined from 5 008 reflections with $I \geqslant 3\sigma(I)$ to a final R of 0.029, crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 8.309(1), b = 12.294(1), c = 13.308(3) Å, α = 96.22(1), β = 95.07(1), γ = 101.34(1), and Z = 2; for (**2**): refined from 1 756 reflections with $I \geqslant 3\sigma(I)$ to a final R of 0.023, crystals are monoclinic, space group $I2/a$, with unit-cell dimensions a = 16.707(3), b = 8.838(1), c = 12.514(2) Å, β = 106.85(1)°, and Z = 4. In both complexes, the co-ordination around Tc is distorted square pyramidal with an apical multiply bonded nitrogen atom [Tc≡N 1.611(3) Å in (**1**) and 1.613(3) Å in (**2**)] and the basal ligands bent away from the nitrido group.

Application of the metastable isomer ^{99m}Tc as an imaging agent in nuclear medicine, has produced rapid development of the inorganic chemistry of technetium, principally as a consequence of the need to design more powerful and specific radiopharmaceuticals.[1] A number of recent investigations have focused on the properties of the $[Tc{=}O]^{3+}$ core, characterizing the wide role of technetium(V) chemistry.[2,3] In particular, the need to obtain lipid-soluble species for brain imaging[4] has led to the synthesis of a series of five-co-ordinate complexes with macrocyclic amino-oxime ligands, containing the Tc=O group in the apical position of a square pyramid.[5]

The $[Tc{\equiv}N]^{2+}$ core constitutes a group isoelectronic with $[Tc{=}O]^{3+}$.[6–9] The nitrido N^{3-} ligand is considered the strongest π donor known which may act as a terminal or bridging atom, and which tends to stabilize the metal in high oxidation states.[10] Recently, new radiopharmaceuticals based on the $[Tc{\equiv}N]^{2+}$ core have been investigated.[11]

As a potential alternative approach to lipophilic square-pyramidal technetium complexes, we investigate here the synthesis of new Tc^{V} complexes, containing the $[Tc{\equiv}N]^{2+}$ core, with bi- and tri-dentate Schiff bases derived from *S*-methyldithiocarbazate, $NH_2NHC(=S)SCH_3$. Square-pyramidal complexes having an apical $Tc^{V}{\equiv}N$ group, with bis(quinoline-8-thiolato), $[TcN(C_9H_6NS)_2]$,[6] and bis(diethyldithiocarbamate), $[TcN(S_2CNEt_2)_2]$,[7] have been reported. With monodentate ligands, only the six-co-ordinate compound $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$,[8] in which an exceptionally long Tc–N bond distance (2.491 Å) to the CH_3CN ligand is observed as a result of the strong *trans* influence of the nitrido group, was reported. A series of complexes of general formula $[TcNL_2]^{0,2-,2+}$ (L = dichalcogeno ligand) have also been prepared, though no structural *X*-ray characterization was carried out.[12]

In this paper, we report the synthesis and characterization of a series of technetium(V)–nitrido complexes with the ligands illustrated, obtained by reduction of the technetium(VI) complex $[TcNCl_4]^-$ or by ligand substitution of the Tc^{V} complex $[TcNCl_2(PPh_3)_2]$. We discuss also the crystal structures of the complexes $[TcNL^1(PPh_3)]$ [H_2L^1 = *S*-methyl 3-(2-hydroxyphenylmethylene)dithiocarbazate] and $[TcN(L^{12})_2]$ (HL^{12} = *S*-methyl 3-isopropylidenedithiocarbazate).

Experimental

General.—Technetium-99 emits a low energy (0.292 keV, *ca.* 4.67×10^{-17} J) β-particle with a half-life of 2.12×10^{-5} years.

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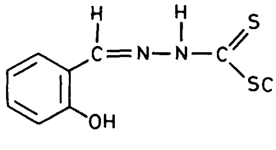
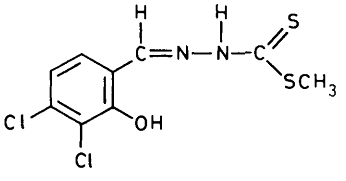
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



H_2L^1



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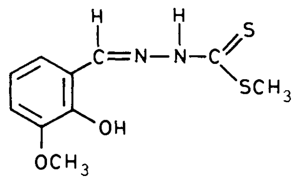

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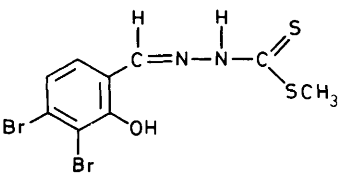

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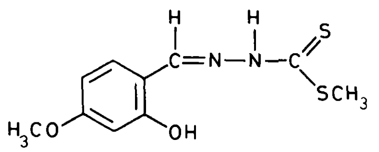

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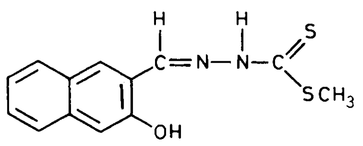

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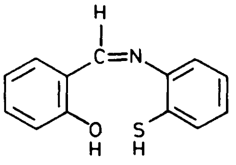

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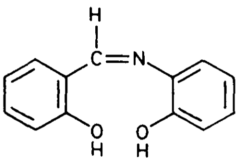

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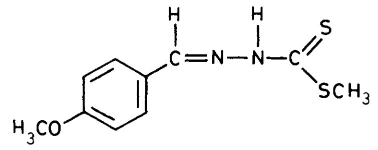
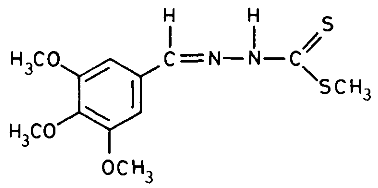
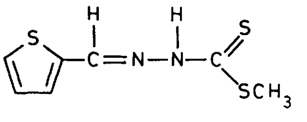


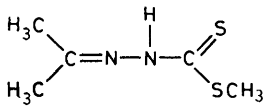
HL^9



HL^{10}



HL^{11}



HL^{12}

When this material is handled in milligram amounts it does not present a serious hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination.

All common laboratory chemicals were reagent grade. Technetium, as $[NH_4][TcO_4]$ in 0.1 mol dm^{-3} ammonia solutions, was purchased from the Radiochemical Centre, Amersham, England. The $[NBu^n{}_4]^+$ and $[AsPh_4]^+$ salts of the tetrachloronitridotechnetate(VI) anion, $[TcNCl_4]^-$, were prepared by reaction of $[TcO_4]^-$ with NaN_3 in the presence of concentrated HCl and of the corresponding cation,[9] while $[TcNCl_2(PPh_3)_2]$ was obtained by reaction of $[TcO_4]^-$ with hydrazine dihydrochloride and triphenylphosphine.[13]

I.r. spectra were recorded on a Perkin-Elmer 577 grating spectrometer using KBr pellets, or in Nujol mulls between CsI discs. Elemental analyses were performed on a Carlo Erba elemental analyzer model 1106; the elemental analyses for radioactive technetium were carried out on a Packard liquid-scintillation instrument, model TRICARB 300C, with Insta-gel as scintillator, after dissolution of the samples in hydrogen peroxide–nitric acid solutions. Magnetic susceptibility measurements were carried out by Evans' method[14] on a Bruker WP 80 MHz spectrometer.

The Schiff bases illustrated (H_2L^1—H_2L^8 and HL^9—HL^{12}) and the ligand $2\text{-}HOC_6H_4CH{=}NPh$ were prepared by methods reported elsewhere,[15,16] while the ligands H_2L^7 and H_2L^8 were obtained by condensation of 2-hydroxybenzenecarbaldehyde with 2-aminothiophenol and 2-aminophenol, respectively.[17]

Synthesis of the Complexes.—$[TcNL(PPh_3)]$ (L = *tridentate ligand*). The $[NBu^n{}_4]^+$ or $[AsPh_4]^+$ salts of $[TcNCl_4]^-$ (0.157 mmol) were treated with a two-fold molar excess of the relevant ligand (H_2L^1—H_2L^7) and a three-fold molar excess of triphenylphosphine (PPh_3) in ethanol–methylene chloride (1:3) solution (20 cm^3). The reaction mixture was stirred and heated slightly (40 °C) for 10 min. The colour changed from orange to yellow and, after slow evaporation of the solvent in air, yellow (or yellow-orange) crystals of the final complex were collected and washed with ethanol and diethyl ether. Yield >90%.

The same compounds were also prepared using $[TcNCl_2$-

$(PPh_3)_2]$ as starting material. In this case, the ligands were added in the stoicheiometric ratio 2:1 (ligand:metal) to a benzene solution of the initial compound. After refluxing for 1 h, the colour changed from pink to yellow and crystals of the final products were recovered by slow evaporation of the solvent in air, and were then washed with ethanol and diethyl ether. Yield $> 90\%$.

$[TcNClL'(PPh_3)]$ (L′ = *bidentate ligand*). A stoicheiometric amount of the appropriate ligand (HL^9—HL^{12}) was added to an ethanol–methylene chloride (1:3) solution (30 cm^3) of the $[NBu^n_4]^+$ or $[AsPh_4]^+$ salts of $[TcNCl_4]^-$ (0.157 mmol), containing a three-fold excess of PPh_3. The mixture was stirred for 30 min at reflux temperature. The resulting yellow solution was evaporated to dryness under reduced pressure and the residue washed with ethanol and diethyl ether. Recrystallization was carried out from ethanol–methylene chloride. Yield $> 80\%$.

An alternative procedure employed $[TcNCl_2(PPh_3)_2]$ without addition of PPh_3. After treating this complex with a stoicheiometric amount of the ligand in boiling benzene for 1 h, the final compounds were recovered using the same isolation procedure as above. Yield $> 80\%$.

$[TcN(L')_2]$. A four-fold excess of the bidentate ligand was added to an ethanol–methylene chloride (1:3) solution (20 cm^3) of $[TcNCl_4]^-$, $[NBu^n_4]^+$ or $[AsPh_4]^+$ salt, or to a benzene solution of $[TcNCl_2(PPh_3)_2]$. The solution was refluxed for 1 h and then evaporated to dryness under reduced pressure. The residue was washed with ethanol and diethyl ether and recrystallized from CH_2Cl_2–EtOH. Yield $> 80\%$.

Crystal-structure Determinations.—The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo-K_α radiation and ω–2θ scan technique.

Cell parameters were obtained from least-squares refinement of 25 centred reflections in the range $9 < \theta < 13°$ for the complex $[TcNL^1(PPh_3)]$ (**1**), and of 24 centred reflections in the range $10 < \theta < 14°$ for the complex $[TcN(L^{12})_2]$ (**2**). The intensity of three standard reflections, monitored every 2 h, showed no significant variation during data collection for both complexes. All data were corrected for Lorentz polarization and absorption [minimum transmission factor = 0.875 for (**1**) and = 0.895 for (**2**)]. Scattering factors and anomalous dispersion parameters were taken from ref. 18; the positions of the Tc atoms were obtained from a Patterson synthesis; all non-H atoms were located in the subsequent Fourier maps. Hydrogen atoms were found from difference Fourier maps and refined only for (**2**). After a few cycles of isotropic refinement, the structures were refined by full-matrix least squares using anisotropic thermal parameters for all non-H atoms. All hydrogen atoms were included in the structure-factor calculations using fixed thermal parameters of 5 Å^2 for structure (**1**), and refined isotropically for (**2**).

Table 1. Crystal data

	(**1**)	(**2**)
Formula	$C_{27}H_{23}N_3OPS_2Tc$	$C_{10}H_{18}N_5S_4Tc$
M	598.6	435.4
Crystal size/mm	0.21 × 0.24 × 0.5	0.14 × 0.31 × 0.45
Space group	$P\bar{1}$	$I2/a$ (alternative $C2/c$ no. 15)
a/Å	8.309(1)	16.707(3)
b/Å	12.294(1)	8.838(1)
c/Å	13.308(3)	12.514(2)
α/°	96.22(1)	90
β/°	95.07(1)	106.85(1)
γ/°	101.34(1)	90
U/Å^3	1 316.5(4)	1 768.4(5)
F(000)	608	880
Z	2	4
D_c/g cm^{-3}	1.512	1.635
D_m/g cm^{-3}	1.55	1.60
μ(Mo-K_α)/cm^{-1}	7.7	12.5
Radiation	Mo-K_α	Mo-K_α
Monochromator	Graphite	Graphite
$\theta_{min.}$—$\theta_{max.}$/°	2—27	2—27
Standard reflections	3	3
T/°C	22	22
Independent reflections	5 729	1 953
Reflections with $I \geqslant 3\sigma(I)$	5 008	1 756
Variables (last cycle)	316	136
Final R, R'*	0.029, 0.041	0.023, 0.035
Final shift/error max.	0.02	0.04
Largest peak (e Å^{-3}) in the final difference map (outside Tc co-ordination sphere)	0.33	0.27
Weighting factor	$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$	$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
S = Error in an observation of unit weight	1.8	1.3

* $R = \Sigma|\Delta F_o|/\Sigma|F_o|$; $R' = (\Sigma w|\Delta F_o|^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

Table 2. Positional parameters (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for complex (**1**)

Atom	x	y	z	Atom	x	y	z
Tc	1 344.2(2)	1 198.6(1)	3 127.9(1)	C(11)	−1 950(3)	2 646(2)	3 966(2)
P	164.2(7)	2 670.3(4)	2 484.0(4)	C(12)	−2 926(4)	3 089(3)	4 615(3)
S(1)	2 375.2(8)	2 244.4(5)	4 705.0(5)	C(13)	−2 908(4)	4 206(3)	4 716(3)
S(2)	4 274.2(9)	1 628.6(6)	6 433.7(5)	C(14)	−1 889(4)	4 902(3)	4 191(3)
O	−710(2)	145(1)	2 405(1)	C(15)	−927(4)	4 453(2)	3 520(2)
N(1)	2 822(3)	1 309(2)	2 415(2)	C(16)	1 624(3)	3 808(2)	2 096(2)
N(2)	2 568(2)	114(2)	4 965(2)	C(17)	3 218(4)	4 116(3)	2 592(2)
N(3)	1 595(2)	−97(2)	4 011(1)	C(18)	4 292(4)	5 034(3)	2 345(3)
C(1)	4 632(4)	354(3)	6 858(2)	C(19)	3 802(5)	5 643(3)	1 608(3)
C(2)	2 986(3)	1 153(2)	5 300(2)	C(20)	2 259(5)	5 329(3)	1 102(2)
C(3)	1 001(3)	−1 147(2)	3 713(2)	C(21)	1 161(4)	4 414(2)	1 342(2)
C(4)	−40(4)	−1 601(2)	2 798(2)	C(22)	−1 376(3)	2 177(2)	1 388(2)
C(5)	−340(4)	−2 762(2)	2 517(3)	C(23)	−950(3)	1 578(3)	557(2)
C(6)	−1 367(5)	−3 272(2)	1 669(3)	C(24)	−2 097(5)	1 132(3)	−277(2)
C(7)	−2 148(4)	−2 637(2)	1 075(2)	C(25)	−3 673(5)	1 303(4)	−279(3)
C(8)	−1 906(3)	−1 498(2)	1 332(2)	C(26)	−4 121(4)	1 870(5)	550(3)
C(9)	−867(3)	−950(2)	2 191(2)	C(27)	−2 974(4)	2 330(3)	1 383(2)
C(10)	−963(3)	3 323(2)	3 403(2)				

Weights for the last cycle were applied according to the schemes given in Table 1 for each structure. All calculations were performed with the SDP system of programs[19] and PARST.[20]

Final positional parameters are given in Tables 2 and 3 for (**1**) and (**2**) respectively. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Results

Elemental analyses and i.r. spectra for the complexes are given in Table 4.

[TcNL(PPh$_3$)] *Complexes*.—The new nitrido–technetium(v) complexes with tridentate Schiff bases are formed quickly, in high yield, from CH_2Cl_2–EtOH solutions of $[TcNCl_4]^-$, in the presence of an excess of the ligand and phosphine, under slight heating. Using [TcNCl$_2$(PPh$_3$)$_2$] as starting material, a longer reaction time, in refluxing benzene, is required.

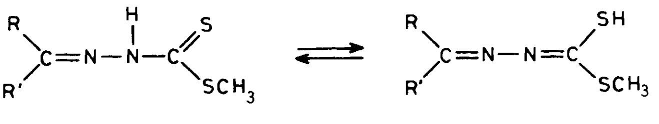
Table 3. Positional parameters ($\times 10^4$) with e.s.d.s in parentheses for complex (**2**)

Atom	x	y	z
Tc	2 500	1 090.5(3)	0
S(1)	3 711.4(3)	68.0(7)	1 238.0(4)
S(2)	3 982.1(4)	− 1 315.9(7)	3 437.9(5)
N(1)	2 500	2 916(3)	0
N(2)	2 033(1)	668(2)	1 412(1)
N(3)	2 537(1)	− 123(2)	2 351(1)
C(1)	3 285(1)	− 390(2)	2 312(2)
C(2)	3 361(2)	− 1 513(3)	4 384(2)
C(3)	1 327(1)	1 097(2)	1 557(2)
C(4)	1 087(1)	707(3)	2 572(2)
C(5)	723(1)	2 017(3)	706(2)

The complexes are soluble in CH_2Cl_2, $CHCl_3$, and acetone, slightly soluble in MeOH, EtOH, Et_2O, and benzene, and nearly insoluble in pentane and water. They are indefinitely stable in the solid state and in solution.

Magnetic susceptibility measurements performed in solution by the Evans' method[14] showed that [TcNL(PPh$_3$)] complexes are diamagnetic: this is consistent with a + 5 oxidation state for technetium with two paired *d* electrons.

The complexes exhibit the Tc≡N stretching vibration at lower frequencies (1 070—1 060 cm^{-1}) compared to the value of *ca.* 1 080 cm^{-1} found in five-co-ordinate $[TcNCl_4]^-$ and [TcNCl$_2$(PPh$_3$)$_2$] complexes.[9] No changes in the absorption band of PPh$_3$ were observed with respect to [TcNCl$_2$(PPh$_3$)$_2$], in which it occurs at 1 095 cm^{-1}.[13] The free ligands show the N–H bond vibration for the α-nitrogen atom of the hydrazinic group, in the range 3 200—3 100 cm^{-1}, but no ν(S–H) absorption, indicating that in the solid state they remain in the thione form. Probably, in solution an equilibrium exists between the thione and thiol forms as shown below.



The C=N bond vibration of the co-ordinated Schiff-base moiety is found at *ca.* 1 600 cm^{-1} for all the ligands, and is characteristic of chelation through the neutral β-nitrogen atom

Table 4. Elemental analyses and principal i.r. bands for technetium–nitrido complexes (calculated values in parentheses)

Complex	Analysis (%) C	H	N	S	Tc	I.r./cm^{-1} ν(Tc≡N)	ν(C=N)	ν(C–S)	ν(Tc–Cl)
[TcNL^1(PPh$_3$)]	53.9	3.9	7.0	10.5	15.7	1 060	1 600	1 005	
	(54.1)	(3.9)	(7.0)	(10.5)	(16.5)				
[TcNL^5(PPh$_3$)]	53.3	4.0	6.7	10.0	15.0	1 065	1 590	1 020	
	(53.4)	(4.0)	(6.7)	(10.2)	(15.7)				
[TcNL^3(PPh$_3$)]	53.5	4.0	6.6	10.1	14.9	1 065	1 590	1 010	
	(53.4)	(4.0)	(6.7)	(10.2)	(15.7)				
[TcNL^4(PPh$_3$)]	43.0	2.9	5.4	8.3	12.5	1 070	1 590	1 010	
	(42.8)	(2.8)	(5.5)	(8.4)	(13.1)				
[TcNL^2(PPh$_3$)]	48.7	3.2	6.2	9.4	14.1	1 070	1 600	1 015	
	(48.5)	(3.2)	(6.3)	(9.6)	(14.8)				
[TcNL^6(PPh$_3$)]	57.2	3.9	6.4	9.6	14.9	1 065	1 600	990	
	(57.3)	(3.9)	(6.5)	(9.8)	(15.2)				
[TcNL^7(PPh$_3$)]	61.4	4.1	4.5	5.2	16.0	1 060	1 605		
	(61.8)	(4.0)	(4.6)	(5.3)	(16.4)				
[TcNClL^9(PPh$_3$)]	51.6	4.1	6.5	9.7	14.6	1 080	1 570	1 020	300
	(51.7)	(4.0)	(6.5)	(9.8)	(15.2)				
[TcNClL^{10}(PPh$_3$)]	50.6	4.3	5.8	8.9	13.0	1 075	1 570	1 020	325
	(50.7)	(4.3)	(5.9)	(9.0)	(13.9)				
[TcNClL^{11}(PPh$_3$)]	47.6	3.4	6.5	15.2	15.1	1 070	1 580	1 015	330
	(47.9)	(3.5)	(6.7)	(15.3)	(15.8)				
[TcNClL^{12}(PPh$_3$)]	48.0	4.3	7.4	11.1	16.7	1 070	1 595	995	330
	(48.3)	(4.2)	(7.3)	(11.2)	(17.3)				
[TcN(L^9)$_2$]	40.4	3.8	11.6	21.5	15.9	1 075	1 580	1 020	
	(40.6)	(3.7)	(11.8)	(21.6)	(16.7)				
[TcN(L^{10})$_2$]	40.3	4.1	9.7	17.8	13.0	1 070	1 580	1 020	
	(40.5)	(4.2)	(9.8)	(18.0)	(13.9)				
[TcN(L^{11})$_2$]	31.0	2.4	12.8	35.4	17.7	1 070	1 570	1 015	
	(30.9)	(2.6)	(12.9)	(35.3)	(18.2)				
[TcN(L^{12})$_2$]	27.5	4.4	16.0	29.6	22.0	1 070	1 590	1 000	
	(27.6)	(4.1)	(16.1)	(29.4)	(22.7)				

and the charged phenolic oxygen atom.[16] The complexes do not show any ν(N–H) bands in the region 3 200—3 100 cm^{-1}, while ν(CS_2), occurring at *ca.* 1 060—1 030 cm^{-1} in the free ligand, shifts to lower frequencies (*ca.* 1 010 cm^{-1}). These observations suggest that the ligands co-ordinate to the technetium atom in the thiol form and behave as tridentate, di-anionic donors through the charged phenolic oxygen atom, the neutral β-nitrogen atom, and the charged thiol sulphur atom. Thus, the co-ordination environment around the central ion can be described as square pyramidal, the equatorial positions being occupied by the tridentate ligand and the phosphine group, and the apical position by the nitride ion.

$[TcNClL'(PPh_3)]$ *and* $[TcN(L')_2]$ *Complexes.*—The reaction of $[TcNCl_2(PPh_3)_2]$ with a stoicheiometric amount of the potentially bidentate Schiff bases leads to production of the monosubstituted $[TcNClL'(PPh_3)]$ complexes. These complexes are also obtained from $[TcNCl_4]^-$ in the presence of an excess of free PPh_3 in the reaction mixture. The same starting complexes can be used to obtain the disubstituted products $[TcN(L')_2]$ by adding excess of ligand to the reaction mixture. The compounds are stable both in the solid state and in solution. They are soluble in CH_2Cl_2, $CHCl_3$, and acetone, but nearly insoluble in all other common solvents.

As observed for the complexes with tridentate ligands, these products are diamagnetic in solution, indicating that the technetium ion is in the +5 oxidation state.

The i.r. spectra show the Tc≡N stretching frequency at *ca.* 1 070 cm^{-1} whereas the C=N bond vibration is found in the range 1 595—1 570 cm^{-1}. Significant bands between 1 020—990 cm^{-1} are assigned to the ν(CS_2) stretching vibration. The monosubstituted complexes show the characteristic band of the PPh_3 group at 1 090 cm^{-1}. No ν(N–H) absorptions are observed, suggesting that these ligands co-ordinate to the metal in the thiol form, as for the tridentate ligands discussed above, and therefore undergo the same thiol $\rightleftharpoons$ thione equilibrium in solution.

The ^1H n.m.r. spectra of the complexes $[TcNL^{12}(PPh_3)]$ and $[TcN(L^{12})_2]$ show a poorly resolved doublet at $\delta = 2.55$, which arises from the non-equivalence of the two methyl groups of the acetone moiety caused by the rigidity of the double bond of the $Me_2C=N$ group.

These observations suggest that the complexes possess a square-pyramidal geometry with an apical Tc≡N group and the bidentate ligand co-ordinated to the central ion, in the basal plane, through the neutral β-imine nitrogen atom and the charged sulphur atom both in mono- and di-substituted complexes.

Discussion

The behaviour of the tridentate and bidentate derivatives of *S*-methyl dithiocarbazate toward the Tc≡N group appears to be governed by two factors: (*i*) the oxidation state of the technetium ion and (*ii*) the presence of 'soft' donors on the ligands.

In all the complexes technetium is in the +5 oxidation state and no Tc^{VI} complexes were isolated. The reduction of the $[Tc^{VI}≡N]^{3+}$ core to the more stable $[Tc^{V}≡N]^{2+}$ core completely parallels the behaviour of the isoelectronic $[Tc^{V}=O]^{3+}$ core, which constitutes a similarly stable group. This fact is satisfactorily explained by observing that the technetium(v) ion, in the $[Tc^{V}≡N]^{2+}$ and $[Tc^{V}=O]^{3+}$ cores, possesses a d^2 closed-shell configuration, in which the two metal electrons occupy a non-bonding *xy* orbital.[21] This configuration is highly stable and generates the peculiar properties of such groups; in particular the weak bonding of the ligands in the plane normal to the Tc≡N or Tc=O bonds, favouring substitution reactions.[22] In the $[Tc^{VI}≡N]^{3+}$ core, technetium has a d^1 electronic configuration with a resulting unpaired electron. The pairing of this electron, with the consequent reduction of the metal centre, permits attainment of the stable $d_{xy}{}^2$ configuration.

Reactivity of $[TcNCl_4]^-$ and $[TcNCl_2(PPh_3)_2]$ towards tridentate, H_2L^7 and H_2L^8, and bidentate, 2-HOC_6H_4-CH=NPh Schiff bases has also been tested. The complex $[TcNL^7(PPh_3)]$ is formed rapidly, in high yield, both from $[TcNCl_4]^-$ and PPh_3, and $[TcNCl_2(PPh_3)_2]$. This compound shows completely analogous properties to those of the complexes discussed above, and the same square-pyramidal geometry can be attributed to it. With the ligands H_2L^8 and 2-HOC_6H_4CH=NPh, no products were obtained, and only the starting materials were recovered. This behaviour is largely in contrast with that shown by the $[TcO]^{3+}$ core, for which stable compounds are formed with tri- or bi-dentate Schiff bases having $[O^-,N,O^-]$, $[O^-,N,S^-]$, or $[O^-,N]$ as donor atoms.[17,23–25]

The $[TcN]^{2+}$ core strongly favours co-ordination with 'soft' donors like dithiocarbamate,[7] quinoline-8-thiolato,[6] dichalcogeno chelating ligands, pseudo-allyl anions $[S(OEt)NR]^-$ [26] and phosphines.[13] The $[TcO]^{3+}$ core, instead, forms stable complexes with both 'hard' and 'soft' ligands. This may partly be attributed to the strong *trans* influence of the Tc≡N multiple bond, which causes the square-pyramidal geometry to be highly preferred and limits the possible co-ordination geometries and modes of bonding. In fact, while technetium(v)–oxo complexes range between the two limits of nearly perfect octahedral dioxo complexes and square-pyramidal oxo complexes, passing through the formation of distorted pseudo-octahedral species having a weakly bound ligand *trans* to the Tc=O moiety,[27,28] only one example of a distorted pseudo-octahedral complex containing the Tc≡N group has been reported.[8] It would be of interest to find ligands able to modify the strong metal-to-nitrido π interaction in order to obtain new co-ordinative modes in technetium–nitrido chemistry.

X-Ray Structure of $[TcNL^1(PPh_3)]$ (**1**).—An ORTEP[29] view of the molecule is shown in Figure 1. Selected bond distances and angles are reported in Table 5.

The crystals consist of monomeric units packed together with

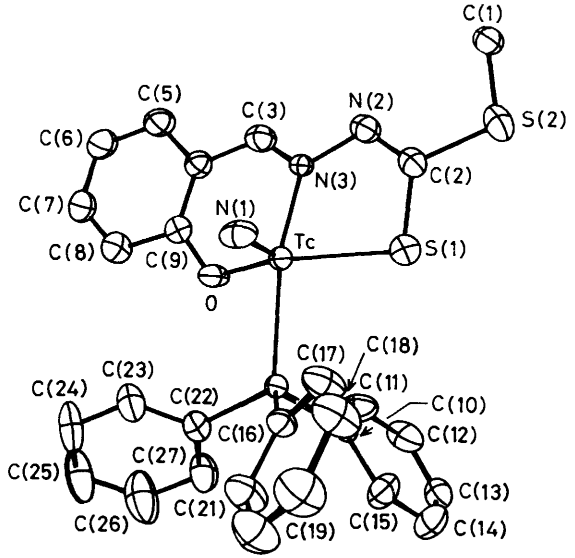


Figure 1. An ORTEP view of complex (**1**) showing the thermal ellipsoids at 40% probability

Table 5. Selected bond distances (Å) and angles (°), with e.s.d.s in parentheses, for complex (**1**)

Tc–P	2.4195(6)	P–C(16)	1.815(3)	O–C(9)	1.324(3)	C(4)–C(9)	1.423(4)
Tc–S(1)	2.3358(8)	P–C(22)	1.818(2)	N(2)–N(3)	1.413(3)	C(5)–C(6)	1.364(5)
Tc–O	2.0215(14)	S(1)–C(2)	1.764(3)	N(2)–C(2)	1.275(3)	C(6)–C(7)	1.378(5)
Tc–N(1)	1.611(3)	S(2)–C(1)	1.791(4)	N(3)–C(3)	1.293(3)	C(7)–C(8)	1.375(3)
Tc–N(3)	2.111(2)	S(2)–C(2)	1.744(3)	C(3)–C(4)	1.421(3)	C(8)–C(9)	1.391(3)
P–C(10)	1.817(3)			C(4)–C(5)	1.403(3)		
P–Tc–S(1)	94.20(3)	Tc–P–C(10)	112.5(1)	N(3)–N(2)–C(2)	112.8(2)	C(3)–C(4)–C(9)	123.4(2)
P–Tc–C	85.70(5)	Tc–P–C(16)	105.7(1)	Tc–N(3)–N(2)	121.7(2)	C(5)–C(4)–C(9)	118.6(3)
P–Tc–N(1)	95.10(10)	Tc–P–C(22)	113.5(1)	Tc–N(3)–C(3)	124.4(2)	C(4)–C(5)–C(6)	121.7(3)
P–Tc–N(3)	158.01(6)	C(10)–P–C(16)	105.7(1)	N(2)–N(3)–C(3)	113.7(2)	C(5)–C(6)–C(7)	119.5(3)
S(1)–Tc–O	141.18(6)	C(10)–P–C(22)	103.3(1)	S(1)–C(2)–S(2)	113.0(1)	C(6)–C(7)–C(8)	120.6(3)
S(1)–Tc–N(1)	107.85(10)	C(16)–P–C(22)	105.2(1)	S(1)–C(2)–N(2)	125.6(2)	C(7)–C(8)–C(9)	121.5(2)
S(1)–Tc–N(3)	79.67(5)	Tc–S(1)–C(2)	97.1(1)	S(2)–C(2)–N(2)	121.4(2)	O(1)–C(9)–C(4)	123.5(2)
O–Tc–N(1)	110.83(10)	C(1)–S(2)–C(2)	102.5(1)	N(3)–C(3)–C(4)	126.0(2)	O(1)–C(9)–C(8)	118.4(2)
O–Tc–N(3)	86.11(6)	Tc–O–C(9)	124.7(2)	C(3)–C(4)–C(5)	117.9(2)	C(4)–C(9)–C(8)	118.1(2)
N(1)–Tc–N(3)	106.89(11)						

Table 6. Distances (d/Å) from weighted least-squares planes through groups of atoms within complex (**1**); e.s.d.s are in parentheses

Plane 1	d	Plane 2	d	Plane 3	d
Tc	0.017(1)	Tc	0.032(1)	S(1)	−0.049(1)
S(1)	−0.033(1)	O	−0.263(2)	P	0.040(1)
N(2)	0.088(2)	N(3)	−0.206(2)	O	−0.207(2)
N(3)	−0.177(2)	C(3)	0.027(3)	N(3)	0.226(2)
C(2)	0.194(3)	C(4)	0.355(3)	Tc*	0.569(1)
		C(9)	0.183(3)		

* Not included in the least-squares plane calculation.

Table 7. Bond distances (Å) and angles (°), with e.s.d.s in parentheses, for complex (**2**)

Tc–S(1)	2.3442(6)	N(2)–N(3)	1.416(2)
Tc–N(1)	1.613(3)	N(2)–C(3)	1.301(3)
Tc–N(2)	2.161(2)	N(3)–C(1)	1.286(2)
S(1)–C(1)	1.742(3)	C(3)–C(4)	1.479(4)
S(2)–C(1)	1.749(2)	C(3)–C(5)	1.485(3)
S(2)–C(2)	1.795(3)		
S(1)–Tc–N(1)	112.67(3)	N(3)–N(2)–C(3)	111.9(2)
S(1)–Tc–N(2)	80.80(4)	N(2)–N(3)–C(1)	114.2(2)
S(1)–Tc–S(1′)	134.64(3)	S(1)–C(1)–S(2)	113.9(1)
S(1)–Tc–N(2′)	91.49(3)	S(1)–C(1)–N(3)	127.3(2)
N(1)–Tc–N(2)	99.95(7)	S(2)–C(1)–N(3)	118.8(2)
N(2)–Tc–N(2′)	160.1(1)	N(2)–C(3)–C(4)	122.3(2)
Tc–S(1)–C(1)	97.6(1)	N(2)–C(3)–C(5)	121.1(2)
C(1)–S(2)–C(2)	101.5(1)	C(4)–C(3)–C(5)	116.6(2)
Tc–N(2)–N(3)	119.7(1)		
Tc–N(2)–C(3)	128.4(1)		

no contacts significantly shorter than the sum of the van der Waals radii.

The co-ordination around the Tc atom is distorted square pyramidal with the nitrido nitrogen atom at the apical position; technetium is displaced by 0.569(1) Å, toward N(1), from the plane defined by the atoms S(1), P, N(3), O. The Tc^V≡N bond length of 1.611(3) Å falls in the range of similar distances found in other nitrido complexes of Tc^V {1.604(6) Å in [TcN(S$_2$CNEt$_2$)$_2$];[7] 1.623(4) Å in [TcN(C$_9$H$_6$NS)$_2$];[6] 1.629(4) Å in [TcN(NCS)$_2$(CH$_3$CN)(PPh$_3$)$_2$][8]}. The tridentate ligand occupies the three co-ordination sites of the base, the fourth position being occupied by a PPh$_3$ group *trans* to N(3).

Bond lengths of 2.3358(8) in this complex and of 2.3559(7) in [TcN(C$_9$H$_6$NS)$_2$][6] between Tc^V and S$^-$ are significantly shorter than Tc^V–S bond distances [av. 2.401(2) Å] found in a nitrido complex where S has a formal charge of $-\frac{1}{2}$.[7] This can be interpreted in terms of decreasing ionic character of the bond between Tc^V and the sulphur ion: in fact, Tc^V is a 'hard' acid which can form stronger and shorter bonds with the 'hard' base R–S$^-$ than with the 'softer' one R–S$^{\frac{1}{2}-}$. This simple acid–base model seems to be supported by comparison of the distances Tc–O$^-$, 2.022(1) Å, and Tc–N, 2.111(2) Å.

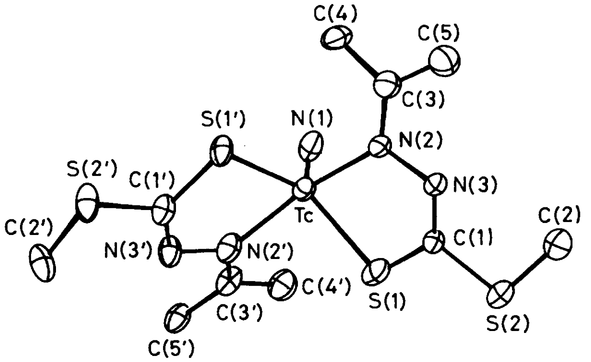


Figure 2. An ORTEP view of complex (**2**) showing the thermal ellipsoids at 40% probability

All the bond distances in the tridentate ligand are normal. The rings formed by chelation are not planar and the displacements of the atoms from least-squares planes are given in Table 6.

X-Ray Structure of [TcN(L^{12})$_2$] (**2**).—An ORTEP[29] view of the molecule is shown in Figure 2. Bond distances and angles are reported in Table 7. The molecule has C_2 symmetry and the Tc–N(1) bond lies on a two-fold crystallographic rotation axis.

The Tc–N(1) distance of 1.613(3) Å indicates the presence of a triple bond and compares well with the values found in other technetium(V)–nitrido complexes. The Tc–S(1) distance [2.3442(6) Å] is affected by the fact that the negative charge of the ligand is localized on S(1), as discussed for (**1**) and as shown by the C(1)–S(1) distance [1.742(3) Å], which agrees well with the value predicted for a single C_{sp^2}–S bond.[30]

The co-ordination around technetium is distorted square pyramidal with the nitrido atom in the apical position. The technetium atom is 0.8443(3) Å above the mean plane S(1), S(1′), N(2), N(2′) towards the N(1) atom. The maximum distortion from square-pyramidal symmetry is caused by the repulsion of the Tc≡N multiple bond being greater towards the

S(1) and S(1′) negatively charged atoms than towards the neutral N(2) and N(2′) ones [N(1)–Tc–S(1) = 112.67(3); N(1)–Tc–N(2) = 99.95(7)°]. The five membered ring Tc, S(1), C(1), N(2), N(3) is not planar, with mean deviations of the atoms in the plane of 0.038(2) Å and maximum deviation of 0.084(2) Å of the N(2) atom. Other structural details are as expected and need no comment.

Acknowledgements

We thank Dr. Patrizia Garuti for helpful discussions and Mr. M. Fratta for elemental analyses.

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Received 21*st July* 1987; *Paper* 7/1326