167. 1,3,5-Trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol, an Efficient Ligand for Hard Trivalent Metal Ions. Determination of the Stability Constants of the Fe^{III}, Al^{III}, and Cu^{II} Complexes in Aqueous Solution

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The complexes $[Fe(tdci)_2]Cl_3$ and $[Al(tdci)_2]Cl_3$ (tdci = 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol) were prepared and characterized by mass spectrometry, NMR spectroscopy, and magnetic-susceptibility measurements. The formation constants were determined in aqueous solution (25°, 0.1M KCl) by potentiometric titration. pK values of $H_3(tdci)^{3+}$: 5.89, 7.62, 9.68; Fe^{III} complexes: $\log \beta_{ML} = 18.8$, $\log \beta_{ML2} = 32.6$; Al^{III} complexes: $\log \beta_{ML} = 14.3$, $\log \beta_{ML2} = 26.4$. The protonated complex $[FeH(tdci)_2]^{4+}$ has also been identified. In contrast to the high stability of the Fe^{III} and Al^{III} complexes, only weak interactions of tdci with Cu^{II} have been observed in aqueous solution (25°, 0.1M KNO_3).

Introduction. – The high affinity of 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci) for Fe^{III} has already been recognized in 1984 [1]. In a subsequent study, a variety of metal complexes has been characterized in aqueous solution [2]. However, several hazards prevented the preparation of tdci in the scale required for an unambiguous identification of the metal complexes and a quantitative investigation of the equilibria in solution. Our first attempt was, therefore, to improve the preparation procedure of tdci [3] [4]. Since this ligand is now readily available, a comprehensive investigation of complex formation has been performed in our laboratory. We report here the synthesis and characterization of the solid, crystalline Fe^{III} and Al^{III} complexes and the potentiometric determination of the stability constants for Fe^{III}, Al^{III}, and Cu^{II} in aqueous solution.

Results. – *Preparation and Characterization of the Al^{III} and Fe^{III} Complexes.* Owing to the high tendency of Al^{III} and Fe^{III} to hydrolyze in aqueous solution and the rather slow rate of complex formation with tdci, the preparation of $[Fe(tdci)_2]Cl_3$ and $[Al(tdci)_2]Cl_3$ was performed in MeOH. Upon addition of H_2O, the compounds precipitated as crystalline solids. Once formed, they could be dissolved in H_2O, forming clear, almost neutral solutions, and the formation of any solid hydrolysis product has not been observed at all. Mononuclearity of the ferric complexes has been established by magnetic-susceptibility measurements of aqueous complex solutions at pH 3.1 and in 2M NaOH. A constant magnetic moment of 5.7 μ_B was observed in the range of 80–260 K. The NMR measurements of the Al^{III} complex (D_2O, pH 7) indicated the presence of one single species. The signals of the free ligand did not appear in the spectrum (< 1%). Thus, only the 1:2 complex, showing D_{3d} symmetry, exists in neutral aqueous solution. Mass spectra were obtained for both metals by using the FAB technique for ionization. It is interesting to note that the spectrum of the Fe^{III} and Al^{III} complex differ characteristically. For the Al^{III} complex $[Al(tdci)_2H_{-2}]^+$ was the dominant species. No other Al-containing ions and

Table 1. *FAB^+ Mass-Spectrometry Data* (glycerol matrix) *for [$Fe(tdci)_2$]Cl_3: Relative Intensities of Major Metal-Containing Ions*

	m/z	Assignment	Rel. intensity [%]	Oxidation state Fe^{II}_x	Fe^{III}_y
				x	*y*
Mononuclear species	576.1	$[Fe(tdci)_2H_{-2}]^+$	100	–	1
	577.1	$[Fe(tdci)_2H_{-1}]^+$	46	1	–
Dinuclear species	629.1	$[Fe_2(tdci)_2H_{-5}]^+$	11	–	2
	630.1	$[Fe_2(tdci)_2H_{-4}]^+$	50	1	1
	631.1	$[Fe_2(tdci)_2H_{-3}]^+$	54	2	–
	666.0	$[Fe_2(tdci)_2O_2]^+$	16	1	1
	667.0	$[Fe_2(tdci)_2O_2H]^+$	15	2	–
Trinuclear species	684.0	$[Fe_3(tdci)_2H_{-6}]^+$	12	2	1
	685.0	$[Fe_3(tdci)_2H_{-5}]^+$	21	3	–
	718.9	$[Fe_3(tdci)_2O_2H_{-3}]^+$	11	1	2
	719.9	$[Fe_3(tdci)_2O_2H_{-2}]^+$	45	2	1
	720.9	$[Fe_3(tdci)_2O_2H_{-1}]^+$	47	3	–
	755.9	$[Fe_3(tdci)_2O_4H_2]^+$	16	2	1
	756.9	$[Fe_3(tdci)_2O_4H_3]^+$	13	3	–

no free ligand $H(tdci)^+$ have been observed. In the spectrum of the Fe^{III} complex $[Fe(tdci)_2H_{-2}]^+$ was also the most intensive metal-containing ion. However, a variety of polynuclear species $[H_aFe^{III}_bFe^{II}_c(tdci)_2O_d]^+$ and an intense signal of the free ligand $H(tdci)^+$ could be detected. The major Fe-containing ions are summarized in *Table 1*. The different reactivity of the Fe^{III} and Al^{III} complex is well understandable, if we consider that the glycerol matrix acts as reducing agent under FAB conditions [5] [6]. Obviously, the $[M^{III}(tdci)_2]^{3+}$ (M = Fe, Al) complexes are inert against ligand exchange in the glycerol matrix, and the dissociation of tdci occurred only after the reduction of Fe^{III} to Fe^{II}.

Stability Constants of the Fe^{III} Complexes. The curve of the acidimetric titration of $[Fe(tdci)_2]^{3+}$ (*Fig. 1, a*) was evaluated assuming $[Fe(tdci)_2]^{3+} + 3\ H^+ \rightleftharpoons [Fe(tdci)]^{3+} + H_3tdci^{3+}$, $K_2 = [[Fe(tdci)_2]^{3+}] \cdot [[Fe(tdci)]^{3+}]^{-1} \cdot [tdci]^{-1}$ as the relevant reaction. However, a systematic deviation $pH_{obs} - pH_{calcd}$ indicated the presence of additional species ($\sigma_{pH} = 0.089$)[1]) and the formation of either the protonated complex $[Fe(tdci)_2H]^{4+}$ (**1**) or of the hydroxo complex $[Fe(tdci)(OH)]^{2+}$ (**2**) were considered for further evaluation. The admission of **1** resulted in a significant diminution of the above mentioned deviation ($\sigma_{pH} = 0.0052$). The improvement obtained by admission of **2** was much smaller ($\sigma_{pH} = 0.031$), and this model was, therefore, rejected. It was not possible to calculate $\beta_{ML} = [[Fe(tdci)]^{3+}] \cdot [Fe^{3+}]^{-1} \cdot [tdci]^{-1}$ from these potentiometric data. Obviously, the decay of $[Fe(tdci)]^{3+}$ is not observed in aqueous solutions with pH $\geqslant$ 3. An exchange titration $[Fe(edta)]^- + 2\ H_3(tdci)^{3+} + 4\ OH^- \rightleftharpoons [Fe(tdci)_2]^{3+} + H_2edta^{2-}$ (H_4edta = ethylenediaminetetraacetic acid) was suitable to evaluate β_{ML} (*Fig. 1, b*). As shown in *Fig. 2, a* for a solution containing edta and tdci in a 1:2 molar ratio, $[Fe(edta)]^-$ was the dominant species in the acidic range of the pH profile, whereas $[Fe(tdci)_2]^{3+}$ is favoured in alkaline media. A species distribution diagram for the Fe^{III}/tdci system as a function of the pH is given in *Fig. 2, b*. Evaluated equilibrium constants are presented in *Table 2*.

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[1]) $\sigma_{pH} = (\Sigma w(pH_{obs} - pH_{calcd})^2 / \Sigma w)^{1/2}$, $w = (pH_{i+1} - pH_{i-1})^{-2}$.

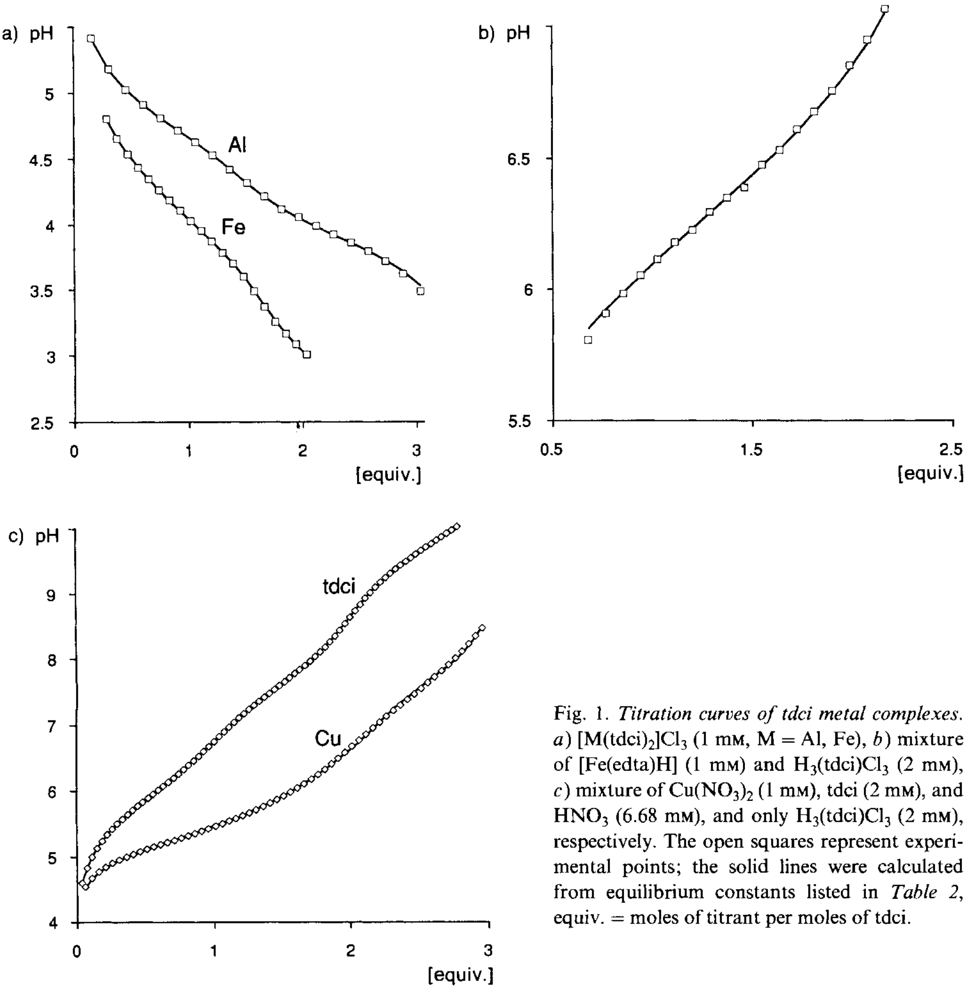


Fig. 1. *Titration curves of tdci metal complexes. a*) $[M(tdci)_2]Cl_3$ (1 mM, M = Al, Fe), *b*) mixture of [Fe(edta)H] (1 mM) and $H_3(tdci)Cl_3$ (2 mM), *c*) mixture of $Cu(NO_3)_2$ (1 mM), tdci (2 mM), and HNO_3 (6.68 mM), and only $H_3(tdci)Cl_3$ (2 mM), respectively. The open squares represent experimental points; the solid lines were calculated from equilibrium constants listed in *Table 2*, equiv. = moles of titrant per moles of tdci.

Stability Constants of the Al^{III} Complexes. In contrast to Fe^{III}, both, β_{ML} and β_{ML_2} could be evaluated from the acidimetric titration of $[Al(tdci)_2]Cl_3$ (*Fig. 1, a*). Again, an improvement of the fit was obtained by admitting an additional complex. However, the concentration of this complex never exceeded 15% of the total amount of Al, and it was not possible to decide unambiguously, whether the protonated complex $[Al(tdci)_2H]^{4+}$ (*Model 1*, $\sigma_{pH} = 0.0088$) or the hydroxo complex $[Al(tdci)(OH)]^{2+}$ (*Model 2*, $\sigma_{pH} = 0.0098$) was present in the solution (*Fig. 2, c* and *2, d*). Both models are in agreement with the above mentioned NMR study, revealing the 1:2 complex to be the only significant species at pH 7. An even better fit was obtained by the consideration of $Al(OH)^{2+}$ ($pK_{Al} = 5.0$ [7]): $\sigma_{pH} = 0.0069$ (*Model 1*) or 0.0074 (*Model 2*). *Fig. 2, e* shows that this complex is formed in the range $3 < pH < 4.5$. Since the amount of $Al(OH)^{2+}$ never exceeds 5% of the equilibrium composition, and a precise value for pK_{Al} was not available, this species has not been considered for the evaluation, presented in *Table 2* and *Fig. 1, a*. The values for β_{ML}

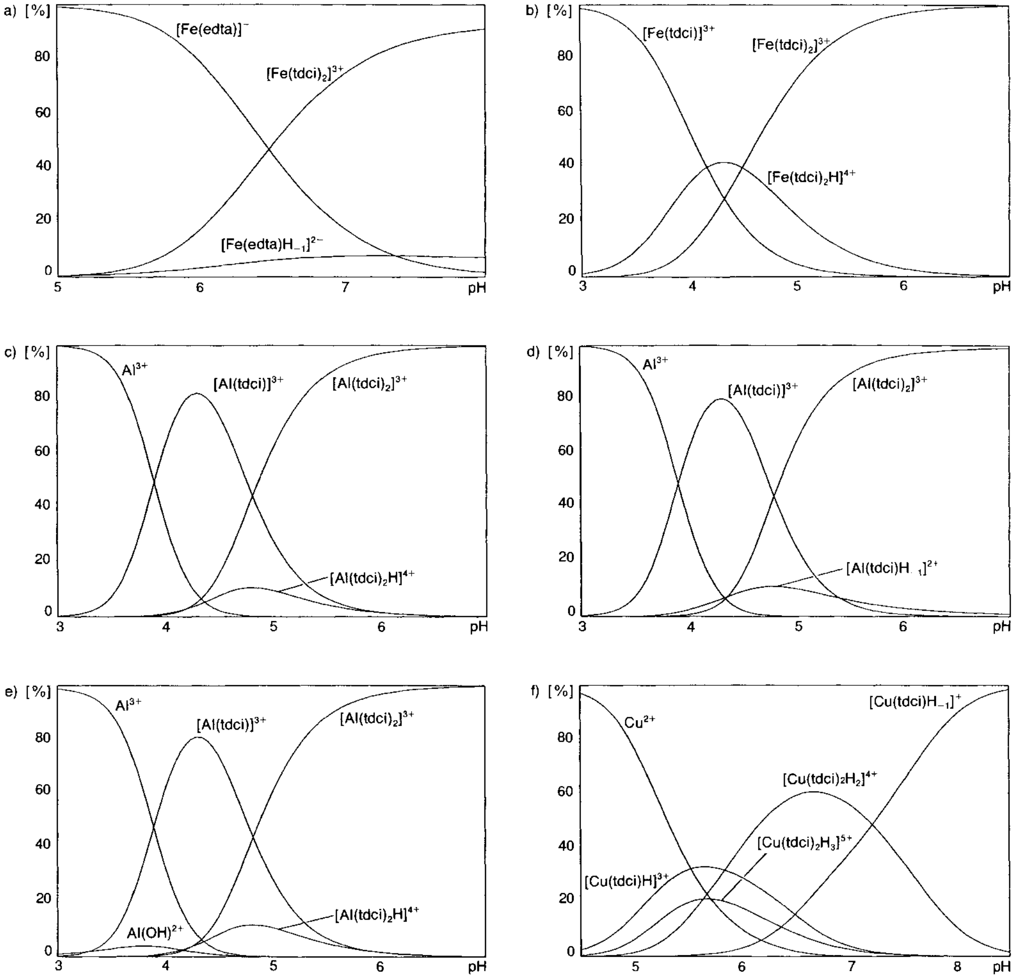


Fig. 2. *Species distribution of equilibrated aqueous solutions. a)* $Fe^{III} = 1$ mM, tdci = 2 mM, and edta = 1 mM, *b)* $Fe^{III} = 1$ mM, tdci = 2 mM, *c)* $Al^{III} = 1$ mM, tdci = 2 mM, *Model 1, d)* $Al^{III} = 1$ mM, tdci = 2 mM, *Model 2, e)* Al^{III}/tdci 'best fit', *Model 1* and $Al(OH)^{2+}$ as additional species with $pK_{AL} = 5.0$ [7]. *f)* Cu = 1 mM, tdci = 2 mM. The species distribution were calculated using the equilibrium constants listed in *Table 2*, for the edta complexes from [21–23].

and β_{ML_2} do not differ significantly by using either *Model* 1 or *Model 2* with or without $Al(OH)^{2+}$ for evaluation.

Complex Formation with Cu^{II}. Since a solid complex of tdci and Cu^{II} was not available, an alkalimetric titration of a solution containing $Cu(NO_3)_2$ and tdci·3 HNO_3 in a 1:2 ratio was performed (*Fig. 1, c*). In contrast to Fe^{III} and Al^{III}, the evaluation of an appropriate model was not trivial. Calculations with SUPERQUAD [8], using $[Cu(tdci)]^{2+}$ (**3**) and $[Cu(tdci)_2]^{2+}$ (**4**) resulted in a rather high σ value. This value could be substantially lowered by admitting additional protonated and deprotonated species. In

Table 2. *Potentiometric Data and Formation Constants of tdci Complexes.* Estimated standard deviations in parentheses (25°, $I = 0.1$).

Initial concentrations	HFe(edta): 1 mM, H_3(tdci)Cl_3: 2 mM	[Fe(tdci)$_2$]Cl_3: 1 mM	[Al(tdci)$_2$]Cl_3: 1 mM		Cu(NO_3)$_2$: 1 mM, tdci: 2 mM, HNO_3: 6.68 mM	H_3(tdci)Cl_3: 2 mM	tdci: 2 mM, HNO_3: 6.52 mM
Inert electrolyte	KCl	KCl	KCl		KNO_3	KCl	KNO_3
Titrant	KOH	HCl	HCl		KOH	KOH	KOH
Type of titration	batch	batch	batch		continuous	continuous	continuous
No. of data points	18	20	20		59	75	60
			Model 1	*Model 2*			
$\log\beta_{H_{-1}ML}$[a])				8.9 (5)	2.26 (5)	$pK_1 = 5.89$[b])	$pK_1 = 5.86$[b])
$\log\beta_{ML}$[a])		18.8 (1)[c])	14.31 (5)	14.3 (1)		$pK_2 = 7.62$[b])	$pK_2 = 7.61$[b])
$\log\beta_{HML}$[a])					15.2 (3)	$pK_3 = 9.68$[b])	$pK_3 = 9.68$[b])
$\log\beta_{ML_2}$[a])	32.6 (1)		26.4 (1)	26.4 (1)			
$\log\beta_{HML_2}$[a])		37.1 (1)[c])	30.6 (5)				
$\log\beta_{H_2ML_2}$[a])					30.21 (5)		
$\log\beta_{H_3ML_2}$[a])					35.9 (5)		
σ_{pH}	0.0114	0.0052	0.0088	0.0098	0.0099	0.0023	0.0020

[a]) $\beta_{H_xML_y} = [H_xM(tdci)_y] \cdot [M]^{-1} \cdot [H]^{-x} \cdot [tdci]^{-y}$.

[b]) $K_i = [H_{3-i}(tdci)] \cdot [H] \cdot [H_{4-i}(tdci)]^{-1}$, estimated standard deviations < 0.01.

[c]) Evaluated constants: $K_2 = [[Fe(tdci)_2]] \cdot [[Fe(tdci)]]^{-1} \cdot [tdci]^{-1}$ $\log K_2 = 13.76$ (5) and $K_{HML_2} = [[Fe(tdci)_2H]] \cdot [[Fe(tdci)]]^{-1} \cdot [tdci]^{-1} \cdot [H]^{-1}$, $\log K_{HML_2} = 18.26$ (5); $\log\beta_{ML} = \log\beta_{ML_2} - \log K_2$, $\log\beta_{HML_2} = \log\beta_{ML} + \log K_{HML_2}$.

the progress of refinement, SUPERQUAD rejected the initially postulated complexes **3** and **4**. The final model is presented in *Table 2* and *Fig. 2, f*.

Discussion. – We recently introduced 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) as a novel and versatile ligand [5]. The presence of two chair conformations, providing either three OH or three NH_2 groups for metal binding, enables the formation of stable complexes with hard and soft metal ions. The larger space filling of the Me_2N groups in tdci impede this conversion (*Scheme 1*). This result is clearly expressed by the low stability and the diversity of the different Cu^{II} complexes (*Table 2*, compare with the Cu^{II} complexes of taci: $\log\beta_{ML} = 12.1$, $\log\beta_{ML_2} = 18.8$ [5]). However, the binding ability of tdci for

Scheme 1

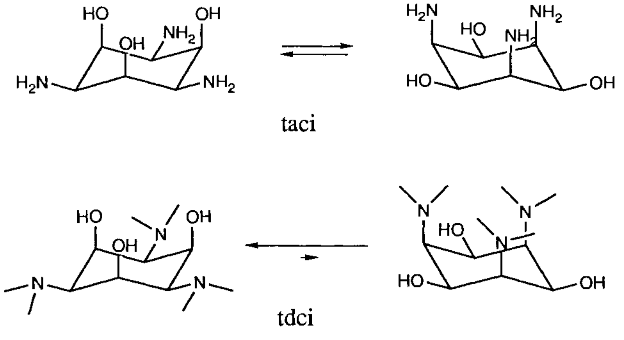


Table 3. *Comparison of Stability Constants of Fe^{III} and Al^{III} Complexes with Tridentate* (β_{ML_2}) *and Hexadentate* (β_{ML}) *Ligands*

Ligand	$\log\beta_{Al}$	$\log\beta_{Fe}$	Ligand	$\log\beta_{Al}$	$\log\beta_{Fe}$
ida[a])	15.1	20.1	edta[a])	16.5	25.0
taci[b])	18.7	–	Desferrioxamin B[d])	22	30.6
tdci[c])	26.4	32.6	hbed[a])	–	39.7

[a]) Iminodiacetic acid (H_2ida), ethylenediaminetetraacetic acid (H_4edta), and *N,N'*-bis(2-hydroxybenzyl)-ethylenedinitrilo-*N,N'*-diacetic acid (H_4hbed) [22].

[b]) 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (taci) [10].

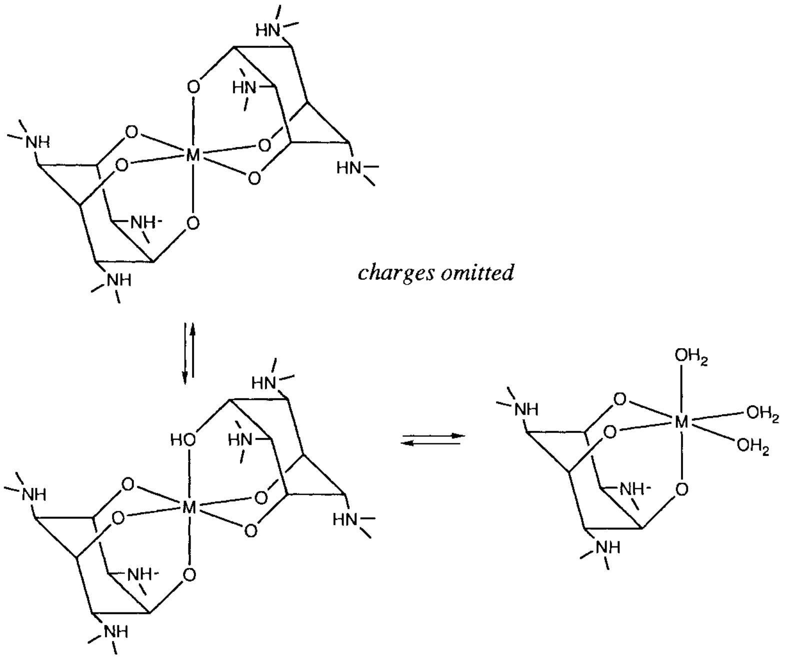
[c]) This work.

[d]) [9].

hard metal ions which are coordinated to the OH groups, is not affected at all. Moreover, it seems that this affinity is even higher, as can be seen by the significantly larger stability of $[Al(tdci)_2]^{3+}$ compared with $[Al(taci)_2]^{3+}$ (*Table 3*). Thus, the introduction of the Me_2N groups generate a powerful and selective ligand for hard cations like Al^{III} and Fe^{III} (*Table 3*).

A free energy relation log K_{FeL} *vs.* log K_{AlL} has been established for octahedrally coordinated Al^{III} and Fe^{III} complexes [9]. The values for the tdci complexes, presented in this investigation, agree well with this relation[2]).

Scheme 2



charges omitted

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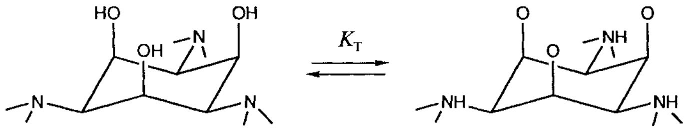
[2]) log $K_{AlL} = 0.3 + 0.71 \cdot \log K_{FeL}$. Compare the experimental value log $\beta_{AlL} = 14.3$ with 13.7, calculated accordingly from log β_{FeL}.

Potentiometric data allow only the calculation of macroscopic constants, and it is not possible to get information about the structure of the individual species. In particular, it is not possible to evaluate the number of different microspecies. In the case of Al^{III} and Fe^{III}, the magnetic and spectroscopic data are in agreement with a structure where the metal ions are bound to the six fully deprotonated hydroxy groups of two ligand molecules (*Scheme 2*). A corresponding structure has been established for $[Al(taci)_2]^{3+}$ [10] and $[Cr(taci)_2]^{3+}$ [11] by X-ray structure analysis. Consequently, in $[Fe(tdci)_2H]^{4+}$ one hydroxy and five alkoxo groups are bound to Fe^{III}.

However, it is not obvious to assign an appropriate structure for the various Cu^{II} complexes. *E.g.*, $[Cu(tdci)H_{-1}]^+$ could either be regarded as a hydroxo complex $[Cu(tdci)(OH)]^+$ or a complex with a deprotonated ligand $[Cu(H_{-1}tdci)]^+$. These considerations are also applicable to the partially protonated forms of tdci: the deprotonation of $H_3(tdci)^{3+}$ can either occur at an OH or ammonium group providing different tautomeric species. A rough estimate for the microscopic acidity of the OH groups in $H_3(tdci)^{3+}$ is given by the values $pK_1 = 8.1$, $pK_2 = 13$, $pK_3 = 18$ observed for the completely methylated 1,3,5-trideoxy-1,3,5-tris(trimethylammonio)-*cis*-inositol [3]. Considering the above mentioned structure of the Al^{III} and Fe^{III} complex, intrinsic, microscopic formation constants can be estimated according to *Scheme 3*.

Scheme 3



L L′

$\log K_T = -15.9$

$$\begin{tikzcd} nL \arrow[r, "K_T^n"] \arrow[rr, bend right, "\beta_n"'] & nL' \arrow[r, "\beta_n^*"] & ML_n \end{tikzcd}$$

	Al	Fe
$\log\beta_1^*$	30	35
$\log\beta_2^*$	58	64

We thank *Beat Müller* for the measurement of the NMR spectra, *Rolf Häfliger* for recording the FAB mass spectra, and *Heinz Samaras* for the preparation of tdci. Financial support of this work by *Kredite für Unterricht und Forschung*, ETH-Zürich, is gratefully acknowledged.

Experimental Part

General. ^1H- and ^{13}C-NMR spectra: *Bruker AC-200* δ[ppm] scale, TSP (= 0 ppm) as internal standard. MS: *VG ZAB-VSEQ*, Dr. *W. Amrein*, Laboratorium für Organische Chemie, ETH Zürich, data given as m/z (%). The samples were dissolved in H_2O and mixed with glycerol prior to the introduction in the spectrometer. Assignments and intensity determinations were performed by the analysis of the isotope patterns assuming a natural isotope distribution. Magnetic measurements of glassy frozen solns. were performed as described in [12]. MeOH was dried according to [13]. Analyses for C,H,N: *D. Manser*, Laboratorium für Organische Chemie, ETH-Zürich. Fe: tris(phenanthrolin)iron [14]. Cl: argentometric titration (Ag/AgCl electrode). Cu: complexometric titration (edta, PAN) [15].

[Fe(edta)H]·2H$_2$O was prepared according to [16]. Anal. calc. for $C_{10}H_{17}N_2O_{10}Fe$: C 31.52, H 4.50, N 7.35, Fe 14.65; found: C 31.23, H 4.45, N 7.13, Fe 14.46.

tdci was prepared according to [3]. Anal. calc. for $C_{12}H_{27}N_3O_3$: C 55.15, H 10.41, N 16.08; found: C 54.89, H 10.51, N 15.97.

[Fe(tdci)$_2$]Cl$_3$. Anh. $FeCl_3$ (9.73 g) was added to MeOH (300 ml). The slurry was allowed to stand for 14 h and then decanted. The content of the clear soln. was found to be 14.7 mg Fe/g. This soln. (46 g; 12.1 mmol Fe) was added to a soln. of 6.64 g (25.4 mmol) of tdci dissolved in 20 ml of MeOH. H_2O (12 ml) was then added to the resulting soln., and a white solid precipitated which was dissolved again by gentle heating. The soln. was allowed to cool down yielding pale yellow crystals which were dried *in vacuo* over P_2O_5. Yield: 70%. Anal. calc. for $C_{24}H_{54}Cl_3FeN_6O_6 \cdot 0.5\,H_2O$: C 41.54, H 7.99, N 12.11; found: C 41.47, H 7.60[3]), N 11.99. The dried product proved to be hygroscopic. The equilibration on air resulted in a defined hydrate. Anal. calc. for $C_{24}H_{54}Cl_3FeN_6O_6 \cdot 14.5\,H_2O$: C 30.47, H 8.84, N 8.88, Cl 11.24, Fe 5.90; found: C 30.77, H 8.19[3]), N 8.84, Cl 11.45, Fe 5.90.

[Al(tdci)$_2$]Cl$_3$. Anh. $AlCl_3$ (4.94 g) was added to solid (liquid N_2) MeOH (50 ml). The mixture was allowed to warm up slowly to r.t., and a clear colorless soln. was obtained. tdci (4.83 g, 18.5 mmol) was then dissolved in 30 ml of MeOH, and 12.2 ml (9.0 mmol Al) of the $AlCl_3$ soln. were added. Upon addition of 3 ml of H_2O, a colorless solid was obtained which was worked up as described for the corresponding Fe^{III} complex. Yield: 75%. ^{1}H-NMR (D_2O): 4.82 (*s*, HDO); 4.77 (*m*, 3 H); 3.03 (*s*, 18 H); 2.99 (*m*, 3 H). ^{13}C-NMR (D_2O): 69.9; 66.1; 44.0. Anal. calc. for $C_{24}H_{54}AlCl_3N_6O_6 \cdot 14.5\,H_2O$: C 31.43, H 9.12, N 9.16; found: C 31.63, H 8.49[3]), N 9.03.

Potentiometric 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 0.1M KNO_3 or 0.1M KCl, respectively. The sample solns. were titrated with 0.1M KOH, 0.05M HCl/0.05M KCl, or 0.1M HCl, dispensed from a *Metrohm 665* piston buret. The ionic strength was adjusted to 0.1 by adding appropriate amounts of KCl or KNO_3 to the test solns. The potential measurements were performed in a water-jacketed beaker at 25° under N_2 (washed previously with an aq. soln. of 0.1M KCl or 0.1M KNO_3). The stability of the electrodes was checked by two calibration titrations prior and after each measurement. For calibration, 100 ml of 2 mM HNO_3 or 2 mM HCl was titrated with 0.1M KOH and the potentials were corrected for liquid junction effects according to [17].

The p*K* determination of the ligand in 0.1M KCl was performed by an alkalimetric titration of an anal. pure sample of $H_3(tdci)Cl_3 \cdot 2H_2O$ [3] (2 mM) which was free of stereoisomers according to its ^{1}H- and ^{13}C-NMR spectrum. A corresponding mixture of tdci (2 mM) and HNO_3 (6.52 mM) was used for the pK determination in 0.1M KNO_3. The stability constants of the Fe^{III} and Al^{III} complexes were performed by acidimetric titrations of solns. containing 1 mM of the complex dissolved as crystalline, anal. pure $[M(tdci)_2]Cl_3 \cdot 14.5\,H_2O$ (M = Al, Fe). Since the equilibration was slow, a batch method was applied, using individually sealed and thermostated sample solns. The edta/tdci exchange titration was performed by a batchwise titration of solns. containing 1 mM $[Fe(edta)]^-$ (applied as crystalline, anal. pure $[Fe(edta)H] \cdot 2H_2O$) and 2 mM $H_3(tdci)Cl_3 \cdot 2H_2O$. Appropriate amounts of KOH were then added, and the solns. were allowed to equilibrate for 48 h. The measurements of the Cu^{II} complexes were performed by an alkalimetric titration of a soln. containing 1 mM $Cu(NO_3)_2$, 2 mM tdci, and 6.68 mM HNO_3. The titration curves of the metal complexes are presented in *Fig. 1*.

Calculation of Equilibrium Constants. In this work, all constants are concentration quotients and pH is defined as $-\log[H]$. The value for the ionic product of H_2O ($I = 0.1$, 25°) was obtained from the calibration titration as $pK_w = 13.79$. The p*K* values of $H_3(tdci)^{3+}$ were calculated using the computer program PKAS [18] [19]. The formation constants of the metal complexes were evaluated by the computer program SUPERQUAD [8]; final refinements were performed using the computer program BEST [18] [20] for an optimal fit σ_{pH} (*Table 2*). For the evaluation of the edta/tdci exchange titration, the following constants for edta were applied with fixed values: p*K* values: 2.1, 2.78, 6.18, and 10.26 [21], $\log K_{Fe(edta)} = 25.0$ [22], and $pK_{Fe(edta)} = 7.37$ [23]. No significant difference was found by using either BEST or SUPERQUAD for the calculation of the equilibrium constants. However, a comparison of the constants evaluated from different titrations exhibited clearly that the standard deviations from SUPERQUAD, calculated from one single curve are underestimated. The standard deviations, presented in *Table 2* are five times higher than those given by SUPERQUAD.

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[3]) The H content of the solid Al^{III} and Fe^{III} complexes of tdci was generally too low, indicating a systematic error of the analysis (interference of solid metal oxides, formed during the combustion?).

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