groups. X-ray crystallography indicates that the compound displays a severely distorted and strained tetrahedral geometry about lead, which is supported by the fact that the compound reacts with CO to eliminate $Fe(CO)_5$. Efforts are continuing to establish the structure of the $[PbFe_2]^{2-}$ intermediate.

The original goal of producing group-14 Zintl-metal carbonylates has unfortunately not yet been achieved by the same methodology applicable to the bismuth system. The $[PbFe_4(CO)_{16}]^{2-}$ cluster, however, does possess some interesting features. First, it represents a clean, high-yield synthesis, which is rare for clusters of this type. Second, it has sites of potential reactivity in the bridging carbonyls and in the two terminal $Fe(CO)_4$ units. These latter metal sites could act as centers for addition of further main-group fragments, which could ultimately give access to the desired Zintl-type clusters. The cluster also possesses potential for undergoing reversible redox cycles involving the formation/breaking of metal–metal bonds as implicated by the known structures of neutral $M[Fe_2(CO)_8]_2$ (M = Sn, Ge). In keeping with this idea, the cluster is found to be oxidized by a variety of reagents including Cu^+, H^+, and CH_3^+. These results and an electrochemical study of the molecule will be presented elsewhere.

Acknowledgment. This work has been generously supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. CHE-8421217). The high-pressure experiments were made possible by a grant from the Atlantic Richfield Foundation, administered by the Research Corp.

Supplementary Material Available: Tables of hydrogen atom positions and anisotropic thermal parameters as well as a stereoview of $[PbFe_4(CO)_{16}]^{2-}$ (2 pages). According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (11 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

Contribution from the Department of Chemistry and Mass Spectrometry Laboratory,
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Nitrosyl Complexes of Technetium: Synthesis and Characterization of $[Tc^I(NO)(CNCMe_3)_5](PF_6)_2$ and $Tc(NO)Br_2(CNCMe_3)_3$ and the Crystal Structure of $Tc(NO)Br_2(CNCMe_3)_3$

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Received November 18, 1985

Reaction of $[^{99}Tc^I(CNCMe_3)_6]^+$ with $NOPF_6$ or with nitric acid in glacial acetic acid leads to the formation of $[Tc^I(NO)(CNCMe_3)_5](PF_6)_2$ in high yield. The complex has been characterized by elemental analysis, infrared and ^1H NMR spectroscopy, cyclic voltammetry, and fast-atom-bombardment mass spectrometry. Attempts to form the manganese nitrosyl congener by reaction of $[Mn(CNCMe_3)_6]^+$ with $NOPF_6$ or NO yielded only the oxidation product $[Mn(CNCMe_3)_6]^{2+}$. Reaction of *tert*-butyl isocyanide with $[Tc(NO)Br_4]^-$ did not yield $[Tc(NO)(CNCMe_3)_5]^{2+}$; instead, $Tc^I(NO)Br_2(CNCMe_3)_3$ was isolated in 30% yield. A crystal structure of this material reveals an approximately octahedral array of ligands. The three isocyanide ligands are meridional with respect to one another and one isocyanide is trans to the nearly linear NO^+ ligand. Crystal data are as follows: space group $P2_1cn$, with $a = 10.985$ (2) Å, $b = 14.250$ (2) Å, $c = 14.677$ (2) Å, $V = 2297.5$ Å^3, ρ(calcd) = 1.556 g cm^{-3} for $Z = 4$ and mol wt 538.29. Final $R_1 = 0.060$ and $R_2 = 0.048$.

Introduction

Several preparations for the manganese isonitrile dications $[Mn(CNR)_6]^{2+}$ (R = alkyl, aryl) have been reported in the literature. These compounds can be prepared by the oxidation of the corresponding monocations $[Mn(CNR)_6]^+$ with nitric acid in glacial acetic acid[1,2] or bromine in ethanol[3] and can also be electrochemically generated.[4] Cyclic voltammetry of the Tc(I)–isocyanide complex $[Tc(CNCMe_3)_6]^+$ in acetonitrile reveals a quasi-reversible one-electron-oxidation wave at +0.83 V vs. SCE, indicating that the corresponding Tc(II) complex $[Tc(CNCMe_3)_6]^{2+}$ is potentially accessible under highly oxidizing conditions. During our attempts[6,7] at the preparation of $[Tc(CNCMe_3)_6]^{2+}$, several routes used to prepare $[Mn(CNCMe_3)_6]^{2+}$ were explored. However, in most instances where a potential NO^+ source was used as the "oxidant", the new complex $[Tc^I(NO)(CNCMe_3)_5]^{2+}$ was the major product isolated. The synthesis and characterization of this new nitrosyl complex of technetium are reported in this paper and the differences in reactivity of $[Mn(CNCMe_3)_6]^+$ and $[Tc(CNCMe_3)_6]^+$ are discussed.

An alternative synthesis of $[Tc(NO)(CNCMe_3)_5]^{2+}$ via the reaction of *tert*-butyl isocyanide with labile $TBA[Tc^{II}(NO)Br_4]$[8] was attempted. However, only two of the four halides were displaced in this reaction. The resulting Tc(I) complex, $Tc(NO)Br_2(CNCMe_3)_3$ was crystallographically characterized to determine the disposition of the isonitrile ligands in the molecule. The synthesis, characterization, and crystal structure of this new compound are reported here.

Experimental Section

Technetium, as $NH_4{}^{99}TcO_4$ in aqueous solution, was obtained as a gift from NEN Products/DuPont, Billerica, MA. ^{99}Tc is a weak β-emitter (0.29 keV, half-life 2.12 × 10^5 years); therefore, all manipulations were carried out in laboratories approved for the use of low-level radioactivity, following precautions detailed elsewhere.[9] The complex $[Tc(CNCMe_3)_6]^+$ was prepared from TcO_4^- as either the chloride or PF_6^- salt, using the procedure of Abrams et al.;[5] $TBA[TcNOBr_4]$ was pre-

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pared as reported by Orvig et al.[8] $NOPF_6$ was of reagent grade (Aldrich) and was dispensed in a drybox. Acetonitrile was dried over calcium hydride, and then distilled and stored over Linde 4A sieves. *tert*-Butyl isocyanide was purchased from Fluka Chemicals and stored at −20 °C. Hexakis(*tert*-butyl isocyanide)manganese(I) hexafluorophosphate was obtained by methathesis of the corresponding iodide salt[10] with ammonium hexafluorophosphate. All other reagents were of reagent grade and were used without further purification unless otherwise specified.

Infrared spectra were recorded on a Perkin-Elmer 283B IR spectrophotometer as KBr pellets. Fourier-transform ^1H NMR spectra were obtained on a Bruker WM 250-MHz instrument with Me_4Si as the internal standard. Melting points were recorded with a Mel-Temp apparatus and are uncorrected. Voltammetric studies were carried out on a PAR Model 174 polarographic analyzer with a stationary Pt electrode. Ferrocene was used as an internal calibrant. The supporting electrolyte was tetra-*n*-butylammonium perchlorate, and dry spectrograde acetonitrile was used as the solvent. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA. Field desorption and fast-atom-bombardment mass spectra were run on a Varian MAT 731 mass spectrometer.

Preparation of Hexakis(*tert*-butyl isocyanide)technetium(I) Nitrate. By the use of the method of Abrams et al., $[^{99}Tc(CNCMe_3)_6]^+$ was prepared in aqueous ethanol from ammonium pertechnetate.[5] After the reaction mixture was cooled, excess NH_4NO_3 was added, and the reaction mixture reduced in volume to 10 mL by rotary evaporation. The dirty white solid was collected by suction filtration, washed with 20 mL of water, and dried in vacuo. The product was then dissolved in a minimal volume of hot methanol and filtered. An equal volume of boiling water was added slowly and the solution volume reduced by half by boiling gently. White needles of $[Tc(CNCMe_3)_6](NO_3)$ formed in 85% yield on cooling. The optical and ^1H NMR spectra and cyclic voltammetry of this material were identical with that of the PF_6 salt prepared by Abrams et al.

Preparation of $[^{99}Tc(NO)(CNCMe_3)_5](PF_6)_2$. Method 1. In a small beaker, $[Tc(CNCMe_3)_6](NO_3)$ (200 mg, 0.30 mmol) was dissolved in 1.5 mL of glacial acetic acid. Concentrated nitric acid (75 μL) was added with stirring. The solution turned deep orange immediately, but turned to yellow over 30 min. Addition of $NaPF_6$ in ice-cold water (600 mg in 6.0 mL) caused the immediate precipitation of yellow needles. After being chilled on ice for 10 min, the product was isolated by suction filtration, washed with 10 mL of ice-cold water and then ether, and dried in vacuo at room temperature to give 232 mg (0.28 mmol, 93%) of $[Tc(NO)(CNCMe_3)_5](PF_6)_2$. The product was recrystallized by the addition of ether to a CH_2Cl_2 solution, followed by chilling to −20 °C; mp 133–135 °C. Anal. Calcd for $C_{25}H_{45}F_{12}N_6OP_2Tc$: C, 35.98; H, 5.44; N, 10.06. Found: C, 36.12; H, 5.29; N, 10.05. IR (KBr): ν_{CN}, 2220 (s), 2240 (s) cm^{-1}; ν_{NO}, 1865 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.65 (s, 4 H), 1.60 (s, 1 H). FAB MS (*m/z*, ion): 689, $[Tc(NO)(CNCMe_3)_5](PF_6)^+$; 544, $[Tc(NO)(CNCMe_3)_5]^+$; 514, $[Tc(CNCMe_3)_5]^+$; 487, $[Tc(NO)(CN)(CNCMe_3)_4]^+$ (base peak). $E_{1/2}$(cathodic) = −0.72 V vs. SCE (1e, irreversible).

Method 2. To 95 mg (0.13 mmol) of $[Tc(CNCMe_3)_6](PF_6)$ in a dry 50-mL side-arm flask was added 5.0 mL of acetonitrile by cannula transfer. The reaction vessel was purged with N_2 and then chilled on ice. Then $NOPF_6$ (23 mg, 0.13 mmol) in 2 mL of N_2-purged acetonitrile was added slowly with stirring. The resulting chrome yellow solution was stirred on ice for 1 h and 15 mL of ether added. The resultant yellow precipitate was isolated by suction filtration, washed with ice-cold water and ether, and dried in vacuo at room temperature. It was recrystallized from CH_2Cl_2/ether as above to give 70 mg (0.084 mmol) of $[Tc(NO)(CNCMe_3)_5](PF_6)_2$ that was identical by ^1H NMR, and IR spectroscopy with the material produced by method 1; 66% yield overall. Anal. Calcd for $C_{25}H_{45}F_{12}N_6OP_2Tc$: C, 35.98; H, 5.44; N, 10.06. Found: C, 35.80; H, 5.42; N, 10.26.

Attempted Reaction of $[Tc(CNCMe_3)_6]PF_6$ with NO Gas. To 65.5 mg (0.088 mmol) of $[Tc(CNCMe_3)]_6PF_6$ under N_2 was added 5.0 mL of dry N_2-purged CH_2Cl_2. The solution was purged with N_2 for 5 min, and then NO gas was bubbled gently through the solution for 1 h. After the solution was purged with N_2 for 10 min, the product was stripped to dryness by rotary evaporation. White, crystalline starting material, as identified by IR and ^1H NMR, was quantitatively recovered.

If both NO gas and *dry air* were bubbled through the above reaction, no starting material remained after 1 h. Very low yields of $[Tc(NO)(CNCMe_3)_5]^{2+}$ could be obtained; however, the predominant product is a white, paramagnetic complex[6,7] that does not contain NO. This complex is unstable and reacts readily with reducing solvents such as ethanol to give $[Tc(CNCMe_3)_6]^+$. Preliminary results indicate that this complex is $[Tc(CNCMe_3)_6]^{2+}$. IR(KBr): ν_{CN}, 2200 (s) cm^{-1}. Mp: 120–124 °C dec. FDMS (*m/z*, ion): 597, $[Tc(CNCMe_3)_6]^+$. The complex $[Mn(CNCMe_3)_6](PF_6)_2$ can be prepared by a similar route (see below).

Attempted Reaction of $[Mn(CNCMe_3)_6]PF_6$ with NO Gas. To 60 mg (0.086 mmol) of $[Mn(CNCMe_3)_6]PF_6$ under N_2 was added 5.0 mL of dry, degassed MeOH. After the reaction was purged with N_2 for 10 min, NO gas was bubbled through the reaction for 30 min. The product was then stripped to dryness by rotary evaporation after the reaction was purged with N_2 to remove NO. Starting material, as identified by TLC and IR and ^1H NMR spectroscopy, was quantitatively recovered.

Reaction of $[Mn(CNCMe_3)_6]PF_6$ with NO/O_2. Preparation of $[Mn(CNCMe_3)_6](PF_6)_2$. In a small round-bottom flask, $[Mn(CNCMe_3)_6]PF_6$ (100 mg, 0.143 mmol) and $NaPF_6$ (60 mg, 0.36 mmol) were dissolved in 5.0 mL of anhydrous MeOH. Gentle streams of NO gas *and* dry air were bubbled through the reaction mixture for 15 min. The pale pink needles that precipitated from the reaction mixture were isolated by suction filtration, washed with cold MeOH (2 × 3 mL), and dried in vacuo at room temperature. The yield of analytically pure $[Mn(CNCMe_3)_6](PF_6)_2$ was 100 mg, 83%; mp 120–121 °C. Anal. Calcd for $C_{30}H_{54}F_{12}MnN_6P_2$: C, 42.69; H, 6.45; N, 9.97. Found: C, 42.59; H, 6.42; N, 9.94. IR (KBr): ν_{CN}, 2175 cm^{-1}. The material prepared by this route is indistinguishable from that prepared by Matteson and Bailey[1] by nitric acid oxidation of $[Mn(CNCMe_3)_6]^+$ in glacial acetic acid.

Preparation of $Tc(NO)Br_2(CNCMe_3)_3$. To 30 mL of deoxygenated methanol was added 285 mg (0.41 mmol) of $TBA[Tc(NO)Br_4]$ followed by 1.0 mL (~9.6 mmol) of *tert*-butyl isocyanide. The red-brown solution was refluxed under nitrogen for 1.5 h and solvent removed by rotary evaporation. The resultant brown oil was dried overnight in vacuo, then redissolved in a minimal volume of CH_2Cl_2, and flash chromatographed on a 2 × 8 cm silica gel column (E. Merck 6H silica gel, TLC grade) conditioned and eluted with CH_2Cl_2. The purple fraction was stripped to dryness by rotary evaporation to give 70 mg (0.13 mmol) of $Tc(NO)Br_2(CNCMe_3)_3$ in 32% yield; mp 138–139.5 °C dec. Crystals for X-ray structure determination were grown by evaporation of an aqueous ethanol solution. Anal. Calcd for $C_{15}H_{27}Br_2N_4OTc$: C, 33.47, H, 5.06; Br, 29.69; N, 10.41. Found: C, 33.55; H, 5.08; Br, 29.62; N, 10.37. ^1H NMR (CD_2Cl_2): δ 1.43 (s, 1 H), 1.47 (s, 2 H). IR (KBr): ν_{CN}, 2230 (m), 2160 (s) cm^{-1}; ν_{NO}, 1755 (vs) cm^{-1}. FDMS (*m/z*): 536, 538, 540 (1:2:1); molecular ion, $C_{15}H_{27}Br_2N_4OTc^+$.

Crystallography. The pale purple crystal of $Tc(NO)Br_2(CNCMe_3)_3$ used for data collection was bounded by the faces (001) and (00$\bar{1}$), 0.05 mm apart; (110) and ($\bar{1}\bar{1}$0), 0.50 mm apart; and (1$\bar{1}$0) and ($\bar{1}$10), 0.59 mm apart. The program ORABS was used to apply an absorption correction. Data were collected at +7 °C on an Enraf-Nonius CAD4F-11 diffractometer using Mo Kα radiation. Details of the data collection, reduction, and refinement procedures have been described elsewhere.[11] A total of 2772 reflections (+*h*,+*k*,+*l*) were collected in the range 3° ≤ 2θ ≤ 55° with the 1407 having $F_o > 4\sigma(F_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (210 variables) using SHELX-76. Final R_1 = 0.060 and R_2 = 0.048. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and were constrained to ride on their respective carbon atoms. Attempts to refine the structure in the centrosymmetric space group *Pmcn* were unsuccessful. Intensity statistics also strongly suggested that the structure was noncentrosymmetric. Refinement of the alternate hand of the structure led to higher *R* values. Although the *b* and *c* cell dimensions are somewhat similar, the structure reported is not tetragonal. If the structure were tetragonal, the intensities of the 0*k*0 and 00*l* reflections should be the same (e.g. 020 and 002 should have the same intensity). This is not the case.

Crystal data are as follows: *a* = 10.985 (2) Å, *b* = 14.250 (2) Å, *c* = 14.677 (2) Å, *V* = 2297.5 Å^3, space group = $P2_1cn$, *Z* = 4, mol wt 538.29, ρ(calcd) = 1.556 g cm^{-3}, μ = 39.8 cm^{-1}. The general equivalent positions for the space group (which is a nonstandard setting of $Pna2_1$) are as follows: x, y, z; $^1/_2 + x, -y, -z$; $x, {}^1/_2 - y, {}^1/_2 + z$; $^1/_2 + x, {}^1/_2 + y, {}^1/_2 - z$.

Final non-hydrogen atom positional parameters appear in Table I, and selected interatomic distances and angles appear in Table II. Figure 1 shows the geometry of $Tc(NO)Br_2(CNCMe_3)_3$ along with the atom numbering.

Results and Discussion

Reactivity. The reaction of nitric acid with $[Tc(CNCMe_3)_6](NO_3)$ in glacial acetic acid leads to the formation of the diamagnetic, 18-electron complex $[Tc(NO)(CNCMe_3)_5]^{2+}$

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Table I. Final Positional Parameters for the Non-Hydrogen Atoms of $Tc(NO)Br_2(CNCMe_3)_3$[a]

atom	*x*	*y*	*z*
Tc	0.0000	0.66280 (7)	0.20797 (9)
Br1	−0.1753 (2)	0.63119 (16)	0.32106 (15)
Br2	0.1956 (2)	0.67963 (13)	0.11674 (15)
N1	−0.0999 (16)	0.6981 (8)	0.1239 (9)
O1	−0.1711 (18)	0.7208 (9)	0.0724 (9)
C11	0.0140 (18)	0.7980 (10)	0.2604 (10)
N11	0.0169 (15)	0.8694 (8)	0.2938 (9)
C12	0.002 (2)	0.9587 (9)	0.3416 (11)
C13	−0.042 (3)	1.0305 (12)	0.2751 (13)
C14	0.124 (3)	0.9853 (17)	0.382 (2)
C15	−0.080 (3)	0.9446 (14)	0.4181 (17)
C21	−0.0037 (18)	0.5206 (10)	0.1757 (10)
N21	−0.0037 (17)	0.4421 (7)	0.1636 (9)
C22	−0.006 (2)	0.3391 (9)	0.1652 (11)
C23	0.073 (2)	0.3087 (13)	0.2441 (15)
C24	0.049 (2)	0.3064 (11)	0.0750 (12)
C25	−0.136 (2)	0.3079 (14)	0.1692 (19)
C31	0.1100 (17)	0.6175 (13)	0.3198 (15)
N31	0.1574 (14)	0.5908 (9)	0.3857 (10)
C32	0.2092 (19)	0.5457 (10)	0.4704 (12)
C33	0.217 (2)	0.4423 (10)	0.4460 (12)
C34	0.3266 (16)	0.5929 (10)	0.4917 (12)
C35	0.1152 (20)	0.5670 (13)	0.5415 (14)

[a] Numbers in parentheses are errors in the last significant digit(s).

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for $Tc(NO)Br_2(CNCMe_3)_3$

Tc–C11	2.080 (15)	Tc–Br1	2.582 (3)
Tc–C21	2.082 (14)	Tc–Br2	2.543 (3)
Tc–C31	2.137 (22)	N11–C11	1.130 (15)
Tc–N1	1.726 (15)	N21–C21	1.133 (15)
N1–O1	1.136 (17)	N31–C31	1.163 (22)
Tc–N1–O1	175.9 (1.6)	C11–Tc–C31	87.3 (7)
Br1–Tc–Br2	170.1 (1)	C21–Tc–C31	83.8 (7)
C11–Tc–C21	170.8 (6)	Tc–C11–N11	175.3 (1.5)
C31–Tc–N1	174.9 (8)	Tc–C21–N21	175.7 (1.3)
		Tc–C31–N31	172.2 (1.7)
Br1–Tc–N1	92.1 (5)	C11–N11–C12	171.1 (1.9)
Br2–Tc–N1	97.7 (5)	C21–N21–C22	170.0 (1.5)
C11–Tc–N1	92.4 (6)	C31–N31–C32	173.1 (1.8)
C21–Tc–N1	96.2 (6)		

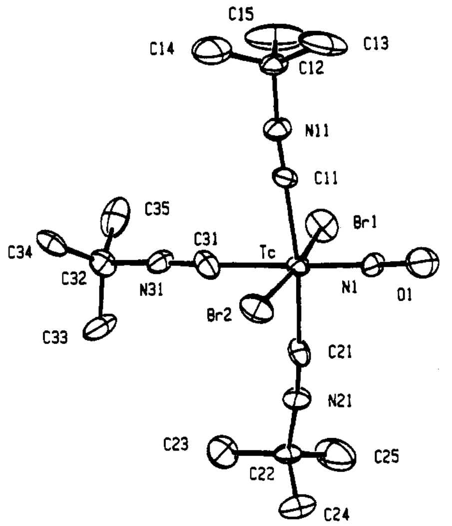

Figure 1. Geometry of $Tc(NO)Br_2(CNCMe_3)_3$ showing the atom-labeling scheme and 30% probability thermal ellipsoids. Hydrogen atoms are not shown.

in high yield. The isolation of this Tc(I) nitrosyl complex stands in contrast with parallel reactions[1,2] with $[Mn(CNR)_6]^+$ (R = alkyl, aryl). The manganese(I) hexakis(isocyanide) cations are smoothly oxidized to $[Mn(CNR)_6]^{2+}$ by treatment with nitric acid; no nitrosyl-containing products are isolated.

$$[Tc(CNCMe_3)_6]^+ + HNO_3 \xrightarrow{HOAc} [Tc(NO)(CNCMe_3)_5]^{2+}$$
ligand substitution

$$[Mn(CNCMe_3)_6]^+ + HNO_3 \xrightarrow{HOAc} [Mn(CNCMe_3)_6]^{2+}$$
oxidation

The same reactivity difference is seen when manganese and technetium hexakis(isocyanide) cations are treated with $NOPF_6$; manganese is oxidized, and technetium undergoes ligand substitution.

$$[Tc(CNCMe_3)_6]^+ + NOPF_6 \xrightarrow{CH_3CN} [Tc(NO)(CNCMe_3)_5]^{2+}$$
ligand substitution

$$[Mn(CNCMe_3)_6]^+ + NOPF_6 \xrightarrow{CH_3CN} [Mn(CNCMe_3)_6]^{2+}$$
oxidation

The reason for this reactivity difference is not completely clear. Cyclic voltammetry of both $[Tc(CNCMe_3)_6]^+$ and $[Mn(CNCMe_3)_6]^+$ shows a quasi-reversible, one-electron-oxidation wave for both complexes. Under the highly oxidizing conditions used (HNO_3/HOAc or $NOPF_6$), simple oxidation of $[Tc(CNCMe_3)_6]^+$ to the dication is not unexpected, although the half-wave potential for the oxidation of $[Tc(CNCMe_3)_6{}^+]$ is considerably higher than that of its manganese[4] congener ($E_{1/2}(Mn^{+\rightarrow 2+}) = 0.56$ V vs. SCE; $E_{1/2}(Tc^{+\rightarrow 2+}) = 0.83$ V vs. SCE (CH_3CN)).

Preliminary results seem to indicate that $[Tc(CNCMe_3)_6]^{2+}$ is, in fact, formed prior to the formation of $[Tc^I(NO)(CNCMe_3)_5]^{2+}$; an unstable paramagnetic technetium dication that does not contain NO can be isolated under certain conditions. In the reaction of $[Tc(CNCMe_3)_6][X]$ with nitric acid in glacial acetic acid, the reaction products formed have proved to be quite sensitive to the counterion present. In reactions using $[Tc(CNCMe_3)_6][X]$ (X = NO_3^-, BPh_4^-), the major product *in solution* after 30 min is $[Tc(NO)(CNCMe_3)_5]^{2+}$. However, if X = PF_6^-, $[Tc(NO)(CNCMe_3)_5](PF_6)_2$ is produced in less than 50% yield; it precipitates directly from the reaction mixture along with what appears to be $[Tc^{II}(CNCMe_3)_6]^{2+}$. It appears that the first product to form in both cases is $[Tc(CNCMe_3)_6]^{2+}$. If this remains in solution, it reacts further to form $[Tc^I(NO)(CNCMe_3)_5]^{2+}$. However, if PF_6^- is present, the unstable dication precipitates from the reaction mixture before further reaction can take place.

As the monocationic 18-electron $[Tc(CNCMe_3)_6]^+$ is substitutionally quite inert, direct ligand substitution (NO^+ for $CNCMe_3$) in the preparation of $[Tc^I(NO)(CNCMe_3)_5]^{2+}$ seems highly unlikely. The intermediacy of a more labile, oxidized technetium species that undergoes ligand substitution and subsequent reduction is more consistent with the findings above. However, this does not explain why the corresponding manganese nitrosyl cannot be isolated under similar reaction conditions. In our hands, the isolated manganese dication either failed to react or underwent slow decomposition when treated with either NO gas or $NOPF_6$.

In similar reactions between $Cr(CNR)_6{}^{2+}$ and NO gas,[12] reductive nitrosylation occurs and $[Cr(NO)(CNR)_5]^{2+}$ species can be isolated quite readily. Many complexes of the type $[M(NO)(CNR)_5]^{n+}$ (M = Cr, Mo, W; R = alkyl, aryl; *n* = 1, 2) have been prepared in the group VI (group 6[24]) triad.[12,13] However, no reference to the preparation of manganese and rhenium congeners of $[Tc(NO)(CNCMe_3)_5]^{2+}$ could be found

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in the literature. The only reference found for the preparation of a complex of this type was reported by Eaborn et al.[14] They reported the preparation of $[Mn(NO)(CNCMe)_5](SO_3F)_2$ by alkylation of $[Mn(NO)(CN)_5]K_3$ with $MeOSO_2F$. No synthetic details or characterization were reported in this communication.

We were not able to make $[Mn(NO)(CNCMe_3)_5]^{2+}$. All synthetic routes attempted led only to oxidation of manganese to $[Mn(CNCMe_3)_6]^{2+}$. Routes included the reaction of $[Mn(CNCMe_3)_6]PF_6$ with $NOPF_6$ or NO gas in the presence of dry air. The latter reaction proceeds rapidly with consummate ease and analytically pure $[Mn(CNCMe_3)_6](PF_6)_2$ could be isolated directly from the reaction mixture in greater than 80% yield. The oxidant in this reaction is clearly not NO but NO_2, as this forms rapidly when NO and O_2 are mixed.[15] If NO gas was used in the absence of air, oxidation to the dication proceeded quite slowly with manganese and no reaction was seen with technetium. The pale pink needles isolated from the reaction of $[Mn(CNCMe_3)_6]^+$ and NO/O_2 are indistinguishable from material prepared by nitric acid oxidation of $[Mn(CNCMe_3)_6]^+$ in glacial acetic acid,[1] although the yield is much higher. This reaction thus appears to be a synthetic improvement over preparations currently in the literature.

Characterization of $[Tc(NO)(CNCMe_3)_5](PF_6)_2$. The nature of the NO ligand is such that this compound could be formulated either as a complex of Tc(III) with a bent NO^- ligand, or as Tc(I) with NO serving as linear NO^+. The IR spectrum of the complex is consistent with the latter formulation.[16] The N≡O stretching mode in the IR of complexes containing "bent" NO^- tends to occur at lower wave numbers (1525–1690 cm^{-1}) than does the corresponding mode for linear NO^+ (1650–1900 cm^{-1}).[17] The very strong ν_{NO} for $[Tc(NO)(CNCMe_3)_5]^{2+}$ falls at 1865 cm^{-1}, comfortably within the latter range. Two isocyanide (C≡N) stretches are also prominent in the spectrum, at 2200 and 2240 cm^{-1}. The high frequency of these bands is a reflection of the 2+ charge on this complex and indicates that π-back-bonding to the isonitrile ligands is not important.[18] The ^1H NMR (CD_2Cl_2) spectrum consists of two singlets at δ 1.65 and 1.60 in a 4:1 ratio, as expected for the equatorial and axial protons in this presumably C_{4v} molecule. Fast-atom-bombardment mass spectrometry (positive mode) shows a molecular ion at *m/z* 689 $[M^{2+} + PF_6^-]$, as well as peaks corresponding to reduction on the probe (*m/z* 544, $[Tc(NO)(CNCMe_3)_5]^+$), loss of NO^+ (*m/z* 514, $[Tc(CNCMe_3)_5]^+$), and dealkylation (*m/z* 487, $[Tc(NO)(CN)(CNCMe_3)_4]^+$). The latter peak is the base peak in the spectrum.

The electrochemical behavior of $[Tc(NO)(CNCMe_3)_5]^{2+}$ is quite different from that of the parent $[Tc(CNCMe_3)_6]^+$. Whereas the hexakis monocation undergoes a quasi-reversible one-electron oxidation at +0.83 V vs. SCE, only an irreversible reduction at −0.72 V vs. SCE is seen with $[Tc(NO)(CNCMe_3)_5]^{2+}$ in CH_3CN.

The complex is soluble in polar organic solvents and is air- and water-stable. It decomposes upon heating in methanol to an as yet uncharacterized product.

$Tc(NO)Br_2(CNCMe_3)_3$. An alternative route to $[Tc(NO)(CNCMe_3)_5]^{2+}$, by reaction of *tert*-butyl isocyanide and $[Tc^{II}(NO)Br_4]^-$ was attempted. This nitrosyl starting material has proved useful[8] for the preparation of other technetium nitrosyls such as $[Tc(NO)Cl_4]^-$ and $[Tc(NO)(NCS)_5]^{2-}$, and it was hoped that the isocyanide ligand would both displace all four bromide ions and reduce the metal center.[19] Reduction did occur; however, only two of the bromides were displaced, and purple, neutral $Tc(NO)Br_2(CNCMe_3)_3$ was the only product isolated in 30% yield. Higher yields have not been obtained, as the product is thermally unstable and decomposes in the reaction mixture as it forms.

This new complex appears to be directly analogous to the product obtained when pyridine and $[Tc(NO)Br_4]^-$ are refluxed.[8] In this case, reduction of the metal center also occurs and $Tc(NO)Br_2(pyr)_3$ is isolated in 87% yield. Even when the complex was refluxed in neat pyridine, the last two bromide ions were not displaced.

Analysis of the isonitrile complex is consistent with its formulation as $Tc(NO)Br_2(CNCMe_3)_3$. The compound is a nonelectrolyte and shows no conductivity in acetonitrile. Its ^1H NMR spectrum shows two singlets at δ1.43 and 1.47 in a ratio of 1:2, as expected for the two types of isocyanide (axial and equatorial) present in the molecule. Two C≡N stretches are seen in the IR spectrum of the complex at 2230 and 2160 cm^{-1}. The medium-intensity band at higher frequency is assigned to the isonitrile bonded trans to the nitrosyl. The high frequency of this band indicates that π-back-bonding to this isonitrile is not important[18] and that the NO ligand trans to it is competing quite effectively for the electron density. The NO stretch is very prominent in the IR spectrum, at 1755 cm^{-1}, and falls comfortably within the range expected for an NO^+ ligand.

X-ray Structure. Because the analytical data previously discussed for $Tc(NO)Br_2(CNCMe_3)_3$ is consistent with either a facial or meridional disposition of isocyanide ligands, an X-ray structure determination was undertaken. An ORTEP diagram of the complex is shown in Figure 1. Selected bond distances and bond angles are listed in Table II. The technetium atom is six-coordinate, with the three isonitrile ligands coordinated meridionally with respect to one another. The two bromide atoms are trans to one another, and one of the isonitrile ligands coordinates in the position trans to the nearly linear NO^+ ligand. The complex is slightly distorted from octahedral geometry, as the four ligands cis to the nitrosyl bend out of the equatorial plane away from the nitrosyl. The bond angles of 170.1 (1)° (Br1–Tc–Br2) and 170.8 (6)° (C11–Tc–C21) reflect this fact.

The Tc–N–O bond angle of 175.9 (1.6)° is nearly linear and confirms the assignment of the ligand as NO^+ rather than NO^-. The Tc–NO bond length is, as expected for coordinated NO^+, quite short at 1.726 (1.5) Å. This bond length compares favorably to the Tc–NO distance of 1.72 Å reported for the only other Tc(I)-nitrosyl complex that has been crystallographically characterized,[20] namely *trans*-$[Tc(NH_3)_4(NO)(H_2O)]Cl_2$. The NO bond length of 1.136 (17) Å is somewhat shorter than that in *trans*-$[Tc(NH_3)_4(NO)(H_2O)]^{2+}$ (1.203 (6) Å), indicating that π-back-bonding, which is expected to lengthen the N–O bond distance, is somewhat less important in $Tc(NO)Br_2(CNCMe_3)_3$. This is not unexpected, as the isocyanide ligand trans to the NO should be better able to complete for electron density than the water ligand trans to NO in *trans*-$[Tc(NH_3)_4(NO)(H_2O)]^{2+}$.

The two isocyanide ligands cis to the nitrosyl have slightly longer Tc–C bond lengths than are seen in $[Tc(CNCMe_3)_6]^+$[21] (average Tc–C bond lengths of 2.08 and 2.03 Å, respectively). The Tc-isocyanide bond trans to the nitrosyl is considerably longer, at 2.137 (22) Å. This lengthening is consistent with the structural trans influence[22] expected at a position axial to the π-back-bonding nitrosyl. This lengthening may also be due to steric interactions with the equatorial bromine and isocyanide ligands, which are bent toward the axial isocyanide. Long metal–ligand bonds axial

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(19) Examples where an isocyanide ligand has served as a reducing agent are many. See, for example: Klendworth, D. D.; Welters, W. W., III; Walton, R. A. *Organometallics* **1982**, *1*, 336. Lloyd, M. K.; McCleverty, J. A. *J. Organomet. Chem.* **1973**, *61*, 261.

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to NO$^+$ have been noted previously in the crystal structures of complexes of the type [Re(NO)X$_4$L]$^-$ (X = Cl, L = pyridine; X = Br, L = EtOH, CH$_3$CN).[23] The technetium–bromide bond distances are unexceptional.

Acknowledgment. We thank the Biomedical Research Support-Shared Instrument Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10RR02243-01). This investigation was also supported (in part) by NIH Grant RR00317, Biotechnology Resources Branch, Division of Research Resources. We also gratefully acknowledge the financial support of NEN/DuPont, North Billerica, MA.

Registry No. [^{99}Tc(CNCMe$_3$)$_6$]NO$_3$, 101998-10-1; [^{99}Tc(CNCMe$_3$)$_6$](PF$_6$)$_2$, 102046-55-9; [^{99}Tc(CNCMe$_3$)$_6$]PF$_6$, 89172-45-2; [^{99}Tc(CNCMe$_3$)$_6$]$^{2+}$, 101998-11-2; [Mn(CNCMe$_3$)$_6$]PF$_6$, 38682-78-9; [Mn(CNCMe$_3$)$_6$](PF$_6$)$_2$, 23039-89-6; ^{99}Tc(NO)Br$_2$(CNCMe$_3$)$_3$, 101998-12-3; TBA[Tc(NO)Br$_4$], 90386-75-7.

Supplementary Material Available: Table S2, final thermal parameters, and Table S3, final hydrogen atom positional parameters (2 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, Table S1, calculated and observed structure factors (6 pages), is being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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(24) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Redox Chemistry of Hydrogen Peroxide in Anhydrous Acetonitrile

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Received December 16, 1985

Under anhydrous conditions H$_2$O$_2$ is oxidized by a single-electron-transfer step to HO$_2$$^\bullet$, which (a) is further oxidized to O$_2$ by a second electron transfer or (b) disproportionates to H$_2$O$_2$ and O$_2$ (k_{MeCN}, 1×10^7 M^{-1} s^{-1}). The oxidation potential in dry acetonitrile (MeCN) for the primary process (H$_2$O$_2$ + A$^-$ → HO$_2$$^\bullet$ + HA + e$^-$) ranges from +2.4 V vs. NHE to +1.8 V in the presence of *p*-MePhSO$_3$$^-$, +1.3 V with NH$_3$, and +1.0 V with picolinate anion. In MeCN, HO$_2$$^\bullet$ is reversibly reduced to HO$_2$$^-$ at +0.64 V vs. NHE. These processes and the associated redox chemistry for H$_2$O$_2$ have been characterized at glassy-carbon (GC) electrodes by linear-sweep voltammetry and the rotated-ring–disk technique. Reduction of H$_2$O$_2$ at Pt (−0.4 V vs. NHE) or at GC (−1.5 V) yields H$_2$ and HO$_2$$^-$; the latter species is unstable (HO$_2$$^-$ + H$_2$O$_2$ → O$_2$$^{\bullet-}$ + H$_2$O + $^\bullet$OH) but can be oxidized to HO$_2$$^\bullet$ at +0.64 V vs. NHE within the time frame of the ring–disk experiment (a few milliseconds).

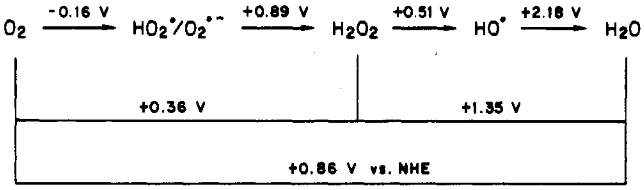
The oxidation–reduction chemistry of dioxygen and of its reduced intermediates (O$_2$$^{\bullet-}$, HO$_2$$^\bullet$, and H$_2O_2$) in aprotic solvents has been a major interest of our group for the past 2 decades.[1,2] Hydrogen peroxide, which is a natural intermediate from aerobic metabolism,[3] can be generated from oxygen reduction or water oxidation and results from the proton-induced disproportionation of superoxide ion.[4]

$$2\mathrm{O_2}^{\bullet-} + 2\mathrm{H}^+ \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad (1)$$

The redox thermodynamics for hydrogen peroxide in aqueous media at pH 7 is summarized within the reduction manifold of Scheme I (with the standard state for O$_2$ unit activity).[5]

However, because of the water-like nature of hydrogen peroxide its redox properties are highly dependent upon the media and the solution acidity. The solvation energies for ionic intermediates have a primary effect on the redox potentials for H$_2$O$_2$. The enhanced solubility of O$_2$ in biomembranes and the presence of the reductive cofactors in the membrane prompts the conclusion that the generation of O$_2$$^{\bullet-}$ and H$_2$O$_2$ occurs in a nonaqueous matrix, which can be modeled by dipolar aprotic solvents such as acetonitrile.[6]

Scheme I



A previous study has discussed the electrochemical reduction of hydrogen peroxide in pyridine[7]

$$\mathrm{H_2O_2} + \mathrm{e}^- \rightarrow {}^1\!/_2\mathrm{H_2} + \mathrm{HO_2}^- \qquad (2)$$

which is followed by a rapid chemical step to yield superoxide as the stable product (unique to pyridine because of its ability to trap $^\bullet$OH).[8]

$$\mathrm{H_2O_2} + \mathrm{HO_2}^- \xrightarrow{\mathrm{py}} \mathrm{O_2}^{\bullet-} + \mathrm{H_2O} + (1/n)[^\bullet\mathrm{py(OH)}]_n \qquad (3)$$

Beyond this the redox chemistry of H$_2$O$_2$ in aprotic media has been neglected. The present study is directed to the electron-transfer oxidation and reduction of H$_2$O$_2$ at glassy-carbon electrodes and to the generation and redox characterization of the intermediate product species, HO$_2$$^\bullet$ and HO$_2$$^-$, in acetonitrile (MeCN).

Experimental Section

Instrumentation. The rotated ring–disk electrode measurements were made with a Pine Instruments Co., Model PIR Rotator with either Pt-Pt- or GC–GC-ring–disk electrodes. The parameters of the electrodes were as follows: Pt–Pt electrode, r_1 = 0.382 cm, r_2 = 0.399 cm, r_3 = 0.422 cm, N = 0.178; GC–GC electrode, r_1 = 0.382 cm, r_2 = 0.416 cm, r_3 = 0.556 cm, N = 0.418. Potential control was provided by a Pine Instruments Co., Model RDE 3 dual potentiostat. The sample solutions and electrode assembly (including a Pt auxiliary electrode in a separate tube with a medium-porosity fritted-glass disk at the end and a Ag/AgCl reference electrode in a Luggin capillary) were contained in a 150-mL

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