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Technetium Complexes of 3,5-Di-*tert*-butylcatechol. Direct Synthesis of Tris(3,5-di-*tert*-butylcatecholato)technetium(VI) and Bis(3,5-di-*tert*-butylcatecholato)(di-*tert*-butylamidophenolato)technetium(VI) from Ammonium Pertechnetate

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Abstract: The reaction between 3,5-di-*tert*-butylcatechol and ammonium pertechnetate in methanol produces a mixture of tris(3,5-di-*tert*-butylcatecholato)technetium(VI) (Tc(DBCat)$_3$) and bis(3,5-di-*tert*-butylcatecholato)(di-*tert*-butylamidophenolato)technetium(VI) (Tc(DBCat)$_2$(DBAP)). The amidophenolate ligand of Tc(DBCat)$_2$(DBAP) appears to result from Schiff-base condensation of ammonia from ammonium ion with catechol. When the reaction is carried out in the presence of excess 3,5-di-*tert*-butylcatechol only small quantities of Tc(DBCat)$_2$(DBAP) are formed. Crystallographic characterization of Tc(DBCat)$_3$ has shown that the molecule crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions a = 15.892 (3) Å, b = 15.878 (4) Å, c = 16.367 (3) Å, β = 93.13 (1)°, and V = 4123 (1) Å^3. The complex molecule is of C_3 symmetry and the average ligand C–O bond length of 1.334 (13) Å is typical of values found for catecholate ligands. As such, the complex is a unique example of Tc(VI). Both Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP) exhibit well-resolved 10-line EPR spectra in solution at room temperature. Coupling to the ^{99}Tc nucleus ($I = {}^9/_2$) of approximately 140 G is consistent with the d^1 Tc(VI) formulation for both complexes. They each undergo reversible one-electron oxidations to cationic complexes with surprising ease, and they each undergo two reversible one-electron reductions to Tc(V) and Tc(IV) forms of the complexes.

Technetium radiopharmaceuticals are becoming routinely used as anatomical imaging agents in nuclear medicine.[1] Two general approaches have been used in the development of tissue-specific imaging agents. Technetium-labeled molecules of defined biodistribution (i.e., antibodies) have been considered for use with the assumption that the in vivo distribution of the technetium-labeled species remains the same as that of the unlabeled carrier. A second approach has involved use of technetium coordination compounds, where biodistribution is controlled by the physical properties of the complex. These relationships are poorly understood, and the development of metal complex radiopharmaceuticals has been largely empirical.

The coordination chemistry of technetium has expanded dramatically over the past 5 years in conjunction with this interest. Clinical applications utilize the metastable ^{99m}Tc isotope in imaging experiments as a high-energy γ emitter with a relatively short $t_{1/2}$ (6.02 h). Inexpensive generators are available that conveniently produce ^{99m}TcO$_4^-$ by the β decay of ^{99}Mo in ^{99}MoO$_4^{2-}$. Developmental studies are frequently carried out on complexes of ^{99}Tc, which is a longer lived β emitter ($t_{1/2} = 2.1 \times 10^5$ years) and less difficult to handle in routine laboratory work. Synthetic procedures often require a prereduction of pertechnetate with Sn(II) or Na$_2$S$_2$O$_4$ prior to complex formation. Products of these reactions generally contain either Tc(III) or the [Tc^{V}O]$^{3+}$ core, by far the most common forms of the metal.

We now describe the products of the reaction between ammonium pertechnetate and 3,5-di-*tert*-butylcatechol. In this reaction, catechol serves as both a reducing agent and a chelating ligand in the formation of the tris(catecholato)technetium(VI) product. Additionally, the +6 charge of the metal is the least common oxidation state for technetium.

Experimental Section

NH$_4{}^{99}$TcO$_4$ was obtained from Oak Ridge National Laboratory and was recrystallized from water prior to use. 3,5-Di-*tert*-butylcatechol and 3,5-di-*tert*-butyl-1,2-benzoquinone were obtained from Aldrich Chemical Co., Re$_2$(CO)$_{10}$ and KReO$_4$ were obtained from Stream Chemical Co., and all were used as received. ^{99}Tc is a β emitter, and all manipulations were carried out in a well-ventilated fume hood by personnel wearing protective coats and gloves.

Synthesis of Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP). NH$_4{}^{99}$TcO$_4$ (0.59 g, 3.31 mmol) and 3,5-di-*tert*-butylcatechol (2.34 g, 10.53 mmol) were dissolved in 80 mL of anhydrous methanol. The resulting solution was freeze–thaw–degassed once under Ar and refluxed for 24 h. The solid product obtained after complete evaporation of the reaction solution was washed with several aliquots of cold methanol. Product separation was achieved by column chromatography using a toluene mobile phase and silica gel as the solid support. Crystals of Tc(DBCat)$_3$ suitable for X-ray crystallography were grown directly from the reaction.

Synthesis of Re(DBCat)$_3$. Re(DBCat)$_3$ was synthesized from Re$_2$(CO)$_{10}$ and 3,5-di-*tert*-butylbenzoquinone by procedures described previously[2] or by the method below: KReO$_4$ (0.47 g, 1.64 mmol) and 3,5-di-*tert*-butylcatechol (1.09 g, 4.91 mmol) were freeze–thaw–degassed for

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(1) (a) *Technetium in Chemistry and Nuclear Medicine*; Deutsch, E.; Nicolini, M.; Wagner, H. N., Jr., Eds.; Cortina International Verona: Verona, Italy, 1983. (b) Pinkerton, T. C.; Desilets, C. P.; Hoch, D. J.; Mikelsons, M. V.; Wilson, G. M. *J. Chem. Educ.* **1985**, *62*, 965. (c) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983**, *30*, 75.

(2) deLearie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 817.

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Table I. Crystallographic Data for Tc(DBCat)$_3$.

chem formula	$TcO_6C_{42}H_{60}$	T, °C	26
fw	759.94	λ(Mo Kα), Å	0.71069
space gp	$P2_1/n$	ρ_{obsd}, g/cm^3	1.20(2)
a, Å	15.892 (3)	ρ_{calcd}, g/cm^3	1.19
b, Å	15.878 (4)	μ, cm^{-1}	3.8
c, Å	16.367 (3)	transm coeff	0.985–0.958
β, deg	93.13 (1)	R	0.0466
V, Å^3	4123 (1)	R_w	0.0534
Z	4		

3 cycles under N_2 in 100 mL of freshly distilled CH_2Cl_2. The resulting solution was refluxed under N_2 for 24 h. Re(DBCat)$_3$ was obtained in low yield and characterized by infrared and EPR spectroscopy.

Physical Measurements. Infrared spectra were recorded on an IBM IR/30 FTIR spectrometer with samples prepared as KBr pellets. UV/vis spectra were recorded on a HP 8451A diode array spectrophotometer. Magnetic susceptibility measurements were made by the Faraday technique using a Sartorius 4433 microbalance, and EPR spectra were obtained on a Varian E-109 spectrometer using DPPH as the g-value standard. ^{1}H NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer, and mass spectra were recorded on a VG 7070EQ mass spectrometer. Cyclic voltammograms were obtained with a BAS-100 electrochemical analyzer in CH_2Cl_2 solutions. A platinum disk working electrode and a platinum wire counter electrode were used. The reference electrode was based on the Ag/Ag$^+$ couple and consisted of a CH_2Cl_2 solution of Ag(PF$_6$) in contact with a silver wire placed in glass tubing with a Vycor frit at one end to allow ion transport. Tetrabutylammonium hexafluorophosphate (TBHP) was used as the supporting electrolyte, and the ferrocene/ferrocenium couple was used as the internal standard. Controlled-potential electrolysis was performed in CH_2Cl_2 solutions using a PAR Model 173 potentiostat with a PAR Model 175 Universal Programmer. A platinum gauze working electrode and a platinum wire counter electrode were used. The counter electrode was separated from the bulk solution with a Vycor frit. The reference electrode was identical with that used for cyclic voltammetry, and TBHP was used as the supporting electrolyte.

Crystallographic Structure Determination on Tc(DBCat)$_3$. A suitable crystal of the complex was mounted on a glass fiber, coated with an amorphous resin, and aligned on a Nicolet P3/F automated diffractometer. Axial photographs indicated monoclinic symmetry for the crystal. Unit cell dimensions given in Table I were calculated from the centered positions of 24 intense reflections with $19° < 2\theta < 26°$. Additional parameters and details of procedures used for data collection, structure determination, and refinement are contained in the supplementary material. The location of the Tc atom was determined from a three-dimensional Patterson map, and phases derived from the refinement of the metal atom were used to locate all non-hydrogen atoms of the structure. Final cycles of least-squares refinement converged with discrepancy indices of $R = 0.047$ and $R_w = 0.053$. Final positional and isotropic thermal parameters for all non-hydrogen atoms are listed in Table II. Tables containing anisotropic thermal parameters, hydrogen atom locations and thermal parameters, and structure factors are available as supplementary material.

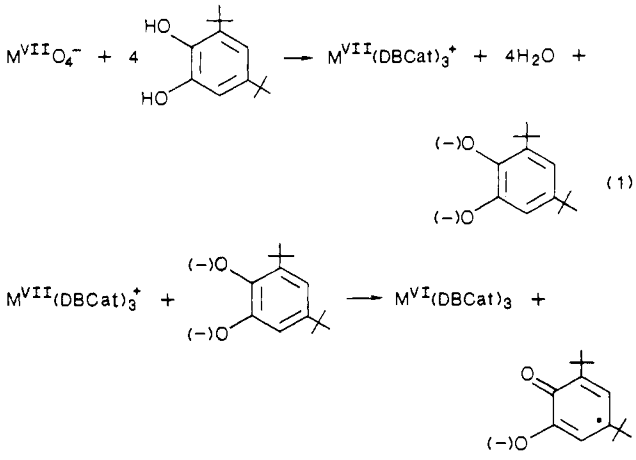
Experimental Results

Simple reactions between NH_4TcO_4 and 3,5-di-*tert*-butylcatechol carried out in methanol solution produce Tc(DBCat)$_3$ in high yield. When stoichiometric proportions of catechol are used, the product obtained is a mixture of Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP). The 3,5-di-*tert*-butylamidophenolate (DBAP) ligand apparently results from Schiff-base condensation of ammonia from the ammonium cation with the catechol.[3] Separation of Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP) may be carried out by using chromatography, and the quantity of Tc(DBCat)$_2$(DBAP) produced in the reaction may be reduced by using an excess of catechol in the reaction mixture. Tc(DBCat)$_3$ is air stable, while Tc(DBCat)$_2$(DBAP) decomposes in air over the period of days. Samples of the complex were stored under argon. The analogous rhenium complex, Re(DBCat)$_3$, was prepared earlier by the photolysis of solutions containing $Re_2(CO)_{10}$ and 3,5-di-*tert*-butyl-1,2-benzoquinone.[2] Reactions between $KReO_4$ and 3,5-di-*tert*-butylcatechol could also be used to form the complex. A 1:4 stoichiometric reaction between pertechnetate or perrhenate and the catechol would produce a cationic product, water, and the deprotonated catecholate (1). The catecholate ion is a relatively

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Tc(DBCat)$_3$

	x/a	y/b	z/c	U_{eq}^{a}
Tc	2042 (1)	1780 (1)	−1794 (1)	46 (1)
O1	2021 (5)	3011 (4)	−1790 (4)	54 (3)
O2	835 (4)	1979 (5)	−1723 (4)	48 (3)
O3	2094 (4)	1635 (5)	−2988 (4)	50 (3)
O4	1771 (4)	583 (4)	−1914 (4)	49 (3)
O5	3263 (4)	1750 (5)	−1633 (4)	45 (3)
O6	2168 (4)	1613 (4)	−616 (4)	43 (3)
C1	1273 (7)	3367 (7)	−1680 (5)	40 (5)
C2	621 (7)	2781 (7)	−1600 (6)	41 (4)
C3	−198 (7)	3040 (7)	−1425 (6)	42 (5)
C4	−311 (7)	3911 (7)	−1406 (6)	45 (5)
C5	323 (8)	4507 (8)	−1520 (6)	47 (5)
C6	1116 (7)	4230 (7)	−1654 (6)	41 (5)
C7	−897 (7)	2404 (7)	−1284 (7)	51 (4)
C8	−1719 (7)	2805 (7)	−1041 (7)	79 (6)
C9	−590 (7)	1829 (7)	−566 (6)	75 (5)
C10	−1087 (6)	1871 (7)	−2061 (7)	71 (5)
C11	123 (8)	5458 (7)	−1524 (8)	57 (5)
C12	−601 (10)	5677 (8)	−1055 (11)	192 (12)
C13	834 (9)	5965 (8)	−1168 (10)	141 (9)
C14	−52 (11)	5733 (8)	−2376 (8)	157 (10)
C15	1841 (6)	894 (7)	−3266 (7)	39 (4)
C16	1609 (7)	311 (7)	−2687 (7)	42 (5)
C17	1238 (6)	−463 (7)	−2863 (7)	46 (5)
C18	1233 (6)	−672 (7)	−3694 (7)	50 (5)
C19	1534 (7)	−143 (7)	−4306 (7)	45 (5)
C20	1814 (6)	652 (7)	−4100 (7)	47 (5)
C21	890 (7)	−1017 (7)	−2207 (7)	54 (5)
C22	259 (7)	−521 (7)	−1745 (7)	73 (5)
C23	1618 (7)	−1348 (7)	−1638 (6)	71 (5)
C24	409 (7)	−1761 (7)	−2586 (7)	81 (5)
C25	1533 (8)	−447 (8)	−5194 (7)	56 (5)
C26	1672 (11)	210 (9)	−5777 (8)	174 (11)
C27	2226 (9)	−1099 (9)	−5220 (8)	133 (8)
C28	761 (9)	−921 (10)	−5461 (8)	132 (9)
C29	3570 (7)	1656 (7)	−867 (6)	42 (4)
C30	2958 (7)	1523 (6)	−307 (6)	39 (4)
C31	3164 (7)	1312 (6)	504 (7)	43 (4)
C32	4011 (8)	1310 (7)	730 (6)	53 (5)
C33	4645 (7)	1504 (6)	195 (6)	42 (4)
C34	4414 (6)	1655 (6)	−622 (6)	41 (4)
C35	2482 (7)	1059 (8)	1094 (7)	56 (5)
C36	1941 (7)	1825 (8)	1274 (6)	80 (5)
C37	2872 (7)	747 (9)	1905 (7)	107 (7)
C38	1940 (7)	333 (7)	715 (7)	76 (5)
C39	5574 (7)	1511 (8)	493 (7)	58 (5)
C40	5684 (8)	2080 (9)	1221 (9)	125 (8)
C41	5839 (8)	665 (9)	769 (11)	167 (11)
C42	6144 (8)	1800 (12)	−101 (9)	209 (13)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.



(1)

M = Tc, Re

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[3] deLearie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1989**, *28*, 644.

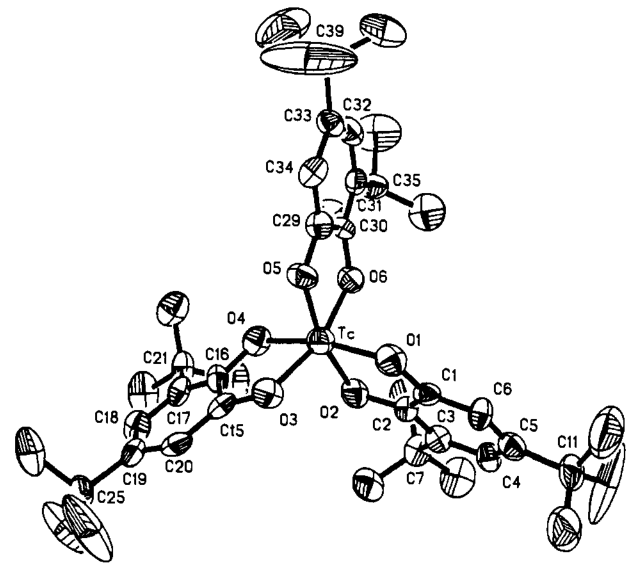

Figure 1. View down the approximate C_3 axis of the Tc(DBCat)$_3$ molecule.

Table III. Selected Bond Lengths (Å) and Angles (Degrees) of Tc(DBCat)$_3$

Bond Lengths: Technetium-Oxygen			
Tc-O1	1.955 (6)	Tc-O4	1.956 (6)
Tc-O2	1.954 (7)	Tc-O5	1.945 (6)
Tc-O3	1.974 (6)	Tc-O6	1.945 (6)
Ligand 1			
O1-C1	1.337 (13)	C4-C5	1.401 (16)
O2-C2	1.336 (13)	C5-C6	1.364 (16)
C1-C2	1.403 (16)	C1-C6	1.394 (16)
C2-C3	1.411 (16)	C3-C7	1.527 (15)
C3-C4	1.395 (15)	C5-C11	1.543 (17)
Ligand 2			
O3-C15	1.317 (13)	C18-C19	1.410 (16)
O4-C16	1.349 (13)	C19-C20	1.374 (16)
C15-C16	1.388 (16)	C15-C20	1.416 (16)
C16-C17	1.385 (16)	C17-C21	1.516 (16)
C17-C18	1.399 (16)	C19-C25	1.532 (16)
Ligand 3			
O5-C29	1.328 (12)	C32-C33	1.404 (16)
O6-C30	1.335 (12)	C33-C34	1.389 (14)
C29-C30	1.389 (15)	C29-C34	1.380 (14)
C30-C31	1.391 (15)	C31-C35	1.544 (16)
C31-C32	1.375 (16)	C33-C39	1.528 (16)
Bond Angles			
O1-Tc-O2	79.7 (3)	O1-C1-C2	113.5 (10)
O3-Tc-O4	78.9 (3)	O2-C2-C1	115.0 (10)
O5-Tc-O6	79.3 (3)	Tc-O3-C15	114.8 (6)
O1-Tc-O3	97.0 (3)	Tc-O4-C16	115.8 (6)
O1-Tc-O5	92.3 (3)	O3-C15-C16	116.5 (10)
O2-Tc-O4	87.3 (3)	O4-C16-C15	112.5 (9)
O2-Tc-O6	90.7 (3)	Tc-O5-C29	116.3 (6)
O4-Tc-O6	88.8 (3)	Tc-O6-C30	115.7 (6)
Tc-O1-C1	116.0 (7)	O5-C29-C34	125.1 (9)
Tc-O2-C2	115.0 (6)	O6-C30-C29	114.3 (9)

strong reducing agent and reduces the cationic complex to the neutral form obtained. The electrochemical properties of the neutral complexes show that further reduction would not readily occur.

Crystallographic Characterization of Tc(DBCat)$_3$. The Tc^{VI}(DBCat)$_3$ molecule has the tris-chelated structure of C_3 symmetry shown in Figure 1; bond distances and angles are given in Table III. The coordination geometry is approximately octahedral, in contrast to the trigonal-prismatic structure of the benzene-1,2-dithiolate analogue, Tc(S$_2$C$_6$H$_4$)$_3$.[4] Distortion toward a prismatic structure is found in the values of the twist angle between triangular faces of the polyhedron. Values of 0 and 60° would be expected for regular trigonal-prismatic and octahedral structures. For this molecule the value is 41.7°, roughly intermediate between the two regular values, but comparable with the value of 37.9° for Re(DBCat)$_3$ and 49.4° for Tc(oxalate)$_3^{2-}$.[2,5] There are no Tc^{VI}–O bond lengths for comparison, but the average value of 1.955 (6) Å for Tc(DBCat)$_3$ agrees with Tc^{V}–O values of 1.957 (3) Å found for both TcO(Cat)$_2^-$ and TcO(S(CH$_2$)$_2$O)$_2^-$,[6,7] and it is shorter than the Tc^{IV}–O value of 1.991 (7) Å for Tc(ox)$_3^{2-}$. The Tc–O length of Tc(DBCat)$_3$ is approximately 0.02 Å longer than the average value of 1.938 (5) Å found for Re(DBCat)$_3$. This difference appears consistent with the slight contraction in effective radius of Re relative to Tc.[8] Radial values for six coordinate Re(V), Re(VI), and Re(VII) are 0.72, 0.69, and 0.67 Å, respectively. Six-coordinate radii for Tc(V) and Tc(VII) are 0.74 and 0.70 Å, and a reasonable estimate for the radius of octahedral Tc(VI) would be 0.71 Å. As in other catecholate structures, the average ligand C–O length is in the 1.33–1.35 Å range at 1.334 (13) Å. One oxygen atom of the structure, O3, shows anomalies in both the Tc–O and C–O lengths. There is the possibility that the crystal contains a mixture of Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP). However, the C–N length should be longer than the C–O length, and the thermal parameters of O3 show no evidence of disorder or partial NH occupancy. Furthermore, high-resolution mass spectral analysis recorded on crystals of Tc(DBCat)$_3$ taken from the sample used for X-ray analysis failed to show the presence of two species with different exact mass values. Attempts at growing crystals from pure samples of Tc(DBCat)$_2$(DBAP) have, so far, failed.

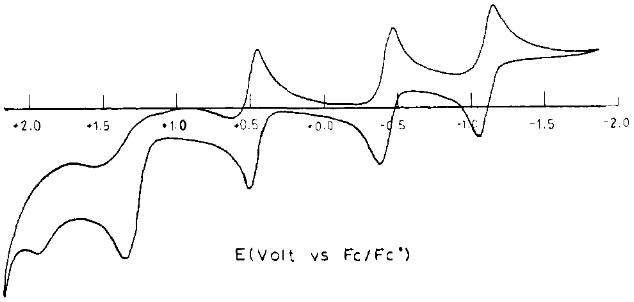

Figure 2. Isotropic EPR spectrum of Tc(DBCat)$_3$ recorded in dichloromethane solution at room temperature. The spectrum is centered about a $\langle g \rangle$ value of 2.0134; the average spacing between lines is 144 G due to coupling to the ^{99}Tc ($I = {}^9/_2$) nucleus.

Spectroscopic Properties of Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP). Infrared spectra on Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP) are quite similar and are similar to spectra recorded on Re(DBCat)$_3$[2] and other di-*tert*-butylcatecholate complexes.[9] Bands that appear for both complexes in the 1000–1650-cm^{-1} region include strong bands at 1582, 1362, and 1143 cm^{-1} and bands of medium intensity at 1636, 1530, 1462, 1377, 1290, and 1098 cm^{-1}.

Both Tc(DBCat)$_3$ and Tc(DBCat)$_2$(DBAP) are highly colored due to intense absorptions in the visible spectrum. Dark blue Tc(DBCat)$_3$ has a band at 594 nm (ϵ 19000 L cm^{-1} mol^{-1}) and a strong band at 232 (23000) with shoulders at 284 and 350 nm. Tc(DBCat)$_2$(DBAP) is deep purple in color with principal bands at 534 (25000) and 232 (28000) nm, shoulders at 284 and 350 nm, and a band of lesser intensity at 440 nm. The intense bands in the visible are thought to be catecholate-to-metal charge-transfer transitions.

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(4) Kawashima, M.; Koyama, M.; Fujinaga, T. *J. Inorg. Nucl. Chem.* **1976**, *38*, 801.

(5) Colmanet, S. F.; Williams, G. A.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1987**, 2305.

(6) Davison, A.; DePamphilis, B. V.; Jones, A. G.; Franklin, K. J.; Lock, C. J. L. *Inorg. Chim. Acta* **1987**, *128*, 161.

(7) Jones, A. G.; DePamphilis, B. V.; Davison, A. *Inorg. Chem.* **1981**, *20*, 1617.

(8) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(9) (a) Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1616. (b) Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962.

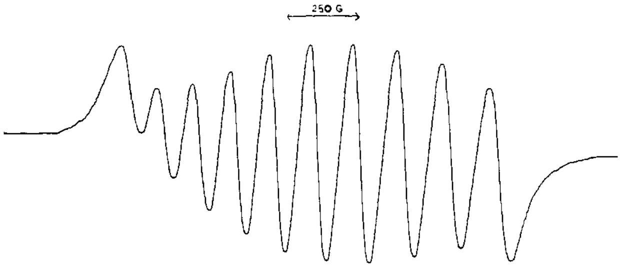


Figure 3. Cyclic voltammogram of $Tc(DBCat)_3$ recorded in dichloromethane solution at a scan rate of 200 mV/s.

Electron-impact mass spectrometry gave parent ion peaks at *m/e* values of 759.5 for $Tc(DBCat)_3$ and 758.5 for $Tc(DBCat)_2(DBAP)$. Exact mass calculations for the two complexes gave values of 759.345 and 758.357 for $TcC_{42}H_{60}O_6$ and $TcC_{42}H_{61}NO_5$, respectively.

Magnetism and EPR Spectra of $Tc(DBCat)_3$ and $Tc(DBCat)_2(DBAP)$. As distorted octahedral complexes of a second-row d^1 metal ion both $Tc(DBCat)_3$ and $Tc(DBCat)_2(DBAP)$ show magnetic moments that are lower than the values expected for the spin-only value. Room-temperature values of 1.28 (1) and 1.38 (1) μ_B have been obtained for the two complexes, showing the effects of spin–orbit coupling. Lower values of 1.18 (1) and 1.26 (1) μ_B were obtained for the related rhenium complexes $Re(DBCat)_3$ and $Re(Cl_4Cat)_3$.[2]

$Tc(DBCat)_3$ and $Tc(DBCat)_2(DBAP)$ both show clearly resolved room-temperature solution EPR spectra. Paramagnetic technetium complexes with a $S = {}^1/_2$ magnetic ground state are rare, and few show simple EPR spectra. The spectrum of $Tc(DBCat)_3$, shown in Figure 2, consists of 10 lines due to coupling to the $I = {}^9/_2$ ^{99}Tc nucleus centered about a $\langle g \rangle$ value of 2.0134. Spacing between lines shows a strong second-order field dependence with separations of 122 G between low-field lines increasing to 169 G between high-field lines. $Tc(DBCat)_2(DBAP)$ shows a nearly identical spectrum centered about a $\langle g \rangle$ value of 2.0193, with an average spacing between lines of 141 G and strong second-order field dependence. These spectra are unique for technetium complexes. The nitridotechnetium(VI) anions $TcNCl_4^-$ and $TcNBr_4^-$ show frozen-solution spectra with $\langle g \rangle$ values of 2.003 and 2.072 and average line spacings of 200 and 174 G, respectively.[10] Stronger hyperfine coupling for the axially symmetric nitridotechnetium(VI) complexes relative to the tris-chelated catecholate complexes parallels the pattern observed for vanadium(IV) complexes where vanadyl species commonly show stronger coupling than simple octahedral complexes.[11] Technetium hyperfine coupling has also been resolved in the spectra of tris(toluene-3,4-dithiolato)technetium[4] and tris(*o*-amidobenzenethiolato)technetium.[12] It is tempting to view these complexes as also containing Tc(VI). However, hyperfine coupling values of 14.1 and 4.0 G, respectively, show clearly the radical nature of the sulfur-donor ligands in these molecules, which differ from the catecholate complexes in both molecular and electronic structures.

Electrochemistry on $Tc(DBCat)_3$, $Tc(DBCat)_2(DBAP)$, and $Re(DBCat)_3$. Solutions prepared with purified samples of $Tc(DBCat)_3$ and $Tc(DBCat)_2(DBAP)$ were studied by using cyclic voltammetry and controlled-potential electrolysis. Both complexes undergo two reversible one-electron reductions, one reversible one-electron oxidation and two irreversible oxidations. The cyclic voltammogram of $Tc(DBCat)_3$ is shown in Figure 3. Reversible reductions of this complex occur at −0.42 and −1.09 V (vs Fc/Fc^+), and the reversible oxidation occurs at +0.45 V. This is followed at more positive potentials by irreversible oxidations at +1.33 and +1.93 V. The CV of $Tc(DBCat)_2(DBAP)$ is qualitatively similar to that of $Tc(DBCat)_3$. Reversible reductions occur at −0.59 and −1.53 V, and the reversible oxidation was found at +0.27 V. The irreversible oxidations occur at +1.06 and +1.68 V.

Table IV. Reversible Redox Couples for the $M(Cat)_3$ (M = Tc, Re) Complexes

	$E°(\Delta E_p)$, mV		
	$M^{VI}(DBSQ)(Cat)_2^+$/ $M^{VI}(Cat)_3$	$M^{VI}(Cat)_3$/ $M^V(Cat)_3^-$	$M^V(Cat)_3^-$/ $M^{IV}(Cat)_3^{2-}$
$Tc(DBCat)_3$	+0.45 (61)[a]	−0.42 (41)	−1.09 (48)
$Tc(DBCat)_2$-(DBAP)	+0.27 (53)	−0.59 (48)	−1.53 (45)
$Re(DBCat)_3$	+0.73 (93)	−0.57 (46)	−1.69 (64)
$Re(Cl_4Cat)_3$	+0.94 (49)	+0.36 (81)	−0.59 (127)[b]

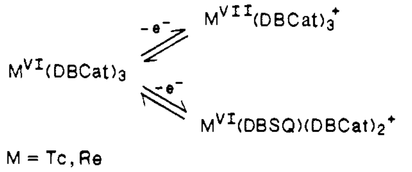
[a] $E°$ values recorded at a scan rate of 200 mV/s and references to the Fc^+/Fc couple. [b] Reference 2.

It is of interest to compare the results of the electrochemical characterization on $Tc(DBCat)_3$ with the redox properties of the Re analogue. We reported earlier only one reduction for $Re(DBCat)_3$.[2] The results obtained on the technetium complexes suggested that a second reduction might lie at more negative potentials. Reinvestigation of the electrochemistry on $Re(DBCat)_3$ revealed the second reduction and gave a result that is similar to the electrochemistry of the two Tc complexes. The rhenium complex undergoes two reversible reductions at −0.57 and −1.69 V, a quasireversible oxidation at +0.73 V, and two irreversible oxidations at +1.07 and +1.37 V. These results are summarized in Table IV and compared with the potentials of related oxidation and reduction processes for $Re(Cl_4Cat)_3$. In this complex the tetrachlorocatecholate ligands result in positive shifts in potential for all three processes.

Electrochemical activity may involve either the quinone ligands or the metal ions. Reduction of the neutral complexes must occur at the metal since the ligands are in the fully reduced catecholate form. Consequently, the two reduction steps correspond to reversible formation of $M^V(Cat)_3^-$ and $M^{IV}(Cat)_3^{2-}$, (M = Tc, Re) (2). Further, the shift to more negative potentials for $Re(DBCat)_3$

$$M^{VI}(DBCat)_3 \overset{e^-}{\rightleftharpoons} M^V(DBCat)_3^- \overset{e^-}{\rightleftharpoons} M^{IV}(DBCat)_3^{2-} \quad (2)$$

relative to $Tc(DBCat)_3$ is consistent with general periodic trends and the increased stability of high oxidation state forms of Re over Tc.[13] The reversible oxidation could potentially occur at either the metal or at one of the catecholate ligands to form a coordinated semiquinone (3). Strong π and σ donation has contributed to the stability of tris(catecholato) complexes of the d^0 metals V(V), Mo(VI), and W(VI),[9,14] and it would not be surprising to find that Tc(VII) and Re(VII) forms resulted from the reversible oxidation reactions. However, the values of the oxidation potentials show that the cationic technetium complex is more stable than the rhenium analogue. This is contrary to expectation for Tc(VII) and Re(VII) species, and oxidation must occur from one ligand to give the $M^{VI}(DBSQ)(DBCat)_2^+$ diradical cation. Controlled-potential electrolysis in CH_2Cl_2 at +0.80 V (Fc^+/Fc) was used to synthesize the oxidation product of $Tc(DBCat)_3$. The resulting complex is purple in color and shows sharp *tert*-butyl resonances at 1.22 and 1.25 ppm in the room-temperature ^1H NMR spectrum. The resolution of this spectrum



(3)

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[10] Baldas, J.; Boas, J. F.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2395.

[11] Jeyierski, A.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1981**, 1.

[12] Kirmse, R.; Stach, J.; Spies, H. *Inorg. Chim. Acta* **1980**, *45*, L251.

[13] (a) Peacock, R. D. *The Chemistry of Technetium and Rhenium*; Elsevier Publishing Co.: New York, 1966. (b) Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B. V.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988. (c) Deutsch, E.; Libson, K.; Vanderheyden, J.-L.; Ketring, A. R.; Maxon, H. R. *Nucl. Med. Biol.* **1986**, *13*, 465.

[14] (a) Cooper, S. R.; Koh, Y. G.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092. (b) Cass, M. E.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 122. (c) deLearie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1988**, *27*, 3842.

indicates that the oxidation product is diamagnetic and that all three ligands are equivalent. Diamagnetism must result either from strong spin–spin coupling between the paramagnetic metal and radical ligand or from charge delocalization within the cationic complex. This observation further suggests that the positively charged complex, which may form initially in the hydrolysis reaction between MO_4^- and catechol in reaction 1, is the Tc(VI) species $Tc^{VI}(DBSQ)(DBCat)_2^+$ rather than $Tc^{VII}(DBCat)_3^+$. Given the negative value of the DBSQ/DBCat couple, catecholate reduction of Tc(VII) to Tc(VI) would be quite favorable.

Discussion

Two unusual examples of Tc(VI) have been obtained from the reaction between NH_4TcO_4 and 3,5-di-*tert*-butylcatechol. Other well-characterized complexes of Tc(VI) are confined to the nitrido anions $TcNX_4^-$ (X = Cl, Br, TcF_6) and the polymeric oxyhalides $TcOX_4$ (X = F, Cl).[10,15,16] In the reaction, catechol serves as an acid to hydrolyze oxo ligands of the pertechnetate ion, as a chelating agent with the metal, and as a reducing agent for Tc(VII). Both $Tc(DBCat)_3$ and $Tc(DBCat)_2(DBAP)$ show well-resolved 10-line EPR spectra in solution at room temperature. Electrochemical characterization has been used to show the stability of the neutral Tc(VI) complexes relative to Tc(V) and Tc(IV) forms and to evaluate the accessibility of cationic forms of the complexes.

Empirical studies have shown that complexes with a single positive charge are particularly effective as heart-imaging agents. Spheroidal complexes appear to bind most effectively with myocardial receptors and the hexakis(isonitrile)technetium(I) complexes are among the most effective myocardial-imaging agents.[17] The *tert*-butylisonitrile complex $Tc(t\text{-}BuNC)_6^+$ provides high-quality images but accumulates in the liver, blocking exposure to the heart. Derivatives with methoxy substituents have shown lower liver accumulation and higher miocardial specificity. Clathrochelating triglyoxime complexes of Tc(III) have been tested with some success,[18] cationic complexes containing phosphine and arsine ligands have been investigated,[19] and even dibenzenetechnetium(I) has been considered for heart-imaging applications.[20]

The catecholate complexes of technetium and rhenium may be of interest in imaging applications. They can be synthesized by procedures that should be easily adapted to a field kit, and they are chemically and kinetically stable in solution. The DBCat complexes included in our present investigation undergo $Tc^{VI}(DBSQ)(DBCat)_2^+/Tc^{VI}(DBCat)_3$ reduction at positive potentials. They are probably too strong as oxidants for use as myocardial-imaging agents, and the lipophilic character of the neutral complexes may promote transfer to the liver. However, catechols are readily available with a wide variety of different substituents, which may be used to shift electrochemical potentials, solubility properties, and stereochemical features. The catechol/pertechnetate reaction could prove useful as a practical route to technetium catecholate complexes that may be of interest as radiopharmaceuticals.

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Supplementary Material Available: Tables containing details of the structure determination and refinement, anisotropic thermal parameters, a complete list of bond distances and angles, and hydrogen atom positions for $Tc(DBCat)_3$ (14 pages); observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(15) Holloway, J. H.; Selig, H. *J. Inorg. Nucl. Chem.* **1968**, *30*, 473.

(16) (a) Edwards, A. J.; Jones, G. R.; Sills, R. J. C. *J. Chem. Soc. A* **1970**, 2521. (b) Guest, A.; Lock, C. J. L. *Can. J. Chem.* **1972**, *50*, 1807.

(17) (a) Jones, A. G.; Kronauge, J. F.; Davison, A. *J. Nucl. Med. Allied Sci.* **1985**, *29*, 200. (b) Linder, K. E.; Davison, A.; Jones, A. G. *J. Nucl. Med. Allied Sci.* **1985**, *29*, 203.

(18) Thompson, M.; Nunn, A. D.; Treher, E. N. *Anal. Chem.* **1986**, *58*, 3100.

(19) (a) Hurst, R. W.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1981**, *20*, 3298. (b) Vanderheyden, J.-L.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1666.

(20) Dean, R. T.; Wester, D. W.; Nosco, D. L.; Adams, M. D.; Coveney, J. R.; Robbins, M. S.; McElvany, K. D.; DeJong, R. *Technetium in Chemistry and Nuclear Medicine 2*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1986; p 147.

The Novel Superacid Systems HSO_3F–$Nb(SO_3F)_5$ and HSO_3F–$Ta(SO_3F)_5$

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Abstract: The in situ oxidation of niobium and tantalum in HSO_3F by bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, results in the formation of solvated Lewis acids $M(SO_3F)_5$, M = Nb or Ta. Both solutes behave as moderately strong, monoprotonic acids, based on electrical conductivity measurements over the concentration range 0–0.05 *m* and on conductometric titrations against KSO_3F. These measurements suggest a general order of acidity, $Au(SO_3F)_3 > Ta(SO_3F)_5 \geq SbF_5 > Nb(SO_3F)_5 > NbF_5$, all giving rise to monoprotonic acids. Supporting evidence comes from ^1H, ^{19}F, and ^{93}Nb NMR spectroscopy and the successful isolation and characterization of complexes of the type $Cs_n[M(SO_3F)_{5+n}]$, with M = Nb or Ta and n = 1 or 2, from these solutions.

1. Introduction

After initial observation by Woolf in 1959,[1] the superacid system HSO_3F–SbF_5, later termed "magic acid",[2] was first investigated in 1965 by means of conductometry, cryoscopy, and ^{19}F nuclear magnetic resonance[3] and applied to the generation of carbonium cations[4] at about the same time. Following these early reports, the system has been subsequently extensively studied[5] and even

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(1) Woolf, A. A. *J. Chem. Soc.* **1955**, 433.

(2) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.

(3) Thompson, R. C.; Barr, J.; Gillespie, R. J.; Milne, J. B.; Rothenbury, R. A. *Inorg. Chem.* **1965**, *4*, 1641.

(4) Olah, G. A.; Comisarow, M. B.; Cupas, C. A.; Pittman, C. U. *J. Am. Chem. Soc.* **1965**, *87*, 2997.

0002-7863/89/1511-4328$01.50/0