that for **3**? The unsymmetrical nature of the ligand backbone in **2** lowers the symmetry of the complex from the C_{2v} observed in the other structure. This means that the angle α is slightly different for each copper center. Projecting the Cu and donor atoms on a plane, in a manner similar to that used by Nishida et al.,[13] we have evaluated α for **2**. An average value of α (0.6 ± 0.2°) used (see Table IV) in our calculations is much closer to the value reported for **3** and gives a value of S(a–s) that correlates very well with $-2J$ (supplementary material).

Even though the overlap integrals evaluated by using data from Jaffe[25] and Kuroda[26] are rough, the fact that α and S(a–s) are quite similar for **2** and **3** appears to correlate nicely with the fact that $-2J$ for **2** and **3** are also quite close. These data suggest that the pyrazolate bridge exerts conflicting influences on the magnetic exchange in the systems. On the one hand, the energy spacing of the pyrazaolate HOMO's indicates that pyrazolate and alkoxide function in a countercomplementary fashion with respect to the exchange process. On the other hand, since the antisymmetric MO's overlap is more effective (note S(a–s) is positive for **1–3**), this overlap factor competes with the energy factor causing the pyrazolate to act in a complementary fashion with respect to the alkoxide ion. Although the precise contribution of each of the bridging species to the magnitude of the exchange interaction was not determined in this work, it appears that an unfavorable energy factor that attenuates magnetic exchange is increasingly offset by a favorable overlap factor in complexes **1–3**.

Summary

A new pyrazolate-bridged binuclear copper(II) complex (**2**) has been synthesized with the asymmetric ligand **4**. The crystal structure of **2** is isostructural with that of **1** and **3**. The magnetic properties of **2** have been evaluated and compared with results reported previously for **1** and **3**. The pyrazolate bridge in **2** appears to participate in a complementary fashion with the alkoxide bridge to enhance the strength of the antiferromagnetic exchange interaction.

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Supplementary Material Available: Tables containing a complete listing of bond lengths and bond angles, positional parameters for hydrogens and their esd's, anisotropic thermal parameters for all non-hydrogen atoms, torsion angles, least-squares planes, and magnetic data and a figure showing the correlation of $-2J$ and S(a–s) for compounds **1–3** (16 pages); a listing of F_o and F_c (10 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

Synthesis and Characterization of a Technetium(III) Nitrosyl Compound: Tc(NO)(Cl)(SC$_{10}$H$_{13}$)$_3$

Nadine de Vries,[†] Jessica Cook,[†] Alan Davison,*[,†] Terrence Nicholson,[‡] and Alun G. Jones[‡]

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Upon the reaction of (*n*-Bu$_4$N)[Tc(NO)Cl$_4$] with 2,3,5,6-tetramethylbenzenethiol, the neutral compound Tc(NO)(Cl)(tmbt)$_3$ is obtained. The infrared spectrum shows a band at 1798 cm^{-1} from the linear nitrosyl group, establishing the metal oxidation state of +3. ^{1}H NMR data indicate that this diamagnetic compound is analogous to a series of trigonal-bipyramidal, 14-electron compounds in which the thiolate ligands are bound in the equatorial plane and the remaining two ligands sit in the axial sites. The X-ray crystal structure of Tc(NO)Cl(tmbt)$_3$ confirms this ligand disposition with the thiolates adopting the "two-up-one-down" conformation. Crystal data for C$_{30}$H$_{39}$NOS$_3$ClTc: monoclinic space group $C2/c$, a = 24.420 (5) Å, b = 14.701 (4) Å, c = 17.500 (4) Å, β = 93.50 (2)°, V = 6271 (5) Å^3 to give Z = 8 for D_{calc} = 1.394 g/cm^3; structure solution based on 7457 reflections converged at R = 0.056, R_w = 0.067.

Introduction

Although the preparation of the first technetium nitrosyl compound was reported in 1963,[1] it was only identified as such 12 years later[2] and, even now, few technetium nitrosyl compounds are known. The isolation of [Tc(NO)Br$_4$]$^-$ has been reported,[3] as well as a limited number of Tc(I) and Tc(II) complexes with nitrosyl groups and various coligands.[4-6] Recently, Thornback et al. published a convenient, high-yield synthesis of (*n*-Bu$_4$N)[Tc(NO)Cl$_4$],[7] which has prompted renewed interest in the technetium nitrosyl core.

We have shown elsewhere[8] the tendency of the ligand 2,3,5,6-tetramethylbenzenethiolate (tmbt) to stabilize technetium(III) complexes. The planar thiolate core Tc(tmbt)$_3$ binds two of a number of different π-accepting ligands (MeCN, *i*-PrNC, CO, py, PEt$_3$) to form five-coordinate, trigonal-bipyramidal compounds. The incorporation of the NO$^+$ group as a π-accepting ligand into such Tc(III) centers is described herein.

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.[9]

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Reagents and solvents were used as received unless otherwise indicated. The nitrosyl complex (*n*-Bu$_4$N)[Tc(NO)Cl$_4$] was

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[†] Massachusetts Institute of Technology.

[‡] Harvard Medical School and Brigham and Women's Hospital.

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prepared by the method of Thornback et al.,[7] and the 2,3,5,6-tetramethylbenzenethiol (Htmbt) was supplied by Michelle Millar.[10] The disulfide $(tmbt)_2$ was prepared by reaction of the thiol with iodine.[11] The ^1H NMR spectrum was recorded on a Varian XL-300 MHz NMR spectrometer, the infrared spectrum on a Mattson Cygnus 100 FTIR spectrometer, and the UV-visible spectrum on an HP 8451A diode-array spectrophotometer. The fast-atom-bombardment mass spectrum was measured on a sample dissolved in a 3-nitrobenzyl alcohol matrix by using a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerating voltage of 8 kV. The FAB gun produced a beam of 6–8-keV xenon neutrals. The elemental analysis was performed by Atlantic Microlab, Norcross, GA.

Preparation of $Tc(NO)(Cl)(tmbt)_3$. The following reaction was performed under a nitrogen atmosphere. To a 50-mL round-bottomed flask containing $(n\text{-}Bu_4N)[Tc(NO)Cl_4]$ (174 mg, 0.339 mmol) and 15 mL of CH_2Cl_2 were added $(tmbt)_2$ (90 mg, 0.5 equiv) and Htmbt (250 mg, 4.5 equiv). The green color of the solution deepened and the turned dark brown upon the addition of 30 μL of 1,1,2,2-tetramethylguanidine. Addition of MeOH (10 mL) caused a final color change to orange, and a solid precipitated upon evaporation of most of the solvent. The orange microcrystalline product was collected and dried in vacuo. Yield: 132 mg, 59%.

Anal. Calcd for $C_{30}H_{39}ClONS_3Tc$: C, 54.58; H, 5.95; Cl, 5.40; N, 2.12; S, 14.57. Found: C, 54.41; H, 6.08; Cl, 5.61; N, 2.16; S, 14.81. IR (KBr): ν(NO) 1798 cm^{-1}. UV-visible (CH_2Cl_2): λ_{max} 268 nm (ϵ 9800 L cm^{-1} mol^{-1}), 334 (7900), 410 (18 000). ^1H NMR (300 MHz; solvent $CDCl_3$, standard Me_4Si): δ_H 2.10–2.46 (36 H, m, $ArCH_3$), 6.95 (2 H, s, Ar *H*), 7.07 (1 H, s, Ar *H*). FABMS(+): *m/z* 660 (5%, M + H), 624 (98, M − Cl), 494 (100, M − tmbt). FABMS(−): *m/z* 659 (100%, M), 592 (30, M − Cl − NO), 459 (12, M − Cl − tmbt), 328 (7, M − 2tmbt − H).

Crystallography. A dark red-orange prismatic crystal of $Tc(NO)Cl(tmbt)_3$ was selected from a sample recrystallized from a 1:1 methylene chloride–methanol mixture that was allowed to slowly evaporate under air. The crystal selected measured 0.2 × 0.3 × 0.5 mm. The diffractometer employed was an Enraf-Nonius CAD-4. The scan mode used was ω–2θ with a maximum 2θ of 54.9°. The quadrants collected were $h, k \pm l$. The reflections collected were hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, giving a total of 7633 reflections. Of those, 7457 were unique and 3712 reflections of $I > 3\sigma$ were used in the final structure refinement. The technetium atom was located by using direct methods. Neutral scattering factors were used throughout the analysis. Extinction effects were not observed. An empirical absorption correction was used from the DIFABS/TEXSAN software of the Molecular Structure Corp. The crystal exhibited no significant decay under X-ray irradiation. Hydrogen atom positions were calculated.

Results and Discussion

The reaction of $(n\text{-}Bu_4N)[Tc(NO)Cl_4]$ with 2,3,5,6-tetramethylbenzenethiol (Htmbt) in the presence of the proton sponge 1,1,2,2-tetramethylguanidine produces an orange technetium(III) trithiolate compound in which the nitrosyl group and one chloride have been retained. The N–O stretch at 1798 cm^{-1} in the IR spectrum confirms that the nitrosyl is linear, formally NO^+,[12] and that the metal is in the +3 oxidation state. Oxidation of Tc(II) to Tc(III) is facile in the presence of either a limited amount of air or a stoichiometric quantity of the disulfide of Htmbt. This compound has also been observed as a product of the reaction of $Tc(tmbt)_3(MeCN)_2$[8] with $(NO)PF_6$ in the presence of chloride ion or when $(Ph_4As)[TcO(tmbt)_4]$[13] is allowed to react with hydroxylamine hydrochloride. However, these alternate routes give only minute quantities of the compound and are of no synthetic utility.

Although this compound is robust and the molecular ion is the base peak in the negative mode FAB mass spectrum, it is barely observable in the FAB(+) spectrum. In the positive mode, ions that gain their positive charge through the loss of the negatively charged ligands, chloride or tmbt, dominate the spectrum.

Table I. Atomic Coordinates for $Tc(NO)Cl(tmbt)_3$

atom	*x*	*y*	*z*
Tc	0.86316 (2)	0.08852 (4)	0.12572 (3)
Cl1	0.91215 (8)	0.2199 (1)	0.0919 (1)
S1	0.92854 (8)	0.1551 (1)	0.2301 (1)
S2	0.94648 (8)	0.0231 (1)	0.1462 (1)
S3	0.82276 (8)	0.1025 (1)	0.0057 (1)
O1	0.8024 (2)	−0.0777 (4)	0.1538 (3)
N1	0.8258 (2)	−0.0111 (4)	0.1446 (3)
C11	0.8534 (3)	0.2671 (5)	0.2494 (4)
C12	0.9040 (3)	0.2795 (5)	0.2898 (4)
C13	0.9211 (3)	0.3673 (5)	0.3078 (4)
C14	0.8863 (4)	0.4392 (5)	0.2885 (5)
C15	0.8349 (3)	0.4280 (5)	0.2504 (4)
C16	0.8174 (3)	0.3412 (5)	0.2295 (4)
C17	0.9401 (3)	0.1990 (6)	0.3115 (5)
C18	0.9763 (4)	0.3871 (6)	0.3472 (5)
C19	0.7999 (4)	0.5112 (6)	0.2347 (5)
C20	0.7628 (3)	0.3252 (6)	0.1872 (5)
C21	0.9406 (3)	−0.0953 (5)	0.1647 (4)
C22	0.9585 (3)	−0.1549 (5)	0.1090 (4)
C23	0.9556 (3)	−0.2483 (6)	0.1221 (6)
C24	0.9356 (4)	−0.2792 (5)	0.1891 (6)
C25	0.9190 (3)	−0.2207 (6)	0.2466 (5)
C26	0.9222 (3)	−0.1268 (5)	0.2349 (4)
C27	0.9793 (4)	−0.1213 (7)	0.0347 (5)
C28	0.9740 (4)	−0.3166 (7)	0.0635 (6)
C29	0.8971 (4)	−0.2579 (7)	0.3191 (6)
C30	0.9072 (3)	−0.0622 (6)	0.2968 (4)
C31	0.7675 (3)	0.0236 (5)	−0.0091 (4)
C32	0.7150 (3)	0.0531 (5)	0.0063 (4)
C33	0.6706 (3)	−0.0042 (6)	−0.0118 (5)
C34	0.6800 (4)	−0.0868 (6)	−0.0434 (5)
C35	0.7322 (4)	−0.1186 (5)	−0.0573 (4)
C36	0.7771 (3)	−0.0634 (5)	−0.0391 (4)
C37	0.7055 (4)	0.1456 (6)	0.0410 (6)
C38	0.6120 (4)	0.0277 (7)	0.0011 (7)
C39	0.7377 (4)	−0.2095 (6)	−0.0959 (5)
C40	0.8344 (4)	−0.0938 (6)	−0.0524 (5)

Table II. Selected Bond Lengths (Å) and Angles (deg) for $Tc(NO)Cl(tmbt)_3$

Tc–N1	1.767 (6)	Tc–S3	2.274 (2)
Tc–S1	2.280 (2)	Tc–Cl	2.366 (2)
Tc–S2	2.259 (2)	N1–O1	1.150 (7)
S1–Tc–S2	115.44 (8)	Cl–Tc–S3	83.85 (7)
S1–Tc–S3	122.68 (8)	N1–Tc–S1	89.1 (2)
S2–Tc–S3	121.40 (8)	N1–Tc–S2	95.0 (2)
Cl–Tc–N1	176.3 (2)	N1–Tc–S3	92.7 (2)
Cl–Tc–S1	93.89 (7)	Tc–N1–O1	176.8 (6)
Cl–Tc–S2	85.59 (7)		

Table III. X-ray Data for the Structure Determination of $Tc(NO)Cl(tmbt)_3$

chem formula $C_{30}H_{39}NOS_3ClTc$	fw = 658.28
a = 24.420 (5) Å	space group = $C2/c$
b = 14.701 (4) Å	T = 22 °C
c = 17.500 (4) Å	γ = 0.71069 Å (graphite monochromated)
β = 93.50 (2)°	μ = 7.40 cm^{-1}
V = 6271 (5) $Å^3$	transm coeff = 1.18–0.92
Z = 8	R = 0.056, R_w = 0.067
ρ_{calc} = 1.394 g/cm^3, ρ_{exp} = 1.31 g/cm^3	GOOF = 1.20

Unlike the technetium nitrosyl compounds reported thus far, $Tc(NO)(Cl)(tmbt)_3$ contains Tc in the +3 oxidation state (d^4) and is diamagnetic. It, therefore, does not exhibit an EPR signal but can be observed by NMR spectroscopy. Comparison of the ^1H NMR spectrum with those of other compounds of the general formula $Tc(tmbt)_3(L)_2$ (L = π-accepting ligand) strongly suggests that this compound shares both the trigonal-bipyramidal geometry and the "two-up-one-down" conformation of the aryl groups.[8,13] The signals arising from the thiolate rings show the characteristic 2:1 integral ratio consistently observed for other compounds in this series. With such an arrangement and dissimilar axial ligands,

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

(11) To a solution of Htmbt (100 mg) in MeOH (20 mL) was added a saturated solution of I_2 in MeOH dropwise until the red-orange color persisted for at least 10 min. The solution was cooled, and 90 mg of the disulfide $(tmbt)_2$ was recovered by filtration.

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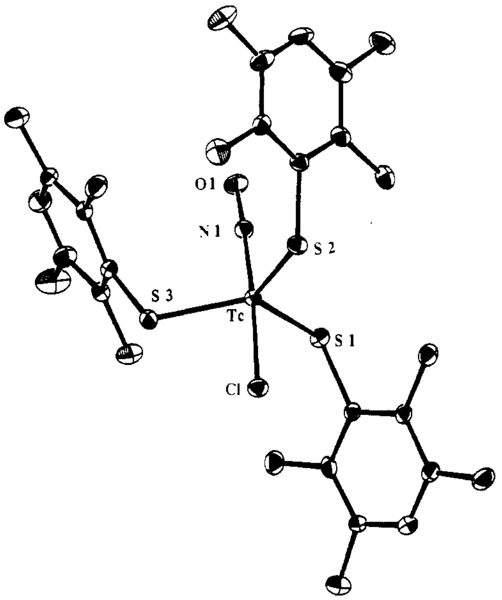

Figure 1. ORTEP diagram, showing 20% probability ellipsoids of Tc(NO)Cl(tmbt)$_3$ with the "two-up-one-down" thiolate ligand arrangement.

two conformations are possible for Tc(NO)(Cl)(tmbt)$_3$. The unique thiolate ring could be on the side of either the chloride or the nitrosyl ligand, and both species could be present in solution. Such is the case for Tc(tmbt)$_3$(MeCN)(CO),[8] in which the two different conformers (present in a 70:30 ratio) give rise to four aromatic proton signals (two sets of two signals). However, the presence of only two aromatic proton signals for the nitrosyl compound suggests that one conformation of Tc(NO)(Cl)(tmbt)$_3$ is favored over the other.

An X-ray crystal structure determination was performed to determine the preferred conformation and confirm the linearity of the nitrosyl ligand. Atomic coordinates for Tc(NO)Cl(tmbt)$_3$ are listed in Table I. Selected bond lengths and angles are listed in Table II, and experimental details for the data collection are used in Table III. The geometry about the technetium atom is trigonal bipyramidal as suggested by the NMR data, with the chloride and nitrosyl nitrogen atoms in the axial positions. An ORTEP diagram of Tc(NO)Cl(tmbt)$_3$ is shown in Figure 1. The equatorial coordination sites are occupied by the three thiolate sulfur atoms. The crystal structure establishes the preferred conformation as that with one of the thiolate aryl groups directed toward the chloride ligand and the remaining two directed toward the nitrosyl ligand. This reflects the fact that the chloride ligand is larger than the nitrosyl ligand and the sterically hindered thiolate ligands adopt the less encumbered conformation. The nitrosyl unit is coordinated in the linear manner as suggested by the infrared data, with the Tc–N–O bond angle of 176.8 (6)°. The Tc–N bond length of 1.767 (6) Å and N–O bond length of 1.150 (7) Å reflect multiple bonding throughout the nitrosyl unit. The Tc–S and Tc–Cl bond lengths are typical of Tc(III) complexes.[8,14]

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Supplementary Material Available: Tables SI–SV, listing respectively complete X-ray data, atomic positional parameters including those of the hydrogens, intramolecular atomic distances, intramolecular bond angles, and anisotropic thermal parameters (16 pages); Table SVI, listing calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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