Technetium(V) and Rhenium(V) Complexes with Schiff-base Ligands containing the ONNNO Donor Atom Set. Crystal Structure of [*N,N'*-3-Azapentane-1,5-diylbis(salicylideneiminato)(3−)-*O,O',N,N',N''*]-oxotechnetium(V)†

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The reactions of quinquedentate Schiff-base ligands derived from salicylaldehyde and diethylenetriamine (H_3L^1) or 3,3'-diamino-*N*-methyldipropylamine (H_2L^2) with $[MO(eg)_2]^-$ (M = Tc or Re; H_2eg = ethylene glycol) have been investigated. The complexes $[MOL^1]$ and $[MOL^2]^+$ were produced and characterized by the usual physicochemical measurements. In particular the crystal structure of $[TcOL^1]$ was determined by single-crystal *X*-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, with $a = 9.459(8)$, $b = 9.437(7)$, $c = 21.768(12)$ Å, $\beta = 99.08(5)°$, and $Z = 4$. *X*-Ray diffraction provided 2 097 observed reflections (up to $2\theta = 50°$) and the structure has been refined by full-matrix least-squares methods to $R = 0.053$. The compound consists of discrete $TcOL^1$ molecules with one methanol molecule of crystallization also present in the crystal lattice. One of the oxygen atoms of the quinquedentate ligand is located *trans* to the technetium–oxo bond, while the remaining four donor atoms occupy the equatorial sites around the Tc atom which resides in a highly distorted octahedral co-ordination environment. The distance between the deprotonated N atom and Tc [1.894(8) Å] is significantly shorter than the average for Tc–N single bond lengths.

In the last few years one of the areas of technetium chemistry investigated has been concerned with Schiff-base type ligands. The flexibility and ductility of these ligands in varying the chemical properties, geometry, co-ordinating sites, and the lateral chains, make possible the synthesis of several types of technetium complexes with different configurations, in which technetium is in different oxidation states.[1]

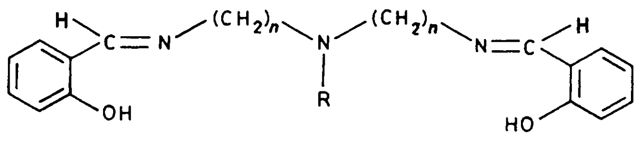
To date the investigations reported in the literature[1] present Schiff-base ligands co-ordinated around technetium with no more than four potential co-ordinating atoms and, with the exception of bidentate ligands,[2,3] the ligand occupying co-ordination sites in the equatorial positions normal to the $Tc{=}O^{3+}$ group.

The potentially quinquedentate ligands H_3L^1 and H_2L^2 behave in different ways, using $[MO(eg)_2]^-$ as the starting material (M = Tc or Re; H_2eg = ethylene glycol). In fact, while the H_3L^1 ligand produces the $[MOL^1]$ compounds, H_2L^2 leads to the $[MOL^2]^+$ compounds.

The complexes were characterized by means of elemental analysis, i.r. and u.v.–visible spectra, magnetic susceptibility, and conductivity measurements, and for $[TcOL^1]$ also by *X*-ray structure analysis.

Experimental

Materials.—Technetium, as $[NH_4][TcO_4]$ in 0.1 mol dm^{-3} ammonia solution, was obtained from the Radiochemical Centre, Amersham; $[NBu_4][MOCl_4]$ and $[NBu_4][MO(eg)_2]$ (M = Tc or Re; H_2eg = ethylene glycol) were prepared as reported in the literature.[4,5]



H_3L^1 ; R = H, *n* = 2

H_2L^2 ; R = Me, *n* = 3

Technetium-99 is a low energy (0.292 MeV) β-particle emitter with a half-life of 2.12×10^5 years. When handled in milligram quantities, ^{99}Tc does not present a serious health 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 of reagent grade.

The ligands were prepared by mixing salicylaldehyde and diethylenetriamine, or 3,3'-diamino-*N*-methyldipropylamine, in ethanol following the procedure detailed below for H_3L^1. To a stirred solution of diethylenetriamine (788 mg, 7.6 mmol) in ethanol (10 cm^3) a solution of salicylaldehyde (2 g, 15.2 mmol) in ethanol (10 cm^3) was added at room temperature; the solution turned yellow immediately and, after 1 h a yellow oil was collected by evaporation of the reaction solvent. The yellow oil can be used as the ligand without further purification; it is soluble in all common organic solvents. To confirm the H_3L^1 formulation of the yellow oil, and to obtain the chloride salt of the ligand, a 1 mol dm^{-3} ethanolic solution of hydrochloric acid was added dropwise to an ethanolic solution of the yellow oil until pH 5 was attained. Pale yellow crystals appeared and were collected by filtration, washed with a few drops of ethanol and with a few cm^3 of diethyl ether (yield 88%). The chloride salt of the ligand can also be used as a reagent. The adduct $H_3L^1{\cdot}HCl$ was soluble in water, slightly soluble in MeCN and

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

Non-S.I. unit employed: eV = 1.6×10^{-19} J.

alcohols, and insoluble in CH_2Cl_2, Me_2CO, and Et_2O (Found: C, 62.3; H, 6.1; Cl, 10.2; N, 12.0. Calc. for $C_{18}H_{22}ClN_3O_2$: C, 62.1; H, 6.4; Cl, 10.2, N, 12.1%). I.r. spectrum: strong sharp absorptions at 1 637 ($\nu_{C=N}$), 1 487, 1 281 (ν_{C-O}), and 752 cm^{-1}; u.v.–visible spectrum (CH_2Cl_2): absorptions at 400, 315, 255, and 225 nm; ^1H n.m.r. ($CDCl_3$, relative to $SiMe_4$): δ 8.38 (s) (imine), 7.46—6.81 (aromatic), 3.75 (t) and 3.03 (t) p.p.m. (methylene groups).

The ligand H_2L^2 was obtained as a yellow oil, soluble in common organic solvents, and was used without further purification. The chloride salt was not obtained. Characterization of the oil was performed. I.r. spectrum: strong absorptions at 1 635 ($\nu_{C=N}$), 1 282 (ν_{C-O}), and 760 cm^{-1}; u.v.–visible spectrum: same pattern as for H_3L^1; ^1H n.m.r. ($CDCl_3$, relative to $SiMe_4$): δ 8.32 (s) (imine), 7.37—6.66 (aromatic), 2.29 (s) (Me), 3.67 (t), 2.48 (t), and 1.88 (m) p.p.m. (methylene groups).

Apparatus.—I.r. spectra, obtained as KBr pellets or Nujol mulls between CsI pellets, were recorded in the range 4 000—250 cm^{-1} on a Perkin-Elmer PE 580B spectrometer. ^1H N.m.r. spectra of the ligands were obtained on a Varian FT80 instrument using $SiMe_4$ as internal reference. Magnetic susceptibility measurements were performed in the solid state using the Faraday method with an assembled Oxford Instrument (DN 700S with NI77 magnet and Cahn 200 microbalance). All the complexes were diamagnetic in character, in agreement with other Tc^V and Re^V complexes containing the $M{=}O^{3+}$ moiety. Conductivity measurements were made in acetonitrile at 25 °C using a Metrohm Herison conductometer, model E518. U.v.–visible spectra were recorded in different solvents using a Cary 17D spectrophotometer.

Syntheses.—$[TcOL^1]$. The salt $[NBu_4][TcOCl_4]$ (34 mg, 0.068 mmol) was dissolved in methanol (5 cm^3). Ethylene glycol (0.5 cm^3) was added to the solution with stirring at room temperature, followed by dropwise addition of a 0.75 mol dm^{-3} methanolic solution of sodium acetate (0.6 cm^3). The initial green colour turned to turquoise and then to violet producing $[NBu_4][TcO(eg)_2]$ *in situ*. The adduct $H_3L^1{\cdot}HCl$ (24 mg, 0.068 mmol) in methanol (10 cm^3) was added to this mixture and the solution immediately became blood-red. After 10 min red crystals precipitated from the reaction solution. These were filtered off, and washed with a few drops of methanol and diethyl ether. The crystals were suitable for *X*-ray analysis without further recrystallization. The product was slightly soluble in CH_2Cl_2, $CHCl_3$, MeCN, diethyl ether, and alcohols.

$[ReOL^1]$. The complex was synthesized by the same procedure used for the $[TcOL^1]$ compound, above.

$[TcOL^2][ClO_4]$. $[NBu_4][TcO(eg)_2]$ was produced *in situ* as described above. A stoicheiometric amount of H_2L^2 oil, previously dissolved in methanol (5 cm^3), was added with stirring at room temperature. The solution became red-brown and no solid appeared within 3 h. An excess of $NaClO_4$ in MeOH was added and a red powder immediately precipitated. This was filtered off, and washed several times with MeOH and Et_2O. The product was slightly soluble in MeCN and CH_2Cl_2, and insoluble in other organic solvents.

$[ReOL^2][BPh_4]$. The complex was prepared following the procedure detailed above for $[TcOL^2][ClO_4]$ and using $NaBPh_4$ as the precipitating salt.

Table 1. Crystal data, data collection, and refinement for $[TcOL^1]{\cdot}MeOH$

Formula	$C_{18}H_{18}N_3O_3Tc{\cdot}MeOH$
M	455.3
Habit	Monoclinic
Crystal dimensions/mm	0.15 × 0.15 × 0.20
Systematic absences	$h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$
Space group	$P2_1/c$ (no. 14)
Unit-cell constants (at 20 °C)	a = 9.459(8), b = 9.437(7), c = 21.768(12) Å; β = 99.08(5)°
U, Z, $F(000)$	1 918.8(2.2) Å^3, 4, 928
μ/cm^{-1}	7.6
D_c,D_m/g cm^{-3}	1.576, 1.56
Diffractometer, scan method	Philips PW 1100, θ—2θ
Scan speed/° min^{-1}, scan width/°	2.40, 1.20
Background time	7 s at each end
2θ limit/°	$3 \leqslant 2\theta \leqslant 50$
No. of data	3 362
No. of 'observed' ($F_o > 3\sigma F_o$)	2 097
Weighting scheme	$w = 1$
Anisotropy	Heteroatoms + carbon atoms nearest to the 'inner core'
No. of parameters	194
$R = (\Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/(\Sigma \lvert F_o\rvert)$	0.053

Table 2. Final fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Tc	0.043 3(1)	0.195 8(1)	0.124 4(0)
O(1)	−0.112 4(6)	0.336 8(6)	0.077 9(3)
O(2)	−0.155 3(6)	0.090 5(6)	0.126 0(3)
O(3)	0.119 3(7)	0.049 3(7)	0.159 5(3)
N(1)	0.080 0(8)	0.170 5(8)	0.032 3(4)
N(2)	0.196 7(8)	0.322 8(9)	0.120 7(4)
N(3)	0.011 7(8)	0.325 3(8)	0.196 3(3)
C(1)	−0.202 6(9)	0.297 2(10)	0.027 2(4)
C(2)	−0.346 7(9)	0.343 3(10)	0.020 3(4)
C(3)	−0.441 5(10)	0.316 0(11)	−0.035 0(4)
C(4)	−0.391 2(11)	0.242 2(11)	−0.084 5(5)
C(5)	−0.251 7(10)	0.196 9(12)	−0.078 6(4)
C(6)	−0.157 7(10)	0.218 6(10)	−0.022 3(4)
C(7)	−0.009 4(10)	0.182 1(11)	−0.019 7(4)
C(8)	0.236 8(10)	0.184 6(14)	0.031 8(5)
C(9)	0.272 0(11)	0.327 1(13)	0.066 5(5)
C(10)	0.208 8(12)	0.448 0(12)	0.161 5(6)
C(11)	0.137 4(11)	0.415 9(11)	0.218 7(5)
C(12)	−0.104 6(10)	0.330 6(10)	0.221 1(4)
C(13)	−0.230 9(10)	0.250 2(10)	0.202 8(4)
C(14)	−0.347 0(12)	0.284 8(12)	0.236 0(5)
C(15)	−0.477 4(13)	0.215 8(14)	0.223 5(5)
C(16)	−0.499 1(12)	0.109 6(13)	0.178 6(5)
C(17)	−0.388 4(11)	0.071 1(11)	0.145 5(5)
C(18)	−0.252 1(9)	0.137 6(10)	0.157 0(4)
O(4)	−0.159 4(11)	0.613 9(12)	0.100 0(5)
C(19)	−0.195 3(17)	0.661 3(19)	0.153 0(8)

Solution and Refinement of the Structure of $[TcOL^1]$.—Red crystals of $[TcOL^1]$ suitable for *X*-ray analysis were crystallized from methanol by slow evaporation. Crystal data and other details of the data collection and structure refinement are given in Table 1. Corrections for Lorentz and polarization effects and for absorption, using an empirical method based on ψ scans[6] of three reflections near $\chi \approx 90°$, were made. The structure was solved by standard heavy-atom methods. Refinement using full-matrix least squares and minimizing the function $w\Delta F^2$ was terminated when the maximum and average shift to error ratios were <0.18 (in MeOH) and <0.04 in positional parameters. In the final cycle a weighting scheme based on counter statistics did not improve the model and to ensure a good observation:parameters ratio, the carbon atoms farthest from the inner core were treated isotropically. No feature corresponding to atoms larger than hydrogen was found in the final difference map. The scattering factors and the real and imaginary components of anomalous dispersion for Tc were

Table 3. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

Tc–O(1)	2.120(6)	C(8)–C(9)	1.55(2)	Tc–N(1)	2.101(8)	C(11)–C(10)	1.54(2)
Tc–O(2)	2.130(6)	C(9)–N(2)	1.47(1)	Tc–N(2)	1.894(8)	C(10)–N(2)	1.48(1)
Tc–O(3)	1.685(6)	C(1)–C(2)	1.42(1)	Tc–N(3)	2.044(8)	C(13)–C(14)	1.44(2)
O(1)–C(1)	1.34(1)	C(2)–C(3)	1.41(1)	O(2)–C(18)	1.30(1)	C(14)–C(15)	1.38(2)
C(1)–C(6)	1.43(1)	C(3)–C(4)	1.43(2)	C(13)–C(18)	1.45(1)	C(15)–C(16)	1.39(2)
C(6)–C(7)	1.44(1)	C(4)–C(5)	1.37(1)	C(12)–C(13)	1.42(1)	C(16)–C(17)	1.41(2)
C(7)–N(1)	1.31(1)	C(5)–C(6)	1.41(1)	C(12)–N(3)	1.30(1)	C(17)–C(18)	1.42(1)
N(1)–C(8)	1.49(1)	O(4)–C(19)	1.33(3)	N(3)–C(11)	1.48(1)		
O(1)–Tc–O(2)	75.7(2)	C(6)–C(7)–N(1)	123.3(9)	O(2)–Tc–N(3)	91.7(3)	C(18)–C(13)–C(12)	127.2(9)
O(1)–Tc–O(3)	161.2(3)	Tc–N(1)–C(7)	129.5(7)	O(3)–Tc–N(1)	102.5(3)	C(13)–C(12)–N(3)	126.3(9)
O(1)–Tc–N(1)	79.8(3)	Tc–N(1)–C(8)	108.1(6)	O(3)–Tc–N(2)	105.3(4)	Tc–N(3)–C(12)	125.2(7)
O(1)–Tc–N(2)	93.5(3)	C(7)–N(1)–C(8)	119.7(8)	O(3)–Tc–N(3)	104.3(3)	Tc–N(3)–C(11)	113.0(6)
O(1)–Tc–N(3)	79.4(3)	N(1)–C(8)–C(9)	102.2(8)	N(1)–Tc–N(2)	77.8(3)	C(12)–N(3)–C(11)	121.8(8)
O(2)–Tc–O(3)	85.7(3)	C(8)–C(9)–N(2)	105.8(9)	N(1)–Tc–N(3)	149.8(3)	N(3)–C(11)–C(10)	106.6(9)
O(2)–Tc–N(1)	104.0(3)	C(9)–N(2)–Tc	121.4(7)	N(2)–Tc–N(3)	81.9(3)	C(11)–C(10)–N(2)	108.2(9)
Tc–O(1)–C(1)	121.5(5)	C(9)–N(2)–C(10)	117.1(9)	Tc–O(2)–C(18)	123.1(6)	C(10)–N(2)–Tc	118.3(7)
O(1)–C(1)–C(6)	122.8(8)	O(2)–Tc–N(2)	168.4(3)	O(2)–C(18)–C(13)	125.1(8)	C_{Ph}–C_{Ph}–C_{Ph}	mean 120.0(9)
C(1)–C(6)–C(7)	120.0(8)						

Table 4. General properties, elemental analysis, principal u.v.–visible and i.r. spectral parameters of the complexes

			Analysis[a]/%					$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})				I.r./cm^{-1}		
Compound	Yield/%	Colour	C	H	N	Cl	Tc					ν(M=O)	ν(C=N)	ν(C–O)
[TcOL^1]	42	Deep red	50.9	4.4	10.1		23.0	545[b]	415	310	270	888	1 623	1 297
			(51.1)	(4.3)	(9.9)		(23.4)	(400)	(2 000)	(3 600)	(4 000)		1 608	
[TcOL^2][ClO$_4$]	50	Orange-red	45.0	4.7	7.0	6.0	17.1	440[c]	310	250	220	935	1 628	1 303
			(44.6)	(4.5)	(7.4)	(6.3)	(17.5)	(8 500)	(20 700)	(46 200)	(94 300)		1 603	
[ReOL^1]	32	Yellow-mustard	42.3	3.6	8.2			465[b]	405	295	260	915	1 621	1 292
			(42.7)	(3.7)	(8.2)			(2 300)	(5 100)	(15 800)	(18 600)		1 608	
[ReOL^2][BPh$_4$]	45		61.7	5.7	5.1			445[d]	315	250	225	957	1 632	1 281
		Olive-green	(61.8)	(5.4)	(4.9)			(900)	(21 300)	(27 200)	(79 800)		1 604	

[a] Calculated values are given in parentheses. [b] In dimethylformamide. [c] In MeCN. [d] In CH_2Cl_2.

taken from ref. 7. Final atomic fractional parameters are given in Table 2. Interatomic distances and angles are presented in Table 3. The program package used was SHELX 76.[8]

Results and Discussion

The two ligands used in the reaction with $[MO(eg)_2]^-$ (M = Tc or Re) are H_3L^1 and H_2L^2, as shown. They are potentially quinquedentate ligands containing the ONNNO donor atom set in which an amine group is located at the middle of the chain joining the two lateral imine groups. These ligands can be compared to the quadridentate (ONNO) Schiff-base ligands derived from salicylaldehyde and diamines. The behaviour of the quadridentate Schiff bases has been thoroughly investigated[9–13] and the reaction mechanism proposed for the formation of [MO(ONNO)X] (M = Tc or Re; X = Cl, Br, OH_2, or –O– bridge) suggests, as a first step, reaction of the two imine groups in the plane normal to the Tc=O direction and, as a consequence, co-ordination of the two phenolic groups as phenolates in the same plane.[12] The reactions already reported[9–11] have concerned ligands with a maximum of four $-CH_2-$ groups in the central chain[10] and have adopted $[MOCl_4]^-$ salts as the starting compounds. The quinquedentate ligands reported here present two main differences compared to the compounds already known: five atom centres in the central chain joining the two imino groups, and the labile $[MO(eg)_2]$ intermediate[14] produced *in situ* by means of a ligand exchange reaction from $[MOCl_4]^-$.

The elemental analyses of the complexes and their general physicochemical properties are reported in Table 4. The complexes synthesized with the H_3L^1 ligand were non-conducting in MeCN and diamagnetic in the solid state. I.r. spectra show ν(M=O) at a low frequency with respect to other oxo-complexes. These results attest to neutral compounds with the metal in the 5+ oxidation state, and the presence of the $M{=}O^{3+}$ core. The elemental analyses support the presence of one ligand per metal centre. I.r. spectra exhibit two stretching vibrations in the range of ν(C=N) characteristic of an imine nitrogen co-ordinated to the central metal. This double stretch, shown also by the already known $[TcOClL_2]$[2] and [TcOL′L][15] complexes (L = bidentate Schiff base and L′ = tridentate Schiff base), is in agreement with the existence of two imine nitrogen–metal bonds in different electronic environments. ^1H N.m.r. spectra were not recorded owing to the low solubility of the complexes.

The *X*-ray structure of [TcOL^1] was also determined and Figure 1 illustrates the geometry and atom-numbering scheme used. The structure contains discrete molecules, without significant intermolecular interactions, and one methanol molecule of crystallization is also present in the crystal lattice. One of the oxygen atoms [O(1)] of the quinquedentate ligand is located *trans* to the technetium–oxo ligand, while the remaining four donor atoms, N_3O, occupy equatorial sites around the Tc atom, which resides in a highly distorted octahedral co-ordination environment. Distortions from an ideal Tc-centred octahedron result in (*i*) the Tc atom lying out of the mean equatorial plane by 0.30 Å towards the oxo ligand; (*ii*) a non-linear O(1)–Tc=O axis of 161.2(3)° accomplished by O(2)–Tc–N(2) and N(1)–Tc–N(3) angles of 168.4(3) and 149.8(3)°, respectively;

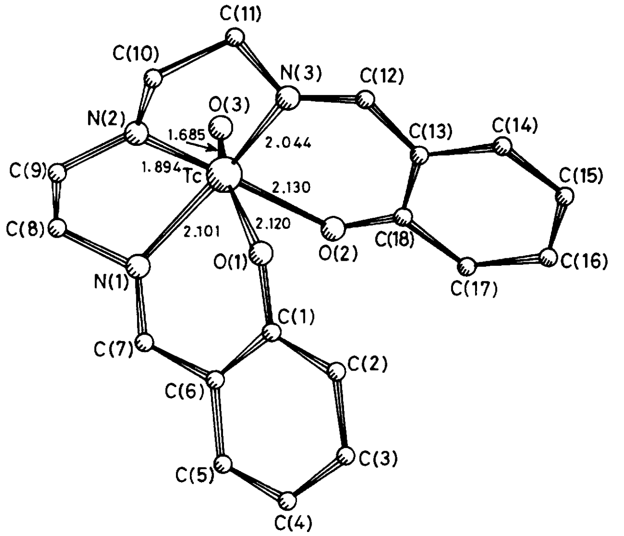

Figure 1. A perspective view of the [TcOL^1] complex showing the atom labelling. The MeOH molecule is omitted for clarity

Table 5. Comparison of Tc–N bond lengths (Å) in oxotechnetium(v) complexes, with co-ordination number (c.n.) five or six

Compound	Tc–N	Ref.
c.n. = 5		
[TcOCl(opsal)]^a	2.06	15
[TcO(NHC$_6$H$_4$S)$_2$]	2.08	*b*
[TcOL^3]^c	1.91,2.09	16
meso-[TcOL^4]^d	1.91,2.08	17
DL-[TcOL^5]^e	1.91,2.07	17
meso-[TcOL^5]	1.91,2.07	17
[TcOL^6]^f	1.91,2.07	17
c.n. = 6		
[TcOCl$_2${HB(pz)$_3$}]^g	2.09,2.26	*h*
cis-[TcOCl(2Me-quin)$_2$]^i	2.18,2.21	3
[TcO(C$_5$H$_9$NO$_2$S)(C$_5$H$_{10}$NO$_2$S)]	2.19	*j*
[TcOCl(salen)]^k	2.05	*j*
[TcO(acen)(H$_2$O)]$^{+\,l}$	2.00	9
[TcOCl(psal)$_2$]^m	2.12,2.19	2
[{TcO(salpd)}$_2$O]^n	2.12	10
[TcOCl(salpd)]	2.12	10
[TcO(opsal)(quin)]^o	2.06,2.19	19
[TcOBr$_2$(OEt)(npy)$_2$]^p	2.14	*q*
[TcOL^1]	1.89,2.04,2.10	This work

[a] opsal = *N*-(2-Oxidophenyl)salicylideneiminate(2−). [b] G. Bandoli and T. I. Gerber, *Inorg. Chim. Acta*, 1987, **126**, 205. [c] H$_3$L^3 = 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime. [d] H$_3$L^4 = 3,9-dimethyl-4,8-diazaundecane-2,10-dione dioxime. [e] H$_3$L^5 = 3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime. [f] H$_3$L^6 = 3,6,9-trimethyl-4,8-diazaundecane-2,10-dione dioxime. [g] HB(pz)$_3$ = Hydrotris(1-pyrazolyl)borate(1−). [h] G. W. Estes, R. C. Elder, and E. Deutsch, *J. Am. Chem. Soc.*, 1979, **101**, 4581. [i] 2Me-quin = 2-Methylquinolin-8-olate(1−). [j] K. J. Franklin, H. E. Howard-Lock, and C. J. Line-Lock, *Inorg. Chem.*, 1982, **21**, 1941. [k] salen = *N,N′*-Ethylenebis(salicylideneiminate)(2−). [l] acen = Ethylenebis(acetylacetonate)(2−). [m] psal = Phenylsalicylideneiminate(1−). [n] salpd = *N,N′*-Propane-1,3-diylbis(salicylideneiminate)(2−). [o] quin = Quinolin-8-olate(1−). [p] npy = 4-nitropyridine. [q] P. H. Fackler, M. E. Kastner, and M. J. Clarke, *Inorg. Chem.*, 1984, **23**, 3968.

(*iii*) significant deviations (up to 0.16 Å) of the N$_3$O atoms defining the 'equatorial' plane; (*iv*) 'bite' angles ranging from 77.8 to 91.7°; and (*v*) a short Tc–N(2) distance of 1.894(8) Å.

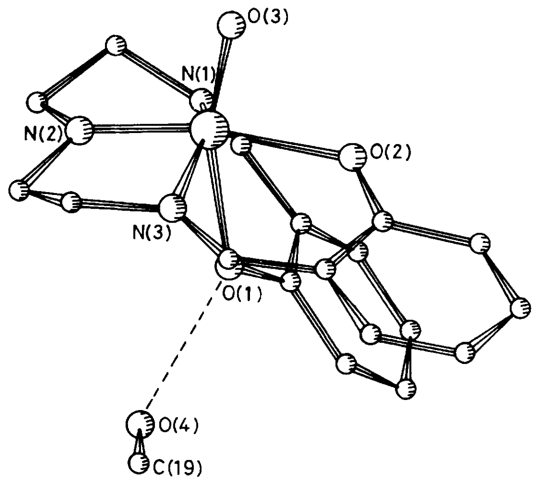

Figure 2. View along the *c* axis showing the O(1) ··· OMe contact

A comparison of the Tc–N bond lengths in oxotechnetium(v) complexes, with co-ordination numbers (c.n.) of 5 and 6, is shown in Table 5. It can be seen that the reported Tc–N distances range from 1.89 {in the [TcOL^1] complex} to 2.26 Å (in [TcOCl$_2${HB(pz)$_3$}], a compound with a considerable oxo-induced structural *trans* effect). Consequently, the observed distance between the deprotonated N(2) atom and Tc is diagnostic of some double bond character (and is strictly comparable to the value found in five technetyl tetradentate amine–oxime complexes[16,17]). Singly bonded nitrogen ligands give rise to much longer Tc–N bond lengths (*ca.* 2.1 Å), whereas from structure determinations of four nitrido technetium(v) complexes[14,18,19] a mean value of 1.61(1) Å is acceptable for the Tc≡N bond. Moreover, angles about the deprotonated N(2) atom are close to 120°, ranging from 117.1(9) to 121.4(7)°, as expected for the sp^2 hybridization of this atom, and N(2), Tc, and the two carbon atoms adjacent to the nitrogen are nearly coplanar. By comparison, angles about the N(1) and N(3) atoms differ considerably from 120°, ranging from 108.1(6) to 129.5(7)°. Moreover, the short Tc–N$_{\text{amido}}$ distance seems to induce weakening of the Tc–O(2) bond *trans* to it (2.13 Å) [in other seven-co-ordinate oxotechnetium(v) complexes with Schiff-base ligands of c.n. = 6[2,3,9,10,20] the Tc–O$_{\text{eq}}$ bond lengths range from 1.95 to 2.02 Å], while the lengthening of the Tc–O(1) bond (2.12 Å), *trans* to Tc=O, can be associated with the O(1) ··· OMe non-bonding distance (2.71 Å) (Figure 2). This interaction is less than the sum of van der Waals radii, although a genuine hydrogen bond is not favoured by the angle O(1) ··· O–Me (123.3°). The Tc–O(3) bond length [1.685(6) Å] is at the longer end of the range expected for technetyl complexes (1.61—1.68 Å).[21]

The complexes obtained using the H$_2$L^2 ligand were conducting in MeCN, Λ_{eq} = 142 and 105 Ω^{-1} cm^2 mol^{-1} respectively for technetium and rhenium complexes, supporting a 1:1 electrolytic character. They showed diamagnetic behaviour and ν(M=O) at the usual values (Table 4). The elemental analysis is in agreement with a formula containing the whole ligand co-ordinated around the metal centre. Two ν(C=N) vibrations were exhibited also by these complexes suggesting the different position of the imine nitrogen–metal bonds. From the above results the proposed formulation of the L^2 complexes is [MOL^2]$^+$ as depicted in Figure 3.

U.v.–visible spectra of all the complexes are quite similar and in agreement with attributing the electronic absorptions to ligand to metal charge-transfer transitions.[3,15,17]

From the results reported above we can conclude that the

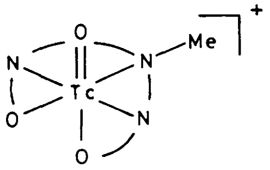

Figure 3. The proposed configuration of $[TcOL^2]^+$

reaction mixture containing $[MO(eg)_2]^-$, treated with the potentially quinquedentate ligands H_3L^1 and H_2L^2 produces complexes in which all five co-ordinating sites are bound to the central core, MO^{3+}. The mechanisms of these reactions in basic media can be completely different compared to those of the quadridentate ONNO ligands. The phenolic oxygen, probably deprotonated, can immediately co-ordinate *trans* to the M=O group and then the other groups, even the deprotonated amine nitrogen, co-ordinate in the plane normal to M=O. From the steric point of view the ligands containing five atoms in the central chain show, even by constructing the molecular models, the capability to surround the metal without high bond strains, in contrast to ligands with shorter central chains. This seems to be the reason why only with the ligand reported here has it been possible to reproduce the more stable electronic configuration obtained for the first time with technetium and bidentate Schiff bases (L) in the complexes $[TcOClL_2]$.[2] The only difference observed in using the H_2L^2 ligand instead of H_3L^1 is that, owing to the impossibility of deprotonation of the amine group, it leads to the production of cationic complexes.

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