Metal Binding of Polyalcohols. Part 2.[1] (*all-cis*-1,3,5-Triaminocyclohexane)cobalt(III), a Facially Co-ordinating, Diamagnetic Probe exemplified by its Complex Formation with *cis*-Inositol†

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Interactions of *cis*-inositol (ino) (cyclohexane-1,2,3,4,5,6-hexol) and 1,3,5-triacetamido-1,3,5-trideoxy-*cis*-inositol (taino) with the Co(tach)$^{3+}$ unit (tach = *all-cis*-1,3,5-triaminocyclohexane) have been examined. Reaction with *cis*-inositol resulted in the formation of [Co(tach)(H$_{-1}$ino)]$^{2+}$, with taino in either [(tach)Co(μ-OH)$_2$(μ-NO$_3$)Co(tach)]$^{3+}$ or [Co(taino)$_2$]$^{2+}$. The crystal structures of [Co(tach)(H$_{-1}$-ino)][NO$_3$]$_2$ **1**, [(tach)Co(μ-OH)$_2$(μ-NO$_3$)Co(tach)][NO$_3$]$_3$·0.75H$_2$O **2**, [Co(taino)$_2$][NO$_3$]$_2$·4H$_2$O **3a** and [Co(taino)$_2$][NO$_3$]$_2$·8H$_2$O **3b** have been determined. The Co^{III} in solid **1** is bound to two hydroxyl groups and one alkoxo group of *cis*-inositol in a *syn*-1,3,5-triaxial arrangement. In aqueous solution, [Co(tach)(ino)]$^{3+}$ reacted as a strong acid. The values pK_1 < 2.0, pK_2 = 4.05(2) and pK_3 = 6.68(2) have been established by potentiometric measurements (0.1 mol dm^{-3} KNO$_3$, 25 °C). In addition, an isomerization reaction [binding of the Co(tach)$^{3+}$ unit to three adjacent hydroxyl groups in an axial–equatorial–axial arrangement] as well as the reversible dissociation of *cis*-inositol have been observed by NMR measurements. Both reactions show a characteristic pH dependence for the equilibrium composition as well as for the reaction rate. The individual microscopic acidity constants of the two isomers were elucidated by ^{1}H NMR-monitored pD titrations. Molecular mechanics calculations were used to rationalize differences in energy between the two isomeric forms. The rather weak binding of neutral polyalcohols to metal ions was confirmed. However, it was also demonstrated that the deprotonated polyols can act as powerful ligands for metal ions.

Polyalcohols (sugars, sugar alcohols, polysaccharides) as well as metal ions play an important role in biological systems and their mutual interactions have been recognized to be crucial for a variety of biochemical processes.[2] An increasing number of studies with this focus is now in progress, and a variety of complexes, where aliphatic or alicyclic polyalcohols are bound to a metal ion, have been described. However, most of the ligands used bear a strongly binding 'anchor'-group like an amine,[3,4] or a carboxylate,[4–6] which enforces sufficient stability on the complex. Co-ordination of additional hydroxyl groups is then promoted by a favourable ΔS. The co-ordination chemistry of true polyalcohols (*i.e.* ligands which co-ordinate the metal exclusively *via* hydroxyl groups) is still poorly developed.[1,7] Particularly kinetic and thermodynamic data of such complexes are not widely available. Investigation of these complexes is complicated by several factors: (*i*) their stability in aqueous solution is usually rather low; (*ii*) the high number of donor groups within the ligand results in a multitude of possible structures; (*iii*) the ability of the aliphatic hydroxyl group to co-ordinate the metal cation either in the protonated (ROH) or deprotonated (RO$^-$) form, combined with a high tendency of the co-ordinated alkoxo group for bridging interactions, results in a complex system of various species, including polynuclear complexes. Since the co-ordination of a ligand is not necessarily coupled to a proton dissociation, the pH method is not generally applicable for determination of the stability of such a complex. Also UV/VIS spectroscopy, another standard method for the identification of individual species and the determination of its stability, not always provides valuable information because the differences in the spectra of the aqua ion and the corresponding complex with an aliphatic polyalcohol are often not significant.

In a previous investigation the complex formation of Fe^{III} with a variety of polyalcohols in alkaline aqueous solutions was studied.[1] It had been shown that mononuclear complexes exist only at high pH and high concentration of these ligands. Lowering the pH resulted in formation of polynuclear species and finally in the formation of solid phases. In subsequent investigations we focused on the structure, stability and reactivity of mononuclear complexes in aqueous solutions in the range $3 \leqslant \text{pH} \leqslant 9$. The (*all-cis*-1,3,5-triaminocyclohexane)-cobalt(III) [=Co(tach)$^{3+}$] unit proved to be a particularly suitable probe to investigate a variety of sugars, sugar alcohols and cyclitols. The present contribution reports the interaction of [Co(tach)]$^{3+}$ with *cis*-inositol (ino) (cyclohexane-1,2,3,4,5,6-hexol) and 1,3,5-triacetamido-1,3,5-trideoxy-*cis*-inositol (taino) in the solid state and in aqueous solution.

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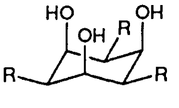
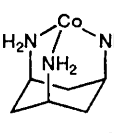
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



ino R = OH
taino R = NHCOMe



$[Co(tach)]^{3+}$

Experimental

The C, H and N analyses were performed by D. Manser, Laboratorium für Organische Chemie, ETH Zürich.

Syntheses.—*cis*-Inositol[8] and *all-cis*-1,3,5-triaminocyclohexane trihydrochloride (tach•3HCl)[9] were prepared according to published procedures.

The complex $[Co(tach)Cl_3]$ was prepared by following the method given by Umehara *et al.*:[10] a solution of $CoCl_2{\cdot}6H_2O$ (1.19 g, 5 mmol) in water (5 cm^3) was added to a solution of tach•3HCl (1.19 g, 5 mmol) and NaOH (604 mg, 15.1 mmol) in water (5 cm^3). Air was bubbled through the solution for 1.5 h. Concentrated HCl (5 cm^3) was added and the resulting solution heated to 80 °C for 15 min. The solution was evaporated *in vacuo* to a total volume of 2 cm^3 and allowed to stand for 3 d at 4 °C. A blue solid was filtered off, washed repeatedly with water and dried *in vacuo*. Yield 50% (Found: C, 24.60; H, 5.15; N, 14.00. Calc. for $C_6H_{15}Cl_3CoN_3$: C, 24.45; H, 5.15; N, 14.25%).

1,3,5-Triacetamido-1,3,5-trideoxy-*cis*-inositol was prepared from 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol[11] in an excess of $(MeCO)_2O$.[12]

Methanolic solutions of (all-cis-1,3,5-*triaminocyclohexane*)-*cobalt*(III) *trinitrate.* The complex $[Co(tach)Cl_3]$ (195 mg, 0.66 mmol) was suspended in MeOH (4 cm^3) and solid $AgNO_3$ (355 mg, 2.09 mmol) added. The slurry was stirred for 5 h at room temperature and then filtered. The solid residue was washed repeatedly with MeOH and the combined solutions were evaporated *in vacuo* to a total volume of 15 cm^3 and used in the following experiments.

[cis-*Inositolato*(1 –)](all-cis-1,3,5-*triaminocyclohexane*)-*cobalt*(III) *dinitrate* **1**. Solid *cis*-inositol (1 g, 5.6 mmol) was added to a methanolic solution of $[Co(tach)][NO_3]_3$ (30 cm^3, 5.6 mmol Co). The slurry was stirred for 20 h at room temperature, resulting in a red solid and a colourless solution. The solid was filtered off and dried *in vacuo* (2.35 g, 86%). Single crystals for X-ray diffraction experiments were obtained by layering a saturated aqueous solution of the complex with EtOH (Found: C, 29.40; H, 5.25; N, 14.05. Calc. for $C_{12}H_{26}CoN_5O_{12}$: C, 29.35; H, 5.35; N, 14.25%). VIS spectrum (water): 535 nm (ε 76 dm^3 mol^{-1} cm^{-1}).

Di-μ-*hydroxo*-μ-*nitrato*-*bis*[(all-cis-1,3,5-*triaminocyclohexane*)*cobalt*(III)] *trinitrate hydrate* **2**. (*a*) *From the reaction of* $[Co(tach)]^{3+}$ *with taino.* A solution of taino (151 mg, 0.5 mmol) in MeOH (1 cm^3) was added to a methanolic solution of $[Co(tach)][NO_3]_3$ (3 cm^3, 0.5 mmol Co). The resulting clear red solution was stirred for 48 h, filtered and then layered with EtOH yielding red crystals which were used for single-crystal X-ray analysis. A modified procedure, where taino was added to a slurry of $[Co(tach)Cl_3]$ prior to the addition of $AgNO_3$, resulted in the same product (Found: C, 21.75; H, 4.90; N, 20.65. Calc. for $C_{12}H_{33.5}Co_2N_{10}O_{14.75}$: C, 21.45; H, 5.05; N, 20.85%).

(*b*) A freshly prepared methanolic solution (5 cm^3) of $[Co(tach)][NO_3]_3$ (0.26 mmol Co) was stirred for 3 d and then evaporated *in vacuo* to a total volume of 1 cm^3. A few drops of water were added and the solution was layered with EtOH. Red needles, yield 54%. VIS spectrum (water): 397 (ε 147) and 514 nm (141 dm^3 mol^{-1} cm^{-1})].

Bis(1,3,5-*triacetamido*-1,3,5-*trideoxy*-cis-*inositol*)*cobalt*(II) *nitrate* **3**. (*a*) *From reductive decomposition of* $[Co(tach)]^{3+}$. Solid taino (201 mg, 0.66 mmol) was added to a methanolic solution (15 cm^3) of $[Co(tach)]^{3+}$. The resulting clear solution was refluxed for 24 h, filtered and evaporated to dryness. Single crystals of composition $[Co(taino)_2][NO_3]_2{\cdot}4H_2O$ **3a** and $[Co(taino)_2][NO_3]_2{\cdot}8H_2O$ **3b** were grown by redissolving the obtained solid in water (2 cm^3) and layering the resulting solution with acetone [Found: C, 32.65; H, 5.80; N, 12.45. Calc. for $C_{24}H_{52}CoN_8O_{23}$ (mixture of **3a** and **3b**): C, 32.75; H, 5.95; N, 12.75%].

(*b*) A solution of taino (303 mg, 1 mmol) in MeOH (2 cm^3) was added to a solution of $Co(NO_3)_2{\cdot}6H_2O$ (146 mg, 0.5 mmol) in MeOH (1 cm^3). The mixture was heated to 60 °C and a few drops of water were added until a clear pink solution was obtained. Orange crystals of $[Co(taino)_2][NO_3]_2{\cdot}8H_2O$ (380 mg, 81%) precipitated at 4 °C within 12 h.

Potentiometric Measurements.—The pK_a values of free *cis*-inositol and of $[Co(tach)(ino)]^{3+}$ were determined by several alkalimetric titrations. The test solutions (100 cm^3) were titrated in a water-jacketted beaker at 25 °C under an atmosphere of nitrogen (washed previously with an aqueous solution of 1 or 0.1 mol dm^{-3} KNO_3) by adding suitable increments of 1 or 0.1 mol dm^{-3} KOH, dispensed from a Metrohm 665 piston burette. The pH ($= -\log[H]$) was measured with a Philips GAH420 glass electrode, an Ag–AgCl reference electrode fitted with a salt bridge (1 or 0.1 mol dm^{-3} KNO_3) and an Orion 720 A pH/mV meter. The potentiometric data and the evaluated equilibrium constants are summarized in Table 1. Calibration was performed by titrating 100 cm^3 of 2×10^{-3} mol dm^{-3} HNO_3 with 1 or 0.1 mol dm^{-3} KOH, revealing a pK_w of 13.78 for 1 mol dm^{-3} KNO_3 and of 13.79 for 0.1 mol dm^{-3} KNO_3. All pK_a values obtained from potentiometric measurements refer strictly to concentration quotients. The data were evaluated with the computer program SUPERQUAD[13] and refined with BEST.[14] The pK_a values of complex **1** were evaluated, considering an average presence of 10% of $[Co(tach)(H_2O)_3]^{3+}$, as estimated from the NMR measurements. Since the pK_a values of this triaqua complex were not known at 25 °C, $I = 0.1$ mol dm^{-3}, the corresponding values for 20 °C, $I = 0.1$ mol dm^{-3} (5.45, 7.65, 9.80) were used as fixed values during the refinement.[15] It is well known[15] that $[Co(tach)(H_2O)_3]^{3+}$ dimerizes slowly to $[(tach)Co(\mu\text{-}OH)_3Co(tach)]^{3+}$. Therefore, the concentrations of the Co-containing components were allowed to vary during the refinement, revealing 0.087 mmol for $\Sigma_i[Co(tach)(H_{-i}ino)]$ and 0.010 mmol for $\Sigma_j[Co(tach)(H_2O)_j(OH)_{3-j}]$. These values confirm, however, that the formation of the pH-inactive dimer is slow,[15,16] allowing the determination of a preequilibrium system consisting exclusively of mononuclear species. The total concentration of H$^+$ added, $[H]_t$, was treated as fixed at 0.20 or 0.30 mmol, respectively.

Spectroscopy.—The UV/VIS spectra were recorded on an Uvikon 940 spectrophotometer, NMR spectra on a Bruker AMX-500 spectrometer (500.13 and 125.9 MHz for ^1H and ^{13}C respectively). Two-dimensional NMR experiments [correlation spectroscopy (COSY) and ^{13}C, ^1H heteronuclear multiple quantum coherence spectroscopy (HMQC)] were performed according to the literature.[17,18] Chemical shifts (δ) are given relative to 3-(trimethylsilyl)[$^2H_4$]propionate (δ 0). Titrations of complex **1** monitored by ^1H NMR spectroscopy were performed by adding appropriate amounts of NaOD to 21 individual sample solutions (D_2O). The samples were allowed to equilibrate for 48 h prior to the NMR and pH measurement. Values[19] of pD (= pH + 0.42) were measured with a glass electrode (Philips) which was calibrated by using aqueous buffer solutions. The titrations were evaluated from the equation $\delta_{calc} = (\delta_0 + K_3[D]\delta_1 + K_3K_2[D]^2\delta_2)/(1 + K_3[D] + K_3K_2[D]^2)$, where δ_0, δ_1 and δ_2 denote the chemical shifts of the species X, DX$^+$ and D_2X^{2+}, respectively, X = [Co(tach)-$(H_{-3}ino)$], $K_3 = [DX]/([X][D])$ and $K_2 = [D_2X]/([DX][D])$. Values for K_3, K_2, δ_1 and δ_2 were obtained from least-squares calculations by minimizing $\Sigma(\delta_{calc} - \delta_{obs})^2$

Table 1 Potentiometric data and evaluated equilibrium constants at 25 °C for *cis*-inositol and $[Co(tach)(ino)]^{3+}$ with estimated standard deviations[a] in parentheses

	cis-Inositol	**1**[b]	
$[KNO_3]$ Medium/mol dm^{-3}	1	0.1	0.1
$[ino]_t$/mol dm^{-3}	4×10^{-3}	1×10^{-3}	1×10^{-3}
$[HNO_3]_t$/mol dm^{-3}	0	0	1×10^{-3}
[KOH] Titrant/mol dm^{-3}	1	0.1	0.1
No. of points	26	39	46
Refined constants	$pK_1 = 12.692(8)$[c]		$pK_1 = 1.69(6)$[c]
		$pK_2 = 4.042(1)$	$pK_2 = 4.05(1)$
		$pK_3 = 6.681(1)$	$pK_3 = 6.670(5)$
σ(pH)[d]	0.004	0.003	0.004

[a] From SUPERQUAD.[13] [b] The presence of 10% $[Co(tach)(H_2O)_3]^{3+}$ was considered by using corresponding pK_a values of 5.45, 7.65 and 9.80 as fixed in the refinement.[15] [c] The standard deviations for these values are underestimated. Considering the low concentration of $[Co(tach)(ino)]^{3+}$ and $H_{-1}ino^-$ at the beginning or at the end of the titration, respectively, the uncertainties of the pK_w as well as the particularly large inaccuracy of the glass electrode for pH < 3 and pH > 11, a value of $pK_1 = 12.7(3)$ for *cis*-inositol and $pK_1 = 1.7(3)$ for $[Co(tach)(ino)]^{3+}$ are reasonable. [d] From BEST,[14] $\sigma(pH) = \{[\Sigma w(pH_{obs} - pH_{calc})]^2/\Sigma w\}^{\frac{1}{2}}$, $w = (pH_{i+1} - pH_{i-1})^{-2}$.

Table 2 The pK_a values and chemical shifts (^1H) of complexes **1a** and **1b** obtained from the ^1H NMR-monitored titration *

Resonance	pK_3	pK_2	δ_0	δ_1	δ_2
A_1	7.14	4.40	3.46	3.66	3.84
A_2	7.13	4.44	2.79	3.21	3.62
B_4	7.78	4.04	3.86	3.93	4.17
B_2	7.75	4.06	3.62	3.86	4.03
B_3	7.82	4.03	3.40	3.58	3.82
B_1	—	3.99	3.44	3.46	3.64

Average pK_3 and pK_2 7.14(1), 4.42(3) for **1a**; 7.78(3), 4.03(3) for **1b**.

* $\sigma = [\Sigma(\delta_{calc} - \delta_{obs})^2/N]^{\frac{1}{2}} = 0.001$ in each case, where N = number of data points.

individually for every resonance (Table 2). The δ_0 values were obtained from the spectrum with pD 12. Mean pK_3 (= log K_3) and pK_2 (= log K_2) values were then calculated as an unweighted average for each of the two isomers **1a** and **1b** (Fig. 4).

Molecular Mechanics Calculations.—These were carried out as described previously,[20] using the commercially available program SYBYL.[21]

Crystal Structure Determination and Refinement.—Diffraction data for compounds **1**, **2**, **3a** and **3b** were collected on three different four-circle diffractometers using graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). A summary of crystal data, intensity measurements and structure refinement is presented in Table 3. The stability of the crystals was checked by measuring standard reflections at an interval of 120 reflections. However, no significant loss of intensity was noted for any of the crystals. All data were corrected for Lorentz and polarization effects. A face-indexed, numerical absorption correction was performed for **1**, **3a** and **3b**. The structures were solved by direct methods using the program SHELXTL PLUS[22] on a MicroVAX II computer. Refinements were performed by using SHELXTL PLUS[22] for **2**, **3a** and **3b** and SHELXL 93[23] for **1**. All non-hydrogen atoms of the complex molecules $[Co(tach)(H_{-1}ino)]^{2+}$, $[(tach)Co(\mu\text{-}OH)_2(\mu\text{-}NO_3)Co(tach)]^{3+}$, and $[Co(taino)_2]^{2+}$ as well as of the NO_3^- counter ions were located and refined by a series of alternating difference electron syntheses and full-matrix least-squares refinements. Additional peaks were interpreted as oxygen positions of non-co-ordinating water molecules. However, O(3w) and O(4w) in the structure of **2** had unusually high displacement parameters. In addition, the elemental analysis indicated the presence of one rather than two water molecules. Therefore, these positions were refined with occupancy factors of 0.5 and 0.25, respectively. In the structure of **3b** two different orientations of the nitrate were found, showing a single position for N but six positions for the three oxygen atoms. This result was interpreted as a static disorder and the six oxygen positions were therefore refined with occupancy factors of 0.5. Anisotropic displacement parameters were used for all non-hydrogen atoms in the final refinement. All expected hydrogen positions of the molecules **2**, **3a** and **3b** were located and included in the refinement with fixed values as obtained from the Fourier difference map. The hydrogen atoms of the non-co-ordinating water molecules were not located. The positions of 15 carbon-, six nitrogen- and five oxygen-bonded H atoms in **1** were located in the Fourier difference map. These positions as well as their isotropic displacement parameters were allowed to vary in the final refinement. The scattering factors were from ref. 24. Atomic coordinates are listed in Table 4, selected bond lengths and angles in Tables 5–8. The bond distances and angles of the organic ligands in **1**, **2**, **3a** and **3b** and of the NO_3^- counter ions all fell in expected ranges.

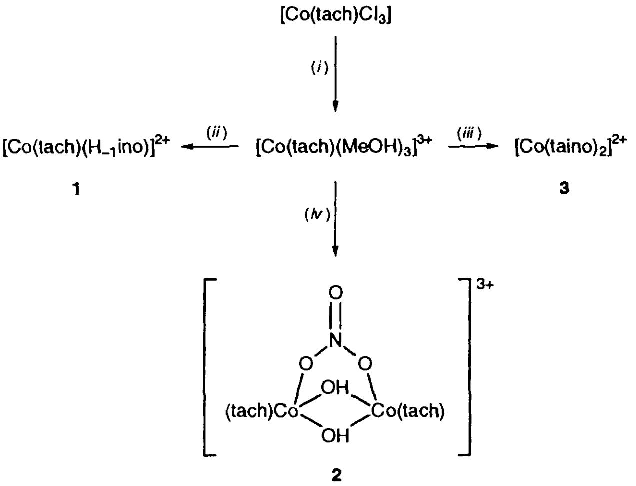
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles. Calculated and observed structure factors are available from the authors upon request.

Results

Syntheses.—The preparation procedure started from the well known, blue $[Co(tach)Cl_3]$ which is insoluble in conventional solvents.[10,15] However, the three Cl^- ligands could be detached by the addition of 3 equivalents of $AgNO_3$ to a slurry of $[Co(tach)Cl_3]$ in MeOH. We formulate the resulting species in the deep red solution as a solvate $[Co(tach)(MeOH)_3]^{3+}$. However, direct co-ordination of NO_3^- to the metal cation cannot be ruled out completely. The subsequent substitution of the co-ordinated solvent molecules by tridentate, facially co-ordinating ligands was investigated by adding *cis*-inositol or 1,3,5-triacetamido-1,3,5-trideoxy-*cis*-inositol to this solution (Scheme 1). The co-ordination of *cis*-inositol to the $[Co(tach)]^{3+}$ moiety was easily verified by the isolation of crystalline $[Co(tach)(H_{-1}ino)][NO_3]_2$ **1**, however, no valid evidence was found for an analogous binding of $[Co(tach)]^{3+}$ to taino. Since the VIS spectra of the intermediate solvent complex and of $[Co(tach)(taino)]^{3+}$ are not expected to differ significantly, the formation of this complex in solution could not be completely ruled out. However, it was not possible to isolate it in the form of a solid compound. The final product of the reaction was either $[(tach)Co(\mu\text{-}OH)_2(\mu\text{-}NO_3)Co(tach)]^{3+}$ **2**, which was formed at room temperature after a period of several days, or $[Co(taino)_2]^{2+}$ **3**, which was obtained at elevated temperature. The latter crystallized either as the

Table 3 Summary of crystal data, intensity measurements and structure refinement for $[Co(tach)(H_{-1}ino)][NO_3]_2$ **1**, $[(tach)Co(\mu\text{-}OH)_2(\mu\text{-}NO_3)Co(tach)][NO_3]_3\cdot 0.75H_2O$ **2**, $[Co(taino)_2][NO_3]_2\cdot 4H_2O$ **3a** and $[Co(taino)_2][NO_3]_2\cdot 8H_2O$ **3b**

Compound	**1**	**2**	**3a**	**3b**
Formula	$C_{12}H_{26}CoN_5O_{12}$	$C_{12}H_{33.5}Co_2N_{10}O_{14.75}$	$C_{24}H_{50}CoN_8O_{22}$	$C_{24}H_{58}CoN_8O_{26}$
M	491.3	671.8	861.7	933.7
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	*Pccn* (no. 56)	$P2_1/n$ (no. 14)	*Pcab* (no. 61)
a/Å	7.187(1)	15.158(3)	10.313(4)	11.66(2)
b/Å	15.692(2)	22.796(5)	11.401(3)	18.51(3)
c/Å	16.347(4)	14.885(3)	16.821(5)	19.77(4)
β/°	90	90	94.26(2)	90
U/Å^3	1843.6(6)	5143(2)	1972.3(1)	4268(14)
Z	4	8	2	4
D_c/kg m^{-3}	1.77	1.74	1.45	1.45
F(000)	1024	2780	906	1972
Crystal size/mm	0.3 × 0.4 × 0.1	0.1 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.6 × 0.6 × 0.6
μ(Mo-Kα)/cm^{-1}	10.11	13.77	5.26	4.99
Diffractometer	Enraf–Nonius CAD4	Picker-Stoe	Syntex P21	Syntex P21
T/K	293	293	293	293
No. measured reflections	8314	3415	2690	3171
No. observed reflections, $I > 2\sigma(I)$	5757	2472	1956	2085
No. parameters	377	353	250	295
Weighting scheme, w^{-1}	$\sigma^2(F_o^2) + (0.0957P)^2 + 1.68P$ $P = [\max(F_o^2,0) + 2F_c^2]/3$	$\sigma^2(F) + 0.0001F^2$	$\sigma^2(F) + 0.0001F^2$	$\sigma^2(F) + 0.001F^2$
Minimum, maximum transmission	0.7102, 0.9015		0.8914, 0.9612	0.7807, 0.8534
Final residual electron density/e Å^{-3}	0.66, −0.45	0.61, −0.40	0.55, −0.33	0.42, −0.33
$R\,[=\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert]$	0.051	0.047	0.051	0.048
$wR_2\{=[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}\}$	0.1292			
$R'\{=[(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$		0.055	0.062	0.068



Scheme 1 (*i*) $AgNO_3$, MeOH; (*ii*) 25 °C, ino; (*iii*) 80 °C, taino; (*iv*) 25 °C, taino

dinitrate tetrahydrate **3a** or the dinitrate octahydrate **3b** from aqueous solutions. To our knowledge, complexes **2** and **3** have not been described in the literature. They can, however, be prepared more conveniently by adding water to a methanolic solution of $[Co(tach)][NO_3]_3$ yielding **2**, or by simply adding $Co(NO_3)_2$ to an aqueous solution of taino, yielding **3**.

Structural Characterization.—Single-crystal X-ray analysis of complexes **1**, **2**, **3a** and **3b** clearly confirmed that the $Co(tach)^{3+}$ moiety is only preserved in **1** and **2**. In **1**, Co^{III} is bound to the three amino groups of tach and to three axial oxygen donors of *cis*-inositol (Fig. 1). The presence of only two nitrates per complex is somewhat unexpected for a cobalt(III) complex. However, the electronic properties (the complex is diamagnetic), the Co–N and Co–O bond lengths and the observed reactivity in aqueous solution clearly indicate the presence of Co^{III}. Consequently, one of the two ligand molecules must bear a negative charge. Indeed, the structure showed that one of the co-ordinated hydroxyl groups of *cis*-inositol is deprotonated. In the electron-density map all H atoms bound to C and N and five of the six bound to O could be located. However, no significant electron density was observed in proximity of O(22). In addition, the Co–O(22) distance of 1.899(2) Å is significantly shorter than the corresponding distances from Co to O(24) [1.939(3) Å] and O(26) [1.940(3) Å]. Moreover, the C–O bond lengths of the co-ordinated alcoholic groups are slightly longer than the corresponding bond distance of the co-ordinated alkoxo group. In turn, the distance from Co to N(15), which is *trans* to O(22), is significantly elongated, indicating a stronger *trans* influence of RO^- compared with ROH (Table 5). It is noteworthy that the mean Co–OH(R) distance of 1.940 Å does not significantly differ from the mean $Co–NH_2(R)$ distance of 1.944 Å.

In complex **2**, two Co(tach) entities are linked together by two symmetric μ-hydroxo bridges and one symmetric μ-nitrato bridge (Fig. 2). The structure can be described as two distorted octahedra, sharing one common edge. The distortion is a consequence of the strain within the four-membered Co(1)–O(1w)–Co(2)–O(2w) ring, resulting in a Co–O–Co angle of 95.5°. The O(1w) ··· O(2w) distance is 2.49(1) Å. The two connected equatorial planes [N(11)–N(15)–O(2w)–O(1w) and N(21)–N(25)–O(2w)–O(1w)] are bent against each other by an angle of 23°. Atoms N(13), Co(1), O(11n), N(1n), O(12n), Co(2) and N(23) all lie approximately in one plane (all deviations from the least-squares mean plane are <0.035 Å). The torsional angle O(11n)–Co(1)–Co(2)–O(12n) is 1.9°. The $Co–O_{nitrato}$ distances (average 1.960 Å) (Table 6) are significantly longer than the $Co–O_{hydroxo}$ distances (average 1.900 Å). In turn, the

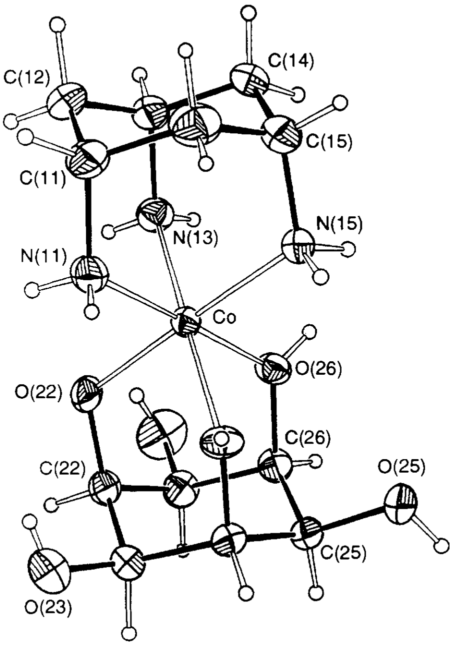


Fig. 1 View of the cation [Co(tach)(H$_{-1}$ino)]$^{2+}$ of compound **1** showing the atom numbering scheme. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary size

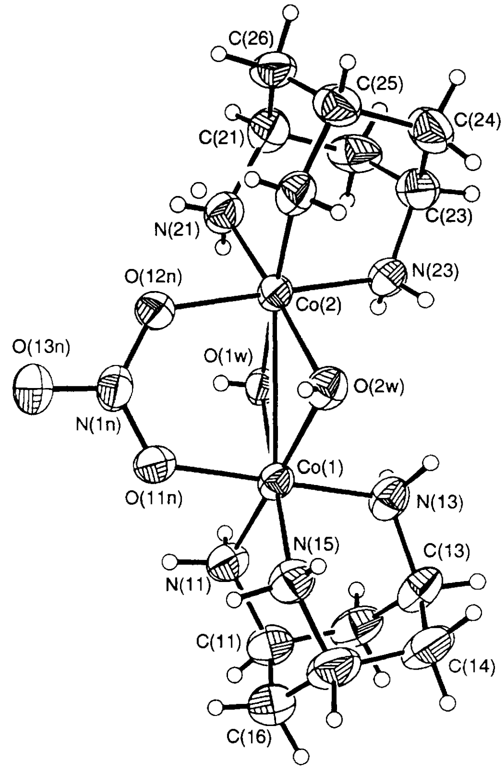


Fig. 2 View of the cation [(tach)Co(μ-OH)$_2$(μ-NO$_3$)Co(tach)]$^{3+}$ of compound **2** showing the atom numbering scheme. Details as in Fig. 1

distances from Co to the nitrogen atoms located *trans* to the nitrate ligands are slightly shorter than the Co–N distances *trans* to Co–OH. However, these differences are barely significant. The Co–N distances fall in the range 1.912(4)–1.954(5) Å (mean 1.933 Å). Although μ-dihydroxo-bridged cobalt(III) complexes are well known, the Co(μ-OH)$_2$(μ-NO$_3$)Co fragment has not been reported. However, analogous μ-carboxylato,[26] -carbonato[27] and -amidino complexes[28] with a similar structure have been described. We note that the average Co–OCO$_2$ distance of 1.901(2) Å in the carbonato-bridged species is significantly shorter than the average Co–ONO$_2$ length in the present complex.

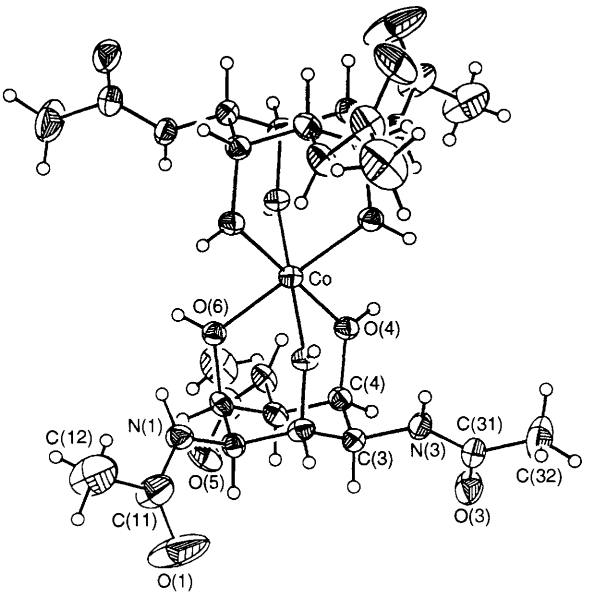


Fig. 3 View of the cation [Co(taino)$_2$]$^{2+}$ of compound **3** showing the atom numbering scheme. Details as in Fig. 1

The structure of [Co(taino)$_2$]$^{2+}$ is presented in Fig. 3. No significant structural differences were found for the cations in the monoclinic tetrahydrate **3a** and the orthorhombic octahydrate **3b**. A variety of cobalt(II) complexes with a CoO$_6$ co-ordination sphere are known having mean Co–O distances in the range 2.07–2.11 Å (average 2.089 Å).[29] Thus, the mean values of 2.058(4) or 2.056(5) Å, respectively, in the present complexes are rather short. A possible explanation may be found in the rigidity of taino. Molecular mechanics calculations, which examined steric strain in the bis complexes [M(L)$_2$]$^{z+}$ (L = 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol) as a function of the M–O bond length revealed minimal strain at 2.06 Å.[25] It is interesting that the recently reported[25] complex [Mg(L)$_2$]$^{2+}$ as well as the present cobalt(II) complex match these requirements (Table 7). The mean Mg–O distance of 2.047(5) Å does not differ significantly from the mean Co–O distance, although the ionic radius of Co^{2+} (high spin, co-ordination number six) is reported[30] to be about 3% larger than that of Mg^{2+}. In addition, the bond angles in the co-ordination spheres of the two metal ions are also strikingly similar (Table 7): differences in average values of inter- and intra-ligand O–M–O angles as well as the C–O–M angles are generally less than 0.1°. The only exception is the *trans* O–M–O angle: in contrast to the previously reported magnesium complex, Co is placed on a crystallographic centre of symmetry enforcing values of 180°.

Reactivity in Aqueous Solution.—Proton NMR spectra of complex **1** in D$_2$O are shown in Fig. 4. In freshly prepared solutions one single component **1a** dominates, exhibiting two triplets (A$_1$ and A$_2$, J = 3.8 Hz) assignable to the axial and the equatorial ring protons of the co-ordinated ino ligand. The three additional signals at δ 1.75 (3 H), 2.08 (3 H) and 2.60 (3 H) correspond to the co-ordinated tach molecule. The observed C_{3v} symmetry clearly indicates the binding of the Co(tach)$^{3+}$ moiety to three axial oxygen donors of *cis*-inositol as observed in the solid state (Fig. 1). However, the emergence of further signals points to the formation of additional species in solution. The identification of the isomer **1b** is based on the presence of four ^{1}H and four ^{13}C resonances for the co-ordinated *cis*-inositol as established by COSY and ^{13}C–^{1}H correlation experiments shown in Fig. 5. The corresponding signals, B$_1$–B$_4$,

Table 4 Fractional atomic coordinates for [Co(tach)(H_{-1}ino)][NO_3]$_2$ **1**, [(tach)Co(μ-OH)$_2$(μ-NO_3)Co(tach)][NO_3]$_3$·0.75H_2O **2**, [Co(taino)$_2$][NO_3]$_2$·4H_2O **3a** and [Co(taino)$_2$][NO_3]$_2$·8H_2O **3b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **1**							
Co	0.0162(1)	0.1205(1)	0.2612(1)	O(26)	0.1783(4)	0.0348(2)	0.3083(2)
N(11)	−0.1443(5)	0.2079(2)	0.2167(2)	C(21)	0.0939(6)	0.0487(3)	0.4503(2)
N(13)	−0.1496(5)	0.0323(2)	0.2225(2)	C(22)	−0.0248(5)	0.1282(2)	0.4354(2)
N(15)	0.1628(4)	0.1163(2)	0.1597(2)	C(23)	0.0988(5)	0.2070(3)	0.4434(2)
C(11)	−0.2157(6)	0.1981(3)	0.1319(3)	C(24)	0.2617(5)	0.2034(2)	0.3829(2)
C(12)	−0.3337(5)	0.1181(3)	0.1261(3)	C(25)	0.3772(4)	0.1225(3)	0.3930(2)
C(13)	−0.2194(6)	0.0374(3)	0.1364(3)	C(26)	0.2542(6)	0.0436(2)	0.3890(2)
C(14)	−0.0574(6)	0.0345(3)	0.0758(3)	N(1)	0.1800(5)	0.1131(2)	0.6850(2)
C(15)	0.0629(5)	0.1142(3)	0.0799(2)	O(11N)	0.1129(7)	0.0449(3)	0.6702(5)
C(16)	−0.0529(7)	0.1949(3)	0.0714(3)	O(21N)	0.1293(8)	0.1815(3)	0.6567(3)
O(21)	−0.0123(6)	−0.0276(2)	0.4496(2)	O(31N)	0.3139(8)	0.1132(3)	0.7301(5)
O(22)	−0.1216(3)	0.1252(2)	0.3602(1)	N(2)	0.8151(5)	0.1495(2)	0.8337(2)
O(23)	−0.0025(5)	0.2833(2)	0.4332(2)	O(12N)	0.6883(7)	0.1479(3)	0.7819(4)
O(24)	0.1864(4)	0.2069(2)	0.3012(2)	O(22N)	0.8651(9)	0.0836(3)	0.8657(3)
O(25)	0.5152(3)	0.1190(2)	0.3313(2)	O(32N)	0.8771(7)	0.2182(3)	0.8519(4)
Complex **2**							
Co(1)	0.9229(1)	0.3560(1)	0.1254(1)	O(1w)	0.9425(2)	0.4381(1)	0.1206(2)
Co(2)	0.8728(1)	0.4567(1)	0.2222(1)	O(2w)	0.8864(2)	0.3749(2)	0.2446(2)
N(11)	0.9639(3)	0.3438(2)	0.0024(3)	O(3w)[a]	0.75	0.25	0.0087(4)
N(13)	1.0409(3)	0.3466(2)	0.1702(3)	O(4w)[b]	0.25	0.25	0.3098(16)
N(15)	0.8963(3)	0.2738(2)	0.1374(3)	N(1n)	0.7470(3)	0.4057(2)	0.0975(3)
N(21)	0.8655(3)	0.5391(2)	0.1883(3)	O(11n)	0.8039(2)	0.3664(2)	0.0768(3)
N(23)	0.9811(3)	0.4687(2)	0.2853(3)	O(12n)	0.7620(2)	0.4447(2)	0.1566(3)
N(25)	0.8033(3)	0.4707(2)	0.3294(3)	O(13n)	0.6753(3)	0.4056(2)	0.0583(3)
C(11)	1.0250(4)	0.2944(3)	−0.0165(4)	N(2n)	0.8904(4)	0.5090(3)	−0.0769(5)
C(12)	1.1094(4)	0.3026(3)	0.0368(5)	O(21n)	0.8745(3)	0.5291(2)	−0.1526(3)
C(13)	1.0960(4)	0.2963(3)	0.1373(4)	O(22n)	0.8926(5)	0.5440(3)	−0.0115(4)
C(14)	1.0478(4)	0.2392(3)	0.1607(5)	O(23n)	0.9002(6)	0.4614(3)	−0.0621(6)
C(15)	0.9638(4)	0.2306(2)	0.1083(5)	N(3n)	0.8180(4)	0.3196(2)	−0.1893(4)
C(16)	0.9789(4)	0.2372(3)	0.0072(4)	O(31n)	0.7821(4)	0.3441(2)	−0.1260(3)
C(21)	0.8849(4)	0.5838(2)	0.2591(4)	O(32n)	0.7821(4)	0.3204(3)	−0.2622(3)
C(22)	0.9795(4)	0.5747(3)	0.2931(5)	O(33n)	0.8883(4)	0.2941(3)	−0.1795(4)
C(23)	0.9896(4)	0.5192(3)	0.3469(4)	N(4n)	1.3469(5)	0.1198(3)	0.3796(6)
C(24)	0.9221(4)	0.5132(3)	0.4207(4)	O(41n)	1.4228(4)	0.1323(3)	0.3766(5)
C(25)	0.8278(4)	0.5217(3)	0.3876(4)	O(42n)	1.3253(5)	0.0731(4)	0.3602(7)
C(26)	0.8180(4)	0.5781(2)	0.3334(4)	O(43n)	1.2925(7)	0.1452(4)	0.4158(12)
Complex **3a**[c]							
Co	0	0.5	0	C(5)	−0.0727(5)	0.6690(5)	0.1621(3)
O(1)	−0.1872(7)	0.9889(4)	−0.0345(4)	C(6)	−0.1625(5)	0.6819(5)	0.0862(3)
O(2)	0.0460(3)	0.6662(3)	−0.0331(2)	C(11)	−0.2293(7)	0.8997(6)	−0.0660(4)
O(3)	0.3253(4)	0.7998(4)	0.2002(2)	C(12)	−0.3188(8)	0.9022(6)	−0.1408(4)
O(4)	0.0861(3)	0.5403(3)	0.1104(2)	C(31)	0.3459(5)	0.7668(5)	0.1313(4)
O(5)	−0.2629(4)	0.6965(4)	0.2632(3)	C(32)	0.4808(6)	0.7561(7)	0.1054(4)
O(6)	−0.1677(3)	0.5748(3)	0.0401(2)	C(51)	−0.2151(6)	0.5977(6)	0.2606(3)
N(1)	−0.1978(4)	0.7944(4)	−0.0369(3)	C(52)	−0.2581(6)	0.4982(6)	0.3106(4)
N(3)	0.2497(4)	0.7379(4)	0.0781(3)	N	0.0768(6)	0.1007(6)	0.6007(4)
N(5)	−0.1181(4)	0.5760(4)	0.2128(3)	O(1n)	0.0556(7)	0.0217(7)	0.6451(5)
C(1)	−0.1135(5)	0.7805(5)	0.0350(3)	O(2n)	0.0001(7)	0.1804(7)	0.5966(5)
C(2)	0.0288(5)	0.7663(5)	0.0170(3)	O(3n)	0.1702(6)	0.0981(5)	0.5615(4)
C(3)	0.1137(5)	0.7519(5)	0.0940(3)	O(1w)	0.7803(4)	0.0762(5)	0.6766(3)
C(4)	0.0689(5)	0.6521(5)	0.1463(3)	O(2w)	0.5380(4)	0.8115(4)	0.3134(2)
Complex **3b**[d]							
Co	0	1.0	0.5	C(12)	0.4411(5)	1.1656(3)	0.5073(3)
O(1)	0.4777(3)	1.0585(2)	0.5711(2)	C(31)	0.2066(5)	0.7815(3)	0.3785(3)
O(2)	0.1392(2)	0.9884(2)	0.4353(1)	C(32)	0.1394(5)	0.7527(3)	0.3211(3)
O(3)	0.3000(3)	0.7594(2)	0.3939(2)	C(51)	0.1666(5)	0.8981(3)	0.7160(2)
O(4)	0.0233(2)	0.8910(2)	0.5202(2)	C(52)	0.0835(5)	0.8903(4)	0.7734(3)
O(5)	0.2682(3)	0.9123(2)	0.7247(2)	O(1w)	0.1591(3)	0.6193(2)	0.7186(2)
O(6)	0.1164(2)	1.0191(2)	0.5733(1)	O(2w)	0.1583(4)	1.0185(2)	0.3102(2)
N(1)	0.3243(3)	1.0582(2)	0.5026(2)	O(3w)	0.0994(3)	0.1340(2)	0.6442(2)
N(3)	0.1554(3)	0.8355(2)	0.4128(2)	O(4w)	0.0222(3)	0.4321(2)	0.3509(2)
N(5)	0.1218(3)	0.8909(2)	0.6541(2)	N	0.1662(4)	0.2067(3)	0.3891(3)
C(1)	0.2930(4)	0.9841(2)	0.5174(2)	O(1n)[a]	0.0587(21)	0.2311(18)	0.3747(19)
C(2)	0.2383(4)	0.9483(2)	0.4551(2)	O(2n)[a]	0.0973(13)	0.1818(11)	0.3475(5)
C(3)	0.2088(4)	0.8706(2)	0.4708(2)	O(3n)[a]	0.1571(9)	0.1478(6)	0.4061(10)
C(4)	0.1342(4)	0.8613(2)	0.5338(2)	O(4n)[a]	0.1527(8)	0.1884(8)	0.4496(5)
C(5)	0.1924(4)	0.8992(2)	0.5942(2)	O(5n)[a]	0.2521(4)	0.2331(2)	0.3643(3)
C(6)	0.2198(4)	0.9783(2)	0.5806(2)	O(6n)[a]	0.1257(23)	0.2444(17)	0.4354(17)
C(11)	0.4159(4)	1.0894(2)	0.5302(3)				

[a] Occupancy factor = 0.5. [b] Occupancy factor = 0.25. [c] All positions except Co are duplicated by the symmetry operation −*x*, 1 − *y*, −*z*. [d] All positions except Co are duplicated by the symmetry operation −*x*, 2 − *y*, 1 − *z*.

Table 5 Selected bond lengths (Å) for $[Co(tach)(H_{-1}ino)]^{2+}$ **1**

Co-N(11)	1.933(3)	O(26)-C(26)	1.434(5)
Co-N(13)	1.933(3)	C(11)-C(12)	1.519(6)
Co-N(15)	1.966(3)	C(11)-C(16)	1.532(7)
Co-O(22)	1.899(2)	C(12)-C(13)	1.518(6)
Co-O(24)	1.939(3)	C(13)-C(14)	1.528(6)
Co-O(26)	1.940(3)	C(14)-C(15)	1.522(6)
N(11)-C(11)	1.487(5)	C(15)-C(16)	1.521(7)
N(13)-C(13)	1.497(5)	C(21)-C(22)	1.532(6)
N(15)-C(15)	1.489(4)	C(21)-C(26)	1.529(5)
O(21)-C(21)	1.420(6)	C(22)-C(23)	1.527(5)
O(22)-C(22)	1.413(4)	C(23)-C(24)	1.534(5)
O(23)-C(23)	1.411(5)	C(24)-C(25)	1.526(5)
O(24)-C(24)	1.442(5)	C(25)-C(26)	1.523(5)
O(25)-C(25)	1.416(4)		

Table 6 Summarized bond lengths (Å) for $[(tach)Co(\mu\text{-}OH)_2(\mu\text{-}NO_3)Co(tach)]^{3+}$ **2**

	Minimum	Maximum	Average
Co···Co			2.814(1)
Co-OH(Co)	1.892(3)	1.908(4)	1.900
Co-O(NO$_2$)	1.959(4)	1.961(4)	1.960
Co-N	1.912(4)	1.954(5)	1.933
C-N	1.477(7)	1.501(7)	1.490
C-C	1.505(8)	1.535(9)	1.519

Table 7 Summarized bond lengths (Å) and interbond angles (°) for $[Co(taino)_2]^{2+}$, **3a** and **3b**, and $[MgL_2]^{2+}$ *

	3a	**3b**	$[MgL_2]^{2+}$
M-O			
minimum	2.040(3)	2.017(5)	2.032(4)
maximum	2.084(4)	2.078(5)	2.080(5)
average	2.058	2.056	2.047
C-O			
minimum	1.426(6)	1.429(6)	1.430(6)
maximum	1.445(6)	1.432(6)	1.440(6)
average	1.436	1.430	1.435
O-M-O (intraligand)			
minimum	85.6(1)	85.2(2)	84.0(2)
maximum	86.9(1)	86.8(2)	88.2(2)
average	86.2	86.1	86.3
O-M-O (interligand, *cis*)			
minimum	93.1(1)	93.2(2)	91.9(2)
maximum	94.4(1)	94.8(2)	95.7(2)
average	93.8	93.9	93.7
O-M-O (interligand, *trans*)	180.0	180.0	177.6
C-O-M			
minimum	121.4(3)	121.1(3)	120.7(3)
maximum	122.4(3)	123.2(3)	123.0(3)
average	121.9	122.1	121.8

* From ref. 25.

in the ^1H NMR spectrum exhibited a 1:2:2:1 ratio indicating C_s symmetry. Thus, the $Co(tach)^{3+}$ moiety is bound to three adjacent hydroxyl groups of *cis*-inositol, forming an axial–equatorial–axial arrangement. The COSY experiment allowed establishment of the correct sequence of the four ^1H resonances of *cis*-inositol in **1b**. The protons in positions 2, 2′ and 4 were identified by their mutual long-range coupling of the W type which is characteristic for protons in equatorial positions. Further coupling (J = 3–4 Hz) is indicative of vicinal protons in an axial–equatorial arrangement. This allowed the assignment of the remaining two resonances, B_1 and B_3, to the three axial protons in positions 1, 3 and 3′. These ^1H NMR characteristics, although consistent with the proposed bonding mode for this isomer, do not, however, exclude a bidentate co-ordination with only the two oxygens in position 2. The ^1H–^{13}C correlation confirmed the tridentate co-ordination mode in that both resonances of the carbon atoms in positions 1 and 2 were considerably shifted towards lower field. Such downfield shifts are characteristic for the formation of five-membered chelate rings. Also, the protons of the co-ordinated tach ligand show different resonances for the two isomers **1a** and **1b**. We note in particular a characteristic downfield shift for one of the ring protons of **1b**. The formation of a third species is indicated by two broad signals, C_1 and C_2, at δ 3.69 and 4.07, easily identified as free *cis*-inositol. Hence, the reactivity in aqueous solution can be characterized by two independent processes: an isomerization reaction and the substitution of *cis*-inositol by three solvent molecules.

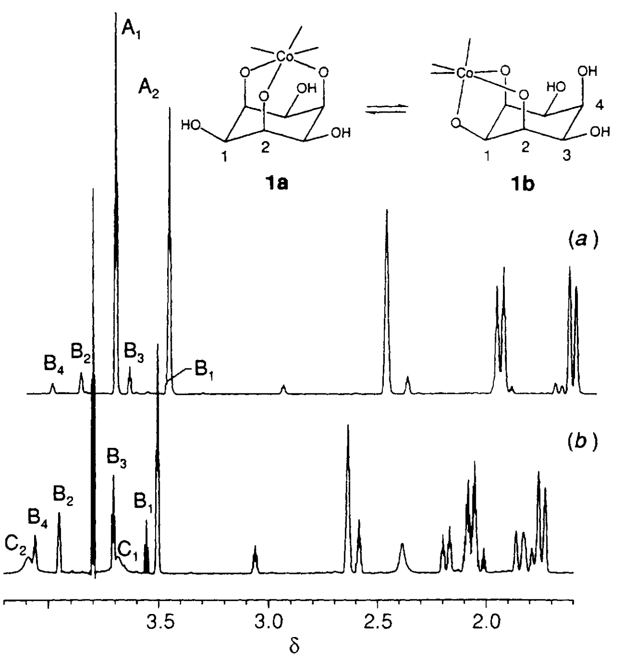


Fig. 4 Proton NMR spectrum of complex **1**: (*a*) immediately after dissolution of solid **1** in D_2O (pD 3.8); (*b*) the same sample after 2 d (pD 4.1). The signals A_1, A_2 and B_1–B_4 refer to the ring protons of the two isomers **1a** and **1b**. The signals C_1 and C_2 refer to free *cis*-inositol. The isomers are shown in their most deprotonated forms. However, protonation occurs at pH < 8 (see text), and if not explicitly specified **1a** and **1b** also include these partially protonated forms

A series of ^1H NMR spectra recorded at variable pD showed characteristic pD-dependent chemical shifts for the signals of isomers **1a** and **1b**, indicative of deprotonation of three co-ordinated hydroxyl groups in the range 1 < pD < 8.5 (Fig. 6). Obviously $[Co(tach)(ino)]^{3+}$ reacts as a strong acid in aqueous solution, forming a series of deprotonated species $[Co(tach)(H_{-x}\text{-}ino)]^{3-x}$ where $0 \leqslant x \leqslant 3$. Since the pD dependence of the signal A_2 is much more pronounced than that of A_1, the former can be assigned to the equatorial hydrogens, adjacent to the co-ordinated alcoholic groups [pD 1.8, δ(A_1) 3.91, δ(A_2) 3.78; pD 8.5, δ(A_1) 3.46, δ(A_2) 2.79]. Also the pD dependences of the four ^1H resonances of **1b** differ characteristically. Resonance B_2 shows the most pronounced change in the range 6 < pD < 8, where the change in resonance B_1 is not significant. This observation indicates that the first protonation of the triply deprotonated **1b** occurs selectively at one of the axial hydroxyl groups at position 2 (Figs. 4 and 6). Above pD 8.5 the equilibrium composition as well as the chemical shifts of the individual hydrogens remained constant with increasing pD (Fig. 6). A titration monitored by ^1H NMR spectroscopy was used to elucidate a set of individual pK_a values for each of the two isomers **1a** and **1b**. The first value could, however, not be determined due to reductive decomposition of the complex below pH 3 (formation of Co^{II}). The evaluation revealed pK_2 = 4.42, pK_3 = 7.14 for **1a** and pK_2 = 4.03, pK_3 = 7.78 for **1b** (D_2O, 25 °C, no inert electrolyte).

Table 8 Selected interbond angles (°) for $[Co(tach)(H_{-1}ino)]^{2+}$ **1** and $[(tach)Co(\mu\text{-}OH)_2(\mu\text{-}NO_3)Co(tach)]^{3+}$ **2**

Complex **1**

N(11)-Co-N(13)	91.0(1)	N(15)-Co-O(26)	89.4(1)
N(11)-Co-N(15)	91.5(1)	O(22)-Co-O(24)	90.9(1)
N(13)-Co-N(15)	91.8(1)	O(22)-Co-O(26)	90.1(1)
N(11)-Co-O(22)	89.0(1)	O(24)-Co-O(26)	88.4(1)
N(11)-Co-O(24)	90.5(1)	Co-N(11)-C(11)	119.0(2)
N(11)-Co-O(26)	178.5(1)	Co-N(13)-C(13)	118.4(2)
N(13)-Co-O(22)	89.1(1)	Co-N(15)-C(15)	118.7(2)
N(13)-Co-O(24)	178.5(1)	Co-O(22)-C(22)	119.1(2)
N(13)-Co-O(26)	90.2(1)	Co-O(24)-C(24)	121.5(2)
N(15)-Co-O(22)	179.0(1)	Co-O(26)-C(26)	121.8(2)
N(15)-Co-O(24)	88.3(1)		

Complex **2**

N(11)-Co(1)-N(13)	90.7(2)	N(11)-Co(1)-N(15)	90.9(2)
N(13)-Co(1)-N(15)	93.1(2)	N(11)-Co(1)-O(1w)	93.2(2)
N(13)-Co(1)-O(1w)	88.7(2)	N(15)-Co(1)-O(1w)	175.6(2)
N(11)-Co(1)-O(2w)	174.9(2)	N(13)-Co(1)-O(2w)	88.5(2)
N(15)-Co(1)-O(2w)	94.2(2)	O(1w)-Co(1)-O(2w)	81.8(1)
N(11)-Co(1)-O(11n)	87.9(2)	N(13)-Co(1)-O(11n)	178.4(2)
N(15)-Co(1)-O(11n)	87.7(2)	O(1w)-Co(1)-O(11n)	90.6(1)
O(2w)-Co(1)-O(11n)	92.8(2)		
N(21)-Co(2)-N(23)	92.2(2)	N(21)-Co(2)-N(25)	91.3(2)
N(23)-Co(2)-N(25)	92.2(2)	N(21)-Co(2)-O(1w)	92.3(2)
N(23)-Co(2)-O(1w)	86.8(2)	N(25)-Co(2)-O(1w)	176.2(2)
N(21)-Co(2)-O(2w)	174.3(2)	N(23)-Co(2)-O(2w)	87.8(2)
N(25)-Co(2)-O(2w)	94.3(2)	O(1w)-Co(2)-O(2w)	82.0(1)
N(21)-Co(2)-O(12n)	87.5(2)	N(25)-Co(2)-O(12n)	88.1(2)
O(1w)-Co(2)-O(12n)	92.9(2)	O(2w)-Co(2)-O(12n)	92.5(1)
Co(1)-O(1w)-Co(2)	95.9(2)	Co(1)-O(2w)-Co(2)	95.2(2)
Co(1)-O(11n)-N(1n)	128.0(3)	Co(2)-O(12n)-N(1n)	126.4(3)
Co(1)-N(11)-C(11)	118.9(4)	C(1)-N(13)-C(13)	119.3(4)
Co(1)-N(15)-C(15)	118.4(4)	Co(2)-N(21)-C(21)	117.7(4)
Co(2)-N(23)-C(23)	119.4(3)	Co(2)-N(25)-C(25)	118.0(3)

In addition, potentiometric measurements (25 °C, 0.1 mol dm^{-3} KNO_3) were used to investigate the acidity constants of complex **1**. Since, the interconversion **1a** $\rightleftharpoons$ **1b** was too rapid to establish a reliable set of individual pK_a values for the two isomeric forms, only an average of the individual, microscopic acidity constants could be evaluated. Again, pK_1 was too low for an accurate determination by the pH method ($\leqslant 2$). The overall values $pK_2 = 4.05(2)$ and $pK_3 = 6.68(2)$ (Table 1) are in good agreement with the microscopic acidity constants obtained from the NMR experiment if one considers the different media (H_2O, 0.1 mol dm^{-3} KNO_3 *vs.* D_2O, no inert electrolyte).[19]

It is well known that the co-ordinated water molecules of $[Co(tach)(H_2O)_3]^{3+}$ also become deprotonated in neutral and alkaline aqueous solution.[15] The corresponding values $pK_1 = 5.45$, $pK_2 = 7.65$ and $pK_3 = 9.80$ (0.1 mol dm^{-3} KNO_3, 20 °C) are, however, considerably higher compared with the pK_a values of the inositol complex. Furthermore, these hydroxo complexes have a pronounced tendency to form hydroxo-bridged dimers. Hence, the complete reaction scheme includes a total of 15 species (Scheme 2): (*i*) the inositol complexes $[Co(tach)(H_{-x}ino)]^{3-x}$, $0 \leqslant x \leqslant 3$, each of the four macrospecies consisting of two isomeric microspecies **a** and **b**; (*ii*) four different species of the aquacomplex $[Co(tach)(H_2O)_3]^{3+}$ and its deprotonated forms $[Co(tach)(H_2O)_{3-x}(OH)_x]^{3-x}$; (*iii*) free *cis*-inositol; and (*iv*) the dinuclear complexes $[Co_2(tach)_2(H_2O)_{6-2x}(\mu\text{-}OH)_x]^{6-x}$, $x = 2$ or 3. The species distribution in solutions of **1** can be calculated using the equilibrium constants from ref. 15 and from the present work. For such a solution with a total Co concentration of 0.05 mol dm^{-3}, the dinuclear $[Co_2(tach)_2(OH)_3]^{3+}$ has a maximum abundance of about 10% at pH 4.5. At higher pH the formation of dinuclear complexes is not significant. This result is in agreement with the complete absence of *cis*-inositol as observed in the NMR spectra of slightly alkaline complex solutions.

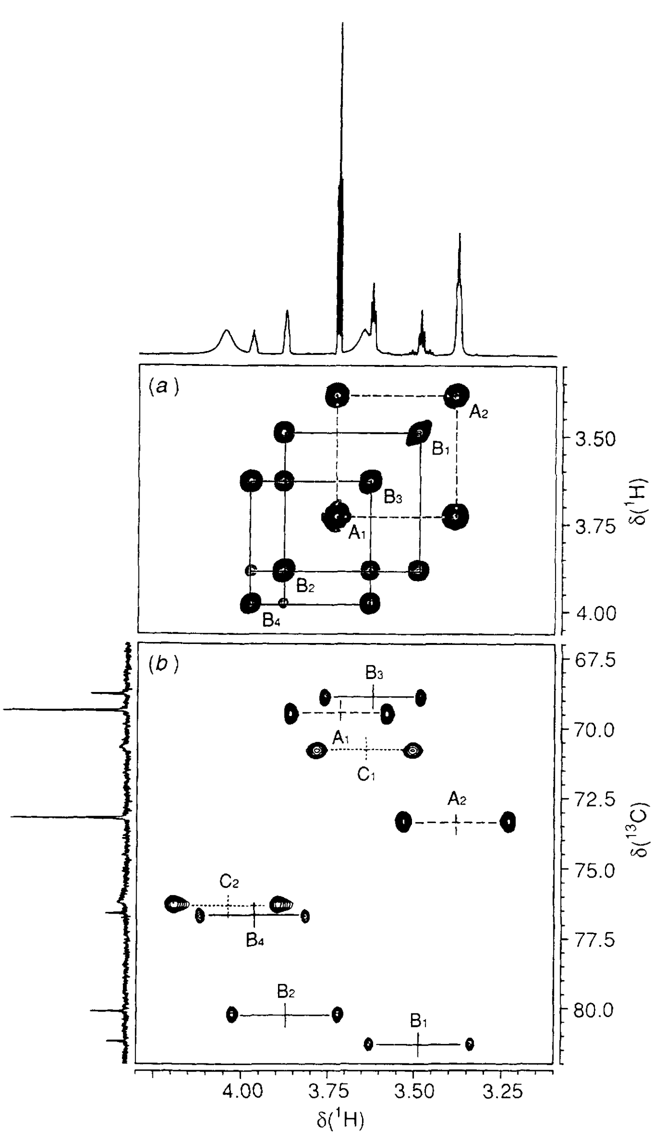


Fig. 5 Section of the ^1H COSY (*a*) and of the ^{13}C–^1H HMQC spectrum (*b*) of complex **1** (D_2O, pD 5.5, no ^{13}C decoupling during acquisition). Details as in Fig. 4

The systematic collection of NMR spectra at intervals of time allowed the investigation of equilibria and kinetics of the reactions (1) and (2) (Figs. 7 and 8). Both reactions produce

$$[Co(tach)(H_{-x}ino)]_a^{3-x} \rightleftharpoons [Co(tach)(H_{-y}ino)]_b^{3-y} + (y-x)H^+ \quad (1)$$

$$[Co(tach)(H_{-x}ino)]^{3-x} + 3H_2O \rightleftharpoons [Co(tach)(H_2O)_y(OH)_{3-y}]^{y+} + (3-y-x)H^+ + ino \quad (2)$$

products, **1b**, $[Co(tach)(H_2O)_3]^{3+}$, which have a different acidity compared with the starting complex **1a**. Consequently the pD increased slightly during the reaction (Fig. 4). An additional buffer for pD adjustment was not used because a possible interaction between the buffer and the $Co(tach)^{3+}$ moiety must be considered. However, the variable pD during the reaction as well as the different degree of protonation, associated with each of the two components **1a** and **1b** in the equilibrium, complicated the analysis of the two reactions. The equilibria were therefore evaluated by using the conditional stability constants[31] $K'(1) = \{\Sigma_i[Co(tach)(H_{-i}ino)]_a\}$-

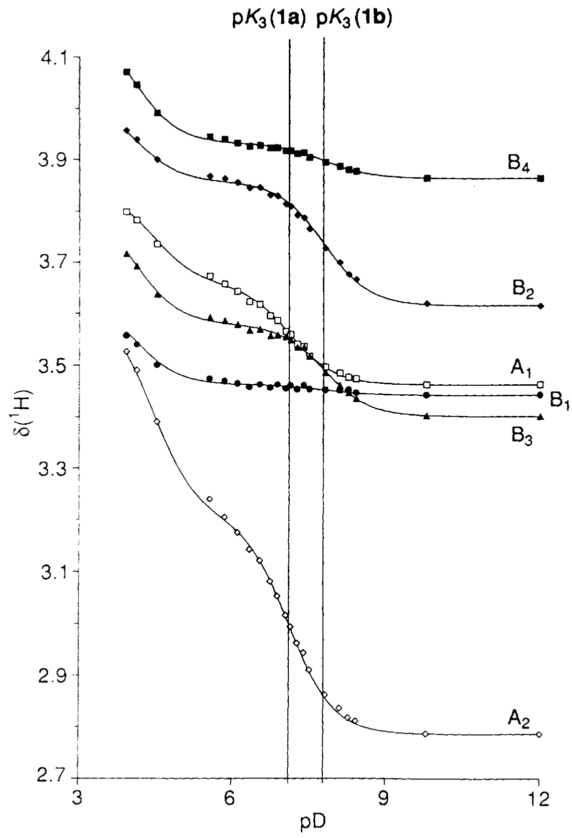


Fig. 6 Chemical shifts of the ring protons of *cis*-inositol in complexes **1a** and **1b** as a function of pD. The points represent experimental values; the lines were calculated from the evaluated data in Table 2. Details as in Fig. 4

Table 9 Conditional equilibrium constants and half-lives for the isomerization and ligand dissociation of complex **1**, in D_2O at 25 °C

pD	$K'(1)$	$-\log K'(2)$	t(**1a**)/min	t(**1b**)/min	t(ino)/min
3.9	2.1	2.1	33	100	350
4.5	1.8	2.4			
6.4	1.4	2.9			
7.3	2.6	4.3			
8.5	5.8	> 5	50	50	—
9.8	5.8	> 5			
12.0	5.8	> 5	< 1	< 1	—

$\{\Sigma_i[\mathrm{Co(tach)(H_{-i}ino)}]_b\}^{-1}$ and $K'(2) = \{\Sigma_{i,m}[\mathrm{Co(tach)(H_{-i}\text{-}ino)}_m]\}\ \{\Sigma_j[\mathrm{Co(tach)(H_2O)}_j\mathrm{(OH)}_{3-j}]\}^{-1}[\mathrm{ino}]^{-1}$ (m = **a** or **b**) and the kinetics was characterized by the corresponding half-lives t(**1a**), t(**1b**) and t(ino) rather than by rate constants (Table 9).

The reactivity of complex **1** in aqueous solution can be summarized as follows. (*i*) In equilibrated complex solutions, isomer **a** predominates over **b** in the entire pH range investigated (Fig. 7). However, a characteristic pH dependence is observed in the range where the co-ordinated hydroxyl groups become deprotonated: the amount of isomer **1b** increased from 30 (pD $\leqslant$ 4) to 41 ($\approx$6.4) then decreased to 15% ($\geqslant$8.5). On the other hand, no pD dependence was observed above pD 9.

(*ii*) A similar pD dependence was observed for the ligand-dissociation reaction (Table 9). Equilibrated complex solution contained up to 30% of free inositol at low pD. However, in neutral or alkaline solutions no decay of $[\mathrm{Co(tach)(H_{-3}ino)}]$ was noted even after several weeks. Obviously, the amount of free inositol formed (if any) was too small for detection by NMR measurements.

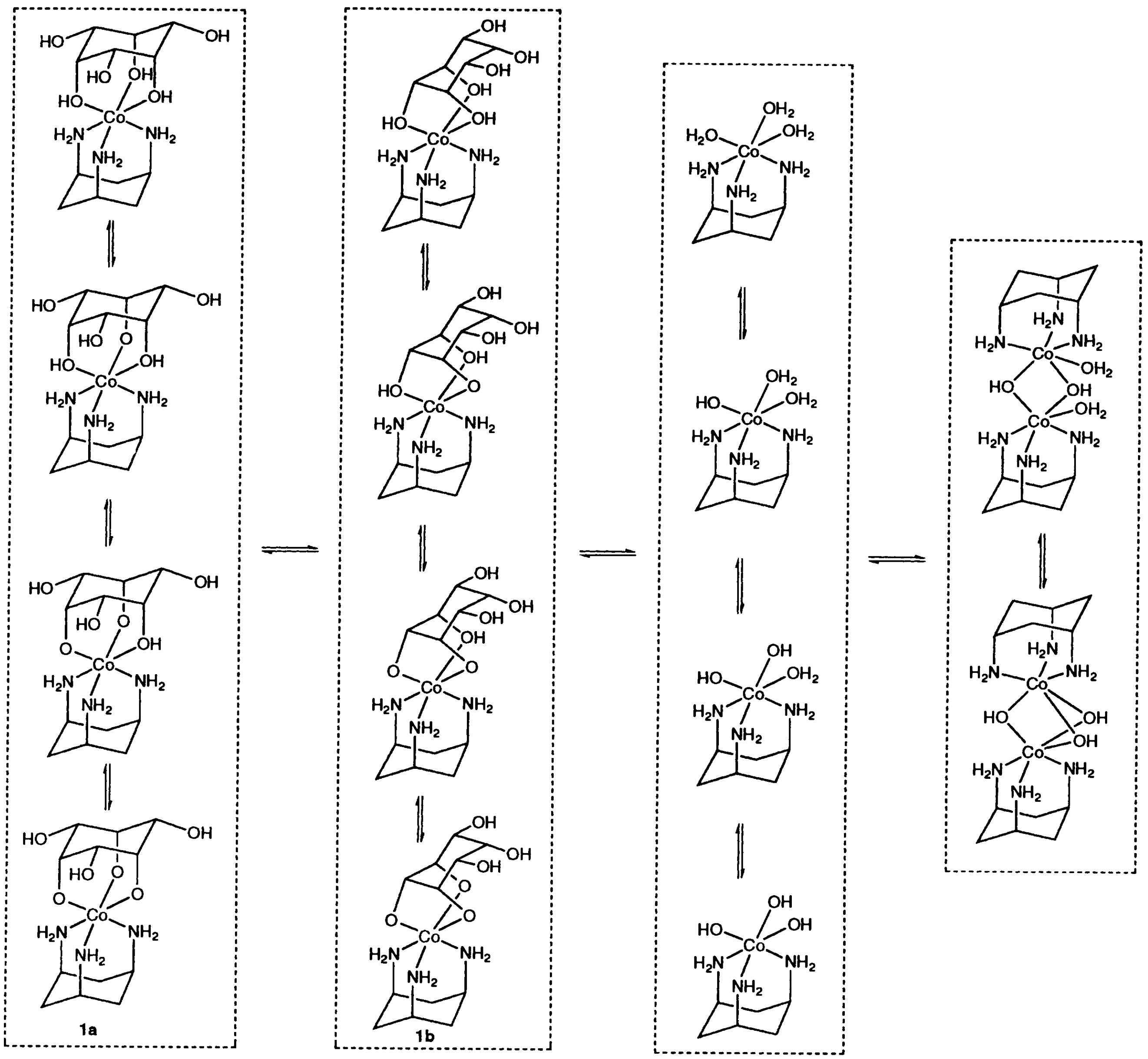
(*iii*) Starting from a solution containing exclusively complex **1a**, the isomerization reaction was considerably faster compared to the dissociation of inositol (Fig. 8). The rate of isomerization was only moderately dependent on pD in the range $3 < \mathrm{pD} < 9$ with a slight increase in rate with decreasing pD. However, the rate increased considerably at high pD. In fact, in solutions with pD > 11, the reaction was too fast to be followed by the NMR technique. Measurements (25 °C), carried out immediately after sample preparation, revealed already complete equilibria.

(*iv*) In strongly acidic solutions (pH < 3) a slow reduction of $\mathrm{Co^{III}}$ to $\mathrm{Co^{II}}$ was observed. Significant amounts of the paramagnetic $\mathrm{Co^{II}}$ were indicated after a period of several days by the disappearance of the signals in the NMR spectrum. Therefore, the determination of the final equilibrium concentrations of isomers **1a**, **1b** and of free *cis*-inositol was not possible in such solutions.

Molecular Mechanics Calculations.—The difference in energy between the two isomers **1a** and **1b** was elucidated by analysing steric strain in the various chelate rings and van der Waals repulsion between hydrogen atoms attached to the co-ordinated donor atoms. We recently reported such results for the $[\mathrm{M(ino)}]^{z+}$ and $[\mathrm{M(ino)(H_2O)_3}]^{z+}$ complexes as a function of the ionic radius of the metal ion M^{z+}. The study revealed a clear preference of small metal ions (r_M < 0.85 Å) for the three axial hydroxyl groups of *cis*-inositol, whereas large metal ions co-ordinate preferably to three adjacent hydroxyl groups in an axial–equatorial–axial arrangement.[20] This result is a consequence of the different types of chelate rings formed in each of the two co-ordination modes. The former co-ordination mode implies the exclusive formation of six-membered chelate rings with a chair conformation (adamantane-type structure). In the latter, two five- and one six-membered chelate ring are formed. It is well known that the formation of five-membered chelate rings is favoured by large metal ions, while six-membered chelate rings are favourable for small metal ions.[32] In this previous study it was also shown that for small metal ions the co-ordination of an additional ligand leads to severe steric strain due to mutual van der Waals repulsions between adjacent donor groups.[20] However, the present calculations revealed that the van der Waals repulsions between the three amino groups of tach and the three hydroxyl groups of *cis*-inositol occur to a significantly lesser extent in the complex where $\mathrm{Co(tach)^{3+}}$ is bound to an axial–equatorial–axial site of *cis*-inositol (isomer **1b**) compared to the complex where it is bound to the three axial hydroxyl groups (isomer **1a**). Subsequent deprotonation of the co-ordinated hydroxyl groups reduces these $\mathrm{NH_2}$–HO repulsions and consequently the triaxial mode (complex **1a**) is more stabilized in the completely deprotonated form. The following strain energies (kJ $\mathrm{mol^{-1}}$) were calculated: $[\mathrm{Co(tach)(ino)}]^{3+}$, 28.8 for isomer **1a**, 30.3 for isomer **1b**; $[\mathrm{Co(tach)(H_{-3}ino)}]$, −1.0 for **1a**, 3.1 for isomer **1b**. For the isomerization reaction $\Delta H \approx \Delta G$ is reasonable, and according to these calculations 36% of isomer **1b** is to be expected in acidic solutions, decreasing to 16% in alkaline solution (pH > 8) where the co-ordinated hydroxyl groups are completely deprotonated. It is noteworthy that these values are in excellent agreement with the observed species distribution obtained from NMR measurements of the equilibrated sample solutions (Fig. 7).

Discussion

Applicability of the Method.—The $\mathrm{Co^{III}(tach)^{3+}}$ unit was tested as a probe for elucidating interactions between metal ions and a polyalcohol L. Our results clearly demonstrate the advantages, but also possible complications, of this method. (*i*) Complexes of the composition $[\mathrm{Co(tach)L}]^{3+}$ can readily be prepared and can be isolated as crystalline solids. (*ii*) The



Scheme 2 Reactions and corresponding species in aqueous solutions of complex **1**. Species of the same isomer which differ in their degree of protonation are enclosed by dashed boxes

$Co^{III}(tach)^{3+}$ entity behaves as a stable and completely inert unit. The dissociation of tach from Co^{III} has never been observed in our experiments. (*iii*) The $Co^{III}(tach)^{3+}$ unit is restricted to a facial co-ordination of three donor groups of the ligand L, promoting the formation of mononuclear species $[Co(tach)L]^{3+}$. This is of importance, since a large number of different types of interactions should be avoided. Otherwise, an unambiguous identification of the species and their various reactions may not be possible. (*iv*) The complexes are diamagnetic and therefore suitable for NMR studies. Their structure and reactivity in aqueous solution can thus easily be investigated. Kinetics and equilibria of isomerization reactions as well as the dissociation of the polyalcohol can be monitored directly. The individual acidity of co-ordinated hydroxyl groups can be elucidated by analysing chemical shifts as a function of pD.

On the other hand, this method is limited due to two types of possible side reactions. (*i*) As is well known, the $Co^{III}(tach)^{3+}$ unit has a high tendency to form hydroxo-bridged dimers.[15,16] Even a low concentration of water in the methanolic solution of the solvate $[Co(tach)(MeOH)_3]^{3+}$ is sufficient for the formation of such species. Since the polyols do not represent a class of high-affinity ligands for Co^{III}, the formation of these dimers competes with the binding of the polyol. Once formed, the co-ordination of the polyol is no longer possible. (*ii*) The reduction of Co^{III} to Co^{II} results in the formation of labile, paramagnetic complexes. The required inertness of the Co(tach) unit is no longer ensured, and the formation of a variety of complexes like $[Co(tach)_2]^{2+}$, $[Co(tach)L]^{2+}$ and $[CoL_2]^{2+}$ must be considered.

In fact the formation of compounds **2** and **3** as well as the reductive decomposition of **1** in acidic aqueous solutions are illustrative examples for such side reactions. It is interesting that $[Co(tach)(ino)]^{3+}$ could be prepared without difficulty, whereas $[Co(tach)(taino)]^{3+}$ could not. Since the two ligands are structurally closely related an explanation for the observed difference is not apparent.

Structure and Stability of $[Co(tach)(ino)]^{3+}$.—We have shown here that the enhanced donor ability of the alkoxo group, compared to the hydroxyl group, gives rise to a dramatic increase in complex stability. This effect is clearly expressed in the structure of $[Co(tach)(H_{-1}ino)]^{2+}$ and has also been confirmed by thermodynamic data. Beside the electrostatic,

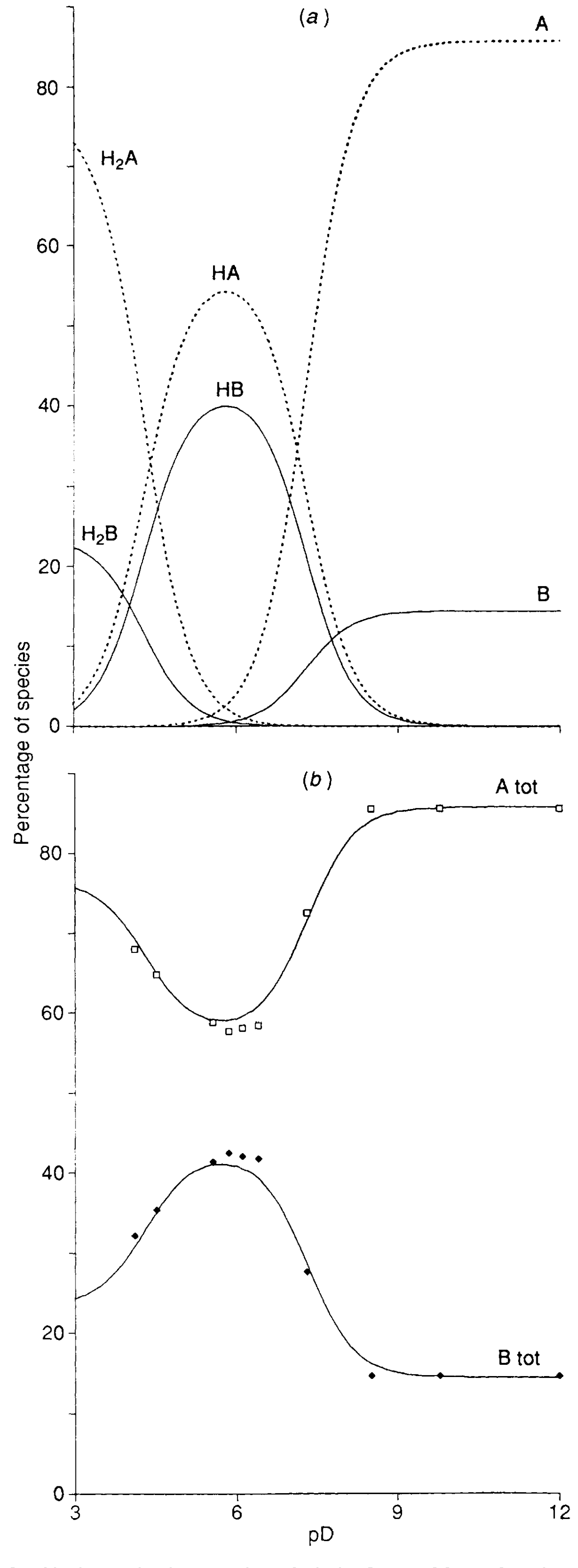


Fig. 7 The isomerisation reaction of **1** in D_2O at 25 °C as a function of pD. (*a*) Calculated distribution of the inositol complexes using the individual microscopic pK_a values (Table 2) and a value of 5.8 for the completely deprotonated $[\mathrm{Co(tach)(H_{-3}ino)}]_a$ A and $[\mathrm{Co(tach)(H_{-3}ino)}]_b$ B. The partially protonated isomers are indicated as HA and HB for $[\mathrm{Co(tach)(H_{-2}ino)}]^+$ and H_2A and H_2B for $[\mathrm{Co(tach)(H_{-1}ino)}]^{2+}$. (*b*) Total amounts $\Sigma_i[\mathrm{Co(tach)(H_{-i}ino)}]_a$ and $\Sigma_i[\mathrm{Co(tach)(H_{-i}ino)}]_b$ as a function of pD. The squares represent experimental points from integration of ^1H NMR signals; the lines were obtained from the accumulation of the calculated concentrations shown in (*a*)

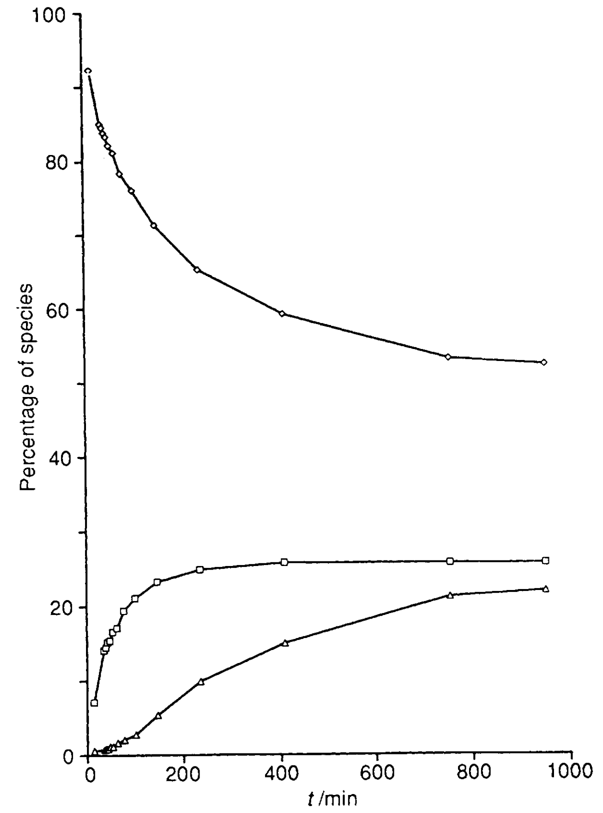


Fig. 8 Species distribution in a solution of complex **1** in D_2O as a function of time, $\mathrm{pD_{start}} = 3.8$, $\mathrm{pD_{end}} = 4.1$. The amount of each species was determined by integration of the corresponding ^1H NMR signals: (◇) **1a**; (□) **1b**; (△) ino

$(\mathrm{Co^{III}{-}O^{-II}H^{I}{-}C} \longrightarrow \mathrm{Co^{III}{-}O^{-II}{-}C})$, the electronic properties of the Co–O bonds as well as steric strain in the ligand sphere also contribute to this effect. The electronic contribution is expressed by the enhanced *trans* influence of the alkoxide ligand. We explain this effect by a partial release of electron density from the deprotonated oxygen donor by a p–d π-type bonding. In addition, the molecular mechanics calculations indicate significant van der Waals repulsion between adjacent hydrogen atoms of the OH and NH_2 donor groups, resulting in a destabilization of the complex in its protonated form. Thus, the strain energy within the ligand as well as van der Waals repulsion between the donor groups in the ligand sphere were recognized to be the basic parameters determining the abundance of different isomers in equilibrated complex solutions. It is interesting that the microscopic acidity constants of the two isomers on the one hand and the overall ratio $\Sigma_i[\mathrm{Co(tach)(H_{-i}ino)}]_a : \Sigma_i[\mathrm{Co(tach)(H_{-i}ino)}]_b$ $[= K'(1)]$ on the other are clearly related. The minimum of $K'(1)$ at about pD 6 indicates a particular stabilization of isomer **1b** at this pH (Fig. 7, Table 9). We interpret this in terms of hydrogen bonding between a hydroxyl group and an alkoxo group in a 1,3-diaxial arrangement. Strong hydrogen bonding for such a geometry is well established in cyclic polyols.[25,33] As a consequence, the abstraction of the third proton from isomer **1a** requires less energy than that from **1b**, since the proton in **1a** is obviously not involved in such a type of interaction. This effect is nicely expressed in the large difference $\mathrm{p}K_3(\mathbf{1b}) - \mathrm{p}K_3(\mathbf{1a}) = 0.64$. Exactly the reverse order has been observed for $\mathrm{p}K_2$, -0.38. Consequently $K'(1)$ increases with decreasing pD in the range $6 \geqslant \mathrm{pD} \geqslant 3$. Using $K'(1) = 5.8$ (pD > 10), observed for the completely deprotonated $[\mathrm{Co(tach)(H_{-3}ino)}]$, as starting value and the individual microscopic acidity constants, the concentrations of the partially protonated forms of **1a** and **1b**, and thus the pD dependence of $K'(1)$ can be calculated. As can be seen in Fig. 7, these calculations are in excellent agreement with the experimental values obtained from integration of ^1H NMR signals.

It is noteworthy that, compared to the co-ordinated water molecules of $[Co(tach)(H_2O)_3]^{3+}$, the acidity of the co-ordinated hydroxyl groups of $[Co(tach)(ino)]^{3+}$ is enhanced by a factor of about 10^3–10^4. Such an enhancement is generally observed for protic chelate complexes relative to their monodentate analogues. It has been explained by an inductive effect of the additional electron-withdrawing hydroxyl groups and a diminution of the effective relative permittivity in the co-ordination sphere.[34] In fact, the acid dissociation constants of the free polyols are also significantly increased relative to water [*cis*-inositol, $pK_a = 12.7$; sorbitol (D-glucitol),[35] $pK_a = 13.6$; glucose,[36] $pK_a = 12.3$].

The substantial increase in stability of the complex, caused by subsequent deprotonation of the co-ordinated hydroxyl groups, is expressed by a decreasing tendency of the polyol to dissociate from the complex, and by the reductive decomposition at low pH. In fact, both reactions, the reduction of Co^{III} to Co^{II} as well as the elimination of *cis*-inositol, were only observed below pH 7.5. Thus, the present study clearly confirms that, in contrast to a neutral polyol, a deprotonated polyalcoholate ligand is a powerful sequestering agent for metal ions in aqueous solution. This conclusion can be illustrated by the consideration of the equilibria (3) and (4) with $K_3/K_4 > 10^{10}$. The enhanced ability

$$[Co(tach)(ino)]^{3+} + 3H_2O \overset{K_3}{\rightleftharpoons} [Co(tach)(H_2O)_3]^{3+} + ino \quad (3)$$

$$[Co(tach)(H_{-3}ino)] + 3H_2O \overset{K_4}{\rightleftharpoons} [Co(tach)(OH)_3] + ino \quad (4)$$

of a deprotonated polyol to co-ordinate a metal ion is therefore a consequence of the increased acidity of the polyol ligand. It should be noted that the co-ordinated polyol is triply deprotonated above pH 7.5, whereas the corresponding hydroxo complex $[Co(tach)(OH)_3]$ is only formed in strongly alkaline solution (pH > 10.5).

Reactivity of $[Co(tach)(ino)]^{3+}$: *Kinetics and Mechanism.*— The kinetics of the isomerization $\mathbf{1a} \rightleftharpoons \mathbf{1b}$ and of the ligand dissociation were monitored by NMR spectroscopy. These measurements show two important results: (*i*) the rate of the isomerization is dependent on pH; however, the dependence of the reaction rate is non-linear and not even monotonic; (*ii*) the isomerization is considerably faster than the ligand dissociation.

Regarding the substitution of a co-ordinated polyol, one would expect that a hydroxyl group is a better leaving group than the corresponding alkoxo group. Accordingly, it has been reported that the hydrolysis of $[Co(NH_3)_5(MeOH)]^{3+}$ showed an increase in rate with decreasing pH and the substitution of the methoxide ligand has been found to be slow.[37] This observation is in good agreement with the result found for pH < 8 in the present study. On the other hand, an acceleration of the ligand substitution with increasing pH, as observed for pH > 10, is well understandable, too. The so-called base catalysis has been discussed at length on the basis of the deprotonation of a co-ordinated amine in a rapid preequilibrium (D CB mechanism).[38] At high pH, the facilitated release of the hydroxyl group is therefore overcompensated by the acceleration due to base catalysis. The enhanced rate of the isomerization reaction compared to the elimination of *cis*-inositol obviously indicates that *cis*-inositol remains co-ordinated through at least one donor atom during the isomerization.

Conclusion

The present investigation demonstrates some fundamental aspects relevant to an improved understanding of interactions between polyalcohols and metal cations. These types of interactions are indeed relatively weak, as long as the metal ion is exclusively bound to the hydroxyl groups of the polyalcohol. However, as soon as co-ordination proceeds with deprotonation, polyols are powerful chelators for metal ions. In this context, the enhanced acidity of the alcoholic hydroxyl group ($pK_{H_2O} - pK_{polyol} \approx 2$–$4$) is of great importance. Considering the pK_a values of trivalent aqua ions[39] like Fe^{3+} (2.2), Al^{3+} (5.0), Cr^{3+} (4.0) and Ga^{3+} (2.6) one realizes that the complexes of these ions with a polyol react as strong acids in aqueous solution. The co-ordinated polyols are deprotonated even at acidic pH values. This is to a lesser extent also true for divalent metal ions like Cu^{2+}, Zn^{2+} and even Mg^{2+} with pK_a values of 8.0, 9.0 and 11.4, respectively.[39] With respect to biological systems, we note that polyols co-ordinate acidic metal ions in the form of a strongly binding polyalkoxide at physiological pH and may well play an important role, *e.g.* in preventing hydrolytic polymerization of such ions.

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