the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. Programs used in this work include locally modified versions of the programs listed in the reference section.[20]

Solution and Refinement of the Structure of [*commo*-3,3′-Fe{3,1,2-$FeC_2B_9H_{11}\}_2][N(CH_3)_4]_2$ (6). Atoms were located by use of direct methods. All calculations were performed on the VAX 11/750 computer of the J. D. McCullough Laboratory for Crystallography. All H atoms on the anion were kept in located positions with an assigned value of U = 0.08 Å^2. All methyl H were included in calculated positions in structure factor calculations with an assigned U value of 0.10 Å^2. No hydrogen parameters were refined. Scattering factors for H were obtained from Stewart et al.[21] and for other atoms were taken from ref 22. Anomalous dispersion terms were applied to the scattering of Fe. The largest peak on a final difference electron density map was 0.8 e/Å^{-3}. Final positional and thermal parameters for non-hydrogen atoms are given in Table VII.

Acknowledgment. We gratefully acknowledge financial support provided by the Office of Naval Research.

Registry No. **5**, 132232-99-6; **6**, 12304-96-0; **7**, 132233-00-2; **8**, 132259-25-7; **9**·Cl, 132233-01-3; K[*nido*-7,8-$C_2B_9H_{12}$], 12304-72-2; [*nido*-9-(4-$C_5H_4N)CO_2CH_3$)-7,8-$C_2B_9H_{11}$], 110433-08-4; [*nido*-10-N-$(C_2H_5)_3$-7,8-$C_2B_9H_{11}$], 132205-46-0; [*nido*-10-$C_6H_5N(CH_3)_2$-7,8-$C_2B_9H_{11}$], 132205-47-1; [*nido*-9-$C_6H_5N(CH_3)_2$-7,8-$C_2B_9H_{11}$], 132205-48-2; [*nido*-9-$HCON(CH_3)_2$-7,8-$C_2B_9H_{11}$], 132205-49-3; [*nido*-9-$CH_3CON(CH_3)_2$-7,8-$C_2B_9H_{11}$], 132205-50-6; [*nido*-10-$N(C_2H_5)_3$-7,9-$C_2B_9H_{11}$], 132205-51-7; [*closo*-1,8-$C_2B_9H_{11}$], 52952-24-6; [*nido*-10-$\{(CH_3)_2CH\}_2NH$-7,9-$C_2B_9H_{11}$], 132205-52-8; [*nido*-10-C_5H_5N-7,9-$C_2B_9H_{11}$], 73066-29-2; 4-$(C_5H_4N)CO_2CH_3$, 2459-09-8; Me_3NH[*nido*-7,8-$C_2B_9H_{12}$], 12543-22-5.

Supplementary Material Available: For **5** and **6**, tables of crystallographic parameters, positional and thermal parameters, and interatomic distances and angles (14 pages); listings of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Investigations of the Technetium–Hydrazido Core. Synthesis and Structural Characterization of $[(n\text{-}C_4H_9)_4N][Tc_2(NNPh_2)_2(C_6Cl_4O_2)_4]\cdot CH_2Cl_2\cdot 2CH_3OH$, a Tc(V)/Tc(VI) Catecholate Complex with the Hydrazido Ligands Adopting the Unusual η^1 Bridging Mode

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Received December 4, 1990

Reaction of the oxo–bis(tetrachlorocatecholate) Tc(V) complex $[(n\text{-}C_4H_9)_4N][TcO(C_6Cl_4O_2)_2]$ (**1**) with *N*,*N*-diphenylhydrazine in CH_2Cl_2 yields the binuclear paramagnetic Tc(V)/Tc(VI) mixed-valence complex $[(n\text{-}C_4H_9)_4N][Tc_2(NNPh_2)_2(C_6Cl_4O_2)_4]\cdot CH_2Cl_2\cdot 2CH_3OH$ (**2**). The structure of the molecular anion of **2** consists of two distorted octahedral Tc centers bridged by two hydrazido(2–) groups bonding in the η^1 mode, an unusual bonding motif for this ligand, having been previously described only for cyclopentadienyl–metal species. Complex **2** is also a unique example of a Tc(V)/Tc(VI) mixed-valence species; the Tc–Tc distance of 2.612 (2) Å is consistent with direct metal–metal interaction. Crystal data for **1**: $P\bar{1}$, $a = 9.579$ (2) Å, $b = 11.705$ (3) Å, $c = 16.391$ (4) Å, $\alpha = 83.95$ (2)°, $\beta = 88.63$ (2)°, $\gamma = 74.51$ (2)°, $V = 1761.3$ (7) Å^3, $Z = 2$, $D_{calc} = 1.60$ g cm^{-3}; 3637 reflections, $R = 0.046$. Crystal data for **2**: $P\bar{1}$, $a = 14.210$ (3) Å, $b = 16.663$ (4) Å, $c = 19.644$ (4) Å, $\alpha = 76.82$ (2)°, $\beta = 80.52$ (2)°, $\gamma = 66.79$ (2)°, $V = 4151.8$ (15) Å^3, $Z = 2$, $D_{calc} = 1.55$ g cm^{-3}; 6999 reflections, $R = 0.075$.

Introduction

The intense contemporary interest in the fundamental coordination chemistry of the synthetic radioactive element technetium is a consequence of its expanding application in diagnostic nuclear medicine.[1-3] Technetium-99 remains the radionuclide of choice for numerous applications by virtue of its reasonable cost, ready availability, and optimal nuclear properties (γ = 140 keV with no particulate emissions, $t_{1/2}$ = 6 h), which allow images of high resolution to be obtained with a low radiation dose to the patient. In order to be clinically useful, a technetium-containing complex must be easily prepared in a radiochemically pure form, must exhibit stability under biological conditions, and must possess useful biodistribution properties. Although a variety of technetium coordination complexes that locate in a particular organ have been described,[4-7] a more general approach exploits the binding of ^{99m}Tc to tumor-localizing monoclonal and polyclonal antibodies.[8-10]

Methods employed in the conjugation of ^{99m}Tc to proteins include the use of diethylenetriaminepentaacetic acid[11] and of N_2S_2 and N_3S[12-18] functionalized ligands and direct reduction[19] of the protein disulfide bonds to form free sulfhydryl groups. Difficulties encountered with these technologies include protein denaturation, nonspecific binding of technetium, and slow kinetics of Tc-labeling.

We have recently described a simple, efficient, and general method for labeling proteins with ^{99m}Tc based on bifunctional

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hydrazine reagents. Tc(V)–oxo precursors were found to add readily under mild conditions to hydrazinopyridine-modified proteins to yield stable ^{99m}Tc-labeled proteins in >90% radiometric yield.[20,21] ^{99m}Tc hydrazinopyridine–polyclonal IgG conjugates have been demonstrated to be useful agents for the imaging of focal sites of infection.[22]

However, the fundamental chemistry of technetium with organohydrazine ligands remains largely unexplored[23-29] and suggests that Tc–oxo precursors do not react via condensation-type reactions to give exclusively Tc–hydrazide species. In the course of our extensive studies of the chemistry of organohydrazines with macroscopic quantities of the long-lived radionuclide ^{99}Tc, we have investigated the reactions of Tc(V)–oxo catecholates, $[TcO(C_6R_4O_2)_2]^-$ (R = H, Cl, Br), models for $[TcO(glucoheptonate)_2]^-$[30] commonly used as a synthetic precursor in the preparation of ^{99m}Tc protein conjugates, with N,N-disubstituted organohydrazines. In this paper, we report the synthesis and structure of the unusual binuclear Tc(V)/Tc(VI) species $[(n\text{-}C_4H_9)_4N][Tc_2(NNPh_2)_2(C_6Cl_4O_2)_4]$, which contains bridging hydrazido(2–) ligands.

Experimental Section

Syntheses. *Caution!* Technetium-99 is a weak β^- emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive material.

Ammonium pertichnetate was purchased from Oak Ridge National Laboratory. Reagents were used as received from the usual commercial sources. Column chromatography was performed with the use of TLC grade silica gel. Infrared spectra were obtained on a Perkin-Elmer 283B infrared spectrophotometer; UV/visible spectra were obtained on a Shimadzu Model UV-160 spectrophotometer. Electrochemical studies were carried out on a BAS 100 electroanalytical system using solutions 3×10^{-3} M in complex in 0.1 M $(n\text{-}Bu_4N)(PF_6)$. EPR measurements were done on a Varian E4 spectrometer.

$[(n\text{-}C_4H_9)_4N][TcO(C_6Cl_4O_2)_2]$ (1). Addition of a solution of $[(n\text{-}C_4H_9)_4N][TcOCl_4]$[31] (0.234 g, 0.47 mmol) in 2 mL of anhydrous methanol to a solution of tetrachlorocatechol (0.224 g, 0.90 mmol) in 5 mL of methanol resulted in a homogeneous orange-red solution. Addition of 3 equiv of NaOMe (based on Tc), followed by 1 mL of 75% $(n\text{-}C_4H_9)_4NCl$ in methanol and 20 mL of H_2O, resulted in a copious orange precipitate. Recrystallization from CH_2Cl_2/ether afforded red-orange block-shaped crystals in 80% yield. Anal. Calcd for $C_{28}H_{36}O_5NCl_8Tc$: C, 39.6; H, 4.24. Found: C, 39.4; H, 4.19. IR (KBr pellet; cm^{-1}): 2965 (m), 2876 (w), 1472 (w), 1401 (s), 1378 (m), 1252 (m), 1238 (m), 969 (m), 809 (s), 739 (w), 700 (w), 613 (s), 590 (m), 576 (m). UV/vis [CH_2Cl_2; λ_{max}, nm (ϵ, cm^{-1} M^{-1})]: 301 (1.4×10^4).

Table I. X-ray Data for the Structure Determinations of **1** and **2**

	1	**2**
empirical formula	$C_{28}H_{36}NO_5Cl_8Tc$	$C_{67}H_{66}N_5O_{10}Cl_{18}Tc_2$
fw	848.2	1935.3
a, Å	9.579 (2)	14.210 (3)
b, Å	11.705 (3)	16.663 (4)
c, Å	16.391 (4)	19.664 (4)
α, deg	83.95 (2)	76.82 (2)
β, deg	88.63 (2)	80.52 (2)
γ, deg	74.51 (2)	66.79 (2)
V, Å^3	1761.3 (7)	4151.8 (15)
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_{calc}, g cm^{-3}	1.599	1.548
D_{obs}, g cm^{-3}	1.61 (1)	1.56 (1)
μ, cm^{-1}	10.48	9.63
λ(Mo Kα), Å	0.71073	0.71073
temp, °C	23	23
R, R_w	0.046, 0.054	0.075, 0.079
goodness of fit	1.17	1.92
$F(000)$	860	1950

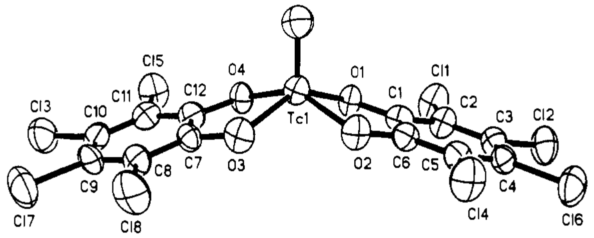

Figure 1. ORTEP view of the molecular anion of **1**, $[TcO(C_6Cl_4O_2)_2]^-$.

$[(n\text{-}C_4H_9)_4N][Tc_2(NNPh_2)_2(C_6Cl_4O_2)_4]\cdot CH_2Cl_2\cdot 2CH_3OH$ (2). To a solution of **1** (0.100 g, 0.12 mmol) in 2 mL of methanol was added *N*,*N*-diphenylhydrazine in slight excess (0.028 g, 0.15 mmol). The deep purple solution was refluxed for 30 min. When the mixture was cooled to −4 °C, a purple precipitate formed, which was collected by filtration and dried in air. The solid was dissolved in CH_2Cl_2 and the solution chromatographed on silica gel. The deep purple fraction, which eluted first, was collected, concentrated to 3 mL, and carefully layered with methanol. After the mixture was allowed to stand for 4 days at room temperature, X-ray-quality crystals of **2** were collected in ca. 20% yield. Anal. Calcd for $C_{64}H_{56}N_5O_8Cl_{16}Tc_2$: C, 43.0; H, 3.16; N, 3.91; Cl, 31.7. Found: C, 43.5; H, 3.36; N, 3.78; Cl, 31.6 (sample had been vacuum-dried to remove CH_2Cl_2 and MeOH of crystallization). IR (KBr pellet; cm^{-1}): 2963 (w), 1522 (m), 1486 (m), 1386 (m), 1326 (m), 1258 (vs), 1231 (s), 988 (s), 811 (m), 791 (m), 756 (m), 691 (m), 688 (m), 571 (m), 470 (m). UV/vis [CH_2Cl_2; λ_{max}, nm (ϵ, cm^{-1} M^{-1})]: 304 (4.83×10^4), 580 (2.40×10^4). $E_{1/2}$ (CH_2Cl_2, 100 mV/s scan speed, Pt working electrode, Ag/AgCl reference; V): −0.456, +0.020, +0.673, +1.049 (all reversible, anodic) (see ref 46 for other examples of Tc–catecholate electrochemical behavior).

X-ray Crystallography. The crystal data and experimental details of the structure determination are given in Table I.

A bright red-orange crystal of complex **1** measuring 0.25 × 0.30 × 0.30 mm was selected. Data were collected on a Siemens R3m/V diffractometer using the ω–2θ scan mode with a maximum 2θ of 45°. The hemisphere $\pm h,\pm h,+l$ was collected. Of 4942 reflections collected, 3637 with $F_o \geq 6\sigma(F_o)$ (Mo Kα, $\lambda = 0.71073$ Å) were deemed observed. An empirical absorption correction was applied. The technetium was located by the Patterson method, and all non-hydrogen atoms were located from subsequent difference Fourier maps. Hydrogen atom positions were calculated. Neutral-atomic scattering factors were used throughout.[32] Extinction effects were not observed.

A deep purple crystal of **2** measuring 0.42 × 0.30 × 0.25 mm was selected, and data were collected in the hemisphere $\pm h,\pm k,+l$. Of 11341 reflections collected under conditions identical with those used for **1**, 6999 with $F_o \geq 6\sigma(F_o)$ were used in the solution and refinement, which also were carried out as for **1**. The final difference map revealed the presence of a methylene chloride molecule of crystallization and four poorly resolved methanol molecules of crystallization, each at ca. 0.5 occupancy, which were included in the final cycles of refinement. Atomic positional parameters for **1** are listed in Table II, and those for **2**, in Table IV.

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients for **1**

	x	y	z	U(eq),[a] Å^2
Tc(1)	508 (1)	2256 (1)	2573 (1)	39 (1)
Cl(1)	3923 (2)	2966 (2)	409 (1)	67 (1)
Cl(2)	2352 (2)	3755 (2)	−1303 (1)	69 (1)
Cl(3)	1610 (3)	3458 (2)	6413 (1)	75 (1)
Cl(4)	−2736 (2)	3646 (2)	167 (1)	67 (1)
Cl(5)	3529 (2)	2662 (2)	4883 (1)	68 (1)
Cl(6)	−971 (3)	4096 (2)	−1429 (1)	70 (1)
Cl(7)	−1746 (3)	4058 (2)	6263 (1)	83 (1)
Cl(8)	−3194 (2)	3874 (2)	4599 (1)	73 (1)
O(1)	1881 (4)	2657 (4)	1774 (2)	40 (2)
O(2)	−867 (5)	2978 (4)	1678 (3)	48 (2)
O(3)	−1006 (4)	3029 (4)	3302 (3)	48 (2)
O(4)	1753 (4)	2581 (4)	3408 (3)	43 (2)
O(5)	658 (5)	815 (4)	2649 (3)	56 (2)
C(1)	1301 (7)	2999 (6)	1013 (4)	40 (2)
C(2)	2077 (7)	3185 (6)	323 (4)	46 (3)
C(3)	1395 (8)	3525 (6)	−445 (4)	48 (3)
C(4)	−113 (8)	3675 (6)	−494 (4)	44 (2)
C(5)	−906 (7)	3487 (6)	220 (4)	43 (2)
C(6)	−212 (7)	3167 (6)	958 (4)	41 (2)
C(7)	−469 (7)	3171 (5)	4034 (4)	38 (2)
C(8)	−1336 (7)	3535 (6)	4698 (4)	46 (3)
C(9)	−672 (8)	3626 (6)	5423 (4)	51 (3)
C(10)	818 (9)	3364 (6)	5500 (4)	53 (3)
C(11)	1671 (7)	2997 (6)	4832 (4)	48 (3)
C(12)	1031 (7)	2909 (6)	4103 (4)	45 (3)
N(1)	6292 (5)	602 (4)	2615 (3)	39 (2)
C(21)	5134 (7)	1786 (5)	2632 (4)	40 (2)
C(22)	5697 (7)	2877 (5)	2527 (5)	47 (2)
C(23)	4486 (8)	3988 (6)	2630 (6)	60 (3)
C(24)	4961 (10)	5102 (7)	2466 (7)	85 (4)
C(25)	7438 (7)	444 (6)	3274 (4)	45 (2)
C(26)	6886 (8)	560 (7)	4134 (4)	55 (3)
C(27)	8127 (8)	371 (7)	4721 (5)	60 (3)
C(28)	7641 (11)	520 (10)	5583 (5)	95 (5)
C(29)	5571 (7)	−411 (6)	2755 (5)	49 (3)
C(31)	3938 (10)	−1567 (7)	2359 (6)	70 (4)
C(32)	2836 (11)	−1733 (8)	1807 (7)	99 (5)
C(30)	4521 (8)	−497 (6)	2110 (5)	58 (3)
C(33)	7028 (7)	603 (6)	1782 (4)	45 (2)
C(34)	8132 (9)	−528 (7)	1613 (5)	63 (3)
C(35)	8705 (12)	−402 (8)	753 (7)	91 (5)
C(36)	7573 (16)	−252 (10)	117 (6)	133 (7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg) for **1**

Tc(1)–O(1)	1.945 (4)	Tc(1)–O(2)	1.959 (4)
Tc(1)–O(3)	1.948 (4)	Tc(1)–O(4)	1.967 (5)
Tc(1)–O(5)	1.646 (5)		
O(1)–Tc(1)–O(2)	82.1 (2)	O(2)–Tc(1)–O(4)	144.7 (2)
O(1)–Tc(1)–O(3)	139.8 (2)	O(2)–Tc(1)–O(5)	106.3 (2)
O(1)–Tc(1)–O(4)	86.1 (2)	O(3)–Tc(1)–O(4)	81.7 (2)
O(1)–Tc(1)–O(5)	86.1 (2)	O(3)–Tc(1)–O(5)	110.0 (2)
O(2)–Tc(1)–O(3)	110.1 (2)	O(4)–Tc(1)–O(5)	109.0 (2)

Results and Discussion

The reaction of $[TcOCl_4]^-$ with 3 equiv of tetrachlorocatechol in methanol, followed by addition of NaOMe and then of water, yields $(n\text{-}Bu_4N)[TcO(C_6Cl_4O_2)_2]$ (**1**) as a copious red-orange precipitate. Recrystallization from CH_2Cl_2/ether affords red crystals of the diamagnetic Tc(V) complex. The spectroscopic characteristics of **1** are similar to those reported for the catecholate complex $(n\text{-}Bu_4N)[TcO(C_6H_4O_2)_2]$.[46] The prominent feature at 969 cm^{-1} is characteristic of the presence of the Tc–oxo unit. The structure of **1**, illustrated at Figure 1, consists of discrete cations and molecular anions, with the Tc adopting square-pyramidal geometry. The metrical parameters listed in Table III are unexceptional and similar to those reported for the analogous catecholate $[TcO(C_6H_4O_2)_2]^-$.[46]

Reaction of $[(n\text{-}C_4H_9)_4N][TcO(C_6Cl_4O_2)_2]$ (**1**) with *N*,*N*-diphenylhydrazine in methylene chloride, followed by addition of methanol, yields lustrous purple crystals of $[(n\text{-}C_4H_9)_4N][Tc_2(NNPh_2)_2(C_6Cl_4O_2)_4]\cdot CH_2Cl_2\cdot 2CH_3OH$ (**2**). The substitution of the terminal oxo group may be formally described as a condensation type reaction, giving H_2O and the Tc–hydrazido unit.[33] Since the average oxidation state of the Tc centers in **2** is +5.5, it would appear that the diphenylhydrazine serves as an oxidant, as well as a ligating group. Although the presence of diphenylamine in the product mixture would seem to confirm the role of the hydrazine, the relatively low yield of product **2** and the presence of several uncharacterized byproducts preclude a definitive conclusion.

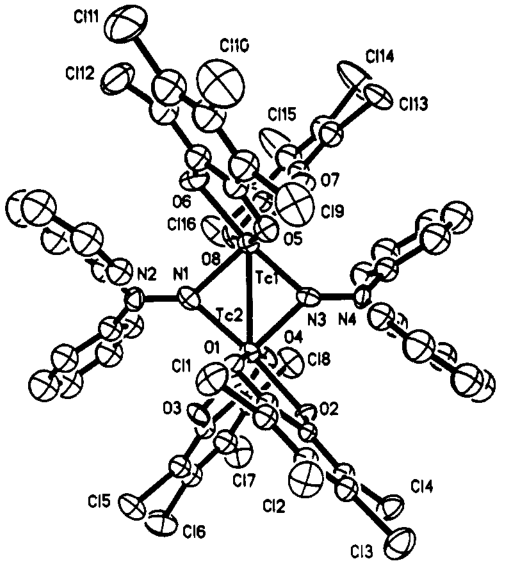

Figure 2. ORTEP view of the molecular anion of **2**, $[Tc_2(NNPh_2)_2(C_6Cl_4O_2)_4]^-$, showing the atom-labeling scheme.

Complex **2** is paramagnetic (by NMR spectroscopy) but EPR silent in various solvents to −77 °C. At lower temperatures, a broad line centered at a g value of about 2.015[34] is observed; detailed EPR studies at liquid-helium temperature are in progress.[35] The infrared spectrum exhibits characteristic bands at 1486 and 1521 cm^{-1}, associated with the hydrazido(2−) ligand. The electronic spectrum of **2** in CH_2Cl_2 displays charge-transfer bands at 580 and 304 nm (ϵ 2.4×10^4 and 4.8×10^4 cm^{-1} M^{-1}, respectively) and a weak band at 12 000 cm^{-1} (ϵ 200 cm^{-1} M^{-1}) in the near-infrared spectrum, which is consistent with an intervalence charge-transfer band. The complex is electrochemically active, exhibiting four successive reversible one-electron oxidations. Such successive one-electron processes are characteristic of ligand-based redox in general and of metal–catecholate complexes specifically.

The structure of complex **2** is illustrated in Figure 2, and metrical parameters are listed in Table V. The structure of the molecular anion of **2** consists of discrete binuclear units $[Tc_2(NNPh_2)_2(C_6CL_4O_2)_4]^-$ with distorted octahedral geometries about the Tc centers. Each technetium bonds to two terminal bidentate catecholato ligands and to the α-nitrogen donors of the two bridging hydrazido(2−) groups. The catecholate ligands are disposed so as to each provide an oxygen donor oriented trans to a bridging hydrazido nitrogen in the $[Tc_2N_2O_4]$ plane and a second oxygen donor in an axial position trans to an oxygen of the second catecholate group bound to the metal center. A consequence of this ligand configuration is inequivalent Tc–O bond distances of 2.04 (1) Å for Tc–O bonds trans to the bridging hydrazido groups and 1.98 (1) Å for those occupying the axial sites trans to another catecholate oxygen. the average Tc–N bond distance, 1.94 (1)

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Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients for **2**

	x	y	z	U(eq),[a] Å^2		x	y	z	U(eq),[a] Å^2
Tc(1)	2527 (1)	7665 (1)	2421 (1)	246 (5)	C(25)	2032 (10)	9298 (9)	833 (7)	328 (33)
Tc(2)	2429 (1)	9040 (1)	2895 (1)	223 (4)	C(26)	3066 (10)	9098 (9)	717 (7)	367 (34)
Cl(1)	5460 (3)	9376 (3)	1394 (2)	424 (17)	C(27)	3539 (13)	8939 (10)	60 (8)	552 (44)
Cl(2)	6990 (3)	9604 (3)	2241 (2)	454 (17)	C(28)	2986 (13)	9015 (11)	−468 (10)	644 (49)
Cl(3)	6454 (3)	9674 (3)	3836 (2)	480 (18)	C(29)	1964 (14)	9234 (12)	−361 (10)	735 (54)
Cl(4)	4352 (3)	9569 (2)	4556 (2)	382 (16)	C(30)	1455 (13)	9380 (11)	295 (8)	542 (43)
Cl(5)	226 (3)	12307 (2)	2707 (2)	436 (16)	C(31)	2906 (10)	6695 (9)	4258 (7)	336 (33)
Cl(6)	−1625 (3)	12602 (3)	3838 (2)	549 (18)	C(32)	1883 (11)	7012 (10)	4386 (8)	420 (36)
Cl(7)	−2001 (3)	10962 (3)	4812 (2)	552 (18)	C(33)	1395 (12)	6494 (10)	4822 (8)	529 (42)
Cl(8)	−491 (3)	9047 (3)	4627 (2)	491 (17)	C(34)	1987 (14)	5666 (12)	5139 (10)	717 (53)
Cl(9)	6179 (3)	6689 (3)	1508 (2)	635 (20)	C(35)	3005 (13)	5320 (12)	5015 (9)	644 (49)
Cl(10)	6553 (4)	5972 (3)	104 (3)	872 (25)	C(36)	3513 (13)	5826 (11)	4564 (8)	564 (44)
Cl(11)	4685 (5)	6095 (4)	−596 (2)	950 (31)	C(37)	4321 (10)	7286 (9)	3982 (7)	319 (32)
Cl(12)	2464 (4)	6816 (3)	145 (2)	715 (25)	C(38)	5087 (10)	7286 (9)	3428 (8)	380 (35)
Cl(13)	2874 (3)	4528 (2)	3481 (2)	447 (16)	C(39)	6009 (12)	7284 (10)	3618 (9)	529 (42)
Cl(14)	716 (4)	4414 (3)	4010 (3)	996 (28)	C(40)	6138 (12)	7266 (10)	4304 (8)	538 (43)
Cl(15)	−1247 (3)	6145 (3)	3896 (4)	1143 (31)	C(41)	5392 (12)	7250 (11)	4838 (9)	584 (45)
Cl(16)	−1059 (3)	7964 (3)	3216 (2)	550 (18)	C(42)	4464 (11)	7253 (9)	4680 (8)	424 (37)
O(1)	3602 (6)	9247 (5)	2282 (4)	254 (36)	C(43)	575 (10)	10141 (9)	1604 (7)	340 (33)
O(2)	3176 (6)	9275 (5)	3585 (4)	260 (37)	C(44)	370 (11)	10944 (10)	1185 (8)	455 (38)
O(3)	1555 (6)	10364 (5)	2770 (4)	290 (37)	C(45)	−563 (12)	11611 (11)	1304 (9)	591 (46)
O(4)	1251 (6)	9058 (5)	3583 (4)	290 (37)	C(46)	−1273 (14)	11465 (12)	1814 (9)	663 (50)
O(5)	3985 (6)	7272 (6)	2065 (4)	319 (38)	C(47)	−1067 (12)	10670 (10)	2207 (8)	494 (40)
O(6)	2460 (7)	7356 (6)	1497 (5)	395 (44)	C(48)	−144 (10)	9992 (10)	2097 (7)	402 (36)
O(7)	2720 (6)	6378 (5)	2840 (4)	268 (36)	N(5)	3201 (8)	2472 (7)	2290 (6)	328 (27)
O(8)	1074 (6)	7783 (5)	2705 (4)	272 (36)	C(49)	2588 (10)	2513 (9)	2995 (7)	339 (33)
N(1)	1985 (7)	8925 (7)	2045 (5)	262 (44)	C(50)	2742 (11)	1602 (9)	3453 (7)	415 (37)
N(2)	1529 (8)	9458 (7)	1495 (5)	295 (48)	C(51)	2098 (12)	1721 (11)	4158 (8)	522 (42)
N(3)	2984 (7)	7778 (6)	3256 (5)	250 (44)	C(52)	2514 (13)	2089 (11)	4628 (9)	643 (49)
N(4)	3410 (8)	7264 (7)	3813 (5)	396 (48)	C(53)	2839 (11)	2028 (10)	1873 (7)	424 (37)
C(1)	4271 (9)	9353 (8)	2600 (6)	239 (29)	C(54)	3372 (12)	1880 (10)	1173 (8)	489 (40)
C(2)	5187 (9)	9430 (8)	2268 (7)	298 (31)	C(55)	2887 (13)	1465 (12)	803 (9)	654 (49)
C(3)	5847 (9)	9526 (8)	2652 (7)	288 (31)	C(56)	3398 (14)	1295 (12)	98 (10)	759 (56)
C(4)	5609 (9)	9568 (8)	3358 (6)	276 (30)	C(57)	3050 (11)	3532 (10)	1914 (8)	456 (39)
C(5)	4677 (9)	9517 (8)	3680 (6)	241 (29)	C(58)	2022 (15)	4020 (13)	1825 (12)	913 (66)
C(6)	4046 (8)	9380 (7)	3323 (6)	184 (27)	C(59)	2076 (19)	5043 (16)	1571 (14)	1173 (86)
C(7)	731 (9)	10585 (8)	3216 (6)	258 (30)	C(60)	1157 (21)	5715 (18)	1558 (15)	1494 (113)
C(8)	40 (10)	11404 (9)	3270 (7)	309 (32)	C(61)	4324 (11)	1955 (10)	2354 (8)	457 (39)
C(9)	−780 (10)	11543 (9)	3758 (7)	354 (34)	C(62)	4779 (12)	2233 (11)	2883 (9)	573 (45)
C(10)	−963 (10)	10809 (9)	4190 (7)	381 (35)	C(63)	5944 (12)	1949 (11)	2731 (9)	598 (46)
C(11)	−296 (10)	9973 (9)	4127 (7)	355 (34)	C(64)	6430 (15)	2027 (13)	3310 (10)	797 (58)
C(12)	547 (9)	9841 (8)	3655 (7)	280 (31)	C(65)	4903 (13)	4849 (12)	7181 (9)	633 (48)
C(13)	4187 (10)	7016 (9)	1450 (7)	333 (33)	Cl(18)	4169 (6)	5482 (5)	6485 (3)	1391 (40)
C(14)	5174 (11)	6692 (10)	1125 (8)	471 (39)	Cl(17)	4742 (6)	5460 (4)	7826 (3)	1080 (36)
C(15)	5320 (12)	6408 (11)	487 (9)	532 (43)	O(82)	816 (16)	1349 (15)	8975 (12)	600 (61)
C(16)	4486 (13)	6442 (11)	188 (9)	599 (46)	C(82)	398 (20)	1923 (18)	9374 (15)	367 (69)
C(17)	3493 (11)	6753 (10)	516 (8)	453 (38)	O(83)	8708 (21)	4810 (18)	2454 (15)	911 (84)
C(18)	3365 (10)	7029 (9)	1154 (7)	366 (34)	C(83)	8054 (34)	4330 (30)	2078 (25)	948 (139)
C(19)	1839 (9)	6278 (8)	3073 (7)	277 (30)	O(86)	9048 (24)	4150 (21)	1282 (17)	1119 (103)
C(20)	1785 (10)	5454 (9)	3395 (7)	371 (34)	C(86)	7921 (33)	4065 (29)	1600 (24)	897 (130)
C(21)	800 (11)	5440 (10)	3641 (8)	452 (38)	O(85)	1613 (15)	2721 (14)	8386 (11)	540 (56)
C(22)	−67 (12)	6187 (10)	3582 (8)	489 (40)	C(85)	483 (31)	2683 (28)	9470 (22)	820 (123)
C(23)	−2 (10)	7001 (9)	3273 (7)	367 (34)	C(87)	698 (35)	4463 (32)	28 (25)	1046 (150)
C(24)	957 (9)	7041 (8)	3015 (6)	252 (30)					

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Å, is consistent with considerable multiple-bond character, while the short N(1)–N(2) and N(2)–N(3) bond lengths suggest delocalization throughout the [Tc_2N_4] moiety. The Tc(1)–Tc(2) bond length of 2.612 (2) Å indicates a significant metal–metal interaction.

Since the metrical parameters associated with the ligands are unexceptional for the descriptions catecholato(2−) and hydrazido(2−), the complex may be formally considered a unique example of a mixed-valence Tc(V)/Tc(VI) species. Alternatively, the nitrogenous ligands may be described as neutral isodiazene groups, which would result in an oxidation-state assignment of Tc(III)/Tc(IV), for which [Tc_2O_2(triazacyclononanetriacetate)$_2$]$^{3-}$ provides a precedent.[36] However, the Tc–Tc bond distance of 2.402 Å for this latter complex is significantly shorter than that of **2** and indicative of considerable metal–metal multiple-bond character. Technetium–technetium bond distances fall in the ranges 2.11–2.20 Å for Tc(II)/Tc(III) and Tc(III)/Tc(III) species,[37–39] 2.33–2.41 Å for Tc(III)/Tc(IV) and Tc(IV)/Tc(IV) complexes,[36,40,41] and 3.65 Å for a Tc(V)/Tc(V) binuclear species.[42] The Tc–Tc bond distance of 2.612 Å in **2** would suggest that the Tc(V)/Tc(VI) assignment is appropriate. Furthermore, the N–N distances for the organohydrazine ligands are consistent

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Table V. Selected Bond Lengths (Å) and Angles (deg) for **2**

Tc(1)–Tc(2)	2.612 (2)		
Tc(1)–O(5)	1.967 (8)	Tc(2)–O(1)	1.988 (8)
Tc(1)–O(6)	2.023 (1)	Tc(2)–O(2)	2.041 (10)
Tc(1)–O(7)	2.039 (8)	Tc(2)–O(3)	2.040 (7)
Tc(1)–O(8)	1.991 (8)	Tc(2)–O(4)	1.966 (8)
Tc(1)–N(1)	1.937 (9)	Tc(2)–N(1)	1.954 (12)
Tc(1)–N(3)	1.935 (12)	Tc(2)–N(3)	1.936 (9)
N(1)–N(2)	1.311 (13)	N(3)–N(4)	1.297 (13)
O(5)–Tc(1)–O(6)	79.0 (4)	O(1)–Tc(2)–O(2)	78.2 (4)
O(5)–Tc(1)–O(7)	89.4 (3)	O(1)–Tc(2)–O(3)	92.5 (3)
O(5)–Tc(1)–O(8)	165.3 (4)	O(1)–Tc(2)–O(4)	167.5 (4)
O(5)–Tc(1)–N(1)	104.1 (4)	O(1)–Tc(2)–N(1)	86.0 (4)
O(5)–Tc(1)–N(3)	85.9 (4)	O(1)–Tc(2)–N(3)	103.1 (4)
O(6)–Tc(1)–O(7)	85.8 (4)	O(2)–Tc(2)–O(2)	86.1 (4)
O(6)–Tc(1)–O(8)	90.7 (4)	O(2)–Tc(2)–O(4)	92.6 (4)
O(6)–Tc(1)–N(1)	91.9 (4)	O(2)–Tc(2)–N(1)	164.0 (4)
O(6)–Tc(1)–N(3)	164.4 (4)	O(2)–Tc(2)–N(3)	91.0 (4)
O(7)–Tc(1)–O(8)	79.4 (3)	O(3)–Tc(2)–O(4)	78.3 (3)
O(7)–Tc(1)–N(1)	165.7 (4)	O(3)–Tc(2)–N(1)	92.1 (4)
O(7)–Tc(1)–N(3)	90.1 (4)	O(3)–Tc(2)–N(3)	163.2 (4)
O(8)–Tc(1)–N(1)	86.5 (4)	O(4)–Tc(2)–N(1)	102.7 (4)
O(8)–Tc(1)–N(3)	103.3 (4)	O(4)–Tc(2)–N(3)	85.3 (4)
N(1)–Tc(1)–N(3)	95.7 (5)	N(1)–Tc(2)–N(3)	95.1 (5)
Tc(1)–N(1)–N(2)	138.7 (10)	Tc(2)–N(1)–N(2)	137.0 (10)
Tc(1)–N(3)–N(4)	138.0 (10)	Tc(2)–N(3)–N(4)	137.0 (10)

with the hydrazido(2–) formalism rather than the isodiazene mode, which would require an N–N distance in the 1.15–1.20-Å range.

Another unusual feature of the structure of **2** is the presence of bridging hydrazido(2–) ligands,[43] a bonding mode that had been restricted to the cyclopentadienyl complexes $[Mo_2(C_5H_5)_2(NO)_2I_2(NNMe_2)]$[44] and $[Ti_2(C_5H_5)_2Cl_2(NNPh_2)_2]$.[45] Furthermore, in these latter complexes, the metal–bridging hydrazido nitrogen distances are unequivalent and the N–N distances lengthened to 1.39 Å. In contrast, the Tc–N distances for **2** are equivalent (1.925 (12)–1.954 (12) Å), while the average N–N distance of 1.31 (1) Å is consistent with the hydrazido(2–) formalism. Complex **2** is a unique example of symmetrically bridging η^1-hydrazido(2–) coordination.

The observation of bridging hydrazido ligands for **2** lends further support to the conclusion that the coordination chemistry of Tc–oxo precursors with organohydrazine ligands does not parallel that of Re–oxo and Mo–oxo species, where direct substitution of the terminal oxo group by a terminal hydrazido unit is the rule. Technetium–hydrazido chemistry is complicated by a tendency toward N–N bond cleavage and formation of Tc–nitrido and Tc–imido species[26] and by the presence of unusual bonding modes. The consequences of these results for bonding on the tracer level have yet to be evaluated.

We are currently investigating the magnetic and spectroscopic properties of **2** and of the related complexes $[Tc_2(NNRR')_2(cat)_4]^-$ (R = R' = CH_3, C_6H_5; R = CH_3, R' = C_6H_5; cat = $C_6Cl_4O_2^{2-}$, $C_6Br_4O_2^{2-}$, $C_6H_4O_2^{2-}$, $C_6H_2(t\text{-Bu})_2O_2^{2-}$).

Acknowledgment. This work was supported by a grant from Johnson Matthey.

Supplementary Material Available: For **1** and **2**, tables listing crystal data, details of the structure solution and refinement, atomic coordinates, bond distances and angles, anisotropic temperature factors, and calculated hydrogen atom positions (18 pages); listings of calculated and observed structure factors (57 pages). Ordering information is given on any current masthead page.

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Fluoride as a Terminal and Bridging Ligand for Copper: Isolation and X-ray Crystallographic Characterization of Monomeric and Dimeric Complexes $[Cu^{II}(TMPA)F]_n^{n+}$ (n = 1 or 2; TMPA = Tris[(2-pyridyl)methyl]amine)

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The copper(I) complex with tripodal tetradentate amine ligand TMPA, $[Cu^I(TMPA)CH_3CN]PF_6$ (**1**; TMPA = tris[(2-pyridyl)methyl]amine), reacts with dioxygen, resulting in breakdown of the hexafluorophosphate anion and providing two distinct fluoride Cu(II) complexes that have been crystallographically characterized. $[Cu^{II}(TMPA)F]_2(PF_6)_2$ (**2**) is a fluoride doubly bridged dimer (axial–equatorial), where each copper ion is pseudooctahedrally coordinated [$C_{36}H_{36}Cu_2F_{14}N_8P_2$, monoclinic $P2_1/n$; a = 11.649 (4), b = 12.942 (4), c = 14.654 (4) Å; β = 110.67 (2)°; Z = 4, V = 2067 (1) Å^3]. However, $[Cu^{II}(TMPA)F]PF_6\cdot CH_2Cl_2$ (**3a**) contains a trigonal-bipyramidal (TBP) coordination environment, with axial fluoride and tertiary amine ligation [$C_{19}H_{20}Cl_2CuF_7N_4P$, orthorhombic $Pcab$; a = 11.869 (2), b = 15.891 (3), c = 26.116 (6) Å; Z = 8, V = 4926 (2) Å^3]. Complex **3a** readily loses its dichloromethane to give $[Cu^{II}(TMPA)PF_6\cdot{}^1/_2H_2O$ (**3b**), which has solution properties (i.e. UV–vis, EPR) characteristic of TBP coordination. Compound **2** breaks down in solution to give the same monomeric structure as **3b**, and solution UV–vis and EPR studies indicate the **3b** structure can also be directly generated by addition of fluoride ion to $[Cu^{II}(TMPA)H_2O](ClO_4)$ (**4**).

In the last two decades, there has been a great deal of effort to synthesize low-molecular-weight complexes to model the function and/or spectroscopic features of copper-containing enzymes[1] and to explore relevant copper coordination chemistry in greater detail.[2] Fluoride ion binding to copper enzymes is of interest due to the use of F^- as a spectroscopic probe for proteins such as hemocyanin and tyrosinase and because of the known

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