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Synthesis, Spectroscopy, and Structural Characterization of Neutral Seven-Coordinate Technetium Xanthate Complexes. X-ray Structure of $[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COC}_4\text{H}_9)_3]$, a Capped Octahedral Technetium(III) Complex

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Reaction of $(\text{Bu}_4\text{N})[\text{TcOCl}_4]$ with triphenylphosphine and an excess of potassium xanthate yields neutral complexes of the general formula $[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COR})_3]$ (R = ethyl, isopropyl, *n*-butyl, neopentyl). The infrared spectra show a single C=S absorption from the exclusively bidentate xanthate ligands. The fast-atom-bombardment mass spectral results show the parent ions and a complex fragmentation pattern that includes two sulfido species. The X-ray structure of $[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COBu}^n)_3]$ confirms the unusual seven-coordinate, capped octahedral geometry, with the technetium and phosphorus atoms each sitting on 3-fold axes and a single crystallographically unique *n*-butyl xanthate ligand. Crystal data for $\text{C}_{33}\text{H}_{42}\text{O}_3\text{PS}_6\text{Tc}$: rhombohedral space group (hexagonal axes) $R3c(h)$, $a = 15.437(4) \text{ \AA}$, $c = 53.49(1) \text{ \AA}$, $V = 11040(4) \text{ \AA}^3$ to give $Z = 12$ for $D = 1.46 \text{ g/cm}^3$; structure solution and refinement based on 1726 reflections converged at $R = 0.043$, $R_w = 0.047$. The ^1H NMR spectra show that the 3-fold molecular symmetry is maintained in solution, with a single set of C—H absorptions from the three xanthate ligands. The ^{99}Tc NMR resonances of these complexes fall in the Tc(V) region and are the first technetium complexes with sulfur ligation to be so characterized.

Introduction

There is considerable interest in the chemistry of technetium due to its increased availability and widespread use in diagnostic nuclear medicine. The favorable nuclear properties of the metastable isotope $^{99\text{m}}\text{Tc}$ ($\gamma = 140 \text{ keV}$, $t_{1/2} = 6 \text{ h}$) allow images of high resolution to be obtained with a low radiation dose to the patient.

The functionally robust, seven-coordinate, 18-electron complexes discussed within possess the capacity for variation at both the axial ligand site and the xanthate terminus, thus allowing manipulation of the complexes' lipophilicity. These complexes are currently being examined at the tracer level for possible application in diagnostic nuclear medicine.

Experimental Section

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

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Reagents and solvents were used as received unless otherwise stated. Potassium xanthate ligands were synthesized by the method of Shupe.³ Routine infrared spectra were obtained on a Mattson Cygnus 100 FTIR instrument. ^{99}Tc NMR spectra were recorded on either a Varian XL-300 or a Varian VXR-500 FTNMR spectrometer and referenced to $[\text{TcO}_4]^-$. Electronic spectra were recorded on an HP 8451A diode array spectrophotometer. Fast-atom-bombardment mass spectra of samples dissolved in a *p*-nitrobenzyl alcohol matrix were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerated voltage of 8 kV. The FAB gun produced a beam of 6–8-keV xenon neutrals. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. SEP-PAK C_{18} cartridges were obtained from Waters Associates. Samples were loaded onto the cartridges until a brown solid could be seen accumulating on the prefilter leading into the reverse-phase packing material.

$[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COC}_2\text{H}_5)_3]$ (1). The complex $(\text{Bu}_4\text{N})[\text{TcOCl}_4]$, 0.07 g, was dissolved in 15 mL of ethanol, to which a warm solution of 0.15 g of PPh_3 in 10 mL of ethanol was added dropwise with stirring until a bright red color persisted. Potassium ethyl xanthate, 0.25 g, dissolved in 15 mL of ethanol was added to the red solution, which caused a rapid color change to dark red-brown. The solution was stirred at room temperature for 15 min, after which 100 mL of distilled water was added. The resulting muddy-brown suspension was loaded onto a SEP-PAK C_{18} cartridge, washed with 10 mL of distilled water, and eluted with ethanol. The resulting rich red-brown solution yielded brown microcrystals after the addition of a few drops of water and refrigeration. Yield: 55–65%. Anal. Calcd for $\text{C}_{27}\text{H}_{45}\text{O}_3\text{PS}_6\text{Tc}$: C, 44.73; H, 4.18; S, 26.54. Found:

C, 44.80; H, 4.12; S, 26.61. IR (KBr): $\nu(\text{C}=\text{S})$ 1229 cm^{-1} . UV-vis (CHCl_3) [λ_{max} , nm (ϵ , $\text{L mol}^{-1} \text{ cm}^{-1}$): 440 (2.58×10^3), 318 (2.30×10^4), 250 (2.46×10^4). ^{99}Tc NMR (CDCl_3 , 22 °C): δ 2859.

$[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COC}_4\text{H}_9)_3]$ (2). The red-brown, tris(*n*-butyl xanthate) complex 2 was prepared analogously to complex 1 with potassium *n*-butyl xanthate. Brown crystals formed with slow evaporation of the eluted ethanol-water solution. Yield: 65–70%. Anal. Calcd for $\text{C}_{33}\text{H}_{42}\text{O}_3\text{PS}_6\text{Tc}$: C, 48.99; H, 5.24. Found: C, 48.87; H, 5.33. IR (KBr): $\nu(\text{C}=\text{S})$ 1235 cm^{-1} . UV-vis [λ_{max} , nm (ϵ , $\text{L mol}^{-1} \text{ cm}^{-1}$): 438 (2.61×10^3), 319 (2.30×10^4), 250 (2.51×10^4). ^{99}Tc NMR (CDCl_3 , 22 °C): δ 2882.

$[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COC}_3\text{H}_7)_3]$ (3). The tris(neopentyl xanthate) complex 3 was prepared analogously to complex 1 with potassium neopentyl xanthate. The brown microcrystalline product was isolated directly from the ethanolic solution without the chromatographic purification. The isolated product contained a minor contamination of potassium chloride which cocrystallized with the product. Yield: 65–70%. Anal. Calcd for $\text{C}_{54}\text{H}_{48}\text{O}_3\text{PS}_6\text{Tc}(\text{KCl})_{1/3}$: C, 49.36; H, 5.53; S, 21.95. Found: C, 49.54; H, 5.53; S, 21.69. IR (KBr): $\nu(\text{C}=\text{S})$ 1241 cm^{-1} . UV-vis [λ_{max} , nm (ϵ , $\text{L mol}^{-1} \text{ cm}^{-1}$): 440 (2.60×10^3), 319 (2.36×10^4), 252 (2.53×10^4). ^{99}Tc NMR (CDCl_3 , 22 °C): δ 2862.

The preparations described above are those used to prepare the crystalline samples used throughout for analytical and spectroscopic analyses. A general method used to synthesize essentially pure samples of the seven-coordinate technetium complexes with a variety of derivatized xanthate ligands is described below.

The water-sensitive complex $(\text{Bu}_4\text{N})[\text{TcOCl}_4]$ was dissolved in absolute ethanol, which gave a yellow-green solution. A warm solution of triphenylphosphine (4-fold excess) dissolved in a minimum amount of absolute ethanol was added dropwise, which caused the color to darken to red. This solution was stirred at room temperature for 15 min. A freshly prepared sample of potassium alkyl xanthate dissolved in a minimum amount of absolute ethanol was added dropwise to the stirred solution of the phosphine and $[\text{TcOCl}_4]^-$. The color darkened with continued stirring, after which a large excess of distilled water was added. The red-brown solution rapidly formed a muddy-brown suspension, which was loaded onto SEP-PAK C_{18} chromatography cartridges, and each sample was washed with 20 mL of distilled water. The major side product, TcO_2 , appears to bind irreversibly to the cartridge, as does the excess phosphine. The excess xanthate was removed in the water wash prior to elution of the complex with ethanol. The red-brown complex was eluted cleanly with absolute ethanol. Thin-layer chromatography and HPLC confirmed the purity of the eluted samples.

Results and Discussion

The chemistry of technetium with dithiocarbamate ligands has been explored in various oxidation states;⁴ however the chemistry with xanthate ligands has remained largely overlooked. It has been previously reported that xanthates may be used as colorimetric agents for the determination of technetium content;⁵

(1) (a) Massachusetts Institute of Technology. (b) Harvard Medical School and Brigham and Women's Hospital.

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Table I. Mass Spectral Results for [Tc(PPh₃)(S₂COR)₃] Derivatives

species	xanthate derivative	mass, <i>m/z</i>
TcL ₃ P ⁺ (= M ⁺)	ethyl	724
(= M ⁺)	isopropyl	767
(= MH ⁺)	<i>n</i> -butyl	809
(= M ⁺)	neopentyl	850
TcL ₃ H ⁺	ethyl	463
TcL ₃ H ₂ ⁺	isopropyl	505
TcL ₃ H ₂ ⁺	<i>n</i> -butyl	548
TcL ₃ H ⁺	neopentyl	585
TcL ₂ P ⁺	ethyl	603
TcL ₂ P ⁺	isopropyl	632
TcL ₂ PH ⁺	<i>n</i> -butyl	660
TcL ₂ P ⁺	neopentyl	687
TcL ₂ ⁺	ethyl	341
TcL ₂ ⁺	isopropyl	369
TcL ₂ H ⁺	<i>n</i> -butyl	398
TcL ₂ ⁺	neopentyl	425
TcS ₂ LP ⁺	ethyl	546
TcS ₂ LP ⁺	isopropyl	560
TcS ₂ LPH ⁺	<i>n</i> -butyl	575
TcS ₂ LPH ⁺	neopentyl	589
TcSL ₂ ⁺	ethyl	373
TcSL ₂ H ⁺	isopropyl	402
TcSL ₂ H ⁺	<i>n</i> -butyl	430
TcSL ₂ ⁺	neopentyl	457

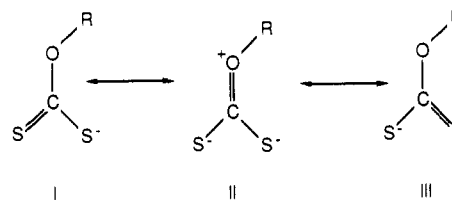
however the synthetic products from these reactions have never been rigorously characterized.

The reaction of the Tc(V) complex (Bu₄N)[TcOCl₄] with triphenylphosphine in acetone or dry ethanol followed by an excess of potassium xanthate readily gives neutral seven-coordinate Tc(III) complexes. The red-brown crystalline products are hydrolytically stable in ethanol-water mixtures, with yields varying from good to excellent. The product can also be obtained directly from the reaction of TcO₄⁻, triphenylphosphine, and potassium xanthate. These results will be presented elsewhere.

The steric bulk of the alkyl xanthate ligand does not appear to influence the mode of coordination. Ethyl xanthate-, isopropyl xanthate-, and neopentyl xanthate-triphenylphosphine adducts are all isolable as crystalline products, with infrared spectra exhibiting single C=S bands near 1235 cm⁻¹, the region associated with the bidentate mode of coordination for xanthate ligands.⁶

The results of the mass spectrometric analyses are listed in Table I. In addition to the parent ions, the decomposition profiles show loss of a single xanthate, [Tc(PPh₃)(xan)₂]⁺, loss of two xanthates from the parent ion, [Tc(PPh₃)(xan)]⁺, and the loss of the phosphine from the tris(xanthate) species, [Tc(xan)₃]⁺. In addition, a species corresponding to the bis(xanthate) complex is common to each of the xanthate derivatives, [Tc(xan)₂]⁺. Two sulfido species are also generated during the mass spectrometric experiment, [TcS₂(xan)(PPh₃)]⁺ and [TcS(xan)₂]⁺. These results may provide insight into the synthesis of technetium sulfido complexes.

Nuclear magnetic resonance employing the ⁹⁹Tc nucleus is proving to be a useful tool for characterization of coordination complexes of technetium. The chemical shifts (relative to [TcO₄]⁻) for a large number of technetium complexes have recently been reported,^{7a} and it has been proven possible to correlate the chemical shift with the oxidation state of the complex. The chemical shifts for the seven-coordinate tris(xanthate) complexes resonate in the region assigned to Tc(V) compounds (800–5500 ppm) and not

**Figure 1.** Resonance structures for the xanthate ligand.**Table II.** X-ray Data for the Structure Determination of Complex 2

empirical formula	C ₃₃ H ₄₂ PS ₆ O ₃ Tc
fw	807.03
cryst system	rhombohedral (hexagonal axes)
<i>a</i> , Å	15.437 (4)
<i>c</i> , Å	53.49 (1)
<i>V</i> , Å ³	11040 (5)
space group	<i>R</i> 3 <i>c</i> (<i>h</i>) (No. 167)
<i>Z</i>	12
<i>D</i> (calcd), g/cm ³	1.456
<i>D</i> (exptl), g/cm ³	1.4
μ , cm ⁻¹	7.75
radiation (λ , Å), graphite monochromated	Mo K α (0.71069)
temp, °C	23
<i>T</i> _{max} , <i>T</i> _{min}	1.22, 0.74
<i>R</i> , <i>R</i> _w	0.043, 0.047
goodness of fit	2.48

the established Tc(III) region (–1329 to –78 ppm). This downfield shift of the technetium NMR resonances for these species can be attributed to a paramagnetic shielding effect. The paramagnetic shielding term, represented by σ_p , is proportional to $-(\Delta E^{-1})$ so that weak-field ligands, such as sulfur donors, will result in a deshielding of the technetium nucleus.^{7b}

Infrared spectroscopy can reflect the degree to which the different canonical forms contribute to the structure.⁶ In the ionic mode of coordination (II), the π -bond character of the C=S bond is lowered, while the σ -bond character of the C—O bond acquires a partial π -bond character. This results in a lowering of the C—S frequency and an enhancement of the C—O frequency. Absorptions from C=S bonds can occur as high as 1220 cm⁻¹ with corresponding C—O absorptions as low as 1020 cm⁻¹ in complexes containing xanthate ligands⁶ coordinated in the nonionic manner (I and III), while the ionic mode of coordination shows absorptions from the C=S bonds as low as 1143 cm⁻¹ and corresponding C—O bond absorptions as high as 1077 cm⁻¹.⁶ The technetium complexes show absorptions from the xanthate C—O bonds near 1040 cm⁻¹, which reflects a partial contribution from the ionic form of the xanthate ligand for these complexes. Further, X-ray structural results (*vide infra*) confirm the presence of partial C—O double bond character. The broad ⁹⁹Tc NMR resonances observed for these complexes, with an average value of 7800 Hz, preclude the assessment of any effects of changing the xanthate alkyl substituents.

The proton NMR spectrum of the isopropyl xanthate derivative establishes a 3-fold molecular symmetry in solution. The spectrum of the isopropyl xanthate derivative [Tc(PPh₃)(S₂COC₃H₇)₃] shows a single set of signals from the CH protons of the isopropyl substituents. A well-defined septet between 5.4 and 5.5 ppm and a sharp doublet at 1.35 ppm, which integrate 1:6, are assigned to the aliphatic CH protons. A complex multiplet between 7.2 and 7.5 ppm, which integrates 5:1 with respect to the septet, is assigned to the phosphine aryl protons. A pentagonal-bipyramidal geometry would likely result in multiple signals from the alkyl protons of the xanthates.⁸

A single-crystal X-ray structural determination was undertaken on red-brown crystals of the *n*-butyl xanthate complex [Tc(PPh₃)(S₂COC₄H₉)₃] to confirm the unusual heptacoordination geometry. Crystal data and experimental details of the structure determination are given in Table II. A dark red prismatic crystal

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Table III. Atomic Positional Parameters for Complex 2

atom	x	y	z
Tc(1)	$2/3$	$1/3$	0.44388 (1)
S(1)	0.7540 (1)	0.4785 (1)	0.47189 (3)
S(2)	0.6179 (1)	0.4593 (1)	0.43459 (2)
P(1)	$2/3$	$1/3$	0.39936 (3)
O(1)	0.6990 (3)	0.6114 (3)	0.46773 (8)
C(1)	0.6914 (4)	0.5286 (4)	0.4586 (1)
C(2)	0.6477 (6)	0.6568 (5)	0.4549 (1)
C(3)	0.555 (1)	0.636 (1)	0.4691 (2)
C(4)	0.469 (1)	0.584 (2)	0.4648 (3)
C(5)	0.418 (1)	0.548 (1)	0.4407 (3)
C(11)	0.5658 (4)	0.3465 (4)	0.38460 (8)
C(12)	0.4708 (4)	0.2974 (5)	0.3943 (1)
C(13)	0.3937 (5)	0.3049 (5)	0.3834 (1)
C(14)	0.4136 (5)	0.3640 (5)	0.3621 (1)
C(15)	0.5084 (5)	0.4144 (5)	0.3520 (1)
C(16)	0.5840 (4)	0.4054 (4)	0.3634 (1)

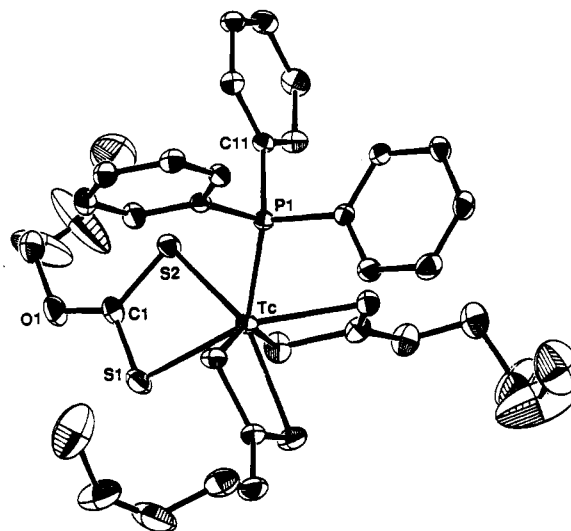
Table IV. Selected Bond Lengths and Angles for Complex 2

Bond Lengths (Å)			
Tc(1)–P(1)	2.381 (2)	Tc(1)–S(1)	2.463 (2)
Tc(1)–S(2)	2.462 (2)	S(1)–C(1)	1.670 (6)
S(2)–C(1)	1.691 (5)	O(1)–C(1)	1.319 (6)
Bond Angles (deg)			
P(1)–Tc(1)–S(1)	127.48 (4)	P(1)–Tc(1)–S(2)	78.36 (3)
Tc(1)–S(1)–C(1)	88.9 (2)	Tc(1)–S(2)–C(1)	88.5 (2)
S(1)–C(1)–O(1)	119.9 (4)	S(2)–C(1)–O(1)	127.0 (5)
S(1)–C(1)–S(2)	113.1 (3)	S(1)–Tc(1)–S(1)	86.83 (6)
S(2)–C(1)–S(2)	116.04 (2)	S(1)–Tc(1)–S(2)	69.41 (5)
S(1)–Tc(1)–S(2)	80.03 (5)	S(1)–Tc(1)–S(2)	153.27 (6)

of complex **2** was selected from a sample recrystallized from an ethanol–water mixture. The crystal selected measured $0.20 \times 0.20 \times 0.35$ mm. The diffractometer employed was a Rigaku AFC-6R. The scan mode used was ω - 2θ , with a maximum 2θ of 54.9° . The octants collected were hkl ($-h + k + l = 3n$) and $h0l$ ($l = 2n$) giving a total of 5986 reflections. Of those, 3131 were unique and 1726 reflections of $I > 3\sigma(I)$ were used in the final structure refinement. The technetium atom was located by using direct methods. Neutral-atom scattering factors were used throughout the analysis.⁹ 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-irradiation. Tables of bond lengths and angles, anisotropic temperature factors, hydrogen atom positions, and calculated and observed structure factors are available as supplementary material.

Structurally characterized seven-coordinate complexes of technetium are rare and with few exceptions display distorted pentagonal-bipyramidal geometry.¹⁰ The complex described here, with capped octahedral coordination geometry, shows both technetium and phosphorus atoms sitting on crystallographically defined 3-fold axes. A single idantate *n*-butyl xanthate ligand and one phenyl group of the coordinated triphenylphosphine are crystallographically unique. The coordination sphere about the technetium consists of the six sulfurs from three bidentate xanthate ligands and the phosphorus of the triphenylphosphine. Table III lists the atomic positional parameters for complex **2**. A structure contains a slight disorder in the alkyl portion of the butyl xanthate ligand, which is reflected in the bond lengths, with a short C(3)–C(4) bond of 1.17 Å. Table IV contains selected bond lengths and angles for complex **2**, while Figure 2 shows the ORTEP diagram of the structure of complex **2**.

The other structurally characterized capped octahedral complex of technetium is the neutral Tc(III) species $[\text{TcCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$,¹¹ with the carbonyl group capping the face defined

Figure 2. ORTEP diagram of $[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COC}_4\text{H}_9)_3]$, with relevant atoms labeled showing 15% probability ellipsoids.

by the three phosphine groups. The xanthate complex shows bond lengths from the technetium to the capped-face sulfur atoms ($\text{Tc}–\text{S}(2) = 2.462$ (2) Å) nearly equivalent to those to the sulfurs in the noncapped face ($\text{Tc}–\text{S}(1) = 2.463$ (2) Å). This suggests that the delocalization of the $\text{C}=\text{S}$ double bond is not influenced by a trans effect imposed by the triphenylphosphine in the pseudo-trans position. These bond lengths are significantly longer than the $\text{Tc}–\text{S}$ bonds in trigonal-bipyramidal technetium(III) tris(thiolate) complexes,¹² which fall between 2.234 (6) and 2.258 (6) Å. The xanthate carbon–sulfur bonds are 1.691 (5) and 1.670 (6) Å, which reflect a degree of multiple bonding. The short carbon–oxygen bond of 1.319 (6) Å suggests that the charge delocalization is distributed throughout the functional portion of the xanthate moiety.

The bond angles about the technetium in the xanthate complex are $\text{P}–\text{Tc}–\text{S}(2) = 78.36$ (3)°, $\text{S}(2)–\text{Tc}–\text{S}(2) = 116.04$ (2)°, and $\text{S}(1)–\text{Tc}–\text{S}(2) = 69.41$ (5)°. For comparison, the average values involving the same positions in $[\text{TcCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$ are 74.2, 112.9, and 77.3°. In capped octahedral coordination, the freedom of the atom in the uncapped face is revealed in the angles around the ligand in the uncapped face, in this case, S(1). These angles are $\text{P}–\text{Tc}–\text{S}(1) = 127.48$ (4)°, $\text{S}(1)–\text{Tc}–\text{S}(1) = 86.83$ (6)°, and $\text{S}(1)–\text{Tc}–\text{S}(2) = 153.27$ (6)°, which are similar to those found in the majority of capped octahedral structures with other central atoms (ca. 127, 90, and 162°).¹³ The differences reflect the bulk of the capping ligand (PPh_3) and the geometric constraints imposed by the small bite angle of the bidentate xanthate ligands.

The phenyl rings of the phosphine ligand are angled along the technetium–phosphorus bond, situated between the blades formed by the coordinated xanthate ligands, thus minimizing steric interactions on the periphery.

The structurally characterized seven-coordinate technetium(III) tris(dithiocarbamate) carbonyl complex $[\text{Tc}(\text{CO})(\text{S}_2\text{CNEt}_2)_3]$ displays distorted pentagonal-bipyramidal geometry,¹⁴ with one arm of one bidentate ligand coordinated trans to the carbonyl group. The analogous rhenium complex $[\text{Re}(\text{CO})(\text{S}_2\text{CNEt}_2)_3]$ has also been shown to adopt this pentagonal-bipyramidal geometry.¹⁵ The difference in coordination geometry between the tris(xanthate) phosphine complexes and the tris(dithiocarbamate) carbonyl species may be attributed to the increased bulk of the axial ligand of triphenylphosphine relative to the carbonyl group, since the two forms of the dithiocarboxylate ligand would be expected to behave the same structurally. Bond lengths and angles

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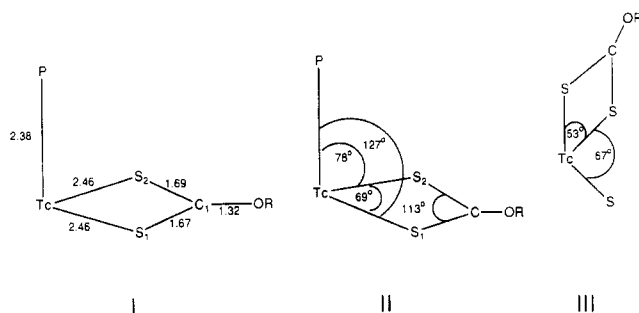


Figure 3. Diagram depicting bond lengths and angles of $[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COC}_4\text{H}_9)_3]$ from various perspectives.

from various perspectives are shown in I and II of Figure 3, while III depicts the bond angles looking down the technetium-phosphorus bond, showing the distorted capped octahedral geometry.

An analogous Tc(IV) complex, the tris(dithiocarbamate) dimethylphenylphosphine complex $[\text{Tc}(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNET}_2)_3](\text{PF}_6)$, synthesized from $[\text{TcCl}_3(\text{PMe}_2\text{Ph})_3]$ has recently been reported; however no crystal structure has been reported for a comparison of the bonding parameters.¹⁶

Summary

In conclusion, we have prepared the first fully characterized technetium xanthate complexes. The functionally versatile, neutral, seven-coordinate complexes show potential as radiopharmaceuticals using the short-lived isotope $^{99\text{m}}\text{Tc}$. The results of the biological studies will be reported elsewhere.

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Supplementary Material Available: Listings of final positional parameters for $[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COBu}^n)_3]$ including hydrogen atoms (Table SI), anisotropic thermal parameters (Table SII), intramolecular bond lengths involving non-hydrogen and hydrogen atoms (Tables SIII and SIV), intramolecular bond angles involving non-hydrogen and hydrogen atoms (Tables SV and SVI), and complete X-ray data collection parameters (Table SVIII) (8 pages); listings of final observed and calculated structure factors (Table SVII) (20 pages). Ordering information is given on any current masthead page.

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Reactivity of Coordinated Phosphate Esters: Pentaamminecobalt(III) Complexes

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The reactivity of two phosphate ester complexes designed to test the efficacy of different modes of activation of phosphate esters by metal ions has been investigated. Ethyl 4-nitrophenyl phosphate coordinated to the pentaamminecobalt(III) moiety liberates nitrophenolate in basic solution 10^6 -fold faster than the free phosphodiester. The reaction proceeds via attack of coordinated amido ion to yield a four-membered N,O chelate phosphoramidate ethyl ester. The four-membered chelate does not display the enhanced reactivity of the five-membered-ring cyclic ethylene phosphates but decays with cobalt-ligand bond rupture and yields finally free ethyl phosphoramidate. The aminolysis is accompanied by some loss of ethyl 4-nitrophenyl phosphate by the $\text{S}_{\text{N}}1(\text{CB})$ mechanism. The binuclear complex (μ -nitrophenyl phosphato)decaamminedicobalt(4+) undergoes aminolysis in basic aqueous media, also by intramolecular attack of coordinated amido ion. The reaction proceeds some 10^2 -fold faster than the analogous aminolysis of the mononuclear complex, (4-nitrophenyl phosphato)pentaamminecobalt(1+). The reaction is also accompanied by some $\text{S}_{\text{N}}1(\text{CB})$ loss of the intact ligand; in this case, the ligand is the mononuclear complex. This study illuminates some of the modes by which metal ions can enhance the reactivity of phosphate esters. In agreement with other studies, the electrostatic and inductive effects are estimated to contribute $\sim 10^2$ -fold to the rate enhancement, while the intramolecularity of the reaction is responsible for the remainder of the observed rate enhancement.

Introduction

Many energy-requiring reactions in living systems obtain their energy from the lysis of phosphoanhydride bonds. The lysis of many phosphate ester, anhydride, and amidate bonds in biological systems is mediated by enzymes that have as a striking feature an almost ubiquitous requirement for metal ions for activity.¹ As part of an ongoing study into the effect of metal ions on the reactivity of phosphate derivatives, the metal complex ions (ethyl 4-nitrophenyl (phosphato)pentaamminecobalt(2+) and (μ -4-nitrophenyl phosphato)decaamminedicobalt(4+) have been synthesized and their reactivity studied.

The (4-nitrophenyl phosphato)pentaamminecobalt(1+), (fluorophosphato)pentaamminecobalt(1+), and (2,4-dinitrophenyl phosphato)pentaamminecobalt(1+) ions studied previously²⁻⁴ react in hydroxide ion solution to yield significant amounts of 4-nitrophenolate, fluoride, and 2,4-dinitrophenolate ions, respectively, by attack of deprotonated ammonia at the phosphorus center. The

reaction proceeds via the chelate phosphoramidate, incorporating the phosphorus into a strained four-membered ring. These observations raised several interesting possibilities with regard to metal ion activated phosphoryl transfer.

The demonstration that a cis-coordinated amido ion was an effective nucleophile toward phosphorus centers of coordinated phosphate esters raised the prospect of synthesis of a chelated phosphoramidate ester. Such an ester should be formed, at least as an intermediate, during the aminolysis of a coordinated phosphodiester. The reactivity of this class of compound is of interest because of the presence of the strained four-membered ring incorporating the phosphorus atom. This ring strain might give rise to an increase in the reactivity at the phosphorus atom by lowering the energy of the transition state for the $\text{S}_{\text{N}}2(\text{P})$ reaction,⁵⁻⁷ as observed for the reactions of five-membered-ring organic phosphate esters.⁸ The prospect of observing substantial reactivity with phosphate esters involved in four-membered rings

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