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1,3,5-Trideoxy-1,3,5-tris((2-hydroxybenzyl)amino)-*cis*-inositol, a Novel Multidentate Ligand Providing Various N,O Coordination Sites. Structure of the Rhenium(V) Complex

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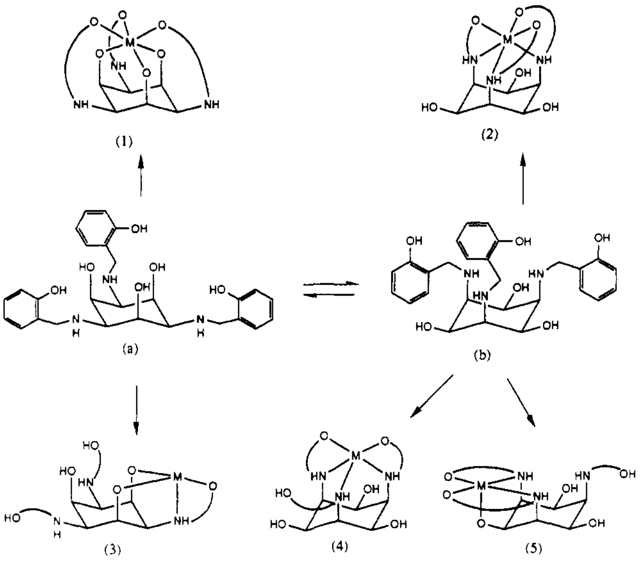
1,3,5-Trideoxy-1,3,5-tris((2-hydroxybenzyl)amino)-*cis*-inositol (H_3thci) has been prepared in our laboratory as a new type of a potentially hexadentate ligand.[1] The various coordination sites of this ligand allow a metal ion to choose selectively a coordination sphere of appropriate softness, size, and number of binding atoms (Scheme I). Hence, this ligand is particularly suitable to elucidate the individual binding properties of metal ions, as shown by the present investigation of the complex Re^VO(thci), which has been readily obtained according to the equation $ReOCl_3(PPh_3)_2$ + H_3thci → ReO(thci) + 3HCl + $2PPh_3$.[2] No particular protection against moisture and air was necessary and no additional base was added during the reaction. The composition ReO(thci)·THF·MeOH has been elucidated by elemental analysis.

The X-ray analysis[3] established structure **5** in the scheme (M = ReO) as the correct one for this particular complex. The amino- and phenoxo groups of two (2-hydroxybenzyl)aminato entities are located in the equatorial positions of a distorted octahedron. The third (hydroxybenzyl)amino moiety does not interact with Re at all. The axial positions of the Re coordination sphere are occupied by the terminal oxygen atom and by a deprotonated hydroxyl group of the cyclohexanetriol fragment (Figure 1). All bond lengths are in the expected range for an octahedrally coordinated Re^VO complex.[4]

Scheme I



ReO(thci) is soluble in MeOH but insoluble in water. However, the compound readily dissolves in diluted aqueous alkali hydroxide. Obviously, the deprotonation of the noncoordinated aromatic hydroxyl group resulted in the formation of an anionic and water-

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(1) H_3thci was obtained by hydrogenation of a 1:3 mixture of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) and salicylaldehyde (25 °C, 12 h, PtO_2 as catalyst in CH_2Cl_2). For the synthesis of taci, see: Hegetschweiler, K.; Erni, I.; Schneider, W.; Schmalle, H. *Helv. Chim. Acta* **1990**, *73*, 97.

(2) An equimolar mixture of $ReOCl_3(PPh_3)_2$ and H_3thci was refluxed in MeOH for 30 min. The clear solution was evaporated to dryness, and the residue was extracted with CH_2Cl_2. Recrystallization of the residue from MeOH/THF gave crystals suitable for X-ray analysis. For the preparation of $ReOCl_3(PPh_3)_2$, see: Parshall, G. W.; Shive, L. W.; Cotton, F. A. *Inorg. Synth.* **1977**, *17*, 110.

(3) Crystal data for $ReO(C_{27}H_{30}N_3O_6)\cdot CH_3OH\cdot C_4H_8O$: pale violet platelet, orthorhombic, $Pca2_1$, $a = 18.525$ (5) Å, $b = 12.460$ (2) Å, $c = 14.379$ (5) Å, $Z = 4$, 7502 reflections collected ($T = 22$°C), 3783 observed with $I > 2\sigma(I)$. The structure was solved by a combination of Patterson and Fourier calculations. In the final refinement, calculated H atom positions were included using a riding model. O(11) appeared to have a nonpositive definite displacement ellipsoid and was therefore refined isotropically. The non-hydrogen atoms of the solvent molecules (THF, MeOH) were also refined with isotropic displacement parameters. $R = 5.50\%$, $R_w = 3.81\%$. Programs used: SHELX76, SHELXS86.

(4) (a) Holloway, C. E.; Melnik, M.; *Rev. Inorg. Chem.* **1989**, *10*, 235 and references therein. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1 and references therein.

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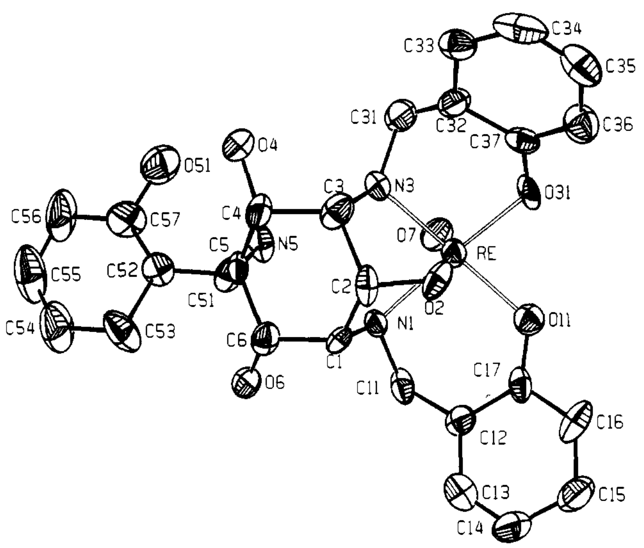

Figure 1. ORTEP drawing (50% probability ellipsoids) of [ReO(thci)]. Selected bond lengths (Å) and bond angles (deg): Re–O(2) = 2.032 (13), Re–O(7) = 1.701 (8), Re–O(11) = 1.960 (7), Re–O(31) = 1.963 (12), Re–N(1) = 2.164 (8), Re–N(3) = 2.163 (8); O(2)–Re–O(7) = 158.6 (4), O(11)–Re–O(7) = 106.9 (3), O(31)–Re–O(7) = 107.9 (4), N(1)–Re–O(7) = 86.4 (4), N(3)–Re–O(7) = 88.6 (3).

soluble species. On the other hand, the compound was not soluble in aqueous hydrochloric acid up to a concentration of 2 M, indicating the absence of any basicity of the noncoordinated amino group. This is quite understandable, since the two N–H bonds of the coordinated amino groups are directed toward the third, noncoordinated nitrogen atom preventing any uptake of an additional proton.

A very stable and inert fragment ReOL (L = 1,4,7-triazacyclononane) has been described recently by Wieghardt and coworkers.[5] It is interesting to note, that an analogous binding of Re(V) to thci with all three nitrogen atoms in a *facial* position, has not been observed under the present conditions (e.g. structure **2**, M = Re, or structure **4**, M = ReO). The observed structure is also in contrast to Angyal's rule for *cis*-inositol,[6] postulating the binding of large cations ($d > 1.6$ Å) to a subsequent axial–equatorial–axial site and the binding of small cations ($d < 1.6$ Å) to a 1,3,5-triaxial site. Re(V) with $d = 1.3$ Å[7] clearly falls in the second category.

The free ligand itself predominantly exists in conformation a according to NMR measurement. The chair conversion, a → b, enforces severe 1,3,5-triaxial repulsion. However, this chair conversion is necessary if more than one nitrogen atom should bind to Re. Thus the result of the present study demonstrates (i) the affinity of Re(V) to the single oxygen atom in combination with an octahedral coordination sphere, expressed by the inability of Re(V) to coordinate six donor atoms of the ligand; (ii) the tendency of the ReO moiety to coordinate hard oxygen donor atoms trans to O_{oxo}; and (iii) the preference for the softer amino group in the cis position of the Re=O bond.[8]

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, thermal parameters, bond lengths, bond angles and H atom coordinates for ReO(thci)·THF·MeOH (12 pages). Ordering information is given on any current masthead page. A table of calculated and observed structure factors (23 pages) is available from the authors on request.

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