manner as a "freer" radical resulting from outer-sphere reduction by a very reactive neutral or negative species. Recent pulse radiolytic experiments by Cohen and co-workers[43] point to substantial differences. Reaction of complexes XIX and XXI with either $CO_2^{-}\cdot$ or $\cdot C(CH_3)_2OH$ yielded the corresponding cobalt(III)-bound isonicotinoyl radicals, the decay of which (to Co^{2+}) may be monitored. The radical from XXI, as expected, decays unimolecularly by internal electron transfer, but those from several other isonicotinoyl complexes, including that from XIX, react predominantly with the parent Co(III) complex in a bimolecular path, (11). No evidence for the latter path is evident in reduction of complex XIX by Eu(II).[44]

$$Co^{III}\text{-}Lig\cdot + Co^{III}\text{-}Lig \rightarrow Co^{III}\text{-}Lig + Co^{2+} + Lig \qquad (11)$$

Although the exact structural features governing the partition between decay paths for radical-cations in Cohen's systems have not been pinpointed, it seems reasonable that a bimolecular reaction between a tripositive ion and a dipositive radical would be less favored in the vicinity of a tripositive Eu^{3+} ion than with the latter species absent. In any event, these differences serve to remind us that electron-transfer reactions, like proton transfers,[45] may be subject to significant kinetic medium effects that can be quite specific both to the nature of the supporting electrolyte[46] and to the particular reaction at hand.[47] In systems featuring a single reaction, these effects are reflected merely in changes in kinetic parameters. Where there are closely balanced competing reactions, however, differential ionic medium effects may operate so that the predominant reaction in one medium may become a minor contributor in another.

Registry No. I, 88129-97-9; II, 88129-99-1; III, 88130-01-2; IV, 28237-77-6; V, 88130-03-4; VI, 28589-22-2; VII, 88130-05-6; VIII, 88130-08-9; IX, 88130-11-4; X, 88130-14-7; XI, 88130-17-0; XII, 88130-20-5; XIII, 88130-23-8; XIV, 88130-26-1; XV, 88130-29-4; XVI, 88130-32-9; XVII, 88130-35-2; $Eu(ClO_4)_2$, 16645-73-1; $V(ClO_4)_2$, 27819-85-8; $U(ClO_4)_3$, 88130-36-3; $Cr(ClO_4)_2$, 13931-95-8.

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(43) Cohen, H.; Gould, E. S.; Meyerstein, D.; Nutkovich, M.; Radlowski, C. A. *Inorg. Chem.* **1983**, *22*, 1374.

(44) If reaction 11 were important in systems involving Eu^{2+} and complex XIX, the net reaction would be second rather than first order in Co(III) in the presence of excess Eu^{3+}. Kinetic profiles for the disappearance of Co(III) (0.001 M) in the presence of 0.08 M Eu^{3+} exhibit no distortion indicative of a second-order component.[4]

(45) See, for example: (a) More O'Ferrall, R. A.; Ridd, J. H. *J. Chem. Soc.* **1963**, 5035. (b) Guthrie, R. D.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5877.

(46) See, for example: (a) Toppen, D. L.; Linck, R. G. *Inorg. Chem.* **1971**, *10*, 2653. (b) Thamburaj, P. K.; Gould, E. S. *Ibid.* **1975**, *14*, 15.

(47) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 3854.

Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, and School of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB, United Kingdom

New Oxotechnetium(V) Complexes of *N*,*N'*-Ethylenebis(acetylacetone imine), *N*,*N'*-Ethylenebis(salicylideneamine), and *o*-Phenylenebis(salicylideneamine). X-ray Structures of the Complexes of *N*,*N'*-Ethylenebis(acetylacetone imine) and *N*,*N'*-Ethylenebis(salicylideneamine)

SILVIA JURISSON,[1a] LEONARD F. LINDOY,[1a,b] KEITH P. DANCEY,[1c] MARY McPARTLIN,[1c]
PETER A. TASKER,[1c] DALJIT K. UPPAL,[1c] and EDWARD DEUTSCH*[1a]

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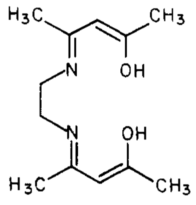
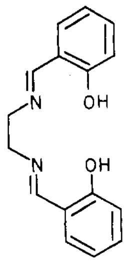
New technetium(V) oxo complexes of tetradentate Schiff base ligands have been synthesized and characterized. X-ray structure determination shows that the *N*,*N'*-ethylenebis(acetylacetone iminato) complex $[TcO(H_2O)(C_{12}H_{18}N_2O_2)]^+$ has a distorted octahedral coordination geometry, containing a *trans*-oxoaquatechnetium(V) core. Such a *trans*-$TcO(OH_2)^{3+}$ core is intermediate between the previously well-characterized monooxo, TcO^{3+}, and *trans*-dioxo, TcO_2^+, cores. The complex was isolated as a mixed chloride/bromide salt $[TcO(H_2O)(C_{12}H_{18}N_2O_2)]Br_{0.25}Cl_{0.75}$, which crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.935$ (4) Å, $b = 9.877$ (4) Å, $c = 7.324$ (3) Å, $\alpha = 87.266$ (9)°, $\beta = 102.498$ (12)°, $\gamma = 97.845$ (9)°, and $R = 0.0215$ for 2370 diffractometer data with $I \geq 3\sigma(I)$. The *N*,*N'*-ethylenebis(salicylideneaminato) complex $[TcOCl(C_{16}H_{14}N_2O_2)]$ also has a pseudooctahedral coordination geometry but contains a *trans*-oxochlorotechnetium(V) core and crystallizes in space group $P2_12_12_1$ with $a = 26.653$ (11) Å, $b = 11.697$ (5) Å, $c = 10.529$ (3) Å, and $R = 0.0642$ for 2105 diffractometer data with $I \geq 3\sigma(I)$.

Introduction

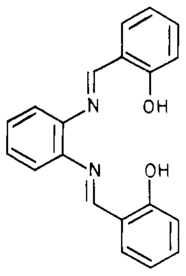
Although technetium has been studied since 1937,[2] much of the development of its coordination chemistry has occurred in the past decade.[3] A large part of this activity has arisen as a consequence of the utility of ^{99m}Tc in nuclear medicine; ^{99m}Tc has virtually ideal nuclear properties for use in radiopharmaceuticals.[4] However, the half-life of ^{99m}Tc is only 6 h and its long-lived daughter, ^{99}Tc ($t_{1/2} = 2.12 \times 10^5$ years), is normally used for preparative and other studies. ^{99}Tc complexes of a range of organic ligands have been reported, and in several cases their biological activity (organ specificity) has been investigated.[3] Although transition-metal complexes of the "classical" tetradentate Schiff base ligands **1–3** have



1, $(acac)_2enH_2$



2, $(sal)_2enH_2$



3, $(sal)_2phenH_2$

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(1) (a) University of Cincinnati. (b) On leave from James Cook University of North Queensland. (c) The Polytechnic of North London.

(2) Perrier, C.; Segrè, E. *J. Chem. Phys.* **1937**, *5*, 712.

(3) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983**, *30*, 75.

(4) Siegal, J. A.; Deutsch, E. *Annu. Rep. Inorg. Gen. Synth. 1975* **1976**, 311.

been known for many years,[5] technetium is one of the few d-block elements for which such complexes have not been prepared. We now report syntheses for $^{99}Tc(V)$ complexes of each of these ligands and the results of X-ray diffraction studies of the complexes of **1** and **2**.

Experimental Section

All common laboratory chemicals were of reagent grade. Salicylaldehyde, acetylacetone, and the diamines were used as obtained without further purification. The tetrabutylammonium bromide (Eastman) was labeled "suitable for polarography". ^{99}Tc was purchased from Oak Ridge National Laboratory as ammonium pertechnetate (30% H_2O_2 was added to oxidize any TcO_2 present prior to synthesizing (n-Bu_4N)[$TcOCl_4$]). Sephadex LH-20 was purchased from Pharmacia Fine Chemicals. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN, or Guelph Laboratories, Ltd., Guelph, Ontario, Canada. Visible–UV spectra were recorded in methanol or dichloromethane on a Cary 210 spectrophotometer at ambient temperature. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 599 spectrophotometer. The ^1H NMR spectra were obtained in dichloromethane-d_2 solution (Me_4Si as an internal reference) by using a Varian T-60 instrument. The Schiff base ligands were synthesized by literature methods.[6] They were purified by recrystallization from absolute ethanol, and their purity was confirmed by their melting points and ^1H NMR spectra. (n-Bu_4N)[$TcOCl_4$] was prepared as described elsewhere;[7] the vis–UV and IR spectral parameters of this material agreed with those reported in the literature.

Aqua[*N*,*N*′-ethylenebis(acetylacetone iminato)]oxotechnetium(V) Bromide. (n-Bu_4N)[$TcOCl_4$] (0.1553 g; 0.311 mmol) was dissolved in absolute ethanol (20 mL), and ligand **1** (0.0716 g; 0.320 mmol) was added. The resulting intense red-brown solution was stirred for ca. 30 min until all the ligand had dissolved. The reaction mixture was rotary evaporated to dryness; the residue was dissolved in a minimum volume of acetone (5–10 mL) and the resulting solution filtered. The filtrate was loaded onto a Sephadex LH-20 column (25 cm × 2.5 cm) prepared in acetone and was slowly eluted (2–3 h) with acetone; several bands were observed. The desired (major) product was red-brown and constituted the second band eluted. This eluted solution containing the product was filtered and solid (n-Bu_4N)Br (ca. 0.2 g) was added. When the mixture was allowed to stand overnight at room temperature, red-brown crystals of the product formed. These were collected by filtration, washed with acetone/ether followed by ether, and then dried over P_2O_5 in vacuo overnight to yield the hemihydrate. Anal. Calcd for $C_{12}H_{19}BrN_2O_{3.5}Tc$: C, 33.82; H, 4.49; N, 6.57. Found: C, 34.05; H, 4.96; N, 6.54. The crystal used for the X-ray study slowly formed when the filtrate from the above preparation was let stand at 0 °C for several days. It was air-dried and subsequently shown to contain a mixture of chloride and bromide anions.

[*N*,*N*′-Ethylenebis(salicylideneaminato)]oxotechnetium(V) Chloride. This was prepared from (n-Bu_4N)[$TcOCl_4$] and $(sal)_2enH_2$ by a method similar to that described above. After the crude reaction product was dissolved in acetone, the bright orange precipitate that remained was removed by filtration and discarded. The filtrate was chromatographed as above, and the red-brown fraction was collected, reduced in volume to 10 mL, and let stand. The red-brown crystals that formed were isolated, washed with acetone/ether, and dried over P_2O_5 in vacuo; yield 32%. Anal. Calcd for $C_{16}H_{14}ClN_2O_3Tc$: C, 46.11; H, 3.39; N, 6.72; Cl, 8.51. Found: C, 45.78; H, 3.63; N, 6.90; Cl, 8.74.

[*o*-Phenylenebis(salicylideneaminato)]oxotechnetium(V) Chloride. This was prepared from (n-Bu_4N)[$TcOCl_4$] by a method analogous to that described above. The product precipitated from the reaction solution and was removed by filtration, washed with absolute ethanol followed by ether, and then dried over P_2O_5 in vacuo. Yield: 72%. Anal. Calcd for $C_{20}H_{14}ClN_2O_3Tc$: C, 51.68; H, 3.04; N, 6.03. Found: C, 51.72; H, 3.40; N, 6.42.

Table I. Crystal Data and Selected[a] Details of the Structure Determinations of $[TcO(H_2O)((acac)_2en)]Br_{0.25}Cl_{0.75}$ and $[TcO((sal)_2en)Cl]$

mol formula	$C_{12}H_{20}Cl_{0.25}Br_{0.75}TcN_2O_4$	$C_{16}H_{14}ClTcN_2O_3$
M_r	402.0	416.9
a/Å	10.935 (3)	26.653 (6)
b/Å	9.877 (3)	11.697 (3)
c/Å	7.324 (3)	10.529 (3)
α/deg	87.27 (2)	(90)
β/deg	102.50 (2)	(90)
γ/deg	97.85 (2)	(90)
Z	2	8
space group	$P\bar{1}$	$P2_12_12_1$
μ(Mo Kα)/cm^{-1}	22.12	9.4
cryst size/mm	0.35 × 0.24 × 0.18	0.35 × 0.25 × 0.30
no. of data in refinement[b]	2370	2105
R[c]	0.0215	0.069
R_w[d]	0.0236	0.072

[a] Further information is available in supplementary Table 1S. [b] Intensity measurements were made on a Philips PW1100 diffractometer using Mo Kα radiation. For both structures unique data with $|F| > 6\sigma(|F_o|)$ were used in refinement. [c] $R = \Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

X-ray Diffraction Studies. The structures were determined by using a Philips PW1100 four-circle diffractometer. Crystal data and details of the refinement of structure are given in the supplementary material (Table 1S) and are summarized in Table I. The dark red-brown crystal of $[TcO(H_2O)((acac)_2en)]Br_{0.25}Cl_{0.75}$ used for the study was isolated from the acetone/ether filtrate obtained after removal of the main batch of product as described above. Refinement of the structure with the halide site having full occupancy Br^- converged to give R = 0.0936 and showed residual peaks of electron density near every atom of the cation. The anisotropic thermal parameters for all atoms were unusually low, with the exception of those of the Br^-, which were relatively high. These results and the method of isolation of the crystal (see above) suggested the possibility that the halide site contained Cl^-. Refinement with full occupancy Cl^- converged to give $R = 0.0581$, with normal thermal parameters for atoms in the cation but with high residual electron density around the halide site. Refinement of the structure was therefore attempted by assuming a mixed Br^-/Cl^- occupancy of the halide site. Difference Fourier maps obtained with C, N, O, and Tc atoms in unrefined positions were examined carefully in the region of the halide site. It was not possible to resolve the electron density into separate maxima for the Br and Cl atoms, and therefore, both atoms were assigned the same positional parameters and fixed thermal parameters (0.05) and their site occupation factors were refined (subject to the constraint that the total occupation was 1.000), giving values of 0.257 and 0.743, respectively. Site occupation factors for Br and Cl were then fixed to 0.25 and 0.75, and the structure was refined normally as outlined in Table 1S (supplementary material), with the halide ions constrained to have the same thermal and positional parameters, and gave $R = 0.0215$ and $R_w = 0.0236$ [where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and $w = 1/(\sigma(F_o))^2$].

The red-brown crystal of $[TcO((sal)_2en)Cl]$ used for the X-ray determination was selected from the crop obtained from the main preparation. Pseudosymmetry between the two molecules in the asymmetric unit led to high correlations between parameters for atoms in part a (molecule 1) and part d (molecule 2) and similar correlations between part b (molecule 1) and part c (molecule 2). Consequently, parameters for molecules 1 and 2 were refined in separate blocks with the equivalent bonds in part a and part d constrained to be equal within 0.02 Å and with similar treatment of bonds in part b and part c.

Results

The three Schiff base complexes were prepared from $[TcOCl_4]^-$ by direct substitution reactions. Vis–UV spectrophotometric data for these complexes in methanol and dichloromethane are listed in Table IV. All show intense absorptions in the 400–500-nm region. Each complex also exhibits an intense absorption in the 900–980-cm^{-1} region of the infrared spectrum. This absorption is due to the Tc=O stretching mode and is indicative of a monooxo Tc(V) species.[3,8] In

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(5) Holm, R. H.; Everett, G. W.; Chakavorty, A. *Prog. Inorg. Chem.* **1966**, 83–214. West, B. O. *New Pathways Inorg. Chem.* **1968**.

(6) McCarthy, P. J.; Hovey, R. J.; Ueno, K.; Martell, A. E. *J. Am. Chem. Soc.* **1955**, *77*, 5820. Lindoy, L. F.; Lip, H. C.; Moody, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 44.

(7) Davison, A.; Trop, H. S.; DePamphilis, B. V.; Jones, A. J. *Inorg. Synth.* **1982**, *21*, 160.

Table II. Fractional Atomic Coordinates and Thermal Parameters (Å^2)[a]

atom	x	y	z	U_{iso} or U_{eq}	atom	x	y	z	U_{iso} or U_{eq}
$[TcO(H_2O)((acac)_2en)]Br_{0.25}Cl_{0.75}$									
Br[b]	−0.10759 (5)	0.18185 (6)	0.01976 (10)	0.0509 (3)*	H(1a1)	0.617 (4)	0.189 (4)	−0.102 (6)	0.08 (1)
Cl[c]	−0.10759 (5)	0.18185 (6)	0.01976 (10)	0.0509 (3)*	H(1a2)	0.531 (4)	0.199 (4)	−0.286 (6)	0.07 (1)
Tc	0.33656 (2)	0.25582 (2)	0.24727 (3)	0.0287 (1)*	H(1a3)	0.505 (4)	0.081 (5)	−0.184 (7)	0.09 (2)
O(1a)	0.4262 (2)	0.1800 (2)	0.0688 (2)	0.037 (1)*	H(3a1)	0.428 (3)	0.395 (3)	−0.273 (5)	0.05 (1)
N(1a)	0.2787 (2)	0.4031 (2)	0.0649 (3)	0.034 (1)*	H(5a1)	0.307 (4)	0.633 (4)	−0.124 (6)	0.07 (1)
C(1a)	0.5342 (4)	0.1765 (4)	−0.1733 (5)	0.047 (2)*	H(5a2)	0.184 (4)	0.543 (4)	−0.249 (5)	0.06 (1)
C(2a)	0.4499 (2)	0.2437 (3)	−0.0804 (3)	0.031 (1)*	H(5a3)	0.312 (4)	0.561 (4)	−0.320 (7)	0.09 (1)
C(3a)	0.4047 (3)	0.3635 (3)	−0.1543 (3)	0.034 (1)*	H(1b1)	0.259 (3)	−0.141 (4)	0.676 (5)	0.06 (1)
C(4a)	0.3213 (2)	0.4364 (2)	−0.0896 (3)	0.028 (1)*	H(1b2)	0.260 (4)	−0.181 (4)	0.461 (6)	0.08 (1)
C(5a)	0.2797 (3)	0.5588 (3)	−0.2043 (4)	0.042 (2)*	H(1b3)	0.376 (4)	−0.104 (4)	0.601 (6)	0.08 (1)
O(1b)	0.3385 (2)	0.0685 (2)	0.3675 (3)	0.037 (1)*	H(3b1)	0.137 (3)	0.042 (4)	0.631 (5)	0.06 (1)
N(1b)	0.1931 (2)	0.2959 (2)	0.3569 (3)	0.033 (1)*	H(5b1)	0.054 (4)	0.363 (5)	0.599 (6)	0.09 (1)
C(1b)	0.2974 (4)	−0.1149 (4)	0.5679 (5)	0.049 (2)*	H(5b2)	0.016 (4)	0.209 (5)	0.631 (7)	0.10 (2)
C(2b)	0.2710 (2)	0.0228 (3)	0.4879 (4)	0.034 (1)*	H(5b3)	−0.026 (4)	0.264 (4)	0.466 (6)	0.07 (1)
C(3b)	0.1810 (3)	0.0878 (3)	0.5413 (4)	0.037 (1)*	HO(w1)	0.116 (4)	0.139 (4)	0.059 (5)	0.04 (1)
C(4b)	0.1428 (2)	0.2158 (3)	0.4793 (3)	0.033 (1)*	HO(w2)	0.172 (4)	0.054 (4)	0.042 (6)	0.06 (1)
C(5b)	0.0390 (3)	0.2596 (4)	0.5571 (5)	0.049 (2)*	H(6a1)	0.167	0.552	0.057	0.05
O(2w)	0.1740 (2)	0.1331 (2)	0.0486 (3)	0.039 (1)*	H(6a2)	0.090	0.410	0.006	0.05
O(3)	0.4590 (2)	0.3380 (2)	0.3895 (3)	0.039 (1)*	H(6b1)	0.071	0.433	0.308	0.05
C(6a1)[d]	0.1640 (4)	0.4589 (4)	0.0886 (5)	0.039 (1)	H(6b2)	0.210	0.500	0.369	0.05
C(6d2)[d]	0.2213 (9)	0.5012 (9)	0.1714 (13)	0.024 (2)	H(6d1)	0.177	0.560	0.085	0.05
C(6b1)[d]	0.1546 (5)	0.4309 (5)	0.2952 (7)	0.039 (1)	H(6d2)	0.283	0.548	0.261	0.05
C(6e2)[d]	0.1254 (10)	0.4127 (10)	0.2652 (13)	0.013 (2)	H(6e1)	0.106	0.466	0.360	0.05
					H(6e2)	0.052	0.383	0.180	0.05
$[TcO((sal)_2en)Cl]$[e]									
Tc(1)	0.21293 (6)	0.25911 (13)	0.20378 (15)	0.0438 (8)*	C(8b)	0.3992 (7)	0.1335 (18)	0.0031 (17)	0.075 (6)
Cl(1)	0.1767 (2)	0.0834 (3)	0.0985 (4)	0.050 (3)*	C(9b)	0.3793 (6)	0.2105 (18)	−0.0731 (20)	0.076 (6)
Tc(2)	0.52645 (6)	0.19214 (13)	0.27228 (15)	0.0459 (9)*	N(1c)	0.4801 (3)	0.3092 (9)	0.1839 (10)	0.042 (3)
Cl(2)	0.5480 (2)	0.3682 (3)	0.4000 (4)	0.056 (3)*	N(1d)	0.5782 (3)	0.2660 (11)	0.1582 (11)	0.054 (4)
N(1a)	0.1634 (4)	0.2116 (12)	0.3393 (10)	0.053 (4)	O(1c)	0.4777 (3)	0.1634 (9)	0.4114 (7)	0.048 (3)
N(1b)	0.2566 (4)	0.1363 (10)	0.2916 (13)	0.062 (4)	O(1d)	0.5784 (3)	0.1173 (9)	0.3801 (9)	0.045 (3)
O(1a)	0.1611 (3)	0.3456 (9)	0.1068 (9)	0.044 (3)	O(3cd)	0.5137 (4)	0.0909 (7)	0.1715 (8)	0.044 (3)
O(1b)	0.2560 (3)	0.2666 (11)	0.0501 (6)	0.050 (3)	C(1c)	0.4042 (5)	0.1798 (17)	0.5243 (15)	0.062 (5)
O(3ab)	0.2373 (4)	0.3627 (8)	0.2862 (12)	0.063 (3)	C(2c)	0.4332 (4)	0.2149 (12)	0.4211 (13)	0.043 (4)
C(1a)	0.0879 (6)	0.4446 (14)	0.0825 (16)	0.051 (5)	C(3c)	0.4131 (5)	0.2957 (11)	0.3347 (11)	0.031 (4)
C(2a)	0.1165 (4)	0.3693 (14)	0.1562 (13)	0.046 (4)	C(4c)	0.4362 (4)	0.3402 (13)	0.2254 (12)	0.037 (4)
C(3a)	0.0949 (6)	0.3204 (15)	0.2655 (14)	0.059 (5)	C(6c)	0.5027 (6)	0.3549 (18)	0.0690 (14)	0.064 (5)
C(4a)	0.1167 (5)	0.2428 (15)	0.3505 (15)	0.055 (4)	C(7c)	0.3644 (5)	0.3411 (15)	0.3579 (16)	0.050 (5)
C(6a)	0.1845 (8)	0.1284 (20)	0.4371 (19)	0.103 (7)	C(8c)	0.3363 (6)	0.3053 (16)	0.4648 (15)	0.059 (5)
C(7a)	0.0461 (6)	0.3611 (18)	0.2996 (21)	0.090 (6)	C(9c)	0.3557 (6)	0.2301 (16)	0.5437 (18)	0.065 (5)
C(8a)	0.0176 (7)	0.4369 (16)	0.2325 (17)	0.071 (5)	C(1d)	0.6581 (5)	0.0561 (14)	0.4375 (16)	0.051 (5)
C(9a)	0.0406 (6)	0.4781 (19)	0.1207 (18)	0.076 (6)	C(2d)	0.6271 (4)	0.1187 (13)	0.3556 (13)	0.041 (4)
C(1b)	0.3291 (6)	0.2541 (18)	−0.0635 (16)	0.063 (5)	C(3d)	0.6499 (4)	0.1756 (12)	0.2527 (12)	0.035 (4)
C(2b)	0.3014 (4)	0.2190 (14)	0.0416 (14)	0.050 (5)	C(4d)	0.6263 (4)	0.2464 (14)	0.1638 (14)	0.050 (4)
C(3b)	0.3230 (6)	0.1460 (15)	0.1335 (14)	0.052 (5)	C(6d)	0.5570 (6)	0.3639 (16)	0.0792 (23)	0.092 (6)
C(4b)	0.2992 (5)	0.1042 (15)	0.2431 (15)	0.054 (5)	C(7d)	0.7031 (4)	0.1644 (14)	0.2383 (16)	0.052 (4)
C(6b)	0.2311 (8)	0.0766 (19)	0.3943 (19)	0.104 (6)	C(8d)	0.7321 (7)	0.0945 (16)	0.3115 (16)	0.069 (5)
C(7b)	0.3719 (6)	0.1006 (17)	0.1125 (18)	0.068 (5)	C(9d)	0.7090 (5)	0.0426 (15)	0.4173 (16)	0.051 (5)

[a] Atoms marked with asterisks were refined anisotropically (see supplementary Table 4S). [b] Site occupation factor 0.25 (see text). [c] Site occupation factor 0.75 (see text). [d] Atoms of ethane bridge are disordered. Two sites for each were resolved, with occupation factors: C(6a1), 0.75; C(6b1), 0.75; C(6d2), 0.25; (C6e2), 0.25. [e] Hydrogen atoms for this structure were inserted in calculated positions (supplementary material).

trans-dioxo Tc(V) complexes, the Tc=O asymmetric stretch is expected to fall in the range 780–900 cm^{-1}. All complexes gave ^{1}H NMR spectra (dichloromethane-d_2) that were in accord with the expected structures. Attempts to characterize the complexes electrochemically were unsuccessful.[9]

The X-ray diffraction analysis of $[TcO(H_2O)((acac)_2en)]Br_{0.25}Cl_{0.75}$ shows the cation to be six-coordinate and have a somewhat distorted octahedral geometry with the TcO^{3+} core lying 0.39 Å above the coordination plane of the $(acac)_2en$ ligand. The Tc=O bond distance of 1.648 (2) Å (Table III) is short relative to comparable bonds in other Tc(V) complexes.[10] The strong structural trans influence of the doubly bonded oxygen results in the axially coordinated water molecule exhibiting a significantly lengthened Tc—O bond (2.3 Å vs. 2.0 Å for a typical single Tc—O bond.[10]

Crystal data together with details of the determination are summarized in Table I; atomic fractional coordinates and isotopic thermal parameters are listed in Table II. Selected bond lengths and angles are listed in Table III, and ORTEP

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(8) Clarke, M. J.; Fackler, P. H. *Struct. Bonding* (*Berlin*) **1982**, *50*, 57.

(9) The electrochemical redox behavior of the Tc complexes proved to be very complex. At room temperature and at normal scan rates, no reversible reduction or oxidation waves were observed (glassy-carbon working electrode; acetonitrile; ∼+1.8V to −2.0 V vs. Ag/AgCl) although much electrochemical activity was evident. When the solution was cooled to ca. −75 °C and scanning was done at fast rates, some electrochemical reversibility was evident. However, because of the overall complexity, no definitive characterization could be made and the redox chemistry of the complexes was not pursued further. The above results are perhaps not surprising since the reduction of Tc(V) to Tc(IV) would probably require the loss of the oxo group, which is not likely to be a reversible process.

(10) Bandoli, G.; Mazzi, V.; Roncari, E.; Deutsch, E. *Coord. Chem. Rev.* **1982**, *44*, 191.

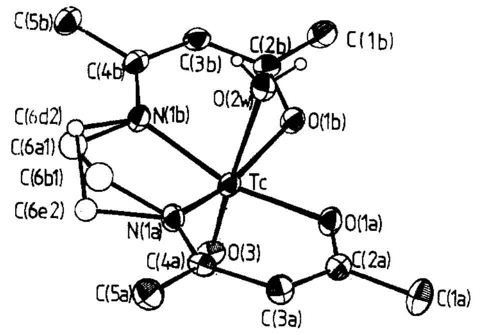

Figure 1. Structure of the $[TcO(H_2O)((acac)_2en)]^+$ cation, showing atom labels used in the tables (30% probability for thermal ellipsoids).

Table III. Selected Bond Lengths and Angles

	$[TcO(H_2O)((acac)_2en)]Br_{0.25}Cl_{0.75}$ (X = O(2w))		$[TcO((sal)_2en)Cl]$ (X = Cl)	
	part a	part b	part ad[a]	part bc[a]
	Bond Lengths/Å			
Tc-N(1)	2.001 (2)	2.003 (2)	2.022 (11)	2.067 (12)
Tc-O(1)	2.020 (2)	2.012 (2)	1.993 (9)	1.987 (8)
Tc-X	2.282 (2)		2.527 (4)	
Tc-O(3)	1.648 (2)		1.626 (11)	
	Bond Angles/deg			
O(1)-Tc-N(1)	92.3 (1)	93.1 (2)	92.9 (4)	93.5 (4)
O(3)-Tc-N(1)	102.3 (1)	101.7 (1)	94.5 (5)	93.4 (5)
O(3)-Tc-O(1)	99.7 (1)	99.3 (1)	100.7 (5)	101.3 (5)
X-Tc-N(1)	79.7 (1)	81.0 (1)	79.9 (4)	80.8 (4)
X-Tc-O(1)	77.7 (1)	78.7 (1)	84.9 (3)	84.1 (3)
O(1)-Tc-O(1)[b]	84.2 (1)		87.8 (4)	
N(1)-Tc-N(1)[b]	82.4 (1)		81.9 (4)	
O(3)-Tc-X	176.8 (1)		172.5 (4)	

[a] Mean values of the two halves of molecules that are correlated by pseudosymmetry, i.e. part a of molecule 1 with part d of molecule 2 and part b of molecule 1 with part c of molecule 2. [b] Denotes an atom in the alternative half of the molecule.

representations are given in Figures 1–3. Figure 3 (supplementary material) shows two $[TcO(H_2O)((acac)_2en)]^+$ cations hydrogen bonded to each other via two coordinated water molecules and two halide anions. The H···X distances of 2.49 and 2.37 Å are consistent with the presence of weak hydrogen bonding.

The $(sal)_2en$ complex contains two independent $[TcO((sal)_2en)Cl]$ molecules per asymmetric unit. These molecules have pseudooctahedral structures (Figure 2 and Table III) with only minor differences in ligand conformations. Crystal data are given in Table I, and atomic fractional coordinates and isotropic thermal parameters are listed in Table II.

Discussion

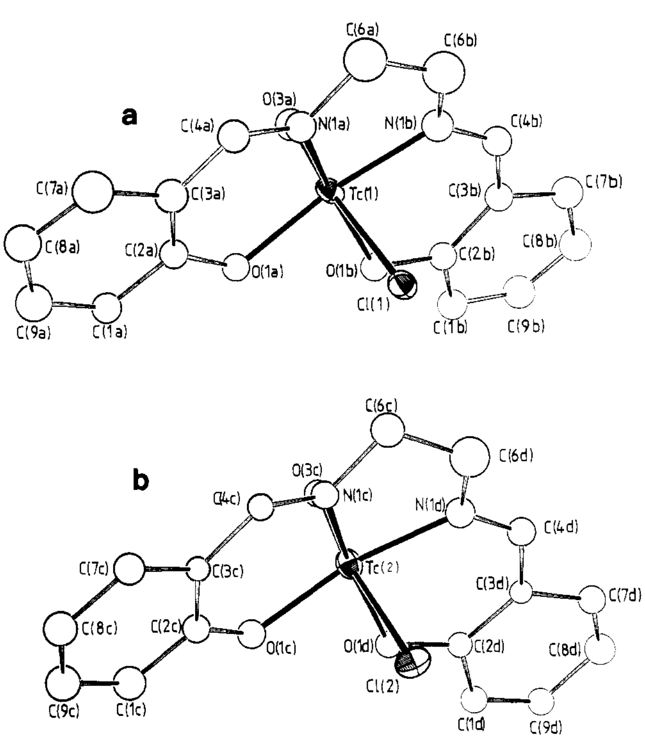

Figure 2. Structures of the two crystallographically independent molecules (a and b) of $[TcO((sal)_2en)Cl]$, showing atom labels used in the tables (30% probability for thermal ellipsoids).

The Tc complexes were all prepared by direct replacement of the chloride ligands on $[TcOCl_4]^-$ by the respective Schiff base ligands. The position of the λ_{max} in the visibile spectrum of each complex varies somewhat between coordinating (methanol) and noncoordinating (dichloromethane) solvents (Table IV). This effect most probably reflects the presence of different solvents in the site trans to the oxo group. Indeed, addition of simple monodentate ligands such as diethylamine or pyridine to these complexes in solution results in major spectral changes that again suggest that the sixth coordination site in each complex is readily occupied by suitable ligands. In agreement with this, the X-ray structure of the $(acac)_2en$ complex shows a water molecule weakly bound in this site. This structural feature is somewhat unusual. Tc(V) chemistry is dominated by the oxo group; a large number of reported Tc(V) complexes contain either the $Tc{=}O^{3+}$ or *trans*-TcO_2^+ cores.[3] The factors determining which of these cores a given Tc(V) complex will contain are not entirely understood, but charge neutralization of the Tc(V) center is clearly important. The $[TcO(H_2O)((acac)_2en)]Br$ complex reported here constitutes the first Tc(V) complex containing the *trans*-$TcO(OH_2)^{3+}$ core to be structurally characterized. This latter arrangement can be considered to be intermediate between the TcO_2^+ and TcO^{3+} cores. The other possible Tc(V) oxo core is $O{=}Tc{-}OH^{2+}$, and complexes containing this core have also recently been synthesized;[11] Davison et al. have

Table IV. Visible-UV Spectrophotometric Parameters

complex	solvent	color	λ_{max}/nm (ϵ/M^{-1} cm^{-1})
$[TcO(OH_2)((acac)_2en)]Br$	methanol	red-brown	418 (3940), 302 sh (6400), 263 sh (9080)
	CH_2Cl_2	red-brown	463 (1900), 302 sh (5080)
$[TcO(OH_2)((acac)_2pn)]Br$	methanol	red-brown	422 (3780), 302 (8860), 260 sh (11 380)
	CH_2Cl_2	red-brown	477 (3580), 291 (9905)
$[TcO(OH_2)((BuOac)_2en)]Br$	methanol	purple-brown	460 (4980), 291 (11 600)
	CH_2Cl_2	violet	512 (5990), 284 (14 490)
$[TcO(OH_2)((Bzlac)_2en)]Br$	methanol	red-brown	455 (6470), 320 (20 580), 296 sh (18 930)
	CH_2Cl_2	red-brown	475 (5090), 304 (16 730)
$[TcO(OH_2)((sal)_2en)]Br$	methanol	red-brown	415 (4900), 342 (17 750), 253 sh (26 670), 224 sh (51 920)
	CH_2Cl_2	red-brown	447 (3225), 332 sh (7470), 256 sh (11 530)
$[TcO(OH_2)((sal)_2phen)]Cl$	methanol	gold-orange	344 (20 680), 295 (22 180)
	CH_2Cl_2[a]	gold	337, 295

[a] Extinction coefficients not determined due to low solubility in CH_2Cl_2. $\epsilon_{337}/\epsilon_{295} = 0.846$.

reported complexes containing the related O=Tc—OR^{2+} core.[12,13]

Since the remaining complexes of type TcOLCl (L = (sal)$_2$en, (sal)$_2$phen) were isolated free of water, their structures were presumed to involve either a square-pyramidal coordination geometry with the oxo ligand occupying the axial site or a six-coordinate structure in which the axial ligands are oxo and chloro. Complexes showing related structures to each of these possibilities are known, but the former is considerably more common.[3] For the latter case, the Tc—Cl bond would be expected to be weak because of the trans influence of the oxo group. It is perhaps significant that [TcO(Ph-sal)$_2$Cl] (where Ph-sal = *N*-phenylsalicylideneaminato) has been shown to have an octahedral geometry, although in this case it is a phenolic oxygen that is trans to the Tc=O bond.[14] The distorted octahedral structure found for the two crystallographically independent [TcO((sal)$_2$en)Cl] molecules differs from the above in that the chloro ligand occupies the position trans to the oxo group. Consequently, the Tc—Cl bonds in the two independent molecules of [TcO((sal)$_2$en)Cl] (Table III) are significantly longer than in other technetium(V) complexes that show[10] lengths in the range 2.33–2.44 Å. The weak nature of the bonds to the atoms trans to the Tc=O units in [Tc(H$_2$O)((acac)$_2$en)]$^+$ and [TcO((sal)$_2$en)Cl] is reflected in the displacements of the Tc atoms from O$_2$N$_2$ coordination planes toward the axial oxo-oxygen atoms (by 0.37 Å in the (acac)$_2$en complex and by 0.28 and 0.25 Å in molecules 1 and 2, respectively, of the (sal)$_2$en complex).

Since many substituted derivatives of the parent Schiff base ligands **1**–**3** have been reported, the synthetic procedure adopted in the present work should be readily applicable to the production of a range of related Tc(V) complexes exhibiting a gradation of structural and electronic properties.[15] Such a variation in properties is expected to result in corresponding changes in the biological activity of the Tc complexes. The availability of such a series of complexes may thus prove useful for the systematic development of new Tc reagents for use in nuclear medicine. An investigation of this type is planned for the future.

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Registry No. [TcO(H$_2$O)((acac)$_2$en)]Br, 87761-77-1; [TcO((sal)$_2$en)Cl], 87761-78-2; [TcO((sal)$_2$phen)Cl], 87761-79-3; [TcO(H$_2$O)((acac)$_2$en)]Br$_{0.25}$Cl$_{0.75}$, 87761-80-6; [TcO(H$_2$O)((acac)$_2$pn)]Br, 87761-81-7; [TcO(H$_2$O)((BuOac)$_2$en)]Br, 87761-82-8; [TcO(H$_2$O)((Bzlac)$_2$en)]Br, 87761-83-9; (*n*-Bu$_4$N)[TcOCl$_4$], 71341-65-6.

Supplementary Material Available: Tables giving full details of the determination and refinement of structures, anisotropic thermal parameters, least-squares planes and deviations, bond lengths and angles, H atom positional parameters, ^{1}H NMR data for all the complexes, and structure factors and Figure 3, showing the hydrogen bonding in [TcO(H$_2$O)((acac)$_2$en)]Br$_{0.25}$Cl$_{0.75}$ (41 pages). Ordering information is given on any current masthead page.

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[11] Vanderheyden, J.-L.; Ketring, A. R.; Libson, K.; Heeg, M. J.; Roecker, L.; Motz, P.; Whittle, R.; Elder, R. C.; Deutsch, E., submitted for publication.

[12] Trop, H. S.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1980**, *19*, 1993.

[13] Related to this latter complex is [TcO(C$_5$H$_9$NO$_2$S)(C$_5$H$_{10}$NO$_2$S)] (where C$_5$H$_{11}$NO$_2$S = D-penicillamine). An X-ray structural determination shows this complex to contain S$_2$N$_2$ equatorial donors with one axial site being filled by an oxo group while the other is occupied by a deprotonated carboxylic oxygen from one of the D-penicillamine ligands: Franklin, K. J.; Howard-Lock, H. E.; Lock, C. J. L. *Inorg. Chem.* **1982**, *21*, 1941.

[14] Bandoli, G.; Mazzi, U.; Clemente, D. A.; Roncari E. *J. Chem. Soc., Dalton Trans.* **1982**, 2455.

[15] Complexes of the type [TcO(H$_2$O)L] where L = *N*,*N*′-1,2-propylenebis(acetylacetone iminato), *N*,*N*′-ethylenebis(*tert*-butoxyacetoacetone iminato), and *N*,*N*′-ethylenebis(benzoylacetone iminato) were also isolated in the present study by using a procedure identical with that described in the Experimental Section. These products gave spectral and chromatographic properties similar to those of [TcO(H$_2$O)((acac)$_2$en)] and are undoubtedly similar in structure to this complex. However the microanalytical data for these products fell slightly outside the expected ranges in each case. The ^{1}H NMR data for all these complexes are included in Table 7S of the supplementary material.

Contribution from the Department of Chemistry,
New Mexico State University, Las Cruces, New Mexico 88003

Kinetics of the Primary Interaction of Pentacyanonitrosylferrate(2–) (Nitroprusside) with Aliphatic Thiols

MICHAEL D. JOHNSON and RALPH G. WILKINS*

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The kinetics of formation and dissociation of adducts of pentacyanonitrosylferrate(2–) (nitroprusside) with a number of aliphatic thiols (RSH) have been measured by the temperature-jump/stopped-flow combination. The second-order rate constant for the formation of Fe(CN)$_5$N(O)SR^{3-} is pH dependent, and this is rationalized by assuming that only the RS$^-$ species is reactive (k_{RS^-}) with 2-mercaptoethanol, 1-pentanethiol, *N*-acetylcysteine, mercaptosuccinate, cysteine, 2-aminoethanethiol, and glutathione. With the three amino thiols, it is found that the forms containing the H$_3$N$^+$–S$^-$ and the H$_2$N–S$^-$ moieties are similar in reactivity. The dissociation of the adducts of nitroprusside with the simpler thiols is pH independent (from 6 to 12), but those of the amino thiols except glutathione are pH dependent and this is ascribed to NH$_2$ protonation weakening the N–S bond. The value of k_{RS^-} (3×10^3–4×10^4 M^{-1} s^{-1} at 25 °C) varies little with the variety of thiols studied, and the associated ΔH^{*} values are similar (~8 kcal mol^{-1}). There is a much larger variation in the adduct dissociation rate constants (from 12 to 3×10^3 s^{-1}) and attendant ΔH^{*} and ΔS^{*} values.

The pentacyanonitrosylferrate(2–) (nitroprusside) ion undergoes addition reactions with a variety of bases (X^{n-}):[1,2]

$$\mathrm{Fe(CN)_5NO^{2-} + X^{n-} \rightleftarrows Fe(CN)_5NOX^{(n+2)-}} \qquad (1)$$

The base may attack either the oxygen or nitrogen atom of the coordinated nitrosyl. Adduct formation (eq 1) is usually heralded by a marked color increase, and this is followed by color fading as further reactions occur. These are usually redox in nature with Fe(CN)$_5$OH$_2$$^{3-}$ (or a polymeric derivative) as the iron product.[1,2] Kinetic data are available for reactions of nitroprusside with OH$^-$,[3,4] SO$_3$$^{2-}$,[5] N$_3$$^-$,[6] NH$_2$OH,[6]

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[1] Swinehart, J. H. *Coord. Chem. Rev.* **1967**, *2*, 385.

[2] Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: New York, 1976; p 134.

[3] Swinehart, J. H.; Rock, P. A. *Inorg. Chem.* **1966**, *5*, 573.

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