1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol, a Ligand with a Remarkable Versatility for Metal Ions

Part XIII 1)

Complex Formation with Rhenium(I) and Rhenium(VII)

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Dedicated to Professor *André Merbach* on the occasion of his 65th birthday

The two neutral complexes $[Re(CO)_3(H_{-1}taci)]$ (**1**) and $[ReO_3(H_{-1}taci)]$ (**2**) (taci = 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol) were synthesized from the conventional Re^{I} and Re^{VII} precursors $(Et_4N)_2[ReBr_3(CO)_3]$ and $[ReO_3(OSnMe_3)]$. The crystal structures of **1** and **2**, which were determined by single crystal X-ray analysis, are virtually isomorphous. Both compounds crystallize in the orthorhombic space group *Pnma*, $Z = 4$; **1**: $a = 14.806(3)$, $b = 8.466(2)$, $c = 9.781(2)$ Å, **2**: $a = 13.050(2)$, $b = 8.732(1)$, $c = 9.061(1)$ Å. In both complexes, the monodeprotonated H_{-1}taci ligand is bonded to the Re center in an N,O,N-coordination mode. The resulting molecular C_s symmetry is retained in the crystal structure and confirmed by IR spectroscopy of solid-state samples. The observed binding mode of the ligand is discussed in terms of steric and electronic effects.

Introduction. – Rigid tridentate ligands that are restricted to facial coordination, such as 1,4,7-triazacyclononane or tris(pyrazolyl)borate (= hydridotris(1*H*-pyrazolato-κN^1)borate(1 –)), have been widely used in transition metal chemistry [1][2]. The specific steric restraints of these chelators allow the design of well-defined coordination geometry, rendering them particularly suitable for the construction of catalysts or as mimics for the metal-binding sites of metalloproteins [3]. In recent times, facially coordinating ligands with a mixed N,O,N donor set, such as bis(1*H*-pyrazol-1-yl)acetate ('scorpionate ligands') received increased attention [4–6]. In our laboratory, we have investigated the coordination chemistry of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) [7][8]. This compound has four different metal binding sites (*Scheme*) with either N,N,N- (*i*), N,O,N- (*ii*), O,N,O- (*iii*), or O,O,O-coordination (*iv*) modes available. All four sites are restricted to facial coordination. The different steric requirements and electronic properties of the four sites give rise to selective binding of different metal ions. Hard and small cations such as Al^{3+} or Mg^{2+} bind selectively to the three O-donors (*iv*) [9][10]. Divalent 3d transition metal cations show a preference for type-(*i*) N,N,N binding [11], whereas the lanthanides undergo type-(*iii*) O,N,O

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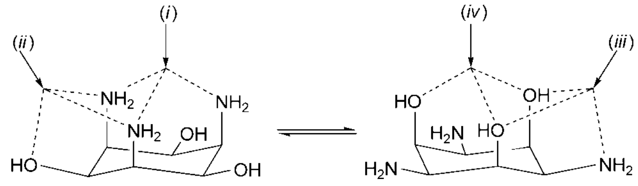
1) Part XII: see [8].

coordination [12]. Interestingly, the type-(*ii*) N,O,N structure has seldom been observed. We found this type of coordination in a complex with the trinuclear $[Mo_3S_4]^{4+}$ core [13] and in an inert complex of Co^{III}, where it was obtained by kinetic rather than thermodynamic control of the formation reaction [11].

Scheme 1. *The Four Possible Coordination Modes of 1,3,5-Triamino-1,3,5-trideoxy*-cis-*inositol* (taci)



The type-(*ii*) structure has also been observed in a series of Re^V complexes with taci derivatives, where additional *ortho*-$CH_2-C_6H_4-OH$ coordinating groups were attached on the amine donors (*Fig. 1*) [14][15]. However, the preferred structure for a Re complex with the simple, unsubstituted taci remained unknown. Moreover, there was no information available on whether a change of the oxidation number would also result in a different structure. More-comprehensive knowledge of the coordination behavior of Re in its various oxidation states would be of considerable interest in the context of the design of stable Re complexes, such as those required for nuclear medicine applications [16]. We have, therefore, prepared two new [Re(taci)] complexes, $[Re(CO)_3(H_{-1}taci)]$ (**1**) and $[ReO_3(H_{-1}taci)]$ (**2**), where the metal center is present in valence states at the low (+ I) and high (+ VII) end of the possible range of oxidation numbers, and report the molecular structure of these two complexes.

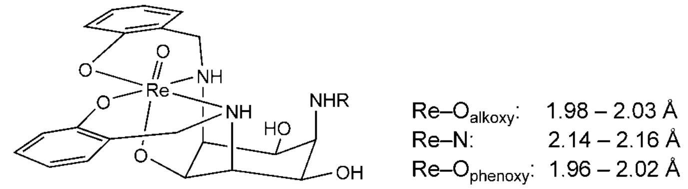


Fig. 1. *Structural diagrams of* Re^V *complexes with extended taci-type ligands as reported in* [14] *and* [15]

Results and Discussion. – The tricarbonyl complex **1** was prepared from the well-known $(Et_4N)_2$-*fac*-$[Re(CO)_3Br_3]$ precursor [17]. The tribromide was dissolved in MeOH and converted into the corresponding solvate derivative (possibly *fac*-$[Re(CO)_3(MeOH)_3]^+$). The liberated Br^- was precipitated as AgBr. Further treatment with taci resulted in the direct formation of the neutral *fac*-$[Re(CO)_3(H_{-1}taci)]$ (**1**), where the taci ligand is present in its monodeprotonated form. Addition of a base was not necessary. The trioxo complex **2** was prepared from $[ReO_3(OSnMe_3)]$ [18]. Both complexes were obtained as white solids. They are air-stable and require no special protection against moisture or oxygen. Some information on the structural properties could be derived from IR spectroscopy. Binding of the *fac*-$[Re(CO)_3]^+$ unit by the three O- or N-donors of taci (type (*i*) or type (*iv*)) would result in a C_{3v} structure for **1**, and two characteristic CO stretching vibrations (symmetry species A and E) would be expected around 1850–2050 cm^{-1} [19][20]. For an asymmetric coordination mode such as type (*ii*) or type (*iii*), the symmetry of the complex is lowered to C_s, the degeneracy of the E-mode is lost, and, consequently, a total of three CO stretching vibrations should be observed. Such IR features have, for example, been reported for a large variety of C_s-symmetric complexes of composition $[Re(CO)_3(bpy)X]$ [21][22] (bpy = 2,2′-bipyridine, X = monodentate ligand). The observation of three CO stretching vibrations in *fac*-$[Re(CO)_3(H_{-1}taci)]$ (**1**) at 2010, 1902, and 1860 cm^{-1} is thus consistent with an asymmetric C_s structure. Moreover, the observation of well-resolved bands is indicative of characteristic differences between the two type of donor groups in terms of σ- and π-bonding properties (*vide infra*). Similarly, the trioxo complex **2** exhibited three strong and well-resolved bands at 934, 914, and 894 cm^{-1}, indicative of Re=O stretching vibrations [20]. For both compounds, the observed positions of these bands are very similar to those reported for related $[Re(CO)_3]^+$ and $[ReO_3]^+$ complexes [4][5][21–32].

Single crystals of **1** and **2** were subjected to X-ray-diffraction analysis. Interestingly, the two crystal structures are virtually isotypic. Both complexes crystallize in the orthorhombic space group *Pnma*. Compared to the $[Re(CO)_3]^+$ unit, the $[ReO_3]^+$ entity is sterically less demanding, and, consequently, the volume of the unit cell of **2** is slightly smaller. The Re-centers of both complexes are bonded to the 'asymmetric' N,O,N site of the taci ligand (*Fig. 2,a* and *b*), which is consistent with the IR characteristics (*vide supra*). The molecular C_s symmetry is retained in the crystal structure: the atoms of the fragments *trans*-OC−Re−O_{taci}−C in **1** and *trans*-O−Re−O_{taci}−C in **2** together with the non-coordinating CH−N group are all placed on a crystallographic mirror plane.

The complexes both exhibit distorted octahedral coordination of the Re-centers. However, deviation from an ideal geometry is much more significant in the oxo complex **2**. This deviation arises mainly from angular deformation within the $[ReO_3]^+$ unit (see *Fig. 2* and *Table 1*) with only minor differences in geometry of the two Re−H_{-1}taci fragments. The charge neutrality of the complexes requires the taci ligand in **1** and **2** to bear a mono-negative charge, which obviously arises from deprotonation of the coordinated alcoholic O-donor. $[Re(CO)_3]^+$ complexes with a (negative) alkoxy ligand and a *fac*-N,O,N coordination are known [23][32]. It has recently been shown that the $[Re(CO)_3(H_2O)_3]^+$ aqua ion is fairly acidic ($pK_a = 7.5$) [33], and thus deprotonation of the coordinated alcoholic hydroxy group of $[Re(CO)_3taci]^+$ is not unrealistic. Such an assignment is also in agreement with the result of our X-ray-diffraction study, where all the H-atoms could be located and refined for both structures. Inspection of the final *Fourier* map did not, however, show corresponding electron density in proximity to the coordinated alkoxy group. Moreover, the deprotonation resulted in the well-known shortening of the C−O bonds with distances of 1.408(13) and 1.409(7) Å for the C−O_{alkoxy} bonds and 1.439(10) and 1.427(5) Å for the C−$O_{hydroxy}$ bonds in **1** and **2**, respectively [9][10]. Additional evidence for deprotonation of the coordinated O-donor comes from the H-bonding scheme. As expected, the coordinated alkoxy groups serve as H-acceptors whilst the non-coordinating OH groups serve as H-donors. These interactions result in a characteristic 2D-sheet structure with layers parallel to the crystallographic *b*, *c* plane. Each complex molecule is H-bonded to four neighbors (*Fig. 2,c* and *d*) by C−O−H ⋯ O_{alkoxy} ⋯

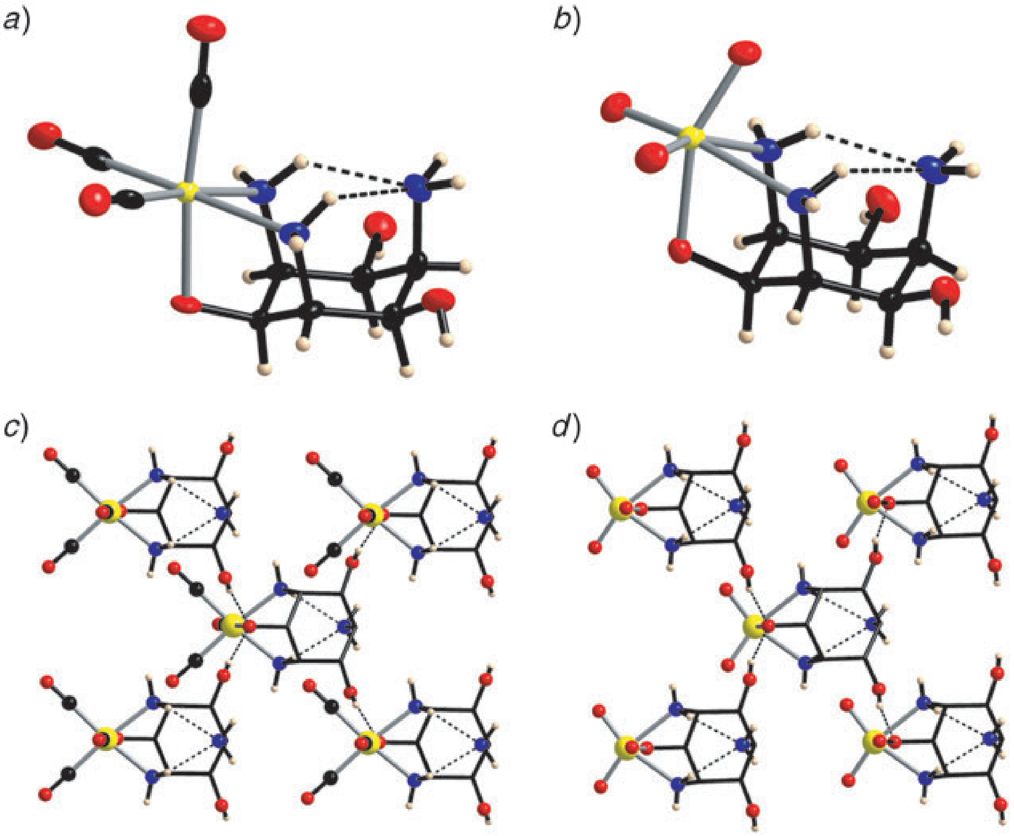


Fig. 2. *Crystal structures of* $[\mathrm{Re(CO)_3(H_{-1}taci)}]$ (**1**) *and* $[\mathrm{ReO_3(H_{-1}taci)}]$ (**2**): a) *and* b) *molecular structures of* **1** *and* **2**, *respectively* (non-H-atoms are shown as vibrational ellipsoids at 50% level, H-atoms as spheres of arbitrary size). c) *and* d) *section of the crystal structures of* **1** *and* **2**, *respectively, showing the H-bonding network* (the cyclohexane frames are represented as a stick model, other non-H-atoms together with NH and OH H-atoms as spheres of arbitrary size; CH H-atoms are omitted for clarity). Color code: Re (yellow), O (red), N (blue), C (black).

Table 1. *Selected Bond Lengths [Å] and Angles [°] for the Complex Molecules in* **1** *and* **2**

	1	**2**		**1**	**2**
$\mathrm{Re{-}O_{taci}}$	2.115(9)	2.039(4)	N–Re–N	76.4(3)	73.8(1)
Re–N	2.227(7)	2.285(4)	$\mathrm{N{-}Re{-}O_{taci}}$	77.1(2)	73.6(1)
Re–C(5)	1.897(17)		$\mathrm{X_{ax}{-}Re{-}O_{taci}}$ a)	172.5(4)	153.0(2)
Re–C(6)	1.915(8)		$\mathrm{X_{eq}{-}Re{-}O_{taci}}$ a)	99.4(3)	92.2(1)
C(5)–O(5)	1.163(21)		$\mathrm{X_{eq}{-}Re{-}N}_{cis}$ a)	98.1(3)	88.6(1)
C(6)–O(6)	1.151(10)		$\mathrm{X_{eq}{-}Re{-}N}_{trans}$ a)	173.9(3)	159.8(1)
Re–O(1)		1.737(4)	$\mathrm{X_{ax}{-}Re{-}N}$ a)	97.1(3)	85.0(2)
Re–O(2)		1.722(3)	$\mathrm{X_{eq}{-}Re{-}X_{eq}}$ a)	87.3(5)	106.5(2)
			$\mathrm{X_{ax}{-}Re{-}X_{eq}}$ a)	86.0(4)	103.7(1)

a) **1**: $\mathrm{X = C_{carbonyl}}$; **2**: $\mathrm{X = O_{oxo}}$

H–O–C interactions, and the O_{alkoxy} donor thus has a distorted tetrahedral environment. Additional intramolecular H-bonds are observed between the coordinated and the non-coordinated NH_2 groups: each of the two coordinated NH_2 groups donates a H-atom to the free NH_2 N-atom. The crystallographic symmetry dictates that this bifurcated structure is entirely symmetric. Interlayer interactions are of the type N–H$\cdots$O between non-coordinating NH_2 and OH groups and between the coordinated NH_2 groups and the O_{oxo} or O_{CO} ligands. However, the long N$\cdots$O distances (3.38 and 3.23 Å for **1**, and 3.11 and 3.22 Å for **2**) indicate that these interactions are rather weak.

The observation of the rare type-(*ii*) structure (*Scheme*) in both complexes **1** and **2** is remarkable and needs to be commented. Site selection is governed by the interplay of steric and electronic factors between the metal center and the donor set. The different steric properties of the four sites have previously been analyzed by molecular-mechanics calculations (*Fig. 3*), and it has been shown that the two adamantane-type structures (*i*) and (*iv*) preferably accommodate very small metal cations [13]. For larger metal ions, there is considerable stabilization of the two asymmetric modes (*ii*) and (*iii*). The minimum strain energy for the type-(*ii*) coordination corresponds to an M–N bond distance of *ca.* 2.3 Å, a value not too far removed from the observed Re–N bond distances of 2.23 and 2.29 Å in **1** and **2**, respectively. However, it should be noted that in terms of simple steric considerations, the type-(*ii*)-coordination mode is always significantly more strained than the type-(*iii*) mode. The additional strain is due mainly to the eclipsed orientation of H–N–C–H and H–N–C–C fragments, which is

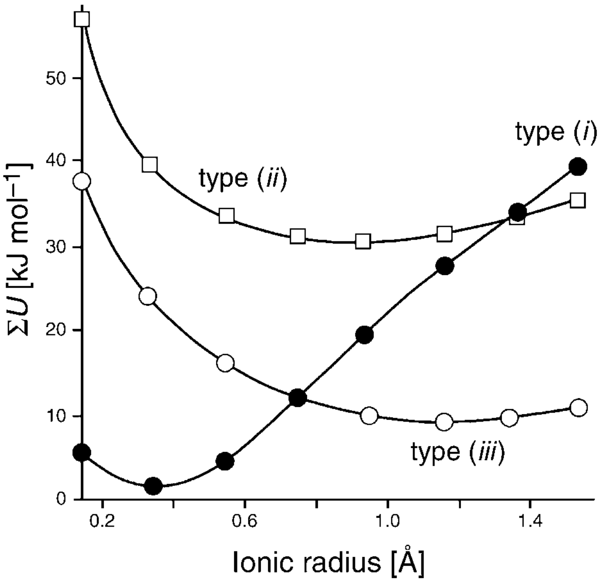


Fig. 3. *Molecular-mechanics calculations for the fragment [M(taci)] where M denotes a generalized metal ion with a constant force field, having an MN_3* (type (*i*)), *MN_2O* (type (*ii*)), *or MNO_2* (type (*iii*)) *structure* (see *Scheme*). The curve for the type-(*i*) and type-(*iv*) structures are virtually identical. The strain energy ΣU is shown as a function of the metal–N-bond distance according to [13] (with permission).

enforced by this particular coordination (*Fig. 4*). Thus, in terms of simple steric interactions, asymmetric coordination is feasible for **1** and **2**, although binding to the O–N–O donor set would be expected to be favored over that to the N–O–N set.

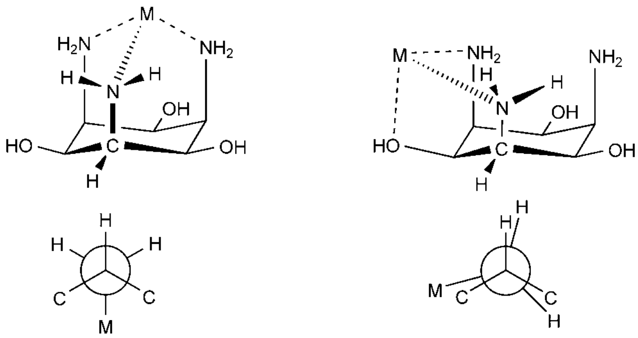


Fig. 4. *Destabilization of the type-(*ii*) coordination of taci.* Ecliptic interactions as indicated result in increased torsional strain.

A negative alkoxy O-atom and an aliphatic amine N-donor are both hard bases in terms of the HSAB terminology, although the N-donor is admittedly somewhat softer [34]. Based on the high oxidation number and the three oxo ligands, the $[Re^{VII}O_3]^+$ unit is expected to be a rather hard *Lewis* acid [35], whereas the $[Re^{I}(CO)_3]^+$ unit is known to be borderline [36]. These differences are, however, not reflected in the molecular structures of **1** and **2**. With respect to the σ- and π-bonding capability of the different donor groups, it is noteworthy that O^{2-} is a very strong σ and a strong π donor, whereas CO is a moderate σ donor and π acceptor; the alkoxy group is a strong σ donor and a weak (but still significant) π donor, whilst the aliphatic NH_2 group is a pure σ donor. In terms of a 'push-pull mechanism', one would thus expect that the coordination of the (deprotonated) alkoxy group would result in a strengthening of the *trans*-Re–C bond in **1** and a weakening of the *trans*-Re–O bond in **2**. Although only barely significant, this behavior is indeed observed (*Table 1*).

When comparing the structural features of **1** and **2**, one might naively expect that corresponding bond distances decrease with increasing oxidation number. Such expectations are supported by inspection of *Shannon*'s effective ionic radii, which are given as 0.77, 0.72, 0.69, and 0.67 for a six coordinate Re with an oxidation number of IV, V, VI, and VII, respectively [37]. Similar behavior is well-established for complexes with 3d transition-metal cations. However, the $Re-O_{taci}$ and $Re-N_{taci}$ bond lengths in the two complexes **1** and **2** differ only slightly (*Table 1*). Moreover, the Re–N bond distance in the Re^{I} complex **1** is shorter than in the Re^{VII} complex **2**. There are only a limited number of reports of X-ray structural data for $[Re^{I}(CO)_3L]$/$[Re^{VII}O_3L]$ pairs with the same tridentate ligand L (for example bis(1-*H*-pyrazol-1-yl)acetate [4][5], triazacyclononane [24][28], tris(pyrazolyl)borate [27][29], and trithiacyclononane [24][38]). Notably, all these examples are in line with our findings. Obviously, the weakening or strengthening of the Re–L bonds caused by the different electronic properties of CO and O^{2-} compensate for the different ionic radii expected for Re in its low and high oxidation states.

Conclusions. – The observed binding of the $[Re^{VII}O_3]^+$ and the $[Re^I(CO)_3]^+$ unit to the mononegative, asymmetric N,O,N donor set of H_{-1}taci$^-$ represents a significant result with respect to the design of selective chelators for these two *Lewis* acids. As outlined in the discussion, a variety of different factors could account for this binding mode in the two complexes. Although it is appealing to explain some of the observed binding properties for the individual species **1** and **2** in terms of relatively simple models such as steric interactions, the HSAB principle or a push-pull mechanism, the adoption of the same structure type for both complexes is not trivial. In particular, the binding of the (deprotonated) alkoxy group (a weak π-donor) *trans* to O_{oxo} in the Re^{VII} complex is unexpected. Of course, one must keep in mind that the observed coordination modes correspond to solid-state structures, and that a particularly stable packing arrangement could partially account for this result. Additionally, relativistic effects, which are of less importance in the chemistry of the 3d transition metals, may be of relevance for the relatively heavy Re center [35][39].

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Experimental Part

General. The chemicals used for the synthetic work were commercially available products of reagent-grade quality and were used as obtained. MeOH and EtOH (reagent grade) were purified by distillation prior to use. $(Et_4N)_2[ReBr_3(CO)_3]$ [17], $[ReO_3(OSnMe_3)]$ [18], and taci [40][41] were prepared according to published methods. IR Spectra (KBr wafer): *Perkin-Elmer-FT-IR-16PC* spectrometer; $\tilde{\nu}$ in cm^{-1}. C,H,N analyses were performed by *D. Manser*, ETH Zürich, Switzerland.

Crystal-Structure Determination[2]). X-Ray diffraction data of **1** and **2** were collected at r.t. on a *Picker-Stoe* (**1**) and *MACH3-Enraf-Nonius* (**2**) four-circle diffractometer, by using graphite monochromated Mo$-K_\alpha$ radiation (λ 0.71073 Å). Crystallographic data are listed in *Table 2*. Corrections for *Lorentz* and polarization effects were performed, and an absorption correction was applied for both data sets. The structures were solved by direct methods (**1**) or the *Patterson* method (**2**) and refined by full-matrix least-squares calculations on F (**1**) or F^2 (**2**) [42][43]. Anisotropic displacement parameters were refined for all non-H-atoms. The H-atoms were located and refined by using variable isotropic displacement parameters.

*Tricarbonyl(1,3,5-triamino-1,3,5-trideoxy-*cis*-inositolato-*$\kappa N^1,\kappa N^3,\kappa O^2$*)rhenium* (*[Re(CO)$_3$(H$_{-1}$taci)]*; **1**). $(Et_4N)_2[ReBr_3(CO)_3]$ (154 mg, 0.2 mmol) was dissolved in MeOH (30 ml). Br^- was removed by quantitative precipitation as AgBr upon addition of $AgNO_3$ (102 mg, 0.6 mmol), dissolved in H_2O (1 ml). The solid AgBr was filtered off and 1 equiv. of solid taci (35.6 mg, 0.2 mmol) was added to the soln. The mixture was refluxed for 2 h (some clouding after 10 min). The suspension was allowed to cool to r.t. and was filtered. The remaining solid was washed with Et_2O and dried under reduced pressure. IR (KBr): 3376*s*, 3350*w*, 3172*m*, 2948*w*, 2010*vs*, 1902*vs*, 1860*vs*, 1604*w*, 1568*m*, 1400*w*, 1348*w*, 1272*w*, 1190*w*, 1100*w*, 1044*s*, 876*w*, 760*w*, 636*w*, 548*w*, 516*m*.

Single crystals of composition $[Re(CO)_3(H_{-1}taci)]$, suitable for X-ray analysis, were grown by slow diffusion of EtOH to an aq. soln. of the complex.

*Trioxo(1,3,5-triamino-1,3,5-trideoxy-*cis*-inositolato-*$\kappa N^1,\kappa N^3,\kappa O^2$*)rhenium* (*[ReO$_3$(H$_{-1}$taci)]*; **2**). $ReO_3(OSnMe_3)$ (82.8 mg, 0.2 mmol) and taci (35.6 mg, 0.2 mmol) were dissolved in MeOH (20 ml) and heated to reflux (some clouding after 30 min). Refluxing was continued for another 3 h, and the suspension was filtered.

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[2]) CCDC 253087 and CCDC 253419 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. *Crystallographic Data for the Re-Complexes* **1** *and* **2**

	1	**2**		**1**	**2**
Empirical Formula	$C_9H_{14}N_3O_6Re$	$C_6H_{14}N_3O_6Re$	μ [mm^{-1}]	9.940	11.789
M	446.4	410.41	T [K]	293(2)	296(2)
Crystal size [mm]	0.15 × 0.08 × 0.08	0.21 × 0.05 × 0.05	θ max [°]	20	26.3
Crystal system	orthorhombic	orthorhombic	Transmission: min, max	0.4214, 0.5739	0.8286, 0.9946
Space group	*Pnma*	*Pnma*	Reflections measured	675	2177
a [Å]	14.806(3)	13.050(2)	Independent reflections	675	999
b [Å]	8.466(2)	8.732(1)	Parameters	126	112
c [Å]	9.781(2)	9.061(1)	R_1 ($I > 2\sigma(I)$)	0.0195 [a])	0.0167 [b])
V [Å^3]	1226.0(5)	1032.5(2)	wR_2 (all data)		0.0347 [b])
Z	4	4	R_w (all data)	0.0235 [a])	
ρ_{cal} [g cm^{-1}]	2.419	2.640	Largest peak/hole [e Å^{-3}]	+0.65, −0.49	+0.64, −0.59
λ [Å] (MoK_α)	0.71073	0.71073			

[a]) Refinement on F. [b]) Refinement on F^2.

The solid was washed with a small amount of MeOH and with Et_2O and was dried under reduced pressure: white powder (61 mg, 74%). IR (KBr): 3336*s*, 3280*s*, 2952*w*, 2924*w*, 2900*w*, 2868*w*, 1600*m*, 1564*m*, 1458*w*, 1380*w*, 1360*w*, 1302*w*, 1272*w*, 1212*w*, 1194*w*, 1170*w*, 1112*m*, 1090*w*, 1056*s*, 1038*m*, 934*s*, 914*s*, 894*s*, 880*m*, 870*m*, 784*m*, 766*m*, 670*m*, 650*m*, 544*m*, 512*m*. Anal. calc. for $[ReO_3(H_{-1}taci)] \cdot 0.5$ MeOH ($C_{6.5}H_{16}N_3O_{6.5}Re$; 426.42): C 18.31, H 3.78, N 9.85; found C 18.55, H 3.69, N 9.78.

Single crystals of composition $[ReO_3(H_{-1}taci)]$, suitable for X-ray analysis, were grown from MeOH.

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