2042 *Inorg. Chem.* **1993**, *32*, 2042–2048

Synthesis of Sulfido and Oxo Complexes of Technetium(V) and Rhenium(V) Containing Dithiolato and Hydrotris(1-pyrazolyl)borato Ligands. Crystal Structures of Dimeric Bis(μ-ethane-1,2-dithiolato)bis(ethene-1,2-dithiolato)technetium(IV) and [Hydrotris(1-pyrazolyl)borato](ethane-1,2-dithiolato)oxorhenium(V)

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Received October 14, 1992

The new technetium(V) sulfido complexes $[TcS(edt)_2]^-$ (**1**) and $[TcSCl_2(HB(pz)_3)]$ (**3**) have been prepared and characterized. These species constitute the first examples of technetium complexes containing a terminal Tc═S bond. Complex **1** was obtained from $[TcCl_6]^{2-}$ by reaction with ethane-1,2-dithiol (H_2edt), while **3** was formed from $[TcOCl_2(HB(pz)_3)]$ by atom transfer from B_2S_3. The rhenium analog of complex **3**, $[ReSCl_2(HB(pz)_3)]$ (**4**), has been also prepared. In the synthesis of **1**, the dimeric Tc(IV) complex $[Tc_2(edt)_2(e{=}dt)_2]$ (**2**) (e═dt = ethene-1,2-dithiolato) was isolated by precipitation. **2** represents the first example of a technetium complex containing two terminal dithiolene and two bridged dithiolato ligands. The conversion of ethane-1,2-dithiolato to ethene-1,2-dithiolato in the reaction of preparation of **1** and **2** seems to play a key role in the formation of the $[Tc{=}S]^{3+}$ core. The X-ray crystal structure of complex **2** showed the Tc atom in a trigonal prismatic array. **2** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 8.624(4)$ Å, $b = 8.064(4)$ Å, $c = 8.303(5)$ Å, $\alpha = 59.01(4)°$, $\beta = 61.22(5)°$, $\gamma = 65.07°$, $V = 422.1(1.1)$ Å^3, $Z = 1$, $R = 0.052$, and $R_w = 0.059$ for 2065 observed reflections with $F > 3\sigma(F)$. The reactions of various monothiols and dithiols with $[MCl_6]^{2-}$ and $[MOCl_2(HB(pz)_3)]$ (M = Tc, Re) are also discussed. The X-ray crystal structure of one product of these reactions, namely the complex $[ReO(edt)(HB(pz)_3]$ (**5**), has been determined. **5** was monomeric with the Re atom in a distorted octahedral environment. It crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 10.109(5)$ Å, $b = 10.246(3)$ Å, $c = 14.997(5)$ Å, $\beta = 94.01(3)°$, $V = 1549.5(1.0)$ Å^3, $Z = 4$, $R = 0.039$, and $R_w = 0.051$ for 4292 observed reflections with $F > 4\sigma(F)$.

Introduction

The widespread use in nuclear medicine of the compounds of the γ-emitting isomer ^{99m}Tc for obtaining diagnostic images of internal organs and the recent introduction of the β-emitting isotopes ^{188}Re and ^{186}Re for the radiotherapy of abnormal tissues have rapidly expanded the studies of the inorganic chemistry of these elements with the aim to find potentially useful radiopharmaceuticals.[4] Specific efforts have been devoted to the synthesis of complexes containing the M≡N, M═O and *trans*-O═M═O (M = Tc, Re) multiple bonds.[5] In particular, a number of ^{99m}Tc-radiopharmaceuticals containing the $[Tc{=}O]^{3+}$ group (^{99m}Tc-HMPAO,[6] ^{99m}Tc-MAG3[7]) are currently in use in the clinical practice as useful diagnostic tools. Very recently, the first class of ^{99m}Tc radiopharmaceuticals containing the $[Tc{\equiv}N]^{2+}$ group has been discovered.[8] These compounds are under preliminary clinical investigation as potential myocardial imaging agents.

The isoelectronic $[M{=}O]^{3+}$, *trans*-$[O{=}M{=}O]^+$, and $[M{\equiv}N]^{2+}$ (M = Tc, Re) groups are characteristic functional moieties for technetium and rhenium in the +5 oxidation state. We studied the possibility to prepare M(V) compounds containing new terminal ME (E = main group element donor atom) multiple bonds and focused our attempts to the synthesis of the isoelectronic metal–sulfido groups $[M{=}S]^{3+}$. We investigated the following two synthetic routes. The first approach was based on the reactions of various starting complexes of technetium and rhenium with mono- and dithiol ligands as possible sources of S^{2-} groups. Only one example of formation of a terminal metal–sulfido bond by reaction of an excess of ethane-1,2-dithiol with $[ReCl_6]^{2-}$ to produce the rhenium(V) sulfido complex $[ReS(edt)_2]^-$ has been reported.[9] Extension of this reaction to technetium was never attempted. The second approach involved the study of oxygen atom transfer reactions between a starting oxo–M(V) complex and a suitable donor of sulfido groups. In particular, we investigate the reactions of oxotechnetium(V) and oxorhenium(V) complexes containing the hydrotris(1-pyrazolyl)borato ligand, $[HB(pz)_3]^-$. This ligand forms a protective steric nook about the metal atom, thereby restricting the complexes to *facial* six-coordinate geometries and possibly allowing the oxo ligand to be substituted by the sulfido ligand. A similar reaction has been previously applied to the synthesis of the first mononuclear sulfidomolybdenum(V) complex, $[MoSCl_2(HB(Me_2pz)_3)]$,[10] and of sulfido-

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0020-1669/93/1332-2042$04.00/0

molybdenum(IV) complexes $[MoS(HB(Me_2pz)_3)(S_2CNR_2)]$ (R = Me, Et, *n*-Pr, *n*-Bu).[11]

We report here the results of this investigation, which led to the synthesis of the first two mononuclear terminal sulfidotechnetium(V) complexes, $[TcS(edt)_2]^-$ and $[TcSCl_2(HB(pz)_3)]$, and of various supplementary complexes containing sulfur ligands. The X-ray crystal structure of the auxiliary Tc(IV) complex $[Tc_2(edt)_2(e{=}dt)_2]$, isolated during the preparation of $[TcS(edt)_2]^-$, will be discussed. This compound represents the first example of a complex containing two terminal dithiolene and two bridging dithiolato ligands and is a rare example of a dimeric technetium complex including only sulfur atoms in the core Tc_2S_8. The crystal structure of the oxorhenium(V) complex $[ReO(HB(pz)_3)(edt)]$ will be also reported. A preliminary report on the preparation of the complexes $[MSCl_2(HB(pz)_3)]$ (M = Tc, Re) has been communicated.[12]

Acronyms and Abbreviations

The following acronyms and abbreviations are used: edt, ethane-1,2-dithiolato; S–Et; ethanethiolato; e=dt, ethene-1,2-dithiolato; bdt, benzene-1,2-dithiolato; tdt, toluene-3,4-dithiolato; dto, dithiooxalato; mnt, 1,2-dicyanoethene-1,2-dithiolato; HB(pz)$_3$, hydrotris(1-pyrazolyl)borato; HB(Me$_2$pz)$_3$, hydrotris(3,5-dimethyl-1-pyrazolyl)borato; DMSO, dimethyl sulfoxide; NBA, nitrobenzyl alcohol; TMS, tetramethylsilane.

Experimental Section

Caution! Technetium-99 emits a low energy β-particle (0.292 MeV) with half-life of 2.12×10^5 years. When handled in milligram amounts, it does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. All operations were performed in a laboratory approved for low-level radioactivity with monitored hoods and gloveboxes.

Reagents. Unless otherwise noted, all chemicals were of reagent grade and were used without further purification. Technetium-99 as $[NH_4][TcO_4]$ was obtained from the Radiochemical Centre, Amersham, England. B_2S_3, H_2edt, and tetraphenylarsonium chloride (AsPh$_4$Cl) were purchased from Aldrich. KHB(pz)$_3$ was prepared as reported elsewhere.[13] The complexes $K_2[MCl_6]$[14] and $[MOCl_2(HB(pz)_3)]$[15] (M = Tc, Re) were synthesized according to literature methods. The Tc(IV) complex $[TcCl_3(HB(pz)_3)]$ was never reported before and was obtained in the following way. A 0.5-mL volume of concentrated HCl was mixed with 5 mL of EtOH in a sealed vial. KHB(pz)$_3$ (0.25 g, 1.0 mmol) was then added to the solution followed by $[AsPh_4][TcOCl_4]$ (0.21 g, 0.33 mmol). The sealed vial was heated for 5 min at 100 °C, and the sudden precipitation of an orange powder was observed. The solid was filtered out, washed with EtOH and Et$_2$O, and recrystallized from CH$_2$Cl$_2$/EtOH to give orange crystals of the final compound. We found that the immediate precipitation of the orange compound was essential for its isolation. When no precipitation occurred, the solution became deep red and, after evaporation, gave only an intractable red-brown oily residue. The product $[TcCl_3(HB(pz)_3)]$ was characterized[16] by elemental analysis, IR, ^{1}H NMR and mass spectra, and magnetic susceptibility measurements in solution by the Evans method.[17]

Measurements. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 984 spectrometer using KBr pellets or Nujol mulls between CsI disks. UV–vis spectra were obtained on a Cary 17D spectrophotometer. Mass spectra were recorded by using a VG 7070E spectrometer with ionization effected by electron impact. FAB mass spectra were recorded in a NBA matrix using a VG 30-250 spectrometer at room temperature. Proton NMR spectra were run on a Bruker AC-200 instrument using TMS as internal reference. Magnetic susceptibilities measurements by the Evans method[17] were performed on the same apparatus. Conductivity measurements in solution were made at 298 K using a Metrohm Herison E518 conductivimeter.

Preparation of $[AsPh_4][TcS(edt)_2]$ (1). $K_2[TcCl_6]$ (0.060 g; 0.15 mmol) was suspended in MeOH (5 mL), and H_2edt (0.1 mL, 1.2 mmol) and triethylamine (0.1 mL, 0.72 mmol) were added to the resulting pale yellow suspension. The mixture was heated at reflux temperature for 5 h under an argon atmosphere. A dark precipitate formed, and the solution was blood-red colored. The mixture was allowed to cool at room temperature and successively filtered to separate the dark precipitate (vide infra). After addition of AsPh$_4$Cl (0.075 g, 0.17 mmol) to the red filtrate, the solution was left stand in the refrigerator overnight to give both dark and white precipitates. These solids were filtered out and washed with acetone until no additional dark precipitate dissolved. The acetone solution was rotoevaporated to dryness and the residue redissolved in the minimum amount of CH$_2$Cl$_2$ (1.5 mL). The resulting dark-red solution was loaded onto a silica-gel column previously conditioned and then eluted with an acetone/CH$_2$Cl$_2$ (1:9) mixture. The second (of three), wide, dark-brown band was collected, and the solution was reduced in volume to 2 mL. Treatment with diethyl ether caused the formation of a blood-red solid, which was filtered out and dried on a vacuum pump. (Yield: 15% based on the starting ^{99}Tc.) Anal. Calcd for $TcC_{28}H_{28}S_5As$: C, 48.13; H, 4.04; S, 22.94. Found: C, 47.76; H, 4.05; S, 22.28. IR (KBr, cm^{-1}): 1482 (m), 1436 (s), 1262 (m), 1080 (m), 997 (m), 742 (s), 735 (s), 689 (m), 520 (m) [ν(Tc=S)], 477 (m), 461 (m). FAB$^-$ MS (DMSO, TEA solution): *m/z* 315 (M$^-$). UV–vis (MeOH, nm): 635, 535 (sh), 455 (sh), 410 (sh), 365, 314 (sh). ^{1}H NMR [(CD$_3$)$_2$CO, 200 MHz]: δ 7.87 (m, 20 H), 3.00 [m(AA′BB′), 8 H]. The complex is diamagnetic in acetone solution.

The reaction described above carried out using $[MCl_6]^{2-}$ (M = Tc, Re) and propane-1,3-dithiol or butane-1,4-dithiol gave rise to intractable oils, while the use of H_2bdt or H_2tdt led to the isolation of the tris-substituted complexes $[M(bdt)_3]^-$ and $[M(tdt)_3]^-$. These compounds have been characterized by element analysis and by comparison of their IR and ^{1}H NMR spectra with those of the identical products and other similar tris-substituted complexes reported previously.[18]

Preparation of $[Tc_2(edt)_2(e{=}dt)_2]$ (2). This product was obtained during the preparation of complex **1**. The dark microcrystalline solid isolated by filtration from the reaction mixture (vide supra) was washed with CH$_3$CN, acetone, MeOH, and diethyl ether and then dissolved in CHCl$_3$ (CH$_2$Cl$_2$) to produce a bright emerald green solution, from which nearly perfect parallelepipeds suitable for X-ray analysis were obtained by slow evaporation in air. (Yield: 20% based on the starting ^{99}Tc.) Anal. Calcd for $Tc_2C_8H_{12}S_8$: C, 17.07; H, 2.15; S, 45.58. Found: C, 17.40; H, 2.25; S, 44.82. IR (KBr, cm^{-1}): 1277 (m), 1231 (m), 841 (m), 722 (s), 368 (m). UV–vis (CH$_2$Cl$_2$, nm): 605, 422, 318, 258. ^{1}H NMR (CDCl$_3$): δ 3.71 (s, 4H), 2.96 (s, 4H), 2.15 (s, 4H). Compound **2** is diamagnetic in CHCl$_3$ solution.

Preparation of $[MSCl_2(HB(pz)_3)]$ [M = Tc (3), Re (4)]. We describe here a slight modification of the procedure reported previously[12] for the synthesis of these complexes, which does not require the use of anhydrous solvents and takes place in shorter reaction times. A solution of $[MOCl_2(HB(pz)_3)]$ (0.38 mmol) in CH$_2$Cl$_2$ (10 mL) was placedd in a test tube, and an argon flow was passed through the solution for 5 min at room temperature. B_2S_3 (0.12 g, 1.0 mmol) was then added as a solid, and the test tube was sealed with a Teflon cap. The resulting suspension

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Table I. ^{1}H NMR Chemical Shifts of Hydrotris(1-pyrazolyl)borate-Containing Complexes[a,b]

	pyrazolyl rings										
	trans to O			trans to Cl			trans to S				
complex	α	β	γ	α	β	γ	α	β	γ	B–H	others
$[TcOCl_2(HB(pz)_3]$	7.26	5.81	7.22	8.45	6.62	7.92				4.50 br q	
$[ReOCl_2(HB(pz)_3]$	7.46	5.95	7.34	8.23	6.57	7.90				4.55 br q	
[ReOCl(S–Et)(Hb(pz)$_3$]	7.47	5.96	7.33	8.32	6.52	7.90	8.24	6.46	7.81		1.57 (t, CH_3), 4.14 (br s, CH_2)
[ReO(S–Et)$_2$(HB(pz)$_3$]	7.69	5.96	7.37				8.32	6.44	7.78		1.52 (t, CH_2), 3.95 (br s, CH_2)
[ReO(edt)(HB)pz)$_3$]	7.25	5.78	7.23				8.42	6.45	7.87		3.95–3.58 (AA′BB′)

[a] $CDCl_3$ solutions. Abbreviations: br = broad; qt = quartet. [b] See Figure 2 for proton assignments; doublet for α and γ protons, triplet for β protons.

was heated at 80 °C in the sealed test tube for 10 min. After the suspension was cooled at room temperature, a weak flow of argon was passed through the reaction solution using a capillary until a gray-white precipitate began to form. This solid was filtered out and discarded, and an additional argon stream was passed through the filtrate. A microcrystalline powder (dark green for Tc and blue-ink for Re) was obtained, washed with hexane, and stored in a sealed vial filled with argon. (Yield: 22% for Tc, 43% for Re based on the starting metal complexes.) Anal. Calcd for $TcC_9H_{10}BN_6SCl_2$: C, 26.05; H, 2.43; N, 20.29; S, 7.72; Tc, 23.86. Found: C, 26.12; H, 2.46; N, 20.32; S, 7.66; Tc, 23.73. IR (Nujol mulls, cm^{-1}): 2510 (m) [ν(B–H)]; 350, 300 (m) [ν(Tc–Cl)]. EI MS (m/z): 414 (M), 379, 381 (M – Cl), 344 (M – 2Cl), 312 (M – 2Cl – S). Anal. Calcd for $ReC_9H_{10}BN_6SCl_2$: C, 21.52; H, 2.01; N, 16.73; S, 6.38. Found: C, 21.54; H, 2.04; N, 16.78; S, 6.29. IR (KBr, cm^{-1}): 2460 (m) [ν(B–H)], 330, 300 (m) [ν(Re–Cl)]. EI MS (m/z): 502 (M), 469, 467, 465 (M – Cl), 432, 430 (M – 2Cl), 400, 398 (M – 2Cl – S). Compounds **3** and **4** are diamagnetic in CH_2Cl_2 solutions.

Preparation of [ReO(edt)(HB(pz)$_3$)] (5). To a suspension of $[ReOCl_2(HB(pz)_3)]$ (100 mg, 0.20 mmol) in EtOH (10 mL) were added H_2edt (0.1 mL, 1.0 mmol) and triethylamine (0.1 mL, 0.72 mmol) at reflux temperature. The resulting brown solution was further heated for 4 h to yield a brown, microcrystalline solid, which was washed with EtOH and diethyl ether and recrystallized from CH_2Cl_2/EtOH to afford red-brown crystals suitable for X-ray analysis. (Yield: 60% based on the starting Re complex.) The same red-brown crystals were obtained from the reaction solution by carrying out the above reaction at room temperature, for 4 days, in the presence of a great excess of the dithiol (1:20). (Yield: 44%.) Anal. Calcd for $ReC_{11}H_{14}BN_6OS_2$: C, 26.03; H, 2.78; N, 16.56. Found: C, 25.51; H, 2.81; N, 15.99. IR (KBr, cm^{-1}): 3152 (w), 3123 (m), 3102 (m), 2517 (m) [ν(B–H)], 951 (s) [ν(Re=O)]. Λ_M (CH_3CN): 2.14 Ω^{-1} cm^2 mol^{-1} (neutral). UV–vis [CH_3CN, nm (ϵ)]: 530 (230) (sh), 375 (3800), 315 (3150). ^{1}H NMR: see Table I.

Preparation of [ReO(S–Et)$_2$(HB(pz)$_3$)] (6). To a suspension of $[ReOCl_2(HB(pz)_3)]$ (150 mg, 0.3 mmol) in EtOH (10 mL) were added HSEt (46 μL, 0.61 mmol) and triethylamine (0.05 mL, 0.36 mmol) at reflux temperature, and the heating was continued for 24 h. The solution was then cooled at room temperature, and its volume reduced by passing a nitrogen stream until a brown powder began to form. The resulting mixture was loaded onto a silica-gel column and eluted with EtOH. The first brown band was collected and evaporated to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2/MeOH at –10 °C affording a brown microcrystalline material. (Yield: 50% based on the starting Re complex.) Anal. Calcd for $ReC_{10}H_{20}BN_6OS_2$: C, 23.95; H, 4.02; N, 16.76. Found: C, 24.07; H, 382; N, 16.30. IR (KBr, cm^{-1}): 3117 (m), 2482 (m) [ν(B–H)], 942 (s), 932 (s) [ν(Re=O)]. Λ_M (CH_3CN): 2.14 Ω^{-1} cm^2 mol^{-1} (neutral). UV–vis [CH_3CN, nm (ϵ)]: 540 (70) (sh), 368 (2050), 246 (2000). ^{1}H NMR: see Table I.

Preparation of [ReOCl(S–Et)(HB(pz)$_3$)] (7). To a suspension of $[ReOCl_2(HB(pz)_3)]$ (150 mg, 0.3 mmol) in EtOH (10 mL) was added HSEt (23 μL, 0.3 mmol) at reflux temperature. The heating was continued for 3 h. The resulting dark green solution deposited a blue-green powder during evaporation of the solvent by passing an argon stream. The precipitate was collected by filtration and purified by column chromatography on Sephadex LH-20 (eluant EtOH). The first dark-green band was recovered, the solvent rotoevaporated, and the residue recrystallized from CH_2Cl_2/hexane at –10 °C. (Yield: 30% based on the starting Re complex.) Anal. Calcd for $ReC_8H_{15}BN_6OSCl$: C, 20.19; H, 3.17; N, 17.66. Found: C, 20.51; H, 3.23; N, 17.81. IR (KBr, cm^{-1}): 3151 (w), 2491 (m) [ν(B–H)], 961 (s) [ν(Re=O)], 336 (w) [ν(Re–Cl)]. Λ_M (CH_3CN): 1.53 Ω^{-1} cm^2 mol^{-1} (neutral). UV–vis [acetonitrile, nm (ϵ)]: 620 (260), 365 (3450), 260 (16 700). ^{1}H NMR: see Table I.

Reactions of $[TcOCl_2(HB(pz)_3)]$ and $[TcCl_3(HB(pz)_3)]$ with H_2edt and HS–Et. The results of these reactions were inconclusive. Mixing excess of H_2edt or HSEt with $[TcOCl_2(HB(pz)_3)]$ or $[TcCl_3(HB(pz)_3)]$ in CH_2Cl_2 or MeOH yielded deep red-violet solutions, which after evaporation under an argon stream gave rise to the precipitation of red-violet powders. The IR spectra of these products showed no band assignable to the Tc=O bond vibration in the range 850–1000 cm^{-1} and showed the presence of the characteristic bands of the $HB(pz)_3^-$ ligand. These results were confirmed by mass spectral analyses. However, treatment of these compounds with various solvents led to extensive decomposition, which prevented their full characterization.

Table II. Crystallographic Data for **2** and **5**

	2	**5**
empirical formula	$C_8H_{12}S_8Tc_2$	$C_{11}H_{14}BN_6OReS_2$
fw	562.6	507.4
cryst system	$P\bar{1}$	$P2_1/c$
a, Å	8.624(4)	10.109(5)
b, Å	8.064(4)	10.246(3)
c, Å	8.303(5)	14.997(5)
α, deg	59.01(4)	
β, deg	61.22(5)	94.01(3)
γ, deg	65.07(3)	
V, Å^3	422.1(1.1)	1549.5(1.0)
Z	1	4
λ, Å (Mo Kα)	0.710 73	0.710 73
D_{calcd}, g cm^{-3}	2.21	2.18
D_{meas}, g cm^{-3}	2.2	2.2
μ, cm–^{1} (Mo Kα)	23.9	82.2
I_{max}/I_{min}	1.0/0.63	1.0/0.71
T, °C	23	21
residuals, %: R, R_w[a]	5.2, 5.9	4.0, 5.2

[a] $R = \sum|\Delta|/\sum|F_o|$; $R_w = (\sum w|\Delta|^2/\sum w|F_o|^2)^{1/2}$

Crystallographic Data Collection and Refinement of the Structure. Single crystals suitable for X-ray analysis were grown by slow evaporation of a $CHCl_3$ solution of **2** and from a CH_2Cl_2/MeOH (1:1) solution of **5**. The crystal structures were determined using a Nicolet Siemens R3m/V diffractometer. Crystallographic data are reported in Table II, while other parameters related to data collection and refinement have been deposited as supplementary material. An empirical method, based on the ψ-scans of six reflections (at $\chi \approx 90°$) at different azimuthal angles, was used for the calculation of the absorption correction. Heavy-atom parameters were found from Patterson synthesis, and all non-H atoms were located in subsequent difference Fourier syntheses. Fractional atomic coordinates and thermal parameters for **2** and **5** are listed in Table III, while Table IV reports some relevant interatomic distances and angles. The SHELXTL-PLUS package of computer programs[19] was employed for the solution and refinement of the structures.

Results

Synthesis. The new technetium(V) sulfido complex $[TcS(edt)_2]^-$ (**1**) was prepared, in low yield, from the reaction of the hexachlorotechnetium(IV) complex $[TcCl_6]^{2-}$ with excess of H_2edt, in MeOH and at reflux temperature. Complex **1** was recovered from the reaction solution after addition of $AsPh_4Cl$. However, **1** does not constitute the main product of the reaction of $[TcCl_6]^{2-}$ with H_2edt. Precipitation of the dimeric, dark-green Tc(IV) complex $[Tc_2(edt)_2(e{=}dt)_2]$ (**2**) was also observed nearly immediately after the mixing of the reagents. Complex **2** is stable

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(19) Sheldrick, G. M. SHELXTL-PLUS: An Integrated System for Solving, Refining and Displaying Crystal Strutures from Diffraction Data. University of Göttingen, Germany, 1987 (for Nicolet R3m/V).

Table III. Fractional Atomic Coordinates of the Non-hydrogen Atoms and Equivalent Thermal Parameters for **2** and **5**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å$^{2\,a}$
		$Tc_2(edt)_2(e{=}dt)_2$ (**2**)		
Tc	0.3376(1)	0.4649(1)	0.5988(1)	0.017
S(1)	0.5757(3)	0.2978(3)	0.3884(4)	0.022
S(2)	0.5754(3)	0.2978(3)	0.7382(3)	0.023
S(3)	0.2072(3)	0.1959(3)	0.7985(4)	0.031
S(4)	0.0429(3)	0.6476(3)	0.6549(3)	0.030
C(1)	0.6718(14)	0.0508(13)	0.5491(16)	0.033
C(2)	0.6731(14)	0.0506(13)	0.7283(14)	0.032
C(3)	–0.0385(17)	0.2833(21)	0.8691(33)	0.095
C(4)	–0.1145(14)	0.4861(19)	0.8148(24)	0.058
		$[ReO(edt)(HB(pz)_3)]_3$ (**5**)		
Re	0.2997(1)	0.1189(1)	0.3837(1)	0.031
O	0.3095(9)	0.1242(12)	0.4969(6)	0.040
S(1)	0.5148(4)	0.1152(45)	0.3470(3)	0.043
S(1a)	0.2957(4)	0.3371(4)	0.3478(3)	0.040
N(1)	0.2343(13)	0.0891(12)	0.2346(9)	0.041
N(2)	0.1435(13)	–0.0086(14)	0.2092(9)	0.046
N(3)	0.0853(13)	0.1037(12)	0.3842(8)	0.033
N(4)	0.0129(12)	0.0104(12)	0.3427(8)	0.037
N(5)	0.2964(11)	–0.0895(11)	0.3732(7)	0.031
N(6)	0.1927(13)	0.1563(13)	0.3352(9)	0.042
B	0.0787(19)	–0.0863(9)	0.2800(12)	0.043
C(1)	0.0075(15)	0.1708(16)	0.4366(10)	0.040
C(2)	–0.1245(17)	0.1150(18)	0.4258(11)	0.048
C(3)	–0.1141(18)	0.0147(18)	0.3653(12)	0.049
C(4)	0.3808(17)	–0.1731(16)	0.4146(11)	0.042
C(5)	0.3251(20)	–0.2983(23)	0.4067(13)	0.063
C(6)	0.2060(18)	–0.0095(18)	0.1189(120	0.047
C(8)	0.2078(17)	0.0878(17)	0.0867(13)	0.048
C(9)	0.2751(15)	0.1450(17)	0.1613(10)	0.040
C(10)	0.5590(20)	0.2856(19)	0.3212(13)	0.063
C(11)	0.4710(17)	0.3843(20)	0.3607(12)	0.055

[a] U_{eq} is defined as one-third the trace of the $\mathbf{U}_{ij}$ matrix.

and does not undergo conversion to **1** when refluxed in $CHCl_3$, also in the presence of excess of H_2edt. In contrast, complex **1** can be converted to the corresponding orange monooxo complex $[TcO(edt)_2]^-$ [20] by refluxing it in CH_2Cl_2 ($CHCl_3$) under aerobic conditions. This indicates that the $[Tc{=}S]^{3+}$ group in **1** is unstable and can easily rearrange to the isoelectronic $[Tc{=}O]^{3+}$ group by transfer of an oxygen atom. The formation of $[TcO(edt)_2]^-$ during the preparation of **1** was prevented by carrying out the reaction under an argon atmosphere.

The complexes $[M^{IV}Cl_6]^{2-}$ (M = Tc, Re) reacted with propane-1,3-dithiol and butane-1,4-dithiol to give intractable oily residues, while their reactions with H_2bdt and H_2tdt afforded the tris-substituted complexes $[M(bdt)_3]^-$ and $[M(tdt)_3]^-$. Identical or similar tris-substituted products have been characterized previously.[18] No evidence of the formation of the $[M{=}S]^{3+}$ cores was found in these preparations.

The reaction of the monooxo complex $[TcOCl_2(HB(pz)_3)]$ with B_2S_3 under strictly anhydrous conditions leads to the formation of the technetium(V) sulfido complex $[TcSCl_2(HB(pz)_3)]$ (**3**), in which the oxo group has been substituted by the sulfido group. The same synthetic procedure carried out with the analogous rhenium complex $[ReOCl_2(HB(pz)_3)]$ gave rise to the sulfido derivative $[ReSCl_2(HB(pz)_3)]$ (**4**). These reactions have been described in detail previously.[12] The compounds **3** and **4** are unstable in solution and are easily converted back to the corresponding monooxo complexes $[MOCl_2(HB(pz)_3)]$ (M = Tc, Re) under aerobic conditions. Their preparations therefore require the careful exclusion of atmospheric oxygen and of water from both the starting materials and solvents. A slight improvement of the synthetic procedure for preparing **3** and **4** was obtained by carrying out the reactions in a sealed test tube filled with argon. This method does not require the use of anhydrous solvents and reactants (see Experimental Section).

Table IV. Selectd Interatomic Distances (Å) and Angles (deg) for **2** and **5**

	Compound **2**		
Tc–S(1)	2.392(5)	Tc–S(1a)	2.392(7)
Tc–S(2)	2.390(6)	Tc–S(2a)	2.394(4)
Tc–S(3)	2.297(6)	C(1)–C(2)	1.49(2)
Tc–S(4)	2.293(5)	C(3)–C(4)	1.39(2)
Tc–Tc′	2.610(3)		
S(1)–Tc–S(2)	74.8(2)	Tc–S(3)–C(3)	109.1(6)
S(1)–Tc–S(3)	91.4(2)	Tc–S(4)–C(4)	110.7(5)
S(1)–Tc–S(4)	142.4(2)	Tc–S(1)–Tc′	66.1(1)
S(2)–Tc–S(3)	91.4(2)	Tc–S(2)–Tc′	66.1(1)
S(2)–Tc–S(4)	142.4(2)	S(1)–C(1)–C(2)	112.8(8)
S(3)–Tc–S(4)	84.4(2)	S(2)–C(2)–C(1)	112.4(8)
Tc–S(1)–C(1)	107.9(4)	S(3)–C(3)–C(4)	119.1(1.5)
Tc–S(2)–C(2)	108.2(4)	S(4)–C(4)–C(3)	116.4(1.3)
	Compound **5**		
Re–O	1.694(9)	Re–N(5)	2.14(1)
Re–S(1)	2.280(4)	N(1)–N(2)	1.39(2)
Re–S(2)	2.299(4)	N(3)–N(4)	1.33(2)
Re–N(1)	2.31(1)	N(5)–N(6)	1.34(2)
Re–N(3)	2.17(1)	B–N mean	1.53(2)
O–Re–S(1)	104.6(3)	N(3)–Re–N(5)	85.3(4)
O–Re–S(2)	101.7(4)	Re–S(1)–C(10)	106.4(7)
O–Re–N(1)	165.4(5)	Re–S(2)–C(11)	103.3(7)
O–Re–N(3)	89.2(4)	S(1)–C(10)–C(11)	113.3(1.4)
O–Re–N(5)	96.5(4)	S(2)–C(11)–C(10)	112.2(1.4)
S(1)–Re–S(2)	87.8(2)	N–B–N mean	107.2(1.1)
S(1)–Re–N(3)	165.4(3)	Re–N–N mean	122.5(8)
S(2)–Re–N(5)	162.3(3)		

When the complex $[ReOCl_2(HB(pz)_3)]$ was reacted with H_2edt and HS–Et, the monosubstituted complexes $[ReO(edt)(HB(pz)_3)]$ (**5**) and $[ReOCl(S{-}Et)(HB(pz)_3)]$ (**7**) and the disubstituted complex $[ReO(S{-}Et)_2(HB(pz)_3)]$ (**6**) were obtained depending on the metal/ligand stoichiometric ratio. Similar products have been reported recently, but their syntheses were carried out under strictly anhydrous conditions using standard Schlenk techniques and dry solvents.[21] Once again, the formation of the $[Re{=}S]^{3+}$ core was not detected in these conditions. In contrast, the same reactions carried out with the complexes $[TcOCl_2(HB(pz)_3)]$ and $[TcCl_3(HB(pz)_3)]$ led to the isolation of deep-violet compunds in very low yields, in which the $[Tc{=}O]^{3+}$ core was lost. We failed however to obtain a full characterization of these products due to their high instability in solution.

Discussion

We discuss first in this section the crystal structures of compounds **2** and **5** in order to clarify their relationships with the structures of other thiol-containing complexes of technetium and rhenium and to make simpler the discussion on the synthesis of the new sulfido complexes **1**, **3**, and **4**.

Crystal Structure of $[Tc_2(edt)_2(e{=}dt)_2]$ (2). The first technetium dithiolate complexes structurally characterized were $\{Tc^VO[SCH_2C(O)S]_2\}$ [22] and $[Tc^VO(edt)_2]^-$.[20] Recently, a number of complexes of this type has been extensively studied, and in particular, the compounds $[Tc^VO(bdt)_2]^-$,[23] $[Tc^V(bdt)_3]^-$,[18] $[Tc^VO(mnt)_2]^-$,[24] $[Tc^{IV}(mnt)_3]^{2-}$,[25] $[Tc^VO(dto)_2]^-$,[26] and $[Tc^VN(dto)_2]^{2-}$ [26] have been fully characterized. Until now, the only examples of dimeric species with Tc–S–Tc bridges are $[(Tc^VO)_2$-

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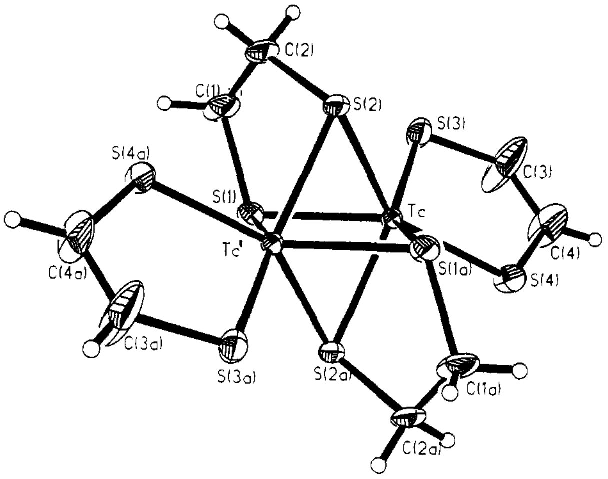

Figure 1. ORTEP (Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1980) diagram of complex **2**. Thermal ellipsoids are at the 50% probability level.

(edt)$_3$] [27] and [Tc$^{IV}_2$(bdt)$_4$]·CHCl$_3$,[28] and relative few complexes of the type [M$^{III}_2$(edt)$_4$] (M = V, Mn, Fe, Co) have been reported.[29] **2**, therefore, represents the first example of a complex containing two terminal dithiolene and two bridging dithiolato ligands. Figure 1 illustrates the molecular geometry and the atom labeling scheme for complex **2**. Two ethanedithiolato groups provide four μ^2-sulfur atoms [S(1), S(2), S(1′), S(2′)] to yield a quadruply bridged Tc(IV) dimer [mean Tc–S$_{br}$ = 2.392(5) Å]. Each technetium atom is additionally coordinated to a terminal ethenedithiolato group [mean Tc–S$_{ter}$ = 2.295(5) Å]. The complex lies on an inversion center and possesses an exact C_i point symmetry. The Tc$_2$S$_8$ inner core contains each technetium atom coordinated in a trigonal prismatic array, as shown by the value of the twisting angle[30] (ϕ = 6.0°) between the upper S(4)S(1′)S(2′) triangular face and the lower S(1)S(2)S(3) triangular face. These two faces are normal to the S(3)TcS(4) plane. The structural parameters listed in Table IV are quite normal and parallel those of the closely similar compound [Tc$_2$(bdt)$_4$]·CHCl$_3$,[28] some minor differences being the Tc–S(1′) bond length (2.392 vs. 2.416 Å), the S(1)···S(2′) contact (2.76 vs 2.81 Å), and the S(2)–Tc–S(4) angle (142.4 vs 140.7°). As expected, the C(1)–C(2) and C(3)=C(4) bond lengths are different being 1.49 and 1.39 Å, respectively, and both the C(1) and C(2) atoms are out 1.14 Å from the S(1)TcS(2) plane. The geometrical features and bond lengths and angles for complex **2** are in good agreement with those found in tris(1,2-dithiolene)[31] and tris(1,2-dithiolato)[18] complexes.

Crystal Structure of [ReO(edt)(HB(pz)$_3$)] (5). An alternative procedure for the preparation of this complex was also described by Degnan et al.,[21] but the determination of its crystal structure was never reported. The molecular geometry and the atom-numbering scheme of complex **5** are shown in Figure 2. The structure consists of discrete molecules, each containing the rhenium atom in a distorted octahedral environment. The equatorial plane of the octahedron is formed by the two sulfur atoms of the dithiolato ligand and the N(3) and N(5) donor atoms of two pyrazole rings. The N(1) atom of the third pyrazole ring and the multiply bonded oxygen are trans to each other in axial positions. Distorions from the ideal octahedral geometry result in (i) the Re atom lying out of the mean of the equatorial plane by 0.31 Å toward the yl-oxygen, (ii) a bent O–Re–N(1) axis of 165.4(5)° accompanied by S(1)–Re–N(3) and S(2)–Re–N(5) angles of 165.4(5) and 162.3(3)°, respectively, and (iii) the N(1)···N(3) edge distance (2.79 Å) being shorter than S(1)···S(2) distance (3.17 Å) and consequently the N(1)–Re–N(3) "bite" angle (77.1°) being narrower than the S(1)–Re–S(2) angle (87.8°). The three pyrazolyl rings are strictly planar, while the five-memberd ReS$_2$C$_2$ ring exhibits an envelope form with C(11) displaced by 0.620 Å above the mean plane of the other four atoms. The bond lengths and angles (Table IV) do not differ significantly from the expected values. The molecular packing of the four molecules in the unit cell does not contain interatomic contacts shorter than the sum of the van der Waals radii.

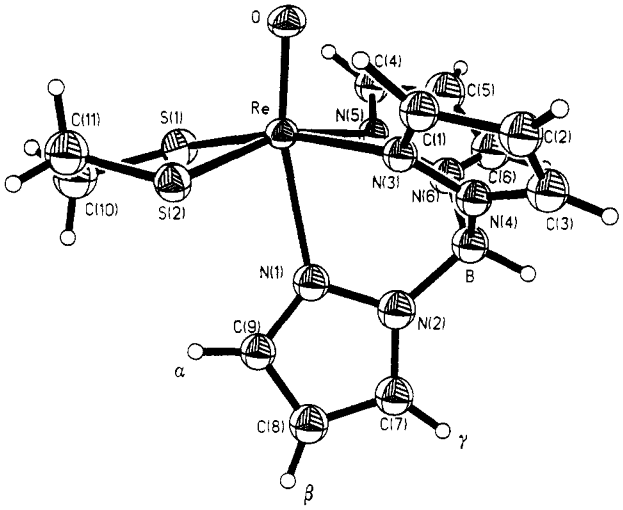

Figure 2. ORTEP diagram of complex **5**. Thermal ellipsoids are at the 50% probability level.

Reactions. According to the literature, the reaction of 2 equiv of H$_2$edt with [Re^{V}OX$_4$]$^-$ (X = Cl, Br) in THF affords the orange complex [Re^{V}O(edt)$_2$]$^-$ by ligand exchange.[32] The same product could be obtained by reduction of [ReO$_4$]$^-$ with NaBH$_4$ in the presence of H$_2$edt.[32] Similarly, the ligand-exchange reaction of H$_2$edt on [Tc^{V}OCl$_4$]$^-$ or [Tc^{V}O(gluconate)]$^-$ in alkaline water/EtOH mixtures or the reduction of [TcO$_4$]$^-$ by sodium dithionite in the presence of excess of H$_2$edt yields the orange [Tc^{V}O(edt)$_2$]$^-$ complex.[32-34] A stable side product, namely the dinuclear complex [(Tc^{V}O)$_2$(edt)$_3$], has been also been reported.[27] A common feature of these reactions is that they give rise to complexes containing the [M=O]$^{3+}$ core (M = Tc, Re) without formation of the isoelectronic [M=S]$^{3+}$ core. In contrast, treatment of the complex [Re^{IV}Cl$_6$]$^{2-}$ with excess of H$_2$edt, in the presence of Et$_3$N, yields the red-brown compound [Re^{V}S(edt)$_2$]$^-$ containing a terminal rhenium–sulfido group.[9] It was proposed that the source of sulfido ligands in this reaction is the dithiolate itself, which should undergo a degradation process with the concomitant formation of ethylene as stable byproduct.[9] In the attempt to prepare the analogous technetium–sulfido complex [Tc^{V}S(edt)$_2$]$^-$, we used to same synthetic approach by treating a suspension of [Tc^{IV}Cl$_6$]$^{2-}$ in MeOH with excess H$_2$edt, in the presence of Et$_3$N as deprotonating agent. Through this route, we successfully isolated the sulfido derivative [Tc^{V}S(edt)$_2$]$^-$ (**1**) along with the dimeric complex [Tc$^{IV}_2$(edt)$_2$(e=dt)$_2$] (**2**). Unexpectedly, we found that complex **2** incorporates two terminal ethene-1,2-dithiolato ligands (e=dt) coordinated to two different Tc(IV) centers, which are further joined by two edt bridges (Figure 1).

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Table V. Comparison of Spectroscopic Properties of $[Me(edt)_2]^-$ Complexes (M = Tc; Re; E = O, S)[a]

	Tc		Re	
	E═O	E═S	E═O	E═S
ν(M═E),[b] cm^{-1}	935	520	952	517
λ_{max} (ϵ)[c]	482 (sh) 433 (sh) 399 (3400) 279 (7750)	635 (40) 535 (sh) 455 (sh) 410 (sh) 365 (5000) 314 (sh)	480 (sh) 416 (600) 362 (sh) 329 (4400)	640 (15) 555 (600) 456 (sh) 403 (4400) 326 (9200)
^1H chem shift (CH_2–CH_2)[d]	3.19–2.95 (AA′BB′)[f]	3.17–2.83[e] (AA′BB′)	2.93–2.81 (m)	2.84–2.72 (m)

[a] Free H_2edt ($CDCl_3$, ppm): δ 2.75 (4H, CH_2–CH_2); 1.69 (2H, S–H). [b] KBr pellets or Nujol mulls. [c] MeCN solutions (10^{-4} mol dm^{-3}): λ (nm), ϵ (dm^3 mol^{-1} cm^{-1}). [d] $CDCl_3$ solutions (ppm). [e] Me_2CO solutions. [f] Multiplicituy, m = multiplet.

It is evident that, under this conditions, the only source of e═dt ligands can be H_2edt, which presumably undergoes an oxidative process with formation of a C═C bond and of molecular hydrogen. In fact, no detectable amounts of H_2e═dt were found in the proton NMR spectrum of free H_2edt and by HPLC analysis. Although in the synthesis of $[Re^VS(edt)_2]^-$ the formation of the analogous rhenium complex of **2** was not observed, the isolation of **2** supports a possible mechanism involving the conversion $H_2edt \rightarrow H_2e$═dt as a preliminary step.[9] It is reasonable to assume that this conversion should require the intervention of the metal ion and the production of some reduced hydrogen species. It remains, however, still obscure the exact pathway generating the production of S^{2-} groups and causing the net reduction of H_2edt to ethylene. We failed to observe any conversion of **2** into **1** by refluxing it in $CHCl_3$, also in the presence of excess of H_2edt. This might indicate that complex **2** is not intermediate in the formation of **1**. Morever, while the net reduction of H_2edt to C_2H_4 in the reaction of $[ReCl_6]^{2-}$ with H_2edt may also account for the formal oxidation from Re^{IV} to Re^V, the fact that the formal oxidation state of the technetium ion in complex **2** remains unchanged compared with the starting $[Tc^{IV}Cl_6]^{2-}$ complex suggests that $[Tc^{IV}_2(edt)_2(e$═$dt)_2]$ is probably a side product in the formation of complex **1**, arising *after* the oxidation of H_2edt to H_2e═dt operated by an undetermined foregoing process. The ethylene production seems to play a key role in the synthesis of the $[M$═$S]^{3+}$ groups (M = Tc, Re) from $[MCl_6]^{2-}$. Attempts to obtain the metal–sulfido bond using propane-1,3-dithiol or butane-1,4-dithiol gave only intractable products, while arenedithiols such as H_2edt and H_2tdt yielded the tris-substituted complexes $[M(bdt)_3]^-$ and $[M(tdt)_3]^-$ [18] and the dimeric species $[Tc_2(bdt)_4]$.[28]

The complexes $[MSCl_2(HB(pz)_3)]$ [M = Tc (**3**), Re (**4**)] containing the terminal M═S bonds have been prepared by substitution of O for S in $[MOCl_2(HB(pz)_3)]$ by treatment of a solution of the monooxo complex in CH_2Cl_2 with solid B_2S_3. This synthetic method has been widely used for the preparation of sulfido complexes with transition metals.[35] Its application to the synthesis of complexes **3** and **4** was strongly assisted by the favorable properties of the tripodal $[HB(pz)]_3^-$ ligand, which provides a sterical protection for the atom transfer between oxygen and sulfur. In contrast, treatment of the monooxo complexes **5**–**7**, obtained by reaction of $[ReOCl_2(HB(pz)_3)]$ with H_2edt and HS–Et, with B_2S_3 did not cause the replacement of the oxo group by the sulfido group, suggesting that also the properties of the other ligands incorporated into the complex are important factors in determining the possibility to obtain the metal–sulfido bond through this route.

Properties of the Complexes. The IR spectrum of $[TcS(edt)_2]^-$ looks identical with that of $[TcO(edt)_2]^-$ except for the lack of the band at 935 cm^{-1} due to the Tc═O stretching and the appearance of a new band at 520 cm^{-1}. We tentatively assign this frequency to the Tc═S stretching (Table V). Similarly, a band at 517 cm^{-1} in the IR spectrum of the homologous complex $[ReS(edt)_2^-$ has been previously assigned to the Re═S bond stretching.[9] The electronic spectrum of $[TcS(edt)_2]^-$ (Figure 3) exhibits a red-shift to longer wavelengths as compared to the oxo analogues.[9] The visible absorption bands can be assigned to thiolate-to-metal charge-transfer transitions, according with the rhenium assignments. The proton NMR spectrum of **1** shows the expected two sets of resonances arising from the aromatic protons of the $[AsPh_4]^+$ counterion (multiplet) and the symmetric AA′BB′ system of the methylene protons of the ethanethiolato ligands (2.83–3.17 ppm) (Table V). Exactly the same behavior is observed in the oxotechnetium derivative in the range 2.95–3.19 ppm. This range is at least halved in $[ReE(edt)_2]^-$ (E = O, S) complexes, resulting in two unresolved multiplets and indicating that the rhenium atom contributes to average the differences between the equatorial and axial protons of the ethanedithiolato ligands, probably as a result of its greater electron density. In addition, all $[ME(edt)_2]^-$ (M = Tc, Re) complexes exhibit a downfield shift for the methylene protons with respect to the free ligand. In particular, $[Tc$═$E]^{3+}$ cores produce a greater downfield

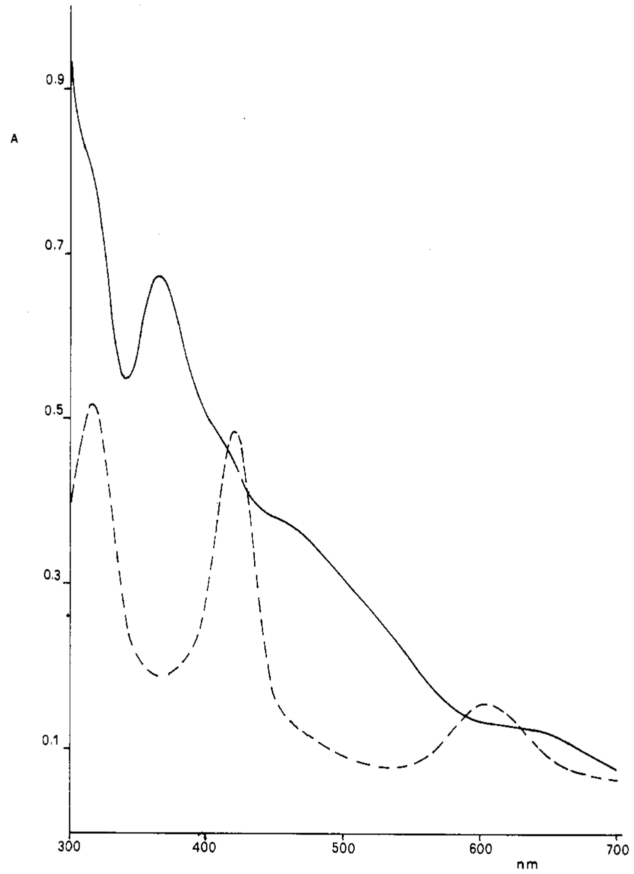

Figure 3. UV–vis spectra (300–700 nm) of a 10^{-4} mol dm^{-3} CH_3CN solution of **1** (solid line) and 10^{-4} mol dm^{-3} CH_2Cl_2 solution of **2** (dashed line).

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(35) Callahan, K. P.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211–3217.

shift than $[Re{=}E]^{3+}$ cores, in accordance with the higher acid character of Tc(V) species.

The new technetium(V)–sulfido complexes $[TcS(edt)_2]^-$ and $[TcSCl_2(HB(pz)_3]$ easily undergo replacement of the sulfido group by the oxo group, in solution and under aerobic conditions, to give the corresponding monooxo analogues $[TcO(edt)_2]^-$ and $[TcOCl_2(HB(pz)_3)]$. This indicates that the $[Tc{=}S]^{3+}$ core is less stable than the isoelectronic $[Tc{=}O]^{3+}$ core, a fact which can be attributed to the change in the periodic properties in passing from oxygen to sulfur. The conversion of the sulfido complex to the oxo analogue could be monitored by UV–vis spectroscopy, following the shift at higher wavelengths of the ligand-to-metal charge-transfer transition. In contrast, the $[Re{=}S]^{3+}$ group possesses a higher stability in comparison with the $[Tc{=}S]^{3+}$ group. The complex $[ReS(edt)_2]^-$ is stable both in solid and in solution, while the complex $[ReSCl_2(HB(pz)_3)]$ undergoes replacement of the sulfido group by the oxo group in solution but at a lower rate than that of the analogous technetium complex. This suggests that also the nature of the other ancillary ligands bound to the metal should contribute to the stabilization of the M=S bond. In particular, ligands possessing negative sulfur donor atoms appear to further stabilize the M=S bond.

The dimeric complex **2** is sparingly soluble only in chlorinated solvents. It is indefinitely stable in solution and in the solid state. Its UV–vis spectrum shows distinct absorptions at 318, 422, and 605 nm (Figure 3). The proton NMR spectrum of **2** exhibits three sharp signals arising from the edt and e=dt ligands, and consistent with a paired d^4–d^4 configuration for the two Tc ions. These data are also consistent with the diamagnetic behavior of this compound in solution.

The properties of the two complexes **3** and **4** have been described in detail elsewhere.[12]

The monooxo complexes **5**–**7** exhibit the diagnostic IR Re=O bond vibration in the usual range around 950 cm^{-1}. The analysis of the proton NMR spectra of complexes **5** and **7** allows one to look both at their structure in solution and at the influence of the coligands on the trans coordinated pyrazolyl protons. The spectrum of **7** shows three sets of coupled protons (integral ratio 1:1:1), each pyrazolyl ring having a different trans substituent. According to the literature,[15] and by comparison with the chemical shifts of the parent compound $[ReOCl_2(HB(pz)_3)]$, the upfield set of signals can be assigned to the protons of the pyrazolyl ring in trans position to the oxo group, as a result of the delocalization of the electron density through the metal–oxygen multiple bond.

Conclusions. The results presented here show that different synthetic routes for the preparation of the terminal $[M{=}S]^{3+}$ (M = Tc, Re) groups are available, but that satisfactory yields of formation of these complexes are difficult to obtain, particularly in the case of technetium sulfido complexes. On the basis of the strong influence on the stability of the M=S multiple bond exerted by the other spectator ligands present in the complex, we may speculate that other compounds with different sets of donor atoms could be more efficient starting materials for the synthesis of derivatives having the $[M{=}S]^{3+}$ core by transfer of S^{2-} sulfur atoms. However, the facile replacement of the sulfido group by the oxo group in solution experienced for the most part by the sulfido complexes reported here seems to prevent the application of this chemistry to the preparation of technetium and rhenium radiopharmaceuticals containing the $[M{=}S]^{3+}$ group in physiological conditions.

Acknowledgment. We are grateful to Dr. A. I. Breikss for her great help in discussing our results. We thank also M. Fratta for elemental analyses and A. Moresco for technical support.

Supplementary Material Available: Tables of full data collection parameters and refinement parameters (Table A), bond distances and angles, least-squares planes, deviations of the relevant atoms, and dihedral angles (Tables B and C) for **2** and **5** and a table of fractional atomic coordinates of the hydrogen atoms for **2** (Table D) (6 pages). Ordering information is given on any current masthead page.