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The formation of tetrameric oxotechnetium(V) and oxorhenium(V) complexes by cyclisation of a potentially multidentate thiocarbohydrazide derivative

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ABSTRACT

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Keywords: Technetium Rhenium Oxo complex Cyclisation X-ray structure Tetrameric complexes of the composition $[MO(L^1)]_4$ (M=Tc, Re), where $(L^1)^{3-}$ represents an asymmetric, trianionic cyclisation product with thiocarbamoylbenzamidinato and mercaptotriazolato donor sites, were formed during reactions of $[TcOCl_4]^-$ or $[ReOCl_4]^-$ with a potentially multidentate ligand derived from thiocarbohydrazide and N-[N',N'-diethylamino(thiocarbonyl)]benzimidoyl chloride.

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N-[(Dialkylamino)(thiocarbonyl)]benzamidines can readily be prepared from *N*-[(dialkylamino)(thiocarbonyl)]benzimidoyl chlorides and amines [1,2]. Recently, we extended the well-known coordination chemistry of bidentate ligands of this type [3] to novel tridentate *N*-[(dialkylamino)(thiocarbonyl)]benzamidines and studied their coordination behavior towards oxorhenium(V) and oxotechnetium(V) cores [3–7]. This also includes benzamidines derived from 4, 4-dialkylthiosemicarbazides, which form surprisingly stable technetium(V) and rhenium(V) complexes [5,7].

In the present communication, we extend our studies to a thiocarbamoylbenzamidine, which has been derived from thiocarbohydrazide (H_4L^0), and its reaction products with common technetium(V) and rhenium(V) precursors. H_4L^0 can readily be prepared as a yellow solid from thiocarbohydrazide and N-[N',N'-diethylamino (thiocarbonyl)]benzimidoyl chloride according to Scheme 1. The identity of the compound was proven by elemental analysis and its IR, NMR and mass spectra [8].

 $\rm H_4L^0$ readily reacts with (NBu₄)[TcOCl₄] or (NBu₄)[ReOCl₄] under formation of reddish brown, microcrystalline solids, which are almost insoluble in common organic solvents (Scheme 2) [9,10]. Their low solubility prevented mass and NMR spectroscopic studies. But the infrared spectra of the complexes suggest coordination of the thiocarbamoylbenzamidine units of the organic ligand by a strong shift of the CN vibrations of $\rm H_4L^0$ from 1643 cm⁻¹ to 1531 (Tc complex) and 1539 cm⁻¹ (rhenium compound), respectively. Such a bathochromic shift is characteristic for thiocarbamoylbenzamidinato complexes and normally goes along with an extended transfer of π -electron density between the CN bonds of the ligand backbone in such compounds [3–7,11]. The crystallization of the products succeeded either from an extremely diluted CH₂Cl₂ solution (CH₂Cl₂ solvate of the rhenium complex) or directly from two-phase reaction mixtures (solvent-free single crystals of the Tc complex and aqua solvate of the Re compound) [10,11].

The results of the X-ray structural determinations [12,13] on [TcO- (L^1)]₄, and the pseudopolymorphs $[\text{ReO}(L^1)]_4 \cdot H_2\text{O}$ and $[\text{ReO}(L^1)]_4 \cdot$ $H_2O \cdot CH_2Cl_2$ confirm the conclusions drawn from the IR spectra, but also show that a more complicate ongoing reaction appeared during the complex formation. The central $\{TcO\}^{3+}$ or $\{ReO\}^{3+}$ units form five- and six-membered chelate rings with one half of the organic ligand, while a ring closure is observed in the remaining part, which yields a triazolethiolato unit. Fig. 1a shows an ellipsoid representation of the asymmetric unit of the technetium complex, while Fig. 1b contains a representation of the complete tetrameric compound. The rhenium complex is isostructural and is therefore not depicted in this communication. Both compounds are tetramers and possess four subunits with each five-coordinate oxotechnetium(V) or oxorhenium(V) cores, the equatorial coordination spheres of which are occupied by the S,N,S donor atom set of the organic ligand, while the remaining fourth position accommodates the sulfur atom of the triazolthiolato moiety of an adjacent asymmetric unit generated from cyclisation of the second half of H₄L⁰ during the complex formation.

The bonding situation inside the monomeric units is unexceptional with TcO and ReO double bond lengths between 1.6 and 1.7 Å and M—S and M—N bonds in the expected range (Table 1). A slight double bond character may be discussed for the relatively short M—N5 bonds, which are 2.011(5)Å ([TcO(L¹)]₄) and 2.029(5)Å ([ReO(L¹)]₄). Similar values are observed in rhenium and technetium complexes

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Scheme 1. Formation of H₄L⁰.

with mixed thiocarbamoylbenzamidinate/thiosemicarbazide coordination spheres [5,7]. The metal atoms in the $[MO(L^1)]_4$ (M=Tc, Re) complexes are situated above the mean planes formed by the donor atoms of the equatorial coordination spheres by 0.741(2)Å (Tc compound) and 0.721(2)Å (Re complex). Such values are normally observed for five-coordinate oxotechnetium(V) and oxorhenium(V) complexes and are commonly explained by the steric bulk of the double bonded oxo ligand [14]. While the five-membered chelate rings are almost planar with maximum deviations of 0.127(3)Å (Tc complex) and 0.126(4)Å (Re complex), the six-membered thiocarbamoylbenzamidinate chelate rings show very strong deviations from planarity. Nevertheless, the C—N bonds inside the rings are all between 1.31 and 1.38Å, which supports a delocalization of the electron density inside the chelate rings.

The formation of N-heterocyclic ring systems is an occasionally observed reaction pattern in the coordination chemistry of thiosemicarbazones and related ligand systems and is normally related to a metal-induced mechanism [15]. This is also highly probable for the reaction under study, since prolonged heating of H_4L^0 in various solvents does not show any evidence for the cyclisation observed in the presence of the rhenium compound. A possible mechanism is given in Scheme 3. As a consequence of the coordination of a $\{\text{ReO}\}^{3+}$ core to one side of H_4L^0 , the nucleophilicity of the remaining hydrazinic nitrogen atoms is increased, which results in a ring closure reaction and the abstraction of diethylamine. The final formation of a tetrameric complex is obtained by coordination of the mercaptotriazolato unit to the fourth equatorial coordination site of an adjacent oxotechnetium unit.





Fig. 1. a) Ellipsoid representation of the asymmetric unit of the molecular structure of $[TcO(L^1)]_4$ with the molecular labelling scheme. Structure determinations were done with SHELX [16] b) Molecular structure of the tetrameric complex $[TcO(L^1)]_4$ [17].



Scheme 2. Reaction of H_4L^0 with (NBu₄)[MOCl₄] complexes (M = Tc, Re).

Table 1

	$[TcO(L^1)]_4/[ReO(L^1)]_4$		$[TcO(L^1)]_4/[ReO(L^1)]_4$
Tc/Re—O10	1.639(5)/1.663(7)	N3—C4	1.314(9)/1.31(1)
Tc/Re—S1	2.304(2)/2.304(2)	C4—N5	1.386(8)/1.377(9)
Tc/Re—N5	2.011(5)/2.029(5)	N5—N6	1.419(7)/1.407(8)
Tc/Re—S8	2.287(2)/2.291(2)	N6—C7	1.277(8)/1.245(9)
Tc/Re—S36′	2.361(2)/2.357(2)	C7—S8	1.744(7)/1.760(7)
S1—C2	1.743(7)/1.741(9)	C33—S36	1.734(6)/1.752(7)
C2—N3	1.348(9)/1.34(1)		
O10—Tc/Re—S8	114.6(2)/114.6(2)	C4—N3—C2	125.8(6)/124.3(7)
O10—Tc/Re—N5	103.5(2)/103.5(2)	N3—C2—S1	1232.6(5)/124.1(7)
O10—Tc/Re—S1	113.8(2)/111.8(2)	Tc/Re—S1—C2	108.0(3)/108.1(3)
O10—Tc/Re—S36′	105.3(2)/105.0(2)	S1—Tc/Re—N5	89.1(2)/89.4(2)
Tc/Re—S8—C7	97.3(2)/97.1(2)	S1—Tc/Re—S36′	85.46(6)/85.93(7)
S8—C7—N6	124.9(5)/124.6(6)	N5—Tc/Re—S8	80.6(2)/80.2(2)
C7—N6—N5	111.0(5)/112.6(6)	S8—Tc/Re—S36′	81.48(6)/82.25(7)
Tc/Re—N5—N6	123.4(4)/122.7(4)	S1—Tc—S8	131.53(8)/133.59(9)
Tc/Re—N5—C4	121.4(4)/120.9(5)	N5—Tc—S36′	150.4(2)/150.8(2)
N5-C4-N3	123.0(6)/124.3(7)		

^{a)}Intramolecular bond lengths and angles in the CH_2Cl_2 solvate of $[ReO(L^1)]_4$ do not significantly differ and are therefore not given separately. Symmetry operation: (') y - 1, 1 - x, 2 - z.



Scheme 3. Proposed mechanism of the formation of the [MO(L¹)]₄ complexes.

All four oxo ligands direct to the center of the voids (distances between neighboring metal atoms: 5.2671(2)Å (Tc complex) and 5.2945(2)Å (Re complex); distances between diagonal metal atoms: 7.2303(3)Å (Tc complex) and 7.2779(3)Å (Re complex)), which are formed between the four metal atoms (Fig. 1b). Consequently, the empty sixth coordination sides point to the outer sphere of the complex and may be matter for the coordination of additional ligands. With a careful selection of bifunctional linker ligands, the tetrameric compound under study can be used as building blocks for supramolecular assemblies.

Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.04.037.

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- [8] Synthesis of H₄L⁰: Thiocarbohydrazide (278 mg, 2.6 mmol) and triethylamine (75 µL, 5.4 mmol) were dissolved in 15 ml dry THF and N-[N',N'-diethyl(thiocarbonyl)]-benzimidoyl chloride (1.31 g, 5.4 mmol) in 5 mL of the same solvent was slowly added. The reaction mixture was stirred for 4 h at room temperature. The colourless solid of (HNEt₃)Cl, which was formed during this time, was filtered off and the solvent of the filtrate was removed in vacuum. The remaining yellow oil was suspended in diethylether and stored for 48 h at 18 °C, which resulted in the formation of a yellow solid, which was carefully washed with diethylether and dried in vacuum. Yield: 1.01 g (70%). Elemental analysis: Calc. for 2g-H₃A₁Ag₅3; C, 55.3; H, 6.3; N, 20.6; S, 17.7 %. Found: C, 56.2; H, 6.3; N, 19.8; S, 17.0%. IR (KBr, v_{max} in cm⁻¹): 3186 (w), 2974 (m), 1643 (m), 1566 (w), 1481 (s), 1346 (m), 1315 (m), 1265 (s), 1134 (m), 1072 (m), 907 (w), 841 (w), 772 (s), 691 (s). ¹H NMR (ô, CDCl₃): 1, 14 (m, 6 H, CH₃), 1.25 (m, 6 H, CH₃), 3.06 (q, 4 H, CH₂), 3.40 (m, 4 H, CH₂), 7.2–8.0 (m, 10 H, arom.), 9.48 (s, 2 H, NH), 10.40 (s, 2 H, NH). ESI⁺ MS: *m/z*: 543.215 [M+H]⁺, 565.197 [M+Na]⁺, 581.17 [M+K]⁺.
- [9] Synthesis of [TcO(L¹)]₄: (NBu₄)[TcOCl₄] (50 mg, 0.1 mmol) was dissolved in 4 ml MeOH and H₄L⁰ (59 mg, 0.1 mmol) was added in 4 ml MeOH. The mixture was stirred at room temperature for 30 min. A very fine, sparingly soluble red precipitate was formed during this time. The solid was dissolved in about 50 ml of warm CH₂Cl₂, from which [TcO-(L¹)]₄ deposited upon cooling and slow evaporation as red microcrystals. Yield: 57 mg (95%). Single-crystals of [TcO

 $[L^1)]_4$ were grown by careful overlayering of a highly diluted CH₂Cl₂ solution of (NBu₄)[TcOCl₄] with a solution of H₄L⁰ in MeOH. Slow diffusion of the two solutions gave a deposit of red crystals at the interface between the two layers. The identity of this product with the bulk, which was prepared following the procedure given above was proven by means of their IR spectra and elemental analyses. Elemental analysis: Calc. for C₈₄H₈₀N₂₈O₄S₁₂RTc₄: Tc, 17.0 %. Found: Tc, 15.9 %. IR (KBr, v_{max} in cm⁻¹): 2974 (w), 1531 (s), 1443 (m), 1350 (s), 1254 (w), 138 (w), 1096 (w), 1072 (w), 961 (m), 945 (m), 775 (w), 729 (m), 683 (m).

- [10] Synthesis of $[ReO(L^1)]_4$: a) (NBu₄)[ReOCl₄] (59 mg, 0.1 mmol) and H₄L⁰ (59 mg, 0.1 mmol) were dissolved in 2 ml MeOH and stirred at room temperature for 30 min. The deposited yellow-brown solid was filtered off and re-dissolved in a large amount (approximately 200 ml) of CH₂Cl₂, from which $[ReO(L^1)]_4$ precipitated as orange-red small crystals. Yield: 63 mg (94%).b) $[ReOCl_3(PPh_3)_2]$ (83 mg, 0.1 mmol) was suspended in 5 ml CH₂Cl₂ and H₄L⁰ (59 mg, 0.1 mmol) was added. A brownish solid was obtained after stirring for 1 h at room temperature. Recrystallisation from about 200 ml CH₂Cl₂ gave an orange-red, crystalline solid of $[ReO(L^1)]_4$ · H₂O· CH₂Cl₂. Yield: 65 mg (91%).Single crystals of $[ReO(L^1)]_4$ · H₂O were obtained following the two-phase reaction described above for the technetium compound. Elemental analysis: Calc. for C₈4H₈₀N₂₈O₅1₂Re₄: C, 37.7; H, 3.0; N, 14.6; S, 14.4%. Found: C, 37.3; H, 2.7; N, 14.3; S, 14.1%. IR (KBr, ν_{max} in cm⁻¹): 2974 (w), 1539 (s), 1443 (m), 1350 (s), 1254 (w), 1138 (w), 1096 (w), 1072 (w), 988 (m), 949 (m), 775 (w), 729 (m), 683 (m).
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- [13] Crystal data for $[ReO(L^1)]_4$: H_2O : tetragonal, space group $P\overline{42}_1c$, a=19.246(1), b=19.246(1), c=14.454(1) Å, V=5353.9(5) Å³, Z=2. STOE-IPDS, Mo K α radiation ($\lambda = 0.71073$ Å), T=200 K, 48033 reflections measured, 7246 independent, 308 parameters, $\mu = 4.802$ mm⁻¹, absorption correction: integration,

T_{min} = 0.2784; T_{max} = 0.6275. Structure solution and refinement: SHELXS-97, SHELXL-97 [16], R1 = 0.0495, wR2 = 0.1258, GooF = 0.956, Flack - 0.02(1), CCDC deposit number: CCDC-815916.*Crystal data for [ReO(L¹)]*₄. *H*₂*O*. *CH*₂*Cl*₂: orthorhombic, space group P22₁2₁, a = 14.124(1), b = 19.076(1), c = 20.398(1) Å, V = 5495.8 (6) Å³, Z = 2. STOE-IPDS, Mo Kα radiation (λ = 0.71073 Å), T = 200 K, 99363 reflections measured, 14879 independent, 647 parameters, μ = 4.728 mm⁻¹, absorption correction: integration, T_{min} = 0.2538; T_{max} = 0.6179. Structure solution and refinement: SHELXS-97, SHELXL-97 [16], R1 = 0.0475, wR2 = 0.1255, GooF = 1.081. Flack 0.001(7). CCDC deposit number: CCDC-815917.

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