to the metal are capable of binding nonsynergistic anions and of affecting the reactivity of the metal.[24,25]　A different spatial arrangement of these clusters of positive charges in the two sites could account for the intersite differences. Refinement at higher resolution of the X-ray three-dimensional structure, which is now available for iron lactoferrin at 3.2-Å resolution,[26] could give the appropriate answers.

The results of the kinetic experiments on other metallotransferrins such as manganese(III) transferrin and copper(II) transferrin give us the opportunity of discussing the role played by the metal in the overall process.

In the case of manganese(III) transferrin, the profiles of the kinetic parameters versus PP concentration strictly resemble those observed for iron transferrin. Again, the data may be reproduced quite well with eq 2. The major difference between the two series of data resides in the fact that for the same values of PP concentration both of the kinetic constants of the manganese derivative are about 1 order of magnitude larger than the corresponding kinetic constants of iron transferrin. This suggests that the same

mechanism of metal release is operative for both derivatives and that the substitution of iron(III) with the more labile manganese(III) ion only causes an increase of the intrinsic rate of the conformational transition.

An analogous interpretative scheme could hold also for the previously investigated copper derivative,[7] even if in the latter case the separation of the linear term from the hyperbolic one is more questionable. This could be ascribed to the fact that for copper transferrin the terms k_1 and k_1' are of comparable magnitude.

Concluding Remarks

The present study suggests that accurately determined experimental data obtained for the iron removal reaction from transferrin by pyrophosphate exhibit a complex pattern and cannot be rationalized on the grounds of simple kinetic models. Indeed, the previous models proposed by Raymond[21] and Bates[20] appear unable to account for them. An extension of the Bates model is needed to interpret the data and to provide a mechanistic support to the empirical Harris equation. In this framework a satisfactory and exhaustive interpretation of the data of PP as well of the effects of chaotropic agents and metal substitution is given. The role of residues of the metal binding cavity that are not directly coordinated to the metal but lie in its immediate surroundings is emphasized, and intersite differences are stressed.

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Synthesis and Characterization of Technetium(V) Complexes with Amine, Alcoholate, and Chloride Ligands

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Two general routes for the preparation of technetium complexes with aromatic amine, chloride, and alkoxide ligands are presented. The reactions of the tetrachlorooxotechnetate(V) anion of $(n\text{-}Bu_4N)[TcOCl_4]$ with pyridine in tetrahydrofuran/alcohol solvent or of the dioxotetrakis(pyridine)technetium(V) cation of $[TcO_2(py)_4]Cl$ with LiCl in sulfuric acid/alcohol both yield a neutral alkoxydichlorooxobis(pyridine)technetium(V) complex. The same isomer appears to result from either route. The analogous thiazole derivatives may be prepared in a like manner. The complex chloro(1,2-ethanediolato)oxo(1,10-phenanthroline)technetium(V), $TcOCl(C_2H_4O_2)(C_{12}H_8N_2)$, is prepared from $(n\text{-}Bu_4N)[TcOCl_4]$ with 1,2-ethanediol and 1,10-phenanthroline in methanol. This complex was characterized by IR, UV/vis, and ^1H and ^{99}Tc NMR spectroscopies and by fast atom bombardment mass spectrometry. Further insight into the bonding in this complex comes from the single-crystal X-ray structure determination. The space group is monoclinic, $P2_1/c$, with $a = 7.440$ (2) Å, $b = 8.928$ (3) Å, $c = 21.355$ (4) Å, $\beta = 92.48$ (2)°, $V = 1417.2$ (7) Å^3, and $Z = 4$. The structure was solved by standard methods and refined to $R = 0.051$ and $R_w = 0.036$ based on 1859 reflections. The oxo and chloride ligands are mutually cis in the highly distorted octahedral coordination sphere. The unusually long Tc–Cl bond length (2.418 (2) Å) is attributed to a trans influence exerted by the coordinated diolate. This effect combined with short lengths for the C–C bond (1.491 (1) Å) and for the O–Tc–O linkage (1.924 (4), 1.902 (3) Å) suggests partial multiple bonding between the technetium and the diolate.

Introduction

Since the discovery[2] of *trans*-$[TcO_2(py)_4]^+$, there has been considerable interest in oxotechnetium(V) complexes with aromatic amine ligands. Some of these compounds have been investigated as potential ^{99m}Tc diagnostic radiopharmaceutical agents,[3] and

they have been used as ligand substitution reagents for the preparation of novel species.[4]

Clarke[5] recently reported a series of mixed-ligand complexes with stoichiometry $TcOX_2(A)_2(OR)$ (A = 4-cyanopyridine, 4-nitropyridine; X = Cl, Br; R = Me, Et) related to the compound $TcOCl_2(bpy)(OEt)$,[6] previously prepared in our laboratory. It had been postulated that these complexes can only be isolated when an electron-withdrawing amine is used. It was speculated, how-

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ever, that similar complexes with unsubstituted pyridine were reaction intermediates in the formation of $[TcO_2(py)_4]^+$ and a series of μ-oxo dimers.[7]

The use of diolate ligands to substitute for the chlorides on $(n\text{-}Bu_4N)[TcOCl_4]$ has been well established for Tc(V) complexes such as $Na[TcO(eg)_2]^8$ (eg = 1,2-ethanediolate), $(n\text{-}Bu_4N)\text{-}[TcO(catecholate)_2]$,[8] and $Na_3[TcO(glucoheptanate)_2]$.[9] The oxotechnetium–bis(diol) complexes have proven extremely useful as a source of the TcO^{3+} core for ligand exchange under mild conditions.[10] Other examples of technetium diolate complexes include the recently described[11] series of complexes TcO(eg)L, prepared by treating $NaTcO(eg)_2$ with L (where L is a polyamino carboxylate ligand). The exact coordination environment of these characteristically pale blue species remains unclear since they do not form single crystals suitable for X-ray diffraction.

Since the non-oxo ligands of dioxotetrakis(pyridine)technetium(V) and oxotetrachlorotechnetate(V) had been shown to be labile, it was reasonable to expect that under appropriate conditions a variety of mixed-ligand complexes with a combination of halides, alkoxides, and aromatic amines could be prepared. Herein we report the preparation of a number of such complexes: $TcOCl_2(A)_2(OR)$ (A = py, thiazole (tz); R = Et, Me) and $TcOCl(AA)(OCH_2CH_2O)$ (AA = bpy, phen). The former series can be prepared without the need for electronegative substituents on the ligands via two different routes: substitution of Cl⁻ for A in $[trans\text{-}TcO_2(A)_4]Cl$ with alcohol solvent and substitution of A for Cl⁻ in $(n\text{-}Bu_4N)[TcOCl_4]$ in THF/alcohol.

Experimental Section

Instrumentation. Fourier transform IR spectra were measured from 4800 to 400 cm⁻¹ on an IBM IR/30S spectrometer with DTGS detector and 2-cm⁻¹ bandwidth. Infrared absorptions from 400 to 200 cm⁻¹ were measured on a Perkin-Elmer 1430A grating spectrometer. ¹H NMR spectra were recorded at 250 MHz on a Bruker WM-250 spectrometer.

Technetium-99 NMR spectra were recorded at 90.232 MHz with a Varian XL-400 instrument. A 15-μs pulse width and 0.15-s acquisition time were used. The spectral width was set at 10^5 Hz and digitized with 30016 data points in the FID weighted with 100-Hz Gaussian line broadening. Since the reference sample $(NH_4[^{99}TcO_4]$ in D_2O, 0 ppm) resonates at 90.032 MHz in this spectrometer, a difference greater than the maximum spectral width (10^5 Hz) obtainable, chemical shifts were calculated manually on the basis of spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. The resulting uncertainty in chemical shift is estimated at ±2 ppm.

Fast atom bombardment mass spectra of samples dissolved in a 3-nitrobenzyl alcohol matrix were recorded with a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV. The source was equipped with an Ion Tech B11N FAB gun producing a beam with 6–8-keV xenon neutrals.

Ultraviolet and visible absorption spectra were recorded on a Hewlett Packard 8451A photodiode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

Syntheses. *Caution!* ⁹⁹Tc is a β^- emitter $(t_{1/2} = 2.1 \times 10^5 \text{ years})$. All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes with precautions outlined elsewhere.[12]

All solvents were of at least reagent grade and used as received, except for MeOH, which was distilled from I_2-activated Mg turnings. Water was passed through a Barnstead Ultrapure ion-exchange column and distilled with a Corning AG-1 glass still. The complexes $(n\text{-}Bu_4N)\text{-}[TcOCl_4]^{12b,13}$ and $[TcO_2(py)_4]Cl^7$ were prepared by literature methods.

Preparation of TcOCl₂(py)₂(OMe). Method 1. Into a disposable vial was weighed 52.94 mg of $(n\text{-}Bu_4N)[TcOCl_4]$ (0.106 mmol) followed by 1 mL of THF to dissolve the solid. Upon addition of 3 drops of pyridine, an intense green color formed. After addition of 0.25 mL of MeOH, a green precipitate gradually formed. The precipitate was redissolved by heating and adding an additional 1.5 mL of THF. The reaction mixture was cooled to −20 °C, where the product crystallized as small plates. The crystals (30.13 mg, 76%) were filtered out with a medium-porosity fritted-glass funnel, washed with cold THF, H_2O, and hexanes, and dried in vacuo at room temperature. This product is soluble with gradual decomposition in CH_2Cl_2 and $CHCl_3$.

Method 2. Into a disposable vial was weighed 22.00 mg of $[TcO_2\text{-}(py)_4]Cl$ (0.046 mmol) followed by 1.50 mL of 0.71 M LiCl (Mallinckrodt) in MeOH. To the resulting orange-brown solution was added with stirring 2 drops of concentrated H_2SO_4 (Mallinckrodt). The blue-green precipitate (12.62 mg, 74%) that formed immediately was filtered out with a fine-porosity fritted-glass funnel, rinsed with MeOH, H_2O, and hexanes, and then dried in vacuo at room temperature. The infrared spectrum of this product is identical with that made by method 1.

Anal. Calcd for $C_{11}H_{13}Cl_2N_2O_2Tc$: C, 35.11; H, 3.58; Cl, 18.66; N, 7.36. Found: C, 35.23; H, 3.49; Cl, 18.91; N, 7.47.

IR (KBr): 3113 (w), 2907 (w), 2813 (w), 1607 (s), 1483 (m), 1451 (s), 1444 (s), 1352 (w), 1244 (w), 1208 (m), 1159 (m), 1120 (s), 1071 (m), 1064 (s), 1048 (m), 1017 (m), 954 (s), 939 (s), 931 (s), 769 (s), 753 (m), 695 (s), 684 (s), 644 (m), 505 (m), 458 (w), 340 (m), 330 cm⁻¹ (m). ¹H NMR (CD_2Cl_2): δ 8.95 (d, 4 H), 7.95 (m, 2 H), 7.55 (t, 4 H), 3.43 (s, bound MeO⁻), 3.35 (s, free MeOH). UV/vis (CH_2Cl_2): λ_{max} (ε) 308 nm (6500 L·mol⁻¹·cm⁻¹), 650 (100).

Preparation of TcOCl₂(py)₂(OEt). Method 1. Into a disposable vial was weighed 22.56 mg of $(n\text{-}Bu_4N)[TcOCl_4]$ (0.045 mmol) followed by 1.5 mL of THF to dissolve the sample. Three drops of pyridine were added with stirring followed by an equal volume of absolute EtOH. Some yellow needles, presumably $[TcO_2(py)_4]Cl$, which formed on cooling to −20 °C, were removed by filtration through paper. A mixture of $CHCl_3$ and EtOH (2:1) was added to the green filtrate, and the resulting solution was concentrated by evaporation. On subsequent cooling to −20 °C, silvery-green plates (5.36 mg, 40%) formed, which were filtered out with a medium-porosity fritted-glass funnel, rinsed with EtOH and hexanes, and dried in vacuo at room temperature. The product is slightly soluble in alcohol and soluble in CH_2Cl_2.

Method 2. Into a disposable vial was weighed 17.76 mg of $[TcO_2\text{-}(py)_4]Cl$ (0.037 mmol) followed by 2 mL of 0.16 M LiCl in absolute EtOH. To the resulting brown solution was added with stirring 2 drops of concentrated H_2SO_4. Within 1 min, small green crystals formed (4.07 mg, 38%), which were filtered out with a medium-porosity fritted-glass funnel, rinsed with EtOH, MeOH, H_2O, and hexanes, and then dried in vacuo at room temperature. The infrared spectrum of this product is identical with that of the product made by method 1.

Anal. Calcd for $C_{12}H_{15}Cl_2N_2O_2Tc$: C, 37.22; H, 3.99; N, 7.28. Found: C, 37.04; H, 3.89; N, 7.20.

IR (KBr): 3098 (w), 3076 (w), 3031 (w), 2977 (w), 2929 (w), 2859 (w), 1608 (m), 1484 (w), 1452 (s), 1355 (w), 1345 (w), 1240 (w), 1215 (m), 1103 (s), 1071 (s), 1049 (m), 1016 (w), 947 (s), 939 (m), 919 (s), 877 (w), 765 (s), 693 (s), 646 (m), 578 (w), 463 (w), 411 (w), 401 cm⁻¹ (w). ¹H NMR (CD_2Cl_2): δ 9.07 (d, 4 H), 8.01 (m, 2 H), 7.61 (t, 4 H), 3.79 (q, 2 H), 1.02 (t, 3 H). UV/vis (CH_2Cl_2): λ_{max} (ε) 646 nm (70 L·mol⁻¹·cm⁻¹).

Preparation of TcOCl(eg)(phen). To 51.61 mg of $(n\text{-}Bu_4N)[TcOCl_4]$ (0.103 mmol) in a disposable vial were added 2.5 mL of MeOH and 1.5 mL of 1,2-ethanediol (Fisher). The resulting blue solution[14] was stirred for several minutes before adding 32 mg of crystalline 1,10-phenanthroline hydrate (Baker, 0.162 mmol) with vigorous stirring. The solution immediately became bright green, and a green microcrystalline precipitate gradually formed. The solid (29.87 mg, 73%) was collected on a medium-porosity fritted-glass funnel, rinsed with methanol and hexanes, and dried in vacuo at room temperature. The product is soluble in $CHCl_3$, CH_2Cl_2, and MeCN; it dissolves with decomposition to a purple product in water.

Anal. Calcd for $C_{14}H_{12}ClN_2O_3Tc$: C, 43.05; H, 3.10; Cl, 9.08; N, 7.17. Found: C, 42.14; H, 3.03; Cl, 8.95; N, 7.04.

IR (KBr): 3435 (s), 3050 (m), 2909 (m), 2888 (m), 2838 (m), 1628 (w), 1579 (w), 1518 (w), 1496 (w), 1457 (w), 1429 (s), 1416 (w), 1343 (w), 1322 (w), 1226 (w), 1205 (w), 1156 (w), 1112 (w), 1024 (s), 1006 (w), 980 (w), 952 (vs), 909 (s), 873 (w), 854 (s), 781 (w), 741 (w), 722 (s), 656 (m), 614 (s), 539 (m), 511 (w), 458 (w), 430 (w), 419 (m), 411

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(14) In order to obtain the blue intermediate, it is crucial that no excess acid remain in the $(n\text{-}Bu_4N)[TcOCl_4]$.

Table I. Crystal Data

compd	$C_{14}H_{12}ClN_2O_3Tc$
fw	390.6
morphology	needle
cryst size, mm	$0.10 \times 0.10 \times 0.35$
systematic absences	$h0l, l = 2n + 1; 0k0, k = 2n + 1$
space group	$P2_1/c$, No. 14
unit cell	
a, Å	7.440 (2)
b, Å	8.928 (3)
c, Å	21.355 (4)
β, deg	92.48 (2)
V, Å^3	1417.2 (7)
Z	4
ρ_{obsd} (ρ_{calcd}), g·cm^{-3}	1.81 (2) (1.830)
T, °C	22
linear abs coeff, cm^{-1}	11.97
abs cor factor A^*	1.11–1.16
max 2θ; reflcns measd	45°; $h,k,\pm l$
std reflcns ($\sigma(I)$)	106 (0.014), 01$\bar{6}$ (0.018)
no. of reflcns measd	2157
R_{int}	0.0197
no. of unique reflcns	1859
final $R,^a$ R_w^a	0.051, 0.036
max, av final Δ/σ	0.25, 0.069
max, min final diff map, e Å^{-3}	0.49, −0.47
secondary extinctn x	−0.000 26
weighting	$w = ((\sigma_F)^2 + 0.000206F_o^2)^{-1}$
$F(000)$	770.2
no. of variables	239
error in observn of unit wt	1.114

$^a R = \sum \|F_o| - |F_c\|/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

cm^{-1} (w). ^{1}H NMR (CDCl$_3$): δ 10.32 (dd, 1 H), 8.98 (dd, 1 H), 8.46 (dd, 1 H), 8.35 (dd, 1 H), 7.98 (m, 1 H), 7.92 (s, 2 H), 7.66 (m, 1 H), 5.99 (ddd, H$_d$; J_{ad} = 3.93 Hz, J_{bd} = 6.08 Hz, J_{cd} = −11.47 Hz), 5.65 (ddd, H$_c$; J_{ac} = 6.08 Hz, J_{bc} = 3.16 Hz), 5.37 (ddd, H$_b$; J_{ab} = −10.96 Hz), 4.61 (ddd, H$_a$). ^{99}Tc NMR (CDCl$_3$): δ 1960 ($\Delta\nu_{1/2}$ = 2 × 10^4 Hz). UV/vis (MeCN): λ_{max} (ϵ) 206 nm (29 900 L·mol^{-1}·cm^{-1}), 222 (32 400), 268 (26 600), 422 (2170), 640 (36). Conductivity (MeCN): 20 Ω·cm^2·mol^{-1}. FABMS(+), m/z [ion, abundance]: 745 [(2M − Cl)$^+$, 0.12%], 726 [(2M + O − 2Cl)$^+$, 0.09%], 390 [(M)$^+$, 2.0%], 355 [(M − Cl)$^+$, 100%], 330 [(M − eg)$^+$, 27.%], 327 (M − Cl − C$_2$H$_4$)$^+$, 28.%], 311 [(M − C$_2$H$_4$ − O)$^+$, 47.%].

Preparation of [TcO$_2$(tz)$_4$]Cl·3H$_2$O. To 76.9 mg of (n-Bu$_4$N)[TcOCl$_4$] (0.154 mmol) were added with magnetic stirring 150 μL of thiazole (Aldrich) and 300 μL of MeOH. To the resulting brown solution was added 3 drops of H$_2$O, causing the appearance of a tan precipitate. The precipitate was redissolved by gently heating with additional MeOH. On cooling to −20 °C, orange crystals formed (63.75 mg, 74%), which were filtered out with a fritted-glass funnel and rinsed with CHCl$_3$, (CH$_3$)$_2$CO, and hexanes. The residual solvent was removed in vacuo for <5 min since prolonged evacuation causes the crystals to desolvate. This product is unstable in solution in the absence of excess thiazole ligand.

Anal. Calcd for C$_{12}$H$_{18}$ClN$_4$O$_5$S$_4$Tc: C, 25.33; H, 2.98; N, 9.97; S, 22.69. Found: C, 25.69; H, 3.23; N, 9.99; S, 22.86.

IR (KBr): 3416 (s), 3100 (s), 3061 (s), 1653 (m), 1505 (m), 1383 (m), 1320 (m), 1246 (m), 1217 (m), 1123 (w), 1092 (w), 1071 (w), 1051 (m), 922 (m), 876 (m), 843 (s), 822 (vs), 789 (m), 756 (m), 629 (s), 554 cm^{-1} (w). ^{1}H NMR (CD$_3$OD/thiazole): δ 9.48 (d, 1 H), 8.24 (d, 1 H), 7.76 (m, 1 H). UV/vis (MeOH/thiazole): λ_{max} 468 nm.

Preparation of TcOCl$_2$(tz)$_2$(OMe). To 49.45 mg of (n-Bu$_4$N)-[TcOCl$_4$] (0.099 mmol) were added with magnetic stirring 100 μL of thiazole, 100 μL of THF, and 100 μL of MeOH. The green precipitate that formed immediately was redissolved by adding 3 mL of THF and heating to boiling. On cooling to −20 °C, green crystals formed (23.17 mg, 60%), which were filtered out with a fine-porosity fritted-glass funnel, rinsed with H$_2$O and hexanes, and then dried in vacuo at room temperature. The product is only appreciably soluble in Me$_2$SO, in which it gradually decomposes.

Anal. Calcd for C$_7$H$_9$Cl$_2$N$_2$O$_2$S$_2$Tc: C, 22.04; H, 2.39; Cl, 18.68; N, 7.34; S, 16.84. Found: C, 21.72; H, 2.34; Cl, 18.32; N, 7.24; S, 16.57.

IR (KBr): 3443 (m), 3117 (m), 3110 (m), 3102 (m), 2808 (w), 1621 (w), 1506 (m), 1444 (w), 1424 (w), 1388 (m), 1318 (w), 1239 (m), 1234 (m), 1102 (s), 1060 (m), 933 (vs), 923 (s), 885 (m), 817 (m), 740 (w), 731 (m), 624 (m), 613 (w), 525 cm^{-1} (m). ^{1}H NMR (Me$_2$SO-d_6): δ 9.70 (d, 2 H), 8.35 (d, 2 H), 8.15 (m, 2 H), 3.42 (s, ≤3 H). UV/vis (Me$_2$SO): λ_{max} (ϵ) 644 nm (≥70 L·mol^{-1}·cm^{-1}). Conductivity (Me$_2$SO): ≤23 Ω·cm^2·mol^{-1}.

Table II. Atomic Positional Parameters ($\times 10^4$) and Temperature Factors (Å$^2 \times 10^3$)

	x	y	z	$U_{eq}{}^a$
Tc	1853 (1)	1642 (1)	3687.3 (2)	38
Cl	4964 (2)	850 (2)	3731 (2)	47
O(1)	−234 (5)	2842 (4)	3478 (2)	50
O(2)	1911 (5)	1434 (4)	2802 (2)	51
O(3)	1061 (6)	116 (4)	4025 (2)	64
N(1)	1997 (6)	2689 (5)	4606 (2)	36
N(2)	3170 (5)	3913 (4)	3579 (2)	31
C(1)	1523 (8)	2042 (7)	5131 (2)	44
C(2)	1385 (8)	2803 (8)	5695 (3)	53
C(3)	1786 (7)	4287 (8)	5723 (3)	43
C(4)	2365 (6)	5025 (6)	5190 (2)	35
C(5)	2865 (7)	6560 (5)	5170 (3)	41
C(6)	3472 (8)	7187 (7)	4644 (3)	48
C(7)	3618 (7)	6329 (5)	4079 (2)	36
C(8)	4323 (8)	6874 (6)	3522 (3)	45
C(9)	4484 (8)	5934 (7)	3032 (3)	46
C(10)	3881 (7)	4467 (6)	3068 (3)	40
C(11)	3074 (6)	4833 (6)	4083 (2)	31
C(12)	2442 (6)	4170 (5)	4642 (2)	40
C(1')	−1061 (10)	2422 (11)	2894 (3)	68
C(2')	388 (10)	2047 (11)	2459 (3)	75

$^a U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$.

Collection of X-ray Data for TcOCl(eg)(phen). The product isolated from the reaction medium was not suitable for single-crystal structure determination. Suitable crystals were grown by slow vapor diffusion of hexane into a CH$_2$Cl$_2$ solution of the complex. Precession photographs revealed the symmetry of the crystal. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range 19.1° < 2θ < 25.7°, recorded on a Syntex P2$_1$ diffractometer with use of Mo Kα radiation (λ = 0.710 69 Å). Crystal data and other parameters related to collection are summarized in Table I. The density was obtained by suspension in a carbon tetrachloride–methylene bromide mixture. Intensities were measured on the P2$_1$ diffractometer with a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[15] Corrections were made for Lorentz and polarization effects, but not for absorption. This will make the maximum error in F_o <1.7%.

Solution of the Structure. The technetium atom was found from a three-dimensional Patterson map, and·refinement with electron density difference syntheses revealed all of the other atoms. At this stage, the temperature factors of the non-hydrogen atoms were made anisotropic. Further refinement by full-matrix least squares, which minimized $\sum(|F_o| - |F_c|)^2$, varied all parameters and was terminated when the maximum shift/error was roughly 0.25. Reflections with $3\sigma_I \geq I \geq -3\sigma_I$ were treated by the method of French and Wilson.[16] Corrections were made for secondary extinctions by the SHELX method.[17] Scattering curves were from ref 18, as were the anomalous dispersion corrections applied to the scattering curves for Tc and Cl.[19] The atom parameters are listed[20] in Table II.

Results and Discussion

The reaction of alcoholic solutions of (n-Bu$_4$N)[TcOCl$_4$] with excess pyridine generally yields TcO$_2$(py)$_4^+$. It has been noted,[21] however, that some water is required to supply the second oxo

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(19) Reference 18, Table 2.3.1, pp 149–150.

(20) All computations were carried out on a VAX 8600 computer. Programs used for initial data treatment were from the XTAL package (Stewart, J. M.; Hall, S. R.; Technical Report TR-1364; University of Maryland: College Park, MD, 1983). The structure was solved with the use of SHELX.[17] Planes were calculated with XTAL, and diagrams were prepared from SNOOPI (Davies, K. "CHEMGRAF suite: Program SNOOPI"; Chemical Design Ltd., Oxford, England.)

(21) Davison, A.; Jones, A. G. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 875.

ligand. When this reaction is performed with scrupulously dried pyridine and alcohol, and unidentified dark green-brown intermediate is formed that will further react with water to produce the dioxotechnetium complex. In tetrahydrofuran, however, the reaction of $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ with pyridine gives a bright emerald green solution that precipitates on addition of ROH (R = Me, Et) as $\text{TcOCl}_2(\text{py})_2(\text{OR})$. The significantly lower dielectric constant of THF compared to methanol is probably of prime importance in favoring formation of the neutral species, since solvents less polar than THF, such as CH_2Cl_2 and CHCl_3, cause the appropriate color change.

The reaction of $\text{TcO}_2(\text{py})_4^+$ with chloride ion in alcohol to form $\text{TcOCl}_2(\text{py})_2(\text{OR})$ is interesting for several reasons. This reaction requires the addition of concentrated sulfuric acid,[22] presumably in order to doubly protonate one oxo ligand, thereby labilizing it. The ability of the alcohol to deprotonate and coordinate under such acidic conditions is quite remarkable. The highly electrophilic technetium is clearly making coordinated alcohols very acidic. Our discovery of a second route to these bis(amine)–dichloride complexes provides mechanistic insight that was heretofore unavailable. The same geometrical isomer is formed by both routes, as is evidenced by their identical IR and NMR spectra. This demonstrates that the trans-labilizing effect is probably unimportant in the determination of geometry that must therefore be controlled by rearrangements to the thermodynamic product.

Thiazole derivatives $[\text{TcO}_2(\text{tz})_4]^+$ and $\text{TcOCl}_2(\text{tz})_2(\text{OR})$ were prepared, demonstrating the generality of the reaction conditions. The similarity of the thiazole and pyridine derivatives suggest that thiazole is acting as an N donor only. This assumption is confirmed by the proton NMR spectra, which show a larger shift than that of the free ligand for the protons α to the nitrogen. Bonding of thiazole through the nitrogen is seen[23] for the divalent ions of Co, Ni, Cu, and Zn.

There is evidence[24] that bleomycin binds Mn^{2+} in part through the 2,4′-bithiazole moiety on this antitumor antibiotic. The donor atoms of this potentially ambidentate ligand that participate in manganese binding could not, however, be uniquely determined. Technetium has been used to radiolabel bleomycin[25] though the chemical nature of this complex also has not been determined. The formation of the relatively stable Tc(V) thiazole complexes suggests that the bithiazole moiety may also play a role in the binding of technetium to bleomycin.

Although the complexes $\text{TcOCl}_2(\text{py})_2(\text{OR})$ are hydrolytically unstable in solution, they are apparently more robust than the analogous complexes made[5] with the poorer donors 4-nitropyridine and 4-cyanopyridine or the thiazole complex reported here. The NMR spectra for the pyridine complexes in CDCl_3 or CD_2Cl_2 show a small resonance corresponding to free alcohol, suggesting that loss of the alkoxide ligand is at least one step in the decomposition process. As expected, the complexes with a chelating diolate ligand, e.g. $\text{TcOCl}(\text{OCH}_2\text{CH}_2\text{O})(\text{phen})$, have enhanced solution stability, making it possible to recrystallize the complex to form single crystals suitable for X-ray diffraction. The diolate derivatives, however, could only be prepared with the bidentate amines 2,2′-bipyridine and 1,10-phenanthroline.

Unlike the monoalcoholate complexes, the diolate species gave readily interpretable positive-mode fast atom bombardment mass spectra. The mass spectra not only confirm the identity of the complexes but also give insight into the hydrolysis products. Since the complex was dissolved in an undried nitrobenzyl alcohol matrix before acquiring the spectra, some hydrolysis could take place on the probe. The low-abundance peak at m/z 726 $(\text{Tc}_2\text{O}_3(\text{eg})_2$-
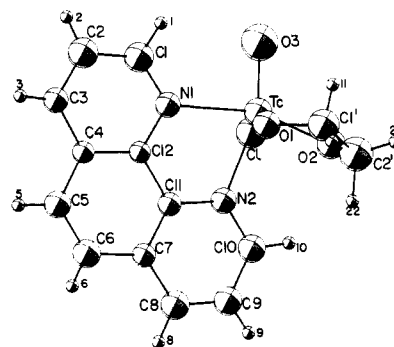

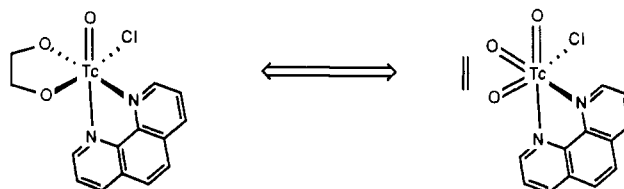**Figure 1.** SNOOPI drawing of TcOCl(eg)(phen), showing the atom-labeling scheme.

Figure 2. Proposed valence bond resonance structures of the ethanediolate moiety.

$(\text{phen})_2^+)$ corresponds to hydrolysis of both chloride ligands. All attempts to isolate this compound from the dark purple hydrolysis mixture have been unsuccessful. The other ion in this mass region with m/z 745 $(\text{Tc}_2\text{ClO}_2(\text{eg})_2(\text{phen})_2^+)$ may correspond to a cluster of two molecules with one of the chlorine atoms dissociated.

Further information on the reactivity of this complex comes from the fragmentation patterns in the molecular ion region of the mass spectrum. The mass of the most abundant ion in this region corresponds to that for loss of the chloride ligand from the parent, which is expected considering the unusually long Tc–Cl bond length (vide infra). A more interesting fragment is the one of mass 327 $(\text{TcO}_3(\text{phen})^+)$ corresponding to that for the loss of chloride and ethylene from the molecule. This ion is reminiscent of the known Tc(VII) species[6] $\text{TcO}_3\text{Cl}(\text{phen})$, suggesting that these two isolable species might be interrelated. Furthermore, the mass spectra of substituted 1,2-diolate complexes show similar losses of the corresponding alkene. In view of this evidence, we have explored the reactivity of $\text{TcO}_3\text{Cl}(\text{phen})$ and discovered[26] that it could be reacted with alkenes to form $\text{TcOCl}(\text{diolate})(\text{phen})$ under mild conditions.

The NMR spectrum of TcOCl(eg)(phen) has seven distinct aromatic proton resonances and four distinct ethanediolate signals. This evidence suggests that the O and Cl atoms have a mutually cis conformation, yielding a completely asymmetrical environment (point group C_1). It was unclear, however, whether a nitrogen or oxygen donor was trans to the oxo ligand. Evidence for the former comes by comparison of the Tc=O stretching frequency $(952\ \text{cm}^{-1})$ to that of $\text{TcO}(\text{eg})(\text{HB}(\text{pyz})_3)^{27}$ (pyz = pyrazole) (953 cm^{-1}), which must have a trans nitrogen.

A single-crystal X-ray structure was obtained in order to better understand the structural features of the diolate mixed-ligand complexes. The molecule is shown in Figure 1, and bond lengths and angles are given in Table III. The technetium atom is six-coordinate but is significantly distorted from normal octahedral geometry. In part, this is because the 1,10-phenanthroline ligand enforces a small N(1)–Tc–N(2) angle $(72.7\ (2)°)$, and in part, it is the effect of the strongly bonded O(3) atom (Tc–O(3) = 1.661 (4) Å) repelling the remaining equatorial ligands (O(3)–Tc–Cl, O(3)–Tc–O(1), and O(3)–Tc–O(2) angles of 95.8 (2), 105.0 (2), and 112.0 (2)°). The Tc–N(2) bond (2.268 (4) Å) is longer than the normal range of Tc–N distances $(2.055\ (6)–2.209\ (6)\ \text{Å})^{28}$

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Table III. Selected Interatomic Distances (Å) and Angles (deg)

Tc–O(1)	1.924 (4)	Tc–O(2)	1.902 (3)	Tc–O(3)	1.661 (4)
Tc–N(1)	2.173 (4)	Tc–N(2)	2.268 (4)	Tc–Cl	2.418 (2)
N(1)–C(1)	1.322 (7)	C(1)–C(2)	1.390 (8)	C(2)–C(3)	1.36 (1)
N(2)–C(10)	1.328 (7)	C(10)–C(9)	1.388 (8)	C(9)–C(8)	1.352 (8)
C(3)–C(4)	1.398 (8)	C(4)–C(5)	1.422 (8)	C(4)–C(12)	1.401 (7)
C(8)–C(7)	1.407 (8)	C(7)–C(6)	1.437 (8)	C(7)–C(11)	1.396 (7)
N(1)–C(12)	1.365 (7)	C(5)–C(6)	1.350 (9)	O(1)–C(1′)	1.418 (8)
N(2)–C(11)	1.359 (6)	C(11)–C(12)	1.429 (7)	O(2)–C(2′)	1.431 (9)
C(1′)–C(2′)	1.491 (1)				
O(3)–Tc–Cl	95.8 (2)	O(3)–Tc–O(1)	105.0 (2)	O(3)–Tc–O(2)	112.0 (2)
O(3)–Tc–N(1)	88.0 (2)	O(3)–Tc–N(2)	160.1 (2)	Cl–Tc–O(1)	159.0 (1)
Cl–Tc–O(2)	87.0 (1)	Cl–Tc–N(1)	94.7 (1)	Cl–Tc–N(2)	81.3 (1)
O(1)–Tc–O(2)	82.9 (2)	O(1)–Tc–N(1)	88.7 (2)	O(1)–Tc–N(2)	80.0 (2)
O(2)–Tc–N(1)	159.7 (2)	O(2)–Tc–N(2)	87.6 (2)	N(1)–Tc–N(2)	72.7 (2)
Tc–N(1)–C(2)	125.0 (4)	Tc–N(1)–C(12)	118.0 (3)	C(12)–N(1)–C(1)	116.7 (4)
Tc–N(2)–C(10)	127.3 (3)	Tc–N(2)–C(11)	115.0 (3)	C(11)–N(2)–C(10)	117.5 (4)
N(1)–C(1)–C(2)	123.6 (6)	C(1)–C(2)–C(3)	119.3 (6)	C(2)–C(3)–C(4)	119.9 (5)
N(2)–C(10)–C(9)	122.6 (5)	C(10)–C(9)–C(8)	120.2 (6)	C(9)–C(8)–C(7)	119.2 (5)
C(3)–C(4)–C(5)	124.7 (5)	C(3)–C(4)–C(12)	116.7 (5)	C(12)–C(4)–C(5)	118.6 (5)
C(8)–C(7)–C(6)	124.7 (5)	C(8)–C(7)–C(11)	117.1 (5)	C(11)–C(7)–C(6)	118.2 (5)
C(4)–C(5)–C(6)	121.5 (5)	N(1)–C(12)–C(4)	123.7 (5)	N(1)–C(12)–C(11)	116.3 (4)
C(7)–C(6)–C(5)	121.2 (5)	N(2)–C(11)–C(7)	123.3 (4)	N(2)–C(11)–C(12)	116.2 (4)
C(11)–C(12)–C(4)	120.0 (5)	Tc–O(1)–C(1′)	111.8 (4)	O(1)–C(1′)–C(2′)	108.1 (6)
C(12)–C(11)–C(7)	120.5 (4)	Tc–O(2)–C(2′)	114.8 (4)	O(2)–C(2′)–C(1′)	110.2 (6)

because of the trans influence of the oxo group O(3) on N(2). Furthermore, Tc–N(1) (2.173 (4) Å) is at the upper limit of normal Tc–N distances and Tc–Cl (2.418 (2) Å) is longer than Tc–Cl bonds normally found in Tc(V) compounds where the chlorine is not trans to the oxo group (range 2.291–2.359 Å, average 2.324 Å).[29-34] This lengthening is due to the trans influence of the strongly bonded O⁻ groups of the ethanediolato moiety. The Tc–O(diol) distances are normal for an RO⁻ group bonded to technetium,[29,30,33,35] but the two differ significantly (Tc–O(1) = 1.924 (4) Å; Tc–O(2) = 1.902 (3) Å). The difference is consistent with Cl having a stronger trans influence than an amine.

Because of the strong trans influence imparted by the ethanediolato group, its bonding might be visualized, as shown in Figure 2, as a resonance hybrid involving primarily a singly bonded 1,2-ethanediolate, but also, to a lesser extent, two doubly bonded oxygens and ethene. The C(1′)–C(2′) distance of the diolate at 1.491 (1) Å is shorter than expected for a single bond but significantly longer than for a double bond. This carbon–carbon bond length is slightly shorter than the equivalent bond (1.498 (5) Å) in (C₅Me₅)ReO(eg),[36] which loses ethene on heating to 150 °C in vacuo.

The bond lengths and angles within the 1,10-phenanthroline group agree well with the averages calculated previously.[37,38] The ligand is significantly nonplanar, being folded about a line passing through the centers of the C(5)–C(6) and C(11)–C(12) bonds. The fold is more pronounced at the C(11)–C(12) end. The di-

hedral angle between the two pyridine rings is 6.5 (2)°, made up of dihedral angles of about 3° between the pyridine rings and the central ring. We assume this fold is to accommodate bonding to the technetium atom, which lies 0.376 (4) Å out of the best plane through the phenanthroline ligand in the same direction as the nitrogen atoms. Nonplanarity of 1,10-phenanthroline ligands has been observed previously, but there appears to be no regular trend in the distortions. Bending of the type observed here has also been observed previously,[37] but in those cases the metal atoms (Na⁺, Rb⁺) lie out of the plane of the ligand in the direction opposite that of the nitrogen atoms.

The ethanediolato ligand is twisted such that *both* carbon atoms lie on the same side of the Tc,O(1),O(2) plane: C(1′) by 0.16 (1) Å and C(2′) by 0.58 (1) Å. We assume that all these distortions are caused by the exigencies of intramolecular repulsions since the packing is unremarkable. Pairs of molecules related by a center of symmetry are arranged to overlap the 1,10-phenanthroline rings and maximize π–π interactions, though the contacts between adjacent molecules are van der Waals.

Conclusions

Ligand substitution reactions of [TcOCl₄]⁻ with pyridine and [TcO₂(py)₄]⁺ with chloride ion yield the same products, TcOCl₂(py)₂(OR). The alkoxide ligand can be formed by deprotonation of either MeOH or EtOH under surprisingly acidic conditions. In an extension of this reaction, the complex TcOCl(eg)(phen) can be prepared. Analysis of this complex reveals very strong bonding between the technetium and the diolate.

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