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Technetium Cyanide Chemistry: Synthesis and Characterization of Technetium(III) and -(V) Cyanide Complexes

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Several new technetium cyanide complexes have been prepared and characterized. The reaction of ammonium hexaiodotechnetate(IV) with postassium cyanide in refluxing aqueous methanol under nitrogen yields potassium heptacyanotechnetate(III) dihydrate, $K_4Tc(CN)_7{\cdot}2H_2O$ (**1**). Infrared and Raman measurements indicate that **1** has a pentagonal-bipyramidal structure (D_{5h}) in both solid and solution. Aqueous solutions of **1** are air sensitive, decomposing to potassium oxopentacyanotechnetate(V) tetrahydrate, $K_2TcO(CN)_5{\cdot}4H_2O$ (**2**). This species can also be prepared from the reaction of $TcO_2{\cdot}xH_2O$ with hot aqueous potassium cyanide solutions. Hydrolysis of **2** in water yields potassium *trans*-dioxotetracyanotechnetate(V), $K_3TcO_2(CN)_4$ (**3**). Preparation of **3** can also be achieved from the treatment of $[TcO_2(Py)_4]ClO_4{\cdot}2H_2O$ with aqueous potassium cyanide. Infrared and Raman measurements on **3** are consistent with the proposed *trans*-dioxo (D_{4h}) structure. Reaction of the oxotetrachlorotechnetate(V) anion, $TcOCl_4^-$, with potassium cyanide in methanol produces *trans*-oxomethoxytetracyanotechnetate(V), $[TcO(OMe)(CN)_4]$ (**4**). The full details of the synthesis and characterization of these interesting technetium(III) and -(V) complexes, as well as observations on the infrared and Raman spectra of *trans*-dioxo metal complexes and the hydrolysis of species **2**, are presented.

Introduction

Technetium cyanide chemistry has remained largely unexplored, even though there are reports in the literature[2] of a wide range of rhenium cyanide complexes with coordination numbers as high as 8[3] and oxidation states as low as zero.[4] Recently, Griffith and co-workers[5] have shown many of those species had been misformulated; nevertheless, there still exists a wide variety of rhenium cyanide complexes.

The d^6 complexes $K_5M(CN)_6$ are known for manganese,[6] technetium,[7] and rhenium.[6,7] The salts are isomorphous by X-ray powder patterns.[7] Raman and infrared studies[8] on the salts show higher C–N stretches and lower M–C stretches as one moves down the group as expected from considerations of d-orbital overlap.

Recently, Griffith and Kiernan[9] have isolated a seven-coordinate rhenium cyanide complex $K_4Re(CN)_7{\cdot}2H_2O$ which appears to have a pentagonal-bipyramidal structure (D_{5h}) on the basis of Raman and infrared as well as X-ray structural evidence.[10]

Rhenium has also been shown to form oxocyano complexes when in the +5 oxidation state; *trans*-$ReO_2(CN)_4^{3-}$ [11] and *trans*-$Re_2O_3(CN)_8^{4-}$ [12] have had their structures confirmed through X-ray crystallographic studies. Protonation of $K_3ReO_2(CN)_4$ leads initially to the formation of $ReO(OH)(CN)_4^{2-}$.[13] In view of such findings, it is surprising that to date no technetium(V) cyano complexes have been reported.

Early polarographic studies[14] on the reduction of pertechnetate ion in the presence of cyanide ion apparently showed to tendency to form a technetium(V) species; however, technetium(IV) species was deemed possible, on the basis of a three-electron reduction wave ($E_{1/2}$ = –0.81 V vs. SCE).[14] Schwochau and Herr[15] had attempted to prepare $TcO_2(CN)_4^{3-}$ but instead isolated a yellow-brown species they formulated as $Tl_3Tc(CN)_4(OH)_3$, formally technetium(IV) exhibiting an infrared band at 905 cm^{-1} which they assigned as a Tc=O stretch, which is surprising in view of their formulation.

For comparison of the chemistries of technetium and rhenium, the synthesis of $Tc(CN)_7^{4-}$ was successfully achieved. During the course of this investigation, it was noticed that, like the rhenium analogue,[5] $Tc(CN)_7^{4-}$ decomposed slowly in oxygenated water. Two different species were identified as decomposition products: $TcO(CN)_5^{2-}$ and *trans*-$TcO_2(CN)_4^{3-}$, both technetium(V) complexes. The $Tc(CN)_4(OH)_3^{3-}$ ion prepared by Schwochau and Herr[15] has to be reformulated as $TcO(CN)_5^{2-}$ by comparison of synthetic and spectroscopic information. Another technetium(V) cyano complex, *trans*-$TcO(OMe)(CN_4)^{2-}$, has been prepared from $TcOCl_4^-$ and cyanide ion in methanol.

The synthesis, characterization, and molecular structure of the new technetium complexes $K_4Tc(CN)_7{\cdot}2H_2O$, $K_2TcO(CN)_5{\cdot}4H_2O$, $K_3TcO_2(CN)_4$, and $(n\text{-}Bu_4N)_2TcO(OMe)(CN)_4$ are discussed.

Experimental Section

All water used was passed through a Barnstead Ultrapure D8902 cartridge followed by distillation using a Corning AG-1 water still prior to use. All other reagents were used as received. All manipulations with $Tc(CN)_7^{4-}$ were done in N_2-purged solvents unless otherwise stated.

$NH_4{}^{99}TcO_4$ in aqueous solution was purchased from New England Nuclear. The concentration was determined by literature method.[16] ^{99}Tc is a weak β emitter (0.292 MeV, half-life 2.12×10^5 years); therefore, all manipulations were carried out in a radiation laboratory with a monitored fume hood. Personnel wore disposable lab coats and gloves at all times. Radioactive wastes, both liquid and solid, were disposed in special receptacles. Samples sent outside of the laboratories' jurisdiction were wipetested for contamination prior to shipment, and all regulations[17] regarding such transportation were followed. All reagents and solvents were used without further purification. Elemental microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

$(NH_4)_2TcBr_6$ and $(NH_4)_2TcI_6$ were prepared by the method of Nelson et al.[18] The preparation of $n\text{-}Bu_4NTcOCl_4$ was performed

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(1) (a) Massachusetts Institute of Technology. (b) Harvard Medical School and Peter Bent Brigham Hospital.
(2) Griffith, W. P. *Coord. Chem. Rev.* **1975**, *17*, 177–248.
(3) Colton, R.; Peacock, R. D.; Wilkinson, *J. Chem. Soc.* **1960**, 1374–8.
(4) Colton, R. "The Chemisty of Rhenium and Technetium"; Interscience: London, 1965; p 141.
(5) Griffith, W. P.; Kiernan, P. M.; Bregeault, J.-M. *J. Chem. Soc., Dalton Trans.* **1978**, 1411–7.
(6) Clauss, D.; Lissner, A. *Z. Anorg. Allg. Chem.* **1958**, *297*, 300–10.
(7) Schwochau, K.; Herr, W. *Z. Anorg. Allg. Chem.* **1962**, *319*, 148–58.
(8) Krasser, W.; Bohres, E. W.; Schwochau, K. *Z. Naturforsch., A* **1972**, *27*, 1193–7.
(9) Kiernan, P. M.; Griffith, W. P. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 377–80.
(10) Griffith, W. P., personal communication.
(11) Fenn, R. H.; Graham, A. J.; Johnson, N. P. *J. Chem. Soc. A* **1971**, 2880–3.
(12) Shandles, R.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1971**, *10*, 2785–8.
(13) Toppen, D. L.; Murmann, R. K. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 139–44.
(14) Colton, R.; Dalziel, J. A. W.; Griffith, W. P.; Wilkinson, G. *J. Chem. Soc.* **1960**, 71–8.
(15) Schwochau, K.; Herr, W. *Z. Anorg. Allg. Chem.* **1962**, *318*, 198–211.
(16) Boyd, G. E. *J. Chem. Educ.* **1959**, *36*, 3–14.
(17) Transportation of radioactive meterials is covered by federal regulations 49CFR173.391-9 and 29CFR11524, 11526. ^{99}Tc is a group 4 radionuclide.

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as described by Davison et al.[19] The *trans*-dioxo(tetrapyridine)technetium(V) cation, $TcO_2(py)_4^+$, can be prepared from $(NH_4)_2TcCl_6$[20] or from the reaction of $TcOCl_4^-$ with pyridine in aqueous methanol.[21]

Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer as either KBr pellets or aqueous solutions in matched AgCl plates (0.5-mm path length). Raman spectra were obtained as either solid samples or aqueous solutions in a capillary by using a Spex Ramalog with the 5145-Å line of an Ar laser. Optical spectra in water or acetonitrile were recorded on a Cary 17 spectrophotometer. Conductivity measurements were made in the concentration range 10-0.1 mM in acetonitrile with a Yellow Springs Model 3403 conductivity cell and a Serfass conductivity bridge.

Magnetic susceptibility measurements were obtained with a home-built Faraday balance using a Varian V-4005 electromagnet with constant-force pole faces and a Cahn RG electrobalance.

Nuclear magnetic resonance measurements of $(n\text{-}Bu_4N)_2TcO(OMe)(CN)_4$ were made on a Varian T 60-MHz spectrometer with CD_2Cl_2 as solvent and tetramethylsilane as the internal calibrant.

Preparation of Potassium Heptacyanotechnetate(III) Dihydrate. To a 50-mL round-bottom flask with side arm and stir bar was added 0.377 g (0.42 mmol) of $(NH_4)_2TcI_6$. The flask was evacuated on a Schlenk line and backfilled with N_2, twice. Another 50-mL round-bottom flask was charged with 1.20 g (18.4 mmol) of freshly ground KCN and then purged thoroughly with N_2. TcI_6^{2-} was partially dissolved in 10 mL of N_2-purged methanol added via a cannula. An aqueous cyanide solution was prepared by the addition of 10 mL of N_2-purged water to the KCN. This solution was transferred via a cannula to the TcI_6^{2-} solution. A heating mantle and a N_2-purged Hopkin's coil condenser were added, and the dark mixture was refluxed under N_2 for 24 h. The resultant orange solution was filtered under N_2, leaving behind a small amount of dark solid. Methanol, N_2 purged, was added until the yellow solid formed appeared to contain all the color of the mixture. The yellow solid was filtered under N_2, washed with two 10-mL portions of N_2-purged metanol, and dried in vacuo. The apparatus was backfilled with N_2, and 0.1 g of KCN was added. Both solids were dissolved with 5-mL of N_2-purged water, added via a cannula. The golden solution was filtered into a N_2-purged three-neck 50-mL round-bottom flask equipped with a Schlenk frit and 50-mL round-bottom flask. Methanol, N_2 purged 20–25 mL, was added, precipitating a yellow solid. This mixture was heated under N_2 to redissolve the solid. The golden solution was quickly filtered and then allowed to cool slowly. The solution was placed in a refrigerator at 5 °C for 24 h. Yellow-orange crystals of $K_4Tc(CN)_7\cdot 2H_2O$ were filtered and washed with methanol prior to drying in vacuo. The yield was 0.056 g on the basis of (28% technetium). Anal. Calcd for $C_7H_4K_4N_7O_2Tc$: C, 17.75; H, 0.85; N, 20.70. Found: C, 17.95; H, 1.30; N, 20.86. IR(KBr): 2090 (s), 2045 (s) cm^{-1}. IR (H_2O): 2089 (s), 2046 (s) cm^{-1}. Raman (solid): 2123 (s), 2114 (s), 2109 (m), 2079 (s) cm^{-1}. Raman (H_2O): 2123 (p), 2110 (p), 2072 (dp) cm^{-1}. Optical spectra in degassed water show bands at 455 (ϵ 90 L mol^{-1} cm^{-1}), 280 (ϵ 790), and 243 nm (ϵ 15 000). The solid is diamagnetic.

Preparation of Potassium Oxopentacyanotechnetate(V) Tetrahydrate. A suspension of $TcO_2\cdot xH_2O$ in water was prepared by the hydrolysis of 0.062 g (0.10 mmol) of $(NM_4)_2TcBr_6$ in 6 mL of water and 1 mL of concentrated NH_4OH. The black solid was centrifuged, the aqueous filtrate was removed, and the solid was washed with 6 mL of water. After centrifugation, the solid was suspended in 6 mL of water and transferred to a 25-mL round-bottom flask equipped with a stir bar. To this suspension was added 0.50 g (7.68 mmol) of KCN, and the mixture was refluxed for 1.5 h, yielding a clear, honey-colored solution. The reaction mixture was transferred to a 100-mL round-bottom flask when cool, and then methanol was added (30 mL) until the yellow solid appeared by heating and then allowed to cool slowly, and the flask was stoppered and placed in a 5 °C refrigerator for 24 h. Pale, greenish yellow crystals of $K_2TcO(CN)_5\cdot 4H_2O$ were filtered onto a medium-porosity fritted filter, washed with methanol, and then dried in vacuo. The yield of green-yellow flakes was 0.012 g (31% on the basis of technetium). Anal. Calcd for $C_5H_8K_2N_5O_5Tc$: C, 15.19; H, 2.04; N, 17.71. Found: C, 14.90; H, 1.00; N, 17.80. IR (KBr): 2095 (m), 2080 (s), 2035 (w–m) (CN); 910 (m) cm^{-1} (TcO). Optical spectra in water reveal bands at 680 (ϵ 60 L mol^{-1} cm^{-1}), 466 (ϵ 680), and 387 nm 46 900). The solid can also be isolated from aerobic recrystallizations of $K_4Tc(CN)_7\cdot 2H_2O$.

Preparation of Potassium *trans*-Dioxotetracyanotechnetate(V). To a 25-mL round-bottom flask with stir bar were added 0.247 g (0.42 mmol) of $TcO_2(py)_4ClO_4\cdot 2H_2O$ and 2.0 g (30.7 mmol) of KCN. Next, 12 mL of water was added, and the mixture was stirred overnight. The resultant yellow solution was filtered to remove some white solid, and methanol was added slowly to the filtrate until crystals began to appear. Additional methanol was added until the total volume was approximately 90 mL. The solid was filtered out on a medium-porosity fritted filter and recrystallized from methanol/water to yield 0.14 g of $K_3TcO_2(CN)_4$ as lemon yellow needles (90% on the basis of technetium). Anal. Calcd for $C_4K_3N_4O_2Tc$: C, 13.63; N, 15.90. Found: C, 13.56; N, 15.42. IR (KBr): 2120 (s) (CN); 785 (s) cm^{-1} (TcO_2). IR (H_2O): 2120 (s) cm^{-1}. Raman (solid): 2110 (s), 2095 (w), 2080 (s), 1971 (s) (CN); 827 (m) cm^{-1} (TcO_2). Raman (H_2O): 2133 (p), 2127 (dp) (CN); 838 (p) cm^{-1} (TcO_2). The optical spectra in water have bands at 460 (ϵ 25 L mol^{-1} cm^{-1}), 325 (ϵ 875), and 248 nm (ϵ 8220). The solid, $K_3TcO_2(CN)_4$, can also be prepared by repeated hydrolysis of either $K_4Tc(CN)_7\cdot 2H_2O$ or $K_2TcO(CN)_5\cdot 4H_2O$.

Preparation of Tetrabutylammonium *trans*-Oxomethoxytetracyanotechnetate(V). A 25-mL round-bottom flask with stir bar was charged with 0.073 g (0.15 mmol) of $n\text{-}Bu_4NTcOCl_4$ and 0.06 g (0.92 mmol) of KCN. Addition of 10 mL of methanol resulted in a plum colored solution and some white solid. The solution was stirred for 1 h, and then 0.18 mL of 75% w/w $n\text{-}Bu_4NCl$ was added. It was followed by 1 mL of water. The solution turned clear, plum colored. It was filtered, and the filtrate was left to stand in a beaker to slowly evaporate. Large lilac needles were separated and washed with 3 mL of water, followed by 20 mL of ether. The solid was dried in vacuo. The yield of $(n\text{-}Bu_4N)_2TcO(OMe)(CN)_4$ was 0.050 g (46% on the basis of technetium). Anal. Calcd for $C_{37}H_{45}N_6O_2Tc$: C, 60.46; H, 10.29; N, 11.43. Found: C, 60.47; H, 10.38; N, 11.00. IR (KBr): 2788 (m) (OMe); 2139 (vw), 2166 (ms) (CN); 1460 (s) (OMe), 1097 (s) (OMe); 932 (vs) cm^{-1} (TcO). NMR: (CD_2Cl_2): δ 3.25 (br, 19 H, OCH_3, $NCH_2CH_2CH_2CH_3$), 1.60 (br, 32 H, $NCH_2CH_2CH_2CH_3$), 1.00 (br, 24 H, $NCH_2CH_2CH_3$). Optical spectra in acetonitrile show bands at 547 (ϵ 45 L mol^{-1} cm^{-1}), 370 (sh), 297 (ϵ 5680). The solid is a 2:1 electrolyte in acetonitrile, $\Lambda_0 = 367$ cm^2 Ω^{-1} $equiv^{-1}$.

Results and Discussion

The synthesis of the yellow-orange potassium heptacyanotechnetate(III) dihydrate from hexaiodotechnetate(IV) in refluxing aqueous methanol is similar to a preparation of the rhenium analogue described by Griffith and Kiernan[9] using hexaiodorhenate(IV). Technetium(IV) halide salts have been shown to undergo reduction easily;[22] in this case, iodide ion is sufficient to reduce technetium(IV) to technetium(III) and cyanide ion is able to stabilize this oxidation state.

mer-Trichlorotris(dimethylphenylphosphine)technetium[23] has been shown to react with 1 mol of carbon monoxide in refluxing ethanol to form the first example of a seven-coordinate complex of technetium.[24] Seven-coordinate complexes can exist in several different geometries: I, pentagonal bipyramidal; II, monocapped trigonal prism; III, monocapped octahedron; IV, tetragonal base–trigonal base. X-ray crystallography[25] has shown that $TcCl_3(PMe_2Ph)_3CO$ is a monocapped octahedron, having C_{3v} symmetry, i.e., structure type III. Potassium heptacyanotechnetate(III) dihydrate, $K_4Tc(CN)_7\cdot 2H_2O$, is only the second seven-coordinate technetium complex to be discovered.

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[18] Nelson, C. M.; Boyd, G. E.; Smith, W. T., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 348–52.

[19] Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M. S.; DePamphilis, B. V.; Jones, A. G., preceding paper in this issue.

[20] Kuzina, A. F.; Oblova, A. A.; Spitsyn, V. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1972**, *17*, 1377–8.

[21] Unpublished results: Trop, H. S. Ph.D. Thesis, M.I.T., May 1979.

[22] Trop, H. S.; Davison, M. A. *J. Inorg. Nucl. Chem.* **1979**, *41*, 271–2.

[23] Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1976**, 125–30.

[24] Mazzi, U.; Bismondo, A.; Kotsev, N.; Clemente, D. A. *J. Organomet. Chem.* **1977**, *135*, 177–82.

[25] Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1978**, 373–80.

Table I. Selected Spectral Data (cm^{-1}) for (n-$Bu_4N)_2TcO(CN)_5\cdot 4H_2O$, ($n$-$Bu_4N)_2TcO(OMe)(CN)_4$, and $K_4Tc(CN)_7\cdot 2H_2O$

complex	IR	Raman
$K_2TcO(CN)_5\cdot 4H_2O$	2095 (ms),[a] 2080 (s),[a] 2035 (w-m),[a] 910 (m)[b]	
(n-$Bu_4N)_2TcO(OMe)(CN)_4$	2790 (m),[c] 2189 (vw),[a] 2116 (ms),[a] 1460 (s),[d] 1097 (s),[e] 932 (vs)[b]	
$K_4Tc(CN)_7\cdot 2H_2O$	2089 (s),[a] 2046 (s)[a]	2123 (s),[a,f] 2110 (s),[a,f] 2072 (s)[a]

[a] CN stretch. [b] TcO stretch. [c] C–H stretch. [d] C–H bond. [e] C–O bend/stretch. [f] Polarized Raman shift.

It was possible to determine the coordination geometry of $K_4Tc(CN)_7\cdot 2H_2O$ through the use of Raman and infrared spectroscopy and observations of similar data obtained on heptacyanometalates whose structures are known. The infrared and Raman data for $K_4Tc(CN)_7\cdot 2H_2O$ are contained in Table I. Both $K_4V(CN)_7\cdot 2H_2O$[26] and $K_4Re(CN)_7\cdot 2H_2O$[10] have been shown to have type I structures, pentagonal bipyramidal, by X-ray crystallography. For such molecules, use of group theory predicts two infrared active ($E_1' + A_2''$) and three Raman active ($2\ A_1' + E_2''$) cyanide stretching modes with no coincidences. In solution, there should be two polarized Raman shifts ($2\ A_1'$ modes). In the case of $K_4Re(CN)_7\cdot 2H_2O$, such behavior is observed.[9] For $K_4V(CN)_7\cdot 2H_2O$, only one broad, unresolved polarized band could be observed.[27] The pentagonal bipyramid offers the least complex spectra in the cyanide stretching region and is the only structure that does not allow coincidences between the infrared- and Raman-allowed modes.

The molybdenum(II) complexes $Na_5Mo(CN)_7\cdot 10H_2O$ and $K_5Mo(CN)_7\cdot H_2O$[28] have been studied recently via X-ray crystallography.[29] One of them, $Na_5Mo(CN)_7\cdot 10H_2O$, appears to be a well-behaved pentagonal bipyramid. However, crystal packing in $K_5Mo(CN)_7\cdot H_2O$ causes a mild distortion from ideal type I symmetry that displaces an equatorial cyanide up out of the equatorial plane slightly. As a result, the solid infrared shows many more bands than the sodium salt. The completely anhydrous salt $K_5Mo(CN)_7$ has been assigned geometry type II on the basis of the infrared[9] and the crystal structure of $K_5Mo(CN)_7\cdot H_2O$[29] although geometry IV cannot be ruled out on the basis of the available data.

Infrared and Raman data[30] for $K_4Mo(CN)_7\cdot 2H_2O$[31] seem to indicate a pentagonal-bipyramidal structure in solution and a monocapped trigonal prism (II) in the solid state.

On the basis of these observations and the results of the Raman and infrared studies on $K_4Tc(CN)_7\cdot 2H_2O$, pentagonal-bipyramidal structure is indicated both in solid and solution. There are two bands in the infrared (A_2'', E_1'; 2090, 2045 cm^{-1}), and the three Raman shifts are noncoincident with the infrared absorptions; in solution, two are polarized ($2\ A_1'$; 2123, 2110 cm^{-1}) while the remaining one is depolarized (E_2'; 2072 cm^{-1}).

Magnetic susceptibility measurements on $K_4Tc(CN)_7\cdot 2H_2O$, a d^4 ion, indicate that the solid is diamagnetic, as expected from the strong-field ground state, $^1A_1'$. The yellow-orange solid dissolved in deoxygenated water (excess cyanide ion present) to yield bright golden solutions with optical absorption bands at 243, 280, and 455 nm. In the presence of oxygen, solutions of $Tc(CN)_7^{4-}$ slowly decompose, as observed by optical spectroscopy. Optical absorption bands at 325 and 378 nm can be observed. Treatment of such solutions with methanol precipitates yellow solids which by infrared spectroscopy reveal several bands in the cyanide stretching region as well as the appearance of bands at 910 and 785 cm^{-1} in the metal–oxygen stretching region.

Table II. Comparison of Stretching Frequencies (cm^{-1}) for t-$MO_2(CN)_4^{x-}$ Complexes

	IR		Raman	
	ν_{CN}	$\nu_{MO_2^-}$ (asym)	ν_{CN}	$\nu_{MO_2^-}$ (sym)
$K_3TcO_2(CN)_4$	2120 (s)	785 (s)	2110 (s), 2080 (s), 2141 (p), 2130[e]	827 (m), 838 (p)[e]
$K_3ReO_2(CN)_4$[a,b]	2125 (s)	768 (s)	2141 (s), 2130 (s), 2141 (p), 2130[e]	871 (m), 881 (p)[e]
$K_4[MoO_2(CN)_4]\cdot 6H_2O$[b,d]	2060 (s)	800 (s)		779
$K_4[WO_2(CN)_4]\cdot 6H_2O$[b,d]	2060 (s)	720 (s)		
$K_2OsO_2(CN)_4$[b,c]	2152 (s)	830 (s)		886 (p)[e]

[a] Reference 33. [b] Reference 34. [c] Reference 35. [d] Reference 31. [e] Solution spectra in water.

Other heptacyanometalates undergo decomposition in solution; for example, $Mo(CN)_7^{4-}$ decomposes in air to $Mo(CN)_8^{4-}$ and MoO_4^{2-},[30] and $V(CN)_7^{4-}$ decomposes to $VO(CN)_5^{3-}$ and $V(CN)_6^{4-}$ in the absence of excess cyanide in anaerobic solutions.[27]

Two species can be obtained from the decomposition of $Tc(CN)_7^{4-}$ in aqueous solution: $K_2TcO(CN)_5\cdot 4H_2O$ and $K_3TcO_2(CN)_4$, both technetium(V) complexes. The preparation and characterization of these two species will be discussed below.

When $K_4Tc(CN)_7\cdot 2H_2O$ was recrystallized from aerobic water/methanol mixtures, yellow-orange crystals of $K_4Tc(CN)_7\cdot 2H_2O$ formed. These were easily separated by the Pasteur method. The infrared spectrum of the former revealed three bands in the cyanide stretching region and on band in the Tc=O stretching region at 910 cm^{-1} (Table I). For a $MX(CN)_5$ system (C_{4v}) group theory predicts three ($2\ A_1 + E$) infrared-allowed cyanide stretching modes; this is what is observed.

It was found that reaction of $TcO_2\cdot xH_2O$, an insoluble black precipitate, with hot, aqueous cyanide also formed $K_2TcO(CN)_5\cdot 4H_2O$ upon crystallization with methanol. This method, interestingly, is identical with the preparation of "$Tc(CN)_4(OH)_3^{3-}$" reported by Schwochau and Herr[15] and is isolated as the thallous salt. The "$Tc(CN)_4(OH)_3^{3-}$" species was observed to have the identical optical spectrum as the yellow $TcO(CN)_5^{2-}$ in aqueous solution with a very strong band at 378 nm and a weaker band around 460 nm. No mention of a weak band at 680 nm (ϵ 25 L mol^{-1} cm^{-1}) as observed in $TcO(CN)_5^{2-}$ was made in the case of "$Tc(CN)_4(OH)_3^{3-}$". Only one broad band was noticed in the cyanide stretching region at 2050 cm^{-1}, and a band at 905 cm^{-1} was assigned to a Tc=O stretch for $Tl_3Tc(CN)_4(OH)_3$. Thus, it seems that $Tc(CN)_4(OH)_3^{3-}$ should be reformulated as $TcO(CN)_5^{2-}$.

The reaction of $ReO_2\cdot xH_2O$ with hot aqueous cyanide led to the isolation of $Tl_3ReO_2(CN)_4$.[15] At this time, there is no report of a species formulated as $Re(CN)_4(OH)_3^{3-}$ or $ReO(CN)_5^{2-}$, although such a species might be implicated in the production of the *trans*-dioxo complex, vide infra. The yellow salt, $K_2TcO(CN)_5\cdot 4H_2O$, hydrolyzes in aqueous solution slowly in the absence of cyanide ion to form $K_3TcO_2(CN)_4$.

The use of n-$Bu_4NTcOCl_4$ as a reagent for exploring oxotechnetium(V) chemistry has been demonstrated recently.[19] In an attempt to prepare $TcO(CN)_5^{2-}$ directly from a technetium(V) precursor, n-$Bu_4NTcOCl_4$ was reacted with 5 equiv

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(26) Levenson, R. A.; Towns, R. L. R. *Inorg. Chem.* **1974**, *13*, 105–9.

(27) Levenson, R. A.; Dominquez, F. J. G.; Willis, M. A.; Young, F. R. III *Inorg. Chem.* **1974**, *13*, 2761–4. Griffith, W. P.; Kiernan, P. M.; O'-Hare, B. P.; Bregeault, J. M. *J. Mol. Struct.* **1978**, *46*, 307–17.

(28) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67–210.

(29) Drew, M. G. B.; Mitchell, P. C. H.; Pygall, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 1071–7.

(30) Rossman, G. F.; Tsay, R.-D.; Gray, H. B. *Inorg. Chem.* **1973**, *12*, 824–9.

(31) Young, R. C. *J. Am. Chem. Soc.* **1932**, *54*, 1402–5.

of potassium cyanide in methanol. Instead of the expected yellow solution, a plum-colored solution resulted, and well-formed lilac needles were obtained upon addition of tetrabutylammonium ion and crystallization from methanol/water. On the basis of elemental analysis, this salt is formulated as $(n\text{-}Bu_4N)_2TcO(OMe)(CN)_4$, an oxotechnetium(V) species. Equivalent conductance measurements in acetonitrile demonstrated that $TcO(OMe)(CN)_4^{2-}$ was a 2:1 electrolyte similar to $(n\text{-}Bu_4N)_2TcCl_6$ in acetonitrile.

Infrared measurements (Table I) and NMR data[32] confirmed the presence of the methoxide ligand and the two bands in the cyanide stretching region (2136 (vw), 2116 (ms) cm^{-1}) are indicative of a trans arrangement for the oxo–technetium–methoxide linkage.

The species $TcO(CN)_5^{2-}$ and $t\text{-}TcO(OMe)(CN)_4^{2-}$ are quite similar differing only in the ligand trans to the oxo ligand. The Tc=O stretch of the methoxide complex appears at 932 cm^{-1} whereas that of the cyano complex occurs at 910 cm^{-1}.

As was noted earlier, in aqueous solution, $K_2TcO(CN)_5\cdot 4H_2O$ hydrolyzes to $t\text{-}TcO_2(CN)_4^{3-}$. Upon repeated recrystallizations from aerobic methanol/water solutions, $K_4Tc(CN)_7\cdot 2H_2O$ yields $K_3TcO_2(CN)_4$ as a yellow crystalline salt. A more direct synthesis involved treatment of an aqueous suspension of $[t\text{-}TcO_2(py)_4]ClO_4\cdot 2H_2O$ with a large excess of potassium cyanide. Addition of methanol to the resultant lemon yellow solution resulted in the formation of $K_3TcO_2(CN)_4$ in high yield.

The molecular structure has been assigned as being *trans*-dioxo by infrared and Raman data. A *trans*-dioxotetracyanometalate ion (D_{4h}) should have on infrared-active mode (E_u) and two Raman-active modes (A_{1g}(p), B_{1g}) in the cyanide stretching region; the metal oxygen stretching region should possess one infrared-active mode (A_{2u}) and one Raman-active mode (A_{1g}(p)). The inversion center allows no coincidences. As can be seen in Table II, $K_3TcO_2(CN)_4$ shows such behavior and is similar to other $t\text{-}MO_2(CN)_4^{x-}$ species whose structures have been confirmed by X-ray crystallography.[11,33,34] Of special interest is the relative position of the symmetric metal–oxygen stretch (Raman active) with respect to the asymmetric metal–oxygen stretch (infrared active). Most linear triatomic systems (or systems that can be viewed as linear triatomics) have $\upsilon_{asym} > \upsilon_{sym}$; $t\text{-}UO_2^{2+}$ systems as well as other inorganics such as CO_2 also demonstrate this property.[38] However, experimentally, *trans*-dioxo species of technetium, rhenium,[35,36] and osmium[36,37]are found to have $\upsilon_{sym} > \upsilon_{asym}$. Molybdenum and tungsten *trans*-dioxo species show the normal trend.[33,36] The *trans*-dioxoruthenium(VI) species $M_2RuO_2Cl_4$ (M = H_3O, Cs, Rb) are unstable,[39] and this has probably precluded Raman studies on these salts. Cotton and Wing[40] had observed differences between UO_2^{2+} species and $RO_2(py)_4^+$ and $OsO_2Cl_4^{2-}$ salts. Calculations of the interaction constants, k_i, derived from **F** matrices[41] for the *trans*-dioxo complexes yielded negative interaction constants for the actinides and positive interaction constants for rhenium and osmium.[40] This observation does not account for the behavior of molybdenum and tungsten; the interaction force constants, k_i, have been determined and are positive.[35] Although the change in sign of k_i for the actinide complexes relative to the d-block complexes is fundamentally quite interesting, the behavior of osmium, technetium, and rhenium cannot be explained from such analysis.

Of possible importance may be the electron-attracting ability of the metal for the oxygen 2pπ orbitals. Since $MoO_2(CN)_4^{4-}$, $WO_2(CN)_4^{4-}$, $TcO_2(CN)_4^{3-}$, $ReO_2(CN)_4^{3-}$, and $OsO_2(CN)_4^{2-}$ are all isostructural and pseudoisoelectronic, the only apparent difference is oxidation state of the transition metal. In fact (within the same row of the periodic table), the symmetric stretching frequency decreases as the oxidation state is lowered. The symmetric stretch would be expected to be more sensitive to changes in π bonding than the asymmetric stretch because of the different nature of the interactions between metal and oxygen in each case.

In the case of the symmetric stretch, the π interactions between the metal and both oxygen atoms will be weakened or strengthened as the molecule vibrates in that mode. In the asymmetric stretch, the change in π interaction that results as one oxygen moves away will be moderated by the increased π interaction of the other oxygen atom as it moves closer to the metal atom. Since π overlap increases down a periodic column, one would expect to see the symmetric stretching frequency also increase. This behavior is indeed observed for technetium and rhenium, with Raman shifts at 838 and 881 cm^{-1} for $K_3TcO_2(CN)_4$ and $K_3ReO_2(CN)_4$, respectively.

The optical spectrum of aqueous $TcO_2(CN)_4^{3-}$ is quite similar to the reported spectrum of aqueous $ReO_2(CN)_4^{3-}$[15] with absorptions at 325 and 248 nm showing the expected bathochromic shift from the 270- and 215-nm absorptions reported for $ReO_3(CN)_4^{3-}$.

The failure of the reaction between $TcOCl_4^-$ and cyanide ion in methanol to form $TcO(CN)_5^{2-}$ was extremely fortunate. The complex $TcO(OMe)(CN)_4^{2-}$ can be viewed as a trapped intermediate in the hydrolysis of $TcO(CN)_5^{2-}$ to $TcO_2(CN)_4^{3-}$. The oxo ligand is apparently a strong trans labilizer; it is not surprising then that $TcO(CN)_5^{2-}$ is stable in aqueous solution only when excess cyanide ion is present. Substitution of the cyanide ion trans to the oxo by solvent[42] leads to $t\text{-}TcO(ROH)(CN)_4^-$ which can also be formed directly from $TcOCl_4^-$ and cyanide in methanol if methanol is coordinated to the technetium atom prior to reaction.[43]

Once the solvent is coordinated, the solvent oxygen is rapidly deprotonated. When methanol is the solvent, this reaction terminates at $t\text{-}TcO(MeO)(CN)_4^{2-}$ because demethylation is energetically unfeasible. When the solvent is water, however, further deprotonation from a $TcO(OH)(CN)_4^{2-}$ intermediate to $TcO_2(CN)_4^{3-}$ is rapid. Protonation of $ReO_2(CN)_4^{3-}$ to $ReO(OH)(CN)_4^{2-}$ requires solutions of approximately 1 M H^+.[13] In the case of $TcO_2(CN)_4^{3-}$, a color change from yellow to deep blue is observed when concentrated perchloric or hydrochloric acid is added. Although the nature of this blue material is currently unknown, the protonation of an oxygen atom in $ReO_2(CN)_4^{3-}$ clearly requires stongly acidic conditions; thus, deprotonation of the $MO(OH)(CN)_4^{2-}$ species would be expected to be rapid in neutral solution.

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(32) A broad multiplet at δ 3.25 contains 19 protons by integration rather than 16 predicted for the methylenes α to the nitrogen on the two tetrabutylammonium cations. Unfortunately, the exact position of the methoxide absorption in this multiplet cannot be determined unequivocally at this time.

(33) Lippard, S. J.; Russ, B. J. *Inorg. Chem.* **1967**, *6*, 1943–7.

(34) Kruse, F. H. *Acta Crystalloys.* **1961**, *14*, 1035–41.

(35) Griffith, W. P. *J. Chem. Soc. A* **1969**, 211–8.

(36) Griffith, W. P. *J. Chem. Soc.* **1964**, 245–9.

(37) Johnson, N. P.; Lock, C. J.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054–66.

(38) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd. ed., Wiley: New York, 1978; p 116.

(39) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 1005.

(40) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 867–73.

(41) Detailed descriptions of **F** and **G** matrices and thier use in complex molecules can be found in: (a) Wilson, E. B.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955; (b) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978.

(42) Whether the mechanism for this substitution is a dissociative or an associative process (or some combination of both) has not been investigated.

(43) Crystals of $n\text{-}Bu_4NTcOCl_4$ obtained from methanol craze violently when dried, suggesting that methanol may be weakly coordinated to technetium. By comparison, $Et_4NReOBr_4\cdot{}^1/_2H_2O$ and $Ph_4AsReOBr_4\cdot CH_3CN$ lose solvent in vacuo at 80 °C.[44]

(44) Cotton, F. A.; Lippard, S. J. *Inorg. Chem.* **1966**, *5*, 9–16.

Reaction of $ReOCl_3(PPh_3)_2$ with $NaEt_2NCS_2{\cdot}3H_2O$ in acetone solution[45,46] forms the well-characterized $Re_2O_3(Et_2NCS_2)_4$[46,47] which contains a linear O=Re—O—Re=O backbone. When the reaction is run in methanol, rather than acetone, the product isolated is *t*-$ReO(OMe)(dtc)_2$.[46] This material is easily converted to $Re_2O_3(dtc)_4$ in methylene chloride. The reaction of $ReOCl_3(PPh_3)_2$ pyridine in wet benzene leads to isolation of $Re_2O_3(py)_4Cl_4$,[48] another linear backbone, whereas reaction in ethanol[37] leads to the formation of $ReO_2(py)_4^+$. Addition of ethanol to $Re_2O_3(py)_4Cl_4$ results in formation of *t*-$ReO(OEt)py)_2Cl_2$ which is further converted to $ReO_2(py)_4^+$ upon addition of wet pyridine.[48]

The formation of the $M_2O_3^{4+}$ unit in $Re_2O_3(dtc)_4$,[45] $Re_2O_3(py)_4Cl_4$,[47] and $K_4Re_2O_3(CN)_8$[13] has been postulated to involve an intermediate *t*-$MO(OH)L_4$ species, which dimerizes and dehydrates to form the *t*-$M_2O_3^{4+}$ core.

Of special interest is the observation that the alkoxide species $ReO(OMe)(dtc)_2$ and $ReO(OEt)(Py)_2Cl_2$ are easily converted to $Re_2O_3(dtc)_4$ and *t*-$ReO_2(py)_4^+$, respectively.[46,48] In the case of $TcO(OMe)(CN)_4^{2-}$, there is no evidence for such a transformation under the mild conditions utilized in the rhenium complexes. Whether this behavior is due to the presence of cyanide ion or represents a fundamental difference between technetium and rhenium cannot be clearly ascertained at this time.

The isolation of $K_4Tc(CN)_7{\cdot}2H_2O$, $K_2TcO(CN)_5{\cdot}4H_2O$, $K_3TcO_2(CN)_4$, and $(n\text{-}Bu_4N)_2TcO(OMe)(CN)_4$ clearly demonstrates that technetium does indeed form a wide variety of cyanide complexes which parallel the known chemistry of its third-row congener, rhenium.

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Registry No. **3**, 73466-61-2; **4**, 73396-83-5; $K_4Tc(CN)_7$, 73396-81-3; $K_2TcO(CN)_5$, 73396-80-2; $(NH_4)_2TcI_6$, 40694-78-8; $(NH_4)_2TcBr_6$, 29462-54-2; $TcO_2(py)_4ClO_4$, 73396-79-9; *n*-$Bu_4NTcOCl_4$, 71341-65-6.

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(45) Rowbottom, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 826–30.

(46) Tisley, D. G.; Walton, R. A.; Wills, D. L. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 523–6.

(47) Fletcher, S. R.; Rowbottom, J. F.; Skapski, A. C.; Wilkinson, G. *Chem. Commun.* **1970**, 1572–3.

(48) Johnson, N. P.; Taha, F. I. M.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2614–6.

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Binding and Activation of Enzymic Substrates by Metal Complexes. 5.[1] Synthesis, Structure, and Properties of Some Acetylenic Complexes of Oxomolybdenum(IV) Dithiocarbamates

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Reaction of $OMo(S_2CNR_2)_2$ (R = Me, Et) with various acetylenes ($C_2R^1R^2$: $R^1 = R^2 = H$; $R^1 = R^2 = Ph$; $R^1 = H$, $R^2 = Ph$; $R^1 = R^2 = CO_2Me$; $R^1 = R^2 = CF_3$; $R^1 = R^2 = COC_6H_5Me$; $R^1 = H$, $R^2 = CO_2Me$) produces the 1:1 complexes $OMo(S_2CNR_2)_2(C_2R^1R^2)$. These reactions have equilibrium constants in the range $\sim 20\,000\ M^{-1}$ (for $R^1 = R^2 = CO_2Me$) to $\sim 20\ M^{-1}$ (for $R^1 = R^2 = H$). Infrared spectroscopy indicates that these products are better described as complexes of Mo(VI) formed by oxidative addition of the acetylenic bond to Mo(IV). The structure of $OMo(S_2CNMe_2)_2(C_2R_2)$ ($R = COC_6H_5Me$) also conforms to this description. The acetylenic C–C bond is 1.267 Å and is perpendicular to the metal–oxygen bond (1.686 Å). The molybdenum–acetylenic carbon bonds are rather short (2.12 Å). NMR spectrometry indicates significant acetylene-to-metal π-electron donation from the position of the deshielded resonance of the bound acetylene in line with the shorter M–C bond. Variable-temperature NMR spectra show all these complexes to have similar structures in solution, which are fluxional, and that the stereochemistry determined in the solid state is conserved in solution. The reaction of $OMo(S_2CNR_2)_2(C_2R^1R^2)$ with water in air gives $Mo_2O_4(S_2CNR_2)_2$ for $R^1 = R^2 = CO_2Me$, for $R^1 = R^2 = CF_3$, and for $R^1 = H$, and $R^2 = CO_2Me$, but with $R^1 = R^2 = COC_6H_5Me$, the complex is stable toward hydrolysis. Under argon, one or the other or both of $OMo(S_2CNR_2)_2$ and $Mo_2O_4(S_2CNR_2)_2$ are formed depending on the conditions. The fate of the acetylenic moiety varies. With alcohols, a thiourethane is formed for $R^1 = R^2 = CO_2Me$ or CF_3 and for $R^1 = H$ and $R^2 = CO_2Me$. The latter also produces dimethyl (*N*,*N*-dimethyldithiocarbamato)fumarate. No reaction occurs with $R^1 = R^2 = COC_6H_5Me$. With R_2NH, except for $R^1 = R^2 = CF_3$ where no reaction occurs, all complexes give $OMo(S_2CNR_2)$ and dimethyl 2-(dialkylamino)maleate.

There are only few well-defined molybdenum(IV) complexes but the chemistry they undergo may well be very important in elucidating the role of molybdenum in enzymes. Molybdenum(IV) has been implicated in the redox cycle of a variety of molybdoenzymes,[3-5] e.g., xanthine oxidase and sulfite oxidase, and certain of its complexes have been used in model studies of these enzymes[6-10] and nitrogenase.[6,10-14] We have

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(1) For Part 4, see L. Ricard, R. Weiss, W. E. Newton, G. J.-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, **100**, 1318 (1978).

(2) (a) Charles F. Kettering Research Laboratory. (b) Institut Le Bel, Université Louis Pasteur de Strasbourg.

(3) E. I. Stiefel, W. E. Newton, G. D. Watt, K. L. Hadfield, and W. A. Bulen, *Adv. Chem. Ser.*, **No. 162**, 353 (1977).

(4) R. C. Bray, *Enzymes, 3rd Ed.*, **12**, 299 (1975); "Proceedings of the 1st Climax International Conference on Chemistry and Uses of Molybdenum", P. C. H. Mitchell, Ed., Climax Molybdenum Co., London, 1973, p 216; *J. Less-Common Met.*, **36**, 413 (1974).

(5) V. Massey, H. Komai, G. Palmer, and G. B. Elion, *J. Biol. Chem.*, **245**, 2837 (1970).

(6) P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **94**, 9640 (1972).

(7) P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 2552 (1975).