

1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol, a New Ligand with a Remarkable Versatility for Metal Ions. 3. Preparation and Characterization of the Aluminum(III), Gallium(III), and Thallium(III) Complexes

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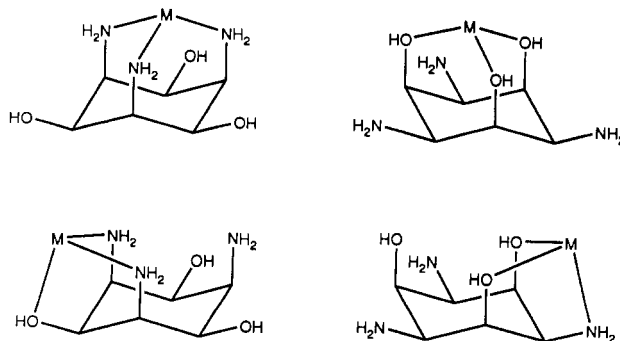
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Solid compounds containing the complexes $\text{Al}(\text{taci})_2^{3+}$, $\text{Ga}(\text{taci})_2^{3+}$, and $\text{Tl}(\text{taci})_2^{3+}$ ($\text{taci} = 1,3,5\text{-triamino-1,3,5-trideoxy-}cis\text{-inositol} = \text{C}_6\text{H}_{15}\text{N}_3\text{O}_3$) have been prepared by combining methanolic solutions of taci and of appropriate metal salts. Single-crystal X-ray analysis revealed an AlO_6 , GaN_3O_3 , and TlN_6 coordination sphere for $\text{Al}(\text{taci})_2\text{Br}_3 \cdot 7\text{H}_2\text{O}$: monoclinic, space group $C2/c$, $Z = 4$, $a = 9.413(1) \text{ \AA}$, $b = 14.560(2) \text{ \AA}$, $c = 20.264(4) \text{ \AA}$, $\beta = 93.36(1)^\circ$; $\text{Ga}(\text{taci})_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$: triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.270(1) \text{ \AA}$, $b = 9.795(1) \text{ \AA}$, $c = 13.524(1) \text{ \AA}$, $\alpha = 92.83(1)^\circ$, $\beta = 88.46(1)^\circ$, $\gamma = 94.15(1)^\circ$; $\text{Tl}(\text{taci})_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$: monoclinic, space group $C2/c$, $Z = 4$, $a = 23.497(12) \text{ \AA}$, $b = 8.811(4) \text{ \AA}$, $c = 14.942(8) \text{ \AA}$, $\beta = 128.82(3)^\circ$. The binding of $\text{Al}(\text{III})$ and $\text{Ga}(\text{III})$ to the hydroxyl groups of taci resulted in an internal proton transfer: $(\text{H}_2\text{N-})_3(\text{C}_6\text{H}_6)(-\text{OH})_3 + \text{M} \rightarrow (\text{H}_3\text{N-})_3(\text{C}_6\text{H}_6)(-\text{O-})_3\text{M}$. The same structures have also been observed in aqueous solution. NMR measurements in D_2O revealed $\text{Al}(\text{taci})_2^{3+}$ and $\text{Ga}(\text{taci})_2^{3+}$ as the major components at pH 7. Hydrolytic polymerization of $\text{Ga}(\text{taci})_2^{3+}$ and $\text{Tl}(\text{taci})_2^{3+}$ was indicated by an increase of the signals of the free ligand in the NMR spectra and the appearance of solid hydrolysis products in slightly acidic solutions ($\text{pH} \leq 4$). Significant hydrolysis of the $\text{Al}(\text{III})$ complex was only observed at temperatures $\geq 80^\circ\text{C}$ after several hours. The hydrolysis of the $\text{Al}(\text{III})$ and $\text{Ga}(\text{III})$ complexes at 25°C was sufficiently slow to investigate a preequilibrium of exclusively mononuclear species. The formation constants $\beta_2 = [\text{M}(\text{taci})_2][\text{M}]^{-1}[\text{taci}]^{-2}$ ($\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$) were determined by acidimetric titrations ($\text{M}(\text{taci})_2^{3+} + 6\text{H}^+ \rightarrow \text{M}^{3+} + 2\text{H}_3(\text{taci})^{3+}$) as well as by alkalimetric titrations ($\text{M}(\text{taci})_2^{3+} + 4\text{OH}^- \rightarrow \text{M}(\text{OH})_4^- + 2\text{taci}$). The two independent methods gave identical values for β_2 within significance. The formation constants $\beta_1 = [\text{M}(\text{taci})][\text{M}]^{-1}[\text{taci}]^{-1}$, and a set of $\text{p}K_i$ values, $\text{p}K_i = [\text{H}_{i-1}\text{M}(\text{taci})_2][\text{H}][\text{H}_{i-1}\text{M}(\text{taci})_2]^{-1}$, where $1 \leq i \leq 4$ and $\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$, were also evaluated. Al^{3+} (25°C , 0.1 M KCl): $\log \beta_1 = 11.8(1)$, $\log \beta_2 = 18.8(1)$, $\text{p}K_1 = 8.1(1)$, $\text{p}K_2 = 8.9(1)$. Ga^{3+} (25°C , 0.1 M KNO_3): $\log \beta_1 = 16.5(1)$, $\log \beta_2 = 25.7(1)$, $\text{p}K_1 = 7.4(1)$, $\text{p}K_2 = 8.7(1)$. The hydrolysis of $\text{Tl}(\text{taci})_2^{3+}$ had already occurred at 25°C to a significant extent in freshly prepared solutions. In addition a slow aging was observed over a period of several weeks. $\text{H}_2\text{M}(\text{taci})_2^+$ was the dominant species in the FAB MS of the Al and Ga complex. The Tl complex was partially reduced in the glycerol matrix, as indicated by the observation of Tl^+ , $\text{Tl}(\text{glycerol})^+$, and $\text{Tl}(\text{taci})^+$.

Introduction

1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (taci) and some N -alkylated derivatives have been investigated in our laboratory as a new class of tridentate ligands.²⁻⁷ The hexamethylated 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci) proved to be a powerful chelator for $\text{Fe}(\text{III})$ ⁶ and thus of interest with respect to its possible application in the treatment of iron overload.⁷ *In vitro* experiments demonstrated that tdci dissolved solid $\beta\text{-FeOOH}$ more rapidly than desferrioxamine B.⁸ Therefore, we were encouraged to investigate the ability of these ligands to form complexes with Al^{3+} and to solubilize the deposits of hydroxy-aluminum silicates associated with the brain lesions of patients suffering from Alzheimer's disease.⁹

Chart I



The coordination behavior of the IIIb group elements in the trivalent state is basically a consequence of the increase in softness and ionic radius in the order $\text{Al}, \text{Ga}, \text{In}, \text{Tl}$. Since taci provides four different metal binding sites with variable softness and size (Chart I), it is interesting to identify the sites as selected by each

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Table I. Potentiometric Data (25 °C, 0.1 M KCl) and Evaluated Equilibrium Constants of Al(III)-*taci* Complexes with Estimated Standard Deviations^a in Parentheses

[Al] _{tot} , mol dm ⁻¹	5 × 10 ⁻⁴	10 ⁻³	10 ⁻³	2 × 10 ⁻³	10 ⁻³	
titrant; [titrant], mol dm ⁻¹	HCl; 0.1	HCl; 0.1	HCl; 0.1	HCl; 0.1	KOH; 0.1	
type of titration	continuous	continuous	batch	continuous	continuous	
evaluated range ^b	0–2.65	0–2.65	0.25–2.785	0–2.65	0–2.25	
no. of data points	38	36	21	36	46	
meas time per point, min	60	60	3000	60	3–15	
log β _{ML} ^c	11.73(3)	11.799(5)	11.73(4)	11.78(1)	11.8 ^d	average 11.8(1)
log β _{ML₂} ^c	18.79(6)	18.860(8)	18.81(7)	18.74(1)	18.765(7)	18.8(1)
log β _{HML} ^c	25.26(9)	25.29(1)	25.26(8)	25.22(1)	25.3 ^d	25.3(1)
log β _{H₁ML} ^c	10.78(15)	10.87(2)	10.7 ^d	10.68(2)	10.527(6)	pK ₁ = 8.1(1) ^e
log β _{H₂ML} ^c					1.632(9)	pK ₂ = 8.9(1) ^e
log β _{H₃ML} ^c					-7.452(8)	pK ₃ = 9.1(1) ^e
log β _{H₄ML} ^c					-17.16(1)	pK ₄ = 9.7(1) ^e
log β _{M(OH)} ^f	-5.0 ^d	-5.0 ^d	-5.0 ^d	-5.0 ^d		
log β _{M(OH)₂} ^f					-23.75 ^d	
σ _{pH} ^g	0.0152	0.0048	0.0147	0.0074	0.0018	

^a From SUPERQUAD. ^b Moles of titrant per moles of *taci*. ^c β_{H_xM_yL_z} = [H_xAl_y(*taci*)_z][Al]^{-y}[H]^{-x}[*taci*]^{-z}. ^d Used as fixed value, not refined. ^e pK_i = -log K_i, K_i = [H_i-Al(*taci*)₂][H][H_{1-i}-Al(*taci*)₂]⁻¹. ^f β_{M(OH)_x} = [Al(OH)_x][H]^x[Al]⁻¹; values from refs 16 and 18. ^g Definition of σ_{pH}; see ref 37.

Table II. Potentiometric Data (25 °C, I = 0.1) and Evaluated Equilibrium Constants of Ga(III)-*taci* Complexes with Estimated Standard Deviations^a in Parentheses

[Ga] _{tot} , mol dm ⁻¹	5 × 10 ⁻⁴ ^b	10 ⁻³ ^b	10 ⁻³ ^c	2 × 10 ⁻³ ^b	10 ⁻³ ^b	
titrant; [titrant], mol dm ⁻¹	HNO ₃ ; 0.1	HNO ₃ ; 0.1	HCl; 0.1	HNO ₃ ; 0.1	KOH; 0.1 M	
inert electrolyte	KNO ₃	KNO ₃	KCl	KNO ₃	KNO ₃	
type of titration	continuous	continuous	continuous	continuous	continuous	
evaluated range ^d	0.0–3.0	0.0–3.0	-0.158 to 2.815	0.0–3.0	0–2.25	
no. of data points	40	40	61	40	80	
meas time per point, min	20	20	25	20	3–15	
log β _{ML} ^e	16.47(2)	16.59(1)	16.58(1)	16.48(1)	16.48 ^f	average 16.5(1)
log β _{ML₂} ^e	25.70(2)	25.71(1)	25.82(1)	25.72(1)	25.76(4)	25.7(1)
log β _{HML} ^e	19.54(3)	19.39(2)	19.49(2)	19.32(2)		19.4(2)
log β _{H₁ML} ^e			10.4(1)			doubtful
log β _{H₂ML} ^e	18.3 ^f	18.3 ^f	18.35(3)	18.3 ^f	18.33(4)	pK ₁ = 7.4(1) ^g
log β _{H₃ML} ^e					9.62(5)	pK ₂ = 8.7(1) ^g
log β _{H₄ML} ^e					0.15(5)	pK ₃ = 9.5(1) ^g
log β _{H₅ML} ^e					-9.38(5)	pK ₄ = 9.5(1) ^g
log β _{M(OH)} ^h	-2.91 ^f	-2.91 ^f	-2.91 ^f	-2.91 ^f	-21.02(6)	pK ₅ = 11.6(1) ^g
log β _{M(OH)₂} ^h	-16.78 ^f	-16.78 ^f	-16.78 ^f	-16.78 ^f		
σ _{pH} ⁱ	0.0057	0.0044	0.0028	0.0062	0.0049	

^a From SUPERQUAD. ^b Ga(*taci*)₂(NO₃)₃. ^c Ga(*taci*)₂Cl₃. ^d Moles of titrant per moles of *taci*. ^e β_{H_xM_yL_z} = [H_xGa_y(*taci*)_z][Ga]^{-y}[H]^{-x}[*taci*]^{-z}. ^f Used as fixed value, not refined. ^g pK_i = -log K_i, K_i = [H_i-Ga(*taci*)₂][H][H_{1-i}-Ga(*taci*)₂]⁻¹. ^h β_{M(OH)_x} = [Ga(OH)_x][H]^x[Ga]⁻¹; values from ref 17. ⁱ Definition of σ_{pH}; see ref 37.

of the four metal ions. Angyal demonstrated that *cis*-inositol preferably binds large cations with an ionic radius $r > 0.8 \text{ \AA}$ to an axial-equatorial-axial site whereas small cations ($r < 0.8 \text{ \AA}$) were selectively coordinated to the triaxial site.¹⁰ This phenomenon certainly reflects the different steric requirement of five membered and six membered chelate rings.¹¹ The comparison of a variety of open chain and macrocyclic ligands containing nitrogen donor atoms revealed a general preference of small metal ions for six membered rings and of large metal ions for five membered rings.¹² The M–N bond lengths and the N–M–N bond angles with minimum strain energy have been determined by a molecular mechanics calculation: 2.5 Å, 69° for five-membered and 1.6 Å, 109.5° for six-membered chelate rings.¹³

In accordance with Angyal's rule, an octahedral MN₆ coordination sphere has been observed for Ni(*taci*)₂²⁺ ($r_{\text{Ni(II)}} = 0.69 \text{ \AA}$), Cu(*taci*)₂²⁺ ($r_{\text{Cu(II)}} = 0.73 \text{ \AA}$), and Zn(*taci*)₂²⁺ ($r_{\text{Zn(II)}} = 0.74 \text{ \AA}$).⁴ Also the structure of the Cr(III) complex ($r_{\text{Cr(III)}} = 0.64 \text{ \AA}$), showing either an CrO₆ octahedron or a facial CrO₃N₃ coordination sphere, agrees with this postulate.³ It is quite clear that Al(III) should bind to the three hydroxyl groups of *taci*.

However, Tl(III) ($r_{\text{Tl(III)}} = 0.95 \text{ \AA}$) is too large for the soft N(1),N-(3),N(5) site and too soft for the rather hard N(1),O(2),N(3) or O(2),N(3),O(4) sites (Chart I). Therefore, the complexes of Ga(III) and Tl(III) have been included in the present investigation to obtain further information about the different types of metal-*taci* interactions as a function of the variable softness and size of the metal ion.

Experimental Section

Spectroscopy, Mass Spectrometry, and Analyses. ¹H and ¹³C NMR spectra were measured on a Bruker AC-200 spectrometer with δ (ppm) scale and sodium (trimethylsilyl)propionate-*d*₄ (=0 ppm) as internal standard. The FAB⁺-MS spectra were run on a VG ZAB VSEQ instrument. Test solutions were prepared by dissolving the samples in water and mixing the resulting solutions with a glycerol matrix prior to the introduction in the spectrometer. CHN analyses were performed by D. Manser, Laboratorium für Organische Chemie, ETH Zürich.

Preparation of the Complexes. *Taci* was prepared according to ref 5. AlCl₃ (anhydrous), AlBr₃ (anhydrous), Ga(NO₃)₃·3H₂O, GaCl₃ (anhydrous), and Tl(NO₃)₃·3H₂O were commercially available products from Fluka, Buchs, Switzerland. The complexes were prepared by the addition of 2 mmol of the metal nitrate, metal chloride, or metal bromide, respectively, dissolved in a suitable amount of CH₃OH (10–60 mL), to a solution of 4.1 mmol of *taci*, dissolved in 40 mL of CH₃OH. The addition was followed by an immediate precipitation of a white solid. In case of Al, the suspension was refluxed for 12 h; the Ga and Tl complexes were allowed to stand at room temperature for 24 h. The white solids

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were then filtered off and redissolved in a small amount of water (10–20 mL). Upon addition of 20–40 mL of EtOH, the desired complexes precipitated in high yields (60–90%). Single crystals were grown by slow diffusion of EtOH to the aqueous complex solutions. Anal. Calcd for $\text{Al}(\text{taci})_2\text{Cl}_3 \cdot \text{H}_2\text{O}$: C, 28.50; H, 6.38; N, 16.62. Found: C, 28.55; H, 6.69; N, 16.71. Calcd for $\text{Al}(\text{taci})_2\text{Br}_3 \cdot 7\text{H}_2\text{O}$: C, 19.29; H, 5.94; N, 11.25; Br, 32.08. Found: C, 19.30; H, 5.73; N, 11.01; Br, 32.37. Calcd for $\text{Ga}(\text{taci})_2\text{Cl}_3 \cdot 2.5\text{H}_2\text{O}$: C, 25.04; H, 6.13; N, 14.60; Ga, 12.11. Found: C, 25.08; H, 6.07; N, 14.78; Ga, 12.02. Calcd for $\text{Ga}(\text{taci})_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$: C, 21.70; H, 5.46; N, 18.98. Found: C, 21.98; H, 5.28; N, 18.98. Calcd for $\text{Tl}(\text{taci})_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$: C, 18.46; H, 4.39; N, 16.14. Found: C, 18.45; H, 4.37; N, 16.09.

Potentiometric Measurements. Acidimetric and alkalimetric titrations were carried out with an Orion 720 A pH/mV meter, a Philips GAH420 glass electrode, and an Ag/AgCl reference electrode, fitted with a salt bridge containing 0.1 M KNO_3 or 0.1 M KCl . The sample solutions were titrated with 0.1 M HNO_3 , 0.1 M HCl , or 0.1 M KOH , respectively, dispensed from a Metrohm 665 piston buret. The ionic strength was adjusted to 0.1 M by adding appropriate amounts of KNO_3 or KCl to the test solutions. The potential measurements were performed as described in ref 4 (see also Tables I and II). Batch titrations were carried out by adding appropriate amounts of the titrant to 21 individually sealed and thermostated sample solutions, allowing an equilibration time of 2–8 days.

Calculations of Equilibrium Constants. In this work, all constants are concentration quotients and pH is defined as $-\log[\text{H}^+]$. Consistent models were evaluated using the computer program SUPERQUAD.¹⁴ Final refinements were performed using the computer program BEST.¹⁵ Only the variables as indicated in Tables I and II were allowed to vary in the refinement (differences between BEST and SUPERQUAD were generally not significant). The pK values of H_3taci were taken from ref 4 (25 °C, 0.1 M KNO_3 , $\text{pK}_1 = 5.95$, $\text{pK}_2 = 7.40$, $\text{pK}_3 = 8.90$) or determined from alkalimetric titrations (25 °C, 0.1 M KCl , $\text{pK}_1 = 5.96$, $\text{pK}_2 = 7.42$, $\text{pK}_3 = 8.91$); $\text{pK}_w = 13.79$ was evaluated by several calibration titrations, the pK values of Al^{3+} (5.0) and Ga^{3+} (2.91) were those from refs 16 and 17. The formation constants $\log[M(\text{OH})_4] \cdot [\text{H}^+]^4 / [M]^{-1}$ of $\text{Ga}(\text{OH})_4^-$ (–16.78) and $\text{Al}(\text{OH})_4^-$ (–23.75) were taken from refs 17 and 18. The concentrations of the reactants corresponded to the values calculated from elemental analyses except for $[\text{Ga}(\text{taci})_2\text{X}_3]_p [\text{H}_{1-p}\text{Ga}(\text{taci})_2\text{X}_2]_{1-p} \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{NO}_3$), where n and p were determined by an optimal adjustment to the titration curve.

X-ray Diffraction Studies. The basic crystallographic data for $\text{Al}(\text{taci})_2\text{Br}_3 \cdot 7\text{H}_2\text{O}$, $\text{Ga}(\text{taci})_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, and $\text{Tl}(\text{taci})_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ are outlined in Table III. Data collection was performed on three different four-circle diffractometers (Table III), using monochromatized $\text{Mo K}\alpha$, or $\text{Cu K}\alpha$, radiation, respectively. No crystal decay was observed during the measurement. The data were corrected for Lorentz and polarization effects.

Al Complex. A numerical absorption correction was applied, based on eight indexed crystal faces. The structure was solved by the Patterson interpretation routine of SHELXS86¹⁹ and refined by full-matrix least-squares calculations using SHELX76.²⁰ The non-hydrogen atoms were refined with anisotropic displacement parameters, except O(W4) which was refined isotropically with an occupancy factor of 0.5. All hydrogen atoms could be localized in the difference fourier map. The H(–C) atoms were refined with variable isotropic displacement parameters, H(–N) and H(–O) were included in the refinement with the bond distances as found in the difference fourier map and with fixed isotropic displacement parameters of 0.04 Å² for H(–N) and 0.05 Å² for H(–O).

Ga Complex. An absorption correction was applied, based on azimuthal scans of six reflections with the diffractometer angle κ near 90°. The structure was solved by direct methods of SHELXS86¹⁹ and refined by

Table III. Crystallographic Data for $\text{Al}(\text{taci})_2\text{Br}_3 \cdot 7\text{H}_2\text{O}$, $\text{Ga}(\text{taci})_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tl}(\text{taci})_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$

	Al complex	Ga complex	Tl complex
chem formula	$\text{C}_{12}\text{H}_{44}\text{AlBr}_3\text{N}_6\text{O}_{13}$	$\text{C}_{12}\text{H}_{36}\text{N}_9\text{O}_{18}\text{Ga}$	$\text{C}_{12}\text{H}_{34}\text{N}_9\text{O}_{17}\text{Tl}$
fw	747.23	664.19	780.83
cryst size, mm	0.50×0.48 $\times 0.17$	0.50×0.40 $\times 0.27$	0.16×0.20 $\times 0.22$
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
crystal system	monoclinic	triclinic	monoclinic
<i>a</i> , Å	9.413(1)	9.270(1)	23.497(12)
<i>b</i> , Å	14.560(2)	9.795(1)	8.811(4)
<i>c</i> , Å	20.264(4)	13.524(1)	14.942(8)
α , deg	90.0	92.83(1)	90.0
β , deg	93.36(1)	88.46(1)	128.82(3)
γ , deg	90.0	94.15(1)	90.0
<i>V</i> , Å ³	2773(1)	1223.0(4)	2410(2)
<i>Z</i>	4	2	4
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Stoe STAD14
<i>T</i> , °C	21	21	21
λ , Å	0.710 73 (Mo $K\alpha$)	1.5418 (Cu $K\alpha$)	0.710 73 (Mo $K\alpha$)
ρ_{calcd} , g/cm ³	1.790	1.804	2.16
μ , cm ^{–1}	44.17	24.53	65.09
transm coeff	0.5074/ 0.1742	1.00/ 0.78	0.2270/ 0.1168
R_w^a , %	4.8	5.2	3.2
R_w^b , %	3.6	6.9	3.1

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}, \quad w = 1/\sigma^2(|F_o|).$$

full-matrix least-squares calculations using SHELX76.²⁰ All non-hydrogen atoms were refined with anisotropic displacement parameters. Here 26 of 30 hydrogen atoms of the $\text{Ga}(\text{taci})_2^{3+}$ molecule and all 6 hydrogen atoms of the water molecules were located in the difference Fourier map. The positions of four additional H(–N) atoms were calculated, and all 36 hydrogen atoms were included in the refinement with variable isotropic displacement parameters.

Tl Complex. An empirical absorption correction (Ψ -scan) was applied. The structure was solved by the Patterson interpretation routine of SHELXS86.¹⁹ The refinement was performed by full-matrix least-squares calculations of SHELX76.²⁰ All non hydrogen atoms were refined with anisotropic displacement parameters. The positions of 6 H(–C) and 6 H(–N) atoms were calculated (riding model) and included in the refinement with constant isotropic displacement parameters of 0.08 Å².

In all calculations, the atomic scattering factors from ref 22 (for Al, Ga, Tl) and from SHELX76²⁰ (for H, C, N, O, Br) were used. The atomic coordinates of the three complexes are listed in Table IV. A summary of bond distances and angles is presented in Tables V and VI.

Results and Discussion

Preparation of the Complexes. The pronounced tendency of Al^{3+} , Ga^{3+} , and Tl^{3+} to hydrolyze in aqueous solution is well established.^{16,17} To avoid competition with hydrolysis, methanol was used as solvent. The combination of methanolic solutions, containing the free ligand on the one hand and the metal as chloride, bromide or nitrate, respectively, on the other, resulted in the immediate precipitation of the complexes as white solids. Once formed, the complexes could be readily dissolved in water, yielding solutions free from solid hydrolysis products. The Tl(III) and Al(III) complexes were obtained as well-defined hydrates $\text{M}(\text{taci})_2\text{X}_3 \cdot n\text{H}_2\text{O}$. However the Ga(III) complex usually proved to be a mixture of the composition $[\text{Ga}(\text{taci})_2\text{X}_3]_p \cdot [\text{H}_{1-p}\text{Ga}(\text{taci})_2\text{X}_2]_{1-p}$ ($0 < p \leq 1$, $\text{X} = \text{Cl}, \text{NO}_3$). The ratio p was poorly reproducible and pure $\text{Ga}(\text{taci})_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ ($p = 1$) could only be obtained by the slow growth of single crystals. Since $\text{Ga}(\text{taci})_2^{3+}$ acted as a weak acid in aqueous solution ($\text{pK} = 7.4$) the incorporation of $\text{H}_{1-p}\text{Ga}(\text{taci})_2^{2+}$ in the solid is quite understandable. The same reactivity has also been found for the Al(III) and Cr(III) complex. In contrast to Ga(III), Cr(III) formed a compound with the well defined composition

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Table IV. Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses for Non-Hydrogen Atoms of Al(taci)₂Br₃·7H₂O, Ga(taci)₂(NO₃)₃·3H₂O and Tl(taci)₂(NO₃)₃·2H₂O

atom	x	y	z	$U_{eq}/U_{iso},^a \text{ \AA}^2$	atom	x	y	z	$U_{eq}/U_{iso},^a \text{ \AA}^2$
Al Complex									
Al	0.25	0.25	0.50	0.0149(2)	C(2)	-0.0198(3)	0.2864(2)	0.4292(2)	0.0200(6)
Br(1)	0.32944(4)	0.33460(3)	0.18859(2)	0.0425(1)	C(3)	-0.0203(3)	0.1923(2)	0.3946(2)	0.0206(6)
Br(2)	0.0	0.46976(4)	0.75	0.0627(2)	C(4)	0.1304(3)	0.1621(2)	0.3813(1)	0.0208(6)
O(2)	0.0531(2)	0.2827(1)	0.4916(1)	0.0185(4)	C(5)	0.1945(3)	0.2343(2)	0.3367(2)	0.0216(6)
O(4)	0.2157(2)	0.1516(1)	0.4400(1)	0.0187(4)	C(6)	0.1984(3)	0.3291(2)	0.3695(1)	0.0207(6)
O(6)	0.2854(2)	0.3288(1)	0.4280(1)	0.0185(4)	O(W1)	0.2943(2)	-0.0097(1)	0.4667(1)	0.0369(6)
N(1)	0.0450(3)	0.4493(2)	0.4119(1)	0.0267(6)	O(W2)	-0.1184(2)	0.3364(2)	0.5819(1)	0.0416(9)
N(3)	-0.0851(3)	0.1235(2)	0.4384(1)	0.0293(6)	O(W3)	0.4952(3)	0.4386(2)	0.4241(1)	0.0401(6)
N(5)	0.3435(3)	0.2073(2)	0.3260(1)	0.0323(6)	O(W4) ^b	0.6470(5)	0.4527(4)	0.7217(3)	0.158(2)
C(1)	0.0458(3)	0.3549(2)	0.3825(2)	0.0216(6)					
Ga Complex									
Ga	0.41905(2)	0.40304(2)	0.74933(2)	0.0128(1)	C(22)	0.7289(2)	0.2336(2)	0.6920(2)	0.0195(5)
O(12)	0.4842(2)	0.5116(2)	0.8683(1)	0.0174(4)	C(23)	0.5993(2)	0.1481(2)	0.7344(2)	0.0171(5)
O(14)	0.2340(2)	0.3462(2)	0.8112(1)	0.0171(4)	C(24)	0.5095(3)	0.0802(2)	0.6499(2)	0.0190(5)
O(16)	0.3397(2)	0.5600(2)	0.6923(1)	0.0174(4)	C(25)	0.4625(3)	0.1822(2)	0.5777(2)	0.0184(5)
N(11)	0.4700(2)	0.7866(2)	0.8079(2)	0.0230(5)	C(26)	0.5946(3)	0.2641(2)	0.5363(2)	0.0200(5)
N(13)	0.2816(2)	0.4099(2)	1.0140(2)	0.0197(4)	N(1N)	-0.0527(2)	0.6875(2)	0.5081(2)	0.0244(5)
N(15)	0.0410(2)	0.4977(2)	0.7066(2)	0.0206(4)	O(1N1)	-0.1425(3)	0.5884(2)	0.5122(2)	0.0452(5)
C(11)	0.3368(2)	0.7062(2)	0.8440(2)	0.0171(4)	O(1N2)	-0.0406(2)	0.7539(2)	0.4319(2)	0.0354(5)
C(12)	0.3825(2)	0.5970(2)	0.9125(2)	0.0161(4)	O(1N3)	0.0289(3)	0.7194(2)	0.5792(2)	0.0413(5)
C(13)	0.2428(2)	0.5178(2)	0.9479(2)	0.0158(4)	N(2N)	0.6806(3)	0.9656(2)	1.0065(2)	0.0296(5)
C(14)	0.1567(2)	0.4486(2)	0.8606(2)	0.0157(4)	O(2N1)	0.6158(3)	0.8515(2)	0.9798(2)	0.0553(6)
C(15)	0.1199(2)	0.5609(2)	0.7932(2)	0.0157(4)	O(2N2)	0.7004(5)	1.0560(3)	0.9496(2)	0.0753(9)
C(16)	0.2547(2)	0.6438(2)	0.7541(2)	0.0165(4)	O(2N3)	0.7154(3)	0.9804(2)	1.0943(2)	0.0502(6)
O(22)	0.8069(2)	0.3072(2)	0.7706(1)	0.0263(4)	N(3N)	0.8307(3)	0.8021(3)	0.7521(2)	0.0331(5)
O(24)	0.3903(2)	0.0025(2)	0.6925(2)	0.0302(4)	O(3N1)	0.7930(2)	0.6835(2)	0.7796(2)	0.0404(5)
O(26)	0.5432(2)	0.3591(2)	0.4731(1)	0.0278(4)	O(3N2)	0.7544(3)	0.8626(3)	0.6990(2)	0.0661(7)
N(21)	0.6107(2)	0.4508(2)	0.6676(2)	0.0175(4)	O(3N3)	0.9498(3)	0.8580(2)	0.7817(2)	0.0437(5)
N(23)	0.5104(2)	0.2335(2)	0.8024(2)	0.0180(4)	O(W1)	1.0074(2)	0.1448(2)	0.8216(2)	0.0448(6)
N(25)	0.3596(2)	0.2782(2)	0.6229(1)	0.0175(4)	O(W2)	0.1596(3)	-0.0156(2)	0.5749(2)	0.0596(7)
C(21)	0.6884(2)	0.3369(2)	0.6182(2)	0.0192(5)	O(W3)	0.9888(3)	0.7645(2)	0.9717(2)	0.0430(6)
Tl Complex									
Tl	0.0	0.0	0.0	0.0191(1)	C(5)	0.1451(3)	0.2116(6)	0.1404(4)	0.021(3)
O(2)	0.0972(3)	-0.0248(5)	0.3365(4)	0.031(3)	C(6)	0.1170(3)	0.2979(6)	0.1946(5)	0.023(3)
O(4)	0.2107(3)	-0.0164(5)	0.1580(4)	0.036(3)	N(1N)	0.1811(3)	-0.4030(6)	0.4152(4)	0.029(3)
O(6)	0.0656(2)	0.4091(5)	0.1124(4)	0.030(3)	O(1N1)	0.3044(3)	0.0350(6)	0.5466(4)	0.044(3)
N(1)	0.0080(2)	0.1461(6)	0.1362(3)	0.037(3)	O(1N2)	0.1601(3)	-0.3080(7)	0.4492(4)	0.055(4)
N(3)	0.1024(2)	-0.1228(5)	0.1587(4)	0.037(3)	O(1N3)	0.1871(3)	-0.3681(5)	0.3409(4)	0.043(3)
N(5)	0.0861(2)	0.1590(6)	0.0227(4)	0.039(3)	N(2N)	0.50	0.1017(9)	0.25	0.027(4)
C(1)	0.0829(3)	0.1984(6)	0.2338(4)	0.020(3)	O(2N1)	0.4861(3)	0.163(1)	0.3047(5)	0.105(5)
C(2)	0.1332(3)	0.0685(7)	0.3073(4)	0.022(3)	O(2N2)	0.50	-0.031(1)	0.25	0.10(1)
C(3)	0.1608(3)	-0.0249(6)	0.2549(5)	0.021(3)	O(W)	0.1133(2)	-0.3643(5)	0.0293(3)	0.032(3)
C(4)	0.1939(3)	0.0769(7)	0.2165(5)	0.024(3)					

^a $U_{eq} = 1/3 \sum_i U_{ij} a_i^* a_j^* a_i a_j$. ^b O(W4) in Al(taci)₂Br₃·7H₂O was refined isotropically.

Table V. Summarized Bond Distances (Å) of the M(taci)₂³⁺ Complexes (M = Al, Ga, Tl) with Estimated Standard Deviations in Parentheses

bond	Al complex		Ga complex		Tl complex	
	av	range	av	range	av	range
M-N			2.101	2.084(2)–2.115(2)	2.316	2.304(5)–2.330(4)
M-O	1.902	1.894(2)–1.912(2)	1.956	1.945(2)–1.969(2)		
C-C	1.530	1.522(4)–1.539(4)	1.532	1.524(3)–1.543(3)	1.527	1.512(7)–1.543(8)
C-N ^a	1.492	1.485(4)–1.498(4)	1.489	1.482(3)–1.499(3)		
C-N ^b			1.488	1.486(3)–1.492(3)	1.484	1.474(6)–1.490(6)
C-O ^a			1.423	1.411(3)–1.436(3)	1.431	1.42(1)–1.438(6)
C-O ^b	1.402	1.400(3)–1.404(4)	1.407	1.407(3)–1.408(3)		

^a Only C-X distances (X = N, O) where X is not coordinated to the metal. ^b Only C-Y distances (Y = O, N) where Y is coordinated to the metal.

[H₁Cr(taci)₂][Cr(taci)₂]₂(SO₄)₄·30H₂O,³ whereas the incorporation of the deprotonated Al complex in the precipitated solid has not been observed at all.

Crystal Structure of Al(taci)₂Br₃·7H₂O, Ga(taci)₂(NO₃)₃·3H₂O and Tl(taci)₂(NO₃)₃·2H₂O. All three metal ions formed mononuclear 1:2 complexes showing an idealized octahedral coordination sphere. As expected, the hard Al³⁺ ion is selectively bound to the six oxygen atoms of the two taci molecules and the deviation from the octahedral geometry is not significant. The present X-ray investigation revealed that the protons of the hydroxyl groups are transferred to the amino groups of taci in the course of coordination. The difference Fourier map showed unambigu-

ously the presence of six NH₃⁺ groups per complex. No peaks assignable to H(-O) were found.

Six of the seven water molecules are bound directly to the coordinated alkoxo groups by hydrogen bonding, forming a second coordination sphere. The entire structure of this Al(taci)₂³⁺·6H₂O aggregate is shown in Figure 1a. An additional water molecule interacts only weakly with the complex. The Al-O distances ($d_{av} = 1.902 \text{ \AA}$) compare well with those observed in tris(lactato)aluminum ($d_{av} = 1.883 \text{ \AA}$),²³ tris(tropolonato)aluminum ($d_{av} = 1.888 \text{ \AA}$),²⁴ tris(isomaltolato)aluminum ($d_{av} = 1.889 \text{ \AA}$),²⁵ aluminichrome A ($d_{av} = 1.895 \text{ \AA}$),²⁶ tris(oxalato)aluminate ($d_{av} = 1.897 \text{ \AA}$),²⁷ tris(1,2-dimethyl-3-hydroxy-4-pyridinonato)alumi-

Table VI. Summarized Bond Angles (deg) of the $M(\text{taci})_2^{3+}$ Complexes ($M = \text{Al, Ga, Tl}$) with Estimated Standard Deviations in Parentheses

angle	Al complex		Ga complex		Tl complex	
	av	range	av	range	av	range
O–M–O _{cis} ^a	89.8	89.6(1)–90.2(1)	92.6	92.2(1)–92.8(1)		
O–M–O _{cis} ^b	90.2	89.8(1)–90.4(1)				
N–M–N _{cis} ^a			87.2	84.6(1)–89.7(1)	84.9	83.2(2)–87.3(2)
N–M–N _{cis} ^b					95.1	92.7(2)–96.8(2)
N–M–O _{cis} ^b			90.0	87.5(1)–93.9(7)		
N–M–N _{trans} ^b					180.0	
O–M–O _{trans} ^b	180.0					
N–M–O _{trans} ^b			175.4	173.3(1)–176.6(1)		
M–O–C	121.6	120.7(2)–122.1(2)	116.9	115.4(1)–118.1(1)		
M–N–C			119.4	118.9(1)–119.8(1)	116.3	115.3(4)–116.9(3)

^a X–M–Y, X and Y are two atoms of the same ligand molecule. ^b X–M–Y', X and Y' are two atoms of two different ligand molecules.

num ($d_{\text{av}} = 1.908 \text{ \AA}$),²⁸ and tris(1-ethyl-3-hydroxy-2-methyl-4-pyridinonato)aluminum ($d_{\text{av}} = 1.912 \text{ \AA}$)²⁹ and are distinctly shorter than the Al–N bond distance observed in diaquanitrilotriacetatoaluminum ($d_{\text{Al–N}} = 2.086(4) \text{ \AA}$).³⁰

In the Ga(III) complex, only one of the two taci molecules is coordinated to the metal by the three alkoxy groups. Again, the protons shifted to the amino groups in the course of coordination. However, the second taci molecule acts as a tridentate N-donor (Figure 1b). The different binding of the two ligands resulted in a facial GaN_3O_3 geometry. The Ga–O ($d_{\text{av}} = 1.956 \text{ \AA}$) and Ga–N ($d_{\text{av}} = 2.101 \text{ \AA}$) distances are distinctly different from each other (Table V) and compare well with those found in a variety of GaL complexes, where a hexadentate ligand L provides both oxygen and nitrogen atoms for metal binding (L = ethylenebis(o-hydroxyphenyl)glycine, $d_{\text{av}}(\text{Ga–O}) = 1.949 \text{ \AA}$, $d_{\text{av}}(\text{Ga–N}) = 2.090 \text{ \AA}$;³¹ L = 1,4,7-triazacyclononane-1,4,7-triacetate, $d_{\text{av}}(\text{Ga–O}) = 1.930 \text{ \AA}$, $d_{\text{av}}(\text{Ga–N}) = 2.090 \text{ \AA}$;³² L = N,N',N''-tris(3,5-dimethyl-2-hydroxybenzyl)-1,4,7-triazacyclononane, $d_{\text{av}}(\text{Ga–O}) = 1.944 \text{ \AA}$, $d_{\text{av}}(\text{Ga–N}) = 2.109 \text{ \AA}$).³³ The three NO_3^- counterions and two of the three water molecules are associated with the $\text{Ga}(\text{taci})_2^{3+}$ moiety by hydrogen bonds.

A view of $\text{Tl}(\text{taci})_2^{3+}$ is shown in Figure 1c. Both ligands coordinate Tl(III) exclusively via nitrogen atoms. In contrast to the almost regular AlO_6 octahedron, the TlN_6 moiety is subjected to a significant trigonal distortion with average angles $\text{N}(i)\text{–Tl–N}(j)$ of 84.9° and $\text{N}(i)\text{–Tl–N}(j)'$ of 95.1° ($\text{N}(i)$ and $\text{N}(j)$ are two atoms of the same ligand and $\text{N}(j)'$ is an atom of the other ligand; see also Table VI). This distortion may be regarded as a stretching along the pseudo-3-fold axis and is probably a consequence of the large diameter of Tl(III).

Complexes of Tl(III) bound exclusively to aliphatic or alicyclic amines are rare.^{34,35} We believe this is the first complete X-ray crystal structure of a Tl(III)–amine complex with a TlN_6

coordination sphere. Wieghardt et al. reported the synthesis and X-ray investigation of the $\text{Tl}(\text{tcc})_2^{3+}$ complex ($\text{tcc} = \text{N,N',N''}$ -trimethyl-1,4,7-triazacyclononane), but the crystals obtained were not suitable for a complete structure determination.³⁵ The observed Tl–N bond distances in $\text{Tl}(\text{tcc})_2^{3+}$ (2.48 \AA) are significantly larger than those found in $\text{Tl}(\text{taci})_2^{3+}$ ($d_{\text{av}}(\text{Tl–N}) = 2.316 \text{ \AA}$). The rather short Tl–N bonds in $\text{Tl}(\text{taci})_2^{3+}$ confirmed that Tl(III) is too large to fit unconstrainedly in the $\text{N}(1), \text{N}(3), \text{N}(5)$ site of taci.

Determination of the Stability Constants. The determination of formation constants of mononuclear complexes was complicated by the hydrolytic polymerization of these complexes. Hydrolysis was indicated by a slow, steady increase of the pH, the liberation of free taci as seen in the NMR spectra, and the deposition of solid hydrolysis products from slightly acidic solutions ($\text{pH} < 4$). Hydrolysis of the Al(III) complexes was generally very slow. Solutions of the mononuclear complexes were stable over a period of several days at room temperature, and liberation of taci was only observed at increased temperature ($> 80^\circ \text{C}$) after several hours. Thus, formation constants could be determined either by continuous titrations or in a batchwise manner (Table I). The hydrolysis of the Ga(III) complexes was considerably faster but still sufficiently slow to allow the determination of a preequilibrium system consisting exclusively in mononuclear complexes. However, to avoid significant interference with hydrolytic polymerization, these measurements must be carried out within less than 15 h. The hydrolytic polymerization of the Tl(III) complexes at 25°C was generally fast compared with the time required for potentiometric measurements.

Acidimetric titrations of the bis complexes were performed at 25°C and an ionic strength of 0.1 (Figures 2a and 3, Tables I and II). For Al(III) and Ga(III), a reasonable fit of the titration curve was obtained by considering $\text{M}(\text{taci})_2^{3+}$ and $\text{M}(\text{taci})_2^{3+}$ as major components in the equilibrium system. $\text{H}_{-1}\text{M}(\text{taci})_2^{2+}$ was recognized as an additional species at $\text{pH} \geq 6$ by the appearance of a buffer region with $\text{equiv} < 0$. According to this model the concentrations of the free aqua ions Al^{3+} and Ga^{3+} are significant in the acidic range. Consequently, the hydrolysis products $\text{Al}(\text{OH})_2^{2+}$ and $\text{Ga}(\text{OH})_2^{2+}$ were included in the refinement using their well-known formation constants.^{16,17,36} The fit could thereby be improved considerably, but some systematic deviation, $\text{pH}_{\text{calc}} - \text{pH}_{\text{obs}}$, was still observed. This deviation disappeared by the inclusion of further species as indicated in Tables I and II and Figure 5. Two different models were tested in the final refinement. Beside the major components $\text{M}(\text{taci})_2^{3+}$, $\text{M}(\text{taci})_2^{3+}$, the deprotonated species $\text{H}_{-1}\text{M}(\text{taci})_2^{2+}$, and the hydrolysis product $\text{M}(\text{OH})_2^{2+}$, a protonated bis complex, $\text{HM}(\text{taci})_2^{4+}$, was considered in model 1, whereas two additional 1:1 complexes ($\text{H}_{-1}\text{M}(\text{taci})_2^{2+}$ and $\text{HM}(\text{taci})_2^{4+}$) were considered in model 2. Model 1 was

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(36) $\text{Ga}(\text{OH})_2^+$, $\text{Ga}(\text{OH})_3$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, and $\text{Al}_2(\text{OH})_2^{4+}$ do not appear significantly in the range $2 \leq \text{pH} \leq 12$.

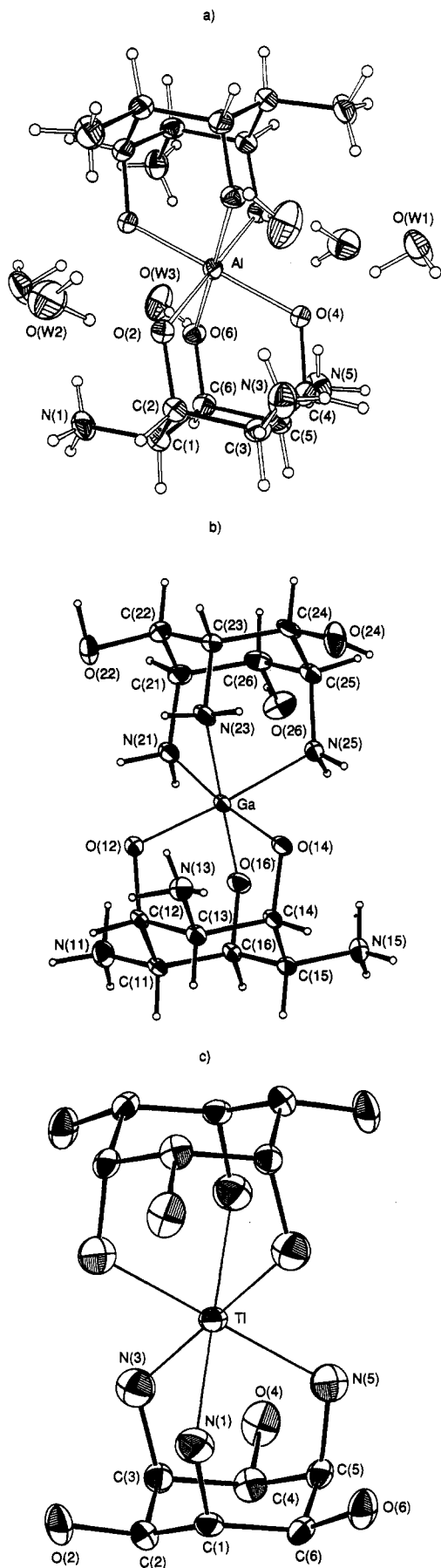


Figure 1. ORTEP drawings of (a) Al(taci)₂³⁺ · 6H₂O, (b) Ga(taci)₂³⁺, and (c) Tl(taci)₂³⁺ with numbering schemes and vibrational ellipsoids at the 50% probability level. The hydrogen atoms in the Al and Ga complex are shown as spheres of arbitrary size.

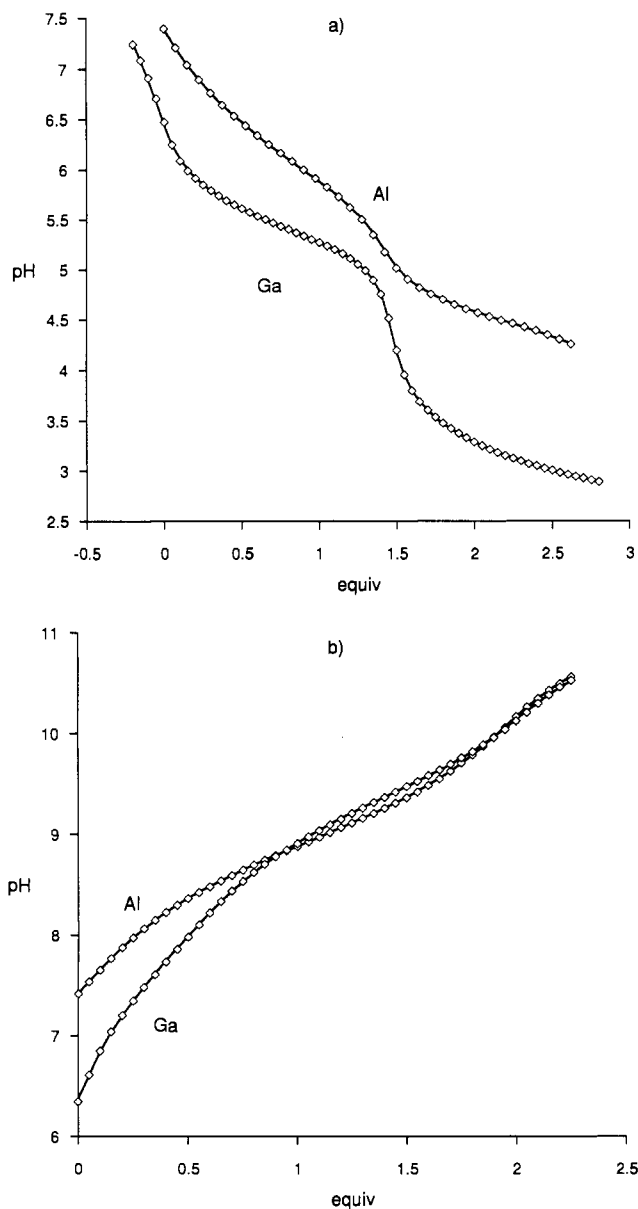


Figure 2. (a) Acidimetric titrations of Al(taci)₂Cl₃ (10⁻³ M) and Ga(taci)₂Cl₃ (10⁻³ M). (b) Alkalimetric titrations of Al(taci)₂Cl₃ (10⁻³ M) and Ga(taci)₂(NO₃)₃ (10⁻³ M). The open squares represent experimental points, and the solid lines were calculated from the equilibrium constants listed in Tables I and II; equiv = moles of titrant added per moles of taci. Only every second point of the alkalimetric titration of Ga(taci)₂(NO₃)₃ is shown for clarity.

avored for Al(III) due to generally lower σ_{pH} values³⁷ and a higher consistency of the evaluated data as obtained from titrations with different Al-concentrations. Model 2 fit better for Ga(III). However, the values of the formation constants of the major species do not differ significantly by using either model 1 or model 2 for evaluation.

It is well known that Al(III) and Ga(III) complexes are readily converted to the very stable Al(OH)₄⁻ and Ga(OH)₄⁻ at high pH. Since the formation constants of the two tetrahydroxo complexes are well established, it has been suggested to use this conversion as a convenient method for the determination of stability constants.^{17,18} To validate our results, obtained from acidimetric titrations, additional alkalimetric titrations of Al(taci)₂Cl₃ (25 °C, 0.1 M KCl) and Ga(taci)₂(NO₃)₃ (25 °C, 0.1 M KNO₃)

(37) $\sigma_{\text{pH}} = (\sum w(\text{pH}_{\text{obs}} - \text{pH}_{\text{calcd}})^2 / \sum w)^{1/2}$, $w = (\text{pH}_{i-1} - \text{pH}_{i+1})^{-2}$.

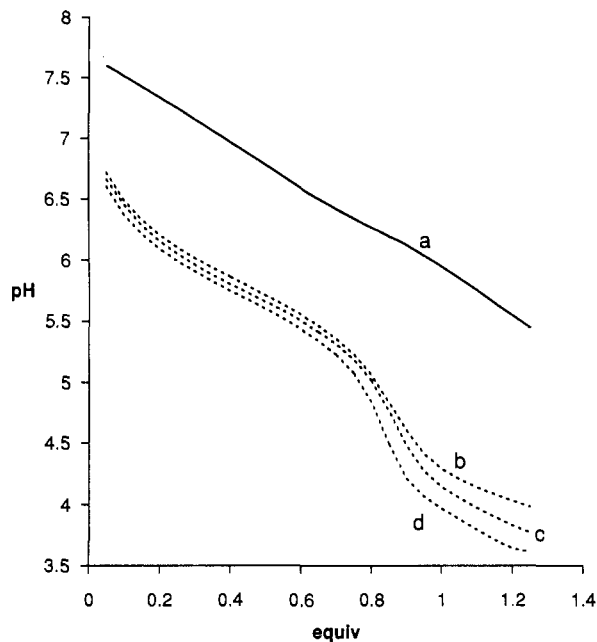
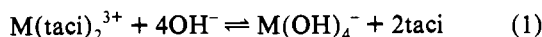
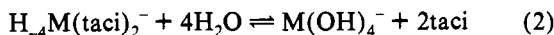


Figure 3. Titration of $\text{Tl}(\text{taci})_2(\text{NO}_3)_3$ (25 °C, 0.1 M KNO_3) with 0.1 M HNO_3 : (a and c) $[\text{Tl}] = 10^{-3}$ M; (b) $[\text{Tl}] = 5 \times 10^{-4}$ M; (d) $[\text{Tl}] = 2 \times 10^{-3}$ M. Dashed lines refer to freshly prepared solutions, and the solid line refers to a solution which was allowed to stand at 25 °C for 14 days; equiv = moles of acid added per moles of taci.

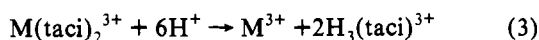
have been performed, and $\beta_{\text{M}(\text{taci})_2}$ has been evaluated according to



However, in the present investigation the evaluation was complicated by rather small fractions of $\text{Al}(\text{OH})_4^-$ ($\leq 40\%$) and $\text{Ga}(\text{OH})_4^-$ ($\leq 20\%$) in the equilibrium system. Moreover, a series of deprotonated species $\text{H}_x\text{M}(\text{taci})_2^{3-x}$ were formed at increasing pH. It is important to note that species such as $\text{M}(\text{OH})_4^-$ ($=\text{H}_4\text{M}$), $\text{M}(\text{H}_3\text{taci})(\text{OH})^-$ ($=\text{H}_4\text{M}(\text{taci})$), and $\text{M}(\text{H}_2\text{taci})_2^-$ ($=\text{H}_4\text{M}(\text{taci})_2$) are equivalent with respect to the amount of base required for their formation. At high pH eq 1 turns to



In the range $10 \leq \text{pH} \leq 11$, taci neither releases nor takes up protons and the equilibrium (2) is not dependent on the amount of titrant added. Hence, no information about equilibrium (2) can be obtained in this range. Since the formation of $\text{Al}(\text{OH})_4^-$ and $\text{Ga}(\text{OH})_4^-$ varies gradually over the wide range of $7 \leq \text{pH} \leq 12$ (Figure 5), the pH method could still be applied for the evaluation of $\beta_{\text{M}(\text{taci})_2}$. The presence of multiply deprotonated species at $\text{pH} \geq 9$ is clearly confirmed by the alkalimetric titrations. However, the evaluated formation constants of $\text{H}_3\text{M}(\text{taci})_2$ and $\text{H}_4\text{M}(\text{taci})_2^-$ are poorly defined, and further experiments will be necessary for an unambiguous identification of these species.³⁸ Nevertheless, alkalimetric titrations proved to be an independent, valuable method to check the values of $\beta_{\text{M}(\text{taci})_2}$ as obtained from acidimetric titrations according to



As seen in Tables I and II, the values obtained according to (1) and (3) are in excellent agreement.

During the acidimetric titration of $\text{Tl}(\text{taci})_2^{3+}$, the formation of a brown solid was observed below pH 4. Therefore, the titration curve could only be evaluated in the range $0 \leq \text{equiv} \leq 1.25$ (Figure 3). Titrations were performed with variable amounts of total Tl (0.5 mM, 1 mM and 2 mM). The observed inflection at equiv ≈ 0.85 is only understandable, if polynuclear hydrolysis products are already present in the freshly prepared solutions.

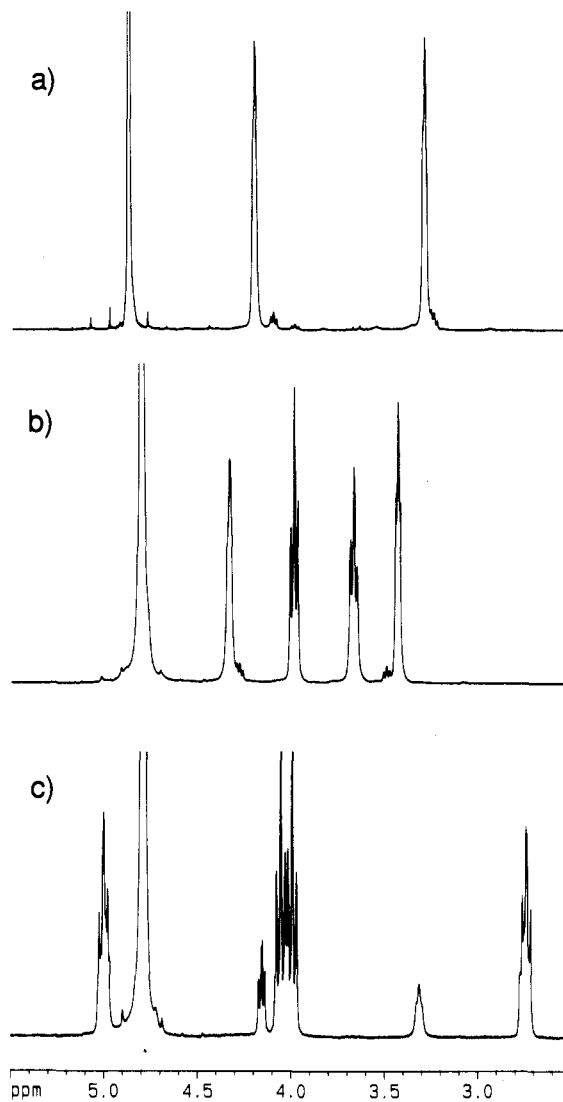


Figure 4. ^1H NMR spectra (D_2O , 25 °C, 0.01 M) of (a) $\text{Al}(\text{taci})_2\text{Cl}_3$, (b) $\text{Ga}(\text{taci})_2\text{Cl}_3$, and (c) $\text{Tl}(\text{taci})_2(\text{NO}_3)_3$.

Moreover, the considerable shift of pH depending on the time (Figure 3) shows that hydrolysis of $\text{Tl}(\text{taci})_2^{3+}$ progresses steadily over a period of 2 weeks, at least. This aging is also indicated in the NMR spectrum by observations of increasing portions of free ligand seen as emerging from hydrolytic decay. In fact, true equilibration times may be exceedingly long at room temperature due to the coupling of hydrolytic decay to very slow aging processes. In order to get some idea of the composition of fresh $\text{Tl}(\text{taci})_2^{3+}$ solutions, we applied several models that involved merely some low polynuclear species. Although a consistent model has not been obtained yet, the present data are in accordance with the decay of $\text{Tl}(\text{taci})_2^{3+}$ in the range $7 \geq \text{pH} \geq 5$ and 10.5 ± 0.5 as reasonable value for $\log K_2$, where $K_2 = [\text{Tl}(\text{taci})_2] / [\text{Tl}(\text{taci})]^{-1}[\text{taci}]^{-1}$. It is interesting to note that a hexanuclear $\text{In}(\text{III})$ complex could be isolated from an aqueous $\text{In}(\text{taci})_2^{3+}$ solution. The composition $\text{OIn}_6(\text{H}_3\text{taci})_4^{4+}$ of this complex has been elucidated by FAB MS and a single-crystal X-ray structure analysis.³⁹

NMR Spectroscopy and Structure in Aqueous Solution. Since potentiometric data do not allow any assignment of a molecular structure to a given macrospecies $\text{H}_x\text{M}_y(\text{taci})_z$, NMR measurements were used for additional characterization of the complexes in aqueous solution. For this purpose, the complexes were

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(39) Hegetschweiler K.; Ghisletta, M.; Fässler, T. F.; Nepser, R. Manuscript in preparation.

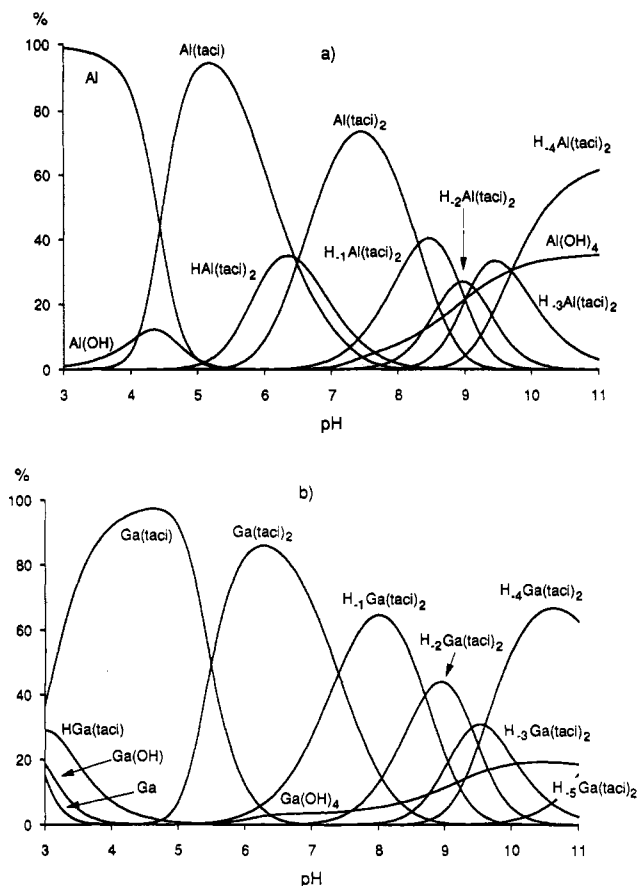


Figure 5. Species distribution in equilibrated solutions containing mononuclear *taci* complexes with $[M]_{\text{tot}}:[taci]_{\text{tot}} = 1:2$, $[M]_{\text{tot}} = 10^{-3}$ moles dm^{-3} : (a) $M = \text{Al}^{3+}$; (b) $M = \text{Ga}^{3+}$. The species concentrations were calculated with the equilibrium constants listed in Tables I and II. $M(\text{OH})_2^+$, $M(\text{OH})_3$ appeared in low abundance³⁶ and are omitted for clarity. Solid hydrolysis products and polynuclear oxo-hydroxo complexes are not considered.

dissolved in D_2O and no additional acid, base, or any buffer was used for a pH adjustment. Therefore, the NMR spectra reflect the species distribution at the starting point of the titration curves in the range $6 \leq \text{pH} \leq 8$.

The ^1H NMR spectrum of the Al(III) complex (Figure 4a) showed one main component with two signals at 4.20 and 3.30 ppm. Additional small signals indicate the presence of less than 10% of minor species. This result agrees with the ^{13}C NMR spectrum, where one main component with two signals (71.6 ppm and 55.5 ppm) was observed as well. Since no significant amount of free *taci* was detected in the spectra, the major component corresponds to the 1:2 complex, as characterized in the solid state by X-ray analysis. Moreover, the NMR data indicated full D_{3d} symmetry for this complex in solution. The existence of a rapid equilibrium with a partial liberation of *taci* (averaged signals) can clearly be ruled out. The addition of free ligand to $\text{Al}(\text{taci})_2^{3+}$ solutions resulted in the appearance of the expected signals of uncoordinated *taci*.

The Ga(III) complex exhibited 4 signals both in the ^1H NMR (Figure 4b) and in the ^{13}C NMR spectrum. Integration confirmed a 1:1:1:1 ratio for the twelve ring protons. Again, signals of a minor component appeared with less than 10% abundance. Obviously, Ga(III) is bound to two different sites of the ligand molecules. Since the spectrum indicates C_{3v} symmetry for the complex, the major component in aqueous solution corresponds to the observed structure in the solid state (Figure 1b).

The evaluation of the potentiometric data revealed two major components $M(\text{taci})_2^{3+}$ and $\text{H}_1M(\text{taci})_2^{2+}$ for Al and Ga in aqueous solution at pH 7.5. The observation of only one dominant species in the NMR spectrum therefore indicates a fast equilibrium

Scheme I. Possible Structure Assignments for $\text{Ga}^{III}(\text{taci})$ Complexes

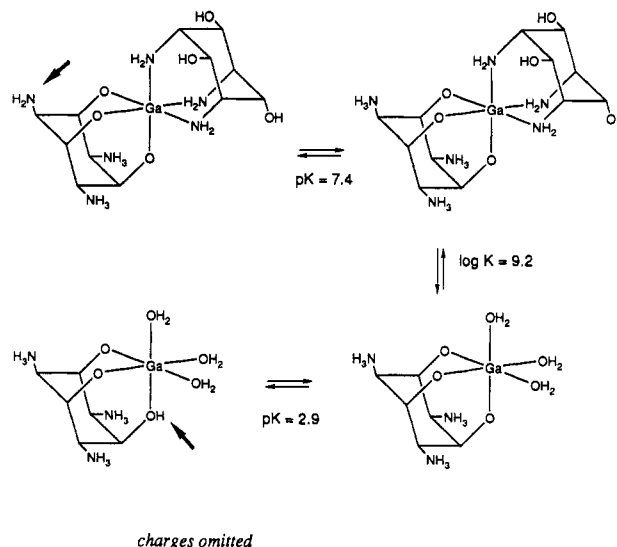


Table VII. FAB⁺ MS Data for $\text{Al}(\text{taci})_2\text{Cl}_3 \cdot \text{H}_2\text{O}$, $\text{Ga}(\text{taci})_2(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tl}(\text{taci})_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (Glycerol Matrix), Showing Relative Intensities of Major Metal-Containing Ions

	% Al	% Ga	% Tl
M^+			100
$M(\text{glyc})^+$			98
$M(\text{taci})^+$			55
$M(\text{taci})\text{O}^+$	21	20	
$\text{H}_2M(\text{taci})_2^+$	100	100	35

$M(\text{taci})_2^{3+} \rightleftharpoons \text{H}_1M(\text{taci})_2^{2+} + \text{H}^+$. The corresponding pK values are $\log \beta(M(\text{taci})_2) - \log \beta(\text{H}_1M(\text{taci})_2) = 7.4$ for Ga and 8.1 for Al. These values fall in the same range as the pK's of the protonated $\text{H}_3(\text{taci})^{3+}$. Thus, acidity and kinetics of these reactions are in accordance with the simple deprotonation of a peripheral NH_3 group of the complex (Scheme I). A corresponding deprotonated Cr(III) complex has recently been observed as well.³

^1H NMR spectra of the Tl(III) complex were measured in D_2O and $\text{DMSO}-d_6$. The latter exhibited individual signals for the protons of the OH groups (5.97 ppm) and the NH_2 groups (5.02 ppm). The large coupling constant Tl-H(-N) of 155 Hz compared with 3 Hz for Tl-H(-O) confirmed the binding of Tl(III) by the three nitrogen atoms. The large difference between the coupling constants of Tl-H(- C_N) (460 Hz) and Tl-H(- C_O) of 6 Hz allowed an unambiguous assignment of the two sets of ring protons. In the spectrum, measured in D_2O (Figure 4c) the corresponding values are 453 Hz for Tl-H(C_N) and 12.6 Hz for Tl-H(C_O). In DMSO, no free ligand could be detected. However, in contrast to Al(III) and Ga(III), a significant amount of the free ligand was observed in D_2O . The existence of individual, sharp signals for the free *taci* and for the complex as well indicated a slow ligand exchange reaction with respect to the NMR time scale. On fact, complete coalescence has not been reached at temperatures $\leq 95^\circ\text{C}$.

Mass Spectrometry. The mass spectra of the three complexes were obtained by the fast atom bombardment (FAB) ionization technique using a glycerol matrix for sample uptake. Beside the usual matrix peaks $\text{H}(\text{gl})_n^+$ and $(\text{H}(\text{gl}) - m\text{H}_2\text{O})^+$ ($1 \leq n \leq 4$, $1 \leq m \leq 2$, gl = glycerol), a set of metal containing species has been assigned (Table VII). In the case of Tl and Ga, these species were easily recognized by their characteristic isotope pattern. The observed distribution is understandable, if one considers that the fragmentation represents essentially solution chemistry in the matrix and that glycerol is acting as a reducing agent under

FAB conditions.^{4,6,40} The pseudo molecular ions $H_2M(taci)_2^+$ were generated by deprotonation of peripheral ammonium or hydroxyl groups. Ligand dissociation is indicated by the presence of 1:1 complexes and of free ligand $H(taci)^+$. The ion $M(taci)-O^+$ has only been found in the spectrum of the Al and Ga compounds. It is reasonable to regard this species as a tetrahedrally coordinated complex of the trivalent metal. However, it is not possible to decide whether this complex exists as $M(taci)-(O)^+$, $M(H_2taci)(OH)^+$ or $M(H_2taci)(H_2O)^+$. In the spectrum of the Ga(III) complex, a small amount of $Ga(taci)^+$, i.e. Ga(I) was detected. The reduction $M(III) \rightarrow M(I)$ became the dominant process for the Tl complex. The large amount of Tl^+ and $Tl(\text{glycerol})^+$ together with $H(taci)^+$ indicate a rather low stability for $Tl(I)-taci$ complexes. The increased tendency to form monovalent species is well established in the series Al, Ga, Tl as a fundamental aspect of their chemical reactivity.

Conclusions

Tridentate ligands, which are sterically constrained to a facial coordination ("tripod ligands") have received repeated attention in literature. 1,4,7-Triazacyclononane,^{35,41} and the tris(borazoly)borate anion,⁴² providing three nitrogen atoms, or the cyclopentadienyltris(dialkylphosphito-*P*)cobaltate anion,⁴³ providing three oxygen atoms, are well-known representatives of this category. *taci* is quite unique in carrying the two coordination sites of the above mentioned ligands combined in one single molecule. It is particularly interesting to study the mutual influence of two *taci* molecules in a 1:2 complex. Such mutual influence of different ligand atoms, coordinated to the same metal ion, has been discussed extensively. Jorgensen introduced the concept of chemical symbiosis: hard bases attached to a Lewis acid increase the affinity for another hard base, and soft bases attached to a Lewis acid lower the affinity for a hard base.⁴⁴ However, it has been shown by Pearson that class b metal ions sometimes behave in an antisymbiotic manner.⁴⁵ The mixed N_3O_3 coordination spheres of $Ga(taci)_2^{3+}$ and $Cr(taci)_2^{3+}$ are instructive models for this chemical antisymbiosis and *taci* is obviously a useful indicator to elucidate the affinity of a given metal ion for a distinct N_3O_3 environment. Two isomers with N_3O_3 -bound Cr(III) and O_6 -bound Cr(III) have been observed,³ whereas only a N_3O_3 -bound Ga(III) complex has been found. Thus, the increased affinity for nitrogen atoms in the series $Al(III) < Cr(III) < Ga(III) < Tl(III)$ is clearly demonstrated by the present investigation.

The observed affinity of Tl(III) to bind six nitrogen atoms of two *taci* molecules is in contrast to the tendency to form polynuclear, partially hydrolyzed *taci* complexes in aqueous solution. The first result indicates a preference of Tl(III) for nitrogen donor atoms. The second result, however, demonstrates also a strong affinity for oxygen atoms. One would expect that the binding characteristics of the alkoxo groups of *taci* and of hydroxide is quite similar, i.e. the high affinity of Tl(III) for oxide or hydroxide suggests also a possibly strong binding to the alkoxo groups. However, such Tl-alkoxo interactions have not been observed yet.

The present investigation demonstrates that *taci* competes barely with hydrolysis of Al^{3+} , Ga^{3+} , and Tl^{3+} in aqueous solution.

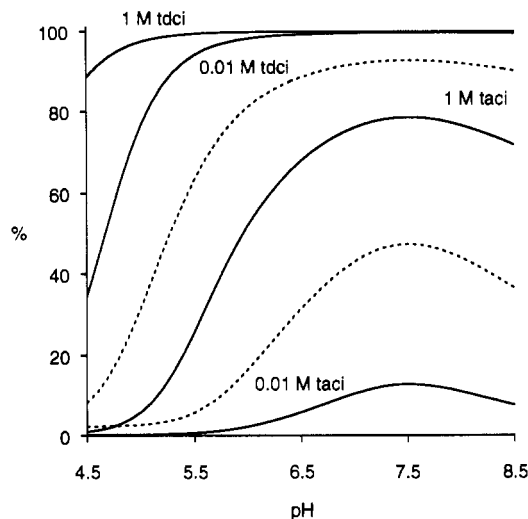


Figure 6. Comparison of the sequestering ability of *taci* and *tdci*. Fraction of the ligand bound to aluminum $\sum_{ij}[H_iAl(L)_j]/[L]_{tot}$, in equilibrated *taci* and *tdci* solutions with excess of solid $Al(OH)_3$ (solid line; $\log K_{so} = -33.5$; dashed line, $\log K_{so} = -32.5$). Total amount of ligand as indicated. Only mononuclear complexes are considered. The concentrations were calculated using the formation constants from Table I for *taci* and from ref 6 for *tdci*.

Table VIII. Comparison of Formation Constants (25 °C, $I = 0.1$) for Selected Tridentate and Hexadentate Ligands

	Al^{3+}		Ga^{3+}	
	$\log \beta_{ML}$	$\log \beta_{ML_2}$	$\log \beta_{ML}$	$\log \beta_{ML_2}$
ida ^a	8.1	15.1	12.8	
pmg ^b	13.7	22.05		
edta ^c	16.5		21.7	
cdta ^d	19.6		22.3	
nota ^e			31.0	
dtpa ^f	18.7		23.2	
edtpo ^g			31.8	
tdci ^h	14.3	26.4	16.6	30.2
<i>taci</i> ⁱ	11.8	18.8	16.5	25.7

^a Iminodiacetic acid ($Al^{51} Ga^{52}$). ^b *N*-phosphonomethylglycine.⁵³ ^c Ethylenediaminetetraacetic acid.⁵¹ ^d Cyclohexanediaminetetraacetic acid ($Al^{51} Ga^{52}$). ^e *N,N',N''*-triazacyclononanetriacetic acid.⁵⁴ ^f Diethylenetriamino-pentaacetic acid ($Al^{51} Ga^{17}$). ^g Ethylenedinitrilotetrakis(methylenephosphonic) acid.¹⁷ ^h 1,3,5-Trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol ($Al^{56} Ga^{38}$). ⁱ 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (this work).

In fact, aqueous solutions of these complexes are supersaturated with respect to solid $Al(OH)_3$, $Ga(OH)_3$, and Tl_2O_3 . In completely equilibrated solutions, significant amounts of the mononuclear complexes are only stable at fairly high *taci* concentrations (Figure 6). This result is of importance, if the dissolution of solid phases is considered as a possible application of *taci*. In contrast to the hexamethylated 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (*tdci*),^{6,38} the sequestering ability of *taci* is obviously not sufficient for this purpose. The reaction rate of the hydrolytic polymerization varies characteristically in the order $Tl(III) > Ga(III) > Al(III)$ in accordance with the well known decrease of the rate constants for the water exchange on the hexaaquaions.⁴⁶

Considering the over all charge of +3 for the 1:2 complexes, the value of 25.7 for $\log \beta_{Ga(taci)_2}$ is still high and falls in the same range as observed for corresponding polyaminocarboxylato and polyaminophosphonato complexes (see Table VIII for a summary of representative complexes). As expected, the stability of $Al(taci)_2^{3+}$ is significantly reduced. Using the well established linear

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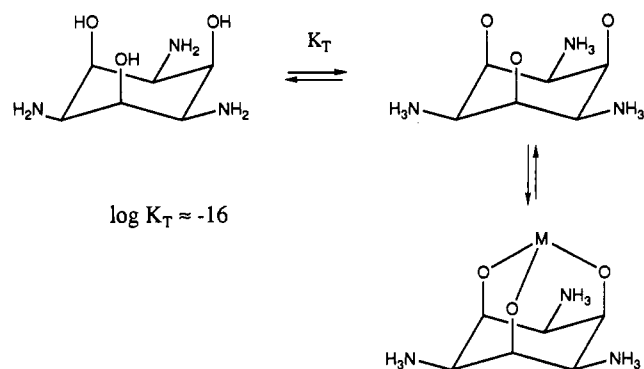
- (46) (a) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545. (b) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 4444. (c) Banyai, I.; Glaser, J. J. *Am. Chem. Soc.* **1990**, *112*, 4703.

free energy relation,⁴⁷ a value of 21 would be reasonable for $\log \beta_{\text{Al}(\text{taci})_2}$.⁴⁸ The observed value of 18.8 is even somewhat lower. The small ionic radius of Al^{3+} (0.51 Å) might be responsible for this finding. According to Angyal,¹⁰ metal ions with a radius below 0.6 Å are even too small to fit in the triaxial site of *cis*-inositol. In addition, the different binding (GaN_3O_3 vs AlO_6) might also contribute to this effect. On the other hand, a surprisingly high stability has been observed for the structurally related $\text{Al}(\text{tdci})_2^{3+}$ ($\log \beta_{\text{Al}(\text{tdci})_2} = 26.4$).⁶ Since *taci* and *tdci* provide essentially the same coordination site for Al^{3+} , the large difference in the stability is not quite evident.

Another unanswered question is the structure of $\text{Ga}(\text{taci})^{3+}$. Is it N-coordinated or O-coordinated? At least for $\text{HGa}(\text{taci})^{4+}$, only O coordination is in agreement with a chemically sensitive model (Scheme I). Provided that $\text{HGa}(\text{taci})^{4+}$ is generated from $\text{Ga}(\text{taci})^{3+}$ by simple protonation, the significant presence of $\text{HGa}(\text{taci})_2^{4+}$ in the acidic range of the pH profile (Figure 5b) indicates O coordination for $\text{Ga}(\text{taci})^{3+}$. In general, *taci* is an interesting example to illustrate the difficulties in identifying microspecies and determining microconstants.^{18,49} Since deprotonation of $\text{H}_3(\text{taci})^{3+}$ can either occur at the hydroxyl groups or ammonium groups, different tautomeric species must be considered. A rough estimate for the microscopic dissociation constants of the hydroxyl groups is given by the comparison with the completely methylated 1,3,5-trideoxy-1,3,5-tris(trimethylammonio)-*cis*-inositol ($\text{p}K_1 = 8.1$, $\text{p}K_2 = 13$, $\text{p}K_3 = 18$).⁵⁰ These values indicate that the zwitter ionic form of *taci*, as observed in the metal complexes, is actually inexistent in aqueous solution (Scheme II) and the internal proton transfer occurred just in the course of complex formation.

As a matter of fact, *taci* is a ligand, where the 3 equiv of base, required for deprotonation, are already incorporated in the molecule. In contrast to other oxygen ligands, no additional base must be added for complex formation. Moreover, the six

Scheme II



ammonium groups in a O_6 -bound 1:2 complex act as a reservoir of weakly acidic protons, allowing an over all charge adjustment according to $\text{H}_x\text{M}^{z+}(\text{taci})_2^{z-x}$, $0 \leq x \leq 6$. Monopositive cations or neutral (and potentially volatile) species can readily be formed, regardless of the oxidation state of the metal and *taci* is therefore a particularly suitable ligand to investigate mass spectra of coordination compounds as illustrated by the series $\text{H}_3\text{M}(\text{taci})_2^+$ ($\text{M} = \text{Sn}, \text{Ti}, \text{Ge}$), $\text{H}_2\text{M}(\text{taci})_2^+$ ($\text{M} = \text{Al}, \text{Ga}$), $\text{H}_1\text{M}(\text{taci})_2^+$ ($\text{M} = \text{Mg}$). The signals of these species have been observed with high intensities in the spectra of the corresponding compounds.

Acknowledgment. We thank Hans-Rudolf Walter for technical assistance in the X-ray measurements and Rolf Häfliger for recording the mass spectra. The NMR measurements have been performed by Beat Müller, and a part of the synthetic work has been done by Heinz Samaras. We are particularly grateful to Dr. Stefano Musso, Prof. Walter Schneider, Prof. Paul Saltman, and Prof. Gerhard Geier for essential advice and discussions and to the ETH Zürich, Kredite für Unterricht und Forschung, for financial support (Project No. 0899/41-0410.5).

Supplementary Material Available: Tables SI–SV, listing crystallographic data, anisotropic displacement parameters, positional parameters of hydrogen atoms, bond distances and bond angles, and Figures S1–S3, showing the FAB⁺-MS of $\text{Al}(\text{taci})_2\text{Br}_3$, $\text{Ga}(\text{taci})_2(\text{NO}_3)_3$, and $\text{Tl}(\text{taci})_2(\text{NO}_3)_3$ (17 pages). Ordering information is given on any current masthead page. A table of calculated and observed structure factors is available from the authors upon request.

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