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Note

Synthesis and Characterization of the “Sulfur-Rich” Bis(perthiobenzoato)(dithiobenzoato)technetium(III) Heterocomplex

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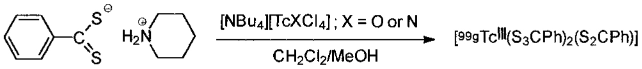
Introduction

Sulfur-coordinated transition metals are known to engage in facile electron and proton-transfer processes that are relevant both in industrial catalysis and biological systems.[1] In this connection, aiming at the elucidation of basic metal sulfide chemistry, induced internal electron transfer reactions involving dithiobenzoato complexes of rhenium have been recently described.[2] The neutral “sulfur-rich” mononuclear Re(III) species [Re(S_3CPh)$_2$(S_2CPh)] (**2**), isolated in quantitative yield by reaction of high-valent [ReS_4]$^-$ with dithiobenzoate disulfide in dry MeCN under an Ar atmosphere, is a remarkable example of contemporary four-electron reduction of a single metal center and of two dithiobenzoate disulfides balanced by the oxidation of coordinated sulfides to S^0. Following a different synthetic approach, we have obtained the identical, thermally stable, dithiobenzoatobis(perthiobenzoato)rhenium(III) complex **2** starting from prereduced [$Re^V(O)Cl_4$]$^-$ and [$Re^{VI}(N)Cl_4$]$^-$ precursors and an excess of dithiobenzoate piperidinium salt in CH_2Cl_2 solutions.[3]

Recently, sulfur-coordinated nitrido−^{99m}Tc−bisdithiocarbamate complexes have shown a promising myocardial uptake in humans,[4] and the agent [^{99m}Tc(N)(NOEt)$_2$] (NOEt = *N*-ethyl-*N*-ethoxy-dithiocarbamate) is now under phase III clinical trials as a new myocardial perfusion agent.[5] The molecular structure of these neutral Tc(V) complexes has been described as square pyramidal with the nitrido group at the apex of the pyramid with four basal dithiocarbamate sulfur donors.[6] The replacement of dithiocarbamate for dithiocarboxylate ligands has produced a new class of ^{99m}Tc agents able to label in vitro leucocytes in whole blood with high yields and selectivity for lymphocytes.[7] In an effort to understand the reason for such a strikingly different biological behavior and to try to enhance the biological properties of ^{99m}Tc-dithiocarboxylato agents, we worked at the elucidation of the molecular structure of our agents by studying the reactivity of the long-lived technetium-99g and of the “cold” congener rhenium with dithiocarboxylate ligands. In this report we describe the reactions of [^{99g}Tc(O)Cl_4][NBu_4] and [^{99g}Tc(N)Cl_4][NBu_4][8] with the dithiobenzoate piperidinium salt[7] (Scheme 1). The resulting deep red complex [^{99g}Tc(S_3CPh)$_2$(S_2CPh)] (**1**) (Figure 1) is isostructural with the green rhenium species **2** described above and represents a rare example of a fully sulfur-coordinated technetium compound. Spectroscopic data and redox behaviors for technetium and rhenium complexes are compared in order to evaluate differences that might be conveniently utilized for the application to nuclear medicine. HPLC concordance experiments established the chemical identity of **1** with the agent produced at the “carrier free” level (^{99m}Tc).[9]

Scheme 1



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(8) The choice of these two prereduced precursors is connected with the availability of similar starting materials containing the mono-oxo or the nitrido groups triply bonded to the metal at the “carrier free” level.

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10.1021/ic0107577 CCC: $22.00

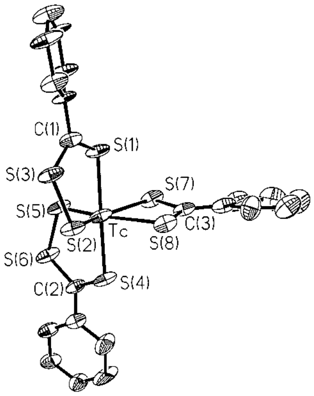

Figure 1. ORTEP diagram of six-coordinate technetium(III) complex [^{99g}Tc(S_3CPh)$_2$(S_2CPh)], **1**. Hydrogen atoms have been omitted for clarity.

Experimental Section

Caution! ^{99g}Tc is a weak β-emitter ($E_\beta = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in a laboratory approved for low-level radioactivity using monitored hoods and gloveboxes. When handled in milligram amounts, ^{99g}Tc does not present a serious health hazard, since common laboratory glassware provides adequate shielding. Bremsstrahlung is not a significant problem, due to the low energy of the β-particles. However, normal radiation safety procedures must be used at all times, especially with solid samples, to prevent contamination and inhalation.

General Method. Technetium as [NH_4][^{99g}TcO_4] was obtained from Oak Ridge National Laboratory. Samples were dissolved in water and treated with excess aqueous ammonia and H_2O_2 (30%, w/w in water) at 80 °C to eliminate residual TcO_2. Solid samples of purified ammonium pertechnetate were obtained by slow evaporation of the solvent with heating at 40 °C. General literature methods were used to prepare the precursor complexes [Tc(O)Cl_4]-[NBu$_4$],[10] [Tc(N)Cl_4][NBu$_4$],[11] and the dithiobenzoate piperidinium salt.[7] THF was distilled twice under dinitrogen over sodium/benzophenone. CH_2Cl_2, Et_2O, and petroleum ether were distilled over $CaCl_2$. Bromobenzene, Mg turnings, CS_2, and piperidine are commercially available from Aldrich (Saint Quentin Fallavier, France).

Carbon, hydrogen, and sulfur analyses were performed on a Carlo Erba Model-1106 elemental analyzer. FT IR spectra were recorded on a Nicolet 510P Fourier transform spectrometer (4000−200 cm^{-1}) in Nujol mull. Proton and carbon NMR spectra were run on a Bruker AC-200 instrument using Si(CH_3)$_4$ as an internal reference and $CDCl_3$ as solvent.

Cyclic voltammetry measurements were performed on a BAS (Bioanalytical System Inc.) CV-1B cyclic voltammograph at 293 K under an atmosphere of dinitrogen by using a conventional three-electrode cell. A platinum-disk electrode (area ca. 10^{-3} cm^2) was used as the working electrode, a platinum wire as the counter electrode, and a silver wire as a quasireference electrode. Controlled potential coulometries were performed using an Amel model 721 integrator, in an H-shaped cell containing, in arm 1, a platinium gauze working electrode and an Ag/Ag$^+$ reference isolated inside a salt bridge by a medium-glass frit and, in arm 2, an auxiliary platinium-foil electrode.

Preparation of [^{99g}Tc(S_3CPh)$_2$(S_2CPh)], 1. To a methanol solution (15 mL) of [Tc(O)Cl_4][NBu$_4$] (0.036 g, 0.072 mmol) was added PhC$S_2^-$$H_2N^+$($CH_2$)$_5$ (0.087 g, 0.36 mmol) in CH_2Cl_2 (5 mL) dropwise, and the solution was stirred at room temperature for 2 h. The dark precipitate was filtered, washed twice with MeOH (5 mL), and dried overnight under a flux of dinitrogen. Yield = 74% (0.033 g). The dark powder was then recrystallized in CH_2Cl_2/petroleum ether (bp = 30−60 °C) to afford dark red crystals suitable for X-ray diffraction analysis. The same product can also be obtained starting from [TcNCl_4][NBu$_4$] using a 1:6 metal/ligand ratio: Yield = 67% (0.035 g). Anal. Calcd for [$C_{21}H_{15}TcS_8$]: C, 40.49, H, 2.42, S, 41.18. Found: C, 40.53, H, 2.43, S, 41.20. ^{1}H NMR: δ_H 7.29 (m, 3H), 7.44 (m, 6H), 7.85 (d, J = 7.5 Hz, 2H), 8.04 (dd, J = 7.5 and 2.0 Hz, 4H). ^{13}C NMR: δ 124.3, 128.1, 128.7, 129.4, 131.6, 132.6, 137.8, 141.9, 226.7, 226.0. FT IR (Nujol mull, cm^{-1}): 1587 (w), 1335 (w), 1311 (w), 1262 (w), 1233 (w), 1117 (w), 1109 (w), 1077 (w), 998 (w), 942 (w), 906 (w), 838 (w), 759 (s), 723 (w), 682 (s), 663 (w), 651 (w), 615 (w), 566 (w), 447 (w).

Table 1. Crystal Data and Details for Data Collection for **1**

chemical formula	$C_{21}H_{15}S_8Tc$
formula weight	621.81
crystal system	monoclinic
space group	$P21/c$
a (Å)	19.951(5)
b (Å)	10.633(3)
c (Å)	11.990(4)
β (deg)	105.75(2)
volume (Å3)	2448(1)
Z	4
temperature	293(2) K
λ (Mo Kα) (Å)	0.71 073
ρ(calc.) (g cm^{-3})	1.687
μ (Mo Kα) (cm^{-1})	1.279
2Θ range (deg)	2.60° ≤ 2Θ ≤ 23.56°
no.obs reflections	3096
$R_1{}^a$, $wR_2{}^b$	0.076, 0.209
GOF	1.073

^{a} $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$. ^{b} $wR_2 = [\Sigma[w[|F_o|^2 - |F_c|^2]]^2/\Sigma(w|F_o|^2)]^{1/2}$

Crystal Structure Determination of 1. The crystal data and details of data collection are given in Table 1. The diffraction intensities of an approximately 0.08 × 0.08 × 0.40 mm needlelike red crystal were collected and corrected for Lorentz polarization and absorption (ψ scan method) effects. A total of 3375 reflections were collected, of which 3096 with $I > 2\sigma(I)$ were used for the structure determination. The structure was solved by the Patterson method using SHELXTL NT[12] and refined by the full-matrix least-squares method on F^2 using SHELXL 93.[13] All hydrogen atoms were placed in calculated positions with their thermal parameters fixed at values of 1.2 times those of their parent atoms. The final difference map was featureless. The relatively high values of the R indices are ascribed to some cracks that developed in the crystal during X-ray exposure and to the rather poor diffracting ability of the sample. As a consequence, the collection was restricted to 2Θ = 47°, since higher angle data bore negative intensity.

Results and Discussion

Reactions of the labile [Tc(O)Cl_4]$^-$ or [Tc(N)Cl_4]$^-$ precursors with the dithiobenzoate piperidinium salt in a dichloromethane/methanol mixture give invariably a dark red com-

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Tc−S(1)	2.349(4)	S(1)−Tc−S(2)	89.6(1)
Tc−S(2)	2.231(4)	S(4)−Tc−S(5)	89.2(1)
Tc−S(4)	2.354(4)	S(7)−Tc−S(8)	68.1(1)
Tc−S(5)	2.227(4)	Tc−S(2)−S(3)	110.0(2)
Tc−S(7)	2.510(4)	Tc−S(5)−S(6)	110.8(2)
Tc−S(8)	2.478(5)	Tc−S(1)−C(1)	110.7(5)
S(2)−S(3)	2.099(6)	Tc−S(4)−C(2)	110.7(5)
S(5)−S(6)	2.075(6)	S(1)−C(1)−S(3)	124.1(9)
S(1)−C(1)	1.67(2)	S(4)−C(2)−S(6)	124.2(9)
S(7)−C(3)	1.67(2)	S(7)−C(3)−S(8)	111.9(9)

pound in reasonable yield. One of the reoccurring features of the Tc(V) and Re(V) oxidation states is the stability of complexes holding the $[M(O)]^{3+}$ or $[M(N)]^{2+}$ cores, which can be usually transferred from compound to compound.[14] However, no retention of the $\mathrm{Tc{=}O}$ or $\mathrm{Tc{\equiv}N}$ stretching vibrations was observed in the IR spectrum. Elemental analysis indicated a quite high sulfur/carbon ratio, and NMR spectra gave sharp signals in a narrow window typical of diamagnetic species. In particular, according to homonuclear decoupling experiments, two set of A_2B_2C phenyl protons (with relative 2:1 integration) were observed, indicating the existence of different dithiobenzoate ligands in the coordination sphere. Correspondingly, the ^{13}C spectrum showed two sets of phenyl and two dithiocarboxy signals. These data strongly support the proposed structure of complex **1** to be identical to that exhibited by the related rhenium compound **2**, as given in Scheme 1. While abstraction of the oxo group operated, for instance, by tertiary phosphines or thiobenzoylhydrazine is a common feature in Tc(V) chemistry,[15] only a few examples of removal of the nitrido group are reported so far. These include reactions with phosphinothiols[16] and aromatic dithiols.[17]

To confirm our hypothesis, a single-crystal X-ray structure determination was undertaken on red crystals of **1**. The technetium ion lies in a distorted trigonal prism environment made up by the six terminal sulfur atoms of three ligands with Tc−S distances ranging from 2.227(4) to 2.510(4) Å (Table 2). The twist angle between the upper and the lower triangular faces is 17.1° compared with the value of 8.9° in **2**. The structure exhibits one dithiobenzoate ligand, forming a four-membered chelate ring and displaying the longest metal-sulfur distances, and two perthiobenzoate ligands, making two five-membered chelate rings around Tc(III). The coordination fashion of these oxidized chelates places the S(1) and S(4) thioketo donors trans to each other [S(1)−Tc−S(4) = 175.4(1)°].

The cyclic voltammogram of **1** in CH_2Cl_2 is shown in Figure 2. A reversible one-electron oxidation is observed at 0.894 V and a further irreversible wave at 1.362 V (E_{an}) is seen. Cathodic scans reveal a reversible reduction at −0.556 V. The oxidations are assigned by coulombometric experiments to the formation of Tc(IV) and Tc(V), respectively, presumably accessing the $4d^3$ [Tc(IV)] and $4d^2$ [Tc(V)] systems. The reduction is assigned to the Tc(III)/Tc(II) couple. The technetium complex **1** is easier to reduce (by 534 mV) and more difficult to oxidize (by 314 mV) than the corresponding rhenium complex **2**. The redox potential gap is at the long end of the range usually observed in pairs of homologous technetium and rhenium complexes.[18]

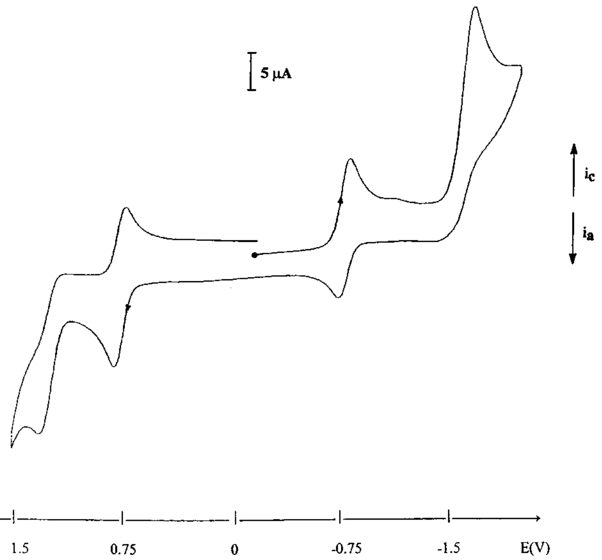

Figure 2. Cyclic voltammogramm of **1**: 3.5×10^{-3} M complex, 0.1 M $[Bu_4N][ClO_4]$ in dry and degassed CH_2Cl_2, −1.7 to +1.6 V, 0.2 V cm^{-1}, Ag wire quasireference electrode.

The existence of the perthio metal linkage M−S−R−S−S has been established in several compounds with different metals such as Cu(II), Ni(II), Zn(II), Pd(II), Pt(II), Fe(III), Os(III), or Mo(IV).[19] Moreover, besides complex **1**, the coordination of perthio fragments upon rhenium has been observed in another monomeric species, $[Re(S)(S_4)(S_3CMe_2)]^-$,[20] and in a number of polynuclear derivatives.[21] However, **2** represents the first example of monomeric Tc(III) species with an unprecedented mixed coordination sphere combining one dithiobenzoate and two perthiobenzoate ligands. Sulfur coordination is common in technetium chemistry,[22] covering different oxidation states (mainly III and V) and various coordination numbers. In these compounds the coordination sphere is often supported by additional nitrogen and/or oxygen donors. Much less frequent

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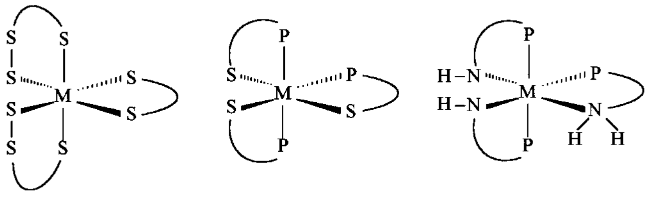

M = Tc, **1**; Re, **2**   **3**   **4**

Figure 3. Schematic view of six-coordinated Tc(III) complexes comprising a lengthened bidentate ligand (on the right side of the molecules).

are coordination spheres entirely supported by sulfur donors. Structurally authenticated examples comprise homoleptic bis-crown thioether Tc(II),[23] hexakis(thiourea)−Tc(III),[24] tris(dicyanoethenedithiolato)−Tc(IV),[25] tris(benzenedithiolato)−Tc(V),[17] the unusual eight-coordinate tetrakis(cyclopentamethylenedithiocarbamate)−Tc(V),[26] and the mixed bis(benzenethiolato) tetrathioether Tc(III) complexes.[27]

Comparison of M−P and M−Cl bond lengths of isostructural mononuclear M(III) complexes (M = Tc, Re) with coordination number six shows that such values are substantially identical (within three standard deviations), in agreement with a trend already observed in pairs of homologous Tc and Re derivatives in oxidation states I and V.[18] M−S distances are comparable as well, except for the pair of "sulfur-rich" homologues **1** and **2**, in which the Tc−S distances are 0.03 Å longer than the corresponding Re−S ones. The contraction of the Re−S distances may account for the unusual value of $\Delta E°$ ($E°_{Re}$ − $E°_{Tc}$), which makes the rhenium(III) compound **2** much more resistant to reduction and easier to oxidize than **1**. On the other hand, the M−S distances cover a very wide range (from 2.198 to 2.493 Å). Several types of metal−sulfur interaction can be identified: (i) M−S of ca. 2.21 and 2.33 Å, respectively, for the sulfur atoms engaged in $^{-}$**S**−SC(Ph)−S and $^{-}$S−SC(Ph)−**S** ligating modes of the technetium−perthiobenzoato moiety; (ii) M−S of ca. 2.28 Å for arenethiolato-type sulfurs −**S**−C(Ph); (iii) M−S of ca. 2.42 Å for thiourea sulfur and (iv) M−S of ca. 2.48 Å for sulfurs facing covalently bonded sulfur. The latter distances are typical of the dithiobenzoate fragment in **1** and of one of the phosphinothiolate fragments in *mer*-[M(2-$Ph_2PC_6H_4S$)$_3$] **3**. Although these two complexes exhibit different coordination spheres (S_6 vs P_3S_3), they possess effective similarities from the electronic point of view. By utilizing the octahedral description sketched in Figure 3, both structures display two apical trans-positioned π-acceptor donors (thio-S in **1** and P in **3**) connected with two strong cis-positioned π-donors. The latters affect seriously the trans-positioned dithiobenzoato (Figure 3.**1**) and "PS" (Figure 3.**3**) ligands. Such a labilizing effect is operating also in the strictly related complex *mer*-[Tc(2-$Ph_2PC_6H_4NH$)$_2$(2-$Ph_2PC_6H_4NH_2$)]$^+$ **4**,[28] in which the third ligand is protonated at the amino function to diminish the electron density at the metal center (Figure 3.**4**). Thus, in this class of Tc(III) complexes it appears that a particular combination of π-donor and π-acceptor atoms tends to drive the system toward five-coordination,[29] resembling the well-characterized trigonal bipyramidal geometry exhibited by a large number of M(III) compounds comprising thiolate and phosphine ligands.[22] In fact, the replacement of phosphine−arenethiolate with phosphine−alkylthiolate ligands in **3**-like compounds, which precludes π-electronic conjugation, gives rise to trigonal bipyramidal arrangements with two π-acceptors (P) at the apexes and three π-donors (S) at the base of the pyramid.[30] Only the capability of the dithiobenzoate (and aromatic phosphinothiolate or phosphinoamine) fragments to delocalize electron density via π-orbitals allows six-coordination to be reached. However, the coordination of this third ligand is greatly affected, and quite long distances are observed. Finally, this electronic requirement explains why the oxidation of a third dithiobenzoate fragment, although accessible from the stoichiometric point of view, does not take place in complexes **1** and **2**.

Conclusion

The diamagnetic "sulfur-rich" technetium(III) complex [^{99g}Tc(S_2CPh)(S_3CPh)$_2$] (**1**) has been characterized both in solid and solution states at the ground level and found to be identical by HPLC concordance experiments with the corresponding Tc-99m agent prepared at the "carrier free" level. The latter displays significant biological properties, being able to label in vitro leukocytes in whole blood with high yields. The established mixed coordination sphere of **1**, which is isostructural to the third-row rhenium complex [Re(S_2CPh)(S_3CPh)$_2$] **2**, comprises a dithiobenzoate and two perthiobenzoate fragments in a distorted trigonal prismatic arrangement. Redox behaviors indicate that the technetium complex is easier to reduce and more difficult to oxidize than the rhenium analogue. The knowledge of the molecular structure of these new "sulfur rich" species makes it now possible to improve their biological activity by subtly tuning the substituents on the dithiobenzoate fragments.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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