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Has the Affinity of High Spin Fe^{III} for sp^3 Nitrogen Donors Been Underestimated?

Kaspar Hegetschweiler,* Michele Ghisletta, Lorenza Hausherr-Primo, and Thomas Kradolfer

Laboratorium für Anorganische Chemie, ETH-Zentrum,
CH-8092 Zürich, Switzerland

Helmut W. Schmalle

Anorganisch-Chemisches Institut, Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Volker Gramlich

Institut für Kristallographie und Petrographie, ETH Zentrum,
CH-8092 Zürich, Switzerland

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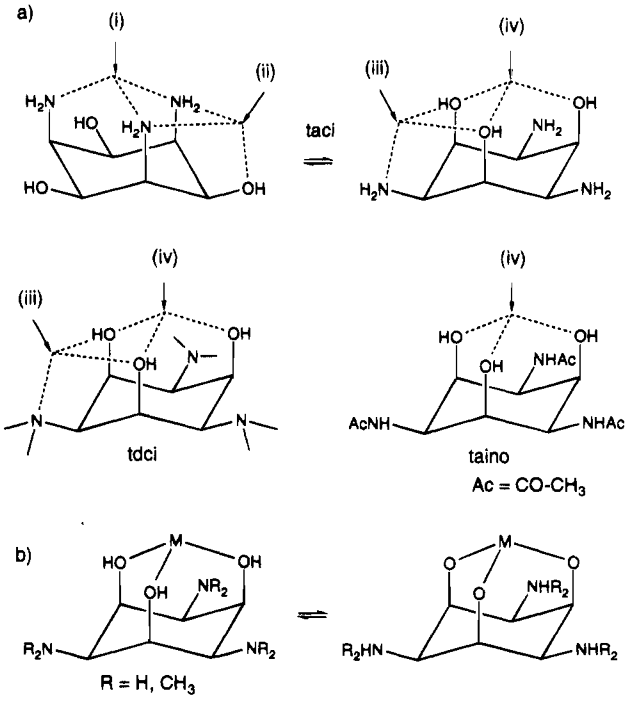
In a series of recent publications we demonstrated that 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) is a useful ligand to elucidate the individual affinity of a metal ion for either nitrogen or oxygen donors.[1−5] Taci has four different binding sites which allow the coordination of a metal ion by three nitrogen atoms (i), one oxygen and two nitrogen atoms (ii), one nitrogen and two oxygen atoms (iii), or three oxygen atoms (iv) (Scheme 1a). Al^{III}, a very hard Lewis acid with a high preference for oxygen donors, forms a bis-type iv complex.[4] In contrast, softer metal ions like Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Tl^{III} all bind exclusively to the nitrogen donors of taci forming a bis-type i structure.[2,4,5] For Ga^{III}, an intermediate type i−type iv coordination with a GaN_3O_3 sphere has been observed.[4] Complex formation with Cr^{III} finally resulted in a mixture of the type i−type iv coordination and the bis-type iv coordination.[1] The versatility of taci is enlarged due to the possibility to coordinate in different tautomeric forms (Scheme 1b). It has been demonstrated that the divalent Mg^{II}, Ca^{II}, Sr^{II}, and Ba^{II} coordinate to OH groups,[5] whereas Al^{III}, Cr^{III}, and Ga^{III} are bound to the zwitterionic form of the ligand.[1,4] For these trivalent cations, a proton transfer from OH to NH_2 is observed, and these metal ions are coordinated to fully deprotonated alkoxo groups. In the present investigation we analyzed the interaction of Fe^{III} with taci. We also demonstrate that the type i coordination mode of the ligand, as well as its ability to coordinate in the zwitterionic form, is easily prevented by introducing suitable substituents to the nitrogen donors.

Scheme 1



Experimental Section

Ligands. 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci),[3] and 1,3,5-triacetamido-1,3,5-trideoxy-*cis*-inositol (taino)[6] were prepared according to the literature.

Metal Complexes. A mixture of $[Fe(taci)_2](NO_3)_3 \cdot 3H_2O$ (**1**) and $[H_{-1}Fe(taci)_2](NO_3)_2 \cdot 2H_2O$ (**2**) was obtained by adding $Fe(NO_3)_3 \cdot 9H_2O$ (1.0 mmol, dissolved in 5 mL of MeOH) to a solution of taci (2.1 mmol in 15 mL of MeOH). The resulting yellowish brown solid was filtered off. Yield: 75%. The solid was redissolved in H_2O and layered with EtOH. The resulting product consisted in single crystals of **1** and **2**. It was, however, not possible to distinguish the two compounds by the naked eye. $[Fe(tdci)_2]Cl_3 \cdot 14.5H_2O$ (**3**) was prepared as described previously.[7] $[H_{-3}Fe(taino)_2] \cdot 12H_2O$ (**4**) was obtained by adding a solution of $FeCl_3$ (4 mmol) and HCl (2 mmol) in 4 mL of H_2O to a solution of taino (8.8 mmol in 20 mL of H_2O). The resulting orange solution (pH 1) was neutralized with 14 mL of 1 M aqueous KOH. A yellow solid precipitated, which was filtered off from the colorless supernatant (pH 7.6). Single crystals were grown from EtOH/hexane. Yield: 65%. Satisfactory C, H, and N analyses were obtained for all compounds.

Mössbauer Spectroscopy. The spectra were measured at 200 K using a conventional spectrometer operating in a constant-acceleration mode and equipped with a ^{57}Co / Rh source and an Oxford bath cryostat.

Crystal Structure Determination. Diffraction data for compounds **1**, **2**, and **4** were collected on three different four circle diffractometers using graphite monochromatized Mo-Kα radiation at 20 °C (Table 1). 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. All data were corrected for Lorentz and polarization effects. A face indexed, numerical absorption correction was performed for **1** and **2**. Direct methods of the program SHELXTL PLUS[8] were used to solve the structures of **1** and **4**. The structure of **2** was solved by the Patterson routine of SHELXS86.[9] All non-hydrogen atomic positions were located in the difference Fourier map and were refined with anisotropic displacement parameters. The refinement was performed by using SHELXTL PLUS for **1** and **4** and SHELXL-93[10] for **2**. The hydrogen atoms of the complex molecules were all located in the difference Fourier map. For **1** and **4**, they were included in the refinement as fixed values with fixed isotropic displacement parameters. The hydrogen atomic positions of **2** were refined with variable isotropic displacement parameters. The atomic coordinates of **2** and **4** are presented in Table 2 and 3, respectively. Compound **1** proved to be isomorphous with the previously reported

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* To whom correspondence should be addressed.

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Ga complex; the coordinates are provided as supplementary material. Summarized bond lengths and angles are given in Table 4.

Table 1. Crystallographic Data for $[Fe(taci)_2](NO_3)_3{\cdot}3H_2O$ (**1**), $[Fe(taci)(H_{-1}taci)](NO_3)_2{\cdot}2H_2O$ (**2**), and $[H_{-3}Fe(taino)_2]{\cdot}12H_2O$ (**4**)

	1	**2**	**4**
chem formula	$C_{12}H_{36}FeN_9O_{18}$	$C_{12}H_{33}FeN_8O_{14}$	$C_{24}H_{63}FeN_6O_{24}$
cryst syst	triclinic	triclinic	trigonal
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)
a, Å	9.308(7)	9.752(3)	18.743(7)
b, Å	9.831(7)	9.765(4)	18.743(7)
c, Å	13.593(12)	13.765(6)	9.985(5)
α, deg	87.43(7)	73.40(3)	90
β, deg	89.07(7)	89.53(3)	90
γ, deg	85.40(6)	62.21(3)	120
V, $Å^3$	1239(2)	1099.2(7)	3038(2)
Z	2	2	3
D_{calc}, g cm^{-3}	1.74	1.72	1.436
diffractometer	Picker-Stoe	Enraf Nonius CAD-4	Syntex P21
transm: min, max	0.8539, 0.9522	0.8195, 0.9122	
no. of measd reflcns	4357	6656	2810
no. of unique reflcns	4357	6402, $R_{int} = 0.023$	880, $R_{int} = 0.060$
no. of obsd reflcns, $I > 2\sigma(I)$	3355	5248	784
no. of params	364	441	84
R^a	0.040	0.034	0.047

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

Table 2. Atomic Coordinates for $[Fe(taci)(H_{-1}taci)](NO_3)_2{\cdot}2H_2O$ (**2**)

atom	*x*	*y*	*z*	U_{eq},[a] $Å^2$
Fe(1)	0.04293(3)	0.05103(3)	0.24144(2)	0.0154(1)
O(12)	−0.0284(1)	−0.0016(1)	0.1289(1)	0.017(1)
O(14)	−0.0108(1)	0.2686(2)	0.1521(1)	0.020(1)
O(16)	−0.1623(1)	0.1248(1)	0.2872(1)	0.019(1)
N(11)	−0.3139(2)	0.0054(2)	0.1910(1)	0.025(1)
N(13)	−0.0497(2)	0.2539(2)	−0.0472(1)	0.022(1)
N(15)	−0.2977(2)	0.4770(2)	0.2313(1)	0.026(1)
C(11)	−0.3101(2)	0.1575(2)	0.1346(1)	0.020(1)
C(12)	−0.1753(2)	0.1196(2)	0.0707(1)	0.018(1)
C(13)	−0.1785(2)	0.2823(2)	0.0160(1)	0.019(1)
C(14)	−0.1601(2)	0.3642(2)	0.0920(1)	0.019(1)
C(15)	−0.2952(2)	0.3949(2)	0.1566(1)	0.021(1)
C(16)	−0.2967(2)	0.2361(2)	0.2132(1)	0.020(1)
O(22)	0.1576(2)	−0.1681(2)	0.5366(1)	0.026(1)
O(24)	0.3955(2)	−0.3888(2)	0.2741(1)	0.033(1)
O(26)	0.4297(2)	0.0711(2)	0.3075(1)	0.029(1)
N(21)	0.1385(2)	0.0891(2)	0.3695(1)	0.020(1)
N(23)	0.1228(2)	−0.1938(2)	0.3460(1)	0.020(1)
N(25)	0.2804(2)	−0.0455(2)	0.2063(1)	0.020(1)
C(21)	0.2924(2)	−0.0387(2)	0.4307(1)	0.019(1)
C(22)	0.2884(2)	−0.1978(2)	0.4837(1)	0.021(1)
C(23)	0.2794(2)	−0.2861(2)	0.4104(1)	0.020(1)
C(24)	0.4110(2)	−0.3128(2)	0.3449(1)	0.022(1)
C(25)	0.4164(2)	−0.1565(2)	0.2890(1)	0.019(1)
C(26)	0.4246(2)	−0.0725(2)	0.3650(1)	0.020(1)
N(1)	0.3657(2)	0.1919(2)	−0.0161(1)	0.027(1)
O(11N)	0.3533(2)	0.2137(2)	0.0688(1)	0.043(1)
O(12N)	0.2602(2)	0.1818(3)	−0.0585(2)	0.066(1)
O(13N)	0.4795(2)	0.1822(3)	−0.0590(1)	0.049(1)
N(2)	−0.1420(3)	−0.3488(3)	0.3900(2)	0.046(1)
O(21N)	−0.0873(3)	−0.3404(3)	0.3073(2)	0.066(1)
O(22N)	−0.1753(3)	−0.2337(3)	0.4237(2)	0.073(1)
O(23N)	−0.1652(4)	−0.4613(4)	0.4336(2)	0.106(1)
O(1W)	0.3341(4)	0.3132(3)	0.3932(2)	0.062(1)
O(2W)	0.0947(3)	0.4610(2)	0.1935(2)	0.056(1)

[a] $U_{eq} = {}^1/_3\Sigma\Sigma U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Table 3. Atomic Coordinates for $[H_{-3}Fe(taino)_2]{\cdot}12H_2O$ (**4**)

atom	*x*	*y*	*z*	U_{eq},[a] $Å^2$
Fe	0.0000	0.0000	0.0000	0.046(1)
O(1)	0.0762(1)	0.0923(1)	−0.1208(1)	0.031(1)
N	0.1629(2)	0.0269(2)	−0.2713(2)	0.038(1)
C(1)	0.0700(2)	0.0843(2)	−0.2641(2)	0.031(1)
C(2)	0.0829(2)	0.0136(2)	−0.3101(2)	0.032(1)
O(2)	0.2188(1)	0.0612(2)	−0.4763(2)	0.060(1)
C(3)	0.2253(2)	0.0488(2)	−0.3574(3)	0.040(1)
C(4)	0.3028(2)	0.0570(3)	−0.3021(3)	0.057(1)
O(1W)	−0.0346(2)	0.1944(2)	0.0305(3)	0.108(1)
O(2W)	−0.2089(2)	0.1230(2)	0.0077(2)	0.104(1)

[a] $U_{eq} = {}^1/_3\Sigma\Sigma U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Table 4. Selected Mean Bond Distances (Å) and Mean Bond Angles (deg) of the Compounds **1**−**4** with Mean Estimated Standard Deviations in Parentheses

	1	**2**	**3**[a]	4
Fe−O	1.96(1)	1.962(1)	2.011(3)	2.005(2)
Fe−N	2.17(1)	2.178(2)		
C−O(−Fe)	1.40(2)	1.411(2)	1.401(4)	1.438(3)
O−Fe−O[b]	92.1(4)	92.18(6)	87.4(1)	87.5(1)
N−Fe−N[b]	84.7(5)	84.77(7)		
C−O−Fe	117.1(8)	117.2(1)	121.3(2)	121.5(1)
C−N−Fe	120.6(9)	120.5(1)		

[a] From ref 11. [b] Intraligand.

Results

Ferric complexes of taci and tdci[7] were prepared by the simple combination of solutions containing Fe^{3+} on the one hand and the ligand (in slight excess) on the other. Both complexes are quite soluble in water (pH 7). The formation of solid hydrolysis products from such solutions was not observed. For the formation of the taino complex **4**, however, 3 equiv of NaOH must be added. In contrast to **1**, **2**, and **3**, this compound consists of neutral molecules. It is insoluble in water but can readily be dissolved in MeOH or EtOH. The two complexes $[Fe(taci)_2]^{3+}$ (**1**) and $[Fe(taci)(H_{-1}taci)]^{2+}$ (**2**) are structurally closely related (Table 4) and differ only in the degree of protonation. An ORTEP representation of **2** is depicted in Figure 1. The presence of only two counterions per Fe^{III} in **2** and the observation of only two hydrogen atomic positions in proximity to N(15) indicate the deprotonation of a peripheral noncoordinating ammonium group. This is also supported by the different lengths of the C−N bonds: N(11)−C(11) = 1.484(2) Å, N(13)−C(13) = 1.485(2) Å and N(15)−C(15) = 1.467(2) Å. In both complexes **1** and **2**, one of the ligands binds the ferric cation by three nitrogen donors, whereas the second is coordinated via three oxygen donors. The type iv coordination mode is coupled with a proton transfer from OH to NH_2. The X-ray structure of the tdci complex **3** has been published elsewhere.[11] In contrast to the taci complexes, Fe^{III} is exclusively bonded to the six oxygen donors of two tdci ligands. Both tdci molecules coordinate as zwitterions with deprotonated alkoxo groups and protonated dimethylammonium groups. An FeO_6 coordination has also been observed for the taino complex **4** (Figure 2). However, the Fourier synthesis clearly showed additional electron density in proximity of O(1). In agreement with the chemical formula $[H_{-3}Fe(taino)_2]$, we interpreted this peak as a H(−O) position. It was, however, not possible to localize the three missing hydrogen atoms unambiguously. Due to the high crystallographic symmetry with only one unique position for the six oxygen atoms, the compound was formulated as $[Fe(H_{-1.5}taino)_2]$. The H(−O) proton is involved in a short hydrogen bond to an adjacent water molecule.

The tdci complex **3** as well as a mixture of the taci complexes **1** and **2** were characterized by Mössbauer spectroscopy in the solid state and as frozen solutions (200 K, no external field). Characteristic differences could be observed for the MN_3O_3

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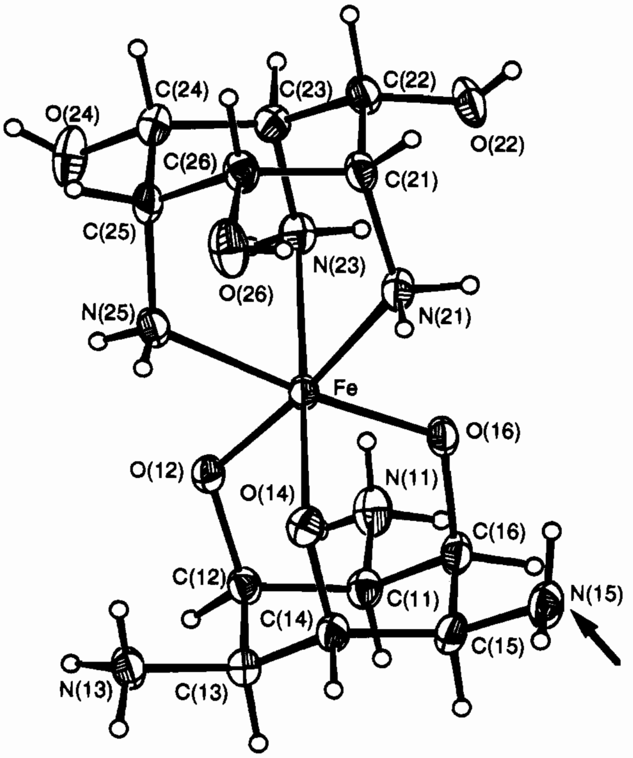

Figure 1. ORTEP drawing of $[Fe(taci)(H_{-1}taci)]^{2+}$ (**2**) with numbering scheme and vibrational ellipsoids at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary size. The missing proton is indicated by an arrow.

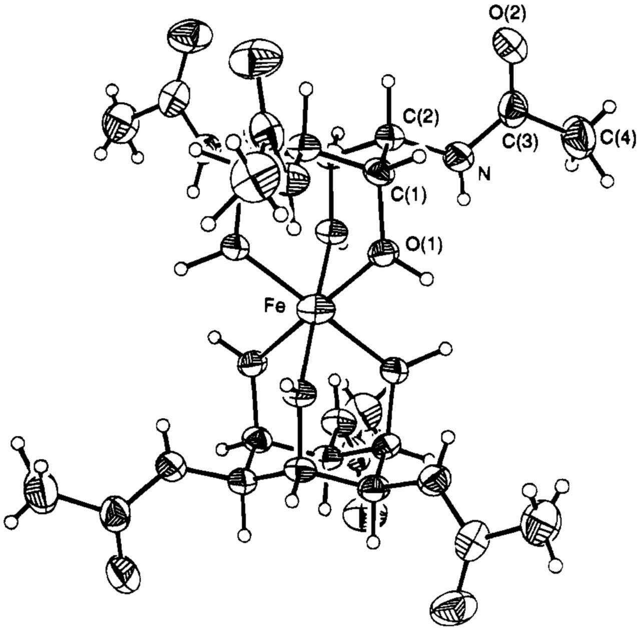

Figure 2. (a) ORTEP drawing of $[H_{-3}Fe(taino)_2]$ (**4**) with numbering scheme and vibrational ellipsoids at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary size.

coordination on the one hand and for the MO_6 coordination on the other, whereas the differences between the solid sample and the frozen solution were not significant. The spectra of **1** and **2** show a slightly asymmetric doublet ($\delta_{\alpha\text{-Fe}} = 0.43 \pm 0.05$ mm s^{-1}) for a crystalline sample and an almost symmetric doublet ($\delta_{\alpha\text{-Fe}} = 0.39 \pm 0.05$ mm s^{-1}) for the frozen solution. These data are in excellent agreement with those reported in ref 12 for Fe^{III} complexes with a related facial FeN_3O_3 coordination. The spectrum of complex **3**, however, shows a strongly broadened singlet for the crystalline sample ($\delta_{\alpha\text{-Fe}} = 0.74 \pm 0.03$ mm s^{-1}) as well as for the frozen solution ($\delta_{\alpha\text{-Fe}} = 0.75 \pm 0.05$ mm s^{-1}).

Discussion

Ligand Design. The high versatility of taci is based on the two almost isoenergetic chair conformations with either hydroxyl groups or amino groups in axial positions. Both forms are stabilized by intramolecular hydrogen bonding.[5,13] Selective ligands can readily be obtained by introducing appropriate bulky substituents to either the oxygen or nitrogen donors.[11] In tdci, the bulky dimethylamino groups impede chair conversion and only the conformation with three axial hydroxyl groups is available for metal binding. Since the tertiary amine represents a stronger base,[14] the coordination in the zwitterionic form is even more favored. Therefore, tdci can readily act as a tridentate oxygen ligand. The 3 equiv of base, required for the deprotonation of the hydroxyl groups, are already incorporated in the molecule.[7,11] For taino, the conformer with three axial nitrogen donors is also destabilized by steric repulsion. Moreover, the nitrogen atoms are now completely deactivated by electron-withdrawing groups. The formation of a zwitterion as well as any metal–nitrogen interactions are no longer possible. Consequently, taino binds a metal ion exclusively by the oxygen donors.[15] Metal binding to the deprotonated oxygen donors is, of course, still possible; however, in this case, taino coordinates as an anion and an external base has to be added for proton abstraction. According to a simple point charge model as used previously,[14] a much higher Coulombic energy is required for the deprotonation of taino compared with the formation of the zwitterionic forms of taci or tdci. These considerations have clearly been confirmed by the present study: In $[Fe(taci)_2]^{3+}$ and $[Fe(tdci)_2]^{3+}$, Fe^{III} coordinates to fully deprotonated alkoxo groups, whereas in $[H_{-3}Fe(taino)_2]$, the oxygens remain partially protonated. Hence, taci, tdci, and taino represent an instructive example for a set of ligands with an increasing amount of restrictions for metal binding (Scheme 1).

Complex Formation with High-Spin Fe^{III}. Fe^{3+} is considered to be a hard Lewis acid with a high affinity for oxygen donors but with a low tendency to coordinate sp^3 nitrogen donors.[16] In fact, the stability of high-spin Fe^{III} complexes with saturated amines is generally low, and the addition of aqueous ammonia to a solution of Fe^{3+} only precipitates the hydrous oxide. The oxophilic nature of Fe^{III} can be illustrated regarding reaction (1): $M\text{-}NH_3 + H_2O \rightarrow M\text{-}OH + NH_4^+$, $K(1) = [M(OH)][NH_4][M(NH_3)]^{-1}$, with log $K(1)$ values of 3.5 for Al^{III}, 3.2 for Fe^{III}, 2.4 for Ga^{III} and −0.3 for Tl^{III}.[17] It should be noted that the observed coordination modes of the previously described $[M(taci)_2]^{3+}$ complexes (M = Al, Ga and Tl), showing an AlO_6, GaN_3O_3 and TlN_6 coordination, are in excellent

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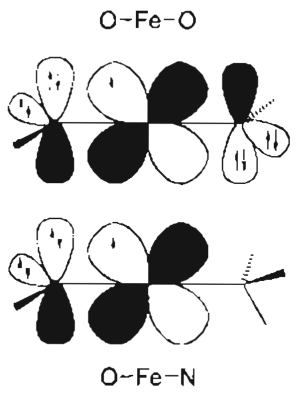
(17) The values of $K(1)$ have been calculated from the well-known formation constants of corresponding hydroxo and ammine complexes. For Al^{III}, Fe^{III}, Ga^{III}, and Tl^{III}, $\beta_1(M\text{-}OH)$ is known experimentally, see: Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1974–1989; Vols 1–6. The values of $\beta_1(M\text{-}NH_3)$ have been estimated, see: Mulla, F.; Marsicano, F.; Nakani, B. S.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 3076. Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.

Scheme 2



agreement with the corresponding values of $K(1)$.[4] Due to the similar values of Al^{III} and Fe^{III}, we expected the formation of a bis-type iv complex for Fe^{III}. However, single crystal analysis (Figure 1) and Mössbauer measurements of **1** and **2** exhibited unambiguously the presence of a type i–type iv coordination in the solid state as well as in aqueous solution. To our knowledge, $[Fe(taci)_2]^{3+}$ is the first example, where a ligand coordinates high-spin Fe^{3+} *exclusively* via sp^3 nitrogen donors in aqueous solution.[18]

It is interesting to note that the Fe–O bond distances of **3** and **4** are significantly longer compared with those of **1** and **2** (Table 4). We explain this effect as a weak *trans* influence of the coordinated alkoxo groups, i.e. by a partial release of electron density from the deprotonated oxygen donors to the metal center by a $p_\pi \rightarrow d_\pi$ type bonding (Scheme 2). Weak $p_\pi \rightarrow d_\pi$ bonding in a high spin Fe^{III} complex with a facial FeO_3N_3 coordination as well as structural criteria for such interactions have recently been reported.[12] In the compounds **1** and **2**, weak $p_\pi \rightarrow d_\pi$ bonding is indicated by the rather short Fe–O bonds and by a widening of the Fe–O–Fe angle. The C–O–Fe angle in **1**–**4** is close to 120°, as expected for an sp^2 hybridization of the oxygen atom (Table 4). However, it should be noted that the structural characteristics of **1** – **4** are not only a consequence of the electronic properties of the ligand–metal bonding. They are also significantly determined by geometric requirements of the rigid ligands.[5,11] On the other hand, weak $p_\pi \rightarrow d_\pi$ bonding is also indicated by the Mössbauer data. Obviously, an increasing number of coordinated alkoxo groups increases the electron density in the d-orbitals of the metal center, causing a stronger shielding of the Fe^{III} nucleus and thus more diffuse s-orbitals. The Mössbauer spectrum of **3** shows indeed a significantly higher isomer shift compared to **1** and **2**. Thus, the Mössbauer data together with the structural parameters clearly indicate a destabilization of the *trans* O–Fe–O structure by antibonding interactions. Consequently, the formation of an FeO_3N_3 structure, as observed in **1** and **2**, is favored. Such $p_\pi \rightarrow d_\pi$ interactions are, however, not significant for Al^{III}, as demonstrated by the AlO_6 coordination of $[Al(taci)_2]^{3+}$.[4]

The results of the present contribution are of importance with respect to the following considerations:

(i) A strongly basic oxygen donor like an alkoxide destabilizes the binding of an additional oxygen in the *trans* position of an octahedrally coordinated Fe^{III} complex. A pure σ-donor like a saturated amine is preferably bound in this position. Consequently, the unexpected preference $N > O$ is observed. Thus, the *general* statement, proposing a high affinity of Fe^{III} for oxygen ligands and a low affinity for sp^3 nitrogen donors must be revised.

(ii) In contrast to Fe^{III}, an AlO_6 coordination is obviously not destabilized, since d-orbitals of suitable energy are not available for such $p_\pi \rightarrow d_\pi$ interactions. Despite the oxophilic nature of both metal ions, as expressed by the similar values of $K(1)$, this effect might cause important differences in the coordination chemistry of the two metal cations. It is, for instance, interesting that anionic ferric hydroxo complexes $[Fe(OH)_n]^{3-n}$ ($n > 3$) play only a minor role in the aqueous chemistry of Fe^{3+}, whereas $[Al(OH)_4]^-$ is a dominant species in alkaline aqueous solutions.[19]

(iii) A facial FeO_3N_3 coordination has been observed in a variety of stable complexes,[20] as well as in metalloproteins.[21] The present study gives also a possible explanation for the particular stability of such a structure.

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Supplementary Material Available: Tables SI–SVI, listing crystallographic data, atomic coordinates of compound **1**, anisotropic displacement parameters, positional parameters of hydrogen atoms, bond distances and bond angles, and Figure S1, showing an ORTEP drawing of compound **1** (11 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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[18] Several ferric hexaamine complexes are known, and some of them are stable in aqueous solution. These complexes contain, however, low-spin Fe^{III}. See for example: (a) Bernhardt, P. V.; Comba, P.; Hambley, T. W.; Lawrance, G. A. *Inorg. Chem.* **1991**, *30*, 942. (b) Pohl, K.; Wieghardt, K.; Kaim, W.; Steenken, S. *Inorg. Chem.* **1988**, *27*, 440.

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