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Technetium(I) Carbonyl Dithiocarbamates and Xanthates

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Technetium(I) tetracarbonyl complexes with diethyldithiocarbamate and methylxanthate ligands $[TcL(CO)_4]$ (L = S_2CNEt_2 and S_2COMe) were prepared. Conditions required for the formation of these complexes were found. The crystal and molecular structure of the xanthate complex was determined by single-crystal X-ray diffraction. $[Tc(S_2CNEt_2)(CO)_4]$ undergoes decarbonylation both in solution and in the course of vacuum sublimation with the formation of a dimer $[Tc(S_2CNEt_2)(CO)_3]_2$ whose structure was determined by single-crystal X-ray diffraction. In donor solvents, $[Tc(S_2CNEt_2)(CO)_4]$ and $[Tc(S_2COMe)(CO)_4]$ undergo decarbonylation with the formation of tricarbonyl solvates $[TcL(CO)_3(Sol)]$. The crystal structure of the pyridine solvate $[Tc(S_2CNEt_2)(CO)_3(py)]$, chosen as an example, was determined by single-crystal X-ray diffraction. The possibility of using bidentate S-donor acidic ligands for tethering the tetracarbonyltechnetium fragment to biomolecules was examined.

Introduction

In the past decade, there has been a great deal of interest in using the $Tc(CO)_3^+$ fragment for technetium labeling of various biomolecules.[1,2] These studies were stimulated by the development by Alberto et al. of an efficient procedure for preparing the water-soluble tricarbonyltriaqua complex $[^{99m}Tc(H_2O)_3(CO)_3]^+$, a convenient precursor for preparing technetium radiopharmaceuticals.[3] To tether the tricarbonyl fragment to biomolecules, it is necessary to fill three vacancies in the coordination sphere of the Tc atom in the tricarbonyl fragment either with a tridentate chelating ligand or with a combination of mono- and bidentate ligands. A possible way to simplify the conjugation is to decrease the required ligand denticity by increasing the number of carbonyl groups in the coordination sphere of the Tc^I atom.[4] In this study, we examined the possibility of using bidentate sulfur-containing coordination cores for binding the tetracarbonyltechnetium fragment $Tc(CO)_4^+$. Previously, Hieber et al.[5] reported that tetracarbonyl complexes of univalent technetium with dithiocarbamate ligands, $[Tc(S_2CNR_2)(CO)_4]$ (R = Me, Et), can be prepared by the reaction of $[TcCl(CO)_5]$ with the corresponding sodium *N*,*N*-dialkyldithiocarbamates in acetone at 50 °C. These data were subsequently cited in handbooks and monographs.[6,7] However, the isolated yellow-brown complexes were characterized only by elemental analysis. The results of our studies[8] suggest that, in a donor solvent such as that used by Hieber et al.,[5] the halogen replacement should be accompanied by decarbonylation with the formation of tricarbonyl complexes. Tetracarbonyl derivatives of technetium are formed only when the replacement reaction is performed in an inert solvent.[8] Later Lorentz et al.,[9] using Hieber's procedure, synthesized "$[Tc(S_2CNEt_2)(CO)_4]$" and characterized the resulting complex by ^{99}Tc NMR spectroscopy. Analysis of the chemical shifts in technetium complexes, performed by Mikhalev,[10] shows that the technetium chemical shift in "$[Tc(S_2CNEt_2)(CO)_4]$" (−1072 ppm, CD_2Cl_2)

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corresponds more likely to technetium tricarbonyl complexes. For tetracarbonyl complexes, the technetium signal should be located in a higher field. To gain understanding of the above contradictory data, we decided to study in more detail the replacement of halogen and carbonyl groups in $[TcCl(CO)_5]$ by bidentate S-donor ligands.

Experimental Section

Materials and Methods. All manipulations were performed in air. Carbon tetrachloride (Fluka, St. Petersburg, Russia) was purified by a standard procedure.[11] Sodium diethyldithiocarbamate trihydrate, $Et_2NCS_2Na\cdot 3H_2O$ (Fluka, St. Petersburg, Russia), was dehydrated before use by heating in a vacuum at 60−70 °C. Sodium methylxanthate was prepared as described in ref 12. The ^1H and ^{99}Tc NMR spectra were recorded with a Bruker CXP-300 spectrometer operating at 300 and 67.5 MHz, respectively, at room temperature (22 ± 2 °C). The ^{99}Tc chemical shifts are given relative to aqueous $KTcO_4$ (negative values correspond to upfield shifts). When spectra of the solutions in CCl_4 were recorded, approximately 5 vol % $CDCl_3$ was added. The IR spectra were recorded with a Shimadzu FT-IR 8700 spectrophotometer in the range 400−4000 cm^{-1}. Samples were prepared as solutions in CCl_4. KBr and CaF_2 cells were used. The Tc content of the compounds synthesized was determined photocolorimetrically with thiourea, after decomposition of the complexes to pertechnetate by treatment with an alkaline solution of hydrogen peroxide.[13]

Synthesis. Chloropentacarbonyltechnetium, $[TcCl(CO)_5]$, was prepared by carbonylation of potassium pertechnetate with a mixture of hydrochloric and formic acids in an autoclave, similarly to the synthesis of $[TcI(CO)_5]$.[4]

$[Tc(S_2CNEt_2)(CO)_4]$. To a dry mixture of $[TcCl(CO)_5]$ (1 mmol) and anhydrous Et_2NCS_2Na (1.2 mmol, 1.2-fold molar excess), we added 8 mL of CCl_4. The resulting heterogeneous mixture was stirred with a magnetic stirrer for 2−3 h and left overnight. On the next day, the mixture was filtered through a paper filter to remove the NaCl precipitate. The filtrate was evaporated in a vacuum at room temperature. The solid residue was sublimed in a rough vacuum (0.1 mmHg) at 40−60 °C. Colorless crystals of composition $[Tc(S_2CNEt_2)(CO)_4]$ were obtained in low yield (~5%). Tc, %: calcd 27.57, found 27.0. IR (CCl_4, cm^{-1}): 2104.2 w, 2017.4 s, 1996.2 m, 1955.7 m. ^{99}Tc NMR (CCl_4, δ, ppm): −1689 ($\Delta\nu_{1/2}$ 700 Hz). ^1H NMR ($CCl_4/CDCl_3$, δ, ppm): 1.25 t (6H, CH_3), 3.71 q (4H, CH_2), J_{HH} = 7.5 Hz.

$[Tc(S_2COMe)(CO)_4]$ was prepared similarly, with $MeOCS_2K$ (1.2-fold molar excess) taken instead of sodium diethyldithiocarbamate. The yield of colorless crystalline $[Tc(S_2COMe)(CO)_4]$ after sublimation was 40−50%. The crystals obtained appeared to be suitable for X-ray structural analysis. Tc, %: calcd 31.13, found 28.9. IR (CCl_4, cm^{-1}): 2110.0 w, 2023.2 s, 2005.8 m, 1965.3 m. ^{99}Tc NMR (CCl_4, δ, ppm): −1689 ($\Delta\nu_{1/2}$ 700 Hz). ^1H NMR ($CCl_4/CDCl_3$, δ, ppm): 4.43 s.

$[Tc(S_2CNEt_2)(CO)_3]_2$. A solution of $[Tc(S_2CNEt_2)(CO)_4]$ in CCl_4 was slowly evaporated in air at room temperature for 2−3 days. In the course of evaporation, the initially colorless solution gradually became yellow, and large yellow crystals precipitated. The crystals appeared to be suitable for X-ray structural analysis. $[Tc(S_2CNEt_2)(CO)_3]_2$ also formed as a yellow residue in the course of vacuum sublimation of $[Tc(S_2CNEt_2)(CO)_4]$. Tc, %: calcd 29.91, found 28.9. IR (CCl_4, cm^{-1}): 2044.4 m, 2029.0 s, 1953.8 m, 1938.3 s, 1928.7 s. ^{99}Tc NMR (CCl_4, δ, ppm): −1039 ($\Delta\nu_{1/2}$ 1200 Hz). ^1H NMR ($CCl_4/CDCl_3$, δ, ppm): 1.30 t (12H, CH_3), 3.89 q (8H, CH_2), J_{HH} = 7.5 Hz.

$[Tc(S_2CNEt_2)(CO)_3(py)]$. A weighed portion of $[TcCl(CO)_5]$ (0.4 mmol) was dissolved upon weak heating in 4 mL of ethanol. Solid Et_2NCS_2Na (0.48 mmol, 1.2-fold molar excess) was added to the resulting solution. The mixture was stirred with a magnetic stirrer for 2 h with weak heating and left overnight. On the next day, the solution was filtered, and pyridine was added to the filtrate (0.6 mmol, 1.5-fold molar excess). The mixture was heated at 40−50 °C for 2 h and then allowed to slowly evaporate at room temperature. Within 10 days, large yellowish crystals of $[Tc(S_2CNEt_2)(CO)_3(py)]$ formed. The crystals appeared to be suitable for X-ray structural analysis. Tc, %: calcd 24.15, found 23.9. IR (CCl_4, cm^{-1}): 2029.0 s, 1930.6 s, 1915.2 m. ^{99}Tc NMR (CCl_4, δ, ppm): −1185 ($\Delta\nu_{1/2}$ 160 Hz). ^1H NMR ($CDCl_3$, δ, ppm): 1.76 t (6H, CH_3), 4.28 q (4H, CH_2), J_{HH} = 7.5 Hz; 7.92 m (2H, 3-H, C_5H_5N), 8.37 t (1H, 4-H, C_5H_5N), 9.43 br.s (2H, 2-H, C_5H_5N).

Crystal Structure Determination. An X-ray diffraction experiment with $[Tc(S_2CNEt_2)(CO)_3]_2$ was performed on a STOE IPDS II diffractometer at room temperature and with $[Tc(S_2COMe)(CO)_4]$ and $[Tc(S_2CNEt_2)(CO)_3(py)]$, with a Bruker Kappa Apex II diffractometer at 100 K. For $[Tc(S_2CNEt_2)(CO)_3]_2$, the absorption correction was introduced, taking into account the crystal shape. The absorption corrections for $[Tc(S_2CNEt_2)(CO)_3(py)]$ were introduced using the *SADABS* program.[14] The structures were solved by direct methods and refined using the *SHELXL-97* program.[15] The structure of $[Tc(S_2COMe)(CO)_4]$ was refined with a twinned crystal consisting of three domains, two of which are turned relative to the first domain by 180°. The contributions of the second and third domains are 0.161 15 and 0.245 18. For this compound, the absorption was taken into account using the *TWINABS* program.[16] The H atoms in the structure of $[Tc(S_2CNEt_2)(CO)_3]_2$ were modeled using a riding model and placed in geometrically calculated positions with isotropic thermal parameters equal to 1.2 (for CH_2 groups) and 1.5 (for CH_3 group) of the equivalent isotropic parameters of the C atoms to which they are bonded. For the other two compounds, the positions of the H atoms were calculated by the algorithm incorporated in the *SHELX* program complex. Anisotropic thermal parameters were calculated for all of the non-H atoms. The crystallographic data and refinement parameters are given in Table 1. The selected bond lengths and angles are given in Tables 2−4.

Results and Discussion

As a starting compound for preparing tetracarbonyltechnetium dithiocarbamate and xanthate complexes, as in ref 5, we chose chloropentacarbonyltechnetium(I). As a solvent for preparing tetracarbonyl complexes, we used CCl_4. Although $[TcCl(CO)_5]$ dissolves in CCl_4 considerably less readily than in acetone, which was used by Hieber et al.,[5] we chose CCl_4 because halogen replacement reactions in pentacarbonyltechnetium halides in donor solvents, according to our observations, are accompanied by decarbonylation and yield only *fac*-tricarbonyl species.[8]

The IR spectrum of the liquid phase obtained after mechanical grinding of $[TcCl(CO)_5]$ with NaS_2CNEt_2 under a CCl_4 layer is shown in Figure 1.

The set of four characteristic bands at 2104.2, 2017.4, 1996.2, and 1955.7 cm^{-1} is similar to that observed in the IR

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Table 1. Crystallographic Data and Refinement Parameters for the Complexes Studied

parameter	$[Tc(S_2COMe)(CO)_4]$	$[Tc(S_2CNEt_2)(CO)_3]_2$	$[Tc(S_2CNEt_2)(CO)_3(py)]$
formula	$C_6H_3O_5S_2Tc$	$C_{16}H_{20}N_2O_6S_4Tc_2$	$C_{13}H_{15}N_2O_3S_2Tc$
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a, Å	6.0895(3)	15.5131(9)	11.5981(9)
b, Å	6.1832(4)	12.0442(10)	10.7273(8)
c, Å	15.0420(10)	13.5538(8)	13.3522(11)
α, deg	79.308(4)	90.00	90.00
β, deg	82.038(4)	103.368(5)	95.615(2)
γ, deg	68.276(3)	90.00	90.00
V, Å^3	515.50(5)	2463.8(3)	1653.3(2)
Z	2	4	4
T, K	100	293	100
D_{calc}, g cm^{-3}	2.044	1.781	1.649
μ, mm^{-1}	1.791	1.493	1.132
radiation	Mo Kα	Mo Kα	Mo Kα
R_σ	0.0501	0.0393	0.0256
R1 ($\lvert F_o \rvert \geq 4\sigma_F$)	0.0426	0.0412	0.0258
wR2 ($\lvert F_o \rvert \geq 4\sigma_F$)	0.1138	0.1145	0.0733
R1 (all data)	0.0597	0.0541	0.0400
GOF	1.010	1.113	1.034

Table 2. Selected Interatomic Distances (d) and Bond Angles (ω) in the Structure of $[Tc(S_2COMe)(CO)_4]$

distance	d, Å	angle	ω, deg
Tc1−C2	1.9366(19)	Tc1−C1−O1	178.29(19)
Tc1−C1	1.943(2)	Tc1−C2−O2	178.86(18)
Tc1−C4	1.989(2)	Tc1−C3−O3	177.62(16)
Tc1−C3	2.0261(19)	Tc1−C4−O4	179.82(19)
Tc1−S2	2.5079(5)	C1−Tc1−C2	90.40(7)
Tc1−S1	2.5085(5)	C1−Tc1−C3	92.87(8)
O1−C1	1.134(2)	C1−Tc1−C4	90.15(8)
O2−C2	1.143(2)	C2−Tc1−C3	92.12(8)
O3−C3	1.125(2)	C2−Tc1−C4	90.68(8)
O4−C4	1.130(2)	C3−Tc1−C4	175.87(7)
S1−C5	1.703(2)	C1−Tc1−S1	99.52(6)
S2−C5	1.694(2)	C1−Tc1−S2	170.20(6)
O5−C5	1.321(2)	C2−Tc1−S1	170.05(6)
O5−C6A	1.444(4)	C2−Tc1−S2	99.31(6)
O5−C6B	1.501(4)	C3−Tc1−S1	88.09(5)
		C3−Tc1−S2	88.10(5)
		C4−Tc1−S1	88.62(6)
		C4−Tc1−S2	88.44(6)

Table 3. Selected Interatomic Distances (d) and Bond Angles (ω) in the Structure of $[Tc(S_2CNEt_2)(CO)_3]_2$

distance	d, Å	angle	ω, deg
Tc−C1	1.915(5)	C1−Tc−S1	100.09(16)
Tc−C2	1.905(5)	C1−Tc−S1	87.10(14)
Tc−C3	1.911(6)	C1−Tc−S2	170.93(16)
Tc−S1	2.5072(13)	C1−Tc−C2	89.0(2)
Tc−S1	2.5723(11)	C1−Tc−C3	89.7(2)
Tc−S2	2.4934(12)	C2−Tc−C3	89.4(3)
C1−O2	1.145(6)	C2−Tc−S1	94.65(19)
C2−O3	1.135(7)	C2−Tc−S1	174.8(2)
C3−O1	1.142(8)	C3−Tc−S1	93.99(18)
S1−C4	1.759(4)	C3−Tc−S1	169.44(15)
S2−C4	1.708(5)	C3−Tc−S2	99.33(15)
C4−N	1.321(6)	S1−Tc−S1	82.71(4)
N−C5	1.473(6)	S1−Tc−S2	70.85(4)
N−C6	1.491(7)	S1−Tc−S2	91.71(4)
C5−C8	1.459(12)	C4−N−C5	121.2(4)
C6−C7	1.483(10)	C4−N−C6	121.6(4)

spectra of technetium tetracarbonyl-β-diketonate complexes[8] and dimers $[TcX(CO)_4]_2$ (X = Cl, Br, I), one of which (X = I) was characterized by single-crystal X-ray diffraction.[17] To isolate $[Tc(S_2CNEt_2)(CO)_4]$ from the solution, carbon tetrachloride was distilled off at reduced pressure, and the dry residue was heated in a vacuum. Upon reaching 40−60 °C, colorless crystals formed on cold walls of the reaction tube. The IR spectrum of the sublimate was similar to the IR spectrum of the reaction mixture before evaporation (Figure 1). Unfortunately, the crystals obtained appeared to be unsuitable for X-ray structural analysis. It should be noted that, in the course of $[Tc(S_2CNEt_2)(CO)_4]$ isolation from the reaction mixture, the major fraction of the product transformed into a poorly soluble yellow precipitate. In the course of both heating of a $[Tc(S_2CNEt_2)(CO)_4]$ solution in CCl_4 and its slow evaporation in air, new bands in the IR spectrum gradually appeared and grew in intensity, and the spectrum acquired the shape shown in Figure 2. A similar set of bands in the carbonyl stretching region was observed for the β-diketonate complexes $[TcL(CO)_3]_2$ (L = anion of acetylacetone, trifluoroacetylacetone, or pivaloyltrifluoroacetone).[8]

As will be shown below, the product of $[Tc(S_2CNEt_2)(CO)_4]$ transformation is the dimer $[Tc(S_2CNEt_2)(CO)_3]_2$. Thus, $[Tc(S_2CNEt_2)(CO)_4]$ is unstable. It should be noted that decarbonylation of this tetracarbonyl complex is reversible, as follows from the dependence of the apparent decarbonylation rate on the efficiency of CO removal from the reaction mixture.

$[Tc(S_2COMe)(CO)_4]$ appeared to be considerably more stable and was isolated in the form of colorless crystals in a reasonable yield (40−50%). $[Tc(S_2COMe)(CO)_4]$ undergoes only slight decarbonylation upon heating of the solution. Even after refluxing in CCl_4, the IR spectrum of the solution contains, along with bands of the starting monomer, only weak doublets at 2054.0 and 2038.6 cm^{-1} and a shoulder at 1950 cm^{-1}. These bands, by analogy with the IR spectrum of the diethyldithiocarbamate dimer, can be tentatively assigned to an impurity of $[Tc(S_2COMe)(CO)_3]_2$.

We failed to isolate pure $[Tc(S_2COMe)(CO)_3]_2$ because of its further decomposition to unidentified insoluble and nonvolatile compounds. Crystals of $[Tc(S_2COMe)(CO)_4]$ grown by vacuum sublimation appeared to be suitable for X-ray structural analysis. Because at room temperature the $[Tc(S_2COMe)(CO)_4]$ crystals decomposed under an X-ray beam,

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Table 4. Selected Interatomic Distances (d) and Bond Angles (ω) in the Structure of [Tc(S_2CNEt_2)$(CO)_3$(py)]

distance	d, Å	angle	ω, deg
Tc1−C3	1.9107(19)	O1−C1−Tc1	179.29(16)
Tc1−C2	1.9188(18)	O2−C2−Tc1	178.33(15)
Tc1−C1	1.9312(19)	O3−C3−Tc1	178.30(19)
Tc1−N2	2.2204(14)	C3−Tc1−C2	88.96(7)
Tc1−S1	2.4978(5)	C3−Tc1−C1	91.55(8)
Tc1−S2	2.5054(5)	C2−Tc1−C1	91.97(8)
C1−O1	1.150(2)	C1−Tc1−S1	169.73(5)
C2−O2	1.15(2)	C2−Tc1−S2	169.25(6)
C3−O3	1.1553(2)	C3−Tc1−N2	176.13(6)
N2−C9	1.348(2)	C1−Tc1−S2	98.77(5)
C9−C10	1.390(2)	C1−Tc1−N2	91.19(7)
C10−C11	1.387(3)	C2−Tc1−N2	93.67(6)
C11−C12	1.386(3)	C2−Tc1−S1	98.29(6)
C12−C13	1.389(2)	C3−Tc1−S1	88.97(6)
C13−N2	1.349(2)	C3−Tc1−S2	90.85(5)
S1−C4	1.7318(16)	N2−Tc1−S1	87.85(4)
S2−C4	1.7246(17)	N2−Tc1−S2	86.03(4)
C4−N1	1.330(2)	S1−Tc1−S2	70.965(15)
N1−C7	1.471(2)	Tc1−N2−C9	122.76(11)
N1−C5	1.477(2)	N2−C9−C10	122.67(16)
C5−C6	1.518(3)	C9−C10−C11	119.04(17)
C7−C8	1.522(3)	C10−C11−C12	118.80(16)
		C11−C12−C13	118.93(17)
		C12−C13−N2	122.81(16)
		C13−N2−C9	117.74(14)
		C13−N2−Tc1	119.50(11)
		Tc1−S1−C4	87.05(6)
		Tc1−S2−C4	86.96(6)
		S2−C4−S1	114.32(9)
		S2−C4−N1	123.15(13)
		S1−C4−N1	122.52(13)
		C4−N1−C7	120.67(15)
		C4−N1−C5	120.74(14)
		N1−C5−C6	112.96(15)
		N1−C7−C8	113.96(15)
		C7−N1−C5	118.37(14)

to obtain a good set of crystal reflections, the experiment was performed at low temperature.

The coordination sphere of the Tc atom in [Tc(S_2COMe)$(CO)_4$] (Figure 3) is an octahedron formed by four C atoms of carbonyl groups and two S atoms of the xanthate ligand. The trans effect is clearly manifested in the molecular structure of [Tc(S_2COMe)$(CO)_4$]: The Tc−C distances for carbonyl groups located in the trans position to the S atoms [Tc1−C2 1.9366(19) Å and Tc1−C1 1.943(2) Å] are shorter by 0.06 Å on average than the Tc−C distances for the carbonyl groups located in the trans position to each other [Tc1−C4 1.989(2) Å and Tc1−C3 2.0261(19) Å]. The Tc−C═O fragments are linear within 3°. It should be noted that the methyl groups of xanthate ligands are disordered with 50% probability relative to the two crystallographically equivalent positions. The total occupancy is 1.0.

The crystal structure of [Tc(S_2COMe)$(CO)_4$] (Figure 4) is built of isolated molecules arranged so that the *trans*-CO groups are parallel to the (−111) plane, whereas the Tc1-S1S2C1C2 least-squares plane is parallel to the (1−11) plane. Tetracarbonyl molecules are packed in bilayer blocks linked by van der Waals bonds via methoxy groups of xanthate ligands.

The ^{99}Tc NMR spectrum of a solution of [Tc(S_2COMe)$(CO)_4$] in CCl_4 consists of one broad (700 Hz) signal at −1689 ppm. A similar signal with the same chemical shift (−1689 ppm) was observed in the ^{99}Tc NMR spectrum of a solution of [Tc(S_2CNEt_2)$(CO)_4$] in CCl_4. It should be noted that the technetium chemical shifts in the spectra of the tetracarbonyl complexes that we synthesized differ essentially from that for "[Tc(S_2CNEt_2)$(CO)_4$]" synthesized by Hieber et al.'s procedure[9] (−1072 ppm).

As noted above, [Tc(S_2CNEt_2)$(CO)_4$] is unstable and transforms upon heating or on storage into a yellow crystalline substance. An X-ray diffraction analysis of the product showed that it was a dimer [Tc(S_2CNEt_2)$(CO)_3$]$_2$ with bridging dithiocarbamate groups (Figure 5).

Taking into account full analogy between the IR spectra of the dimer and tricarbonyl-β-diketonate complexes [Tc(β-diketonate)$(CO)_3$]$_2$ that we synthesized previously, the X-ray structural data obtained indirectly confirm the interpretation of the structure of the β-diketonate complexes in solution, made in our early study.[8]

The coordination polyhedron of the Tc atom is a distorted octahedron formed by three C atoms and three S atoms (Figure 5). The two octahedra share a common S···S edge to form a dimer. Thus, one S atom of the dithiocarbamate ligand (S1) is coordinated to two Tc atoms, and the other (S2), to one Tc atom. The dithiocarbamate ligands in the dimeric molecule are in the cisoid position relative to the TcS1S1Tc quadrangle. The two technetium octahedra are slightly bent relative to each other. The Tc−CO distances

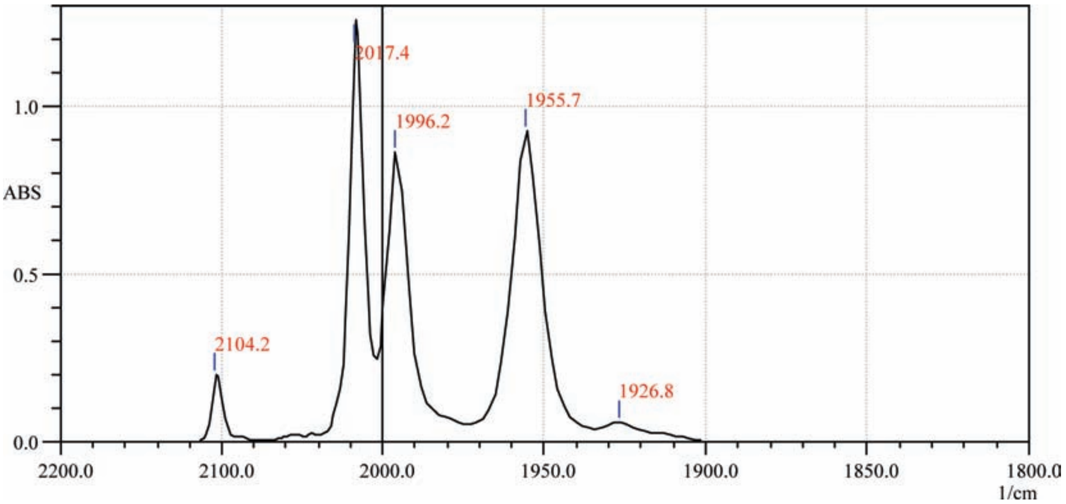

Figure 1. IR spectrum of a solution of [Tc(S_2CNEt_2)$(CO)_4$] in CCl_4.

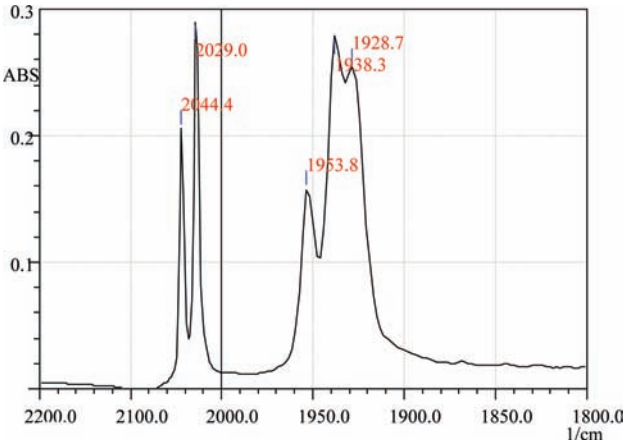

Figure 2. IR spectrum of the product of [Tc(S_2CNEt_2)$(CO)_4$] transformation in CCl_4.

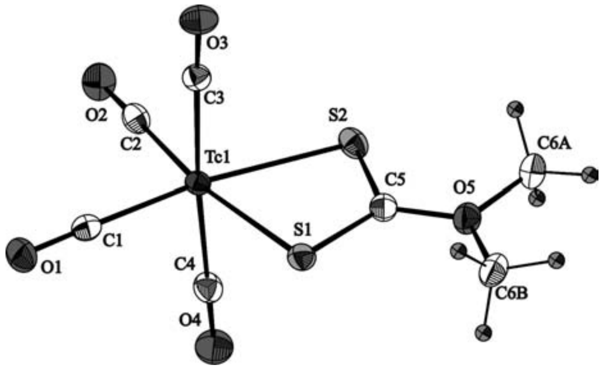

Figure 3. Molecular structure of [Tc(S_2COMe)$(CO)_4$]. Thermal vibration ellipsoids are shown on the 50% probability level.

in the *fac*-tricarbonyl fragments vary in the range 1.905−1.915 Å. A similar dimeric complex $[Tc(CO)_3(salbut)]_2$ [salbut = 2-(1-butylnitrilomethylidyne)phenolato] was prepared by Takayama et al.[18] by dimerization of [Tc(salbut)$(CO)_3$(CH_3CN)] in benzene. In contrast to the dithiocarbamate dimer, this complex has a transoid structure: the bridging bidentate O, N-donor ligands are located on different sides of the TcOOTc plane. Because this dimer has a center of symmetry, its IR spectrum is considerably simpler than that of [Tc(S_2CNEt_2)$(CO)_3]_2$ and contains three bands (2024, 1920, and 1885 cm^{-1}, KBr pellets).

The crystal structure of [Tc(S_2CNEt_2)$(CO)_3]_2$ (Figure 6) is built of isolated dimeric molecules arranged in the staggered mode to form layers parallel to the (011) plane.

The dithiocarbamate dimer [Tc(S_2CNEt_2)$(CO)_3]_2$ is poorly soluble in nonpolar organic solvents. Nevertheless, we were able to record its ^{99}Tc NMR spectrum in a CCl_4 solution. As we expected, with a decrease in the number of carbonyl groups in the coordination sphere of Tc, the ^{99}Tc NMR signal was appreciably shifted downfield (−1038 ppm) relative to the signal for the tetracarbonyl complex (−1689 ppm). In polar organic solvents, [Tc(S_2CNEt_2)$(CO)_3]_2$ readily dissolves upon gentle heating, apparently owing to cleavage of the bridged structure and formation of the monomeric solvate [Tc(S_2CNEt_2)$(CO)_3$(Sol)]. For example, the IR

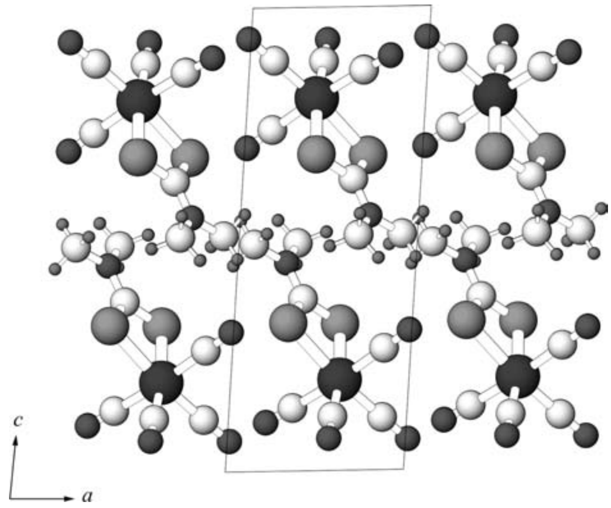

Figure 4. Projection of the crystal structure of [Tc(S_2COMe)$(CO)_4$] onto the (010) plane. The O, S, Tc, and C atoms are shown by gray, light-gray, dark-gray, and white spheres, respectively; the methoxy groups are disordered.

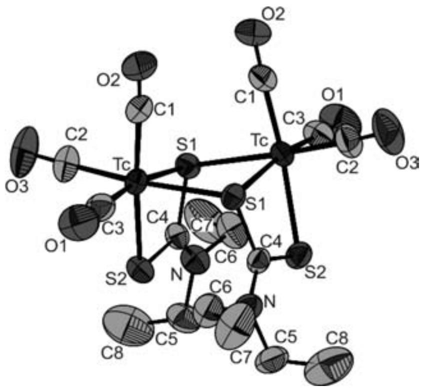

Figure 5. Molecular structure of [Tc(S_2CNEt_2)$(CO)_3]_2$. Thermal vibration ellipsoids are shown on the 50% probability level. H atoms are not shown.

spectrum of the solution obtained by dissolving [Tc(S_2CNEt_2)$(CO)_3]_2$ in acetonitrile at 40−50 °C contains two bands at 2029.0 and 1922.9 cm^{-1}, assignable to the *fac*-tricarbonyl fragment occurring in a more symmetrical surrounding than in the dimer molecule. The ^{99}Tc NMR spectrum consists of a single narrow signal at −1189 ppm. Its position is typical of tricarbonyl complexes. An attempt to isolate the tricarbonyl complex formed resulted in the formation of yellow crystals of the initial dimer. As shown by Takayama et al.,[18] the dimer $[Tc(salbut)(CO)_3]_2$ undergoes similar cleavage in coordinating solvents with the formation of monomers [Tc(salbut)$(CO)_3$(Sol)] (where Sol = py, CH_3CN). The IR spectrum of [Tc(salbut)$(CO)_3$(py)] contains in the carbonyl stretching region three bands (2018, 1914, and 1880 cm^{-1}, KBr pellets), confirming its *fac*-tricarbonyl structure. With the aim of isolating and characterizing the presumed complex [Tc(S_2CNEt_2)$(CO)_3$(sol)], we chose pyridine as the neutral ligand. Because pyridine is a considerably stronger donor than acetonitrile, we suggested that [Tc(S_2CNEt_2)$(CO)_3$(py)] would be more stable and that it would be possible to isolate it pure. Indeed, after the treatment of [TcCl$(CO)_5$] in ethanol with sodium diethyldithiocarbamate and then pyridine, we obtained large yellowish crystals. The X-ray structural

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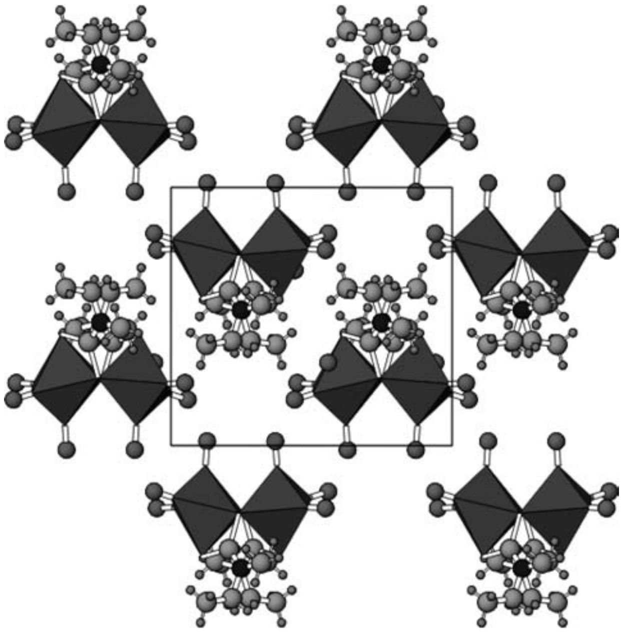

Figure 6. Crystal structure of $[Tc(S_2CNEt_2)(CO)_3]_2$.

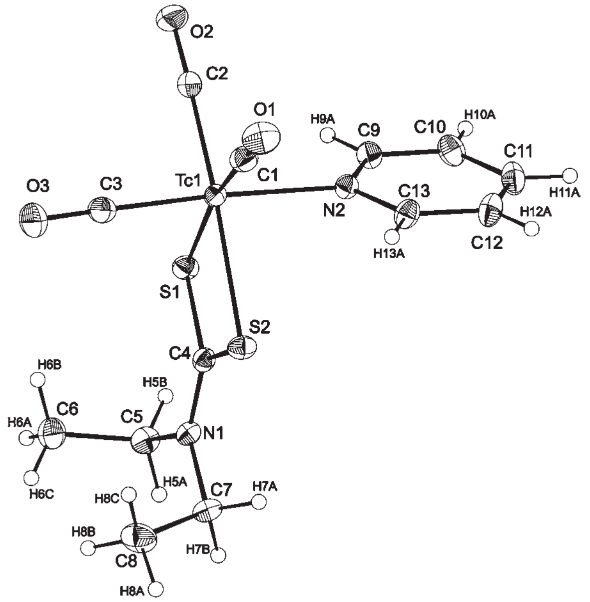

Figure 7. Molecular structure of $[Tc(S_2CNEt_2)(CO)_3(py)]$. Thermal vibration ellipsoids are shown on the 50% probability level.

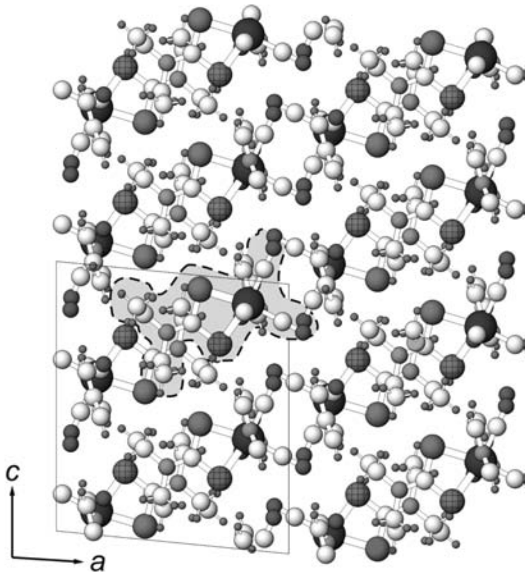

Figure 8. Molecular structure of $[Tc(S_2CNEt_2)(CO)_3(py)]$, projection onto the (010) plane. The O, N, Tc, and C atoms are shown as gray, light-gray, dark-gray, and white spheres, respectively, and the S atoms, as gray cross-hatched spheres. The dashed line bounds the molecule of the complex.

analysis allowed the product to be identified as $[Tc(S_2CNEt_2)(CO)_3(py)]$. The IR spectrum of the solution of the complex in CCl_4 contained in the carbonyl stretching region three bands at 2029.0, 1930.6, and 1915.2 cm^{-1}, characteristic of the *fac*-tricarbonyl fragment. The ^{99}Tc NMR spectrum of this solution contained a single narrow signal at −1185 ppm ($\Delta\nu_{1/2} = 160$ Hz), i.e., in the region typical of tricarbonyl complexes.[10]

In the crystal structure of $[Tc(CO)_3S_2CNEt_2(Py)]$, there is one crystallographically independent Tc atom coordinated by three C atoms of the carbonyl groups (mean Tc−C bond length 1.920 Å), N atom [Tc−N2 2.220(1) Å], and two S atoms (mean Tc−S bond length 2.502 Å). Thus, the coordination polyhedron of the Tc atoms is a weakly distorted octahedron (Figure 7). The Tc−C=O fragments in the structure of the complex are linear within 1.7°. The angles between the carbonyl groups in the cis position are 90 ± 2°.

The crystal structure of $[Tc(S_2CNEt_2)(CO)_3(py)]$ (Figure 8) consists of isolated $[Tc(S_2CNEt_2)(CO)_3(py)]$ molecules. The complexes $[Tc(S_2CNEt_2)(CO)_3(py)]$ are linked in the crystal structure by van der Waals interactions. The molecules of the complexes are packed in stacks parallel to the (10−1) plane, with the C3−Tc1−N2 axes oriented along the [010] direction.

Thus, we found that the necessary condition for formation of the tetracarbonyltechnetium diethyldithiocarbamate and methylxanthate complexes by replacement of the chloride ligand and carbonyl group in $[TcCl(CO)_5]$ with the corresponding S-donor ligand is performing the replacement in an inert noncoordinating solvent without heating. The technetium "tetracarbonyl dithiocarbamate" complexes obtained by Hieber et al. are, most likely, tricarbonyl derivatives. To confirm this assumption, we repeated the synthesis of tetracarbonyltechnetium diethyldithiocarbamate following Hieber et al.'s procedure. A mixture of $[TcCl(CO)_5]$ and sodium diethyldithiocarbamate was heated in acetone at 50 °C for 1 h. After cooling, the mixture was filtered.

The IR spectrum of the filtrate in the carbonyl stretching region appeared to be similar to the spectrum of the dithiocarbamate dimer $[Tc(S_2CNEt_2)(CO)_3]_2$ in CCl_4 (Figure 2). The ^{99}Tc NMR spectrum of the reaction mixture contained a broad signal at −1087 ppm ($\Delta\nu_{1/2}$ 520 Hz, $I = 100$ arb. units) and a narrow signal at −1271 ppm ($\Delta\nu_{1/2}$ 60 Hz, $I = 30$ arb. units). By analogy with the chemical shifts of the complexes structurally characterized in this study ($[Tc(S_2CNEt_2)(CO)_3]_2$ −1039 ppm and $[Tc(S_2CNEt_2)(CO)_3(py)]$ −1185 ppm), these signals can be assigned to the dimer $[Tc(S_2CNEt_2)(CO)_3]_2$ and the monomer $[Tc(S_2CNEt_2)(CO)_3(acetone)]$, respectively. Apparently, the solvate with the weak ligand (acetone) decomposes at 50 °C with the formation of a dimer.

Thus, our results show that replacement of the carbonyl group and chloride ligand in $[TcCl(CO)_5]$ by diethyldithiocarbamate and methylxanthate ligands in hot acetone (as described by Hieber et al.) leads to the formation of tricarbonyl complexes. Such behavior of pentacarbonyltechnetium halides is due to their high reactivity toward the replacement of carbonyl groups. We have shown previously[19] that pentacarbonyltechnetium halides [TcX(CO)$_5$] (X = Cl, Br, I) react at elevated temperature with donor solvents (Sol = CH_3CN, THF) to form tricarbonyl complexes in the form of monomeric disolvates [TcX(CO)$_3$(Sol)$_2$] or dimeric monosolvates [TcX(CO)$_3$(Sol)]$_2$. The solvent molecules present in the coordination sphere of the Tc atom in these complexes are weakly bonded with the central atom, are eliminated in the course of attempted vacuum sublimation of the complexes, and can be readily displaced by another, stronger ligand. On the other hand, the replacement of carbonyl groups in the complex by a σ-donor ligand leads to labilization of the halogen atom.[20] Therefore, it can be assumed that, under the conditions described by Hieber et al., [TcCl(CO)$_5$] first undergoes decarbonylation with formation of the tricarbonyl complex with acetone, after which the acetone and halogen are displaced from the coordination sphere of the Tc atom by a stronger bidentate S-donor ligand.

It should be noted that the complex [Tc(S$_2$COMe)(CO)$_4$] is considerably more resistant to thermal decarbonylation than the starting pentacarbonyl chloride. The IR spectra of a solution of [Tc(S$_2$COMe)(CO)$_4$] in CCl_4 undergo no significant changes after storage for 24 h at room temperature, whereas [TcCl(CO)$_5$] under these conditions undergoes practically complete decarbonylation with the formation of [TcCl(CO)$_4$]$_2$ within 24 h.[21]

Enhanced stability of [Tc(S$_2$COMe)(CO)$_4$] suggests the possibility of using bidentate S-donor ligands as chelating cores for tethering technetium in the form of a tetracarbonyl fragment to various biomolecules. However, to assess this possibility, it is also necessary to evaluate the stability of the synthesized tetracarbonyl complexes under physiological conditions. Because the tetracarbonyl complexes in question are hydrophobic and their solubility in water is very low, we chose another donor solvent, acetonitrile. The IR spectrum of a freshly prepared solution of [Tc(S$_2$COMe)(CO)$_4$] in acetonitrile contains bands at 2113.8, 2025.1, 2005.8, and 1963.4 cm^{-1} and is similar to the IR spectrum of the solution of this complex in CCl_4. In other words, the tetracarbonyl fragment in the donor solvent is preserved. However, with time the intensity of the tetracarbonyl bands starts to decrease, and new bands with frequencies corresponding to those of tricarbonyl species appear in the spectrum: 2038.6 and 1934.5 cm^{-1} Thus, in a donor solvent, [Tc(S$_2$COMe)(CO)$_4$] undergoes slow decarbonylation at room temperature. After refluxing of the acetonitrile solution of [Tc(S$_2$COMe)(CO)$_4$], the IR spectrum in the carbonyl stretching region contains only the above two bands belonging to the tricarbonyl fragment. In the ^{99}Tc NMR spectrum, there is a single narrow signal at −1349 ppm ($\Delta\nu_{1/2}$ 60 Hz), apparently belonging to [Tc(S$_2$COMe)(CO)$_3$(MeCN)].

Thus, tetracarbonyl complexes with S-donor dithiocarbamate and xanthate ligands show limited resistance to decarbonylation, which restricts the possibility of technetium tethering to biomolecules in the form of a tetracarbonyl fragment and the subsequent use of the conjugates obtained.

Supporting Information Available: Crystal data for [Tc(S$_2$COMe)(CO)$_4$] (CCDC 676886), [Tc(S$_2$CNEt$_2$)(CO)$_3$]$_2$ (CCDC 723049), and [Tc(S$_2$CNEt$_2$)(CO)$_3$(py)] (CCDC 755287) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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