$[Me_2bpy]Re(CO)_3Cl$, 103667-38-5; *fac*-$[(CO_2Me)_2bpy]Re(CO)_3Cl$, 138518-62-4; *fac*-$[Ph_2bpy]Re(CO)_3Cl$, 134438-71-4; *fac*-$[bpy]Re(CO)_3Cl$, 55658-96-3; *fac*-$[Cl_2bpy]Re(CO)_3Cl$, 126205-15-0; *fac*-$[(NO_2)_2bpy]Re(CO)_3Cl$, 116840-68-7; *fac*-$[(NO_2)_3bpy]Re(CO)_3Etpy$, 138518-63-5; *fac*-$[(NO_2)_2bpy]Re(CO)_3Etpy^-$, 138518-64-6; *fac*-$[Me_4bpy]Re(CO)_3Etpy$, 138518-65-7; *fac*-$[(MeO)_2bpy]Re(CO)_3Etpy$, 138518-66-8; *fac*-$[Me_2bpy]Re(CO)_3Etpy$, 138518-67-9; *fac*-$[bpy]Re(CO)_3Etpy$, 138518-68-0; *fac*-$[Ph_2bpy]Re(CO)_3Etpy$, 138518-69-1; *fac*-$[Cl_2bpy]Re(CO)_3Etpy$, 138518-70-4; *fac*-$[(CO_2Me)_2bpy]Re(CO)_3Etpy$, 138518-71-5.

Supplementary Material Available: A table containing all elemental analyses for the complexes described in the Experimental Section (1 page). Ordering information is given on any current masthead page.

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Kinetic and Structural Studies on the Oxotetracyanotechnetate(V) Core: Protonation and Ligation of Dioxotetracyanotechnetate(V) Ions and Crystal Structure of 2,2′-Bipyridinium *trans*-Oxothiocyanatotetracyanotechnetate(V)

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The tetracyanodioxotechnetate(V) ion undergoes protonation reactions in acidic aqueous solutions, forming the $[TcO(OH)(CN)_4]^{2-}$ (**1**) and $[TcO(OH_2)(CN)_4]^-$ (**2**) complexes. A dimeric species, $[Tc_2O_3(CN)_8]^{4-}$ (**3**), is rapidly formed from the hydroxo oxo complex, and it is therefore impossible to isolate complex **1**. The coordinated water of $[TcO(H_2O)(CN)_4]^-$ can be displaced by monodentate ligands such as thiocyanate. The reaction with thiocyanate ions gives $[TcO(NCS)(CN)_4]^{2-}$ (**4**), the composition and structure of which was confirmed by means of an X-ray crystal structure determination. 2,2′-Bipyridinium oxothiocyanatotetracyanotechnetate(V) ($C_{25}H_{18}N_9OSTc$) crystallizes in the monoclinic space group, $C2/c$, with $a = 18.210$ (4) Å, $b = 19.473$ (1) Å, $c = 15.501$ (3) Å, $\beta = 107.501$ (14)°, $Z = 8$, $\rho_{calc} = 1.490$ g cm^{-3}. A final R value of 6.4% resulted from refinement of 1868 observed reflections. The first acid dissociation constant of **2** (at 15.0 °C), the forward and reverse rate constants, and the equilibrium quotient for the reaction (at 25.0 °C)

$$trans\text{-}[TcO(H_2O)(CN)_4]^- + NCS^- \underset{k_{-1}}{\overset{k_1,\,K_1}{\rightleftharpoons}} trans\text{-}[TcO(NCS)(CN)_4]^{2-} + H_2O$$

have been determined in 1.0 M (KNO_3) ionic strength aqueous medium as $10^{-2.90(5)}$, 22.2 (3) $M^{-1}\ s^{-1}$, 0.43 (4) s^{-1}, and 54 (2) M^{-1}, respectively.

Introduction

Technetium-99m agents are widely used in diagnostic nuclear medicine, while rhenium-186 and rhenium-188 agents are being actively investigated for radiotherapy.[5] In some cases the proposed use of radiorhenium for therapy is predicted on the chemistry and biodistribution of the analogous technetium agent. Since one can qualitatively predict that aspects of the chemistries of technetium and rhenium will not exactly be analogous,[5,6] it becomes important for the use of radiorhenium in nuclear medicine to quantitively assess the extent to which the solution chemistries of technetium and rhenium differ. Many diagnostic technetium agents contain the radioactive metal in the +5 oxidation state. Thus, in this paper we focus our attention on the comparative aqueous solution chemistry of analogous Tc(V) and Re(V) centers.

It was shown previously that the $[MO_2(CN)_4]^{n-}$ ions of Mo(IV), W(IV), and Re(V) may undergo successive protonation reactions to form the corresponding hydroxo oxo and aqua oxo species.[7] It was further shown that the aqua ligand in the $[MO(H_2O)(CN)_4]^{m-}$ ions may be substituted by mono- and bidentate (for the Mo(IV) and W(IV) systems only) ligands.[7,8] These studies lead to predictions regarding other known dioxo tetracyano complexes, that of Tc(V) and Os(VI).[9] It was recently shown that the $[OsO(H_2O)(CN)_4]$ complex is a too strong acid and $[OsO_2(CN)_4]^{2-}$ can therefore not be protonated.[9] In the case of Tc(V), however, the periodicity and the known chemistry of the neighboring metals suggested that protonation and subsequent ligand substitution should be possible. The investigation of these phenomena in the Tc(V) system is described herein.

Experimental Section

General Considerations. 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 any serious health hazard since ordinary laboratory glassware and other materials provide adequate shielding. Brehmstralung 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, especially when solid samples are handled, to prevent contamination and inadvertent inhalation.

Unless otherwise noted, all chemicals were of reagent grade. $NH_4{}^{99}TcO_4$ was purchased from Oak Ridge National Laboratory and was purified as described previously.[10] (n-Bu_4N)[$TcOCl_4$] was prepared by the method of Davison.[11] All experiments were performed aerobically

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using triply destilled water. UV/visible measurements were performed on Varian Cary and Hitachi 230-70 spectrophotometers, respectively, while infrared spectra were recorded on a Perkin-Elmer Ft333 instrument in KBr disks. FAB mass spectra were measured in the negative ion mode using a VG 30-250 spectrometer (VG Instruments Inc.) and a glycerol matrix at the probe temperature. Xenon was used as the primary beam gas, and the ion gun was operated at 7 kV and 1 mA. Data were generally collected over the mass range 100–1400 Da at 3 s/scan. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN. Technetium analyses were done on a Sciex 777 mass spectrometer with freshly prepared $K^{99}TcO_4$ as primary standard.

Preparation of Complexes. Potassium Tetracyanodioxotechnetate(V), $K_3TcO_2(CN)_4$. $K_3TcO_2(CN)_4$ was prepared directly from $(n\text{-}Bu_4N)TcOCl_4$ in the following way: 100 mg of $(n\text{-}Bu_4N)TcOCl_4$ (0.2 mmol) was added to a solution of 100 mg of pyridine (1.3 mmol) in 1 mL of MeOH. The resulting mixture was stirred for about 5 min while the color changed from red to orange and a precipitate of $[TcO_2(py)_4]Cl$ formed. A 100-mg amount of KCN (1.5 mmol) in 2 mL of 1/1 H_2O/methanol was then added to this mixture, and the color changed to yellow-orange following the dissolution of the solid $[TcO_2(py)_4]Cl$. Bright yellow crystals of $K_3[TcO_2(CN)_4]$ started forming after 5–10 min. Crystallization was completed by the addition of 2 × 20 mL portions of MeOH. The solid was removed by filtration and recrystallized from water/methanol (70 mg, yield >75%). The visible/UV and infrared spectra of this material are identical to that reported previously.[11]

Tetramethylammonium Aquaoxotetracyanotechnetate(V) Dihydrate, $[(CH_3)_4N][TcO(H_2O)(CN)_4]\cdot 2H_2O$. A solution that contained 12 mg of $(CH_3)_4NCl$ (0.11 mmol) in 2.5 mL of H_2O was acidified to a pH of about 1 by the addition of one drop of 5 M HNO_3. A second solution containing 65 mg of $K_3[TcO_2(CN)_4]$ (0.18 mmol) in 2.5 mL of H_2O was similarly acidified (whereupon it turned blue) and added to the first. The resulting mixture was refrigerated at 5 °C. Blue, excessively twinned platelike crystals of $[(CH_3)_4N][TcO(OH_2)(CN)_4]\cdot 2H_2O$ were obtained (30 mg, yield >40%) after 5–20 h, during which time the color of the solution slowly changed to light green, indicating the formation of the dimeric species, $[Tc_2O_3(CN)_8]^{4-}$. Anal. Calcd for $C_8H_{18}N_5O_4Tc$: C, 27.7; N, 20.2; H, 5.19; Tc, 28.5. Found: C, 27.9; N, 20.2; H, 5.25; Tc, 28.5. IR (cm^{-1}): 2154 (m) (CN), 1483 (s) ($N\text{-}CH_3$), 1384 (m) ($N\text{-}CH_3$), 1029 (s) (Tc=O). Visible/UV (0.1 M HCl): 608 nm (ϵ = 21 M^{-1} cm^{-1}). FAB-MS: *m/e* 219 ($M - H_2O$). Cell dimensions determined by the Weissenberg method showed the compound to be isomorphous to the Re(V) analogue:[12] orthorhombic space group *Pmmn* with a = 12.11 Å, b = 9.04 Å, c = 7.10 Å, and Z = 2.

Cadmium (μ-Oxo)bis(tetracyanooxotechnetate(V)) Decahydrate, $Cd_2[Tc_2O_3(CN)_8]\cdot 10H_2O$. A solution of 40 mg of $K_3TcO_2(CN)_4$ (0.11 mmol) in 3 mL of H_2O was acidified to a pH of ca. 1 by the addition of one drop of 5 M HNO_3 (upon which the color immediately changed from yellow to blue). This solution was mixed with a second that contained 50 mg of $CdCl_2$ (0.27 mmol) and one drop of 5 M HNO_3 solution in 3 mL of H_2O, and the resulting mixture was placed in a refrigerator (ca. 5 °C). After 5–10 h twinned purple crystals were obtained from the greenish-blue solution (20 mg, yield >20%). Anal. Calcd for $C_8H_{20}CdN_8O_{13}Tc_2$: C, 11.7; H, 1.9; N, 13.6; Cd, 27.3; Tc, 24.1. Found: C, 12.0; H, 1.7; N, 13.9; Cd, 26.1; Tc, 23.4. IR (cm^{-1}): 2146 (w) (CN), 2131 (s) (CN), 960 (w) (Tc=O), 700 (vs, b) (Tc–O–Tc). Visible/UV (H_2O): 605 nm (ϵ > 1000 M^{-1} cm^{-1}).

Potassium (μ-Oxo)bis(oxotetracyanotechnetate(V)) Hexahydrate, $K_4[Tc_2O_3(CN)_8]\cdot 6H_2O$. To a solution that contained 40 mg of $K_3TcO_2(CN)_4$ (0.11 mmol) in 2 mL of water was added 1 drop of 0.5 M HNO_3. The solution immediately turned green. After ca. 2 min 5 mL of ethanol was added, which resulted in the precipitation of a purple microcrystalline product (20 mg, yield >25%). Anal. Calcd for $C_8H_{12}K_4N_8O_9Tc_2$: K, 21.7; Tc, 27.6. Found: K, 21.6; Tc, 27.1. IR (cm^{-1}): 2147 (w) (CN), 2133 (s) (CN), 956 (w) (Tc=O), 700 (vs, b) (Tc–O–Tc). The visible/UV spectrum in water is identical to that described above for the cadmium salt but is much more soluble in water than the Cd^{2+} salt.

2,2′-Bipyridinium Tetracyanooxothiocyanatotechnetate(V), $(2,2'\text{-}bpyH)_2[TcO(NCS)(CN)_4]$. A solution which contained 6 mg of $K_3TcO_2(CN)_4$ (0.017 mmol) in 2 mL of H_2O was acidified to a pH of about 1 by addition of 1 drop of 5 M HNO_3. A second solution, containing 5 mg of 2,2′-bipyridine (0.032 mmol), 20 mg of NaNCS (0.25 mmol), and two drops of 5 M HNO_3 in 3 mL of H_2O, was prepared. After both were cooled to about 5 °C, the solutions were mixed and kept cold. Green needles, suitable for X-ray structure determination, were obtained after about 10 h (yield >50%). Anal. Calcd for $C_{25}H_{18}N_9OSTc$: C, 50.72; H, 3.05; N, 21.3. Found: C, 50.71; H, 3.05; N, 21.3. IR (cm^{-1}): 2136 (w) (CN), 2066 (s) (SCN), 1004 (s) (Tc=O). Visible/UV (H_2O): 415 nm (ϵ = 4000 M^{-1} cm^{-1}).

Table I. Crystallographic Data for $(2,2'\text{-}bpyH)_2[TcO(NCS)(CN)_4]$

formula	$C_{25}H_{18}N_9OSTc$	fw	591.5
a, Å	18.210 (4)	space group[a]	$C2/c$ (No. 15)
b, Å	19.473 (1)	T, °C	22
c, Å	15.501 (3)	λ, Å	0.71067
β, deg	107.507 (14)	ρ_{obsd}, g cm^{-3}	1.50
V, $Å^3$	5276.8 (5)	ρ_{calcd}, g cm^{-3}	1.490
Z	8	μ, cm^{-1}	5.89
$R(F_o)$[b]	0.064	no. of reflcns	3561
$R_w(F_o)$[c]	0.048	no. of obsd reflcns	1868 ($I > 3\sigma(I)$)

[a] Reference 15. [b] $R = [(\sum \Delta F)/(\sum F_o)]$. [c] $R_w = [(\sum w(\Delta F)^2)/(\sum w(F_o)^2]^{0.5}$.

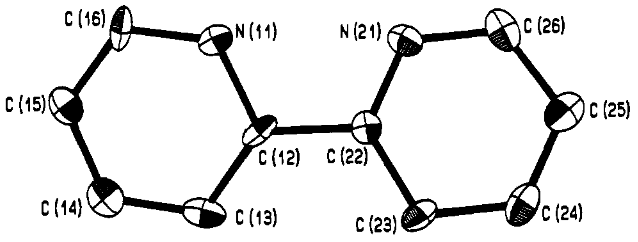

Figure 1. Perspective view of a $(2,2'\text{-}bpyH)^+$ cation showing the distortion and atom-numbering scheme. The first digit refers to the ring, second to the atom in the ring.

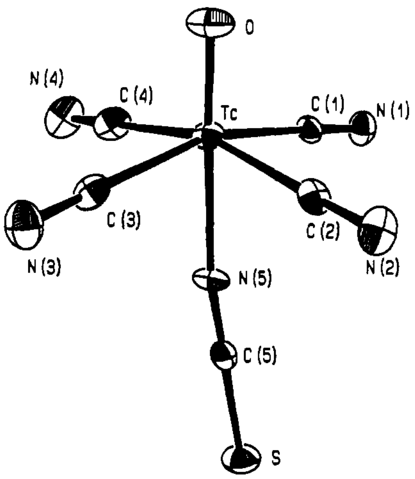

Figure 2. Perspective view of the $[TcO(NCS)(CN)_4]^{2-}$ anion showing the atom-numbering scheme.

Kinetic Measurements. The rate of formation of the *trans*-$[TcO(NCS)(CN)_4]^{2-}$ ion was followed on a Hi-Tech stopped-flow instrument located at Argonne National Laboratory; this instrumentation and the associated data collection systems have been described previously.[13] All the kinetic measurements were performed in solutions of ionic strength 1.0 M (KNO_3) with the uncertainty in temperature measurements ±0.1 °C. Tc(V) concentrations of 5×10^{-5} M were used throughout this study.

Crystallography. Three-dimensional intensity data were collected on an Enraf-Nonius CAD-4F diffractometer with monochromated Mo Kα radiation. The structure was solved by the heavy-atom method, using the SHELX76 and -86 systems[14] of programs. Hydrogen atoms were not located. Crystal data and intensity collection parameters are summarized in Table I.

Results and Discussion

Structure. The structure consists of discrete $[TcO(NCS)(CN)_4]^{2-}$ and monoprotonated 2,2′-bipyridinium ions. The

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($Å^2 \times 10^3$) of $(2,2'\text{-bpyH})_2[TcO(NCS)(CN)_4]$ with Esd's in Parentheses

	x/a	y/b	z/c	U_{eq}[a]
Tc	2822.8 (7)	3404.7 (7)	3784.7 (8)	51.7 (7)
S	2418 (2)	3481 (3)	513 (2)	82 (1)
N(5)	2666 (5)	3549 (6)	2357 (6)	55 (3)
C(1)	3924 (7)	3103 (6)	3718 (9)	48 (3)
N(1)	4491 (6)	2912 (6)	3660 (8)	66 (3)
C(5)	2559 (6)	3520 (7)	1590 (8)	50 (3)
C(3)	1674 (8)	3778 (8)	3401 (9)	61 (4)
O	2952 (5)	3269 (6)	4846 (6)	89 (3)
C(2)	2375 (8)	2438 (7)	3285 (9)	56 (4)
N(3)	1065 (7)	3871 (7)	3204 (9)	91 (4)
N(2)	2138 (7)	1906 (6)	3037 (9)	77 (4)
C(15)	−1644 (9)	6789 (9)	1797 (9)	69 (5)
C(12)	−500 (9)	6030 (7)	1357 (8)	50 (4)
N(11)	−508 (6)	6759 (6)	1363 (7)	57 (3)
C(13)	−1102 (10)	5655 (8)	1547 (9)	71 (5)
C(22)	177 (7)	5737 (7)	1116 (8)	49 (4)
C(23)	337 (8)	5036 (7)	1268 (9)	61 (4)
N(21)	603 (7)	6184 (6)	797 (7)	68 (3)
C(14)	−1672 (9)	6059 (9)	1784 (9)	72 (5)
C(24)	998 (9)	4810 (8)	1037 (10)	74 (5)
C(26)	1247 (9)	5958 (9)	596 (10)	80 (5)
C(16)	−1066 (9)	7131 (8)	1578 (9)	70 (5)
C(25)	1449 (9)	5264 (8)	711 (10)	77 (5)
C(32)	−45 (7)	1478 (8)	1160 (8)	56 (4)
C(42)	−390 (8)	797 (8)	1273 (9)	53 (4)
N(31)	621 (6)	1439 (6)	900 (8)	69 (4)
N(41)	−20 (7)	238 (7)	1062 (8)	77 (4)
C(33)	−341 (8)	2102 (7)	1327 (9)	61 (4)
C(34)	42 (9)	2702 (8)	1237 (10)	74 (5)
C(35)	700 (10)	2672 (9)	962 (11)	82 (5)
C(36)	1001 (10)	2043 (10)	795 (12)	94 (6)
C(43)	−1027 (8)	760 (9)	1579 (9)	70 (5)
C(44)	−1275 (9)	57 (12)	1712 (11)	95 (6)
N(4)	3393 (7)	4989 (7)	3903 (10)	94 (5)
C(4)	3196 (8)	4432 (8)	3853 (10)	72 (5)
C(46)	−275 (12)	−416 (9)	1165 (13)	106 (6)
C(45)	−894 (12)	−488 (13)	1461 (13)	123 (8)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j(a_i a_j)$.

Table III. Selected Interatomic Bond Distances (Å) and Angles (deg) in $(2,2'\text{-bpyH})_2[TcO(NCS)(CN)_4]$ with Esd's in Parentheses

Tc–N(5)	2.162 (9)	Tc–C(1)	2.120 (12)
Tc–C(3)	2.124 (14)	Tc–O	1.612 (8)
Tc–C(2)	2.104 (14)	Tc–C(4)	2.10 (2)
S–C(5)	1.612 (12)	N(5)–C(5)	1.148 (12)
C(1)–N(1)	1.128 (13)	C(3)–N(3)	1.12 (2)
C(2)–N(2)	1.145 (14)	N(4)–C(4)	1.14 (2)
C(12)–N(11)	1.42 (2)	C(12)–C(13)	1.42 (2)
C(12)–C(22)	1.51 (2)	C(22)–C(23)	1.40 (2)
C(22)–N(21)	1.356 (14)	C(32)–C(42)	1.50 (2)
C(32)–N(31)	1.390 (14)	C(32)–C(33)	1.39 (3)
C(42)–N(41)	1.37 (2)	C(42)–C(43)	1.38 (2)
N(5)–Tc–C(1)	79.8 (4)	N(5)–Tc–C(3)	81.6 (4)
C(1)–Tc–C(3)	161.3 (5)	N(5)–Tc–O	177.9 (5)
C(1)–Tc–O	98.9 (5)	C(3)–Tc–O	99.8 (5)
N(5)–Tc–C(2)	79.8 (4)	O–Tc–C(2)	98.7 (5)
N(5)–Tc–C(4)	82.5 (5)	O–Tc–C(4)	99.1 (6)
C(2)–Tc–C(4)	162.2 (5)	Tc–N(5)–C(5)	169.5 (12)
Tc–C(1)–N(1)	176.3 (12)	S–C(5)–N(5)	179.4 (12)
Tc–C(3)–N(3)	179.5 (13)	Tc–C(2)–N(2)	178.1 (13)
Tc–C(4)–N(4)	179 (2)	N(11)–C(12)–C(22)	113.1 (13)
C(13)–C(12)–C(22)	126.7 (12)	C(12)–C(22)–C(23)	118.2 (13)
C(12)–C(22)–N(21)	116.7 (12)	C(23)–C(22)–N(21)	125.1 (13)
C(42)–C(32)–N(31)	114.8 (14)	C(42)–C(32)–C(33)	123.6 (13)
N(31)–C(32)–C(33)	121.6 (14)	C(32)–C(42)–N(41)	115.0 (13)
C(32)–C(42)–C(43)	121 (2)	N(41)–C(42)–C(43)	124 (2)
N(11)–C(12)–C(13)	120.2 (14)		

Table IV. Comparison of the Most Important Distances and Angles in the $[MO(H_2O)(CN)_4]^{m-}$ (A) and $[MO(NCS)(CN)_4]^{n-}$ (B) Ions, M = Tc(V), Re(V), Mo(IV), and W(IV)

complex	distance/angle	Re(V)[a]	Tc(V)[b]	Mo(IV)[c]	W(IV)[d]
A	M=O, Å	1.667 (8)		1.668 (5)	
	$M-H_2O$, Å	2.142 (7)		2.271 (4)	
	$O{=}M{-}C_{av}$, deg	98.4		98.2	
	Δ,[e] Å	0.30		0.34	
B	M=O, Å	1.67 (1)	1.612 (8)		1.61 (2)
	M—NCS, Å	2.12 (1)	2.162 (9)		2.23 (2)
	$O{=}M{-}C_{av}$, deg	98.3 (3)	99.1 (5)		98.9 (8)
	M—N—CS, deg	169 (1)	170 (1)		177 (2)
	Δ,[e] Å	0.30	0.33		0.35
	M—CN,[f] Å	2.11 (1)	2.11 (2)		2.14 (3)

[a] References 16a and 7c. [b] This work. [c] Reference 16b. [d] Reference 16c. [e] Displacement of the metal ion from the plane formed by the four cyano carbons, toward the oxo ligand. [f] Average bond distance.

atom-numbering schemes of both a $(2,2'\text{-bpyH}^+)$ cation and the Tc(V) anion are shown in Figures 1 and 2, respectively, while the fractional atomic coordinates and equivalent thermal parameters are reported in Table II. The most important interatomic bond distances and angles are summarized in Table III.

It is interesting to note that the structure contains two monoprotonated 2,2′-bipyridinium cations, whereas the analogous Re(V) complex is isolated with a single, diprotonated 4,4′-bipyridinium cation;[16] i.e., $[2,2'\text{-bpyH}]_2[TcO(NCS)(CN)_4]$ vs $[4,4'\text{-bpyH}_2][ReO(NCS)(CN)_4]$. The difference most likely stems from the different hydrogen-bonding characteristics of the 2,2′- and 4,4′-bipyridinium isomers. In the monoprotonated 2,2′-bipyridinium cation, the distortion which results from the intra-ring N···H···N hydrogen bonding is quite obvious (see also Figure 1): the N···N distances are 2.68 (2) and 2.66 (2) Å, compared to 3.03 (2) and 2.97 (2) Å between the carbons at the 3-positions. The two pyridine rings are bent about 12° in the direction of the hydrogen-bonded nitrogen atoms. The distortion is further exemplified by the N–C2–C2′ angles of 113–117°, which are significantly less than the normal 120°.

The structure determination establishes that only the aqua ligand of $[TcO(H_2O)(CN)_4]^-$ is displaced upon reaction with excess thiocyanate; i.e. under the reaction conditions employed, the cyano ligands are substitution inert. The atoms coordinated to the Tc(V) center form a distorted octahedron (see Figure 2) with the Tc–C–N chains being essentially linear. The NCS^- ligand is coordinated via the nitrogen atom; this is consistent with the hard and soft acid/base theory, since the Tc(V) center is clearly a "hard" acid. Thus, the geometry of the $[TcO(NCS)(CN)_4]^{2-}$ ion is very similar to the coordination mode observed in the Re(V) and W(IV) systems; a comparison of some important bond parameters for these three related complexes (*trans*-$[MO(NCS)(CN)_4]^{n-}$, M = Tc(V), Re(V), and W(IV)) is given in Table IV.

The data in Table IV show that for the distorted octahedral *trans*-$[MO(NCS)(CN)_4]^{2-}$ (M = Tc, Re) structure, the Tc=O bond is slightly shorter than the Re=O bond (1.612 (8) vs 1.67 (1) Å; Δ = 0.06 Å). This result is consistent with what is observed for related 5-coordinate Tc(V) and Re(V) pairs; for $[MO(SCH_2CH_2S)_2]^-$ the difference is 0.1 Å,[17] for $[MOCl_4]^-$ the difference is 0.02 Å,[18] and for [MO(DBDS)]⁻ (where DBDS represents *N,N*′-bis(mercaptoacetamido)butane-1,4-diamine) the difference is 0.06 Å.[19] In *trans*-$[MO(NCS)(CN)_4]^{2-}$ (M = Tc, Re) the slightly shorter Tc=O is accompanied by a longer *trans*-Tc–NCS bond (2.162 (9) vs 2.12 (1) Å); the latter reflects the greater structural trans effect (STE)[20] exerted by the shorter,

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Table V. Kinetic and Equilibrium Data for Different $[MO(H_2O)(CN)_4]^{n-}$ Complexes at 25.0 °C and μ = 1.0 M, M = Mo(IV), W(IV), Tc(V), and Re(V)

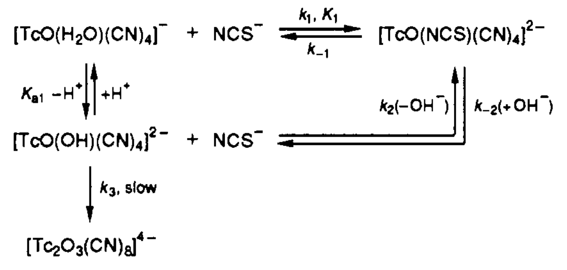
param	Mo(IV)[a]	W(IV)[a]	Tc(V)[b]	Re(V)[c]
pK_{a2}	>14	>14	≈5[d]	4.2
pK_{a1}	10.0	7.8	2.90[e]	1.4
k_{NCS^-},[f] $M^{-1}\ s^{-1}$	>100	2.9 (1)	22.2 (3)	3.5×10^{-3}
k_{aq},[f,g] s^{-1}		2.12 (5)	0.43 (4)	4.8×10^{-5}
K_1,[g] M^{-1}		1.4 (1)	54 (2)	87 (7)

[a] References 8a and 8f. [b] This work. [c] Reference 22. [d] Estimated. [e] 15.0 °C. [f] For reaction $[MO(H_2O)(CN)_4]^{n-} + NCS^- \rightleftharpoons [MO(NCS)(CN)_4]^{m-} + H_2O$. [g] Aquation.

stronger Tc═O linkage. The greater STE of the Tc═O bond leads directly to the aqua ligand of $[TcO(H_2O(CN)_4]^-$ being a weaker acid than the aqua ligand of the analogous Re(V) complex (Table V) and can reasonably be associated with the greater lability of ligands coordinated trans to the Tc═O linkage[21] (vide infra). The shorter Tc═O bond also leads directly to the Tc center being further displaced than the Re from the plane of the four cyano ligands. It is noteworthy that the significant differences in bond lengths between Tc and Re that are observed along the M═O axis are not observed in the perpendicular M–C bonds; both Tc–C and Re–C bonds are equivalent at 2.11 Å (Table IV).

Kinetics. We have extensively studied the protonation and substitution reactions of the $[MO_2(CN)_4]^{n-}$ complexes, where M represents Mo(IV), W(IV), or Re(V). From the periodic relationships among Mo, W, Tc, and Re it was anticipated that the Tc(V) system would not differ dramatically from the three systems already studied. However, this prediction could not be verified by means of spectrophotometric or potentiometric titrations due to a fast reaction, which was later identified as the fast formation (half-life >10 s) of a dimer, $[Tc_2O_3(CN)_8]^{4-}$, at pH values between 2 and 5. At pH values less than 1, solutions of the monomer are fairly stable and display the characteristic spectrum predicted from the previously studied Mo(IV), W(IV), and Re(V) systems. At around pH 1, the ligation of $[TcO(H_2O)(CN)_4]^-$ by NCS^- can be easily monitored as it is accompanied by a significant change in the visible spectrum; the spectrum changes according to well-defined, first-order kinetics. No reaction is, however, observed at pH values where $[TcO_2(CN)_4]^{3-}$ is the predominant species in solution.

Since only the aqua ligand is substituted by the thiocyanate ions, even at high $[NCS^-]$ (verified by the structure determination), the following reaction scheme represents the chemistry of the system:



In order to determine the stability constant governing ligation of $[TcO(H_2O)CN)_4]^-$ by NCS^-, the concentration of the thiocyanate was varied from 0.025 to 0.2 M at $[HNO_3]$ = 0.25 M; this $[H^+]$ was chosen on the basis of the Re(V) system and from visible/UV stability studies which showed that at this $[H^+]$ $[TcO(H_2O)(CN)_4]^-$ is the main Tc species present in solution. Figure 3 shows the data (as a plot of absorbance vs $[NCS^-]$) resulting from this stability constant determination. Equation 1

$$A = \frac{A_M = K_1 A_{ML}[NCS^-]}{1 = K_1[NCS^-]} \qquad (1)$$

may be derived from Beer's law, mass balance, and the definition of K_1 (see above reaction scheme), where A_M is the absorbance of the solution containing only the aqua species, and A_{ML} the absorbance of the solution containing only $[TcO(NCS)(CN)_4]^{2-}$. The absorbance vs $[NCS^-]$ data of Figure 3 were fitted to eq 1 using a nonlinear least-squares program. The resulting calculated value of K_1 is reported in Table VI.

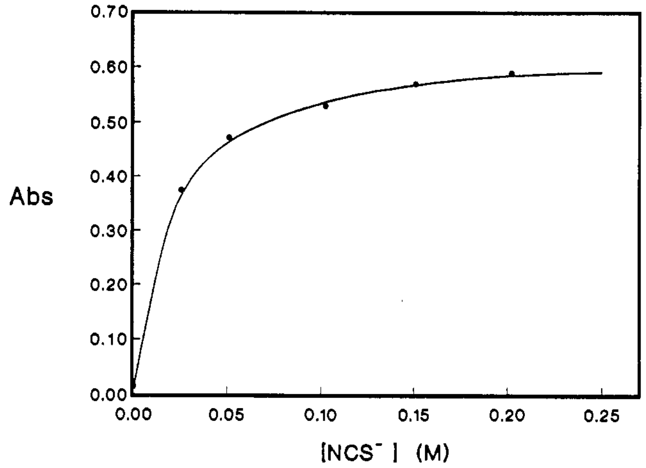


Figure 3. Plot of absorbance vs $[NCS^-]$ at $[HNO_3]$ = 0.25 M, μ = 1.0 M (KNO_3), T = 25.0 °C, λ = 410 nm, and [Tc(V)] = 5×10^{-5} M.

Table VI. Kinetic and Equilibrium Data Determined from the Reaction between $[TcO(H_2O)(CN)_4]^-$ and NCS^- Ions at μ = 1.0 M (KNO_3) with Temperature Accurate to ±0.1 °C

param	temp, °C	result
k_1,[a] $M^{-1}\ s^{-1}$	25	22.2 (3)
	15	9.21 (7)
	3	2.34 (3)
k_1,[b] $M^{-1}\ s^{-1}$	15	8.5 (2)
$\Delta S^*(k_1)$, $J\ K^{-1}\ mol^{-1}$		−9 (12)
$\Delta H^*(k_1)$, $kJ\ mol^{-1}$		62 (4)
k_{-1},[a] s^{-1}	25	0.43 (4)
	15	0.13 (2)
	15	0.17 (1)[c]
	3	0.042 (9)
k_{-1},[b] s^{-1}	15	0.02 (9)
$\Delta S^*(k_{-1})$, $J\ K^{-1}\ mol^{-1}$		21 (24)
$\Delta H^*(k_{-1})$, $kJ\ mol^{-1}$		82 (8)
K_1,[d] M^{-1}	25	54 (2)
k_2,[b] $M^{-1}\ s^{-1}$	15	$<10^{-5}$
pK_{a1}[b]	15	2.90 (5)

[a] Figure 5. [b] Figure 4. [c] Calculated, assuming at 15 °C $K_1 = k_1/k_{-1}$ = 54 M^{-1}. [d] Figure 3.

Within the reaction scheme above, the observed pseudo-first-order rate can be expressed as

$$k_{obsd} = \frac{(k_1 + k_2K_{a1}/[H^+])[NCS^-]}{1 + K_{a1}/[H^+]} + k_{-1} + k_{-2}[OH^-] \qquad (2)$$

if the rate of dimerization is assumed to be negligible compared to that of NCS^- ligation. From the reaction scheme it is also seen that the concentration of the aqua species decreases with an increase in pH, which also corresponds with an increase in the concentration of the hydroxo species. The hydroxo ligand in $[TcO(OH)(CN)_4]^{2-}$ is expected to be much less labile than the aqua ligand in $[TcO(H_2O)(CN)_4]^-$, as was observed in the corresponding Re(V), Mo(IV), and W(IV) systems.[8] This expectation is confirmed by the data of Figure 4, which clearly show a decrease in k_{obsd} with an increase in pH.

At pH values less than 3 ($[OH^-] < 10^{-11}$ M) the contribution of $k_{-2}[OH^-]$ to the observed first-order rate constant is negligible. Under these conditions eq 2 may be simplified to eq 3. Thus,

$$k_{obsd} = \frac{(k_1 + k_2K_{a1}/[H^+])[NCS^-]}{1 + K_{a1}/[H^+]} + k_{-1} \qquad (3)$$

the intercepts of the k_{obsd} vs $[NCS^-]$ plots (Figure 5) provide values

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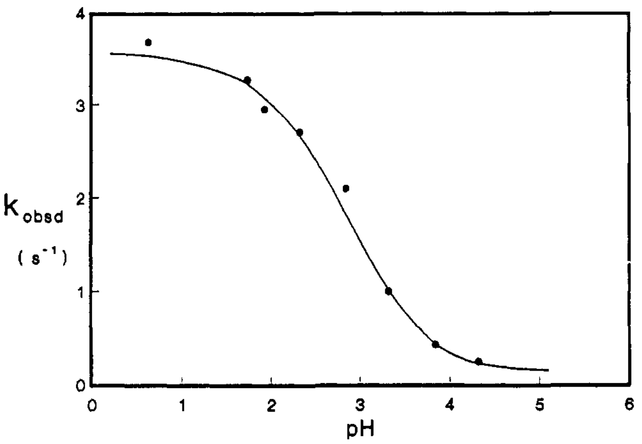

Figure 4. Plot of k_{obsd} vs pH at 15.0 °C, μ = 1.0 M (KNO_3), [NCS^-] = 0.4 M, and [Tc(V)] = 5×10^{-5} M.

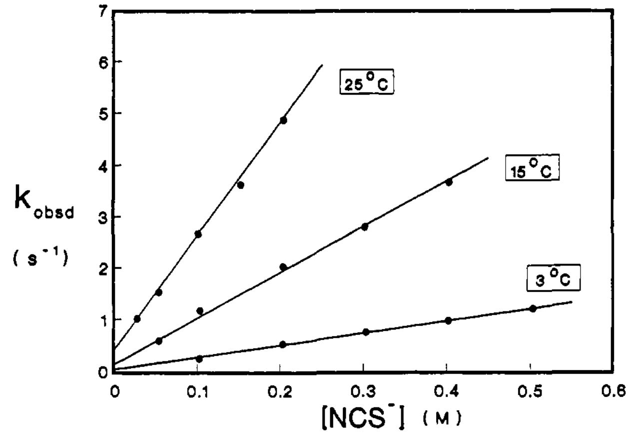

Figure 5. Plot of k_{obsd} vs [NCS^-] at [HNO_3] = 0.25 M, μ = 1.0 M (KNO_3), λ = 410 nm, and [Tc(V)] = 5×10^{-5} M. Temperature is accurate to ±0.1 °C.

of the reverse rate constants, k_{-1}. Furthermore, the data of Figure 4 may be fitted by means of a nonlinear least-squares program to eq 3, yielding values of k_1, k_{-1}, k_2, and K_{a1}; see Table VI. The pK_{a1} value obtained by this nonlinear least-squares analysis, 2.90 (5), is in excellent agreement with that predicted from earlier studies on the analogous Mo(IV), W(IV), and Re(V) systems. This analysis also provides a k_2 value which is essentially zero (within experimental error), confirming that the hydroxo complex does not undergo detectable ligation under the conditions employed.

The pK_{a2} value reported in Table V for $[TcO(H_2O)(CN)]^-$ was estimated from the Re(V) system since pK_{a1} and pK_{a2} in $[ReO(H_2O)(CN)_4]^-$ differ by ca. 2 pH units and the Tc(V) solutions are quite stable at pH $\approx$ 6.5 (i.e., no significant formation of the postulated dimeric species, $[Tc_2O_3(CN)_8]^{4-}$, formed when significant amounts of the $[TcO(OH)(CN)_4]^{2-}$ complex are present, was detected). This suggests pK_{a2} for the Tc(V) system to be ca. 5.

At [H^+] = 0.25 M, [H^+] $\gg K_{a1}$, and thus eq 3 simplifies to eq 4. The data shown in Figure 5 were fitted to eq 4, yielding

$$k_{obsd} = k_1[NCS^-] + k_{-1} \qquad (4)$$

the values of k_1 and k_{-1} at different temperatures; see Table V. These values are in good agreement with those obtained from the pH dependence study (Figure 4).

The activation parameters governing the k_1 and k_{-1} steps were obtained by fitting the k_1, k_{-1} vs temperature data to the Eyring-Polanyi equation (Table V). The $\Delta H^*(k_1)$ of 62 (4) kJ mol⁻¹ compares well, as to be expected, with that determined for the identical reaction in the Re(V) (79 (8)[22]) and W(IV) (73 (4)[8] kJ mol⁻¹) systems. The $\Delta S^*(k_1)$ value of −9 (12) J K⁻¹ mol⁻¹ does not distinguish between a dissociative or associative activation, in agreement with the results found for the NCS^- ligation of the corresponding Re(V)[22] and W(IV)[8] complexes: −28 (20) and 8 (9) J K⁻¹ mol⁻¹. The same reasoning holds for the $\Delta H^*(k_{-1})$ and $\Delta S^*(k_{-1})$ values, although less accurately determinable.

The distinction between mechanisms is more usefully inferred from the structural parameters observed for the $[MO(L)(CN)_4]^{n-}$ complexes of Mo(IV), W(IV), Re(V), and Tc(V). In all these complexes the central metal atom is significantly displaced from the plane formed by the four cyano-carbon atoms toward the oxo ligand. This ensures that a substantial steric hinderance would be encountered within an associative mechanism wherein both the aqua and thiocyanate ligands is associated with the coordination site trans to the oxo ligand. Moreover, a dissociative mechanism is favored by the large structural trans effect generated by the oxo ligand.[20,21] The greater STE observed for the Tc(V) complex (relative to the Re(V) complex) nicely accounts for the more rapid rate of water displacement by thiocyanate for the Tc(V) complex (the values of k_{NCS^-} are 22.2 M⁻¹ s⁻¹ and 0.0035 M⁻¹ s⁻¹ [22] for the Tc(V) and Re(V) complexes, respectively).

The marked greater reactivity of the Tc(V) complex relative to its Re(V) analogue (about a factor of 7000) is even more noteworthy in light of the fact that in closely related reactions Mo(IV) reacts only about 200 times faster than W(IV).[8] While a comprehensive explanation of these rate differences is not yet possible, all structural and kinetic data currently in hand are consistent with a dissociative mode of activation for displacement of the water coordinated trans to the oxo ligand in the $[MO(H_2O)(CN)_4]^{n-}$ complexes.[8] The most conclusive piece of evidence gathered to date is the positive volume of activation[23] (+10.6 (5) cm⁻³ mol⁻¹) observed for the reaction of N_3^- ions with $[WO(H_2O)(CN)_4]^{2-}$.

Both this dissociative mode of activation and the much greater reactivity of the Tc(V) center compared to that of the Re(V) are of particular relevance to nuclear medicine. In the preparation of ^{99m}Tc radiopharmaceuticals or in the labeling of antibodies with ^{99m}Tc, "transfer" ligands are often used to stabilize the required oxidation state, and then the actual labeling is accomplished by simple ligand substitution onto the "transfer complex".[6] Since substitution onto Tc(V) and Re(V) centers appears to be dissociative in character, the most effective way to optimize labeling conditions would be to vary the nature of the transfer ligand rather than to vary the antibody concentration or the chelating moiety attached to the antibody. Furthermore, the great reactivity of technetium compared to that of rhenium will be of importance in developing therapeutic radiorhenium analogues to known diagnostic ^{99m}Tc radiopharmaceuticals; for example, diphosphonates such as methylenediphosphonate or hydroxyethylidenediphosphonate may be labeled with ^{186}Re for therapy[24] or with ^{99m}Tc for diagnosis.[5] The kinetic observations in this work imply that more stringent reaction conditions will be required to prepare radiorhenium analogues to ^{99m}Tc radiopharmaceuticals, and this indeed appears to be the case for ^{186}Re and ^{99m}Tc diphosphonates.[5,24] This difference in reactivities between Tc(V) and Re(V) centers needs to be taken into account before procedures that are available for certain technetium complexes are applied to the preparation of the rhenium analogues.

This investigation into the basic chemistry has identified some fundamental kinetic similarities among the $[MO_2(CN)_4]^{n-}$ complexes of Tc(V), Re(V), Mo(IV), and W(IV) and the protonated forms thereof but has also highlighted some important differences. Further related studies are planned to delineate those periodic relationships which are of importance to understand the prepa-

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ration and biological mechanisms of action of analogous complexes which have radiopharmaceutical applications.

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Registry No. $K_3TcO_2(CN)_4$, 138666-75-8; $[(CH_3)_4N][TcO(H_2O)(CN)_4]$, 138666-77-0; $Cd_2[Tc_2O_3(CN)_8]$, 138666-78-1; $K_4[Tc_2O_3(CN)_8]$, 138666-79-2; $(2,2'\text{-bpyH})_2[TcO(NCS)(CN)_4]$, 138666-81-6; $(n\text{-}Bu_4N)TcOCl_4$, 92622-25-8.

Supplementary Material Available: Listings of anisotropic thermal parameters, interatomic bond distances and angles, and crystallographic details (4 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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Electron-Transfer Reactions of Encapsulated Transition Metal Complexes. Oxidation of (4,4'-Bipyridine)pentaammineruthenium(II) by (Ethylenediaminetetraacetato)cobaltate(III)

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The encapsulation of pentaammine(ligand)ruthenium(II) (ligand = pyrazine or bipyridine) with cyclodextrins was investigated. The equilibrium constants ranged from ~20 to 100. The effect of encapsulation on electron-transfer rates was also determined, and a specific orientation of reactants within the precursor complex is discussed.

Introduction

During the last 3 decades, considerable progress has been made in understanding the mechanistic details of outer-sphere electron-transfer reactions. Recently, several excellent review articles have appeared on this subject.[1] One aspect which has remained relatively unexplored, however, is the nature of reactant orientation within the precursor complex.

Orientational effects have been postulated by researchers studying redox reactions of metalloproteins possessing heme rings.[2] For example, Sutin and others suggest that in cytochrome *c* the electron is passed to the iron center via the solvent-exposed edge of the porphyrin ring.[3] Using simple transition metal complexes, Haim and co-workers have examined the outer-sphere electron-transfer reactions for a series of pentaammine(*N*-heterocycle)ruthenium complexes with varying redox partners.[4] Haim postulated that, for certain couples, electron transfer occurred via the ammine ligands of the ruthenium complex while, for others, the *N*-heterocycle was involved. His discussion was based upon the Marcus cross relation for outer-sphere processes where the separation distance between the two metal centers at the point of electron transfer may be roughly assessed. Meyer also showed that intimate contact between coordination spheres occurs in outer-sphere electron transfer.[5] Studies by Lappin and co-workers have offered evidence for stereoselectivity in the ion-pair precursor structure from oxidation studies of cobalt(II) complexes.[6]

In order to provide a greater understanding of the role of noncoordinating ligands (thereby precursor complex orientation) in the outer-sphere electron-transfer process, we have begun a series of studies on the effect of encapsulation of aromatic ligands on the rate of redox reactions. Selective encapsulation was accomplished using cyclodextrins (CD's) (see Figure 1), which are known to possess high affinities toward aromatic organic species.[7]

$$X_5M\text{–bpy} + CD \overset{K_{CD}}{\rightleftharpoons} X_5M\text{–(bpyCD)}$$

In this study, we have measured the oxidation rate of $[Ru(NH_3)_5(4,4'bpy)]^{2+}$ with $[Co(EDTA)]^-$ in the presence of dimethyl-β-cyclodextrin (dmβCD). In addition, the equilibrium constants for the encapsulation of coordinated ligands were independently determined using spectrophotometric techniques.

Table I. Equilibrium Constants for Cyclodextrin/Metal Inclusion Complexes

complex	CD	K_{CD}	ref
$[Ru(NH_3)_5(bpy)]^{2+}$	dmβ	98 ± 8[a]	this work
$[Ru(NH_3)_5(pyz)]^{2+}$	dmβ	19 ± 1[a]	this work
$[Ru(NH_3)_5(bpy)]^{2+}$	α	23 ± 3[a]	this work
ferrocenecarboxylate	β	483	*b*
carbplatin	dmβ	295	*c*
carbplatin	α	165	*c*

[a] 0.05 M sodium bicarbonate (pH = 8.5), T = 25.0 °C, from spectral data (supplementary Table IIA–C). [b] Osa, T.; Kobayashi, N. *Chem. Lett.* **1986**, 421. [c] Alston, D.; Lilley, T. H.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1600.

Experimental Section

The metal complexes $Na[Co(EDTA)]$, $[Ru(NH_3)_5(4,4'bpy)](PF_6)_2$, and $[Ru(NH_3)_5(pyz)](PF_6)_2$ were prepared using literature methods.[8,9] Their visible spectra agree with literature reports. The 0.05 M sodium bicarbonate (Aldrich) buffer was prepared using a Beckman pH meter. Heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (Cyclolab or Sigma) was chosen because of its correct interior dimensions for including the bipyridyl moiety and its high solubility in water.[10]

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