

Contribution from the Medical Products Division,
Union Carbide Corporation, Tuxedo, New York 10987**Technetium Complexes of Aliphatic Thiols. Synthesis and Characterization of Oxobis(1,2- and 1,3-dithiolato)technetate(V) Anions**

E. F. BYRNE* and J. E. SMITH

Received October 18, 1978

The tetraphenylarsonium salts of oxobis(dithiolato)technetate(V) anions of the general formula $\text{TcO}(\text{L})_2^-$, where L = the dianions of 1,2-dimercaptoethane, 1,2-dimercaptopropane, and 1,3-dimercaptopropane, have been synthesized. The complexes were characterized by UV-visible, IR, Raman, proton NMR, and carbon-13 NMR spectroscopy as well as electrophoresis, chemical analysis, and magnetic susceptibility. Chemical and spectral data are consistent with a square-pyramidal structure, previously determined by X-ray diffraction analysis. The observed diffraction powder pattern for $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$ matched closely with the pattern calculated from the single-crystal X-ray diffraction data.

Introduction

The coordination chemistry of technetium in the higher oxidation states, particularly III–VI, has begun to draw a growing interest in view of the possible relevance to the field of nuclear medicine.¹ Technetium-99m, a 140 keV γ emitter with a half-life of 6 h, is widely used in the nonsurgical examination of internal organs by radioactive imaging because of its ready availability and desirable nuclear properties. Various chemical forms of ^{99m}Tc are presently the most widely used radiopharmaceuticals for imaging of the brain, liver, lung, and skeleton.^{2,3} The chemical nature of most ^{99m}Tc imaging agents, however, is speculative because only nanomolar amounts of ^{99m}Tc are used in diagnostic imaging procedures. With long-lived ⁹⁹Tc, a 0.3 MeV β emitter with a half-life of 2.12×10^5 years, rather than short-lived ^{99m}Tc, macroscopic amounts of technetium compounds can be isolated and their structures determined by conventional chemical and spectroscopic methods.

The apparent coordination of technetium to sulfur-containing ligands in several ^{99m}Tc radiopharmaceuticals^{4–8} has stirred an interest in determining the oxidation state and coordination geometry of technetium chelates with aliphatic thiols. For this reason the complexation of technetium to 1,2- and 1,3-dithiolates was investigated.

In this paper, we describe the synthesis of a new type of technetium(V) complex, oxobis(dithiolato)technetate(V) anions of the general formula $[\text{TcO}(\text{S-X-S})_2]^-$, where X = CH_2CH_2 , $\text{CH}_2\text{CH}(\text{CH}_3)$, and $\text{CH}_2\text{CH}_2\text{CH}_2$. The literature has previously recorded little concerning oxotechnetium(V) compounds,^{9–11} although rhenium^{9–12} and molybdenum^{9,13} as well as other neighboring elements form such compounds in abundance. The oxobis(dithiolato)technetate(V) anions were isolated as tetraphenylarsonium salts and characterized by chemical analysis, electrophoresis, and magnetic susceptibility. The UV-visible, infrared, Raman, proton NMR, and carbon-13 NMR spectral data of the complexes are presented and discussed. The X-ray powder pattern for $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$ is presented and compared to the pattern calculated from the single-crystal X-ray diffraction data.

The square-pyramidal structure of the 1,2-dimercaptoethane complex $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$, determined by X-ray crystallography, was recently reported¹⁴ and found to be similar to that of the closely related compound $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{TcO}(\text{SC}(\text{O})\text{CH}_2\text{S})_2]$.¹⁵ The $\text{Tc}^{\text{V}}\text{OS}_4$ core of these complexes is similar to the isoelectronic $\text{Mo}^{\text{IV}}\text{OS}_4$ ¹⁶ core of $\text{MoO}[(n\text{-C}_3\text{H}_7)_2\text{NCS}_2]_2$ and the $\text{Mo}^{\text{V}}\text{OS}_4$ ¹⁷ core of $[\text{Mo}_2\text{S}_4(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$. In all these structures the metal atom is displaced above the plane generated by the four sulfur atoms toward the apical oxygen.

Experimental Section

Analytical and Physical Measurements. Chemical analyses of carbon, hydrogen, and sulfur were performed by the Schwarzkopf

Microanalytical Laboratory, Woodside, NY. Oxygen percentages were determined from neutron activation analyses by Nuclear Products and Services, Union Carbide Corp., Tuxedo, NY. Arsenic analyses were performed by the Sterling Forest Analytical Laboratory, Union Carbide Corp., Tuxedo, NY. Technetium percentages were determined by direct counting of ⁹⁹Tc β decay by using an Eberline Model HP-210 pancake monitor. Analytical data for the technetium dithiolate complexes prepared in this study are given in Table I.

Electrophoresis experiments were performed with a CAMAG 67-701 thin-layer electrophoresis cell in 0.025 M NaH_2PO_4 at 600 V for 40 min on Whatman No. 1 paper. Electrophoresis migrations were recorded on a Model 930 Vanguard radiochromatogram scanner.

UV and visible spectra were recorded in acetonitrile or aqueous solution on a Cary 118 spectrophotometer.

Infrared spectra were recorded from 4000 to 250 cm^{-1} on a Beckman Model IR-20A-X spectrophotometer. Spectra were run on solid samples prepared as KBr or CsI pellets.

Raman spectra were recorded to 4000 cm^{-1} on a Jarrell-Ash Model 25-300 spectrophotometer equipped with a Coherent Model 52 MG argon-krypton mixed-gas laser operating on either the 4880-Å argon line or the 5682-Å krypton line. Spectra were run on solid samples in sealed glass capillary tubes.

Magnetic susceptibilities of the crystalline solids were measured at ambient temperature with a Faraday balance at the Massachusetts Institute of Technology.¹⁹

The ¹³C NMR spectra were recorded on a Bruker Model HFX-90 spectrometer at 31 °C in CDCl_3 . The ¹H NMR spectra were recorded on both Varian Model T-60 and Varian Model HR-220 spectrometers at ambient temperature in CDCl_3 . Proton and carbon-13 chemical-shift values are reported as δ from tetramethylsilane.

The X-ray powder pattern of $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$ was obtained with a Debye-Scherrer camera on a sample sealed in a Lindeman capillary tube.

Reagents and Syntheses. $\text{NH}_4^{99}\text{TcO}_4$ was obtained from Oak Ridge National Laboratories and was purified by recrystallization from dilute nitric acid. The compounds 1,2-dimercaptoethane, 1,2-dimercaptopropane, and 1,3-dimercaptopropane were purchased from Aldrich Chemical Co. Sodium borohydride and tetraphenylarsonium chloride were purchased from Ventron Corp.

The technetium dithiolate complexes were formed by reducing NH_4TcO_4 with NaBH_4 in the presence of the dithiol in an ethanol solution and were isolated as the tetraphenylarsonium salts.

$[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$. A solution of NaBH_4 (167.5 mg, 4.43 mmol) in 25 mL of absolute ethanol was added to a solution of NH_4TcO_4 (54.3 mg, 0.30 mmol) and 1,2-dimercaptoethane (300 mg, 3.19 mmol) in 25 mL of absolute ethanol. The dark brown solution that formed immediately was stirred for 4 h. Ethanol was then removed by rotary evaporation, leaving a dark brown residue. A bright orange complex was extracted from the brown residue with 100 mL of diethyl ether. The ether solution was filtered, dried over anhydrous MgSO_4 , and reduced to a volume of 10–15 mL. Approximately 25 mL of anhydrous methanol was added to the solution, and the volume was once again reduced to about 10 mL by rotary evaporation. The remaining orange solution was added to a solution of tetraphenylarsonium chloride (141.5 mg, 0.34 mmol) in 10 mL of methanol. Crystals began to form after a few minutes, and the solution was cooled in an ice bath for 1 h. The crystals were filtered, washed with cold MeOH followed by diethyl ether, and air-dried to give 204.8 mg

Table I. Analytical Data for Technetium Dithiolate Complexes

compd	% calcd					% found						
	C	H	O	S	As	Tc	C	H	O	S	As	Tc
[Ph ₄ As][TcO(SCH ₂ CH ₂ S) ₂]	49.26	4.14	2.34	18.79	10.97	14.50	49.22	4.54	2.05	20.36	7.60	14.69
[Ph ₄ As][TcO(SCH ₂ CH(CH ₃)S) ₂]	50.69	4.55	2.25	18.04	10.54	13.93	52.07	4.43	2.25	17.32	10.41	14.22
[Ph ₄ As][TcO(SCH ₂ CH ₂ CH ₂ S) ₂]	50.69	4.55	2.25	18.04	10.54	13.93	51.10	4.51	2.16	18.65	11.70	14.30

Table II. Electrophoresis of Pertechnetate and Technetium Dithiolate Complexes

compd	electrophoresis migration ^a
NH ₄ TcO ₄	-13.5
[Ph ₄ As][TcO(SCH ₂ CH ₂ S) ₂]	-6.8
[Ph ₄ As][TcO(SCH ₂ CH(CH ₃)S) ₂]	-6.5
[Ph ₄ As][TcO(SCH ₂ CH ₂ CH ₂ S) ₂]	-6.9

^a Reported in cm. Negative values indicate that the compound migrated toward the anode. Determined in 0.025 M NaH₂PO₄ at 600 V for 40 min on Whatman No. 1 paper.

(64.4% yield) of orange crystals. This material decomposed to a brown oil at 230–235 °C. It was soluble in acetone, chloroform, ethanol, and acetonitrile, slightly soluble in methanol, and insoluble in water and diethyl ether.

[Ph₄As][TcO(SCH₂CH(CH₃)S)₂]. A solution of NaBH₄ (618.7 mg, 16.4 mmol) in 50 mL of absolute ethanol was added to a solution of NH₄TcO₄ (221.1 mg, 1.22 mmol) and 1,2-dimercaptopropane (1.28 g, 11.84 mmol) in 50 mL of absolute ethanol. The dark brown solution that formed immediately was stirred for 6 h and left to stand overnight. Ethanol was then removed by rotary evaporation. The bright orange complex was extracted from the brown residue with 100 mL of diethyl ether. The ether solution was filtered, dried over anhydrous MgSO₄, and reduced to a volume of about 25 mL. Approximately 50 mL of anhydrous methanol was added to the solution and the volume was once again reduced to about 25 mL. The solution was then added to a solution of tetraphenylarsonium chloride (502.4 mg, 1.20 mmol) in 5 mL of methanol. A light orange powder was precipitated by the addition of diethyl ether and was filtered, washed with diethyl ether, and dissolved in acetone. The acetone solution was filtered to remove any residual tetraphenylarsonium chloride and reduced to a volume of about 25 mL. The addition of diethyl ether resulted in the precipitation of a dark orange powder that was filtered and air-dried to yield 132.2 mg (19.0%); mp 130–135 °C. The product was soluble in acetone, chloroform, acetonitrile, methanol, and ethanol and insoluble in water and diethyl ether.

[Ph₄As][TcO(SCH₂CH₂CH₂S)₂]. A solution of NaBH₄ (675.0 mg, 17.86 mmol) in 50 mL of absolute ethanol was added to a solution of NH₄TcO₄ (207.1 mg, 1.14 mmol) and 1,3-dimercaptopropane (1.29 g, 11.95 mmol) in 50 mL of absolute ethanol. The dark brown solution that formed immediately was stirred for several hours. The ethanol was removed by rotary evaporation, and the orange complex was extracted from the brown residue with acetone. The acetone solution was filtered and the acetone removed. The product was dissolved in 25 mL of methanol, and the solution was filtered and added to a solution of tetraphenylarsonium chloride (576 mg, 1.38 mmol) in 10 mL of MeOH. Diethyl ether was added to precipitate a light orange solid. The orange solid was dissolved in acetone and the solution filtered to remove any residual tetraphenylarsonium chloride. The acetone solution was reduced to about 25 mL, and diethyl ether was added to precipitate a dark orange powder. The product was filtered, washed with diethyl ether, and air-dried to yield 237.1 mg (34.1%). This material decomposed to a brown oil at 195–200 °C. It was soluble in acetone, chloroform, acetonitrile, methanol, and ethanol and insoluble in water and diethyl ether.

Results and Discussion

The orange products obtained from the NaBH₄ reduction of NH₄TcO₄ in the presence of dithiols in ethanolic solution were characterized by standard physical and chemical techniques. Electrophoresis of the technetium dithiolate complexes shows that they are negatively charged, migrating toward the anode approximately half the distance of TcO₄⁻. The migration distances for a typical electrophoresis run are found in Table II. Many additional runs were performed,

Table III. Infrared and Raman Tc=O Stretches of Technetium Dithiolate Complexes

compd	ν(Tc=O), cm ⁻¹	
	infrared	Raman
Ph ₄ AsTcO(SCH ₂ CH ₂ S) ₂	940 s	930 s
Ph ₄ AsTcO[SCH ₂ CH(CH ₃)S] ₂	925 s	930 s
Ph ₄ AsTcO(SCH ₂ CH ₂ CH ₂ S) ₂	945 s	930 s

Table IV. UV-Visible Absorptions of Na⁺ and Ph₄As⁺ Salts of Oxobis(dithiolato)technetate(V) Anions

compd	Na ⁺ salt ^a		Ph ₄ As ⁺ salt ^b	
	λ _{max} , nm	ε _{max}	λ _{max} , nm	ε _{max}
TcO(SCH ₂ CH ₂ S) ₂ ⁻	390	2 400	390	3 000
	270	7 700	270	16 400
	240	13 300	263	16 100
	210	23 400	257	15 500
TcO[SCH ₂ CH(CH ₃)S] ₂ ⁻	390	2 500	390	3 100
	270	6 600	270	14 300
	240	12 300	263	14 600
	210	21 800	257	14 000
TcO(SCH ₂ CH ₂ CH ₂ S) ₂ ⁻	450	3 200	450	3 200
	285	7 600	269	12 100
	255	13 000	263	13 400
	225	25 600	257	12 400
			223	55 900

^a The Na⁺ salts were obtained from the ether or acetone extracts as orange oils. Spectra were recorded in aqueous solution.

^b Spectra were recorded in acetonitrile solution.

and the migration rate of the technetium dithiolates was always 0.50 ± 0.03 times that of pertechnetate.

The results of the chemical analyses of the tetraphenylarsonium salts of the oxobis(dithiolato)technetate(V) anions are summarized in Table I. These data indicate that the complexes contain two dithiolate ligands per technetium, have a net charge of minus one, and may contain an oxygen atom in the coordination sphere. The presence of an oxygen atom was also suggested by the infrared and Raman data. Both the infrared and Raman spectra of each of the technetium dithiolate complexes showed a strong band in the 920–950 cm⁻¹ region (see Table III), typical of the Tc=O stretch.¹⁹ Davison and co-workers¹⁵ have recently isolated a similar oxotechnetium(V) complex and have shown that the Tc=O stretch occurs at 950 cm⁻¹ in both the infrared and Raman spectra. These Tc=O absorptions can be compared to the well-studied Re=O¹² and Mo=O¹³ stretches. Other absorptions expected for the dithiolate ligands as well as the characteristic absorptions of the tetraphenylarsonium group were also observed for the technetium dithiolate complexes. (A complete listing of the infrared and Raman absorptions of the technetium dithiolates is given in the supplementary data.)

The UV-visible absorptions of the sodium and tetraphenylarsonium salts of the oxobis(dithiolato)technetate(V) anions are summarized in Table IV. The 1,2-dithiolate complexes have characteristic absorptions at 390, 270, 240, and 210 nm. The absorptions of the 1,3-dithiolate complexes are slightly shifted and are observed at 450, 285, 255, and 225

Table V. Proton and Carbon-13 NMR Data^a for Dithiols and Metal Dithiolate Complexes

	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
$\text{HSCH}_2\text{CH}_2\text{SH}$	2.9 (singlet)	28.62
$\text{Ph}_4\text{AsTcO}(\text{SCH}_2\text{CH}_2\text{S})_2^b$	3.1 (singlet)	39.13
$\text{Sn}(\text{SCH}_2\text{CH}_2\text{S})_2^c$	3.2 (singlet)	35.76
$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{SH}^d$ (α)	2.8 (triplet)	22.21
	(β) 1.9 (quintet)	36.51
$\text{Ph}_4\text{AsTcO}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_2^b$ (α)	2.7 (triplet)	31.68
	(β) 2.2 (quintet)	36.24

^a Spectra recorded in CDCl_3 . All values reported in ppm relative to internal Me_4Si standard. ^b Also observed for tetraphenylarsonium ion: $\delta(^1\text{H}) = 7.8, 7.7, \text{ and } 7.3$; $\delta(^{13}\text{C}) = 134.8, 132.9, \text{ and } 131.4$ ppm. ^c For synthesis see ref 22. ^d $\delta(^{13}\text{C})$ values obtained from ref 21.

nm. The tetraphenylarsonium salts show absorptions typical of the tetraphenylarsonium group at 270, 263, 257, and 221 nm as well as absorption at 390 nm for the 1,2-dithiolates and an absorption at 450 nm for the 1,3-dithiolate. These absorptions can be compared to those of a similar compound, the oxobis(thiomercaptoacetato)technetate(V) complex,¹⁵ which has λ_{max} 415 nm and ϵ_{max} 3700.

All of the oxobis(dithiolato)technetate(V) complexes are weakly paramagnetic and possess magnetic moments that are field-strength dependent. The effective moments at 298 K between 1910 and 13810 G range from 2.11 to 0.82 μ_{B} for $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$, from 2.60 to 1.00 μ_{B} for $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}(\text{CH}_3)\text{S})_2]$, and from 2.76 to 1.07 μ_{B} for $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_2]$. Other oxotechnetium,¹⁵ oxorhenium,¹² and oxomolybdenum¹³ complexes having a d^2 configuration and local C_{4v} symmetry possess magnetic moments with similar values and field dependence. It has been suggested^{12,13,15} that this behavior is due to temperature-independent paramagnetism. (A listing of the magnetic susceptibility of the technetium dithiolates at 298 K as a function of field strength is given in the supplementary data.)

The ^1H and ^{13}C NMR spectra of 1,2-dimercaptoethane, 1,3-dimercaptopropane, $\text{Ph}_4\text{AsTcO}(\text{SCH}_2\text{CH}_2\text{S})_2$, and $\text{Ph}_4\text{AsTcO}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_2$ are summarized in Table V. The proton spectra of the technetium dithiolates showed the expected resonances with only small shifts relative to the free dithiols. The α -carbon resonances of 1,2-dimercaptoethane and 1,3-dimercaptopropane were shifted approximately 10 ppm downfield upon complexation to technetium. This shift in the α -carbon resonance is similar to that observed for $\text{Sn}(\text{SCH}_2\text{CH}_2\text{S})_2$ (see Table V) and can be compared with the shift observed when a 1,3-dithiol is oxidized to a cyclic disulfide.²⁰ The ^1H and ^{13}C NMR spectra of the technetium dithiolates also showed the resonances expected for the tetraphenylarsonium counterion. No ESR spectrum was observed for any of the technetium dithiolate complexes at 298 or 77 K.

The assignment of the structure of the technetium dithiolate complexes as oxobis(dithiolato)technetate(V) ions was confirmed by determining the structure of the 1,2-dimercaptoethane complex by single-crystal X-ray diffraction.¹⁴ The structure of $\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2^-$ is approximately square pyramidal. The technetium atom is 0.76 Å above the plane formed by the four sulfur atoms with an average Tc-S bond distance of 2.30 Å. The oxygen atom constitutes the apex of the square pyramid with a Tc=O bond distance of 1.64 Å. The structure is very similar to that found recently for the oxobis(thiomercaptoacetate) anion.¹⁵

The powder pattern of $[\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$ was obtained and compared with the powder pattern calculated from the single-crystal X-ray data. The calculated and observed patterns, which are shown in Figure 1, agree well. This confirms that the polycrystalline material used for physical and chemical measurement was the same as the single crystal

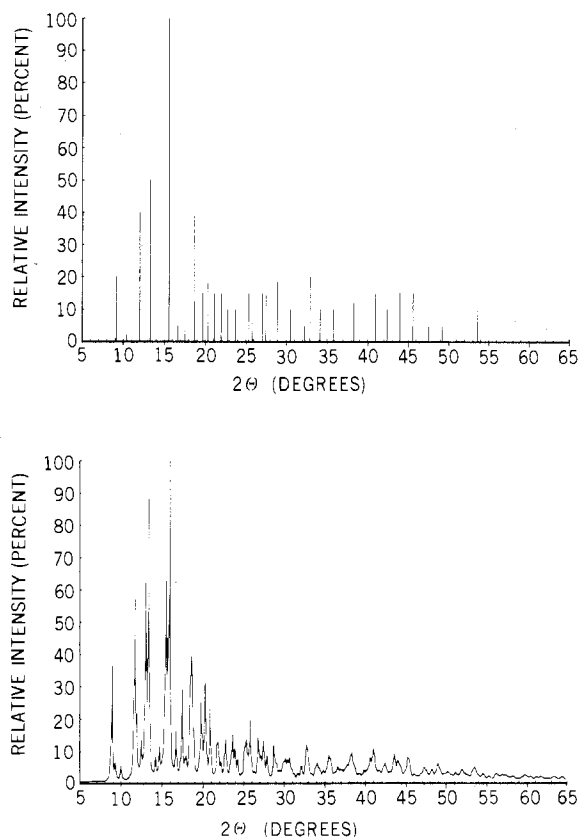


Figure 1. Observed (upper) and calculated (lower) powder patterns of $\text{Ph}_4\text{AsTcO}(\text{SCH}_2\text{CH}_2\text{S})_2$.

used for the X-ray structure determination.

The structure of the technetium dithiolate complexes described in this paper may be relevant to a number of current $^{99\text{m}}\text{Tc}$ radiopharmaceuticals that contain sulfur, particularly 2,3-dimercaptosuccinic acid⁵ and dihydrothioctic acid⁶ which contain the 1,2- and 1,3-dithiol groups, respectively. Although we have not yet isolated pure crystalline ^{99}Tc complexes of 2,3-dimercaptosuccinic acid and dihydrothioctic acid, the infrared, Raman, and UV visible spectra of the compounds obtained strongly suggest that the bonding is analogous to the well-characterized oxobis(1,2- and 1,3-dithiolato)technetate(V) species. The infrared and Raman spectra of the 2,3-dimercaptosuccinic acid and dihydrothioctic acid reaction products show strong Tc=O bands at 940 and 930 cm^{-1} , respectively. The UV-visible spectrum of the 2,3-dimercaptosuccinic acid complex shows absorptions at 390, 270, 240, and 210 nm, typical of the technetium 1,2-dithiolate complexes. The UV-visible spectrum of the dihydrothioctic acid complex shows the typical absorptions of the technetium 1,3-dithiolate complex at 445, 285, 255, and 225 nm.

The complexes characterized in this study have contained only ^{99}Tc , but the corresponding $^{99\text{m}}\text{Tc}$ complexes have also been synthesized with 1,2-dimercaptoethane, 1,2-dimercaptopropane, 1,3-dimercaptopropane, 2,3-dimercaptosuccinic acid, and dihydrothioctic acid. The $^{99\text{m}}\text{Tc}$ complexes of these ligands have been demonstrated to be equivalent to the ^{99}Tc complexes by electrophoresis and paper chromatography. In addition, the ^{99}Tc and $^{99\text{m}}\text{Tc}$ complexes of 1,2-dimercaptoethane were shown to be equivalent by biodistribution in mice.²²

Studies of the type described in this paper are needed because the area of technetium chemistry is relatively unexplored. The chemical compositions, oxidation states, and coordination geometries of most routinely used technetium imaging agents are presently unknown. Future bioinorganic research on technetium-ligand interactions should lead to a

better understanding of the currently used agents and, in addition, should lead to a more rational design of new diagnostic organ imaging agents.

Acknowledgment. We thank Mr. Harvey Trop and Professor Alan Davison of the Massachusetts Institute of Technology for determining the magnetic susceptibilities of the complexes and for many helpful discussions and suggestions.

Registry No. [$\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{S})_2]$, 69216-12-2; [$\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}(\text{CH}_3)\text{S})_2]$, 70209-06-2; [$\text{Ph}_4\text{As}][\text{TcO}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_2]$, 70178-66-4; $\text{NH}_4^{99}\text{TcO}_4$, 34035-97-7.

Supplementary Material Available: Tables listing the infrared and Raman spectral data and the magnetic susceptibility data (3 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) P. Valk, J. McRae, A. J. Bearden, and P. Hambright, *J. Chem. Educ.*, **53**, 542 (1976).
- (2) J. A. Siegel and E. Deutsch, *Annu. Rep. Inorg. Gen. Synth.*, **4**, 311 (1975).
- (3) W. C. Eckelman and S. M. Levenson, *Int. J. Appl. Radiat. Isot.*, **25**, 67 (1977).
- (4) B. Johannsen, R. Syhre, H. Spies, and R. Munze, *J. Nucl. Med.*, **19**, 816 (1978).
- (5) I. Ikeda, O. Inove, and K. Kurata, *J. Nucl. Med.*, **18**, 1222 (1977).
- (6) A. K. Tonkin and F. H. Deland, *J. Nucl. Med.*, **15**, 539 (1974).
- (7) I. Ikeda and T. Sakaguchi, *Int. J. Appl. Radiat. Isot.*, **28**, 387 (1977).
- (8) J. Steigman and P. Richards, *Semin. Nucl. Med.*, **4**, 269 (1974).
- (9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972, pp 965-90.
- (10) R. D. Peacock, "The Chemistry of Technetium and Rhenium", Elsevier, Amsterdam, 1966.
- (11) R. Colton, "The Chemistry of Rhenium and Technetium", Wiley-Interscience, New York, 1966.
- (12) W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
- (13) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
- (14) J. E. Smith, E. F. Byrne, F. A. Cotton, and J. C. Sekutowski, *J. Am. Chem. Soc.*, **100**, 5571 (1978).
- (15) B. V. DePamphilis, A. G. Jones, M. A. Davis, and A. Davison, *J. Am. Chem. Soc.*, **100**, 5570 (1978).
- (16) L. Richard, J. Estienne, P. Karagianidis, P. Toledano, J. Fisher, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974).
- (17) G. Bunzey and J. H. Enemark, *Inorg. Chem.*, **17**, 682 (1978).
- (18) We wish to thank Professor Alan Davison and Mr. Harvey Trop for obtaining the magnetic susceptibilities.
- (19) M. Baluka, J. Hanuza, and B. Jezowska-Trzebiatowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **20**, 271 (1972).
- (20) J. V. Paukstellis, E. F. Byrne, T. P. O'Connor, and T. E. Roche, *J. Org. Chem.*, **42**, 3941 (1977).
- (21) E. W. Abel and D. A. Armitage, *Adv. Organomet. Chem.*, **5**, 1 (1967).
- (22) E. F. Byrne and J. E. Smith, to be submitted for publication in *J. Nucl. Med.*

Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331

Synthesis and Chemistry of the (η^6 -Arene)tris(pyridine)molybdenum(I) Cation

W. E. SILVERTHORN

Received December 8, 1978

The new, highly reactive, paramagnetic compounds [$(\eta^6\text{-arene})\text{Mo}(\text{py})_3$] PF_6 (arene = benzene or toluene) have been prepared by the reaction of pyridine (py) with [$(\eta^6\text{-arene})_2\text{Mo}$] PF_6 . The pyridine ligands are readily replaced by 1-methylimidazole (1-Me-Im) yielding [$(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(1\text{-Me-Im})_3$] PF_6 . The pyridine complexes also react with carbon monoxide yielding *trans*- $[\text{Mo}(\text{CO})_2(\text{py})_4]\text{PF}_6$ which readily and reversibly loses one molecule of carbon monoxide under nitrogen affording the compound $[\text{Mo}(\text{CO})(\text{py})_4]_n^{n+}(\text{PF}_6^-)_n$ ($n \geq 2$). Magnetic susceptibility and electrochemical data are also reported.

Introduction

We have previously reported the synthesis of a series of "electron-rich" 18-electron molybdenum complexes of the type ($\eta^6\text{-arene})\text{MoL}_3$ (arene = benzene or toluene; L = a tertiary phosphine or phosphite ligand) as part of a systematic search for highly reactive molybdenum systems.^{1,2} However, the chemistry of these compounds was found to be limited by their kinetic inertness toward ligand substitution reactions. Recently, an investigation into the synthesis of related 17-electron molybdenum(I) complexes has been undertaken in order to obtain more reactive systems. This paper reports the preparation and characterization of the new paramagnetic cations [$(\eta^6\text{-arene})\text{Mo}(\text{py})_3$] $^+$ (arene = benzene or toluene), [$(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(1\text{-Me-Im})_3$] $^+$, and the carbon monoxide reaction products *trans*- $[\text{Mo}(\text{CO})_2(\text{py})_4]$ $^+$ and $[\text{Mo}(\text{CO})(\text{py})_4]_n^{n+}$. Part of this work has been briefly communicated.³

Experimental Section

Physical Measurements. The infrared spectra were obtained on a Perkin-Elmer Model 237 grating spectrophotometer. The magnetic susceptibilities were obtained at room temperature by using the Gouy method. The conductivity measurements were carried out by using previously described methods.⁴ The carbon monoxide liberation measurements were made on a high-vacuum line and the carbon monoxide gas was identified by infrared spectroscopy. The electrochemical experiments were carried out at room temperature at a platinum electrode by using a PAR Model 170 electrochemistry system. A saturated calomel reference electrode was used.

Materials. Literature methods were used to prepare ($\eta^6\text{-C}_6\text{H}_6$) $_2\text{Mo}$,⁵ ($\eta^6\text{-CH}_3\text{C}_6\text{H}_5$) $_2\text{Mo}$,⁶ and [$(\eta^6\text{-C}_6\text{H}_6)_2\text{Mo}$] I .⁷ Reagent grade pyridine was distilled from CaH_2 before use. The 1-methylimidazole was

obtained from Aldrich Chemical Co. and used without further purification. Common solvents were reagent grade and used without further purification. Ammonium hexafluorophosphate was purchased from Alfa. Tetra-*n*-butylammonium hexafluorophosphate⁸ and $[\text{Ni}(\text{py})_6](\text{PF}_6)_2$ ⁹ were prepared by published methods. All reactions and purifications were carried out under a prepurified nitrogen or argon atmosphere.

Preparations. Bis(η^6 -benzene)molybdenum(I) Hexafluorophosphate, [$(\eta^6\text{-C}_6\text{H}_6)_2\text{Mo}$] PF_6 . The crude iodide salt obtained by treating a benzene solution of 5.1 g of ($\eta^6\text{-C}_6\text{H}_6$) $_2\text{Mo}$ with 2.6 g of iodine was isolated and taken up in 300 mL of warm methanol. The solution was filtered over Filter Aid and 5 g of NH_4PF_6 dissolved in 25 mL of degassed methanol quickly added. A yellow crystalline solid precipitated almost immediately. After the mixture stood at -15°C for 2 h, the solid was collected, washed with 25 mL of cold methanol (2 \times), and dried in vacuo; yield 6.1 g (76%).

Bis(η^6 -toluene)molybdenum(I) Hexafluorophosphate, [$(\eta^6\text{-MeC}_6\text{H}_5)_2\text{Mo}$] PF_6 . A rapidly stirred solution of 12.3 g of (MeC_6H_5) $_2\text{Mo}$ in 250 mL of benzene was treated dropwise with a solution of 5.5 g of iodine in 74 mL of benzene. The crude iodide salt was collected and taken up in 250 mL of warm methanol. The dark orange solution was filtered over Filter Aid and 11.5 g of NH_4PF_6 in 25 mL of degassed methanol quickly added. The warm solution was reduced under vacuum to a volume of ca. 100 mL. After the mixture stood for 12 h at -15°C , the yellow crystals were collected, washed with 35 mL of cold methanol, and dried in vacuo; yield 14.8 g (79%).

(η^6 -Benzene)tris(pyridine)molybdenum(I) Hexafluorophosphate, [$(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{C}_5\text{H}_5\text{N})_3$] PF_6 . A solution of 1.8 g of [$(\eta^6\text{-C}_6\text{H}_6)_2\text{Mo}$] PF_6 in 5 mL of pyridine was warmed to 55°C for 1.5 h. A total of 50 mL of 95% ethanol was then added slowly at room temperature and the solution cooled to -15°C for 5 h. The dark maroon crystalline solid was collected, washed with 15 mL of cold 95% ethanol, and dried