formation. Such optimization may have been the selective pressure for the predominance of $n = 2$–4 γEC peptides in nature. Peptides of the $n = 1$ type (glutathione) will serve as a matrix for CdS formation, but stability is low and GSH-coated particles show facile accretion.[34] Cd(II) complexes with γEC peptides longer than $n = 4$ are predicted to be less effective in nucleating CdS crystallite formation perhaps by virtue of enhanced stability of Cd–cysteinyl thiolate clusters. The importance of sulfide in metal detoxification is highlighted by the isolation of sulfide-deficient *S. pombe* mutants that exhibit cadmium hypersensitivity.[15]

The increased stability of *S. pombe* CdS crystallites does not imply that *S. pombe* is more resistant to cadmium salts than *C. glabrata*. The yeast *C. glabrata* is highly resistant to toxicity of cadmium salts. Formation of CdS crystallites is only one cellular detoxification mechanism in this organism. The other mechanisms have not been elucidated.

The crystallites exhibit properties analogous to those of semiconductor clusters. The yeast CdS particles are quantum crystallites that luminesce and mediate electron transfer to methyl viologen. The latter two properties are attributed to the localization of excited electrons on the surface of the particles.[31] Luminescence in synthetic CdS semiconductor clusters is attributed to the recombination of a photogenerated electron and an existing hole.[28] The electronic state of the electron is not apparent in the absorption spectrum.[28] Luminescence correlates with particle size and is influenced by surface adsorbed cations. Cations are known to quenched the luminescence of synthetic colloidal CdS.[30] The effect is attributed to electron scavenging at the surface of the particles. Electrons are also scavenged by methyl viologen at the surface. Under anaerobic conditions, the reduced dye is stable against facile oxidation, but a significant back-reaction occurs that is attributed to reoxidation of the dye by trapped holes (h+) in the particle.[30] The presence of hole scavengers has been shown to inhibit this route of oxidation in some but not all studies.[35,36] Crystallites formed in vitro with γEC peptides exhibit corresponding excited electronic state properties.

The effectiveness of γEC peptides in stabilizing discrete sizes of CdS crystallites either in vivo or in vitro may enable the peptides to be used as a matrix for other types of mineralization where discrete particle size is desired. As metal–sulfide clusters are used as photosensitizing and catalytic agents,[30,37] discrete sizes of these quantum particles may yield more predictable properties. Presently, synthetic semiconductor clusters are typically coated with nonspecific organic polymers, leading to a wide spectrum of particle sizes.

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(34) Dameron, C. T.; Winge, D. R. *J. Biol. Chem.*, in press.

(35) Gratzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.

(36) Kuczynski, J.; Thomas, J. K. *Langmuir* **1985**, *1*, 158.

(37) Kuczynski, J.; Thomas, J. K. *Chem. Phys. Lett.* **1982**, *88*, 445.

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Technetium Nitrido Complexes with Amine and Thiolate Ligands: Structural Characterization of $TcN(SC_6HMe_4)_2(NHC(NMe_2)_2)_2$, a Complex with Coordinatively Bound 1,1,2,2-Tetramethylguanidine

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A methanol solution of the Tc(VI) complex $(Ph_4As)[TcNCl_4]$ is reduced in the presence of pyridine to give the orange Tc(V) complex $[TcN(OH)(py)_4](Ph_4B)$ (**1**). As in the oxo analogue $[TcO_2(py)_4](Ph_4B)$, the pyridine ligands on **1** are labile and undergo exchange with free pyridine in solution. The TcO_2^+ and $TcN(OH)^+$ cores also appear to be similar electronically, since the ^{99}Tc NMR chemical shifts for these two compounds are not significantly different. Compound **1** reacts with 2,3,5,6-tetramethylbenzenethiolate (tmbt) to give quantitative yields of the robust compound *trans*-$TcN(tmbt)_2(py)_2$ (**2**). In an attempt to prepare $[TcN(tmbt)_4]^-$, $[TcNCl_4]^-$ was allowed to react with Htmbt in the presence of the "noncoordinating" base 1,1,3,3-tetramethylguanidine (TMG). Instead of the desired tetrathiolate complex, $TcN(tmbt)_2(TMG)_2$ (**3**), a rare example of TMG coordination, was obtained. This compound shows dimer formation in fast atom bombardment spectra, and the decomposition of this species was studied by tandem mass spectrometry. The structure of **3** was confirmed by a single-crystal X-ray structure determination (crystal data: molecular formula = $C_{30}H_{52}N_7S_3Tc$, monoclinic, $a = 9.006$ (3) Å, $b = 24.815$ (3) Å, $c = 15.992$ (2) Å, $\beta = 96.57$ (2)°, space group = $P2_1/n$, $Z = 4$, final $R = 0.048$, final $R_w = 0.057$).

The nitrido and oxo groups are isoelectronic,[2] but despite the large number of oxotechnetium compounds known, few nitrido compounds were reported until recently. In 1981, Baldas et al. reported the preparation and crystallographic characterization of the first technetium nitrido complex, $TcN(S_2CNEt_2)_2$.[3] Soon after, the same authors reported the synthesis of $(Ph_4As)[TcNCl_4]$,[4] a convenient starting material for the further exploration of complexes containing the $Tc\equiv N$ bond. This complex has been shown to undergo ligand exchange and yield products in which displacement of chlorides is accompanied by a one-electron reduction of the metal. Part of the current effort in exploring technetium nitrido complexes is directed toward the preparation of the nitrido analogues of oxo compounds, which have proven useful in diagnostic nuclear medicine.[3,5]

We have recently explored the chemistry of oxotechnetium(V) complexes with sterically hindered arenethiolate ligands. Reaction of $(n\text{-}Bu_4N)[TcOCl_4]$ with 2,3,5,6-tetramethylbenzenethiolate (tmbt) yields the five -coordinate anionic species $(n\text{-}Bu_4N)[CO(tmbt)_4]$.[6,7] When the reaction is performed in the presence of

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(1) (a) Massachusetts Institute of Technology. (b) Harvard Medical School.

(2) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369.

(3) Baldas, J.; Bonnyman, J.; Pojer, P. M.; Williams, G. A.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1981**, 1798.

(4) Baldas, J.; Boas, J. F.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2395.

(5) Baldas, J.; Bonnyman, J. *Int. J. Appl. Radiat. Isot.* **1985**, *36*, 919.

(6) Davison, A.; de Vries, N.; Dewan, J. C.; Jones, A. G. *Inorg. Chim. Acta* **1986**, *120*, L15.

0020-1669/90/1329-1348$02.50/0

pyridine, a neutral trithiolate compound TcO(tmbt)$_3$(py) is formed, which proves to be a robust oxygen atom transfer catalyst. Our success in this area has led us to explore the chemistry of the technetium nitrido core with the same ligands.

Experimental Section

Caution! Technetium-99 is a weak β^- emitter (E = 0.292 MeV, $t_{1/2}$ = 2.12 × 10^5 years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[8]

Syntheses. Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Reagents and solvents were used as received unless otherwise indicated. The nitrido complexes (Ph$_4$As)[TcNCl$_4$][4] and Na[TcNCl$_4$][9] were prepared by the methods of Baldas et al., and the Htmbt was supplied by Michelle Millar.[10] ^{1}H and ^{99}Tc NMR spectra were recorded on a Varian XL-300 FTNMR spectrometer, infrared spectra on a Mattson Cygnus 100 FTIR spectrometer, and UV–visible spectra on an HP 8451A diode array spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

[TcN(OH)(py)$_4$](Ph$_4$B) (1). Pyridine (0.5 mL) was added to a solution of Na[TcNCl$_4$] (0.10 mmol) in wet MeOH (20 mL), and the color of the solution changed from orange to dark purple. Subsequent addition of Na(Ph$_4$B) (100 ng, 3 equiv) in MeOH (2 mL) caused feathery orange crystals to deposit within 1 h. Yield: 69.9 mg (94%).

Anal. Calcd for $C_{44}H_{41}BN_5OTc{\cdot}H_2O$: C, 67.44; H, 5.53; N, 8.94. Found: C, 67.27; H, 5.45; N, 8.91; Cl, trace. IR (KBr): ν(TcN) 1050 cm^{-1}. UV–vis (20:1 acetone/pyridine): λ_{max} 470 nm (ϵ 160 L mol^{-1} cm^{-1}). ^{1}H NMR (acetone-d_6, 5% py): δ 6.77 (t, 4 H, Ph$_4$B), 6.91 (t, 8 H, Ph$_4$B), 7.33 (br s, 8 H, Ph$_4$B), 7.56 (t, 8 H, py β-H), 8.06 (t, 4 H, py γ-H), 8.95 (d, 8 H, py α-H), 4.08 (s, 1 H, OH). FABMS(+) *m/z* (%), assignment: 368 (100), [TcN(OH)(py)$_3$ + H]; 447 (30), [TcN(OH)(py)$_4$ + H].

TcN(tmbt)$_2$(py)$_2$ (2). Pyridine (1 mL) was added to a solution of (n-Bu$_4$N)[TcNCl$_4$] (35 mg, 0.07 mmol) in methylene chloride (15 mL), and the reaction mixture was allowed to stir for 1 min until the color changed from orange to brown. A solution of Htmbt (63 mg, 5 equiv) in methylene chloride was added. When the mixture regained its original bright orange color, an equal volume of methanol was added and the methylene chloride was then removed under reduced pressure. Orange crystals deposited and were collected, washed with methanol, and dried in vacuo. Yield: 36.7 mg (89%).

Anal. Calcd for $C_{30}H_{36}N_3S_2Tc$: C, 59.88; H, 6.03; N, 6.98; S, 10.66. Found: C, 59.82; H, 6.00; N, 7.11; S, 10.76. IR (KBr): ν(TcN) 1055 cm^{-1}, UV–vis (CH$_2$Cl$_2$): λ_{max} 244 nm (ϵ 19000 L cm^{-1} mol^{-1}), 270 (16000), 308 (12000), 474 (900). ^{1}H NMR (CDCl$_3$): δ 1.95 (s, 6 H, CH_3ArS), 2.35 (s, 6 H, CH_3ArS), 6.42 (s, 2 H, SArH), 6.80 (br, 4 H, py β-H), 7.26 (t, 2 H, py γ-H), 8.17 (br, 4 H, α-H). FABMS(+) *m/z* (%), assignment: 775 (100), TcN(tmbt)$_4$H$_2$)$^+$; 886 (33), Tc$_2$N$_2$(tmbt)$_4$; 1044 (4), Tc$_2$N$_2$(tmbt)$_4$(py)$_2$. FABMS(−) *m/z* (%), assignment: 443 (100), TcN(tmbt)$_2$; 608 (10), TcN(tmbt)$_3$; 886 (2); 1044 (1).

TcN(tmbt)$_2$((Me$_2$N)$_2$CNH)$_2$ (3). Over a period of 10 min, 1,1,2,2-tetramethylguanidine (TMG) (250 μL, 10 equiv) was added dropwise, under a nitrogen atmosphere, to a stirring solution of (Ph$_4$As)[TcNCl$_4$] (125 mg, 0.20 mmol) and Htmbt (110 mg, 3 equiv) in methylene chloride (10 mL). After the color of the reaction mixture changed from orange to brown and back to orange, an equal volume of hexanes was added and the solvent was allowed to evaporate slowly. Yellow-orange X-ray-quality crystals grew from the resulting oil. They were collected, washed with hexanes, and dried in vacuo. Yield: 18.8 mg (14%).

IR (KBr): ν(TcN) 1057, ν(NH) 3311 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.9–3.1 (m, 36 H, ArCH_3 and NHC(N(CH_3)$_2$)$_2$), 3.87 (s, 2 H, NH), 6.72 (s, 2 H, ArH). FABMS(+) *m/z* (%), assignment: 342 (100), Tc$_2$N$_2$(TMG)H; 393 (35), Tc$_2$N$_2$(tmbt)H$_2$; 508 (12), Tc$_2$N$_2$(tmbt)(TMG)H$_2$; 558 (18), Tc$_2$N$_2$(tmbt)$_2$H$_2$; 673 (20), Tc$_2$N$_2$(tmbt)$_2$(TMG)H; 887 (1), Tc$_2$N$_2$(tmbt)$_4$H; 952 (1), Tc$_2$N$_2$(tmbt)$_3$(TMG)$_2$H; 1002 (1), Tc$_2$N$_2$(tmbt)$_4$(TMG)H; 1116 (1)8 Tc$_2$N$_2$(tmbt)$_4$(TMG)$_2$H. FABMS(−) *m/z* (%), assignment: 443 (100), TcN(tmbt)$_2$; 608 (7), TcN(tmbt)$_3$; 886 (2), Tc$_2$N$_2$(tmbt)$_4$.

Mass Spectrometry. Fast atom bombardment mass spectra were measured on samples dissolved in a 1:1 methylene chloride/3-nitrobenzyl alcohol or 1:1 methylene chloride/triethanol amine by using a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun operating at an accelerating voltage of 8 kV. FABM/MS was carried out by using all four sectors of a JEOL HX110/HX110 tandem high-resolution spectrometer, an instrument of E$_1$B$_1$E$_2$B$_2$ configuration. Collision-induced decomposition took place in the third field-free region; thus both MS-1 (E$_1$B$_1$) and MS-2 (E$_2$B$_2$) were operated as double-focusing instruments using −10-kV accelerating potential. The collision cell was operated at −3 kV so that the collision energy was 7 kV. Helium was used as the collision gas at a pressure sufficient to reduce the precursor ion signal by 50%–80%. FABMS/MS spectra (linked scans of MS-2 at constant B/E ratio) were recorded as profiles during 2-min scans with 30-Hz filtering. Resolution in both MS-1 and MS-2 was 1:1000. MS-2 was calibrated with a solution of CsI in glycerol in the negative-ion mode.[11]

Table I. X-ray Data for the Structure Determination of **3**

$TcS_2N_6C_{30}H_{52}$	space group = $P2_1/n$
fw = 675.83	T = 22 °C
a = 9.006 (3) Å	λ = 0.710 69 Å,
b = 24.815 (3) Å	graphite monochromated
c = 15.992 (3) Å	ρ_{calcd} = 1.879 g/cm^3,
β = 96.57 (2)°	ρ_{exp} = 1.84 g/cm^3
V = 3574.0 (3) Å^3	μ = 6.79 cm^{-1}
Z = 4	transm coeff = 1.07–0.77
	R = 0.048
	R_w = 0.057

Table II. Atomic Positional Parameters for **3**

atom	x	y	z
Tc1	0.11486 (6)	0.10878 (3)	0.31557 (4)
S1	0.1622 (2)	0.05856 (9)	0.1932 (1)
S2	−0.0663 (2)	0.17058 (8)	0.3566 (1)
N1	0.2457 (6)	0.0986 (2)	0.3918 (4)
N3	−0.0428 (6)	0.0486 (2)	0.3404 (3)
N4	0.1951 (6)	0.1733 (2)	0.2455 (4)
N32	−0.1490 (6)	0.0712 (2)	0.4632 (4)
N33	−0.2874 (6)	0.0232 (2)	0.3585 (4)
N42	0.2519 (7)	0.2022 (3)	0.1136 (4)
N43	0.4252 (6)	0.1538 (3)	0.2000 (4)
C11	0.0606 (8)	−0.0027 (3)	0.1810 (4)
C12	0.1116 (8)	−0.0480 (3)	0.2272 (5)
C13	0.035 (1)	−0.0973 (3)	0.2154 (5)
C14	−0.089 (1)	−0.0985 (4)	0.1574 (6)
C15	−0.142 (1)	−0.0551 (5)	0.1101 (5)
C16	−0.0669 (8)	−0.0061 (4)	0.1212 (5)
C17	0.249 (1)	−0.0450 (4)	0.2892 (5)
C18	0.082 (1)	−0.1480 (4)	0.2632 (7)
C19	−0.282 (1)	−0.0607 (6)	0.0479 (6)
C21	−0.0240 (8)	0.2398 (3)	0.3347 (4)
C22	−0.1080 (8)	0.2655 (3)	0.2662 (5)
C23	−0.082 (1)	0.3197 (4)	0.2523 (5)
C24	0.020 (1)	0.3463 (4)	0.3079 (7)
C25	0.103 (1)	0.3220 (4)	0.3736 (6)
C26	0.0841 (8)	0.2680 (4)	0.3870 (5)
C27	−0.222 (1)	0.2351 (3)	0.2098 (5)
C28	−0.166 (1)	0.3491 (4)	0.1778 (7)
C29	0.215 (1)	0.3558 (5)	0.4306 (7)
C31	−0.1572 (8)	0.0483 (3)	0.3861 (4)
C32	−0.008 (1)	0.0774 (4)	0.5158 (5)
C33	−0.2725 (9)	0.1025 (4)	0.4893 (4)
C34	−0.3792 (9)	−0.0031 (4)	0.4153 (5)
C35	−0.3205 (9)	0.0089 (4)	0.2700 (5)
C41	0.2866 (8)	0.1764 (3)	0.1876 (5)
C42	0.096 (1)	0.2118 (5)	0.0828 (6)
C43	0.0360 (1)	0.2335 (4)	0.0736 (5)
C44	0.4901 (9)	0.1258 (4)	0.1334 (5)
C45	0.4904 (8)	0.1408 (4)	0.2849 (5)
C110	−0.123 (1)	0.0416 (5)	0.0712 (5)
C210	0.178 (1)	0.2390 (4)	0.4565 (5)

Single-Crystal X-ray Crystal Structure Determination of 3. Orange prisms were grown by slow evaporation of a solution of **3** in methylene chloride/hexane. Crystal data are presented in Table I, and atomic positional parameters, in Table II. A monoclinic crystal of approximate dimensions 0.4 × 0.4 × 0.6 mm was chosen, and the space group was determined unambiguously to be $P2_1/n$. A total of 8806 refections (of

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(7) de Vries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3728.

(8) Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B. V.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988.

(9) Baldas, J.; Bonnyman, J.; Williams, G. A. *Inorg. Chem.* **1986**, *25*, 150.

(10) Department of Chemistry, SUNY, Stony Brook, NY. Thiols were prepared according to: Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533.

(11) Sato, K.; Asada, T.; Kunihiro, F.; Kammei, Y.; Kubota, E.; Costello, C. E.; Martin, S. A.; Scoble, H. A.; Biemann, K. *Anal. Chem.* **1987**, *59*, 1652.

which 8307 were unique, $R_{\mathrm{int}} = 0.012$) were collected on an Enraf-Nonius CAD-4 diffractometer ($2\theta_{\mathrm{max}} = 55°$; octants collected $+h,+k,\pm l$; scan mode ω–2θ). Solution and refinement of the structure were carried out by using SHELX-76 and the TEXSAN programs of the Molecular Structure Corp. Neutral-atom scattering factors[12] were used throughout, and no extinction effects were observed. The structure was solved by using Patterson methods, an absorption correction was applied by using DIFABS, and all non-hydrogen atoms were refined anisotropically. At least one hydrogen atom on each methyl group and both imine hydrogen atoms, H31 and H41, were found in the difference map, and the others were refined from their calculated positions.

Results and Discussion

The technetium nitrido anion $[TcNCl_4]^-$ is reversibly hydrolyzed in aqueous base to a purple gelatinous material that retains the $Tc{\equiv}N$ group.[9] The reaction of $Na[TcNCl_4]$ with pyridine in wet methanol initially appears to proceed identically, but upon addition of $Na(Ph_4B)$, the tetrapyridine complex $[TcN(OH)(py)_4](Ph_4B)$ (**1**) is precipitated as an orange crystalline material. Isolation of a similar complex, $[TcN(py)_4]Cl_2$, upon reaction of $(n\text{-}Bu_4N)[TcNCl_4]$ with pyridine in refluxing acetone was recently reported by Abram et al.[13] Comparison of the spectroscopic data (^1H NMR, IR, and UV-visible) and elemental analyses confirms that these are similar but distinct species. Consistent with the above assignments, the $Tc{\equiv}N$ stretch found at 1070 cm^{-1} in the IR spectrum of $[TcN(py)_4]Cl_2$ is lowered to 1055 cm^{-1} upon coordination of hydroxide, presumably trans to the nitrido group. This hydroxide ligand appears to be weakly bound, since the molecular ion is not observed in the FABMS(+) spectrum, and the peak at highest mass corresponds to $[TcN(py)_4]^+$. Interestingly, Abram et al. commented that, by analogy to oxotechnetium systems, this complex would in fact be expected to bind a sixth ligand.[13]

The cation $[TcO_2(py)_4]^+$ [14,15] is the oxo analogue of the cation of **1**, and the two species share many properties. Most notable is that the pyridine ligands on both complexes are labile and that these compounds decompose in solutions that do not contain excess pyridine. ^1H NMR studies indicate that compound **1** equilibrates with free pyridine-d_5 in less than 1 min. The exchange is slow on the NMR time scale (~3 ms), however, as distinct ^1H signals are observed for the pyridine ligands on the complex and free pyridine. The same properties have been observed for the oxo complex.[16] Technetium-99 NMR spectroscopy, a technique that is very sensitive to the electronic environment of the metal,[17] also shows the similarity between these two complexes. Chemical shifts range over 8000 ppm, and distinct regions have been observed for the shifts of similar ^{99}Tc complexes.[18,19] Although Tc(V) oxo and dioxo species exhibit an especially wide range of shifts from 810 to ~5500 ppm, the similarity between compound **1** and $[TcO_2(py)_4]^+$ is further emphasized by the relatively small difference (175 ppm) in their chemical shifts.[18]

Reaction of either isolated compound **1** or $[TcN(OH)(py)_4]^+$ prepared in situ with an excess of 2,3,5,6-tetramethylbenzenethiol (Htmbt) yields solely the robust orange compound *trans*-$TcN(tmbt)_2(py)_2$ (**2**). In contrast, $[TcOCl_4]^-$ reacts with Htmbt and pyridine to give the tris(thiolate) complex $TcO(tmbt)_3(py)$.[7] In both systems the neutral product prevails. The ^1H NMR spectrum of **2** contains two sharp and clearly distinct signals arising from the methyl groups on the arenethiolate rings. Excluding coincidental overlap of resonances, only a transoid arrangement of ligands around the base of a square pyramid could give rise to such high symmetry. Thus, compound **2** not only shares the same coordination sphere as the previously reported complex bis(8-quinolinethiolato)nitridotechnetium(V)[8] but also appears to have the same geometry, including the mutually trans arrangement of the sulfur and nitrogen donor atoms. Another interesting feature of the ^1H NMR spectrum is that the two pyridine ligands give rise to only three signals and must be equivalent and rotating freely.

Table III. Selected Bond Distances and Angles for **3**

	Bond Lengths (Å)		
Tc1–N1	1.615 (6)	Tc1–S1	2.398 (2)
Tc1–N3	2.130 (6)	Tc1–S2	2.385 (2)
Tc1–N4	2.128 (6)		
	Bond Angles (deg)		
N1–Tc1–N3	101.2 (3)	N4–Tc1–S2	86.9 (2)
N1–Tc1–N4	104.6 (3)	N3–Tc1–N4	154.2 (2)
N1–Tc1–S1	110.6 (2)	S1–Tc1–S2	138.54 (8)
N1–Tc1–S2	110.8 (2)	C11–S1–Tc1	113.5 (2)
N3–Tc1–S1	88.4 (2)	C21–S2–Tc1	113.1 (2)
N3–Tc1–S2	84.7 (2)	C31–N3–Tc1	132.9 (5)
N4–Tc1–S1	81.9 (2)	C41–N4–Tc1	134.1 (5)

Although it has not been isolated from the reaction of $[TcNCl_4]^-$ with tmbt and pyridine, the tetrathiolate species $[TcN(tmbt)_4]^-$ has been observed in both the positive- and negative-mode fast atom bombardment mass spectra of **2** along with the trithiolate nitrido species and strong and numerous dimer peaks. Dimer formation in the FAB matrix is often observed, and the dimers may have fragmented to form new species, $[TcN(tmbt)_3]^-$ and $[TcN(tmbt)_4]^-$, in which the ligands of the original monomers have been exchanged. Alternatively, they may be present as impurities in the sample. In either case, the presence of these species and the fact that the tetrathiolate oxotechnetium analogue is easily formed and quite stable encouraged us to attempt the preparation of $[TcN(tmbt)_4]^{2-}$.

The base 1,1,3,3-tetramethylguanidine (TMG) is an excellent proton sponge because the positive charge resulting from protonation can be delocalized throughout the molecule. The lone pair on the bare nitrogen is thus diffuse and lacks directionality. This combined with the steric demands of TMG generally prevents it from acting as either a nucleophile or a ligand, and TMG has found widespread application in both organic and inorganic syntheses as a nonnucleophilic and noncoordinating base. The reaction of $[TcNCl_4]^-$ with Htmbt using TMG as the proton sponge should favor the formation of the tetrathiolate nitrido species that was observed in the mass spectrum of **2**. However, the product of this reaction was in fact $TcN(tmbt)_2(TMG)_2$ (**3**), in which two TMG ligands are bound to the metal. ^1H NMR data suggest that the amine and thiolate ligands are, as in compound **2**, bound in a transoid fashion across the base of a square pyramid.

X-ray Structure Determination of $TcN(tmbt)_2(TMG)_2$. A suitable crystal of **3** was chosen and subjected to a single-crystal X-ray structure determination. The compound proved indeed to have two covalently bound TMG ligands. The ORTEP diagram of **3** is shown in Figure 1, and selected bond lengths and angles are presented in Table III. The compound has square-pyramidal geometry with the nitrido group in the apical position and the thiolates and TMG ligands alternating around the base. In the previously reported complex, $TcN(8\text{-quinolinethiolato})_2$, the base of the square pyramid is highly distorted with the sulfur atoms bent down away from the apical nitrido at an angle of 112.19 (2)° and the nitrogen atoms making a smaller angle of 98.8 (6)°. A similar effect is seen in compound **3**, although the distortion is not as pronounced. The N1–Tc–S1 and N1–Tc–S2 angles are 110.6 (2) and 110.8 (2)°, respectively, while the N1–Tc–N3 and N1–Tc–N4 angles are 101.2 (3) and 104.6 (3)°. Although the TMG ligands might be expected to be loosely bound, the Tc–N31 and Tc–N41 distances, 2.128 (6) and 2.130 (6) Å, fall well within the range of expected values for a Tc(V)–N bond (2.002 (2)[20]–2.197 (3) Å[21]) are are slightly shorter than that found for

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[12] *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

[13] Abram, U.; Abram, S.; Spies, H.; Kirmse, R.; Stach, J.; Köhler, K. *Z. Anorg. Allg. Chem.* **1987**, *544*, 167.

[14] Kusina, A. F.; Oblova, A. A.; Spitsyn, V. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1972**, *17*, 1377.

[15] Trop, H. S. Ph.D. Thesis, Massachusetts Institute of Technology, 1979; p 64.

[16] Pearlstein, R. M.; Davison, A. Unpublished results.

[17] Kronauge, J. F.; Pearlstein, R. M.; Thornback, J. R.; Jones, A. G.; Davison, A. *J. Nucl. Med.* **1987**, *28*, 602; Abstract 187.

[18] O'Connell, L. A.; Pearlstein, R. M.; Davison, A.; Thornback, J. R.; Kronauge, J. F.; Jones, A. G. *Inorg. Chim. Acta* **1989**, *161*, 39.

[19] Davison, A.; Kronauge, J. F.; Jones, A. G.; Pearlstein, R. M.; Thornback, J. R. *Inorg. Chem.* **1988**, *27*, 3245.

Table IV. FABMS(−) and Collision-Induced Decomposition FABMS/MS(−) Data for **3**[a]

ion	m/z (%)	ion	m/z (%)	ion	m/z (%)
		Precursor			
$TcN(tmbt)_2^-$	443 (100)	$TcN(tmbt)_3^-$	608 (7)	$Tc_2N_2(tmbt)_4^-$	886 (2)
		Products			
$TcNS(tmbt)^-$	309 (93)	$[TcN(tmbt)_2 - H]^-$	442 (95)	$Tc_2N_2S(tmbt)_3^-$	753 (95)
$[TcN(tmbt) - H]^-$	277 (25)	$TcNS(tmbt)^-$	309 (32)	$Tc_2N_2(tmbt)_3^-$	721 (60)
$TcNS_2^-$	177 (58)	$TcNS_2^-$	177 (10)	$Tc_2N_2S_2(tmbt)_2^-$	620 (24)
				$Tc_2N_2S(tmbt)_2^-$	588 (20)
				$Tc_2N_2S_3(tmbt)^-$	487 (12)
				$Tc_2N_2S_2^-$	290 (5)

[a] Except for minor variation in the relative abundances, the CIDMS/MS spectra of these ions in the spectrum of **2** were identical.

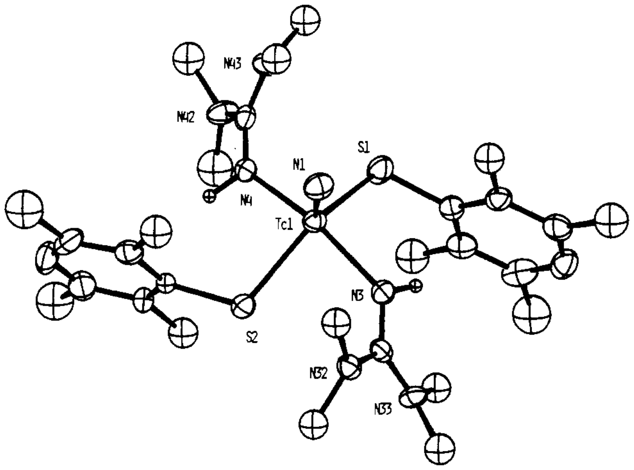
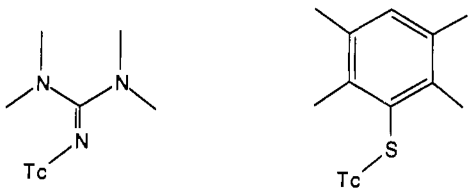


Figure 1. ORTEP diagram of $TcN(tmbt)_2(TMG)_2$ showing the atom-labeling scheme and 30% probability ellipsoids. With the exception of H31 and H41, the hydrogen atoms have been omitted for clarity.

TcN(8-quinolinethiolato) (2.135 (2) Å).[9] The Tc–S bond lengths (2.398 (2) and 2.385 (2) Å), however, are long as compared to the values found for other structurally characterized Tc(V) oxo complexes with thiolate ligands (2.283 (1)[7]–2.319 (3)[22] Å) and also to that seen in $TcN(8\text{-quinolinethiolato})_2$ (2.3559 (7) Å). The Tc≡N distance (1.615 (6) Å), too, is lengthened from that found in the Tc(VI) starting material (1.581 (5) Å),[4] which is consistent with the lowering of the IR stretching frequency from 1076 cm^{-1} in the Tc(VI) tetrachloride complex to 1057 cm^{-1}.

Compound **3** is the first crystallographically characterized transition-metal complex of TMG. The only other example of a structurally characterized compound containing covalently bound TMG is a cyclic enediol λ^5-phosphazole (CEP–TMG) in which TMG has been crystallographically determined to be found to phosphorus.[23,24] This compound is the product of a rare example of nucleophilic attack of TMG on 4,5-dimethyl-2-oxo-1,3,2-dioxaphosphole. Comparison of this structure with that of the technetium compound **3** shows little difference in the bond distances and angles of the TMG group with one exception. In the λ^5-phosphazole structure, the bound nitrogen has been deprotonated whereas in **3** the imine protons on both ligands were found in the difference Fourier map, confirming the oxidation state as +5. The presence of the protons is further substantiated by the infrared and ^{1}H NMR spectra of compound **3**. In the IR spectrum, the NH stretch is observed as a sharp band at 3311 cm^{-1} and there is also a ^{1}H NMR signal of integration 2H at 3.87 ppm which can be assigned to the imine protons. Deprotonation in the CEP–TMG compound is reflected by the smaller P–N–C bond angle (128.0 (2)°) as compared to the Tc–N–C angles of **3**, which have the average value of 133.5 (5)°. The diminished angle found in CEP–TMG can be attributed to the larger size of a lone pair as compared to a hydrogen atom.



TMG tmbt

Figure 2. Schematic representations of the TMG and tmbt ligands.

Tandem Mass Spectrometry. The question remains as to the origin of the tetrathiolate material $[TcN(tmbt)_4]^-$ observed in the mass spectra of the bis(pyridine) compound **2**. In an attempt to trace its formation, tandem mass spectral studies were performed on **2** and also on **3** for comparative purposes. The FABMS(+) spectrum of **3** shows many dimeric species, most of which retain TMG, but the FABMS(−) spectrum is nearly identical with that of the bis(pyridine) compound **2**. The only notable exception is a small peak for **2** at m/z 1044 corresponding to $(Tc_2N_2(tmbt)_4(py)_2)$, whose analogue in the spectrum of **3** occurs at 1116 $(Tc_2N_2(tmbt)_4(TMG)_2)$. Collision-induced decomposition (CID) of the negative ions formed by both compounds leads to a series of FABMS/MS(−) products (Table IV) in which both aryl rings and entire ligands are lost. The precursor at m/z 886, which is assigned the dimeric formula $[Tc_2N_2(tmbt)_4]^-$, decomposes to give only species in which the dimeric core remains intact while ligands and aryl rings are lost. This indicates that the dimeric units are closely associated and that the monomeric tetra- and trithiolate species are not products arising from their decomposition. The CID spectra obtained for the same ions in the spectrum of **2** and **3** were virtually identical. In addition, the CID spectrum of the /z 1044 ion in the spectrum of **2** gave products at m/z 886, 608, and 433 but, as before, no $TcN(tmbt)_4$ of $TcN(tmbt)_3$ species.

Comments. Coordination of TMG is extremely rare. In fact Drago and Longhi reported the only examples of transition-metal complexes of TMG in 1965. This series comprised homoleptic complexes of a number of late transition metals.[25] The chloride salts of metals were dehydrated and allowed to react with TMG in a noncoordinating solvent. The technetium system presented here is unprecedented in that the reaction can occur in the presence of an excess of another good ligand, tmbt. Furthermore, although nominally the structures of TMG and tmbt are quite similar (Figure 2), the shorter metal-to-ligand and X–C (X = S, N) bond distances in TMG pull the ligand in closer to the metal, providing more steric overcrowding at the metal than at the thiolate.

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(20) Jurrisson, S.; Linday, K. F.; Dancey, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 227.

(21) Wilcox, B. E.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 2962.

(22) DePamphilis, B. V.; Jones, A. G.; Davison, A.; Davis, M. D. *J. Labelled Compd. Radiopharm.* **1979**, *16*, 26.

(23) Ramirez, F.; Ricci, J. S., Jr.; Okazaki, H.; Marecek, J. F.; Lewy, M. *Phosphorus Sulfur* **1984**, *20*, 279.

(24) Ramirez, F.; Okazaki, H.; Maracek, J. F. *Synthesis* **1975**, 638.

(25) Longhi, R.; Drago, R. S. *Inorg. Chem.* **1965**, *4*, 11.

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Supplementary Material Available: An ORTEP diagram of 3 and Tables SI–SVI, listing respectively complete X-ray data, hydrogen atom positional parameters, intramolecular atomic distances, intramolecular bond angles, least-squares planes, and anisotropic thermal parameters for 3 (11 pages); Table SVII, listing calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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Molecular and Crystal Structures of a "Platinblau" Analogue, Bis(μ-acetamido)dichlorobis(dimethyl sulfoxide)diplatinum(II), and of *cis*-(Acetonitrile)dichloro(dimethyl sulfoxide)platinum(II)

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The reaction of K[Pt(DMSO)Cl_3] with acetonitrile in aqueous solution produces *cis*-Pt(DMSO)(CH_3CN)Cl_2 after a few days, but if the compound is allowed to stay in solution, a green compound can be isolated after several weeks. The green species can also be synthesized more rapidly by adjusting the pH of the solution to about 8.0 with NaOH. The crystal structures of the two compounds were determined by X-ray diffraction. *cis*-Pt(DMSO)(CH_3CN)Cl_2 is monoclinic with space group $P2_1/n$, $a = 9.566$ (4) Å, $b = 9.996$ (4) Å, $c = 9.995$ (3) Å, $\beta = 93.18°$, and $Z = 4$. The structure was refined to $R = 0.036$ and R_w 0.030. The Pt–Cl(2) bond (2.282 (2) Å) in trans position to the CH_3CN is shorter than the other Pt–Cl(1) bond (2.324 (2) Å). The Pt–S bond is normal (2.225 (2) Å) while the Pt–N bond is also short (1.976 (7) Å). The green compound was found to be a dinuclear species bis(μ-acetamido)dichlorobis(dimethyl sulfoxide)diplatinum(II). The crystals are triclinic, space group $P\bar{1}$ with $a = 8.944$ (6) Å, $b = 10.228$ (7) Å, $c = 11.180$ (10) Å, $\alpha = 83.31$ (7)°, $\beta = 66.73$ (6)°, $\gamma = 68.06$ (5)°, and $Z = 2$, and the structure was refined to $R = 0.027$ and $R_w = 0.035$. The acetamido-bridged dimer is the head-to-tail isomer with Pt···Pt distance = 3.008 (0.3) Å. The Pt–N bonds (2.011 (6) and 2.017 (6) Å) are in cis position to the DMSO ligands while the Pt–O bonds (2.064 (5) and 2.039 (5) Å) are trans to DMSO. The Pt–S bonds (2.185 (2) and 2.198 (2) Å) are slightly shorter than normal. The acetamido ligands are planar. The dihedral angle between the two square-planar Pt planes is 137.1°. This compound is believed to be an analogue of "platinblau" which probably contains bridging acetamido bidentate ligands.

Introduction

Yellow *cis*-Pt(CH_3CN)$_2$$Cl_2$ has been known for a long time,[1] and its cis configuration has been confirmed a few years ago.[2] When it is treated with aqueous silver sulfate or nitrate and the resulting solution left to stand in air, an intense blue color is formed. "Platinblau" or platinum blue was the name originally assigned to the blue compound formed.[3] It was suggested that "platinblau" contained deprotonated acetamide anions bound to platinum(II), the acetamide ligand being obtained by reaction of water with coordinated acetonitrile. The empirical composition was found to be Pt(CH_3CONH_2)$_2$·H_2O. The infrared spectrum has shown an absorption band at 1623 cm^{-1}, which was assigned to a carbonyl stretching vibration. But attempts to obtain "platinblau" by direct combination of platinum(II) with acetamide were not successful. It has been assigned a variety of monomeric and polymeric structures mostly of platinum(II). Chernyaev and his co-workers[4] suggested the presence of chelate acetamido ligands, but later, without presenting any evidence, they suggested a linear structure containing the unit H_2O–Pt–Pt–OH_2.[5] One structure involving diazocyclobutadiene as a ligand was also suggested in 1959.[6] In 1964, Gillard and Wilkinson[7] argued that the chemical and spectroscopic evidence best fitted a polymeric structure involving acetamido bridges, with the water molecules hydrogen-bonded within the crystal. Brown, Burbank, and Robin[8] purified the blue compound and on the basis of a new elemental analysis and their results on a blue trimethylacetamide complex suggested a new formulation that could be written as a tetravalent complex with two hydroxo ligands $Pt^{IV}(CH_3CONH)_2(OH)_2$.

More recently, "platinum blues" have been obtained from the reaction of cisplatin, (*cis*-Pt(NH_3)Cl_2) with pyrimidines, especially uracil derivatives.[9] Cisplatin is a good antitumor agent, and it has been suggested that "platinum blues", which also have good antitumor properties, might be promising as second-generation platinum antitumor drugs. But these compounds have shown to be difficult to characterize. *cis*-Diammineplatinum pyrimidine blues were suggested to be amorphous polymers of varying chain lengths.[9,10] Lippard et al. have prepared several of these compounds with α-pyridone and uracil derivatives. Three such platinum blues were characterized crystallographically.[11,12] These were found to be tetranuclear mixed-valence platinum(2.25) compounds with bridging α-pyridonate or 1-methyluracilate lig-

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(1) Hoffmann, K. A.; Bugge, G. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1772.

(2) Rochon, F. D.; Melanson, R.; Howard-Lock, H. E.; Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1984**, *62*, 860.

(3) Hoffmann, K. A.; Bugge, G. *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 312.

(4) Chernyaev, I. I.; Nazarova, L. A. *Izv. Sekt. Platiny Drugikh Blagorodn. Met., Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR.* **1951**, *26*, 101. Barkovskii, V. F.; Kul'berg, L. M. *Ibid.* **1954**, *28*, 235.

(5) Chernyaev, I. I.; Shenderetskaya, E. V.; Nazarova, L. A.; Antsyshkina, A. S. *Proceedings of the 7th International Conference on Coordination Chemistry*; Stockholm, 1962; p 260.

(6) Orgel, L. E. *International Conference on Coordination Chemistry*; Special Publication 13; The Chemical Society: London, 1959; p 96.

(7) Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2835.

(8) Brown, D. B.; Burbank, R. D.; Robin, M. B. *J. Am. Chem. Soc.* **1969**, *91*, 2895.

(9) Davidson, J. P.; Faber, P. J.; Fischer, R. G., Jr.; Mansy, S.; Peresie, H. J.; Rosenberg, B.; VanCamp, L. *Cancer Chemother. Rep.* **1975**, *59*, 287.

(10) (a) Lippert, B. *J. Clin. Hematol. Oncol.* **1977**, *7*, 26. (b) Thompson, A. J.; Roos, I. A. G.; Graham, R. D. *J. Clin. Hematol. Oncol.* **1977**, *7*, 242. (c) Flynn, C. M., Jr.; Viswanathan, T. S.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1977**, *39*, 437. (d) Macfarlane, R. D.; Torgenson, D. F. *Science* **1976**, *191*, 920.

(11) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827.

(12) O'Halloran, T. V.; Mascharak, P. K.; Williams, I. D.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 1261.

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