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Communication

# Mono- and Dinuclear Tricarbonyltechnetium(I) Complexes with Thiosemicarbazones

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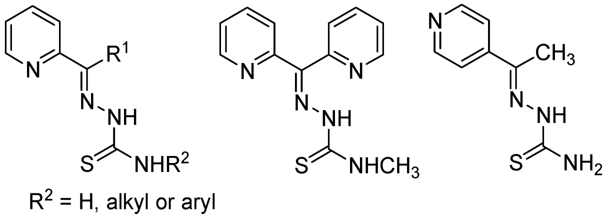
$[NEt_4]_2[Tc(CO)_3Cl_3]$ reacts with thiosemicarbazones derived from 2,2′-dipyridyl ketone ($HL^3$) and 4-acetylpyridine ($HL^4$) to form stable technetium(I) complexes of the compositions $[Tc(CO)_3Cl(HL^3–N^{py},N^{py})]$ and $[Tc_2(CO)_6Cl_2(\mu\text{-}HL^4–N^{py},S)]$. Whereas exclusively the pyridine nitrogen atoms are involved in coordination in the monomeric complex, the binuclear compound represents the first technetium complex with a coordinated thiosemicarbazone functionality.



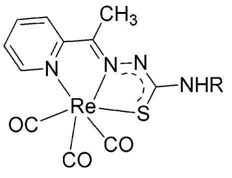
**$HL^1$** ($R^1 = CH_3$)
**$HL^2$** ($R^1 = NH_2$)

**$HL^3$**

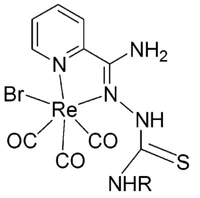
**$HL^4$**

Thiosemicarbazones are versatile ligands that can coordinate as neutral ligands or in their deprotonated form. Numerous metal complexes have been studied chemically and by X-ray crystallography.[1] Some of them show interesting biological behavior, such as antibacterial, antiviral, antineoplastic, or antimalarial activity.[2]

However, to the best of our knowledge, there is no structural information about technetium complexes with thiosemicarbazones. Early reports exclusively refer to attempts to prepare $^{99m}$Tc complexes at a concentration level of approximately $10^{-9}$ mol/L.[3] The first rhenium thiosemicarbazone complexes, $[Re^{III}(L^1)_2]^+$ cations with $HL^1$ = 2-acetylpyridine thiosemicarbazones, were published in 2003. They were prepared by a reductive ligand exchange starting from $[ReOCl_3(PPh_3)_2]$ or perrhenate.[4a] Stable rhenium(V) complexes can be isolated when 2-acetylpyridineformamide thiosemicarbazones are used instead of $HL^1$.[4b] A strong influence of the nature of the substituents in the periphery of the thiosemicarbazones on the structures of the products has also been found for tricarbonylrhenium(I) complexes. A series of neutral complexes of the composition $[Re(CO)_3Br(HL)]$ has been prepared from $[Re(CO)_5Br]$ and ferrocenecarbaldehyde thiosemicarbazone or methylacetoacetate thiosemicarbazone.[5] The presence of an additional pyridine ring in the periphery of the thiosemicarbazone ($HL^1$, $HL^2$) results in the coordination of the tricarbonylrhenium(I) unit to this donor function. Syntheses and structures of corresponding complexes with the potentially tridentate ligands $HL^1$ and $HL^2$ have been reported very recently.



**I**



**II**

Whereas $HL^1$ deprotonates during the reaction with $[NEt_4]_2[Re(CO)_3Br_3]$ and forms $[Re(CO)_3(L^1)]$ complexes (**I**) with strongly distorted, facially coordinated thiosemicarbazones, a bidentate N,N coordination of $HL^2$ is observed in the $[Re(CO)_3Br(HL^2)]$ (**II**) complexes. To date, all attempts to isolate

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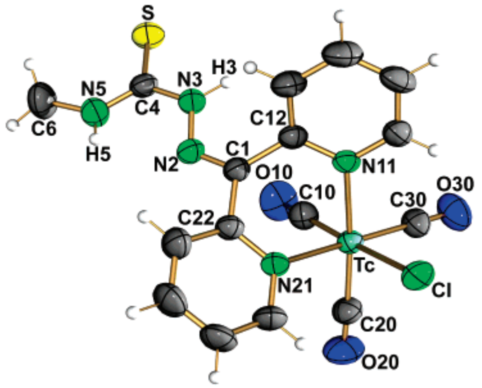

**Figure 1.** Ellipsoid representation[11] of $[Tc(CO)_3Cl(HL^3{-}N^{py},N^{py})]$ (thermal ellipsoids represent 50% probability).

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) in $[Tc(CO)_3Cl(HL^3{-}N^{py},N^{py})]^{a,b}$

| | | | |
|---|---|---|---|
| Tc−N11 | 2.000(3) | Tc−N21 | 2.194(3) |
| Tc−Cl | 2.475(1) | C1−N2 | 1.281(4) |
| N2−N3 | 1.352(4) | N3−C4 | 1.370(4) |
| C4−N5 | 1.317(4) | C4−S | 1.664(3) |
| Cl−Tc−C10 | 178.5(1) | Cl−Tc−C20 | 90.5(1) |
| Cl−Tc−C30 | 94.8(1) | Cl−Tc−N11 | 86.27(7) |
| Cl−Tc−N21 | 86.47(7) | C10−Tc−C20 | 88.8(2) |
| C10−Tc−C30 | 86.1(2) | C10−Tc−N11 | 94.3(1) |
| C10−Tc−N21 | 92.8(1) | C20−Tc−C30 | 89.4(2) |
| C20−Tc−N11 | 176.6(2) | C20−Tc−N21 | 95.6(2) |
| C30−Tc−N11 | 92.2(1) | C30−Tc−N21 | 175.0(2) |
| N11−Tc−N21 | 83.0(1) | | |

[a] Mean values taken for two independent molecules. For individual bond lengths see Table S4. [b] Tc−C bonds are in the range between 1.883(4) and 1.904(4) Å.

technetium analogues of these compounds failed. Attempted reactions between $[NEt_4]_2[Tc(CO)_3Cl_3]$ and $HL^1$ or $HL^2$ only lead to oily products and/or decomposition of the organic ligands. In the present communication, we describe the reactions of $[NEt_4]_2[Tc(CO)_3Cl_3]$ with $HL^3$ and $HL^4$ and the structures of the isolated products.

The addition of $HL^3$ to a solution of $[NEt_4]_2[Tc(CO)_3Cl_3]$ in methanol results in the formation of an orange-red solid of $[Tc(CO)_3Cl(HL^3{-}N^{py},N^{py})]\cdot 0.5MeOH$ (**III**).[6] The IR frequency of the C=S bond at 760 cm$^{-1}$ is almost uninfluenced by the complex formation, and the NH proton signals in the $^1$H NMR spectrum of the products appear at the same positions as in uncoordinated thiosemicarbazone.These facts strongly indicate that the thiosemicarbazone site of $HL^3$ is not involved in the coordination of the metal and that only one or two pyridine rings bind to technetium. This is confirmed by the X-ray crystal structure of the compound.

$[Tc(CO)_3Cl(HL^3{-}N^{py},N^{py})]\cdot 0.5MeOH$ crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent molecules per unit cell.[7] Figure 1 depicts an ellipsoid representation of one of the complex molecules. Selected bond lengths and angles are summarized in Table 1. The coordination spheres of the technetium atoms are distorted octahedra with main distortions in the N−Tc−N angles [83.2(1)° and 82.8(1)°] due to the restricting bite angles of the six-membered chelate rings. $HL^3$ coordinates technetium as a neutral, bis-pyridine ligand. The thiosemicarbazone unit remains unaffected. This bonding mode can be understood by the well-documented preference of $\{Tc(CO)_3\}^+$ centers to bind to aromatic amines,[8] which can also be used for the specific labeling of histidine-rich sites in peptides and proteins for nuclear medical purposes.[9] The bond lengths and angles of the thiosemicarbazone subunit in complex **III** closely resemble the bonding situation in the noncoordinated compound.[10] Hydrogen atoms H3 and H5 form hydrogen bonds to Cl and S atoms of neighboring molecules. These interactions and additional hydrogen bonds due to the solvent MeOH establish a three-dimensional network. Details are shown in Figure S1 and Table S1 of the Supporting Information.

The formation of a monomeric technetium complex with $HL^3$ is, however, surprising with respect to the behavior of the analogous tricarbonylrhenium(I) complex $[NEt_4]_2[Re(CO)_3Br_3]$, which reacts with $HL^3$ to form the dimeric complex $[Re_2(CO)_6Br(L^3)]$ (**IV**) (see also Scheme 1). Similar complexes with this unusual coordination mode of $[L^3]^-$ as formally pentadentate ligand have also been obtained starting from $[Re(CO)_3X(CH_3CN)_2]$ complexes (X = Cl or Br).[10] The two rhenium atoms in complex **IV** are linked by a singly deprotonated thiosemicarbazone, which establishes two five-membered chelate rings to one metal atom and one six-membered ring to the other. This results in a conjugated $\pi$-system inside the thiosemicarbazone backbone.

For technetium, we could not find any evidence for the formation of such dimers. This has been confirmed by a $^{99}$Tc NMR experiment in acetonitrile-$d_3$ as the solvent. Only two signals at −1132 and −1057 ppm are observed during the reaction of $[NEt_4]_2[Tc(CO)_3Cl_3]$ with $HL^3$, which can be assigned to the precursor and $[Tc(CO)_3Cl(HL^3)]$, respectively. The latter signal is practically the only $^{99}$Tc resonance that

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(6) $[Tc(CO)_3Cl(HL^3)]\cdot 0.5MeOH$:$HL^3$ (14 mg, 0.05 mmol) was added to a solution of $[NEt_4]_2[Tc(CO)_3Cl_3]$ (55 mg, 0.1 mmol) in EtOH (5 mL). The reaction mixture was heated on reflux about for 2 h and then stirred at room temperature for 1 h. The resulting orange-red solution was filtered, and a yellow precipitate was filtered off (10 mg, 40%). Yellow-orange single crystals were obtained after slow concentration of a MeOH solution of the complex. For spectroscopic data see Table S3.

(7) X-ray crystal structure calculations: $[Tc(CO)_3Cl(HL^3)]\cdot 0.5MeOH$: CAD4 (Enraf Nonius), $\underline{C}_{16.5}H_{15}N_5O_{3.5}ClSTc$, orange-yellow blocks, triclinic, space group $P\bar{1}$, $a$ = 8.006(1) Å, $b$ = 13.830(2) Å, $c$ = 18.781(2) Å, α = 97.44(1)°, $\beta$ = 91.18(1)°, $\gamma$ = 98.47(1)°, $V$ = 2037.8(4) Å$^3$, Z = 4. $D_{calc}$ = 1.646 g/cm$^3$, $\theta$ = 3−27°, 10 791 reflections collected, 8865 independent, $\mu$ = 0.970 mm$^{-1}$ (no absorption correction applied), solved by direct methods and refined by full-matrix least-squares procedures using SHELXS and SHELXL (Sheldrick, G. M. University of Göttingen, Germany), 515 parameters, R = 0.0442, wR = 0.1171. $[Tc_2(CO)_6Cl_2(\mu\text{-}HL^4)_2]\cdot 2CH_3CN$: Bruker Smart CCD, $C_{26}H_{26}N_{10}{-}O_6Cl_2S_2Tc_2$, orange-red plate, monoclinic, space group $C2/c$, $a$ = 29.416(7) Å, $b$ = 7.584(2) Å, $c$ = 15, 540(4) Å, $\beta$ = 92.57(1)°, $V$ = 3463(1) Å$^3$, Z = 4. $D_{calc}$ = 1.737 g/cm$^3$, $\theta$ = 2.62−27.54°, 16431 reflections collected, 3927 independent, $\mu$ = 1.128 mm$^{-1}$ (absorption correction SADABS, $T_{min}$ = 0.8926, $T_{max}$ = 0.9563), solved by direct methods and refined by full-matrix least-squares procedures using SHELXS and SHELXL (G. M. Sheldrick, University of Göttingen, Germany), 222 parameters, R = 0.0287, wR = 0.0575.

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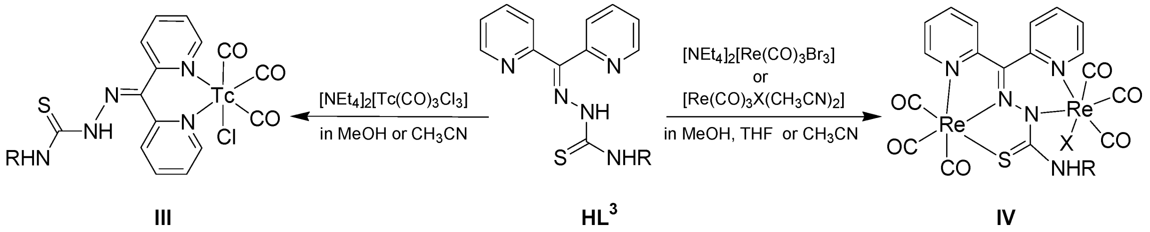
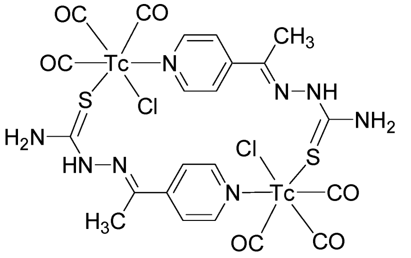
**Scheme 1.** Reactions of HL$^3$ with Common Tricarbonylrhenium(I) and -Technetium(I) Precursors



can be detected after a 2-h refluxing period. The addition of a supporting base such as $NEt_3$ did not result in the deprotonation of the thiosemicarbazone and the formation of a dimeric compound of type **IV**. The reasons for the different behaviors of technetium and rhenium are not yet clear. It might be attributable not only to differences in the acidity of the tricarbonylmetal centers, but also to factors such as the high tendency of the $\{Tc(CO)_3\}^+$ core to bind to aromatic amines,[8,9] and the slightly different reactivities of the intermediately formed solvent complexes $[M(CO)_3(solv)_3]^+$ should play a role.

A dimeric product of the composition $[Tc_2(CO)_6Cl_2(\mu\text{-}HL^4)_2]\cdot 2CH_3CN$ (**V**) is formed during reactions of $[NEt_4]_2[Tc(CO)_3Cl_3]$ with HL$^4$ in acetonitrile.[12] The 4-position of the nitrogen atom in the pyridine ring prevents chelate formation, as has been observed for tricarbonylrhenium(I) complexes with ligands of the types HL$^1$ and HL$^2$.[4,5] This results in a head-to-tail coordination of two $\{Tc(CO)_3\}^+$ units.



**V**

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) in $[Tc_2(CO)_6Cl_2(\mu\text{-}HL^4{-}N^{py},S)_2]$[a,b]

| | | | |
|---|---|---|---|
| Tc−N11 | 2.219(2) | Tc−S′ | 2.5498(9) |
| Tc−Cl | 2.5304(8) | C1−N2 | 1.289(3) |
| N2−N3 | 1.376(3) | N3−C4 | 1.349(3) |
| C4−N5 | 1.314(4) | C4−S | 1.716(3) |
| Cl−Tc−C10 | 178.64(9) | Cl−Tc−C20 | 94.4(8) |
| Cl−Tc−C30 | 89.61(8) | Cl−Tc−N11 | 87.83(6) |
| Cl−Tc−S′ | 89.61(2) | C10−Tc−C20 | 87.3(1) |
| C10−Tc−C30 | 90.2(1) | C10−Tc−N11 | 92.3(1) |
| C10−Tc−S′ | 89.04(9) | C20−Tc−C30 | 90.4(1) |
| C20−Tc−N11 | 92.1(1) | C20−Tc−S′ | 176.16(8) |
| C30−Tc−N11 | 156.50(9) | C30−Tc−S′ | 88.40(9) |
| N11−Tc−S′ | 89.20(6) | Tc−S′-C4′ | 108.44(9) |

[a] Symmetry transformation: $-x + 1/2, -y + 1/2, -z + 1$. [b] Tc−C bonds are in the range between 1.892(3) and 1.916(3) Å.

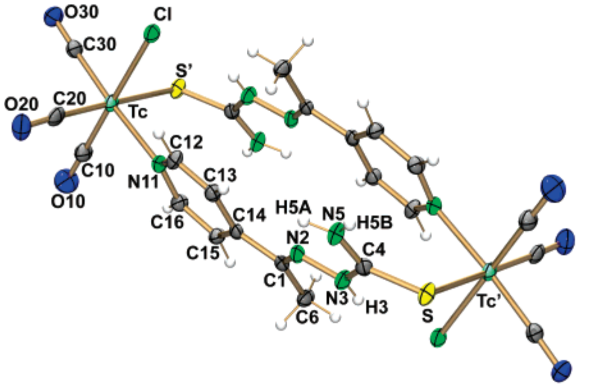


**Figure 2.** Ellipsoid representation[11] of $[Tc_2(CO)_6Cl_2(\mu\text{-}HL^4{-}N^{py},S)_2]$ (thermal ellipsoids represent 50% probability).

The molecular structure of **V** is a centrosymmetric dimer formed by two bridging S,N11-thiosemicarbazones.[7] It represents the first structurally characterized technetium complex that contains a coordinated thiosemicarbazone ligand. Figure 2 depicts the molecular structure of the compound along with the atomic labeling scheme. The technetium atoms are octahedrally coordinated by three carbonyl carbon atoms in fac arrangements, a chloro ligand, and the N11 and S atoms of two thiosemicarbazone ligands. Selected bond lengths and angles are listed in Table 2. Despite the fact that thiosemicarbazone is not deprotonated in **V**, considerable delocalization of π-electron density is indicated by the elongation of the C4−S bond (e.g., compared to the situation in **IV**) and some bond-length equalization in the skeleton of the ligand. The configuration of the thiosemicarbazone[10] with respect to the C1−N2(*E*), N2−N3(*E*), and N3−C4(*E*) bonds is maintained after coordination in the bridging units. The complexes are connected by a network of hydrogen bonds involving H5A, H5B, and H3 (Table S2 and Figure S2, Supporting Information). The solvent molecules are located in channels along the crystallographic *b* axis.

More studies on the reactivity of the presented complexes (particularly on the potential of complexes of the type **III** to serve as building blocks in the synthesis of bimetallic complexes) and with ligands having other substituents in their periphery are currently being carried out in our laboratory.

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**Supporting Information Available:** Spectroscopic data of the complexes, tables, and figures of the hydrogen bonds in $[Tc(CO)_3Cl(HL^3{-}N^{py},N^{py})]$ and $[Tc_2(CO)_6Cl_2(\mu\text{-}HL^4{-}N^{py},S)]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) $[Tc_2(CO)_6Cl_2(HL^4)_2]\cdot 2CH_3CN$:HL$^4$ (0.19 mg, 0.1 mmol) was added to a solution of $[Et_4N]_2[Tc(CO)_3Cl_3]$ (55 mg, 0.1 mmol) in $CHCl_3$ (6 mL). The reaction mixture was heated on reflux for about 1 h. The yellow solid formed was filtered off and redisolved in $CH_3CN$. Orange-red crystals of X-ray quality precipitated upon slow concentration. For spectroscopic data see Table S3.