166. 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol, a New Ligand with a Remarkable Versatility for Metal Ions

Part 2[1])

Safe and Efficient Ligand Preparation and Structure of the Free Ligand and the Co^{III} Complex

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A new, convenient, and safe route to 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) was investigated by hydrogenation of azo-coupled derivatives of phloroglucinol. In the presence of acetic anhydride, the reduction of trisphenylazophloroglucinol (H_2/Pd(5%) on C) resulted in the formation of tri-, hexa-, and nona-acetylated derivatives of triaminophloroglucinol. All three compounds are air-stable, colorless solids. However, the succeeding hydrogenation to the cyclohexane derivative failed. Trisodiumtris(*p*-sulfonatophenylazo)phloroglucinol could be hydrogenated in a one-pot reaction to the desired taci · 1.5 H_2SO_4 using a Pt/Rh oxide as catalyst. taci provides two distinct chair conformations with either three amino or three hydroxy groups for metal binding. The unique metal-binding properties are discussed in terms of minimal conformational changes required for coordination. Conformational analysis, based on X-ray structural data of $[BiCl_6][H_3(taci)] \cdot 2\ H_2O$ (*Pnma*, $a = 24.314$ (5) Å, $b = 10.215$ (2) Å, $c = 7.422$ (8) Å, $R = 5.8\%$) and $[Co(taci)_2(NO_3)_3] \cdot 2H_2O$ (*C*2/*c*, $a = 22.912$ (8) Å, $b = 8.942$ (2) Å, $c = 14.731$ (3) Å, $\beta = 128.66$ (2)°, $R = 4.9\%$) and the previously investigated $[Cr(taci)_2]^{3+}$ revealed an almost ideal chair conformation in all three molecules.

Introduction. – 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (taci) received attention lately owing to the unusual acidity of the OH groups and the metal-binding properties [1–3]. taci has first been prepared by *Quadbeck* and *Röhm* in 1956 [4], and the (all-*cis*)-configuration has been elucidated 1966 by *Lichtenthaler* and *Leinert* [5]. Despite of the remarkable molecular structure – cyclohexane derivatives with three substituents in a stable *syn*-1,3,5-triaxial arrangement are rare – no further investigations on this compound have been reported until 1990. This is particularly a consequence of the tedious and dangerous preparation procedure, where the explosive trinitroso- and trinitrophloroglucinol, and the instable triaminophloroglucinol must be isolated as intermediates.

A comprehensive study in our laboratory demonstrated that taci is a remarkably versatile ligand. A variety of complexes with divalent, trivalent, and tetravalent metal ions has been prepared and characterized, and possible applications in medicine have been considered [6]. However, the above mentioned difficulties in synthesizing this ligand

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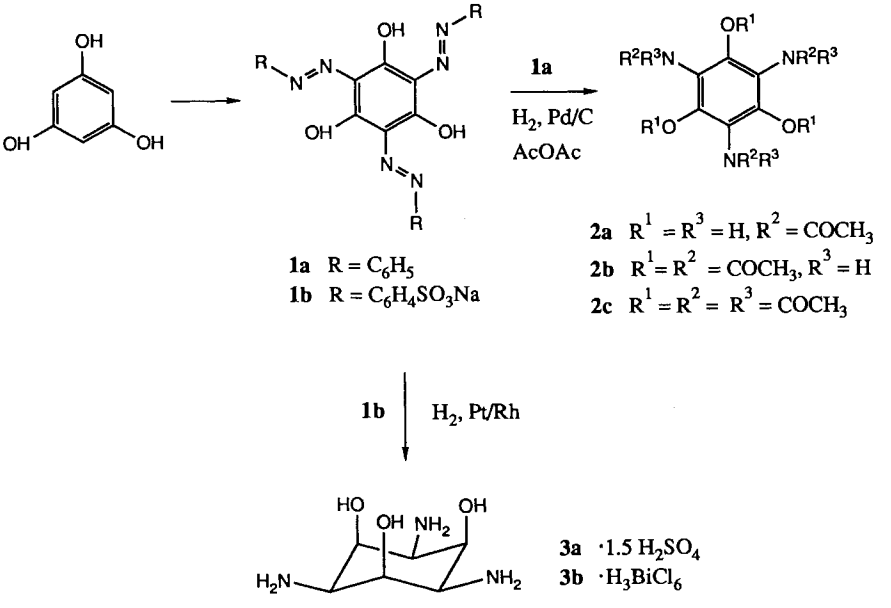
prevented the preparation of taci in a larger scale. The catalytic hydrogenation of triaminophloroglucinol is an efficient way to prepare taci with acceptable yield provided that the major handicaps *i*) a long reaction time, *ii*) the above mentioned explosive intermediates, and *iii*) a rather tedious purification procedure can be eliminated.

We present here a simple, safe, and convenient two-step procedure for the preparation of taci and discuss the unique steric properties of this ligand based on the crystal structures of the protonated, free ligand $[H_3(taci)]^{3+}$ and the complex $[Co(taci)_2]^{3+}$.

Results and Discussion. – *Synthesis.* The coupling reaction of diazonium salts with phenols and the subsequent reduction of the azo compound is a well established method for the introduction of amino groups in the aromatic ring system. Already *Perkin* (1897) [7] described the preparation of the red tris(phenylazo)phloroglucinol (**1a**). Considering the high air sensibility of triaminophloroglucinol, the direct hydrogenation of **1a** to taci would be favorable. This is, however, not possible, because **1a** is completely insoluble in H_2O, the only solvent which prevents the precipitation of solid taci. Since traces of precipitated taci deactivate the catalyst, complete solubility of taci during the entire reaction is required for a successful hydrogenation.

A stabilized derivative of triaminophloroglucinol could be obtained by the reduction of **1a** with H_2/Pd on C in the presence of Ac_2O. Depending on the reaction conditions, the triacetate **2a**, the hexaacetate **2b**, or the nonaacetate **2c** could be isolated (*Scheme 1*). All three derivatives are colorless and air-stable solids. However, in contrast to the unsubstituted triaminophloroglucinol an unspecific hydrogenation (→ **2a**) or even no H_2 uptake at all (→ **2b**, **2c**) has been observed. This result demonstrates clearly that the interaction of the free NH_2 groups with the surface of the catalyst is essential for a stereospecific

Scheme 1

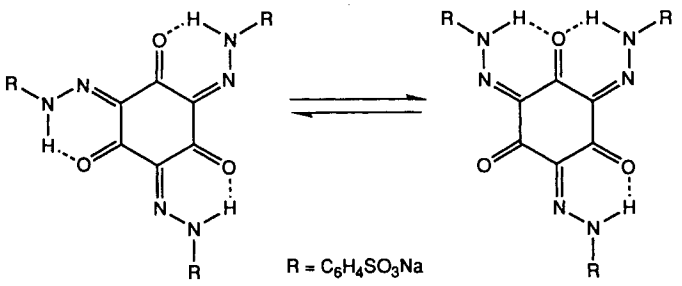


process. In agreement with this consideration, a rather unspecific hydrogenation of hexahydroxybenzene has been reported [8].

In a recent investigation, derivatives of triaminophloroglucinol have been used as precursors for organic cation radicals [9]. At least an easy access for such compounds is now available; on the other hand, acetylated derivatives of triaminophloroglucinol are obviously of no use regarding the aim of the present investigation.

More success was obtained by using the water-soluble trisodiumtris(*p*-sulfonatophenylazo)phloroglucinol (**1b**). According to the ^{1}H- and ^{13}C-NMR spectra in (D$_6$)DMSO, this compound exists in two isomeric trioxo forms rather than in the tautomeric triazo form [10] (*Scheme 2*). Compound **1b** could be readily hydrogenated in aqueous H_2SO_4. According to the H_2 uptake, a three-step kinetics was observed: *i*) the fast

Scheme 2



reduction of the azo groups, *ii*) the hydrogenation of 4-aminobenzenesulfonic acid, and *iii*) the hydrogenation of triaminophloroglucinol. The undesired 4-aminocyclohexanesulfonic acid could be easily removed from the reaction mixture, and a final purification was obtained by preparing the purple [Ni(taci)$_2$SO$_4$]·2H$_2$O (**4a**)[2]) followed by the release of the protonated ligand as taci·1.5H$_2$SO$_4$ (**3a**).

Catalytic Hydrogenation of Triaminophloroglucinol. A screening of a variety of catalysts was performed for the optimization of the critical hydrogenation. Triaminophloroglucinol was prepared *in situ* by using trinitrophloroglucinol as starting material. Activity and selectivity of the investigated catalysts are presented in *Fig. 1*. The activity of the catalysts was determined by measuring the H_2 uptake in the first 5 h. After a reaction time of 20 h, the hydrogenated product was analyzed by ^{13}C-NMR spectroscopy. The selectivity of the catalyst was determined as the amount of the desired taci compared to the total amount of hydrogenated species. Four major by-products were detected and characterized by 2D-COSY ^{1}H-NMR spectroscopy.

2,4,6-Triamino-2,4,6-trideoxy-*epi*-inositol (**5a**) and (all-*cis*)-2,4,6-triaminocyclohexane-1,3-diol (**5b**) were mainly formed by using Rh_2O_3 or PtO_2/Rh_2O_3. Both, the formation of a 'wrong' stereoisomer and hydrogenolysis are well known side reactions for the hydrogenation of polyhydroxy benzenes [8] [11]. By using PdO_2, PtO_2, Pt(5%) on C, Pt(5%) on Al_2O_3, Rh(4%) + Pt(2%) on Al_2O_3, Pd(4%) + Rh(1%) on C,

[2]) A NiN_6 chromophore was unambiguously elucidated by UV/VIS spectrometry [12].

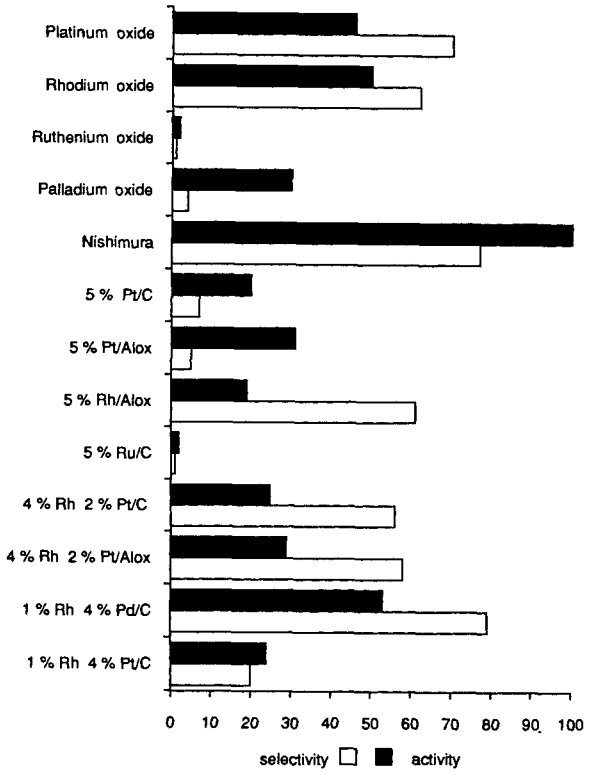
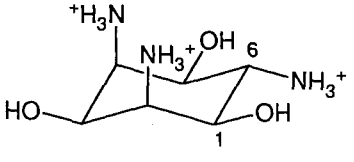
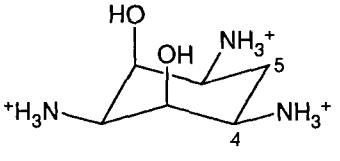


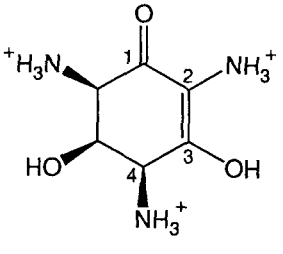
Fig. 1. *Activity and selectivity of different catalysts for the hydrogenation of triaminophloroglucinol*



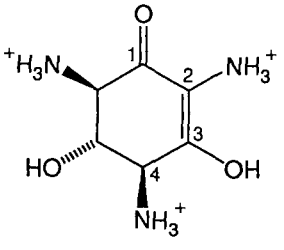
5a



5b



6a



6b

Rh(4%) + Pt(2%) on C, Pt(4%) + Rh(1%) on C, the two diastereoisomeric α,β-unsaturated cyclohexanones **6a** and **6b** have been detected as major by-products. The observed C_{2v} symmetry of **6a** and **6b** in the NMR spectra (D_2O) is a consequence of a fast equilibrium between two tautomeric forms for both compounds [13]. The formation of unsaturated cyclohexanones obviously indicate a premature stagnancy of H_2 uptake.

The present investigation clearly demonstrates that the Rh-Pt catalyst according to *Nishimura* [14] is the most efficient catalyst for the hydrogenation of triaminophloroglucinol. The variation of H_2 pressure showed no significant influence on the reaction rate and the selectivity in the range 20 bar $\leq p(H_2) \leq$ 100 bar. A temperature above 30° rather promotes the above mentioned side reactions.

Structural Studies. The tripositive H_3taci^{3+} formed a variety of almost insoluble and well crystallizing compounds with trinegative anions of appropriate size. Crystals of $[BiCl_6][H_3(taci)]$ (**3b**), suitable for X-ray analysis, have been isolated from 6M HCl (*Fig. 2*).

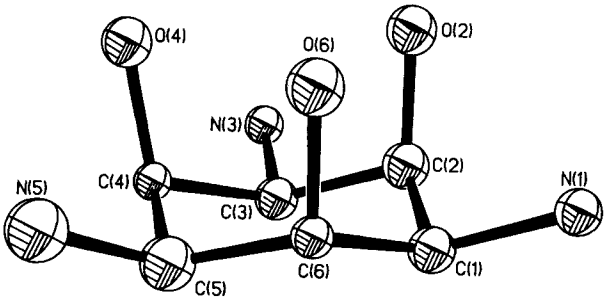


Fig. 2. *Molecular structure of 1,3,5-triammonio-1,3,5-trideoxy-*cis-*inositol* (**3b**). Thermal ellipsoids at the 50% level.

The corresponding Co^{III} complex, showing the expected CoN_6 chromophore[3]) was readily prepared according to standard methods, and crystals of the composition $[Co(taci)_2(NO_3)_3] \cdot 2H_2O$ were used for the present crystal structure determination (*Fig. 3*). Two isomeric Cr^{III} complexes providing either a CrO_3N_3 or a CrO_6 coordination sphere have previously been described [3]. Conformational analysis revealed an almost ideal chair conformation for taci in the metal complexes and for the free ligand in the protonated form. The puckering parameters Q, φ, and θ, according to *Cremer* and *Pople* [17] are presented in *Table 1*[4]).

Most of the established polydentate ligands like diaminoethane, nta, edta, or desferrioxamine have a flexible structure providing a variety of different conformations in solution. The coordination of a metal to those ligands requires a particular, usually unfavorable conformation. These restrictions result in adverse contributions on ΔS and

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[3]) The observed bands $\lambda_1 = 338$ nm ($\varepsilon = 102$) and $\lambda_2 = 470$ nm ($\varepsilon = 84$) fall in the range expected for d–d transitions in the CoN_6 chromophore as found in $[Co(en)_3]^{3+}$: $\lambda_1 = 339$ nm ($\varepsilon = 98$), $\lambda_2 = 466$ nm ($\varepsilon = 87$) [15]; $[Co(NH_3)_6]^{3+}$: $\lambda_1 = 339$ nm ($\varepsilon = 60$), $\lambda_2 = 475$ nm ($\varepsilon = 55$) [16].

[4]) The total puckering amplitue Q is defined by $Q^2 = \Sigma_j z_j^2$, where z_j denotes the displacement of the atom C(j) from the mean plane of the C_6 ring. θ and φ describe different types of conformations: $\theta = 0$ or $\theta = \pi$ (chair), $\theta = \pi/2$, $\varphi = 0$ (boat), $\theta = \pi/2$, $\varphi = \pi/2$ (twist boat).

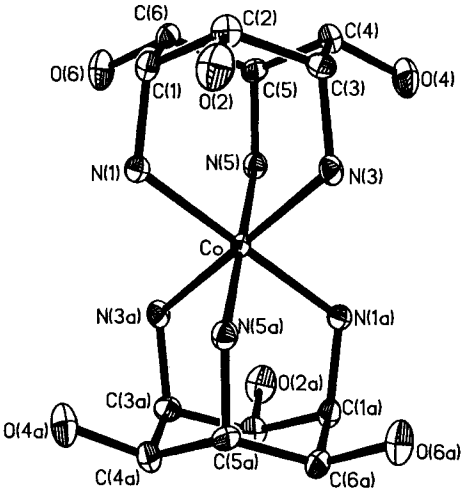


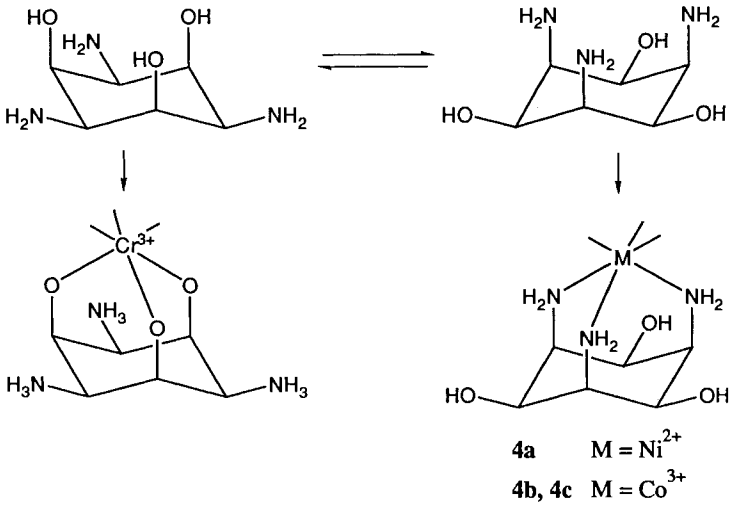
Fig. 3. *Molecular structure of bis(1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol)cobalt(III)* (**4c**). Thermal ellipsoides at the 50% level.

Table 1. *Puckering Parameters* Q, θ, *and* φ *for the Cyclohexane Ring in* $[Co(taci\text{-}N^1,N^3,N^5)_2]^{3+}$, $[Cr(taci\text{-}O^2,O^4,O^6)_2]^{3+}$, *and* $[H_3taci]^{3+}$

	$[Co(taci\text{-}N^1,N^3,N^5)_2]^{3+}$	$[Cr(taci\text{-}O^2,O^4,O^6)_2]^{3+}$	$[H_3(taci)]^{3+}$
Q [Å]	0.57	0.62	0.56
θ [°]	1.51	1.22	–2.68
φ [°]	–60.2	43.5	–34.3

ΔH for metal binding. It is a remarkable uniqueness of the rigid taci that the ligand atoms in both of the possible chair conformations are already optimal arranged for metal binding (*Scheme 3*).

Scheme 3



4a M = Ni^{2+}

4b, 4c M = Co^{3+}

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Experimental Part

General. M.p.: *Büchi 510*; not corrected. VIS/UV Spectra: *Uvikon 810*, $\lambda_{max}(\varepsilon)$ in nm. IR Spectra: *Perkin-Elmer 883*, in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AC-200* and *Varian Unity 500*, δ[ppm] scale, TSP or TMS (= 0 ppm) as internal standard. MS: *VG ZAB-VSEQ* (FAB) and *VG Tribrid* (EI), Dr. *W. Amrein*, Laboratorium für Organische Chemie, ETH-Zürich, data given as *m/z* (%). C,H,N Analyses: *D. Manser*, Laboratorium für Organische Chemie, ETH-Zürich.

Tris(phenylazo)phloroglucinol (= *2,4,6-Tris(phenylazo)benzene-1,3,5-triol*; **1a**) was prepared by the reaction of phloroglucinol with a soln. of benzenediazonium chloride [18] according to [7]. Recrystallization from $PhNO_2$/EtOH (yield 76%). TLC ($CHCl_3$): R_f 0.50. VIS/UV ($CHCl_3$): 488 ($6.6 \cdot 10^4$), 377 ($3.8 \cdot 10^4$). IR (KBr): 3060, 3011, 1601, 1582, 1475, 1450, 1407, 1310, 1222, 1187, 1157, 1098, 1077, 1048, 995, 903, 851, 791, 755, 684, 644, 507, 495, 468. ^1H-NMR ($CDCl_3$) 16.33 (*s*, 3 H); 7.65 (*m*, 6 H); 7.47 (*m*, 6 H); 7.31 (*m*, 3 H). MS (EI^+): 438.1 (44), 361.0 (22), 92.0 (100). Anal. calc. for $C_{24}H_{18}N_6O_3$ (438.45) C: 65.75, H 4.14, N 19.17, O 10.95; found: C 65.39, H 4.13, N 19.11, O 10.95.

Tris(acetamido)phloroglucinol (= *2,4,6-Tris(acetylamino)benzene-1,3,5-triol*; **2a**). A suspension of **1a** (2.5 g, 5.7 mmol) and 5.5 g (54 mmol) AcOAc and 250 mg Pd(5%) on C in CH_2Cl_2 (100 ml) was hydrogenated at 50 bar and 22° for 10 h. After filtration, the solid residue was extracted with H_2O (50 ml). The aq. soln. was evaporated *in vacuo* to a total volume of 10 ml. A white solid precipitated which was recrystallized from $(i\text{-}Pr)_2O$/EtOH. Yield 0.3 g (18%). IR (KBr): 3345, 3303, 1662, 1637, 1568, 1540, 1498, 1368, 1309, 1263, 1178, 1140, 1034, 992, 938, 917, 810, 762, 701. ^1H-NMR ((D_6)DMSO): 9.39 (*s*, 3 H); 9.32 (*s*, 3 H); 2.11 (*s*, 9 H). ^{13}C-NMR ((D_6)DMSO): 170.6; 144.4; 107.9; 22.6. MS (EI^+): 297.2 (77), 255.1 (70), 212.1 (72), 170.1 (87), 43.0 (70), 28.0 (100). Anal. calc. for $C_{12}H_{15}N_3O_6$ (297.27) C: 48.49, H 5.09, N 14.14; found: C 48.63, H 4.87, N 13.90.

Tris-O-acetyltris(acetylamino)phloroglucinol (= *2,4,6-Tris(acetylamino)benzene-1,3,5-triyl Triacetate*; **2b**). A suspension of **1a** (2.5 g, 5.7 mmol), Ac_2O (6.0 g, 59 mmol) and Pd(5%) on C (0.25 g) in acetone (100 ml) were hydrogenated for 6 h (22°, 50 bar). The mixture was allowed to stand for 12 h and was then filtered. The solid residue was washed with 50 ml of hot acetone, and the combined solns. were evaporated *in vacuo* to 50 ml. Crude **2b** precipitated at r.t. within 2 d. Recrystallization from H_2O (65%). M.p. 223° (dec.). IR (KBr): 3234, 3020, 2938, 1775, 1664, 1531, 1462, 1372, 1284, 1251, 1188, 1139, 1045. ^1H-NMR (D_2O): 2.26 (*s*, 9 H); 2.10 (*s*, 9 H). ^{13}C-NMR (D_2O): 175.7; 172.4; 145.2; 125.0; 25.6; 24.0; 22.1. MS (EI^+): 423.2 (0.03), 297.1 (11), 279.2 (37), 43.0 (100). Anal. calc. for $C_{18}H_{21}N_3O_9$ (423.38) C: 51.06, H 5.00, N 9.92, O 34.01; found: C 50.78, H 5.14, N 9.89, O 34.09.

Tris-O-acetyltris(diacetylamino)phloroglucinol (= *2,4,6-Tris(diacetylamino)benzene-1,3,5-triyl Triacetate*; **2c**). A soln. of **2b** (1.0 g, 2.4 mmol) in Ac_2O (20 ml) was refluxed for 4 h and then evaporated *in vacuo* to 5 ml. Upon addition of EtOH (10 ml) and hexane (20 ml), crude **2c** precipitated. The product was dissolved in 5 ml of CH_2Cl_2, and 40 ml of EtOH were added. Slow evaporation of the solvent resulted in the formation of colorless crystals (yield 39%). M.p. 171°. IR (KBr): 3017, 2943, 1792, 1740, 1721, 1458, 1428, 1371, 1265, 1229, 1155, 1061, 1036, 1000, 969. ^1H-NMR ($CDCl_3$): 2.34 (*s*, 18 H); 2.22 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 171.4; 166.4; 146.3; 126.4; 25.6; 20.0. MS (EI^+): 549.2 (0.3), 423.1 (0.4), 297.1 (12), 279.1 (84), 43.0 (100). Anal. calc. for $C_{24}H_{27}N_3O_{12}$ (549.49) C: 52.46, H 4.95, N 7.65, O 34.94; found: C 52.31, H 4.97, N 7.77, O 34.82.

Screening of Catalysts. Catalysts applied as metal oxides: PtO_2, Rh_2O_3, RuO_2, PdO_2 (all from *Engelhard*), Rh_2O_3/PtO_2 (45.4% Rh, 19.5% Pt, *Degussa*); catalysts applied as supported metals on C: Pt(5%), Ru(5%) (both from *Engelhard*), Rh(4%)/Pr(2%), Rh(1%)/Pt(4%) (both from *Degussa*), Rh(1%)/Pd(4%) (*Heraeus*); catalysts applied as supported metals on Al_2O_3: Pt(5%), Rh(5%) (both from *Engelhard*), Rh(4%)/Pt(2%) (*Degussa*).

Standard Procedure. A suspension of trinitrophloroglucinol (7.2 mmol) [2], 200 mg of the catalyst, 22 ml of aq. 1M H_2SO_4, and 80 ml of H_2O were placed in a 300-ml autoclave (stainless steel) fitted with a glass inset and a stirrer (*HAST B*) and hydrogenated for 20 h (22°, 1500 rpm). If metal oxides were used as catalysts, a preliminary reduction (hydrogenation for 1 h) to the elemental form was performed. The activity of the catalysts was determined by measuring the drop in pressure in a small high-pressure reservoir (37 ml). The pressure in the autoclave was kept constant at 50 bar. For the determination of the selectivity, a sample (5 ml) was taken from the reaction mixture (under Ar) and evaporated *in vacuo* to 1 ml. D_2O (1 ml) was then added and the species

distribution determined by integration of ^{13}C-NMR signals in the aliphatic range of the spectrum. For a complete relaxation of all ^{13}C nuclei, a pulse-repetition rate of 5 s was applied.

NMR Data of By-products. (D_2O) ^{1}H-NMR of **5a**: 4.66 (*t*, *J* = 4, H–C(3)); 4.46 (*dd*, *J* = 6, 8.5, H–C(1), H–C(5)); 4.04 (*dd*, *J* = 6, 4, H–C(2), H–C(4)); 3.94 (*t*, *J* = 8.5, H–C(6)). ^{1}H-NMR von **5b**: 4.53 ('*t*', *J* ≈ 3, H–C(1), H–C(3)); 3.80 (*ddd*, *J* = 2.8, 4, 12, H–C(4), H–C(6)); 3.78 (*t*, *J* = 3.2, H–C(2)); 2.3–2.4 (*m*, 2 H–C(5)). ^{13}C-NMR of **5a** and **5b**: 68.8; 68.5; 67.9; 54.2; 53.6; 52.8; 52.6; 25.5. ^{1}H-NMR of **6a**: 4.80 (*t*, *J* = 2.8, H–C(5)); 4.40 (*d*, *J* = 2.8, H–C(4), H–C(6)). ^{1}H-NMR of **6b**: 4.12–4.22 (A_2B system, *J* = 10). ^{13}C-NMR of **6a** and **6b**: 177.4; 104.4; 103.6; 69.1; 67.2; 57.8; 55.2.

*Trisodiumtris[(*para-*sulfonatophenyl)azo]phloroglucinol* (**1b**). Sulfanilic acid (42 g) was used to prepare a soln. of 4-diazobenzenesulfonic acid according to [19]. However, 55 ml of conc. aq. HBr instead of HCl were used. The soln. was added to a soln. of $NaCO_3$ (100 g) and phloroglucinol (10 g) in 400 ml of H_2O, and the temp. was kept below 10° by cooling with ice. The mixture was allowed to stand for 1 h. Conc. aq. HBr (120 ml) and solid NaBr (300 g) were then added, and a red solid precipitated. Recrystallization from H_2O/acetone gave 43 g (70%) of **1b**. IR (KBr): 3433, 1608, 1578, 1482, 1419, 1312, 1196, 1122, 1033, 1006, 834, 723, 711, 637, 567, 370, 337. UV/VIS: 237 ($4.5 \cdot 10^5$), 375 ($8.1 \cdot 10^5$), 483 ($1.4 \cdot 10^6$). ^{1}H-NMR ((D$_6$)DMSO): 15.64 (*s*, 3 H); 7.60–7.80 (*m*, 12 CH, major isomer); 15.64 (*s*, NH); 15.00 (*s*, NH); 14.96 (*s*, NH); 7.60–7.80 (*m*, 12 CH, minor isomer). ^{13}C-NMR ((D$_6$)DMSO): 178.0, 146.2, 141.7, 129.4, 127.3, 116.6 (major isomer); 178.3, 177.9, 175.0, 146.3, 146.1, 145.9, 141.7, 130.4, 129.8, 128.6, 127.3, 116.6 (minor isomer). Anal. calc. for $C_{24}H_{15}N_6Na_3O_{12}S_3 \cdot 2\ H_2O$ (780.61): C 36.93, H 2.45, N 10.77, Na 8.84; found: C 37.02, H 2.38, N 10.65, Na 8.99.

Catalytic Hydrogenation of **1b**. Rh-Pt catalyst [14] (0.5 g) and 0.4M aq. H_2SO_4 (50 ml) were placed in a 300-ml autoclave (stainless steel) fitted with a glass inset and a stirrer (*HAST B*). The catalyst was prereduced by hydrogenation (1 h, 50 bar, 22°, 1500 rpm). Compound **1b** (5 g) was then added and the hydrogenation continued under unchanged conditions for additional 10 h. The catalyst was then filtered off, and the colorless soln. was evaporated *in vacuo* to 50 ml. After the addition of 50 ml of MeOH a white solid precipitated (2.0 g). According to NMR, the product contained 80% of the desired **3a** and the two by-products **5a** (10%) and **5b** (10%). The remaining 4-aminocyclohexanesulfonic acid (**5c**) was precipitated as a white solid by adding 50 ml of Et_2O to the mother liquour. ^{1}H-NMR (D_2O) of **5c**: 3.50 (*m*, 1 H); 2.95 (*m*, 1 H); 1.75–2.15 (*m*, 8 H). ^{13}C-NMR (D_2O) of **5c**: 58.6; 50.2; 28.9; 24.5.

*Bis(1,3,5-triamino-1,3,5-trideoxy-*cis-*inositol)nickel(II) Sulfate Dihydrate* (**4a**). A suspension of 2.0 g of above mentioned, crude **3a** and 20 ml of H_2O was adjusted to a pH of 11 by the addition of conc. aq. NH_3. $NiSO_4 \cdot 6\ H_2O$ (0.67 g), dissolved in 10 ml H_2O was then added. The suspension was allowed to stand for 12 h at 5°. The pink solid was filtered and recrystallized from H_2O: 0.93 g (53%) of **4a**. UV/VIS: 332 (6.1), 520 (6.1), 835 (5.6). Anal. calc. for $C_{12}H_{30}N_6NiO_{10}S \cdot 2\ H_2O$ (545.21): C 26.44, H 6.29, N 15.41; found: C 26.48, H 6.34, N 15.70. MS (FAB$^+$): 411.1 (100, $[H_{-1}Ni(taci)_2]^+$), 509.1 (29, $[Ni(taci)_2(HSO_4)]^+$).

*1,3,5-Triammonio-1,3,5-trideoxy-*cis-*inositol Sulfate* (**3a**). H_2SO_4 (0.6 g) was added to a soln. of 0.93 g of **4a** in 20 ml of H_2O (80°). A color change from pink to green was noted. MeOH (20 ml) was added, and the mixture was allowed to stand for 12 h at r.t. The resulting white solid was recrystallized from H_2O/MeOH: 0.97 g (88%) of **3a**. Characterization: see [2].

*1,3,5-Triamino-1,3,5-trideoxy-*cis-*inositol* (*taci*) was prepared according to [2]. Recrystallization from EtOH (91%).

*1,3,5-Triammonio-1,3,5-trideoxy-*cis-*inositol Hexachlorobismutate* (**3b**). $BiCl_3$ (360 mg) was dissolved in 1 ml of conc aq. HCl, and 200 mg of taci, dissolved in 2 ml H_2O, were then added. The precipitated, white solid (690 mg, 95%) was redissolved in 60 ml of 4M HCl, and the soln. was allowed to evaporate slowly in an open beaker at r.t. The resulting crystals were suitable for the X-ray diffraction study. Anal. calc. for $C_6H_{18}N_3O_3BiCl_6 \cdot 2\ H_2O$ (637.96): C 11.30, H 3.48, N 6.59; found: C 11.34, H 3.47, N 6.68.

*Bis(1,3,5-triamino-1,3,5-trideoxy-*cis-*inositol)cobalt(III) Chloride* (**4b**). A soln. of taci (3.2 g) in 70 ml of H_2O was partially neutralized by the addition of 0.75 ml of 6M aq. HCl. $CoCl_2 \cdot 6\ H_2O$ (2.1 g) were addcd and stirred under a gentle flow of O_2 for 14 h. The soln. was then evaporated *in vacuo* to 40 ml, and 40 ml of conc. aq. HCl and 10 ml of EtOH were added. An orange solid crystallized at 4°. Recrystallization from H_2O/EtOH: 3.6 g (78%) of **4b**. UV/VIS (H_2O): 338 (102), 470 (84). ^{1}H-NMR (D_2O): 4.07 (*t*, *J* = 3.8, 3 H); 2.87 (*t*, *J* = 3.8, 3 H). ^{13}C-NMR (D_2O): 65.6; 51.9. MS (FAB$^+$): 483.0 (4, $[Co(taci)_2Cl_2]^+$), 448.0 (23, $[Co(taci)_2Cl]^+$), 447.0 (27, $[H_{-1}Co(taci)_2Cl]^+$), 412.0 (73, $[H_{-1}Co(taci)_2]^+$), 411.0 (56, $[H_{-2}Co(taci)_2]^+$), 271.0 (100, $[Co(taci)Cl]^+$), 235.0 (49, $[H_{-1}Co(taci)]^+$). Anal. calc. for $C_{12}H_{30}N_6O_6Cl_3Co$ (519.70): C 27.73, H 5.82, N 16.17, Cl 20.47, Co 11.34; found: C 27.71, H 5.89, N 16.23, Cl 20.30, Co 11.15.

*Bis(1,3,5-triamino-1,3,5-trideoxy-*cis-*inositol)cobalt(III) nitrate dihydrate* (**4c**) was obtained by a stoichiometric addition of 3.0 equiv. of 0.1M aq. $AgNO_3$ (Ag electrode) to 0.18 g of **4b**, dissolved in 15 ml of H_2O. The

resulting suspension was filtered through *Celite* and layered with EtOH. The obtained orange crystals were suitable for X-ray diffraction studies.

X-Ray Diffraction Studies. Crystal-structure determinations were performed on a *Nicolet P21* four-circle diffractometer (MoK_α radiation, $\gamma = 0.71073$ Å, graphite-monochromatized). The structures were solved by direct methods and difference *Fourier* calculations of the program *Siemens* SHELXTL PLUS (VMS) [20]. In the full-matrix least-squares refinement, all non-H-atoms of the Co complex **4c** were refined with anisotropic displacement parameters. The positions of the H–(N) protons were those found in the difference *Fourier* map. In the Bi compound **3b**, the Bi- and Cl-atoms were refined with anisotropic displacement parameters, all other were refined isotropically. For both compounds, the six positions of the H–(C) atoms were calculated using a riding model with

Table 2. *Crystallographic Data for Triammonio-1,3,5-trideoxy-*cis-*inositol Hexachlorobismutate Dihydrate* (**3b**) *and Bis(1,3,5-triamino-1,3,5-trideoxy-*cis-*inositol)cobalt(III) Nitrate Dihydrate* (**4c**)

Compound	$[BiCl_6][H_3(taci)]\cdot 2H_2O$	$[Co(taci)_2(NO_3)_3]\cdot 2H_2O$
Crystal dimensions	0.1 × 0.1 × 0.1	0.09 × 0.09 × 0.2
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*, No. 62	*C*2/*c*, No. 15
a [Å]	24.314 (5)	22.912 (8)
b [Å]	10.215 (2)	8.942 (2)
c [Å]	7.422 (8)	14.731 (3)
β [°]	90.0	128.66 (2)
V [Å^3]	1843 (2)	2356 (1)
Z	4	4
μ(MoK_α) [cm^{-1}]	104.3	8.23
Min/Max transmission		0.8950/0.9433
Maximum value (sin θ)/λ	0.538	0.595
Measured reflections	2791	2297
Unique reflections	1277	2143
Observed reflections	941[a])	1461[a])
No. of parameter	71	212
R[b]) [%]	5.8	4.9
R_w[c]) [%]	5.5	5.7

[a]) $I \geq 4\sigma(I)$. [b]) $R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma F_o$. [c]) $R_w = (\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w|F_o|^2)^{1/2}$, $w = 1/\sigma^2(|F_o|)$.

Table 3. *Selected Bond Distances* [Å] *of Triammonio-1,3,5-trideoxy-*cis-*inositol Hexachlorobismutate Dihydrate* (**3b**) *and Bis(1,3,5-triamino-1,3,5-trideoxy-*cis-*inositol)cobalt(III) Nitrate Dihydrate* (**4c**). Estimated Standard Deviations in Parentheses.

	$[BiCl_6][H_3(taci)]\cdot 2H_2O$	$[Co(taci)_2(NO_3)_3]\cdot 2H_2O$
Co–N(1)		1.999 (6)
Co–N(3)		1.991 (4)
Co–N(5)		2.009 (5)
C(1)–C(2)	1.56 (3)	1.544 (7)
C(2)–C(3)	1.58 (3)	1.527 (8)
C(3)–C(4)	1.54 (3)	1.545 (8)
C(4)–C(5)	1.54 (3)	1.535 (7)
C(5)–C(6)	1.58 (3)	1.533 (8)
C(1)–N(1)	1.48 (4)	1.506 (8)
C(2)–O(2)	1.45 (2)	1.444 (7)
C(3)–N(3)	1.51 (3)	1.503 (9)
C(4)–O(4)	1.42 (4)	1.439 (7)
C(5)–N(5)	1.51 (3)	1.509 (8)
C(6)–O(6)	1.45 (2)	1.444 (6)

constant displacement factors of 0.08 Å^2. Crystallographic data are listed in *Table 2*, selected bond lengths are presented in *Table 3*. Atom coordinates, an entire list of bond distances and bond angles, temperature factors, and structure factors are available from the authors upon request.

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