# Synthesis and Characterization of Technetium(v) Oxo-complexes with Quadridentate Schiff-base Ligands: *X*-Ray Structures of μ-Oxo-bis-{oxo[*N*,*N*′-propane-1,3-diylbis(salicylideneiminato)]technetium(v)} and Chloro-oxo[*N*,*N*′-propane-1,3-diylbis(salicylideneiminato)]-technetium(v) †

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The reactions of quadridentate Schiff-base ligands derived from salicylaldehyde and diamines with $[TcOCl_4]^-$ have been investigated. The complexes $[NBu_4][TcOCl_3(Hsalpd)]$ ,$[NBu_4][TcOCl_3(Hsalbd)]$, $[\{TcO(salpd)\}_2O]$, [TcOCl(salpd)], and [TcOCl(salbd)][salpd = *N*,*N*′-propane-1,3-diylbis-(salicylideneiminate), salbd = *N*,*N*′-butane-1,4-diylbis(salicylideneiminate)] were isolated from the reaction mixture in ethanol. The complexes have been characterized by elemental analysis and by i.r. spectroscopy. The crystal structures of $[\{TcO(salpd)\}_2]O$ (1) and [TcOCl(salpd)] (2) have been determined from three-dimensional *X*-ray data: (1), monoclinic, space group $P2_1/c$, $a$ = 15.041(2), $b$ = 12.630(3), $c$ = 16.522(4) Å, β = 95.35(3)° and $Z$ = 4; (2), orthorhombic, space group $Pn2_1a$, $a$ = 12.010(4), $b$ = 11.702(4), $c$ = 11.625(6) Å, and $Z$ = 4. The structures have been solved by Patterson and Fourier methods and refined by least-squares methods to $R$ 0.059 for (1) and 0.076 for (2). The 'dimeric' structure of (1) consists of two crystallographically independent and chemically well separated TcO(salpd) moieties bridged by an oxygen atom with the bridging Tc–O–Tc angle symmetrically imposed at 180°. A novel feature is the presence of the almost linear O=Tc–O–Tc=O group. The technetium atoms have octahedral co-ordination, with the equatorial plane formed by the $N_2O_2$ donor set, and the chelate ligand, as a whole, is very nearly planar. The structure of (2) consists of discrete molecules of [TcOCl(salpd)] with a pseudo-octahedral co-ordination around technetium. The salpd ligand occupies the four equatorial positions, whereas the Cl and the oxygen are *trans* to each other in axial positions. The two salicylaldimine groups are bent in an 'umbrella shape'. Bond distances (Å) in the 'inner core': (1), Tc=O 1.68, Tc–O(bridging) 1.90, Tc–O 2.01, and Tc–N 2.12 Å; (2), Tc=O 1.66, Tc–O 1.98, Tc–N 2.12, Tc–Cl 2.44 Å, estimated standard deviations being 0.01 Å for (1) and 0.02 Å for (2).

Technetium(v) oxo-compounds are of interest both for their wide range in co-ordination numbers and configurations and for their use as radiopharmaceuticals.[1] Schiff-base ligands on the other hand offer high versatility in their substituent groups. Thus the possibility exists of designing technetium complexes with peculiar biological properties.

A number of technetium(v) complexes contain either the $TcO^{3+}$ or *trans*-$TcO_2^+$ core; the $TcO^{3+}$ complexes can be five-,[2-5] six-,[6-8] or seven-co-ordinate,[9] while the reported $TcO_2^+$ complexes are six-co-ordinate.[10-12] At present only two *X*-ray structure determinations of technetium complexes with Schiff-base ligands are available.[13,14]

With the above considerations in mind we have studied the reactions of tetrachloro-oxotechnetate(v) complex with Schiff-base ligands derived from salicylaldehyde and propane- or butane-diamine. *X*-Ray structure determinations were performed for two of the isolated compounds, one containing the $Tc_2O_3^{4+}$ core and the other the $TcO^{3+}$ core.

## Experimental

*Materials.*—Technetium as $[NH_4][TcO_4]$ in 0.1 mol dm$^{-3}$ ammonia solution was purchased from the Radiochemical Centre, Amersham. The salts $[AsPh_4][TcOCl_4]$ and $[NBu_4]$-$[TcOCl_4]$ were prepared by methods reported elsewhere.[13-15] *N*,*N*′-Propane-1,3-diylbis(salicylideneimine), $H_2salpd$, and *N*,*N*′-butane-1,4-diylbis(salicylideneimine), $H_2salbd$, were prepared by mixing (in ethanol) salicylaldehyde and the corresponding diamine in 2 : 1 stoicheiometric ratio and filtering the yellow solid after concentration to small volume. Other materials were reagent grade chemicals.

*Apparatus.*—Infrared spectra of samples as Nujol mulls between CsI discs were recorded on a Perkin-Elmer 580B spectrophotometer in the range 4 000—200 cm$^{-1}$. *X*-Ray data were collected with an automatic Philips PW1100 diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.7107 Å).

*Syntheses.*—$[NBu_4][TcOCl_3(Hsalpd)]$. The salt $[NBu_4]$-$[TcOCl_4]$ (0.1 g) was treated with an excess of $H_2salpd$ (0.12 g) in EtOH (20 cm$^3$) and stirred at room temperature for 15 min. Immediately an orange precipitate appeared. After filtration the powder was washed with EtOH and dried with $Et_2O$ (yield 85%).

$[\{TcO(salpd)\}_2O]$ (1). The salt $[AsPh_4][TcOCl_4]$ (0.1 g) was treated with an excess of $H_2salpd$ (0.9 g) in EtOH (20 cm$^3$) and stirred at room temperature for 1 h. The pale green solution, after addition of the ligand, changed immediately to orange-red and an orange precipitate appeared. After filtration the mother-liquors gave deep red-brown crystals (yield 30%).

[TcOCl(salpd)] (2). The salt $[NBu_4][TcOCl_4]$ (0.2 g) was treated with an excess of $H_2salpd$ (0.26 g) in EtOH (25 cm$^3$) and heated under reflux until the initial precipitate had disappeared (usually 15—20 h). The mixture was cooled, a grey precipitate filtered off, and the solution left to concentrate

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† *Supplementary data available* (No. SUP 23993, 20 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

**Table 1.** Crystal data, data collection, and refinement for [{TcO(salpd)}$_2$O] (1) and [TcOCl(salpd)] (2)

| | (1) | (2) |
|---|---|---|
| Formula | $C_{34}H_{32}N_4O_9Tc_2$ | $C_{17}H_{16}ClN_2O_3Tc$ |
| $M$ | 838.3 | 430.7 |
| Habit | Monoclinic | Orthorhombic |
| Crystal dimensions (mm) | 0.20 × 0.15 × 0.23 | 0.10 × 0.10 × 0.15 |
| Systematic absences | $h0l$, $l \neq 2n$, $0k0$, $k \neq 2n$ | $0kl$, $k + l \neq 2n$; $hk0$, $h \neq 2n$ |
| Space group | $P2_1/c$ (no. 14) | $Pn2_1a$ (alternative setting of no. 33) |
| Unit-cell constants | $a$ = 15.041(2), $b$ = 12.630(3), $c$ = 16.522(4) Å, $\beta$ = 95.35(3)° | $a$ = 12.010(4), $b$ = 11.702(4), $c$ = 11.625(6) Å |
| $U$, $Z$, $F$(000) | 3 125.0 Å$^3$, 4, 1 688 | 1 633.8 Å$^3$, 4, 864 |
| $D_c$/g cm$^{-3}$ | 1.781 | 1.751 |
| $D_m$/g cm$^{-3}$ * | 1.77 | 1.76 |
| $\mu$/cm$^{-1}$ | 8.4 | 10.4 |
| Temperature/°C | 20 | |
| Scan method | $\theta$—$2\theta$ | |
| Scan speed/° min$^{-1}$ | 1.80 | |
| Scan width/° | 1.20 | |
| Background time | 10 s at each end | |
| No. of standard reflections | 3 | |
| (Monitoring frequency and e.s.d.) | (3 h, 3%) | |
| $2\theta$ limit/° | $3 < 2\theta < 42$ | $3 < 2\theta < 44$ |
| No. of data | 4 384, 694 $h$, $k$, $\pm l$ equivalents | 3 027, 1 069 independent |
| No. of 'observed' ($F_o > 3\sigma_F$) | 1 958 | 788 |
| Weighting scheme | 1 | |
| Anisotropy | Heteroatoms + carbon atoms nearest to the 'inner core' | Tc and Cl |
| $R = (\Sigma\|\|F_o\| - \|F_c\|\|)/(\Sigma\|F_o\|)$ | 0.059 | 0.076 |

* By flotation in hexane–1,2-dibromoethane.

**Table 2.** Final fractional atomic co-ordinates (× 10$^4$) with e.s.d.s in parentheses [a]

| | Compound (1) | | | | | | Compound (2) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Molecule (A) | | | Molecule (B) | | | | | | |
| Atom | $X/a$ | $Y/b$ | $Z/c$ | $X/a$ | $Y/b$ | $Z/c$ | Atom | $X/a$ | $Y/b$ | $Z/c$ |
| Tc | −286(1) | 1 394(1) | −369(1) | 5 767(1) | −579(1) | 4 261(1) | Tc | 5 441(2) | 7 500 [b] | 6 168(2) |
| O(1) | −1 551(7) | 1 244(9) | −62(7) | 5 500(8) | −2 041(10) | 4 646(6) | Cl | 4 397(6) | 9 173(7) | 5 542(7) |
| O(2) | −805(7) | 831(11) | −1 450(7) | 4 749(8) | −897(9) | 3 433(6) | O(1) | 5 755(16) | 6 195(17) | 6 611(17) |
| O(3) | −308(10) | 2 692(11) | −593(9) | 6 637(8) | −887(10) | 3 726(7) | O(2) | 6 622(16) | 7 895(15) | 5 047(16) |
| O(4) [c] | 0 000 | 0 000 | 0 000 | 5 000 | 0 000 | 5 000 | O(3) | 6 324(19) | 8 543(20) | 7 151(17) |
| N(1) | 162(10) | 1 803(12) | 834(10) | 6 709(10) | −369(14) | 5 289(9) | N(1) | 4 480(19) | 6 772(19) | 4 823(19) |
| N(2) | 1 028(9) | 1 303(13) | −750(9) | 5 829(9) | 1 023(10) | 3 839(8) | N(2) | 4 175(19) | 7 517(36) | 7 421(20) |
| C(1) | −1 836(11) | 1 421(15) | 650(11) | 5 785(13) | −2 493(16) | 5 346(12) | C(1) | 6 578(25) | 7 962(24) | 3 967(25) |
| C(2) | −1 325(12) | 1 770(15) | 1 350(11) | 6 400(11) | −2 072(15) | 5 915(10) | C(2) | 7 433(33) | 8 433(36) | 3 260(32) |
| C(3) | −361(14) | 1 911(15) | 1 405(11) | 6 813(11) | −1 050(17) | 5 866(10) | C(3) | 7 413(30) | 8 480(34) | 2 121(29) |
| C(4) | 1 116(14) | 1 956(20) | 1 114(14) | 7 201(15) | 668(19) | 5 405(13) | C(4) | 6 505(34) | 8 095(33) | 1 491(29) |
| C(5) | 1 670(14) | 2 318(18) | 456(15) | 7 295(12) | 1 254(15) | 4 637(13) | C(5) | 5 678(30) | 7 497(48) | 2 051(29) |
| C(6) | 1 800(12) | 1 459(19) | −177(12) | 6 429(12) | 1 789(15) | 4 286(10) | C(6) | 5 644(27) | 7 572(38) | 3 288(27) |
| C(7) | 1 182(13) | 1 007(14) | −1 477(12) | 5 391(11) | 1 293(14) | 3 184(10) | C(7) | 4 696(27) | 6 873(29) | 3 776(29) |
| C(8) | 555(13) | 681(16) | −2 140(11) | 4 743(11) | 761(13) | 2 653(9) | C(8) | 3 505(29) | 6 074(29) | 5 136(27) |
| C(9) | −371(13) | 562(16) | −2 074(12) | 4 411(11) | −265(13) | 2 843(10) | C(9) | 2 747(27) | 6 574(28) | 6 120(27) |
| C(10) | −882(14) | 157(17) | −2 797(13) | 3 671(12) | −665(15) | 2 338(11) | C(10) | 3 289(23) | 6 597(24) | 7 271(22) |
| C(11) | −510(18) | −84(21) | −3 471(17) | 3 300(12) | −99(15) | 1 666(11) | C(11) | 4 066(23) | 8 213(26) | 8 253(24) |
| C(12) | 413(16) | −10(19) | −3 504(14) | 3 662(13) | 837(15) | 1 455(11) | C(12) | 4 947(23) | 9 064(24) | 8 562(22) |
| C(13) | 926(13) | 425(16) | −2 850(12) | 4 349(12) | 1 271(16) | 1 956(11) | C(13) | 4 598(29) | 9 754(29) | 9 490(28) |
| C(14) | −1 723(14) | 1 934(17) | 2 099(12) | 6 678(11) | −2 683(14) | 6 658(10) | C(14) | 5 321(30) | 10 536(29) | 9 957(31) |
| C(15) | −2 630(15) | 1 779(18) | 2 094(13) | 6 259(13) | −3 600(18) | 6 762(12) | C(15) | 6 428(37) | 10 643(39) | 9 439(34) |
| C(16) | −3 129(14) | 1 407(20) | 1 430(14) | 5 671(14) | −4 020(17) | 6 211(13) | C(16) | 6 743(18) | 9 942(19) | 8 484(17) |
| C(17) | −2 755(13) | 1 216(16) | 706(12) | 5 430(13) | −3 498(17) | 5 482(12) | C(17) | 5 968(22) | 9 176(26) | 8 039(23) |

[a] Standard deviations are in terms of the last significant digit. [b] To fix origin. [c] Site occupation factor: 0.5.

to small volume. A dark red powder was collected. This solid shows the presence of two products. By washing with a small amount of $CH_2Cl_2$ the required compound was obtained. Yield 35%. The other product was identified as [{TcO(salpd)}$_2$O].

[NBu$_4$][TcOCl$_3$(Hsalbd)]. The salt [NBu$_4$][TcOCl$_4$] (0.1 g) was dissolved in EtOH (25 cm$^3$) and H$_2$salbd (0.12 g) was added to the solution. Immediately an orange precipitate appeared. After 10 min at room temperature the solid was filtered off and washed with EtOH and Et$_2$O. Yield 86%.

**Table 3.** Elemental analysis and general properties of technetium Schiff-base complexes

| Compound | Yield/% | Colour | M.p. (°C) [a] | Analysis [b]/% C | H | N | Cl |
|---|---|---|---|---|---|---|---|
| $[NBu_4][TcOCl_3(Hsalpd)]$ | 85 | Orange | 137 | 54.3 (53.2) | 7.9 (7.2) | 6.1 (5.6) | 13.8 (14.3) |
| $[NBu_4][TcOCl_3(Hsalbd)]$ | 87 | Orange | 130 | 54.5 (53.8) | 7.8 (7.3) | 6.0 (5.5) | 13.5 (14.0) |
| $[\{TcO(salpd)\}_2O]$ | 30 | Red-violet | 215 | 51.0 (50.6) | 4.2 (4.1) | 6.2 (6.3) | 8.2 (8.0) |
| [TcOCl(salpd)] | 40 | Orange-red | 185 | 47.8 (47.4) | 3.6 (3.7) | 6.7 (6.5) | 8.6 (8.2) |
| [TcOCl(salbd)] | 45 | Orange-red | 190 | 49.1 (48.6) | 4.2 (4.1) | 6.2 (6.3) | 8.2 (8.0) |

[a] Measurements produced decomposition to a black powder. The data are uncorrected. [b] Calculated values are given in parentheses.

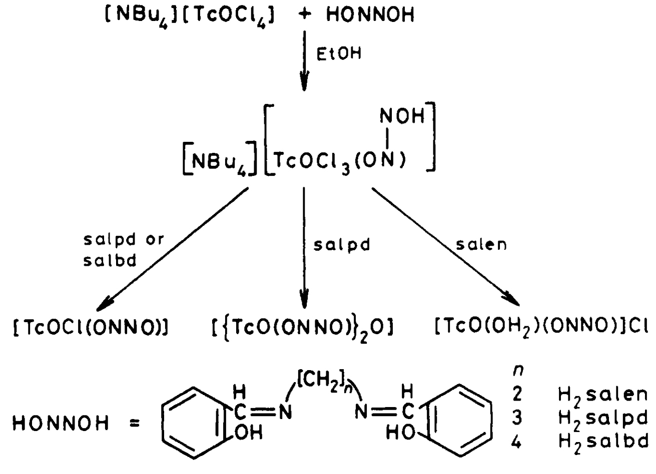
**Table 4.** Principal i.r. bands ($cm^{-1}$) of technetium Schiff-base complexes

| Compound | ν(Tc=O) | ν(C=N) | ν(C–O) | ν(O–H) |
|---|---|---|---|---|
| $[NBu_4][TcOCl_3(Hsalpd)]$ | 942s | 1 656m, 1 600s | 1 280m | 3 420br |
| $[NBu_4][TcOCl_3(Hsalbd)]$ | 940s | 1 650m, 1 610s | 1 280m | 3 000br |
| $[\{TcO(salpd)\}_2O]$ | ν(Tc–O–Tc) 685s | 1 630s | 1 290m | — |
| [TcOCl(salpd)] | 930s | 1 620s | 1 270s | — |
| [TcOCl(salbd)] | 940s | 1 612s | 1 290s | — |

[TcOCl(salbd)]. The salt $[NBu_4][TcOCl_4]$ (0.1 g) was dissolved in EtOH (25 $cm^3$) and $H_2salbd$ (0.12 g) was added to the solution. The mixture was heated under reflux for 15 h and the orange solid which had initially appeared reacted completely. The solution was left to cool and concentrate to small volume. The precipitate was filtered off and washed with $Et_2O$. Recrystallization from $CH_2Cl_2$ gave fine red-orange plates. Yield 25%.

*Solution and Refinement of the Structures of the Compounds* $[\{TcO(salpd)\}_2O]$ (1) *and* [TcOCl(salpd)] (2).—Crystal data and other details of the data collection and structure refinement are given in Table 1. Unit-cell parameters were obtained from a least-squares fit of 2θ, χ, and φ for 25 reflections in the range $20 < 2\theta < 26°$. Corrections for Lorentz and polarization effects were made, also absorption using an empirical method based on ψ scans [16] of reflections near $\chi = 90°$. The structures were solved by standard heavy-atom methods. The paucity of diffraction data (mainly the small amount of high-angle data) did not allow a more accurate structure determination of compound (2) [bond lengths and angles affected by high estimated standard deviations (e.s.d.s)], but the stereochemistry of the technetium atom was unambiguously determined. Refinement using full-matrix least squares and minimizing $\Sigma w(|F_o| - |F_c|)^2$ was terminated when the maximum (average) shift to error ratio for compound (1) was <0.15 (average 0.06) in positional parameters. In the final cycle a weighting scheme of the type $w = n/\sigma_F^2 + mF^2$ did not improve the models and for compound (1) the 2,0,0 reflection was suppressed because of an uneven background (probably beam stop at low 2θ). No feature corresponding to atoms larger than hydrogen atoms was found in the final difference maps. The scattering factors and the real and imaginary components of anomalous dispersion for Tc were taken from ref. 17.

Final atomic fractional positional parameters are given in Table 2. All computations were performed on a CDC Cyber 76 computer using Sheldrick's SHELX 76 program package [18] with minor local modifications.



**Scheme.** Summary of the products of the reactions

## Results and Discussion

The reaction of $[TcOCl_4]^-$ with quadridentate Schiff-base ligands derived from salicylaldehyde and diamines leads to peculiar complexes depending on the length of the aliphatic chain of the diamine group (Scheme). Deutsch and co-workers [1] using *N,N'*-ethylenebis(salicylideneimine), $H_2salen$, as ligand prepared and isolated the compound $[TcO(OH_2)(salen)]^+$ in which the water molecule is weakly co-ordinated *trans* to the oxo-oxygen. *X*-Ray analysis [14] of the complex $[TcO(OH_2)(acen)]Br$ [acen = *N,N'*-ethylenebis(acetylacetone iminate)] has revealed a similar structure to that of the salen compound.

By using propane-1,3-diamine, the $H_2salpd$ ligand thus obtained produced first a $NBu_4^+$ salt of $[TcOCl_3(Hsalpd)]^-$ in which the ligand is bidentate through one half only, and then two different products compared with the salen compound: $[\{TcO(salpd)\}_2O]$ (1) and [TcOCl(salpd)] (2). By using butane-1,4-diamine, the $H_2salbd$ ligand thus obtained produced only the 'half-co-ordinated' compound and [TcOCl(salbd)]. The yields of the quadridentate Schiff-base complexes are always low and it is reasonable to assume that all the types of complexes have been formed but only the most stable in the crystalline form can be isolated and characterized. However, it should be noted that in all the complexes the Schiff-base ligand is in the same plane perpendicular to the Tc=O bond. This is in contrast with the behaviour of bidentate Schiff-base

**Table 5.** Selected interatomic distances (Å) and angles (°)

| | Compound (1) | | | | | Compound (2) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | (A) | (B) | | (A) | (B) | | | | |
| Tc—O(1) | 2.02(1) | 2.00(1) | Tc—O(2) | 2.01(1) | 2.00(1) | Tc—Cl | 2.44(1) | Tc—O(3) | 1.98(1) |
| Tc—N(1) | 2.10(2) | 2.12(1) | Tc—N(2) | 2.13(1) | 2.14(1) | Tc—O(1) | 1.66(1) | Tc—N(1) | 2.12(2) |
| Tc—O(3) | 1.68(1) | 1.69(1) | Tc—O(4) | 1.90(1) | 1.90(1) | Tc—O(2) | 1.98(1) | Tc—N(2) | 2.11(2) |
| O(1)—C(1) | 1.31(2) | 1.32(2) | O(2)—C(9) | 1.32(2) | 1.32(2) | O(2)—C(1) | 1.26(3) | O(3)—C(17) | 1.34(4) |
| C(1)—C(2) | 1.40(2) | 1.36(3) | C(8)—C(9) | 1.41(3) | 1.43(2) | C(6)—C(7) | 1.51(4) | C(11)—C(12) | 1.50(4) |
| C(2)—C(3) | 1.45(3) | 1.44(3) | C(7)—C(8) | 1.44(3) | 1.42(2) | C(7)—N(1) | 1.25(3) | C(11)—N(2) | 1.27(3) |
| C(3)—N(1) | 1.29(3) | 1.28(2) | C(7)—N(2) | 1.30(2) | 1.26(2) | N(1)—C(8) | 1.47(4) | N(2)—C(10) | 1.52(4) |
| N(1)—C(4) | 1.48(2) | 1.51(3) | N(2)—C(6) | 1.44(2) | 1.47(2) | C(8)—C(9) | 1.57(4) | C(9)—C(10) | 1.49(4) |
| C(4)—C(5) | 1.50(3) | 1.49(3) | C(5)—C(6) | 1.53(3) | 1.53(2) | $C_{ph}$—$C_{ph}$ (mean) | 1.40(3) | | |
| O(1)—Tc—N(1) | 90.7(5) | 90.0(5) | O(2)—Tc—N(2) | 90.7(5) | 91.2(5) | Cl—Tc—O(1) | 162.1(7) | O(1)—Tc—O(2) | 104.9(9) |
| N(1)—Tc—N(2) | 93.9(6) | 95.5(6) | O(1)—Tc—O(2) | 83.9(4) | 82.5(4) | Cl—Tc—O(2) | 89.1(6) | O(1)—Tc—O(3) | 105.5(9) |
| O(1)—Tc—N(2) | 171.1(5) | 170.9(5) | O(2)—Tc—N(1) | 171.8(6) | 169.9(5) | Cl—Tc—O(3) | 87.3(7) | O(1)—Tc—N(1) | 89.0(9) |
| O(3)—Tc—O(4) | 167.0(5) | 165.7(4) | O(3)—Tc—O(1) | 98.5(6) | 98.1(6) | Cl—Tc—N(1) | 79.8(6) | O(1)—Tc—N(2) | 87.6(1.0) |
| O(3)—Tc—N(1) | 88.1(6) | 87.1(6) | O(3)—Tc—N(2) | 89.3(7) | 89.3(6) | Cl—Tc—N(2) | 80.1(7) | | |
| O(3)—Tc—O(2) | 98.7(6) | 100.2(5) | O(4)—Tc—O(1) | 91.3(3) | 89.9(3) | O(2)—Tc—N(1) | 89.9(8) | O(3)—Tc—N(2) | 89.0(9) |
| O(4)—Tc—N(1) | 83.2(4) | 80.7(4) | O(4)—Tc—N(2) | 81.7(4) | 83.9(4) | O(2)—Tc—N(2) | 165.9(1.2) | O(3)—Tc—N(1) | 164.6(9) |
| O(4)—Tc—O(2) | 90.8(4) | 92.6(3) | Tc—O(4)—Tc′ | 180.0 * | | N(1)—Tc—N(2) | 96.9(6) | O(2)—Tc—O(3) | 81.5(8) |
| Tc—O(1)—C(1) | 127.2(1.0) | 128.0(1.1) | Tc—O(2)—C(9) | 127.4(1.1) | 126.9(1.0) | Tc—O(2)—C(1) | 129.8(1.9) | Tc—O(3)—C(17) | 127.9(1.8) |
| O(1)—C(1)—C(2) | 126.6(1.6) | 125.3(1.8) | O(2)—C(9)—C(8) | 126.6(1.7) | 126.0(1.4) | O(2)—C(1)—C(6) | 123.9(2.7) | O(3)—C(17)—C(12) | 124.9(2.6) |
| C(1)—C(2)—C(3) | 123.9(1.7) | 125.5(1.6) | C(9)—C(8)—C(7) | 123.5(1.8) | 121.7(1.4) | C(1)—C(6)—C(7) | 123.4(2.8) | C(17)—C(12)—C(11) | 126.0(2.5) |
| C(2)—C(3)—N(1) | 127.8(1.7) | 128.3(1.6) | C(8)—C(7)—N(2) | 128.8(1.8) | 132.6(1.6) | C(6)—C(7)—N(1) | 124.9(2.9) | C(12)—C(11)—N(2) | 122.4(2.5) |
| C(3)—N(1)—C(4) | 113.4(1.7) | 117.6(1.5) | C(7)—N(2)—C(6) | 116.4(1.5) | 119.9(1.4) | C(7)—N(1)—Tc | 124.5(2.1) | C(11)—N(2)—Tc | 127.3(2.0) |
| N(1)—C(4)—C(5) | 113.6(1.8) | 114.1(1.6) | N(2)—C(6)—C(5) | 113.5(1.6) | 111.1(1.5) | Tc—N(1)—C(8) | 118.2(1.8) | Tc—N(2)—C(10) | 114.7(1.6) |
| C(4)—C(5)—C(6) | 113.2(1.9) | 113.4(1.7) | Tc—N(1)—C(3) | 123.6(1.3) | 122.4(1.3) | C(7)—N(1)—C(8) | 117.3(2.5) | C(11)—N(2)—C(10) | 117.9(2.3) |
| Tc—N(1)—C(4) | 123.0(1.3) | 119.5(1.2) | Tc—N(2)—C(7) | 122.6(1.2) | 120.0(1.1) | N(1)—C(8)—C(9) | 115.7(2.6) | N(2)—C(10)—C(9) | 114.9(2.3) |
| Tc—N(2)—C(6) | 120.7(1.2) | 120.0(1.0) | | | | C(8)—C(9)—C(10) | 114.0(2.6) | $C_{ph}$—$C_{ph}$—$C_{ph}$ (mean) | 119.8(2.0) |

* Symmetry imposed: Tc′ at $-x$, $-y$, $-z$.

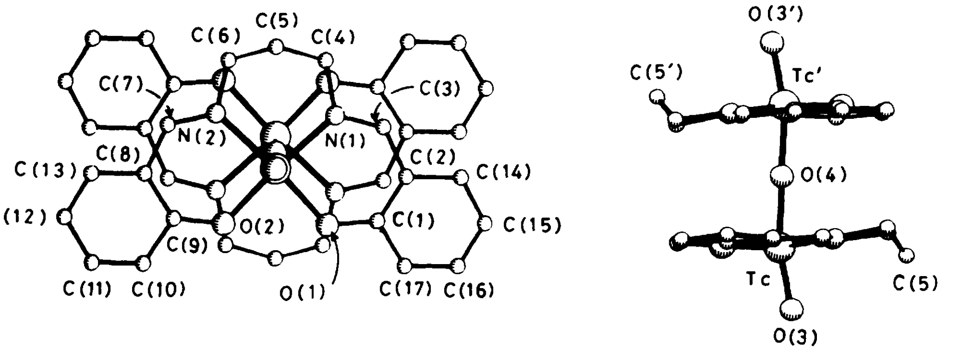


**Figure 1.** PLUTO drawings of the molecule (1) showing the atom numbering. The complex is viewed perpendicular (on the left) and parallel (on the right) to the O(1), N(1), N(2), O(2) mean plane

ligands which in analogous complexes show two ligands in two different perpendicular planes.[1]

*Characterization of the Complexes.*—The anionic compounds are orange powders soluble in $CH_2Cl_2$, $CHCl_3$, and $Me_2CO$, slightly soluble in MeOH and MeCN, and insoluble in $Et_2O$. Elemental analyses are consistent with the formulations proposed (Table 3). I.r. spectra of $[NBu_4][TcOCl_3(Hsalpd)]$ and $[NBu_4][TcOCl_3(Hsalbd)]$ show ν(C=N) at 1 656 and 1 650 $cm^{-1}$ for the non-co-ordinated imino-group and at 1 600 and 1 610 $cm^{-1}$ for the co-ordinated one, respectively; ν(Tc=O) was found at 943 and 940 $cm^{-1}$ and the absorptions at 3 420 and 3 400 $cm^{-1}$ were assigned to ν(O–H) of the non-co-ordinated phenolic group (Table 4).

The compound $[\{TcO(salpd)\}_2O]$ (1) is a dark brown solid slightly soluble in $CH_2Cl_2$, $CHCl_3$, and hot MeCN, insoluble in EtOH, MeOH, and $Et_2O$. Red-violet crystals suitable for *X*-ray analysis were produced by slow evaporation of $CH_2Cl_2$ solutions. The elemental analysis is in agreement with the proposed formulation. The i.r. spectrum shows ν(C=N) at 1 630 $cm^{-1}$ and ν(Tc–O–Tc) at 685 $cm^{-1}$. No absorption can be attributed to ν(Tc=O). The *X*-ray analysis will be discussed below.

The [TcOCl(salpd)] (2) and [TcOCl(salbd)] complexes are light orange crystals very soluble in the common polar solvents. Crystals suitable for *X*-ray analysis were collected from $CH_2Cl_2$–$Et_2O$ solutions. Elemental analyses are consistent with the proposed formulations. Infrared spectra show ν(C=N) at 1 620 and 1 612 $cm^{-1}$ for salpd and salbd compounds respectively and ν(Tc=O) at 930 and 940 $cm^{-1}$; ν(Tc–Cl) is not assigned owing to the absorption of other vibrations in the region 300—250 $cm^{-1}$.

**Table 6.** Other geometrical data

Compound (1)[a]

(*i*) Displacements (Å) of atoms from selected mean planes[b]

| Atom | Plane (A) | (B) | (C) |
|---|---|---|---|
| Tc | 0.12 (0.12) | 0.03 (−0.04) * | 0.02 (0.08) * |
| O(1) | −0.01 (0.00) * | −0.02 (0.04) * | |
| O(2) | 0.01 (0.00) * | | 0.00 (−0.04) * |
| O(3) | 1.77 (1.78) | | |
| O(4) | −1.79 (−1.79) | | |
| N(1) | 0.01 (0.00) * | −0.02 (0.04) * | |
| N(2) | −0.01 (0.00) * | | −0.03 (−0.08) * |
| C(1) | −0.07 (−0.24) | −0.02 (−0.01) * | |
| C(2) | −0.04 (−0.33) | 0.04 (−0.02) * | |
| C(3) | −0.04 (−0.23) | −0.01 (−0.01) * | |
| C(4) | −0.07 (0.01) | −0.14 (−0.02) | −0.27 (−0.08) |
| C(5) | 0.58 (0.70) | 0.44 (0.48) | 0.45 (0.60) |
| C(6) | −0.19 (−0.11) | −0.38 (−0.50) | −0.24 (−0.22) |
| C(7) | −0.06 (0.10) | | 0.00 (0.01) * |
| C(8) | −0.06 (0.10) | | 0.04 (0.08) * |
| C(9) | −0.10 (−0.04) | | −0.03 (−0.05) * |

(*ii*) Dihedral angles (°)

| | | | |
|---|---|---|---|
| (A)–(B) | 3.0 (8.3) | (B)–(C) | 6.3 (7.7) |
| (A)–(C) | 3.4 (1.1) | (D)–(E) | 5.0 (8.3) |

Mean planes

(D) C(1), C(2), C(14), C(15), C(16), C(17)
(E) C(8), C(9), C(10), C(11), C(12), C(13)

(*iii*) Torsion angles (°)

| | |
|---|---|
| N(1)–C(4)–C(5)–C(6) | 70.4 (75.0) |
| C(4)–C(5)–C(6)–N(2) | 76.9 (80.3) |

(*iv*) Other distances (Å)

| | | | |
|---|---|---|---|
| O(1) · · · N(1) | 2.94 (2.92) | Tc–C(1) | 3.00 (3.01) |
| O(2) · · · N(2) | 2.95 (2.96) | Tc–C(3) | 3.01 (3.01) |
| O(1) · · · O(2) | 2.70 (2.64) | Tc–C(7) | 3.04 (2.98) |
| N(1) · · · N(2) | 3.09 (3.16) | Tc–C(9) | 3.00 (2.99) |

Compound (2)

(*i*) Displacements (Å) of atoms from selected mean planes

| Atom | Plane (A) | (B) | (C) |
|---|---|---|---|
| Tc | −0.23 | −0.34 | 0.33 |
| O(1) | −1.85 | | |
| O(2) | −0.01 * | 0.01 * | |
| O(3) | 0.02 * | | 0.00 * |
| N(1) | 0.01 * | −0.02 * | |
| N(2) | −0.04 * | | 0.01 * |
| C(1) | 0.47 | 0.00 * | |
| C(6) | 0.79 | −0.07 * | |
| C(7) | 0.39 | 0.08 * | |
| C(8) | −0.31 | 0.12 | |
| C(9) | 0.20 | | |
| C(10) | −0.46 | | −0.18 |
| C(11) | 0.41 | | −0.01 * |
| C(12) | 0.71 | | 0.01 * |
| C(17) | 0.50 | | 0.00 * |
| Cl | 2.19 | | |

(*ii*) Dihedral angles (°)

| | | | |
|---|---|---|---|
| (A)–(B) | 157.8 | (B)–(D) | 1.9 |
| (A)–(C) | 21.6 | (C)–(E) | 2.9 |
| (B)–(C) | 136.6 | (D)–(E) | 138.6 |

Mean planes

(D) C(1), C(2), C(3), C(4), C(5), C(6)
(E) C(12), C(13), C(14), C(15), C(16), C(17)

(*iii*) Torsion angles (°)

| | | | |
|---|---|---|---|
| C(1)–C(6)–C(7)–N(1) | 16.7 | C(8)–C(9)–C(10)–N(2) | 73.9 |
| C(6)–C(7)–N(1)–C(8) | 178.7 | C(9)–C(10)–N(2)–C(11) | 124.5 |
| C(7)–N(1)–C(8)–C(9) | −137.8 | C(10)–N(2)–C(11)–C(12) | 172.9 |
| N(1)–C(8)–C(9)–C(10) | −67.8 | N(2)–C(11)–C(12)–C(17) | −2.5 |

(*iv*) Other distances (Å)

| | | | |
|---|---|---|---|
| N(1) · · · O(2) | 2.90 | N(2) · · · O(3) | 2.86 |
| O(2) · · · O(3) | 2.59 | N(1) · · · N(2) | 3.16 |
| O(1) · · · O(2) | 2.89 | O(1) · · · O(3) | 2.90 |
| O(1) · · · N(1) | 2.67 | O(1) · · · N(2) | 2.62 |

[a] Values in parentheses refer to molecule (B). [b] Atoms defining the plane are indicated by an asterisk.

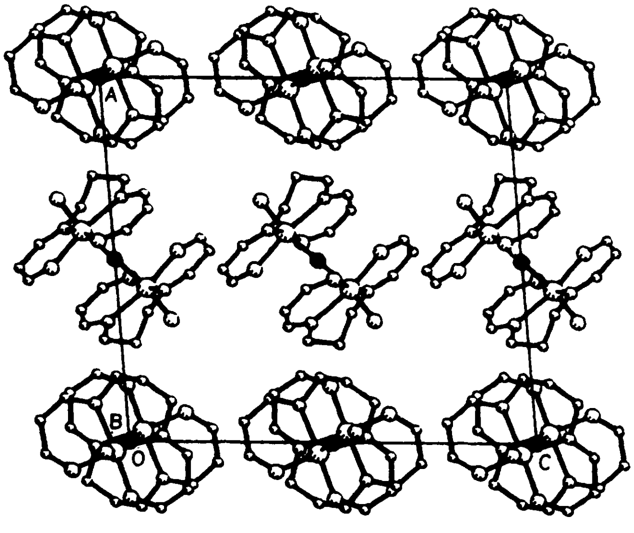


**Figure 2.** Packing of the molecules (1) in the unit cell. For clarity, only the 'inner core' is represented

*X*-Ray structure analysis of compound (1) has conclusively identified the almost linear $Tc_2O_3^{4+}$ group. Trop [19] postulated that this group was formed in dimeric $[\{TcO(S_2CNEt_2)_2\}_2O]$ by the action of sodium diethylcarbamate on $[TcOCl_4]^-$ in acetone. By analogy with the corresponding, structurally characterized, rhenium complex,[20] it is thought to have a linear O=Tc–O–Tc=O structure.

The $Tc_2O_3^{4+}$ core can be thought of as being derived from that of $TcO^{3+}$ with a bridging oxygen occupying the sixth position *trans* to two oxotechnetium groups. The sixth position appears to be labile in $[TcO(OH_2)(acen)]Br$,[14] with the shortest Tc=O distance reported (1.61 Å) and the water molecule, *trans* to Tc=O, at 2.3 Å (*cf.* 2.0 Å for a typical single Tc–O bond [21]); the overall co-ordination geometry is that of a distorted octahedron with all equatorial bonds directed away from the Tc=O linkage. On the contrary, complex (1) shows a very slight deviation from octahedral geometry, with the technetium atom displaced by 0.12 Å from the mean plane of the $N_2O_2$ donor atoms, towards the Tc=O.

The crystal structure of compound (1) consists of two independent and chemically well separated TcO(salpd) moieties (A) and (B), each having a crystallographically

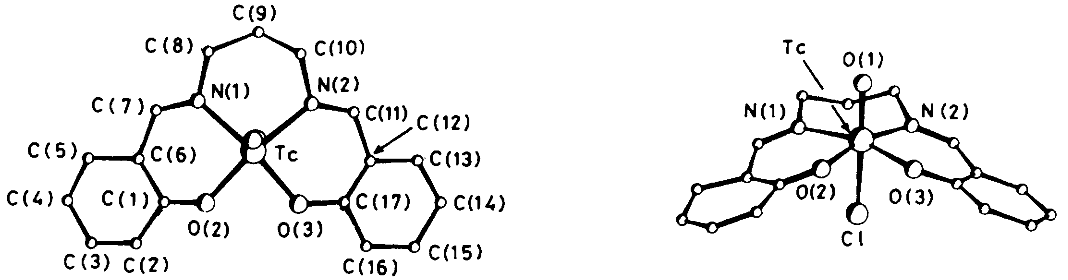


**Figure 3.** PLUTO drawings of the molecule (2) showing the atom numbering. The complex is viewed perpendicular (on the left) to the O(2), N(1), N(2), O(3) mean plane and the 'umbrella shape' is shown on the right

imposed centre of symmetry at (0,0,0) and (½,0,½), where the O(4) atoms reside. Bond lengths and angles (Table 5) within molecules (A) and (B) are normal [21] and details of the molecular shape are best appreciated by consideration of the displacements of appropriate atoms from the mean planes calculated through various parts of the molecules (Table 6). There are only minor differences between the geometries of (A) and (B) and no bond distances differ by more than two standard deviations, although molecule (A) exhibits an overall higher degree of planarity and the torsion angles in the propane-1,3-diamine are quite different. Therefore, discussion of distances and angles will refer to the mean value for molecules (A) and (B). The co-ordinated atoms $N_2O_2$ are slightly displaced from coplanarity and the Tc(salpd) unit, except for the C(5) atom, is almost planar, as depicted in Figure 1, which also shows the atom-labelling scheme. Consequently, all the dihedral angles, reported in Table 6 for compound (1), approach 0°.

The bridging Tc–O distance is 1.90(1) Å, which may be compared with 1.91 Å found in $[\{ReO(S_2CNEt_2)\}_2O]$.[20] This value is intermediate between the average Tc=O length (*ca.* 1.65 Å in $TcO^{3+}$ complexes and *ca.* 1.75 Å in $TcO_2{}^+$ complexes) and the average Tc–O single bond (*ca.* 2.01 Å).[21] Although the O(3)–Tc–O(4) group would be expected to be linear, the observed angle is within 13° of linearity. Another point concerns the lengthening of the Tc–N distances (mean 2.12 Å) compared with the average Tc–O distances of 2.01 Å in the equatorial plane. These longer Tc–N bond lengths are not consistent with the 0.04 Å larger covalent radius of nitrogen compared with oxygen.[22] A simplified packing of compound (1) is presented in Figure 2.

Figure 3 shows a view of the complex (2) and defines the atom-labelling scheme. Crystals of (2) consist of discrete molecules of [TcOCl(salpd)] with a pseudo-octahedral co-ordination around the technetium. The salpd ligand, as in compound (1), occupies the four equatorial positions, where as the Cl and the Tc=O oxygen are *trans* to each other in axial positions. The technetium atom is practically equidistant (+0.33, −0.34 Å) (Table 6) from the planes defined by the two salicylideneimine units, deviating towards the Tc=O oxygen. The angle between the two salicylideneimine groups is 138.6° and these two groups are therefore bent in a 'umbrella shape' (Figure 3). The bond lengths and angles in the 'inner core' do not merit any comment.

In both complexes (1) and (2) there are no unusual intermolecular contacts and the bond distances and angles within the quadridentate Schiff base are in general agreement with mean values reported for several such complexes.[23] In any event, the differences should not be regarded as being chemically significant because of the low accuracy of the structure determination of compound (2).

In conclusion, identification of the $O{=}Tc{-}O{-}Tc{=}O^{4+}$ group adds to the existing family of oxotechnetium(v) cores, and we note that the $O{=}Tc{-}OH_2{}^{3+}$,[14] $O{=}Tc{-}OH^{2+}$,[24] and $O{=}Tc{-}OR^{2+}$ [25] cores have been found or postulated. Thus, the oxotechnetium(v) systems may provide a firm foundation upon which subsequent development and elaboration of technetium chemistry will be based.*

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* *Note added at proof*: A paper on new oxotechnetium(v) complexes with Schiff-base ligands has recently appeared (S. Jurisson, L. F. Lindoy, K. P. Dancey, M. McPartlin, P. A. Tasker, D. K. Uppal, and E. Deutsch, (*Inorg. Chem.*, 1984, **23**, 227).

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*Received 19th December* 1983; *Paper* 3/2230