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# Tricarbonyl complexes of rhenium(I) and technetium(I) with thiourea derivatives

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## Abstract

*fac*-$[M(CO)_3X_3]^{2-}$ complexes (M = Re, X = Br; M = Tc, X = Cl) react with thiourea derivatives under formation of stable rhenium(I) and technetium(I) complexes. The composition of the products can be controlled by the steric requirements of the ligands and their ability to form chelates. The products of reactions with tetramethylthiourea, $Me_4tu$ (**I**), *N,N*-diethylthiocarbamoylbenzamidine, $H_2Et_2tcb$ (**II**), and morpholinylthiocarbamoylbenzamidine, $H_2morphtcb$ (**III**), have been studied by X-ray crystallography showing that the products belong to three different structural types. A mononuclear complex of the composition *fac*-[Re$(CO)_3Br(Me_4tu)_2$] has been isolated with tetramethylthiourea, whereas the thiocarbamoylbenzamidines deprotonate and act as N,S-chelating ligands. This results in the formation of a dimeric [Tc$(CO)_3$(HEt$_2$tcb-N,S)]$_2$ complex with a central, almost square Tc$_2$S$_2$ unit and a monomeric compound of the composition [Tc$(CO)_3$(Hmorphtcb-N,S)(H$_2$morphtcb-S)]. The latter compound contains a neutral, S-bonded morpholinylthiocarbamoylbenzamidine in the unusual imine form in addition to a chelate-bonded Hmorphtcb$^-$ ligand.
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*Keywords:* Rhenium; Technetium; Carbonyl; Thiourea; Crystal structure

## 1. Introduction

Radioactive nuclides of technetium and rhenium are of considerable interest for nuclear medical purposes [1–3]. $^{99m}$Tc complexes ($^{99m}$Tc: pure $\gamma$-emitter, $E_\gamma = 140$ keV, half-life $T_{1/2} = 6$ h) are used in many standard procedures in diagnostic nuclear medicine [2], while rhenium compounds are under discussion for palliative treatment of cancer and radioimmunotherapy [3–5]. A new approach is the labelling of biomolecules with low-valent organometallic rhenium compounds for radio-immunotherapy [6,7] and their technetium analogues for diagnostic purposes. The application of carbonyl complexes became possible with the development of a low-pressure synthesis of $[M(CO)_3X_3]^{2-}$ (M = Tc, X = Cl; M = Re, X = Br) [8–10].

$[M(CO)_3X_3]^{2-}$ anions have been shown to be excellent starting materials for the synthesis of further rhenium(I) and technetium(I) tricarbonyl complexes [11]. A huge number of ligand exchange procedures have been described and most of them are directed towards the labelling of biomolecules and mainly deal with nitrogen and oxygen donor atoms [12,13]. Comparably less is known about ligand exchange reactions of [Re$(CO)_3Br_3$]$^{2-}$ or [Tc$(CO)_3Cl_3$]$^{2-}$ with ligands having a thione functionality [14]. Recently, it was shown that thiourea and thiourea derivatives are able to replace the bromo ligands in [Re$(CO)_3Br_3$]$^{2-}$ under mild conditions, and a few complexes such as [Re$(CO)_3$(tu)$_3$]$^+$ (tu = thiourea), [Re$(CO)_3$Br(HEt$_2$btu)] (H$_2$Et$_2$btu = *N,N*-diethylbenzoylthiourea) and [Re$(CO)_3$(HEt$_2$tcb)]$_2$ (H$_2$Et$_2$-tcb = *N,N*-diethylthiocarbamoylbenzamidine) could be isolated and structurally characterized [15]. Continuing this work, we studied the influence of substituents in the periphery of the ligands on the structure of the products and extended the work to technetium.

Here, we describe reactions of $[M(CO)_3X_3]^{2-}$ complexes (M = Tc, X = Cl; M = Re, X = Br) with tetramethylthiourea, $Me_4tu$ (**I**), *N,N*-diethylthiocarbamoylbenzamidine,

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$H_2Et_2tcb$ (**II**) and *N,N*-morpholinylthiocarbamoyl-benzamidine, $H_2morphtcb$ (**III**). All the ligands have thiocarbonyl donor sites, which are able to coordinate to metal ions. Ligands (**II**) and (**III**) can bind as monodentate ligands or as chelators depending on the metal [16,17].
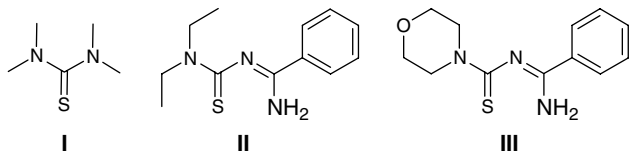


## 2. Experimental

### 2.1. Synthesis

Caution. $^{99}Tc$ is a weak β-emitter ($E_{max} = 292$ keV, $T_{1/2} = 2.12 \times 10^5$ s). Shielding is not necessary when small amounts are used as applied for this investigation, since the β-particles do not penetrate glass walls and secondary X-rays (bremsstrahlung) only play a significant role when larger amounts of $^{99}Tc$ are used. However, special care in the manipulation of radioactive materials is required to avoid contamination and incorporation.

$[Et_4N]_2[Tc(CO)_3Cl_3]$ was prepared from tetrabutylammonium pertechnetate, $BH_3 \cdot THF$ and $[Et_4N]Cl$ under an atmosphere of CO [9]. $[Et_4N]_2[Re(CO)_3Br_3]$ was a donation of Professor Roger Alberto (University of Zurich, Switzerland). $H_2Et_2tcb$ and $H_2morphtcb$ were synthesized following literature procedures [18]. Tetramethylthiourea was purchased commercially (Aldrich) and used without further purification.

### 2.1.1. [Re(CO)₃(Me₄tu)₂Br]

$[Et_4N]_2[Re(CO)_3Br_3]$ (77 mg, 0.1 mmol) was dissolved in 2 ml of water and $Me_4tu$ (47 mg, 0.35 mmol) was added. After stirring at room temperature for 2 h, the solvent was removed under vacuum. The residue was recrystallized by slow evaporation of a $CHCl_3$/iso-propanol solution giving colourless needles.

Yield: 22 mg (36% based on Re). Anal. Calc. for $C_{13}H_{24}BrN_4O_3S_2Re$: C, 25.4; H, 3.9; N, 9.1; S, 10.4. Found: C, 24.1; H, 3.7; N, 8.1; S, 9.2%. IR(KBr) (cm$^{-1}$): $\nu$(CO) 2010, 1886. FAB$^+$ − MS: $m/z$ 535 [Re(CO)₃(Me₄tu)₂]$^+$, 506 [Re(CO)₂(Me₄tu)₂]$^+$, 373 [Re(CO)₂(Me₄tu)]$^+$.

### 2.1.2. [Tc(CO)₃(HEt₂tcb-N,S)]₂

$[Et_4N]_2[Tc(CO)_3Cl_3]$ (55 mg, 0.1 mmol) and $H_2Et_2tcb$ (120 mg, 0.5 mmol) were dissolved in 50 ml of methanol and two drops of $Et_3N$ were added. The mixture was heated under reflux for 2 h and reduced in volume to

about 5 ml. A yellow precipitate was formed upon cooling, which was separated and recrystallized from $CH_2Cl_2$/MeOH.

Yield: 25 mg (30% based on Tc). IR(KBr) (cm$^{-1}$): $\nu$(CO) 2014, 1926, 1896; $\nu$(NH) 3338. $^1$H NMR ($\delta$, $CDCl_3$) (ppm): 8.01 (s, NH, 2H), 7.51 (m, phenyl, 10H), 3.84 (m due to hindered rotation, CH₂, 8H), 1.29 (m due to hindered rotation, CH₃, 12H). $^{99}Tc$ NMR ($\delta$, $CDCl_3$) (ppm): −1020 (s, $\Delta\nu_{1/2} = 4878$ Hz).

### 2.1.3. [Tc(CO)₃(Hmorphtcb-N,S)(H₂morphtcb-S)]

$[Et_4N]_2[Tc(CO)_3Cl_3]$ (55 mg, 0.1 mmol) and $H_2morphtcb$ (125 mg, 0.5 mmol) were dissolved in 40 ml of methanol and two drops $Et_3N$ were added. The mixture was heated under reflux for 2 h and reduced in volume to about 10 ml. Colourless crystals were deposited from this solution within two days.

Yield: 56 mg (83% based on Tc). IR(KBr) (cm$^{-1}$): $\nu$(CO) 2018, 1914, 1903. $^1$H NMR ($\delta$, $CDCl_3$) (ppm): 11.84 (s, NH, 2H), 10.44 (s, NH, 1H), 6.5–7.8 (m, phenyl, 10H), 3.3–4.4 (m, morph, 16H). $^{99}Tc$ NMR ($\delta$, $CDCl_3$) (ppm): −1132 (s, $\Delta\nu_{1/2} = 2598$ Hz).

### 2.2. Physical measurements

Routine IR spectra were recorded as KBr discs on a 5 SXC Nicolet IR spectrometer with DTGS-detector. FAB$^+$ mass spectra were recorded on an TSQ spectrometer (Finnigan) with xenon as primary beam gas. The ion gun was operated at 8 kV and 100 μA; nitrobenzylalcohol was used as matrix. The $^1$H NMR and $^{99}Tc$ spectra were recorded in $CDCl_3$ on a Jeol 400MHZ spectrometer with TMS as internal standard. A 0.1 m solution of $K^{99}TcO_4$ in $D_2O$ was used as standard for the $^{99}Tc$ spectra ($\delta = 0$).

### 2.3. X-ray diffraction

The X-ray data were collected on an Enraf Nonius CAD 4 diffractometer at room temperature ($[Tc(CO)_3$(HEt₂tcb-N,S)]₂) or a Bruker SMART CCD 1000 device ([Tc(CO)₃(Hmorphtcb-N,S)(H₂morphtcb-S)] and [Re(CO)₃(Me₄tu)₂Br]) with Mo Kα radiation ($\lambda = 0.71073$ Å). Standard procedures were applied for data reduction [19], structure solution [20,21] and refinement [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom H(22) in [Tc(CO)₃(Hmorphtcb-N,S)(H₂morphtcb-S)] and the hydrogen atoms H(1) and H(21) in [Tc(CO)₃(HEt₂tcb-N,S)]₂ have been derived from the difference Fourier maps and included in the structure-factor calculations. All other hydrogen atoms were placed at calculated positions and refined with the 'riding model' option of SHELXL 97. One phenyl ring in [Tc(CO)₃(Hmorphtcb-N,S)(H₂morphtcb-S)] is disordered and split positions have been considered in the structure calculation

Table 1
X-ray structure data collection and refinement data

|  | [Re(CO)$_3$Br(Me$_4$tu)$_2$] · CHCl$_3$ | [Tc(CO)$_3$(HEt$_2$tcb-N,S)]$_2$ | [Tc(CO)$_3$(Hmorphtcb-N,S)(H$_2$morphtcb-S)] |
|---|---|---|---|
| Formula | C$_{14}$H$_{25}$BrCl$_3$N$_4$O$_3$ReS$_2$ | C$_{30}$H$_{32}$N$_6$O$_6$S$_2$Tc$_2$ | C$_{27}$H$_{29}$N$_6$O$_5$S$_2$Tc |
| Molecular weight | 733.96 | 832.74 | 679.68 |
| Crystal system | Triclinic | Triclinic | Orthorhombic |
| $a$ (Å) | 9.669(5) | 9.995(1) | 8.659(5) |
| $b$ (Å) | 11.043(5) | 10.523(2) | 20.607(5) |
| $c$ (Å) | 12.773(5) | 17.130(4) | 32.427(5) |
| $\alpha$ (°) | 73.88(1) | 100.75(2) | 90 |
| $\beta$ (°) | 71.91(1) | 97.76(1) | 90 |
| $\gamma$ (°) | 73.70(1) | 92.97(1) | 90 |
| $V$ (Å$^3$) | 1217(1) | 1748.4(6) | 5786(4) |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $Pbca$ |
| $Z$ | 2 | 2 | 8 |
| $D_{calc}$ (g cm$^{-3}$) | 2.003 | 1.582 | 1.560 |
| $\mu$ (mm$^{-1}$) | 7.157 | 0.959 | 0.690 |
| Absorption correction | SADABS | None | None |
| $T_{min}/T_{max}$ | 0.287/0.517 | – | – |
| No. of reflections | 15,106 | 8766 | 44,143 |
| No. independent | 7343 | 7367 | 4932 |
| No. parameters | 257 | 424 | 412 |
| $R_1(F)/wR_2(F_2)$[a] | 0.033/0.081 | 0.047/0.085 | 0.040/0.100 |
| Goodness-of-Fit | 1.021 | 1.007 | 1.076 |
| CCDC deposit | CCDC-225725 | CCDC-225726 | CCDC-225727 |

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

applying a site occupation of 0.55/0.45. More information on crystal data and structure refinement is summarized in Table 1.

## 3. Results and discussion

The reaction of [Re(CO)$_3$Br$_3$]$^{2-}$ with an excess of tetramethylthiourea yields [Re(CO)$_3$Br(Me$_4$tu)$_2$]. No evidence could be found for the formation of the [Re(CO)$_3$(Me$_4$tu)$_3$]$^+$ cation, whereas the tris-thiourea derivative dominates when non-alkyl-substituted thiourea is used in the same reaction [15].

[Re(CO)$_3$Br(Me$_4$tu)$_2$] is readily soluble in CHCl$_3$ or CH$_2$Cl$_2$, but only slightly soluble in alcohols. The carbonyl part of the IR spectrum shows the typical pattern for a facial arrangement of CO ligands and is similar to the previously reported tricarbonylrhenium(I) thiourea complexes such as the neutral [Re(CO)$_3$Cl(tu)$_2$] (2023, 1914 cm$^{-1}$ [23]) and the cationic [Re(CO)$_3$(tu)$_3$]$^+$ (2020, 1918, 1888 cm$^{-1}$ [15]). The FAB$^+$ mass spectrum shows no signal for the molecular ion of the neutral complex. The base peak of the spectrum at $m/z = 535$ can be assigned to the [Re(CO)$_3$(Me$_4$tu)$_2$]$^+$ cation. Further fragmentation proceeds by the subsequent loss of complete ligands ($m/z = 506$ [Re(CO)$_2$(Me$_4$tu)$_2$]$^+$, 373 [Re(CO)$_2$(Me$_4$tu)]$^+$).

Colourless plates suitable for X-ray diffraction could be obtained from a CHCl$_3$/iso-propanol solution. The

compound crystallizes as CHCl$_3$ solvate. The structure of the complex is shown in Fig. 1. Selected bond lengths and angles are summarized in Table 2.

The rhenium atom is coordinated through a *facial* arrangement of three carbonyl groups, two tetramethylthiourea ligands and one bromo ligand in a slightly distorted octahedral arrangement. The Re–C bond length are between 1.894(4) and 1.920(5) Å. The mean value for the Re–S distances is 2.529 Å. This is slightly longer than in [ReO(Me$_4$tu)$_4$](PF$_6$)$_3$ (2.339(3) Å) [24], but in the same range as in [Re(CO)$_3$(tu)$_3$]$^+$ and can be
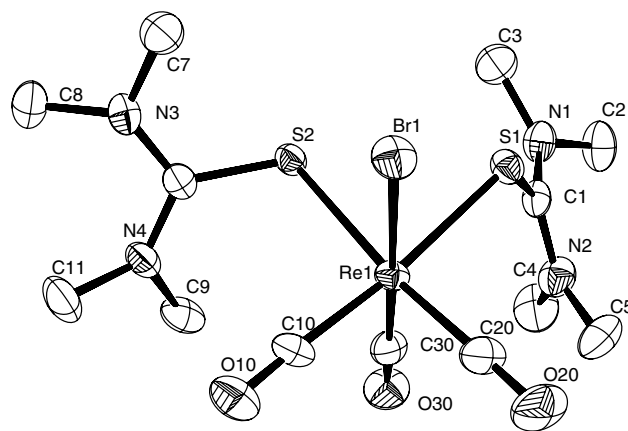


Fig. 1. Ellipsoid representation [19] of the molecular structure of [Re(CO)$_3$Br(Me$_4$tu)$_2$]. Thermal ellipsoids represent 50% probability.

Table 2
Selected bond lengths (Å) and angles (°) in [Re(CO)$_3$Br(Me$_4$tu)$_2$]

| *Bond lengths* | | | |
|---|---|---|---|
| Re1–C10 | 1.920(5) | C10–O10 | 1.137(6) |
| Re1–C20 | 1.900(4) | C20–O20 | 1.159(6) |
| Re1–C30 | 1.894(4) | C30–O30 | 1.164(5) |
| Re1–S1 | 2.530(1) | S1–C1 | 1.723(4) |
| Re1–S2 | 2.540(1) | S2–C6 | 1.726(4) |
| Re1–Br1 | 2.648(1) | | |
| *Bond angles* | | | |
| C10–Re1–C20 | 89.1(2) | C30–Re1–S1 | 97.5(2) |
| C10–Re1–C30 | 89.4(2) | C30–Re1–S2 | 94.2(1) |
| C10–Re1–S1 | 172.4(1) | C30–Re1–Br1 | 178.7(1) |
| C10–Re1–S2 | 95.7(1) | S1–Re1–S2 | 80.56(4) |
| C10–Re1–Br1 | 90.4(1) | S1–Re1–Br1 | 82.60(4) |
| C20–Re1–C30 | 91.5(2) | S2–Re1–Br1 | 84.59(4) |
| C20–Re1–S1 | 94.0(2) | Re1–S1–C1 | 111.9(2) |
| C20–Re1–S2 | 172.6(1) | Re1–S2–C6 | 109.9(1) |
| C20–Re1–Br1 | 89.7(1) | | |

explained by the strong structural *trans* influence of the carbonyls.

The C–Re–S angles are slightly larger than 90° which reduces interactions between the methyl substituents of the thiourea ligands and the carbonyl groups. Although tetramethylthiourea is not extremely bulky and a rhenium complex with four Me$_4$tu ligands, [Re-O(Me$_4$tu)$_4$]$^{3+}$ has been isolated recently [24], the coordination of three of these ligands in *facial* positions is prevented. Attempts to force the coordination of a third Me$_4$tu ligand by the addition of an excess of Me$_4$tu and three equivalents of Ag(NO$_3$) to the reaction mixture were not successful.

*N,N*-Dialkylthiocarbamoylbenzamidines form chelate complexes as singly deprotonated N,S-donor ligands with a large number of metals including rhenium and technetium [17,25]. The six-membered chelate rings of the corresponding rhenium(V) and technetium(V) oxo and nitrido complexes are almost planar and show an extended π-system with almost equal C–N bond lengths [25].

Reactions of [NEt$_4$]$_2$[Tc(CO)$_3$Cl$_3$] with *N,N*-dialkylthiocarbamoylbenzamidines give complexes of different compositions depending on the alkyl groups attached. With H$_2$Et$_2$tcb (**II**), a dimeric complex is formed, where the *N,N*-diethylthiocarbamoylbenzamidine is singly deprotonated and acts as a bridging ligand between two technetium atoms via its sulfur atom. This co-ordination mode of the ligand has previously been observed for the analogous rhenium complex [15].

[Tc(CO)$_3$(HEt$_2$tcb-N,S)]$_2$ is air-stable as a solid and in solution. The compound is readily soluble in CH$_2$Cl$_2$ or CHCl$_3$ and slightly soluble in alcohols. It can be obtained as yellow plates from CH$_2$Cl$_2$/MeOH solutions. The carbonyl region of the IR spectrum gives evidence for the *facial* coordination of the CO ligands. They are slightly shifted to higher wavenumbers compared with the values of [Re(CO)$_3$(HEt$_2$tcb-N,S)]$_2$. The

$^1$H NMR spectrum shows the signals of the ethyl groups to be split into multiplets due to hindered rotation. The $^{99}$Tc NMR spectrum gives one broad signal ($\Delta v_{1/2} = 4878$ Hz) at $\sigma = -1020$ ppm, which is in the expected range for technetium(I) tricarbonyl complexes with sulphur-containing ligands [12].

The compound crystallizes in the triclinic space group $P\bar{1}$ with two dimeric units per unit cell. The dimeric units are generated by inversion symmetry with the centre of inversion positioned in the centre of the almost square Tc$_2$S$_2$ ring. The molecular structure of one of the two symmetry-independent species is shown in Fig. 2. There are no significant differences between the independent molecule. Therefore, significant bond lengths and angles of only one of the species are summarized in Table 3.

The coordination environments of the technetium atoms are almost octahedral with facially bonded CO ligands. A distorted planar arrangement can be found for the six-membered chelate rings (maximum variation from planarity: 0.227(2) Å, r.m.s. 0.1632). All carbon–nitrogen bonds of this chelate system are equal within 0.06 Å which suggests an extended π-system. This type of coordination was observed previously for a number of HR$_2$tcb$^-$-chelates [16,17,25] and only a few exceptions have been reported where the ligands bind as neutral, monodentate thiocarbamoylbenzamidines via their thiourea functionality [26].

The reaction of [NEt$_4$]$_2$[Tc(CO)$_3$Cl$_3$] with the morpholinyl-substituted thiocarbamoylbenzaminide, H$_2$-morphtcb (**III**), gives a neutral monomeric complex with one chelating Hmorphtcb$^-$ ligand and one non-deprotonated H$_2$morphtcb ligand: [Tc(CO)$_3$(Hmorphtcb-N,S)(H$_2$-morph-tcb-S)]. The carbonyl part of the IR spectrum shows the typical CO-bands indicating the presence of the {Tc(CO)$_3$}$^+$ core. One broad signal ($\Delta v_{1/2} = 2598$ Hz) at $\sigma = -1132$ ppm can be observed by $^{99}$Tc NMR.
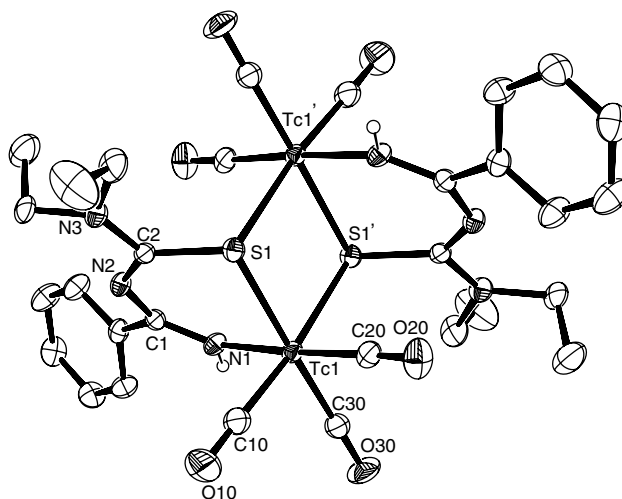


Fig. 2. Ellipsoid representation [19] of the molecular structure of one symmetry-independent dimer of [Tc(CO)$_3$(HEt$_4$tcb-N,S)]$_2$. Thermal ellipsoids represent 30% probability.

Table 3
Selected bond lengths (Å) and angles (°) in [Tc(CO)$_3$(HEt$_2$tcb-N,S)]$_2$

| Bond lengths | | | |
|---|---|---|---|
| Tc1–C10 | 1.872(6) | S1–C2 | 1.880(5) |
| Tc1–C20 | 2.036(6) | C2–N2 | 1.383(7) |
| Tc1–C30 | 1.891(6) | N2–C1 | 1.316(6) |
| Tc1–N1 | 2.273(4) | N1–C1 | 1.320(6) |
| Tc1–S1 | 2.440(1) | N3–C4 | 1.536(8) |
| Tc1–S1′ | 2.525(1) | N3–C6 | 1.544(8) |
| | | | |
| Bond angles | | | |
| C10–Tc1–C20 | 92.6(2) | C10–Tc1–S1 | 96.0(2) |
| C10–Tc1–N1 | 90.0(2) | C20–Tc1–C30 | 88.0(2) |
| C10–Tc1–S1′ | 173.6(2) | C20–Tc1–S1 | 92.1(2) |
| C20–Tc1–N1 | 177.1(2) | C30–Tc1–N1 | 93.4(2) |
| C20–Tc1–S1′ | 91.5(2) | C30–Tc1–S1′ | 99.3(2) |
| C30–Tc1–S1 | 178.2(2) | N1–Tc1–S1′ | 85.9(1) |
| N1–Tc1–S1 | 86.4(1) | Tc1–S1–C2 | 104.1(1) |
| S1–Tc1–S1′ | 78.91(5) | S1–C2–N2 | 134.2(3) |
| C2–N2–C1 | 127.2(4) | N2–C1–N1 | 123.7(5) |
| C1–N1–Tc1 | 137.2(4) | Tc1–S1–Tc1′ | 101.09(5) |
| C10–Tc1–C30 | 85.8(2) | | |

The values for a second, symmetry-independent molecule are identical within the standard deviations.

Symmetry operation: $1 - x, 1 - y, 1 - z$.

Colourless needles suitable for an X-ray structure determination were obtained directly from the reaction mixture. A representation of the structure of the complex is shown in Fig. 3. Selected bond lengths and angles are summarized in Table 4. The technetium atom has a slightly distorted octahedral environment with three facially coordinated carbonyls. The chelating ligand is deprotonated and forms an almost planar chelate ring with similar nitrogen–carbon bonds as in the
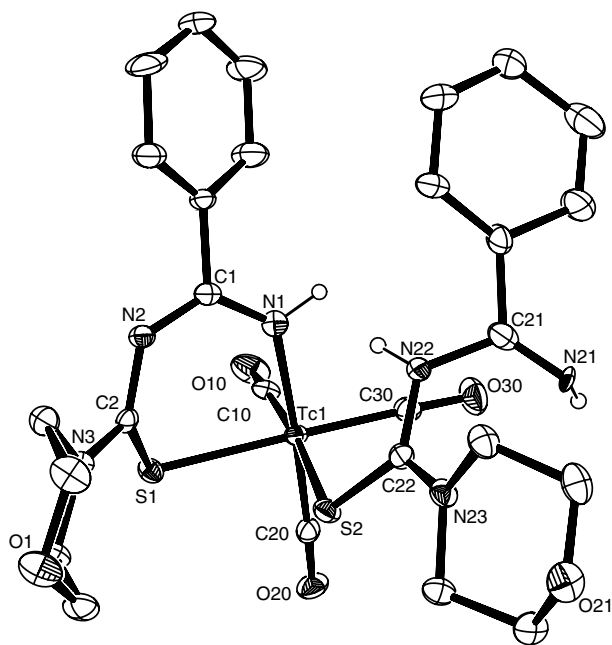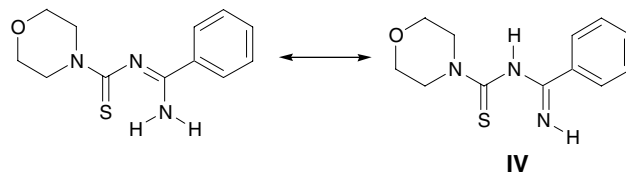


Fig. 3. Ellipsoid representation [19] of the molecular structure of [Tc(CO)$_3$(Hmorphtcb-N,S)(H$_2$morphtcb-S)]. Thermal ellipsoids represent 30% probability.

Table 4
Selected bond lengths (Å) and angles (°) in [Tc(CO)$_3$(Hmorphtcb-N,S)(H$_2$morphtcb-S)]

| Bond lengths | | | |
|---|---|---|---|
| Tc1–C10 | 1.916(5) | N2–C1 | 1.314(5) |
| Tc1–C20 | 1.890(5) | N1–C1 | 1.271(5) |
| Tc1–C30 | 1.925(5) | N3–C2 | 1.326(5) |
| Tc1–N1 | 2.157(3) | S2–C22 | 1.697(4) |
| Tc1–S1 | 2.477(1) | C22–N22 | 1.391(6) |
| Tc1–S2 | 2.527(2) | N22–C21 | 1.409(6) |
| S1–C2 | 1.738(4) | C21–N21 | 1.194(6) |
| C2–N2 | 1.353(5) | C21–C40 | 1.49(2) |
| | | | |
| Bond angles | | | |
| C10–Tc1–C20 | 85.5(2) | C10–Tc1–C30 | 91.9(2) |
| C10–Tc1–N1 | 95.6(2) | C10–Tc1–S1 | 89.8(1) |
| C10–Tc1–S2 | 174.2(1) | C20–Tc1–C30 | 90.2(2) |
| C20–Tc1–N1 | 176.4(2) | C20–Tc1–S1 | 89.8(1) |
| C20–Tc1–S2 | 91.4(2) | C30–Tc1–N1 | 93.2(2) |
| C30–Tc1–S1 | 178.3(2) | C30–Tc1–S2 | 93.1(2) |
| N1–Tc1–S1 | 86.83(8) | N1–Tc1–S2 | 87.26(9) |
| S1–Tc1–S2 | 85.28(4) | Tc1–S1–C2 | 102.0(1) |
| C2–N2–C1 | 126.5(4) | S1–C2–N2 | 124.0(3) |
| C1–N1–Tc1 | 130.9(3) | N2–C1–N1 | 127.4(4) |
| Tc1–S2–C22 | 111.4(2) | N22–C21–N21 | 122.1(4) |
| S2–C22–N22 | 120.5(3) | C22–N22–C21 | 123.3(4) |

[Tc(CO)$_3$(HEt$_2$tcb-N,S)]$_2$ dimer. The second thiocarbamoylbenzamidine ligand acts as a neutral monodentate electron donor. The Tc–S2 bond length of 2.527(2) Å is slightly longer than the Tc–S1 bond (2.477(1) Å).

An interesting structural feature in [Tc(CO)$_3$(Hmorphtcb-N,S)(H$_2$morphtcb-S)] is the bond length situation in the non-deprotonated H$_2$morptcb ligand. The distances between N22–C21 and N22–C22 (1.409(6) and 1.391(6) Å) are close to a single bond and the distance between C(21)–N(21) (1.194(6) Å) can be regarded as a carbon–nitrogen double bond. This strongly indicates that this ligand is coordinated as an imine (**IV**) despite the nitrogen atom not directly contributing to the complex formation. This tautomeric form is supported by the formation of an intramolecular hydrogen bond between the nitrogen atoms N22 and N1 (distances N22–H22 0.83(4), H22···N1 2.08(5), N22···N1 2.893(5) Å, angle N22–H22–N1 163(4)°) and a weaker intermolecular hydrogen bond between N21 and N3′ (symmetry operation $1.5 - x, 0.5 - y, z$; distances N21–H21 0.77, H21···N3′ 2.69, N21···N3′ 3.117(5) Å; angle N21–H21–N3′ 117°) and is, to the best of our knowledge, without precedent in the chemistry of *N,N*-dialkylthiocarbamoylbenzamidines [28].



In [TcN(Hmorphtcb-N,S)$_2$] and [TcO(Hmorphtcb-N,S)$_2$]Cl [25a] as in complexes with numerous other

Scheme 1.

metals, the ligands coordinate either as bidentate, monoanionic chelate ligands or as monodentate S-bonded thioureas. The latter coordination mode is found in $[Ag(H_2Et_2tcb-S)_2]^+$ [26], and the bond lengths in the ligands are close to those in the non-coordinated $H_2Et_2tcb$ [27] and indicate the enamin form.

$[Tc(CO)_3(Hmorphtcb-N,S)(H_2morphtcb-S)]$ can be regarded as an intermediate in the formation of the dimeric complex. This has been verified by a $^{99}Tc$-NMR experiment. When $[Tc(CO)_3(Hmorphtcb-N,S)(H_2mor-phtcb-S)]$ and $[NEt_4]_2[Tc(CO)_3Cl_3]$ are heated under reflux for a prolonged time, the signals of these compounds at −1132 and −868 ppm slowly decrease and a new signal appears at −1043 ppm which most probably belongs to $[Tc(CO)_3(Hmorphtcb-N,S)]_2$ (cf. the chemical shift of $[Tc(CO)_3(HEt_2tcb-N,S)]_2$ at −1020 ppm). Unfortunately we have not yet been able to isolate $[Tc(CO)_3(Hmorphtcb-N,S)]_2$ in pure from such mixtures due to the formation of numerous decomposition products in these solutions, but the CO frequencies in the IR spectra and the $^{99}Tc$ NMR signals strongly indicate this course of the reaction. The reverse experiment, the prolonged heating of $[Tc(CO)_3(HEt_2tcb-N,S)]_2$ with an excess of $H_2Et_2tcb$ did not give any evidence for the formation of $[Tc(CO)_3(HEt_2tcb-N,S)(H_2Et_2tcb-S)]$, and the dimeric technetium complex could be recovered almost quantitatively (Scheme 1). The reason for the different behaviour of the two *N,N*-dialkylthiocarbamoylbenzamidines is not yet clear. We assume that the formation of the imine form as a consequence of the monodentate complex formation is preferred with the morpholinyl-substituted ligand. The rapid formation of the observed intramolecular hydrogen bond may then contribute to the stabilization of the monomeric complex.

In the present study we could show that steric factors as well as polarization effects due to the substituents in the periphery of thiourea ligands can significantly influence the structure of the rhenium(I) and technetium(I) tricarbonyl complexes.

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