where the quantity in parentheses is a $3j$ symbol. The above $3j$ symbol is not zero only if $J_z = J_z'$ and $|J - J'| \geq 1$. The reduced matrix element can now be separated into an orbital and a spin part

$$\langle \gamma SLJ|k_zL_z + g_eS_z|\gamma'S'L'J'\rangle =$$
$$k_z(-1)^{S+L+J'+1}\begin{Bmatrix} J & 1 & J' \\ L' & S & L \end{Bmatrix}[(2J+1)(2J'+1)L(L+1)(2L+1)]^{1/2} +$$
$$g_e(-1)^{S'+L'+J+1}\begin{Bmatrix} J & 1 & J' \\ S' & L & S \end{Bmatrix}[(2J+1)(2J'+1)S(S+1)(2S+1)]^{1/2} \quad (A4)$$

where the quantities in braces are $6j$ symbols. It can easily be shown that the reduced matrix element is not zero only for $\gamma = \gamma'$, $S = S'$, and $L = L'$. Equation A4 can also be used to calculate matrix elements of S_z alone by simply setting k_z to zero and dividing the result by g_e. The necessary $3j$ and $6j$ symbols are obtained from easily programmable equations.[29]

(29) Rotenberg, M.; Bivins, R.; Metropolis, N.; Wooten, J. K., Jr. *The 3j and 6j Symbols*; MIT Press: Cambridge, MA, 1959.

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Synthesis and Structure of an Amino Sugar–Schiff Base Complex of Technetium(V) Containing Salicylaldehyde in an Unusual Coordination Mode

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The technetium(V) complex TcOL(sal), where L represents dianionic *N*-salicylidene-D-glucosamine and sal represents monoanionic salicylaldehyde, has been synthesized and characterized. This neutral species precipitates from a concentrated methanol solution after reaction of a 5-fold excess of the glucose derivative with $TcOCl_4^-$. The presence of chelated salicylaldehyde in the final compound does not appear to result from hydrolysis of the Schiff base ligand L prior to coordination since the reaction of $TcOCl_4^-$, L, and salicylaldehyde in a 1:1:1 stoichiometric ratio does *not* yield TcOL(sal). It thus appears that the formation of TcOL(sal) is a kinetically controlled process. The crystal structure of the title compound, (*N*-salicylidene-D-glucosaminato)(salicylaldehydato)oxotechnetium(V), was determined by X-ray analysis using counter data. The technetium atom is in a distorted octahedral coordination environment with the three donor atoms of the Schiff base ligand (i.e., the neutral aldimine nitrogen atom, the anionic phenolic oxygen atom of the Schiff base moiety, and the anionic hydroxylic oxygen atom of the glucopyranose ring) occupying the plane normal to the Tc=O linkage. The coordination shell is completed by the binding of a salicylaldehyde ligand through a charged phenolic oxygen atom and a neutral carbonyl oxygen atom in positions cis and trans to the Tc=O linkage, respectively. This unusual coordination mode of salicylaldehyde, in which the neutral atom is trans to the M=O linkage, has not been previously observed in oxo complexes containing similar ligands and presumably results from the formation of this complex by a kinetically controlled process. The length of the Tc—O bond trans to Tc=O is 2.360 (9) Å, while the displacement of the Tc atom out of the mean equatorial plane toward the oxo group is 0.422 (1) Å. This complex crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 6.533$ (2) Å, $b = 12.649$ (4) Å, $c = 23.675$ (7) Å, and $V = 1956$ (1) Å^3 with $Z = 4$, for 1445 observed reflections with $I > 2\sigma(I)$.

Introduction

There is great interest in developing ^{99m}Tc radiopharmaceuticals suitable for monitoring the metabolic function of the brain and heart because of the ideal nuclear properties and availability of this isotope.[1] Glucose is an important substrate for brain and heart metabolism and hence it would be desirable to incorporate this sugar into the design of a ^{99m}Tc radiopharmaceutical. The ultimate goal of this design is an agent in which technetium-99m is linked to a glucose molecule in a manner such that the biodistribution of the metabolically active sugar is not altered or destroyed. In principle, such agents can be prepared by using bifunctional chelating agents (BCA) in which one functional group strongly coordinates to the technetium center (e.g., EDTA, DTPA, thiosemicarbazone, thiols, or dithiols[1-12]) and a second functional group provides the biologically active substrate or binds to it. This BCA approach is applied here in the preliminary development of a radiopharmaceutical wherein technetium is bonded to a chelating Schiff base functionality, which in turn is linked to a metabolically active glucose molecule.

A number of Schiff base complexes of Tc(V) and Tc(III) have been recently reported,[13-20] illustrating the efficiency of this class

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(1) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, F. L. *Prog. Inorg. Chem.* **1982**, *30*, 75-139.
(2) Lanteigne, D.; Hnatovich, D. J. *Int. J. Appl. Radiat. Isot.* **1984**, *35*, 617-621.
(3) Seifert, S.; Noll, B.; Muenze, R. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 1393-1398.
(4) Noll, B.; Seifert, S.; Muenze, R. *Int. J. Appl. Radiat. Isot.* **1983**, *34*, 581-584.
(5) Burgi, H. B.; Anderegg, G. A.; Blauenstein, P. *Inorg. Chem.* **1981**, *20*, 3829-3834.
(6) Brenner, D.; Davison, A.; Lister-James, J.; Jones, A. L. *Inorg. Chem.* **1984**, *23*, 3793-3797.
(7) DePamphilis, B. V.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1983**, *22*, 2292-2297.
(8) Davison, A.; Jones, A. G.; Orvig, C.; Sohn, M. *Inorg. Chem.* **1981**, *20*, 1629-1632.
(9) Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B. V.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988-1992.
(10) DePamphilis, B. V.; Jones. A. G.; Davies, M. A.; Davison, A. *J. Am. Chem. Soc.* **1978**, *100*, 5570-5571.
(11) Smith, J. E.; Byrne, E. F.; Cotton, F. A.; Sekutowsky, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 5571-5572.
(12) Pinkerton, T. C.; Desilets, C. P.; Hoch, D. J.; Mikelsons, M. V.; Wilson, G. M. *J. Chem. Educ.* **1985**, *62*, 965-973.
(13) Ichimura, A.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 2134-2139.
(14) Jurisson, S. S.; Dancey, K.; McPartlin, M.; Tasker, P. A.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4743-4749.

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Table I. Crystal Data for TcO(Glusal)(sal)

composition	$TcO_9NC_{20}H_{20}$
fw	516.38
cryst size, mm	0.12 × 0.14 × 0.31
space group	$P2_12_12_1$
unit cell params, Å	6.533 (2), 12.649 (4), 23.675 (7)
V, Å^3	1956 (1)
Z	4
ρ(calcd), g cm^{-3}	1.75
ρ(obsd) g cm^{-3}	1.73
μ(Mo Kα), cm^{-1}	7.6
radiation	Mo Kα
monochromator	graphite
$\theta_{min} - \theta_{max}$, deg	2–27
std reflcns	2 (stable)
temp, °C	22
no. of indep reflcns	2460
no. of reflcns with $I > 2\sigma(I)$	1445
no. of variables (last cycle)	280
final R_1,[a] R_2[a]	0.054, 0.057
final shift/error max	0.17
largest peak (eÅ^3) in final difference map	1.1
weighting	$1/w^2 = 1/\sigma^2(I) + 0.03I$
error in an observn of unit weight	1.3

[a] $R_1 = \sum|\Delta F_o|/\sum|F_o|$; $R_2 = (\sum w|\Delta F_o|^2/\sum w|F_o|^2)^{1/2}$.

of ligands in stabilizing different technetium centers. The structures of the Tc(V) derivatives are dominated by the electronic requirements of the tightly bonded Tc=O core. In particular, it has been observed that bidentate, monoanionic Schiff base ligands invariably give rise to complexes in which an anionic oxygen atom is situated trans to the Tc=O multiple bond.[20] This phenomenon is also observed in oxorhenium(V) complexes of bidentate Schiff bases[21-24] and of salicylaldehyde[25] and it is believed to hold for all monoanionic, bidentate ligands with N,O^- or O,O^- donor atom pairs.[26] Our preliminary investigations into the interactions of glucose–Schiff base bifunctional chelating agents with technetium(V) have led to the first example in which this general structural phenomenon is not observed. We report herein the results of these synthetic and structural investigations and comment on their relevance to the preparation of technetium-99m function-imaging radiopharmaceuticals.

Experimental Section

General Information. Technetium-99 emits a low-energy (0.292-MeV) β-particle with a half-life of 2.12×10^5 years. When this material is handled in milligram amounts, it 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. Technetium, as $[NH_4][TcO_4]$ in 0.1 mol dm^{-3} ammonia solution, was purchased from Radiochemical Centre, Amersham, U.K. $[As(C_6H_5)_4][TcOCl_4]$ was prepared as reported elsewhere.[9,27] IR spectra were recorded on a Perkin-Elmer 599 grating spectrometer using KBr pellets or in Nujol mulls between CsI disks. UV–vis spectra were recorded on a Cary 210 spectrophotometer at room temperature. Elemental analyses were performed on a Carlo Erba elemental analyzer Model 1106; the elemental analyses for the radioactive technetium compounds were carried out on a Packard liquid-scintillation instrument, Model TRI-CARB 300 C, with Insta-gel as scintillator, after dissolution of the samples in hydrogen peroxide–nitric acid solutions. *N*-Salicylideneglucosamine ($GlusalH_2$) and methyl *N*-salicylidene-3,5,6-triacetylglucosaminide (AcGlusalH) were prepared by the methods of Irvine and Earl.[28,29] Methanolic solutions of these ligands are stable for long periods, but in ethanol hydrolysis to salicylaldehyde (salH) and glucosamine occurs to a considerable extent. In acetone, tetrahydrofuran, and dimethyl sulfoxide, hydrolysis takes place rapidly upon dissolution as confirmed by UV–vis spectrophotometry, which detects the immediate presence of absorption bands due to free salH.

Preparation of Complexes. The salt $[As(C_6H_5)_4][TcOCl_4]$ (0.1 g) was treated with a 5-fold molar excess of $GlusalH_2$ in methanol, and the reaction mixture was stirred at room temperature for 15 min. The solution quickly became dark red. After slow evaporation of the solvent under an argon stream, red crystals of the final complex were collected and washed with methanol, H_2O, and ethanol and finally with Et_2O (yield, 90%).

Anal. Calcd. for TcO(Glusal)(sal): C, 46.43; H, 3.90; N, 2.71; O, 27.83; Tc, 19.13. Found: C, 47.08; H, 4.03; N, 2.85; O, 27.95; Tc, 18.41.

The reaction between $[As(C_6H_5)_4][TcOCl_4]$ with a 5-fold molar excess of AcGlusalH in methanol, at room temperature, proceeds readily upon mixing of the reagents, and the solution color turns to dark red. However, evaporation of the reaction solution leads to a brown-red

Table II. Positional (×10^4) and Thermal (Å^2 × 10^3) Parameters with Esd's in Parentheses

	x	y	z	B_{eq}
Tc	7366 (2)	4511.8 (7)	1386.1 (4)	2.23 (1)
O(1)	9454 (13)	4981 (7)	1079 (4)	3.4 (2)
O(2)	5419 (14)	4861 (6)	769 (4)	3.2 (2)
O(3)	7226 (12)	2981 (5)	1154 (3)	2.8 (2)
O(4)	8230 (12)	3990 (6)	2128 (4)	2.7 (2)
O(5)	4164 (13)	3998 (7)	1757 (4)	3.2 (2)
O(6)	9013 (12)	4475 (7)	3031 (3)	2.9 (2)
O(7)	12716 (14)	6600 (7)	2849 (4)	4.2 (2)
O(8)	2140 (14)	7423 (6)	2310 (4)	4.1 (2)
O(9)	12909 (24)	3658 (10)	3525 (6)	10.5 (4)
N(1)	6497 (14)	5763 (7)	1844 (4)	2.3 (2)
C(1)	5160 (18)	6473 (9)	1688 (5)	2.5 (2)
C(2)	4155 (19)	6508 (9)	1170 (5)	2.5 (2)
C(3)	4280 (19)	5739 (8)	747 (5)	2.3 (2)
C(4)	3163 (19)	5882 (10)	260 (6)	3.2 (2)
C(5)	1949 (22)	6765 (12)	183 (7)	4.8 (4)
C(6)	1779 (22)	7478 (12)	587 (7)	4.4 (3)
C(7)	2846 (24)	7359 (10)	1083 (6)	3.8 (3)
C(8)	3110 (18)	3375 (10)	1505 (6)	3.5 (3)
C(9)	3671 (20)	2673 (10)	1070 (6)	3.0 (3)
C(10)	5758 (23)	2507 (10)	909 (6)	3.2 (3)
C(11)	6161 (22)	1764 (11)	491 (7)	5.1 (4)
C(12)	4595 (26)	1170 (11)	245 (6)	4.8 (4)
C(13)	2561 (28)	1332 (13)	400 (6)	5.7 (4)
C(14)	2105 (23)	2102 (11)	799 (6)	4.8 (3)
C(15)	7412 (20)	5768 (7)	2421 (4)	2.2 (2)
C(16)	7694 (19)	4617 (8)	2584 (5)	2.8 (2)
C(17)	11044 (18)	4936 (9)	2988 (5)	2.2 (2)
C(18)	10717 (20)	6117 (10)	2898 (5)	2.7 (3)
C(19)	9555 (19)	6324 (9)	2389 (6)	2.9 (3)
C(20)	12161 (20)	4679 (9)	3510 (5)	3.7 (3)

(15) Jurisson, S.; Lindoy, L. F.; Dancey, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 227–231.
(16) Bandoli, G.; Nicolini, M.; Mazzi, U.; Refosco, F. *J. Chem. Soc., Dalton Trans.* **1984**, 2505–2511.
(17) Wilcox, B. E.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 2962–2967.
(18) Bandoli, G.; Mazzi, U.; Wilcox, B. E.; Jurisson, S.; Deutsch, E. *Inorg. Chim. Acta* **1984**, *95*, 217–223.
(19) Du Preez, J. G. H.; Gerber, T. I. A.; Fourie, P. J.; Van Wyk, A. J. *Inorg. Chim. Acta* **1984**, *82*, 201–205.
(20) Bandoli, G.; Mazzi, U.; Clemente, D. A.; Roncari, E. *J. Chem. Soc., Dalton Trans.* **1982**, 2455–2459.
(21) Bertolasi, V.; Ferretti, V.; Sacerdoti, M.; Marchi, A. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 971–974. Sacerdoti, M.; Bertolasi, V.; Gilli, G.; Duatti, A. *Ibid.* **1984**, *C40*, 968–970.
(22) Gilli, G.; Sacerdoti, M.; Bertolasi, V.; Rossi, R. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 100–104. Bertolasi, V.; Sacerdoti, M.; Gilli, G.; Mazzi, U. *Ibid.* **1982**, *B38*, 426–429.
(23) Roncari, E.; Mazzi, U.; Rossi, R.; Duatti, A.; Magon, L. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 169–173.
(24) Marchi, A.; Duatti, A.; Rossi, R.; Magon, L.; Mazzi, U.; Pasquetto, A. *Inorg. Chim. Acta* **1984**, *81*, 15–19.
(25) Duatti, A.; Rossi, R.; Marchi, A.; Pasquetto, A.; Mazzi, U. *Inorg. Chim. Acta* **1984**, *81*, 21–24.
(26) Bertolasi, V.; Ferretti, V.; Gilli, G.; Duatti, A.; Marchi, A.; Magon, L., submitted for publication.
(27) Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. D.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024–3029.
(28) Irvine, J. C.; Earl, J. C. *J. Chem. Soc.* **1922**, *121*, 2376–2381.
(29) Adam, J. M.; Hall, L. D. *J. Chem. Soc., Chem. Commun.* **1979**, 234–235. Adam, J. M.; Hall, L. D. *Can. J. Chem.* **1982**, *60*, 2229–2237.
(30) Cromer, D. T.; Waber, J. J. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table III. Bond Distances (Å) with Esd's in Parentheses

Tc-O(1)	1.656 (9)	C(2)-C(3)	1.398 (16)
Tc-O(2)	1.987 (9)	C(2)-C(7)	1.390 (18)
Tc-O(3)	2.015 (6)	C(3)-C(4)	1.376 (18)
Tc-O(4)	1.959 (9)	C(4)-C(5)	1.382 (19)
Tc-O(5)	2.360 (9)	C(5)-C(6)	1.319 (22)
Tc-N(1)	2.001 (9)	C(6)-C(7)	1.374 (22)
O(2)-C(3)	1.338 (14)	C(8)-C(9)	1.408 (19)
O(3)-C(10)	1.271 (16)	C(9)-C(10)	1.431 (20)
O(4)-C(16)	1.385 (14)	C(9)-C(14)	1.407 (20)
O(5)-C(8)	1.205 (16)	C(10)-C(11)	1.390 (20)
O(6)-C(16)	1.376 (14)	C(11)-C(12)	1.397 (22)
O(6)-C(17)	1.453 (14)	C(12)-C(13)	1.394 (25)
O(7)-C(18)	1.446 (16)	C(13)-C(14)	1.389 (21)
O(8)-C(19)	1.429 (14)	C(15)-C(16)	1.517 (14)
O(9)-C(20)	1.381 (18)	C(15)-C(19)	1.569 (17)
N(1)-C(1)	1.306 (15)	C(17)-C(18)	1.524 (17)
N(1)-C(15)	1.491 (14)	C(17)-C(20)	1.472 (17)
C(1)-C(2)	1.392 (17)	C(18)-C(19)	1.448 (18)

Table IV. Bond Angles (deg) with Esd's in Parentheses

O(1)-Tc-O(2)	97.2 (4)	C(4)-C(5)-C(6)	120.3 (1.4)
O(1)-Tc-O(3)	105.3 (4)	C(5)-C(6)-C(7)	120.1 (1.4)
O(1)-Tc-O(4)	106.1 (4)	C(2)-C(7)-C(6)	121.6 (1.3)
O(1)-Tc-O(5)	172.9 (4)	O(5)-C(8)-C(9)	128.8 (1.2)
O(1)-Tc-N(1)	100.8 (4)	C(8)-C(9)-C(10)	122.4 (1.2)
O(2)-Tc-O(3)	89.1 (3)	C(8)-C(9)-C(14)	117.9 (1.2)
O(2)-Tc-O(4)	156.7 (4)	C(10)-C(9)-C(14)	119.7 (1.2)
O(2)-Tc-O(5)	76.6 (3)	O(3)-C(10)-C(9)	121.9 (1.2)
O(2)-Tc-N(1)	92.4 (4)	O(3)-C(10)-C(11)	120.1 (1.3)
O(3)-Tc-O(4)	86.2 (3)	C(9)-C(10)-C(11)	118.0 (1.3)
O(3)-Tc-O(5)	78.3 (3)	C(10)-C(11)-C(12)	121.5 (1.4)
O(3)-Tc-N(1)	153.5 (4)	C(11)-C(12)-C(13)	120.6 (1.3)
O(4)-Tc-O(5)	80.2 (3)	C(12)-C(13)-C(14)	119.1 (1.5)
O(4)-Tc-N(1)	82.1 (4)	C(9)-C(14)-C(13)	120.9 (1.4)
O(5)-Tc-N(1)	76.4 (3)	N(1)-C(15)-C(16)	106.1 (8)
Tc-O(2)-C(3)	124.7 (8)	N(1)-C(15)-C(19)	108.4 (8)
Tc-O(3)-C(10)	127.7 (8)	C(16)-C(15)-C(19)	109.5 (9)
Tc-O(4)-C(16)	115.7 (7)	O(4)-C(16)-O(6)	111.5 (9)
Tc-O(5)-C(8)	120.2 (9)	O(4)-C(16)-C(15)	112.5 (9)
C(16)-O(6)-C(17)	117.7 (8)	O(6)-C(16)-C(15)	113.4 (9)
Tc-N(1)-C(1)	125.5 (8)	O(6)-C(17)-C(18)	106.0 (9)
Tc-N(1)-C(15)	112.7 (6)	O(6)-C(17)-C(20)	107.8 (9)
C(1)-N(1)-C(15)	121.6 (9)	C(18)-C(17)-C(20)	113.8 (1.0)
N(1)-C(1)-C(2)	125.9 (1.1)	O(7)-C(18)-C(17)	107.4 (1.0)
C(1)-C(2)-C(3)	125.5 (1.1)	O(7)-C(18)-C(19)	109.3 (1.0)
C(1)-C(2)-C(7)	116.4 (1.1)	C(17)-C(18)-C(19)	111.5 (1.0)
C(3)-C(2)-C(7)	117.9 (1.1)	O(8)-C(19)-C(15)	105.9 (9)
O(2)-C(3)-C(2)	125.6 (1.1)	O(8)-C(19)-C(1)	112.6 (1.0)
O(2)-C(3)-C(4)	115.9 (1.0)	C(15)-C(19)-C(18)	110.3 (1.0)
C(2)-C(3)-C(4)	118.5 (1.0)	O(9)-C(20)-C(17)	113.8 (1.1)
C(3)-C(4)-C(5)	121.4 (1.3)		

powder that decomposes upon dissolution in common solvents, thus preventing its characterization.

Collection of X-ray Data. Crystal data and other crystallographic parameters describing the title compound are given in Table I. Intensity data were collected on an Enrof-Nonius CAD-4 diffractometer with monochromated Mo Kα radiation and the $\theta/2\theta$ scan technique ($0 \le h \le 8$, $0 \le k \le 16$, $0 \le l \le 30$). Cell parameters were obtained by least-squares fitting of diffractometer angular values of 25 reflections having $9 < \theta < 14°$. Intensities were corrected for Lorentz polarization. Absorption corrections were negligible (minimum transmission factor = 96.4%; $\mu R = 0.11$) and were thus omitted. Scattering factors and anomalous scattering corrections were taken from ref 30.

Solution and Refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares analysis with anisotropic temperature factors used for all atoms but hydrogen. Hydrogen atoms were given calculated positions (C-H distance of 0.90 Å and fixed isotropic B's of 5.0 Å^2) except for the three hydroxyl hydrogen atoms of the sugar moiety, which were maintained fixed in the positions found from the difference map calculated after the first anisotropic refinement. Weights were applied according to the scheme given in Table I, and final statistical parameters are reported in the same table. Final positional and equivalent isotropic vibrational parameters[31] are shown in Table II. Tables of observed and calculated structure factors and anisotropic thermal parameters have been deposited as supplementary material. Bond distances and angles are given in Tables III and IV. All calculations were done with the CAD-4 SDP system of programs[32] and PARST.[33] A view of the molecule with the atom-labeling scheme is shown in Figure 1. The molecule is chiral in a noncentrosymmetric space group, and the solution given corresponds to the enantiomer with the smaller R factor ($R = 0.054$ for the solution reported, and $R = 0.057$ for the other enantiomer).

Results and Discussion

Synthesis and Reactivity. The formation of the red complex TcO(Glucal)(sal) from $TcOCl_4^-$ and excess $GlusalH_2$ in methanol occurs quickly, in high yield, at room temperature. The solvent seems to play an important role in the reaction, since the use of ethanol drastically decreases the yield of the final complex, while in tetrahydrofuran (THF), acetone, and dimethyl sulfoxide (Me_2SO) no product can be isolated. These observations presumably result from the different extents that $GlusalH_2$ hydrolyzes in these various solvents to give a salH and glucosamine. In THF, acetone, and Me_2SO, the $GlusalH_2$ ligand undergoes rapid hydrolysis, which is easly monitored by UV-vis spectrophotometry, and thus the main species present in solution immediately upon dissolution are SalH and glucosamine; under these conditions, no products can be isolated. In ethanol, hydrolysis occurs to some extent, and thus the yield of Schiff base complex in this solvent is decreased. In methanol, the ligand is stable over a long period, and thus a high yield of the desired Schiff base complex is obtained in this solvent.

Independent experiments show that in methanol, at room temperature, reaction of equimolar amounts of $TcOCl_4$, $GlusalH_2$, and salH does not yield any isolable TcO(Glusal)(sal) product. This observation is consistent with the known lack of reactivity of salH toward $TcOCl_4^-$[34] and square-pyramidal TcOCl(L) complexes[35] (L = tridentate, dianionic ligand) under the same experimental conditions. Thus, it is very unlikely that the coordinated sal of TcO(Glusal)(sal) originates from the reaction solution (i.e., from the hydrolysis of a *noncoordinated* Glusal ligand). It is much more likely that the coordinated sal$^-$ moiety originates from hydrolysis of a *coordinated* Glusal ligand. A plausible, but admittedly speculative, reaction mechanism incorporating this feature is shown in Figure 2. This proposed mechanism for the formation of TcO(Glusal)(sal) assumes that a Glusal moiety first coordinates as a tridentate ligand in the plane normal to the Tc=O linkage. A second Glusal moiety then coordinates, but it can only function as a bidentate ligand since there are only two coordination sites available on the TcO(Glusal)Cl intermediate. It is proposed that this bidentate coordination occurs with the anionic phenolic oxygen atom in the equatorial plane and the neutral imine nitrogen atom trans to the Tc=O linkage. In this coordination mode, hydrolysis of the Schiff base ligand directly yields a sal$^-$ ligand with the neutral carbonyl oxygen atom trans to the oxo group. This hydrolysis of the coordinated Schiff base may be enhanced by the strong trans electronic and labilizing effects known to be induced by coordinated oxo groups.[31] This proposed mechanism nicely accounts for the presence of an unusually coordinated sal$^-$ ligand in TcO(Glusal)(sal) (i.e., with the neutral carbonyl oxygen atom trans to the Tc=O linkage) since its generation is kinetically controlled.

The apparently facile hydrolysis of tridentate Schiff base ligands coordinated to technetium(V) will be important to the development of ^{99m}Tc radiopharmaceuticals. While this hydrolysis could be detrimental in many situations, it could also be used to advantage in the design of ^{99m}Tc radiopharmaceuticals that will decompose under certain situations encountered in vivo.

(31) Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.
(32) Frenz, B. A. In *Computing in Crystallography*; Schenck, H., Olthoff-Hazekamp, R., Van Koningsveld, H. Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; p 41.
(33) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95-100.
(34) Mazzi, U.; Roncari, E.; Bandoli, G.; Clemente, D. A. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 163-166.
(35) Mazzi, U.; Refosco, F.; Tisato, F.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* in press.

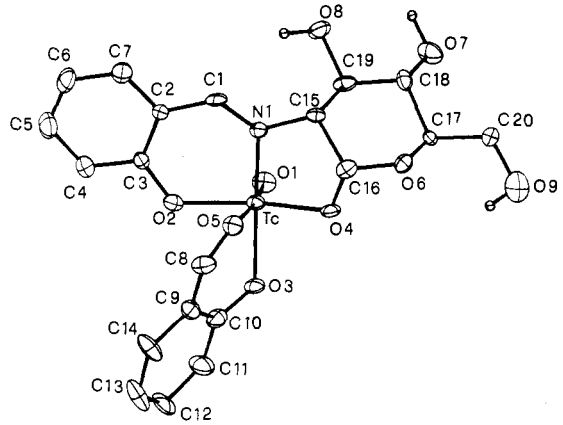

Figure 1. ORTEP[41] view of the molecule showing the thermal ellipsoids at 40% probability. The C–H hydrogens are omitted for clarity.

Properties. The complex TcO(Glusal)(sal) is nearly insoluble in all common solvents and is slightly soluble in methanol and H_2O. It is indefinitely stable in the solid state, but it slowly decomposes in solution. Faraday measurements show that it is diamagnetic in the solid state, but its solution instability precludes meaningful NMR measurements.

The IR spectrum of the complex exhibits a Tc=O stretching frequency at 970 cm^{-1}, which is at the upper limit of the 980–820-cm^{-1} range considered characteristic for this bond vibration.[1] This observation is indicative of a short Tc=O bond distance and, consequently, of a distorted-octahedral geometry for this complex. Quasi-octahedral or "umbrella-shaped" square-pyramidal complexes possess longer Tc=O bonds and exhibit Tc=O vibrations at lower frequencies. The C=N vibration of the Schiff base ligand is observed at 1600 cm^{-1} and is characteristic of chelation through the imine nitrogen atom and the phenolic oxygen atom. An intense broad band centered at 3300 cm^{-1} is attributed to the O–H stretches of the hydroxyl groups of the glucopyranose ring.

Crystal Structure of (*N*-Salicylidene-D-glucosaminato)(salicylaldehydato)oxotechnetium(V). The structure consists of discrete monomeric units linked by weak hydrogen bonds among the sugar moieties. There are no significantly short intermolecular contacts. Some intramolecular hydrogen bonds are present, i.e. O(8)–H···N(1), O(9)–H···O(6), and O(7)–H···O(8) (O···N = 2.93 (1) Å; average O···O = 2.92 (1) Å).

The coordination environment around Tc can be described as a distorted octahedron. If the axial positions are defined to be those of the oxo group and of the trans carbonyl oxygen atom of the salicylaldehydato ligand, the equatorial positions are occupied by the nitrogen and two anionic oxygen atoms of the tridentate ligand and by the phenolic oxygen atom of the salicylaldehydato moiety. The principal distortion from octahedral geometry is produced by the steric requirements of the oxo group as shown by the average O_{oxo}=Tc—L_{cis} angle of 102.3 (4)° or alternatively, by the 0.422 (1) Å displacement toward O(1) of Tc from the mean N(1),O(2),O(3),O(4) plane. None of the five- or six-membered rings formed by chelation are planar, the $\sum(\Delta/\sigma)^2$ values being 77.3 for Tc, N(1), C(1), C(2), C(3), and O(2), 724.0 for Tc, O(4), C(15), C(16), and N(1) and as high as 4500 for Tc, C(8), C(9), C(10), O(3), and O(5). The two phenyl rings are planar within the experimental errors, and the sugar ring is in its usual chair configuration.

The Tc–O_{oxo} distance of 1.656 (8) Å is indicative of a strong triple bond. Comparisons with some Tc(V) complexes containing the fragment O_{oxo}=Tc(V)—O_{trans} are reported in Table V. In this table are listed three different geometrical descriptors: Tc=O_{oxo} and Tc—O_{trans} distances, O_{oxo}—Tc—L_{cis} average angles, and the related quantity Δ, which is the Tc displacement from the average plane of the four cis ligands (L) in the direction of the O_{oxo} ligand. The present molecule displays the longest Tc—O_{trans} bond ever observed (2.359 Å), coupled with a correspondingly short Tc=O_{oxo} distance; the range of the latter (1.684–1.648 Å) is much narrower than that of the former (1.885–2.359 Å). All data of Table V can be easily rationalized in terms of the structural trans effect caused by the multiple Tc=O_{oxo} bond[36] and relative donor capabilities of the trans oxygen-donating ligands. When the trans ligand is alcoholate (RO^-), the strongest Lewis base, the Tc=O_{oxo} distance is relatively long and the Tc—O_{trans} distance is very short at 1.855 Å. This latter distance is as short as the shortest Tc—O_{cis} lengths encountered. In this situation the coordination is nearly octahedral with an average O_{oxo}=Tc—L_{cis} angle of 91.1° and a Δ value as small as 0.05 Å. Trans coordination of weaker donors (in the order phenolate, carboxylate, water, and aldehyde) causes a progressive lengthening of the trans Tc—O bond and an increasing pyramidalization of the coordination polyhedron, as measured by the increasing values of both O_{oxo}=Tc—L_{cis} mean angles and Δ. This can be seen as a transition from nearly pure octahedral to square-pyramidal geometry, which has been also observed in several Tc(V) oxo complexes.[1,18]

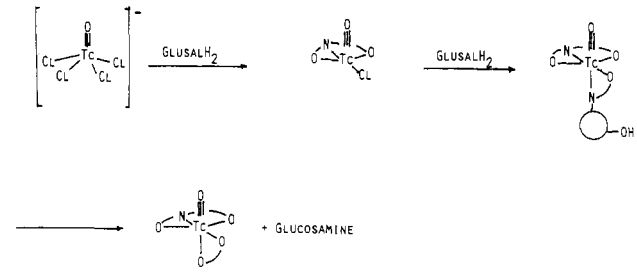

Figure 2. Possible mechanism of formation of the complex TcO(Glusal)(sal). Key: O–N–O = $Glusal^{2-}$; O–N–◯–OH = $GlusalH^-$; O–O = sal^-.

The most interesting feature of the TcO(Glusal)(sal) structure lies in the unusual position of the neutral carbonyl oxygen atom of the sal^- ligand trans to the Tc=O multiple bond. In all reported structures of oxotechnetium(V) and oxorhenium(V) complexes with bidentate, monoanionic ligands containing N,O^- or O,O^- donor atoms,[17,20-22,26] it has been invariably observed that such ligands are bonded with the charged oxygen atom trans to the oxo group. Though no oxotechnetium(V) complexes with sal^- have been reported,[34] octahedral oxorhenium(V)[25] and nitrene–rhenium(V)[37] complexes with this ligand have been prepared. In both cases that the sal^- ligand is arranged in the usual position with the charged oxygen atom trans to the Re=O or Re=N—R linkage. In a more directly analogous case, reactions of square-pyramidal complexes of the type TcO(L)Cl (where L is a tridentate O^-,N,O^- ligand) with bidentate N,O^- Schiff bases[35] led to octahedral complexes in which the bidentate base is coordinated with the charged oxygen atom trans to the Tc=O. It therefore appears to be a general rule that when cis and trans positions in M=O complexes are spanned, a bidentate N,O^- or O,O^- ligand will coordinate so as to place the more basic O^- oxygen atom trans to the M=O linkage. The fact that the sal^- ligand of TcO(Glusal)(sal) fails to follow this rule presumably results from the unique mechanism of formation of this complex. Whereas all the complexes that comprise the general rule were prepared by substitution of the N,O^- or O,O^- ligand onto a metal center, TcO(Glusal)(sal) appears to be formed by hydrolysis of a coordinated

(36) Shustorovich, E. M.; Porai-Koshita, M. A.; Buslaev, Yu. A. *Coord. Chem. Rev.* **1975**, *17*, 1–39.

(37) Marchi, A.; Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *Transition Met. Chem. (Weinheim, Ger.)* **1984**, *9*, 299–302.

(38) Zuckman, A.; Freeman, G. M.; Troutner, D. E.; Volkert, W. A.; Holmes, R. A.; Van Derveer, G.; Barefield, E. K. *Inorg. Chem.* **1981**, *20*, 2386–2389.

(39) Fackler, P. H.; Kastner, M. E.; Clarke, H. J. *Inorg. Chem.* **1984**, *23*, 3968–3972.

(40) Franklin, K. J.; Howard-Lock, H. E.; Lock, C. J. L. *Inorg. Chem.* **1982**, *21*, 1941.

(41) Johnson, C. K. "ORTEP"; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

Table V. Relevant Bond Distances (Å) and Angles (deg) in Tc(V) Octahedral Oxo Complexes with Esd's in Parentheses

compound	$d_{Tc-O_{oxo}}$	$d_{Tc-O_{trans}}$	O(trans) belonging to	mean angle O_{oxo}–Tc–L_{cis}	Δ^a	ref
$TcOBr_2(OEt)(Npy)_2$	1.684 (6)	1.855 (6)	R–O^-	91.1 (3)	0.05	39
$TcOCl(oxMe)_2$	1.649 (3)	1.994 (3)	Ar–O^-	96.2 (1)	0.22	17
$TcO(pam)_2$	1.657 (4)	2.214 (4)	R–COO^-	100.9 (2)	0.42	40
$\{TcO(H_2O)[(acac)_2en]\}^+$	1.648 (2)	2.282 (2)	H_2O	100.7 (1)	0.37	15
TcO(Glusal)(sal)	1.656 (8)	2.359 (8)	Ar–CHO	102.4 (4)	0.42	this work

$^a\Delta$ = displacement of the Tc atom from the mean plane of the cis ligands toward O_{oxo}. oxMe = 2-methyl-8-quinolate; $(acac)_2en$ = *N,N'*-ethylenebis(acetylacetone iminato); Npy = 4-nitropyridine; pam = D-penicillaminato.

Schiff base ligand (Figure 2). Thus, the coordination mode of sal^- in TcO(Glusal)(sal) appears to be kinetically controlled, and the steric requirements of the tridentate $Glusal^{2-}$ ligand presumably prevent sal^- from rearranging to the thermodynamically more favored coordination mode.

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Registry No. TcO(Glusal)(sal), 108343-78-8; $GlusalH_2$, 19124-29-9; $[As(C_6H_5)_4][TcOCl_4]$, 97101-52-5.

Supplementary Material Available: Complete listings of bond distances and angles and tables for anisotropic thermal parameters, hydrogen atom positional parameters, and least-squares planes (6 pages); a table of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

Notes

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Interruption of Conjugation in Transition-Metal-Bound Polyenes: A Reinvestigation of the X-ray Crystal Structure of (Hexamethylbenzene)tricarbonylchromium

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The lowering of symmetry in polyenes π-bound to transition metals and transition-metal fragments has been the subject of controversy for over 20 years.[1] As the accuracy of X-ray crystallographic investigations improve, more accurate values for C–C bond lengths may be determined in polyene rings of organometallic compounds. Early room-temperature X-ray crystallographic studies of $(C_6H_6)Cr(CO)_3$ showed equal C–C bond lengths, within experimental error, in the complexed benzene ring.[2,3] However, a more accurate low-temperature study, which combined X-ray and neutron diffraction, showed C–C bond length alternation.[4] The average difference was 0.017 (2) Å. A low-temperature X-ray study of $(C_6(CH_3)_6)Mo(CO)_3$ indicated that the bond length differences in this analogue averaged 0.036 (9) Å,[5] twice the value seen for $(C_6H_6)Cr(CO)_3$. It has been postulated[6] that long–short C–C bond length alternation should be seen for all $(C_6R_6)M(CO)_3$ (M = Cr, Mo, W) complexes. Small C–C bond length alternation has also been observed in X-ray crystallographic studies of $(C_5(CH_3)_5)M(CO)_2$ (M = Co,[7] Rh[8]) and $(C_5H_5)M(CO)_3$ (M = Mn,[9a] Re[9b]). In almost all cases, room-temperature X-ray studies[2,3,7,8,9] of these and similar complexes have not detected any consistent polyene distortion. The increased accuracy of the low-temperature studies is due to reduction of the carbon atom thermal motions, which obscure their exact positions in room-temperature X-ray studies.

Since an earlier room-temperature X-ray study of $(C_6(CH_3)_6)Cr(CO)_3$ showed no polyene ring distortion,[10] we decided

Table I. Crystallographic Data

formula	$C_{13}H_{18}CrO_3$
fw	298.30
cryst system	orthorhombic
space group	*Pbca*
syst absences	$0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$
a	13.622 (1) Å
b	13.369 (2) Å
c	15.162 (3) Å
vol	2761.2 Å^3
Z	8
d_{calcd}	1.43 g·cm^{-3}
data collection instrument	Enraf-Nonius CAD-4
radiation (graphite monochromated)	Mo Kα (λ = 0.710 73 Å)
cryst–detector dist	21 cm
detector aperture	2.0–2.6 mm horiz; 2.0 mm vert
scan type	ω–θ
scan rate	2–20°/min (in ω)
scan width	(0.7 + 0.350 tan θ)°
max 2θ	60°
no. of unique reflcns	4024
high peak in final diff map	0.28 (6) e/Å
temp	177 ± 1 K

refinement	full data	high angle
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2571	1076
no. of params refined	245	172
R_1[a]	0.031	0.025
R_2[b]	0.046	0.032
esd of an observn of unit wt	1.32	0.793

$^a R_1 = \sum(|F_o| - |F_c|)/\sum(F_o)$. $^b R_2 = (\sum[w(|F_o| - |F_c|)^2]/\sum[w(|F_o|)^2])^{1/2}$; $w = 4(F_o)^2/\sigma^2(F_o^2)$.

(1) (a) Jellinek, F. *J. Organomet. Chem.* **1963**, *1*, 43. (b) Jellinek, F. *Nature (London)* **1960**, *187*, 871. (c) Cotton, F. A.; Dollase, W. A.; Wood, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 1543. (d) Ibers, J. A. **J. Chem. Phys.** *1964*, *40*, 3129.
(2) (a) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 2271. (b) Corradini, P.; Allegra, G. *Atti Acad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1959**, *26*, 511. (c) Allegra, G. *Atti Acad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1961**, *31*, 241.
(3) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314.
(4) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1973, *B29*, 2515.
(5) Chesick, J. P.; Koshland, D. E.; Myers, S. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2013.
(6) Chinn, J. W.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930.
(7) Byers, L. F.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277.
(8) Lichtenberger, D. L.; Blevins, C. H., II; Ortega, R. B. *Organometallics* **1984**, *3*, 1614.
(9) (a) Fitzpatrick, P. J.; Le Page, Y.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2852. (b) Fitzpatrick, P. J.; Le Page, Y.; Butler, I. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1052.
(10) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1298.

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