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Complex Formation of Vanadium(IV) with 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol and Related Ligands[†]

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The complex formation of vanadium(IV) with 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) and 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci) was studied in aqueous solution and in the solid state. The formation constants of $[V^{IV}O(taci)]^{2+}$, $[V^{IV}O(tdci)]^{2+}$, and $[V^{IV}(tdci)_2]^{4+}$ and of the deprotonation product $[V^{IV}(tdci)_2H_{-1}]^{3+}$ were determined (25 °C, 0.1 M KNO_3). Cyclic voltammetry measurements established a reversible one-electron transfer for the $[V^{IV}(tdci)_2H_{-m}]^{(4-m)}$/$[V^{III}(tdci)_2H_{-n}]^{(3-n)}$ couple ($0 \leq n, m \leq 6$) with a strongly pH-dependent $E^{1/2}_{obs}$ (+0.15 V at pH 5, –0.57 V at pH 13.5). Slightly more negative potentials were measured for the taci complexes. An additional quasi-reversible electron transfer at strongly positive potentials (1.2–0.5 V) was assigned to the $[V^{V}(taci)_2H_{-m}]^{(5-m)}$/$[V^{IV}(taci)_2H_{-n}]^{(4-n)}$ couple. The structures of $[V^{IV}(taci)_2](SO_4)_2\cdot 12H_2O$ (**1**), $[V^{IV}(tdci)_2][V_4{}^{V}O_{12}]\cdot 14.5H_2O$ (**2**), and $[V^{IV}(tdci)_2H_{-1}]Cl_3\cdot 15H_2O$ (**3**) were determined by single-crystal X-ray analysis. The cations of **1**–**3** exhibit a structure of approximate D_{3d} symmetry. The vanadium centers have an almost regular octahedral geometry. The coordinated oxygen donors are deprotonated, and their protons are transferred to the amino groups which act as internal bases. For both ligands, EPR measurements support the formation of non-oxo V^{IV} complexes, with a d_{z^2} ground state, in aqueous solution above pH 7. The spectral features are indicative of hexacoordinated complexes with a geometry distorted toward a trigonal prism. Finally, a mechanism is proposed for the decomposition of $[V^{IV}L_2H_{-x}]^{(4-x)}$ (L = taci and tdci) in strongly alkaline media (pH ≈ 13).

Introduction

The chemistry of vanadium(IV) is dominated by the oxovanadium (VO^{2+}) cation. Only a few non-oxo complexes have been fully characterized. The biological significance of non-oxo vanadium centers was illustrated previously,[1] and complexes of this type were reported for amavadin, a low molecular weight V^{IV} compound with mixed carboxylate–hydroxylamine coordination, present in mushrooms of the genus *Amanita*[2] and in the cofactor in vanadium nitrogenase.[3]

Tris chelated non-oxo vanadium(IV) complexes with coordination modes VN_6,[4] VO_3S_3,[5] VS_6,[6] VO_6,[7] and VO_4N_2[8]

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[†] 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol, a Ligand with a Remarkable Versatility for Metal Ions. XI. Part X: ref 29.

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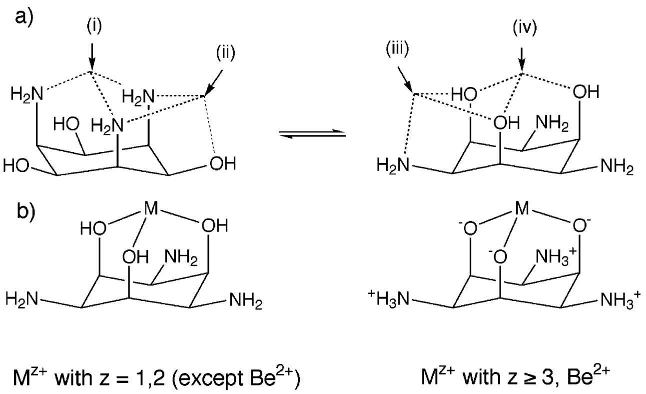
were reported. To our knowledge only five of them, all with a VO_4N_2 coordination,[8e−8h] are bis complexes of tridentate ligands. Generally, six-coordinate non-oxo complexes of V^{IV} exhibit a severe distortion from octahedral geometry. With ligands forming a five-membered chelate ring such as *o*-catechols, *o*-mercaptophenols, and dithiolenes, the geometry is close to a trigonal prism and there is a switch of the ground state from d_{xy} to d_{z^2}.[9] The twist angle between the triangular faces of the coordination polyhedron is ca. 0° in [V^{IV}(dithiolene)$_3$],[6c] 3.0° in [V^{IV}(*cis*-1,2-diphenylethene-1,2-dithiolato)$_3$],[6d] 44.5° in [V^{IV}(maleonitriledithiolato)$_3$]$^{2-}$,[6e] and 56.0° in [V^{IV}(acetylacetonato)$_3$]$^{+}$.[10]

Scheme 1



M^{z+} with z = 1,2 (except Be^{2+}) M^{z+} with z ≥ 3, Be^{2+}

1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (taci) is a tridentate ligand which can bind a metal center through an {N,N,N}, {N,N,O}, {N,O,O}, or {O,O,O} mode (indicated as i−iv in Scheme 1).[11] The {O,O,O} donor set is somewhat harder than the {N,N,N} set. Therefore, soft metal ions such as Ni^{II}, Cu^{II} and Zn^{II} prefer an {N,N,N} coordination,[12] while a hard ion like Al^{III} preferentially binds to the three oxygen donors.[13] Complexes of type iv with a highly charged cation can further be stabilized by an intramolecular transfer of the protons from oxygen to nitrogen donors (generation of a zwitterionic form with the amino groups serving as a base). For 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci) the bulky dimethylamino groups enforce the conformation with the $-N(CH_3)_2$ groups in an equatorial position. Therefore, tdci is a selective ligand for hard and highly charged metal ions.[14] Strong interactions with selective binding of the metal center to the alkoxo groups are thus expected for the V^{IV}−taci and V^{IV}−tdci systems. We report here synthetic, potentiometric, spectroscopic, electrochemical, and structural studies on V^{IV}−taci and V^{IV}−tdci systems and describe the first examples of a bis chelated non-oxo complex with the V^{IV} center bonded exclusively to six oxygen donors.

Experimental Section

Materials, Instrumentation, and Analyses. Taci and tdci were prepared as described.[15] All other chemicals were commercially available products of reagent grade quality. IR spectra were recorded on a Bruker Vector 22 FT IR spectrometer equipped with a Golden Gate ATR unit. The UV−vis spectra of the spectrophotometric titrations (next section) were recorded using a diode array spectrophotometer (J&M, Tidas-UV/NIR/100-1) combined with an immersion probe (Hellma); the spectra of the solid samples were measured in H_2O using an Uvikon 941 spectrophotometer. C, H, N-analyses were performed by H. Feuerhake (Institut für Anorganische Chemie, Universität des Saarlandes). ICP-MS measurements (determination of V and Cl) were carried out by P. Weis (Prof. H. P. Beck, Institut für Anorganische und Analytische Chemie at the Universität des Saarlandes).

Potentiometric and Spectrophotometric Titrations. All titrations of the V^{IV}−tdci and V^{IV}−taci systems were performed at 25 °C/0.1 M KNO_3 in a batchwise manner.[14] Each titration curve consisted of 18−24 data points, and each point corresponded to an individual 10-mL sample, sealed in a double-jacketed beaker. The samples were allowed to equilibrate for 7−14 days. The pH was measured with a Metrohm 713 pH/mV-meter and a Metrohm combined glass electrode (internal Ag/AgCl reference), which was calibrated by acid−base titrations. For the V−taci system, the total

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vanadium to total taci molar ratio in the two independent experiments was 1:4. The V−tdci system was investigated by three independent batches with total vanadium to total tdci molar ratios of 1:2, 1:3, and 1:4. Each sample of the 1:3 V−tdci batch was also investigated spectrophotometrically (350−700 nm).[16]

Calculation of Equilibrium Constants. All equilibrium constants were calculated as concentration quotients with pH = −log [H$^+$] using the computer program HYPERQUAD.[17] The pK_w (13.79),[18] the pK_a values of tdci (5.93, 7.64, 9.68)[19] and taci (5.95, 7.40, 8.90),[12] and the total concentrations of V, L, and H$^+$ were treated as fixed values. The hydrolytic species [V^{IV}O(OH)]$^+$ (log β_{10-1} = −5.94),[20] [(V^{IV}O)$_2$(OH)$_2$]$^{2+}$ (log β_{20-2} = −6.95),[20] [V^{IV}O(OH)$_3$]$^-$ (log β_{10-3} = −18.0),[21] and [(V^{IV}O)$_2$(OH)$_5$]$^-$ (log β_{20-5} = −22.0)[21] were assumed with fixed formation constants. For [V^{IV}O(OH)]$^+$ and [(V^{IV}O)$_2$(OH)$_2$]$^{2+}$ the values of the formation constants were adjusted to the appropriate ionic strengths by use of the Davies equation.[22] However, all the simple hydrolytic species did not form to any significant extent. In the final evaluation the three titration curves of the V−tdci system were combined to one data set and evaluated together. Similarly the two curves of the V−taci system were evaluated in one step. The spectroscopic data for the V−tdci system were evaluated using the computer program SPECFIT.[23] For this purpose, the spectrum of [V^{IV}O(H$_2$O)$_5$]$^{2+}$ was measured separately and was imported without refinement. Free tdci and its protonation products H$_x$tdci^{x+} do not absorb at the investigated wavelengths. Due to very weak absorption, [V^{IV}O(tdci)]$^{2+}$ was considered colorless as well.

EPR Measurements. All the solutions were prepared by dissolving first VOSO$_4$·5H$_2$O in H$_2$O (4 mM). The ligand was then added until an appropriate ligand to metal molar ratio was reached. The solutions were stirred and handled under a flow of Ar. Anisotropic EPR spectra were recorded on aqueous solutions with an X-band (9.15 GHz) Varian E-9 spectrometer at 120 K or at room temperature. As usual for low-temperature measurements, a few drops of DMSO were added to the samples to ensure a good glass formation. The EPR spectra of the non-oxo complexes were simulated with the computer program Bruker WinEPR SimFonia at a microwave frequency of 9.15 GHz. The line widths in the *x*, *y*, and *z* directions were 1, 5, and 1 mT for taci and 1, 5, and 0.8 mT for tdci. The Lorentzian/Gaussian ratio was 1.00 for both systems.

The decomposition of the non-oxo complex [V^{IV}(tdci)$_2$H$_{-x}$]$^{(4-x)}$ was studied using a solution of 0.05 mmol of VOSO$_4$·5H$_2$O in 50 mL of H$_2$O. Tdci (0.2 mmol) was added, and the pH was adjusted to 12.55, 13.00 or 13.55 with 1 M KOH. EPR spectra recorded at 120 K were used to monitor the [V^{IV}(tdci)$_2$H$_{-x}$]$^{(4-x)}$ concentration as a function of time. The intensity of the $M_I = -5/2$ perpendicular component of the anisotropic spectrum was taken as an approximate measure of the species concentration.

Electrochemistry. Cyclic voltammograms were recorded in 0.1 M KNO$_3$, using a BAS C2 cell, a BAS 100B/W 2 potentiostat, a Pt counter electrode, and an Ag/AgCl reference at ambient temperature (23 ± 3 °C). The pH was adjusted using 3-(cyclohexylamino)propanesulfonic acid (CAPS) and 3-morpholinopropanesulfonic acid (MOPS) as buffers. The total vanadium concentration was 0.01 M, and the total ligand concentration 0.04 M. Measurements at positive potentials (E > 200 mV, V^V/V^{IV} couple) were performed using a Pt working electrode. The range with negative potentials (E < 200 mV, V^{IV}/V^{III} couples) was investigated using a Hg (hanging drop) working electrode. All potentials were calculated relative to the normal hydrogen electrode (NHE), with a value of +0.46 V for the [Fe(CN)$_6$]$^{3-/4-}$ couple (0.01 M NaOH).

Preparation of [V^{IV}(taci)$_2$](SO$_4$)$_2$·4H$_2$O. VOSO$_4$·5H$_2$O (85 mg, 336 μmol) was added to a solution of taci·3HCl·1.5H$_2$O (200 mg, 638 μmol) in H$_2$O (2.5 mL). To the resulting blue suspension was added aqueous KOH (0.1 M) until a clear yellow solution was obtained (the amount of KOH was about 12−14 mL, and the final pH was 7). The solution was refluxed for 30 min and then allowed to cool slowly to room temperature. Yellow crystals formed (98 mg, 43%), which were dried in vacuo. Anal. Calcd for C$_{12}$H$_{38}$N$_6$O$_{18}$S$_2$V (M_r = 669.54): C, 21.53; H, 5.72; N, 12.55. Found: C, 21.31; H, 5.89; N, 12.78. UV/vis: λ_{max} (log ϵ) = 369 nm (3.2), 289 nm (3.4), 216 nm (3.7). IR (cm^{-1}): 2879 br, 1623, 1518, 1396, 1364, 1212, 1025, 887, 769.

Preparation of [V^{IV}(tdci)$_2$][V$^V_4$O$_{12}$]·8H$_2$O. Tdci·3HCl·2H$_2$O (100 mg, 246 μmol) was dissolved in a mixture of H$_2$O (2 mL) and EtOH (6 mL). Na$_3$VO$_4$ (90 mg, 489 μmol) was added. The mixture was stirred until complete dissolution. The clear yellow solution was evaporated slowly in air to a final volume of 1 mL. A small amount of yellow crystals formed (36 mg, 33%), which could be used for the X-ray diffraction study. A vacuum-dried sample was used for elemental analysis. Anal. Calcd for C$_{24}$H$_{70}$N$_6$O$_{26}$V$_5$ (M_r = 1113.56): C, 25.89; H, 6.34; N, 7.55. Found: C, 25.75; H, 6.11; N, 7.63. IR (cm^{-1}): 3030, 1462, 1410, 1186, 1159, 1113, 999, 903, 768.

Preparation of [V^{IV}(tdci)$_2$H$_{-2}$]Cl$_2$·10H$_2$O. To a solution of tdci·3HCl·2H$_2$O (100 mg, 246 μmol) in H$_2$O (5 mL) were added VOSO$_4$·5H$_2$O (62 mg, 245 μmol) and 2 mL of 2 M aqueous NaOH (pH ≈ 10). A color change to orange was observed. The solution was allowed to evaporate slowly at room temperature in air to a final volume of 0.5 mL. A small amount of orange crystals (16 mg, 8%) formed which could be used for the single-crystal X-ray diffraction study. The crystals disintegrated rapidly on air (loss of water of crystallization). For the elemental analysis, a small sample was dried in vacuo. The resulting powder was then allowed to equilibrate open to the air at ambient conditions for a few days until a constant weight was reached. Anal. Calcd for C$_{24}$H$_{72}$Cl$_2$N$_6$O$_{16}$V (M_r = 822.71): C, 35.04; H, 8.82; N, 10.21; V, 6.19; Cl, 8.62. Found: C, 35.13; H, 10.10; N, 10.40; V, 6.39; Cl, 8.96. IR (cm^{-1}): 3316 br, 1634, 1462, 1402, 1359, 1284, 1182, 1155, 1108, 1000, 953, 886, 833, 543.

Crystal Structure Determination. X-ray diffraction data for [V^{IV}(taci)$_2$](SO$_4$)$_2$·12H$_2$O (**1**), [V^{IV}(tdci)$_2$][V$^V_4$O$_{12}$]·14.5H$_2$O (**2**), and [V^{IV}(tdci)$_2$H$_{-1}$]Cl$_3$·15H$_2$O (**3**) were collected with a STOE STADI4 four circle diffractometer (**1**, **2**) or with a STOE IPDS diffractometer (**3**), using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Possible disintegration (loss of water of crystallization) was prevented by sealing the crystals in a glass capillary. Additionally, complex **3** was cooled to 215 K. A compilation of the crystallographic data is given in Table 1. No indication of decay was

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Table 1. Crystallographic Data for $[V^{IV}(taci)_2](SO_4)_2 \cdot 12H_2O$ (**1**), $[V^{IV}(tdci)_2][V^{V}_4O_{12}] \cdot 14.5H_2O$ (**2**), and $[V^{IV}(tdci)_2H_{-1}]Cl_3 \cdot 15H_2O$ (**3**)

	1	**2**	**3**
empirical formula	$C_{12}H_{54}N_6O_{26}S_2V$	$C_{24}H_{83}N_6O_{32.5}V_5$	$C_{24}H_{83}Cl_3N_6O_{21}V$
fw	813.67	1230.66	949.25
cryst system	monoclinic	monoclinic	trigonal
space group	$P2_1/c$ (No. 14)	$I2/m$ (No. 12)	$R\bar{3}$ (No. 148)
a, Å	14.145(3)	13.720(3)	17.371(4)
b, Å	11.361(2)	14.309(3)	17.371(4)
c, Å	21.047(4)	14.430(3)	13.077(8)
α, deg	90	90	90
β, deg	91.98(3)	108.40(3)	90
γ, deg	90	90	120
V, Å^3	3380.3(11)	2688.1(10)	3417(2)
Z	4	2	3
T, K	293(2)	293 (2)	215(2)
D_{calcd}, g cm^{-3}	1.599	1.520	1.384
μ, mm^{-1}	0.520	0.930	0.471
cryst size, mm	0.4 × 0.3 × 0.3	0.5 × 0.4 × 0.4	0.15 × 0.15 × 0.15
θ_{min}, θ_{max}, deg	1.94, 25.00	1.79, 25.00	2.06, 24.12
transm (min, max)	0.9141, 0.9971	0.9256, 0.9979	
data set	−16/16; 0/13; −25/0	−16/15; 0/17; 0/17	−19/19; −19/19; −14/14
tot./unique data	5965, 5965	2470, 2470	7218, 1196
params/restraints	640/0	260/0	108/0
R_1, wR_2 [$I > 2\sigma(I)$]	0.0360, 0.0946	0.0542, 0.1688	0.0600, 0.1541
R_1, wR_2 (all data)	0.0449, 0.1034	0.0636, 0.1814	0.1028, 0.1740
max peak/hole, e Å^{-3}	0.397/−0.385	1.034/−0.361	0.292/−0.843

observed for any of the crystals during data collection. All data sets were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied to the data sets of **1** and **2** (SADABS). The structures were solved by direct methods[24] and refined by full-matrix least-squares calculations on F^2.[25] Anisotropic displacement parameters were used for all non-hydrogen atoms. The H atoms of **1** were located and refined with isotropic displacement parameters. The H(−C) positions in **2** and **3** were calculated using a riding model with $U_{iso} = 1.2U_{eq}$ of the pivot atom.

Results and Discussion

Crystal Structures. Single crystals of $[V^{IV}(taci)_2](SO_4)_2 \cdot 12H_2O$ (**1**), $[V^{IV}(tdci)_2][V^{V}_4O_{12}] \cdot 14.5H_2O$ (**2**), and $[V^{IV}(tdci)_2H_{-1}]Cl_3 \cdot 15H_2O$ (**3**) were grown from aqueous solutions. The tdci complex **2** was obtained from Na_3VO_4 as vanadium source. Obviously V^V was partially reduced to V^{IV} in the course of the reaction, probably with tdci acting as reducing agent. A view of the $[V^{IV}(taci)_2]^{4+}$ cation is shown in Figure 1. The tdci complexes **2** and **3** have a closely related geometry. A selection of bond lengths and angles for all three cations is listed in Table 2. The three mononuclear bis complexes represent examples of the rather rare octahedral non-oxo compounds of V^{IV}, with the vanadium center bonded exclusively to the oxygen donors of two tripodal ligand moieties. The alcoholic groups are deprotonated, and their protons transferred to the peripheral amino groups. In the two 4+ cations of compounds **1** and **2** the ligands are therefore present in their neutral zwitterionic forms (Scheme 1b). The protonated amino groups are, however, weakly acidic and can be further deprotonated in alkaline solution (vide infra). The $[V^{IV}(tdci)_2H_{-1}]^{3+}$ cation of compound **3,** which crystallized around pH 10, is an illustrative example for such a partially deprotonated species.

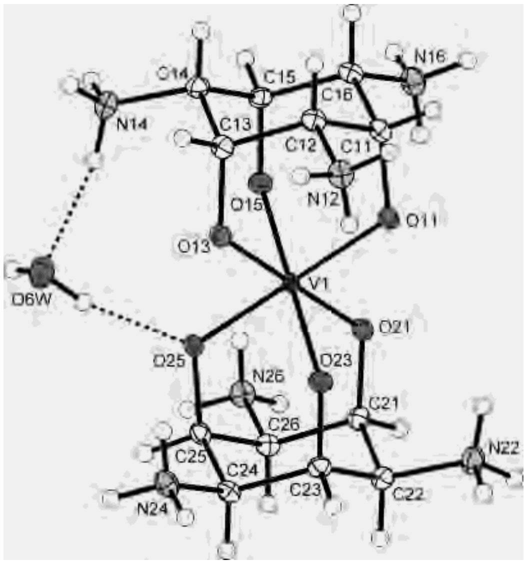

Figure 1. Molecular structure of $[V^{IV}(taci)_2]^{4+}$ with numbering scheme and displacement ellipsoids at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary size. In addition, one of six water molecules, which surround the equator region of the complex cation, is shown.

Table 2. Summary of Bond Distances (Å) and Angles (deg) for the VO_6 Moieties of $[V^{IV}(taci)_2](SO_4)_2 \cdot 12H_2O$ (**1**), $[V^{IV}(tdci)_2][V^{V}_4O_{12}] \cdot 14.5H_2O$ (**2**), and $[V^{IV}(tdci)_2H_{-1}]Cl_3 \cdot 15H_2O$ (**3**)

			O−V−O		
complex		V−O	intraligand, cis	interligand, cis	interligand, trans
1	min	1.921(1)	88.59(7)	90.35(7)	179.20(6)
	max	1.939(1)	89.70(7)	91.64(7)	179.76(6)
	mean	1.929	89.13	90.87	179.57
2	min	1.927(3)	88.52(14)	91.17(10)	
	max	1.932(2)	88.83(10)	91.48(14)	
	mean	1.930	88.73	91.27	180.0
3		1.921(3)	88.73(11)	91.27(11)	180.0

The cations of **1**−**3** all exhibit a double-adamantane structure of approximate D_{3d} symmetry, with the vanadium centers in an almost regular octahedral coordination environ-

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(24) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(25) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

ment. The V$-$O$_{alkoxo}$ bond distances fall in the range 1.92$-$1.94 Å. These values are in good agreement with a +IV valency for the vanadium centers (bond valence calculations indicate values of 4.06, 4.05, and 4.14 for **1**$-$**3**, respectively).[26] In the corresponding $[V^{III}(tdci)_2]^{3+}$ cation, the V$-$O distance is $-$ as expected $-$ somewhat longer;[27] the observed value of 1.965(2) Å is consistent with a valency of +III.

As it is known, an octahedron can be viewed as a special case of a D_{3d}-trigonal antiprism, consisting of two parallel and exactly staggered equilateral triangles. Several parameters allow one to distinguish a trigonal prism from an octahedron.[28] Particularly, the twist angle Φ is 0° for a trigonal prism with the two triangles eclipsed and 60° for a regular octahedron with the two triangles staggered. For **1**$-$**3**, the triangles are defined by the three oxygen donors of each ligand molecule. The corresponding parameters are listed in Table S1 (Supporting Information). The calculations show that the geometry is very close to a regular octahedron with Φ twist angles of 56.9, 55.3, and 55.4°, respectively.

The hydrophilic $[V^{IV}(taci)_2]^{4+}$ cation of **1** is a versatile building block for hydrogen-bonded networks.[29] The alkoxo groups serve as strong hydrogen acceptors, and the six peripheral ammonium groups, as hydrogen donors. A total of six water molecules are arranged around the equatorial region of $[V^{IV}(taci)_2]^{4+}$. All six water molecules donate a hydrogen atom to a coordinating alkoxo group and accept an "axial" hydrogen atom of an ammonium group (Figure 1). The formation of such a $[ML_2]^{4+}\cdot 6H_2O$ entity was previously observed for related taci and tdci complexes of trivalent metal ions.[13,14] Further hydrogen bonding in **1** resulted in a variety of cation$-$cation and cation$-$anion interactions. The cations are arranged in layers parallel to the crystallographic $a-b$ plane. Each $[V^{IV}(taci)_2]^{4+}\cdot 6H_2O$ entity has four nearest cationic neighbors with cation$-$cation interactions consisting of N$-$H$\cdots$O(H)$-$H$\cdots$O$_{alkoxo}$ bridges. The cation$-$anion interactions lead to chains along the crystallographic b axis. They are of the type N$-$H$\cdots$O$-$SO$_2$$-O\cdots$H$-N, O_{alkoxo}\cdots$H$-O-H\cdots$O(SO$_3$)$\cdots$H$-O-H\cdots$O$_{alkoxo}$, and O$_{alkoxo}\cdots$H$-O-H\cdots$O(H$_2$)$\cdots$H$-O-H\cdots$O$_{alkoxo}$. Further cross-linking of these chains parallel to the crystallographic c axis is achieved by additional anion$-$cation interactions of the type N$-$H$\cdots$O$-$SO$_2$$-O\cdots$H$-$N via the ($x$, 0.5 $-$ y, z + 0.5) glide plane.

The $[V^{IV}(tdci)_2]^{4+}$ cation is somewhat less hydrophilic than $[V^{IV}(taci)_2]^{4+}$ and, therefore, the hydrogen-bonded network is less complex. In analogy to the taci complex, $[V^{IV}(tdci)_2]^{4+}$ is surrounded by six water molecules which form a ring structure around the equator. Six additional water molecules give rise to a second hydration sphere. They are hydrogen bonded to the water molecules of the first sphere.[14] In **2**, the 4+ charge of the $\{[V^{IV}(tdci)_2]^{4+}\cdot 6H_2O\}\cdot 6H_2O$ aggregate is balanced by the well-known tetravanadate $[V_4O_{12}]^{4-}$ anion. The entire packing can be derived from a cubic face-centered (NaCl type) structure, with the cations and anions forming each a distorted densest sphere packing. Additional water molecules are located along the tetrahedral holes of this packing. The $[V_4O_{12}]^{4-}$ anion was located on a C_{2h} site. The crystallographic site symmetry did, however, not coincide with the molecular symmetry, and consequently the anion was found to be disordered. The disorder was described by two centrosymmetric, superimposed models of the anion with separate oxygen positions (occupancies = 0.5) but common vanadium positions (occupancies = 1.0; see Figure S2, Supporting Information). The cyclic structure of the $[V_4O_{12}]^{4-}$ anion with a centrosymmetric conformation is well established.[30] In **2**, one of the V$-$O$_{term}$ bonds appears to be unusually short (1.475(6) Å). This value is probably an artifact of the disorder and does not correspond to the real V$-$O distance.

The crystal structure of **3** is isotypic with the chloride salts of the Al, Fe, Ga, and In complexes $[M^{III}(tdci)_2]Cl_3\cdot 15H_2O$.[14] In all these structures the Cl$^-$ counterion and one of the water molecules share a position randomly. Since the charge of the cation can be compensated either by partial deprotonation of a zwitterionic tdci ligand or by incorporation of Cl$^-$, the amount of Cl cannot be established by charge balance considerations alone. The diffraction data for the vanadium complex could be refined either as $[V^{IV}(tdci)_2]Cl_4\cdot 13.5H_2O$, $[V^{IV}(tdci)_2H_{-1}]Cl_3\cdot 15H_2O$, or $[V^{IV}(tdci)_2H_{-2}]Cl_2\cdot 16H_2O$. Due to the rapid disintegration of the crystals, a direct analysis of Cl was not possible. The V:Cl ratio of the dried product was in the range of 1:2.0$-$1:2.5 (see previous section). However, this value does not necessarily reflect the Cl$^-$ content in the crystals, since some loss of HCl was observed during the drying procedure. The assignment with 3 Cl$^-$ counterions, as presented in Table 1, is based on a careful inspection of the electron density and minimization of the R factors.

Potentiometry and UV$-$Vis Spectrophotometry. In strongly acidic solution (pH < 3) vanadium(IV) exists as the pale blue VO^{2+}(aq) and the ligands are fully protonated (H_3L^{3+}). In slightly acidic solutions (4 < pH < 6), an almost colorless 1:1 complex $[V^{IV}OL]^{2+}$ is formed. At higher pH, this species is converted into the yellow bis complex $[V^{IV}L_2]^{4+}$, in which the ligands are present in the neutral zwitterionic form (Figure 1). The noncoordinating ammonium groups are then deprotonated stepwise, forming a series of products $[V^{IV}L_2H_{-x}]^{(4-x)}$. The fully deprotonated $[V^{IV}L_2H_{-6}]^{2-}$ species is finally formed in strongly alkaline solution (Scheme 2).

The formation constants and pH-dependent species distribution of vanadium(IV) complexes were investigated by potentiometric titrations. Since the bis complexes were of an intense yellow color, their formation could also be followed spectrophotometrically. The absorption at 370 nm, with an ϵ_{max} value of about 4000 M^{-1} cm^{-1}, originates from a metal-reduction charge-transfer transition which dominates

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(26) Brese, N. E.; Keeffe, M. O. *Acta Crystallogr., Sect. B* **1991**, *B47*, 192.

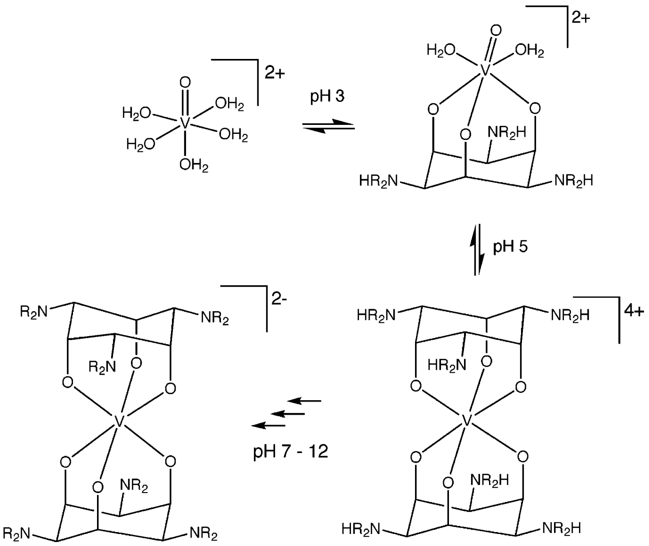
(27) Hegetschweiler, K.; Zubieta, J. Unpublished work.

(28) Avdeef, A.; Fackler Jr., J. P. *Inorg. Chem.* **1975**, *14*, 2002.

(29) Hegetschweiler, K.; Finn, R. C.; Rarig Junior, R. S.; Sander, J.; Steinhauser, S.; Wörle, M.; Zubieta, J. *Inorg. Chim. Acta* **2002**, *337*, 39.

(30) Zhang, Y.; Zapf, P. J.; Meyer, L. M.; Haushalter, R. C.; Zubieta, J. *Inorg. Chem.* **1997**, *36*, 2159.

Scheme 2. Reactions of the Vanadium(IV)−taci and Vanadium(IV)−tdci Systems in Aqueous Solution[a]



[a]The formal charges on the protonated nitrogen (+1) and deprotonated oxygen (−1) atoms are omitted for clarity.

Table 3. Experimental Data and Evaluated Formation Constants for the Potentiometric Titration of the Vanadium(IV)−tdci and Vanadium(IV)−taci System with 0.10 M KOH at 25 °C (0.1 M KNO_3)

exptl param	L = tdci			L = taci
tot. L:tot. V	2:1	3:1	4:1	4:1
tot. V, mM	0.9685	0.4867	1.9087	0.2734
pH range	3.22−6.00	3.60−6.06	2.94−6.16	3.8−6.4
no. of data pts	24	21	18	2 × 23
equilibratn time, h	168	168	168	288

	evaluated consts log $\beta_{xyz}{}^{a,b}$	
xyz/species	L = tdci	L = taci
110/$[VOL]^{2+}$	14.6(1)	13.1(1)
122/$[VL_2]^{4+}$	36.6(1)	
121/$[VL_2H_{-1}]^{3+}$	30.0(1)	28.7(2)
22−2/$[(VO)_2L_2(OH)_2]^{2+}$		20.3(3)

[a] pK_a values for tdci: 5.93, 7.64, 9.68.[19] pK_a values for taci: 5.95, 7.40, 8.90.[12] [b] $\beta_{xyz} = [(VO)_xL_yH_z][VO]^{-x}[L]^{-y}[H]^{-z}$.

the electronic absorption spectra in the visible region.[7a,b,31] However, the measurements were complicated by the observations that equilibration below pH 9 proved generally to be slow, and solid products precipitate around pH 4 (tdci) or pH 6 (taci). Moreover, some slow decomposition of the complexes was observed above pH 9, as indicated by fading of the yellow color with the final product being colorless (vide infra). The rate of this decomposition strongly depended on pH and temperature. Due to slow equilibration, complex formation in the pH range 3−7 was investigated by batch titrations. Precipitation was suppressed by raising the total ligand to total metal molar ratios to 2, 3, and 4 for tdci and 4 for taci. Moreover, the total metal concentration in the vanadium(IV)−taci system was kept below 0.3 mM (Table 3).

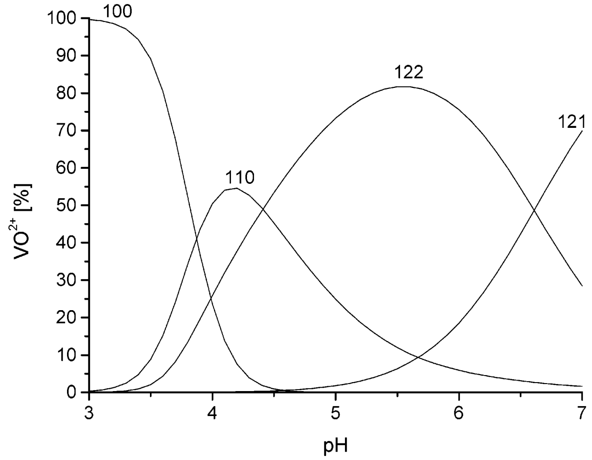


Figure 2. Species distribution in the vanadium(IV)−tdci system with a molar ratio of total V^{IV}:total tdci = 1:3 and total V^{IV} = 0.5 mM. The formation constants listed in Table 3 were used for the calculations. The species are labeled as 100 ($[VO]^{2+}$), 110 ($[VO(tdci)]^{2+}$), 122 ($[V(tdci)_2]^{4+}$), and 121 ($[V(tdci)_2H_{-1})]^{3+}$).

Table 4. Experimental Parameters and Evaluated Formation Constants for the Spectrophotometric Titration of the Vanadium(IV)−tdci System

exptl params	
tot. V:tot. tdci molar ratio	1:3
pH range	3.59−6.43
wavelengths (nm)	350−700

xyz/species	evaluated consts log β_{xyx}
110/$[VOL]^{2+\,a}$	13.9 (1)
122/$[VL_2]^{4+}$	36.91(3)
121/$[VL_2H_{-1}]^{3+}$	30.4(2)

[a] The 110 species ($[VO(tdci)]^{2+}$) was considered as colorless.

The formation of $[V^{IV}O(taci)]^{2+}$ was unambiguously established around pH 4. However, the rather low metal concentration and the large excess of the ligand prevented an unambiguous determination of the formation constants of further species, although the formation of the bis complexes was clearly indicated at higher pH by UV−vis spectroscopy. A variety of models were tested by least-squares calculations, and the experimental data could be satisfactorily fitted by more than one. The model shown in Table 3, which includes $[(V^{IV}O)_2L_2(OH)_2]^{2+}$ as an additional species, was finally selected to account for the formation of a diamagnetic intermediate which was substantiated by EPR spectroscopy around pH 5 (vide infra).

The elucidation of the vanadium(IV)−tdci system was more successful. The formation constants of $[V^{IV}O(tdci)]^{2+}$ and $[V^{IV}(tdci)_2]^{4+}$ could be determined (Table 3) unambiguously, and a pK_a of 6.6 was assigned to the first deprotonation of $[V^{IV}(tdci)_2]^{4+}$. A pH-dependent species distribution plot is shown in Figure 2. UV−vis spectra further confirmed the selected model. The formation constants derived from the spectrophotometric measurements (Table 4) are in reasonably good agreement with the values obtained by pH-metric methods. The spectroscopic data also allowed the calculation of a spectrum for each individual species (Figure 3).

The formation of such $[ML_2]^{4+}$ complexes (L = taci and tdci) and of the corresponding deprotonation products is well established for a number of tetravalent metal ions.[13,14] The pK_{a1} = 6.6 of $[V^{IV}(tdci)_2]^{4+}$ is in good agreement with the values found for $[Ti(tdci)_2]^{4+}$ (6.67), $[Sn(tdci)_2]^{4+}$ (6.76), and $[Ge(tdci)_2]^{4+}$ (6.82).[14] The following pK_{a2}, pK_{a3}, and pK_{a4}

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(31) Von Dreele, R. B.; Fay, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 7935.

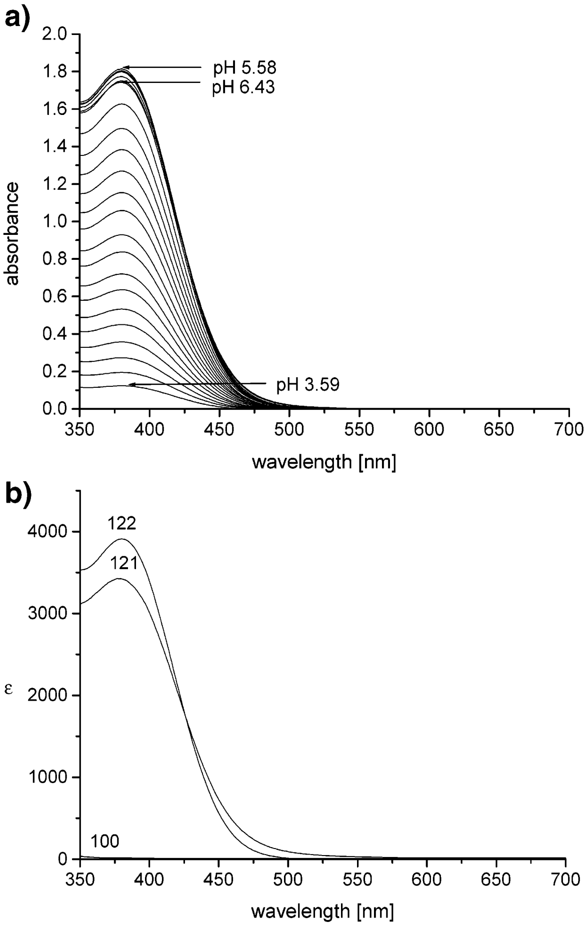

Figure 3. (a) Spectral changes for the vanadium(IV)−tdci system during a titration experiment at total $V^{IV} = 0.5$ mM and total tdci = 1.5 mM. (b) Calculated individual spectra of $[V(tdci)_2]^{4+}$ (122) and $[V(tdci)_2H_{-1}]^{3+}$ (121).

values were reported for the subsequent deprotonation steps: 8.06, 9.63, 11.17 for Ti^{4+}, 8.04, 9.69, 11.02 for Sn^{4+}, and 8.10, 9.44, 10.43 for Ge^{4+}.[14] Complexes with a pentavalent metal center such as $[Ta(tdci)_2]^{5+}$ are slightly stronger acids, and a complete set of six pK_a values (4.5, 5.7, 7.2, 9.3, 10.5, 11.2) could be determined (25 °C, 0.1 M KCl).[32] $[V^{IV}(tdci)_2]^{4+}$ reacts in a similar way in alkaline solution. Evidence for the further deprotonation products was provided by an overlapping buffer region from pH 7 up to pH 11 and by the characteristic pH dependence of the redox properties (cyclic voltammetry; vide infra). Owing to the decomposition above pH 9, a quantitative determination of the higher pK_a's was not possible. Since the pK_a's of the peripheral ammonium groups are essentially dependent from the charge of the metal center, the values of 8.1, 9.6, and 10.9, which represent averages of the Ge, Ti, and Sn derivatives, can, however, be regarded as reasonable estimates for pK_{a2}, pK_{a3}, and pK_{a4} of $[V^{IV}(tdci)_2]^{4+}$. Thus, in strongly alkaline media it is likely that $[V^{IV}(taci)_2H_{-6}]^{2-}$ and $[V^{IV}(tdci)_2H_{-6}]^{2-}$ are formed.

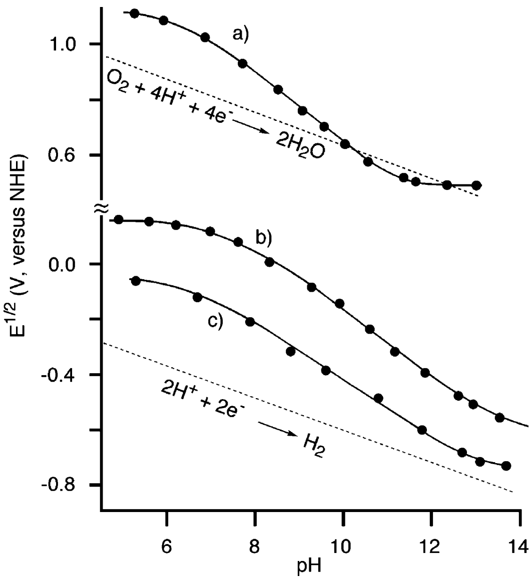

Figure 4. Observed redox potentials $E^{1/2}_{obs}$ as a function of pH: (a) $[V^{V}(taci)_2H_{-m}]^{(5-m)}/[V^{IV}(taci)_2H_{-n}]^{(4-n)}$ system; (b) $[V^{IV}(tdci)_2H_{-m}]^{(4-m)}/[V^{III}(tdci)_2H_{-n}]^{(3-n)}$ system; (c) $[V^{IV}(taci)_2H_{-m}]^{(4-m)}/[V^{III}(taci)_2H_{-n}]^{(3-n)}$ system.

Cyclic Voltammetry. Cyclic voltammetry revealed a quasi-reversible redox behavior for both the $[V^{IV}(tdci)_2H_{-m}]^{(4-m)}/[V^{III}(tdci)_2H_{-n}]^{(3-n)}$ and $[V^{IV}(taci)_2H_{-m}]^{(4-m)}/[V^{III}(taci)_2H_{-n}]^{(3-n)}$ couples, with a cathodic peak current depending linearly on the square root of the scan rate. The quasi reversible behavior was maintained with increasing scan rates. Even at 800 mV/s the peak separation ΔE did not increase significantly (depending on pH, ΔE fell in the range of 70−150 mV). This behavior is only understandable if the same coordination geometry is retained in the oxidized and reduced form. For both complexes the observed redox potential $E^{1/2}_{obs}$ strongly depended on H^+ concentration with a characteristic sigmoid shape for the $E^{1/2}_{obs}$ versus pH curve (Figure 4). This result is in agreement with a stepwise deprotonation of the six peripheral ammonium groups as already indicated by the potentiometric studies. Due to the higher charge of the oxidized form, the vanadium(IV) complexes have somewhat lower pK_a's:

$$[V^{IV}L_2]^{4+} + e^- \rightleftharpoons [V^{III}L_2]^{3+} \quad pH < pK_1\,(V^{IV}) \qquad (i)$$

$$[V^{IV}L_2H_{-x}]^{(4-x)} + e^- + yH^+ \rightleftharpoons$$
$$[V^{III}L_2H_{y-x}]^{(3+y-x)} \quad pK_1\,(V^{IV}) < pH < pK_6\,(V^{III}) \quad (ii)$$

$$[V^{IV}L_2H_{-6}]^{2-} + e^- \rightleftharpoons [V^{III}L_2H_{-6}]^{3-} \quad pH > pK_6\,(V^{III}) \quad (iii)$$

The reactions i and iii represent plateau regions with an $E^{1/2}_{obs}$ independent of pH, assignable to an electron transfer between the fully protonated and the fully deprotonated species. For $[V(tdci)_2]^{4+/3+}$ a redox potential $E^{1/2}$ of 0.15(2) V (versus NHE) is observed. For $[V(taci)_2]^{4+/3+}$ this value cannot be determined directly because the plateau region (i) cannot be reached (the bis complexes are not enough stable below pH 5). $E^{1/2} = 0.0 \pm 0.1$ V (versus NHE) can only be estimated by extrapolation. On the other hand, the $[V^{III}L_2]^{3+}$ complexes could also not be fully deprotonated in aqueous solution and the plateaus corresponding to reaction iii are

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[32] Hegetschweiler, K.; Raber, T.; Reiss, G. J.; Frank, W.; Wörle, M.; Currao, A.; Nesper, R.; Kradolfer, T. *Angew. Chem.* **1997**, *109*, 2052; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1964.

not accessible as well. This is in accord with the findings of previous reports where the pK_a values of the corresponding complexes with other M^{3+} and M^{4+} centers were determined.[13,14] The potentials for the fully deprotonated $[VL_2H_{-6}]^{2-/3-}$ couples must thus again be estimated by extrapolation. Approximate values are −0.8 and −0.7 V (versus NHE) for the taci and tdci complexes, respectively. In the $6 < pH < 13$ range, the investigated vanadium complexes are partially deprotonated, and the observed slope $\partial(E^{1/2}_{obs})/\partial(pH)$ of −0.10 V/pH (taci) and −0.13 V/pH (tdci) can be explained in terms of a combined proton and electron transfer as shown in reaction ii with a ratio H^+/e^- of about 2 (Figure 4). In comparison with taci, the plateau (i) of the tdci complex is extended to higher pH. Obviously, $[V^{IV}(tdci)_2]^{4+}$ is somewhat less acidic than $[V^{IV}(taci)_2]^{4+}$. We also note that the slope $\partial(E^{1/2}_{obs})/\partial(pH)$ is slightly more negative for the tdci system, indicating that the difference in acidity between $[V^{III}L_2]^{3+}$ and $[V^{IV}L_2]^{4+}$ is higher for L = tdci.

Efforts to verify a further reduction of V^{III} to V^{II} were not successful. However, an extension of the CV measurements to more positive potentials exhibited an additional quasi-reversible one-electron oxidation of $[V^{IV}(taci)_2]^{4+}$ in the range $5 \leq pH < 14$. For scan rates up to 800 mV/s, the peak separation ΔE remained approximately constant. This shows again that $[V^{IV}(taci)_2]^{4+}$ can be oxidized electrochemically to $[V^{V}(taci)_2]^{5+}$ with retention of the non-oxo structure. The corresponding oxidation of $[V^{IV}(tdci)_2]^{4+}$ was not observed.[33] The oxidation of the V^{IV}−taci complex showed a similar sigmoid pH profile as described above for the reduction to V^{III}. In analogy to the equations i−iii, the observed pH dependence for the V^{V}/V^{IV} couple can be expressed by the equations

$$[V^{IV}(taci)_2]^{4+} \rightleftharpoons [V^{V}(taci)_2]^{5+} + e^- \qquad (iv)$$

$$[V^{IV}(taci)_2H_{-x}]^{(4-x)} \rightleftharpoons [V^{V}(taci)_2H_{-x-y}]^{(5-y-x)} + e^- + yH^+ \qquad (v)$$

$$[V^{IV}(taci)_2H_{-6}]^{2-} \rightleftharpoons [V^{V}(taci)_2H_{-6}]^{-} + e^- \qquad (vi)$$

The increased positive charge of the 5+ species resulted again in a further increase of acidity[32] and − as a consequence − in an additional shift of the two plateau regions to lower pH. Because of this shift, the reduction potential for reaction (vi) can now be determined directly. $E^{1/2}$ for the fully deprotonated $[V^{V}(taci)_2H_{-6}]^{-}/[V^{IV}(taci)_2H_{-6}]^{2-}$ couple is +0.50 V (versus NHE). The value for the fully protonated $[V^{V}(taci)_2]^{5+}/[V^{IV}(taci)_2]^{4+}$ system (iv) must again be estimated by extrapolation: $E^{1/2} = 1.15$ V (vs NHE). The slope $\partial(E^{1/2}_{obs})/\partial(pH)$ is −0.14 V/pH and falls in a similar range as observed for the V^{IV}/V^{III} couples, indicative of a transfer of ca. 2.4 protons/electron in the intermediate range (v) of the pH profile.

Our CV studies established that $[V^{V}(taci)_2]^{5+}$ is a rather strong oxidizing agent. The corresponding $E^{1/2}$ value of 1.15 V is slightly higher than the value of 1.0 V reported for $[V^{V}O_2]^{+}/[V^{IV}O]^{2+}$.[34] The subsequent deprotonation of the six peripheral ammonium groups reduced this value to +0.50 V. It can thus be expected that the direct oxidation of $[V^{IV}(taci)_2]^{4+}$ by O_2 is difficult and could − if ever − only occur in the narrow pH range 11−12 (Figure 4). $[V^{III}(taci)_2]^{3+}$ and $[V^{III}(tdci)_2]^{3+}$ are reducing agents of moderate strength; the corresponding redox potentials of 0.0 and +0.15 V are somewhat lower than the potential reported for the $V^{IV}O^{2+}(aq)/V^{3+}(aq)$ couple (+0.34 V).[34] In the fully deprotonated form, both complexes $[V^{III}(taci)_2H_{-6}]^{3-}$ ($E^{1/2} = -0.8$ V) and $[V^{III}(tdci)_2H_{-6}]^{3-}$ ($E^{1/2} = -0.7$ V) are strong reducing agents.

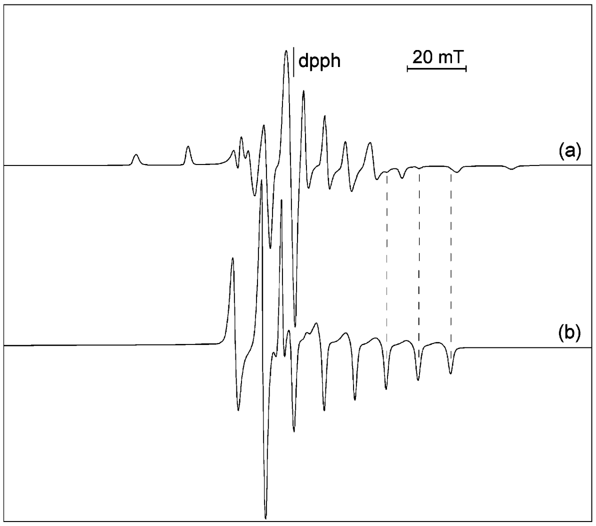

Figure 5. Anisotropic EPR spectra recorded on the vanadium(IV)−tdci system at a molar ratio of 1:2 and total V^{IV} concentration of 4 mM: (a) pH = 5.00 ("normal" oxovanadium(IV) spectrum of the mono chelated complex); (b) pH = 6.55 (non-oxo vanadium(IV) spectrum of the bis chelated complex). Diphenylpicrylhydrazyl (dpph) is used as standard field marker ($g_{dpph} = 2.0036$).

It is noteworthy that $[V^{III}(taci)_2]^{3+}$ and its deprotonation products are slightly stronger reducing agents than the corresponding tdci complexes. This is rather unexpected because tdci is more efficient in chelating metal cations with a high positive charge.[14] However, it should be kept in mind that redox potentials reflect the difference in stability of the trivalent and tetravalent forms, whereas the formation constants account for the stability in reference to the aqua species. Indeed our potentiometric study substantiated that $[V^{IV}(tdci)_2]^{4+}$ is more stable than $[V^{IV}(taci)_2]^{4+}$.

EPR Spectroscopy. The complexation scheme elucidated by potentiometric and spectrophotometric methods was substantiated by EPR measurements. The spectra of vanadium(IV)−tdci and vanadium(IV)−taci systems recorded in aqueous solution supported the formation of mono chelated complexes $[VOL(H_2O)_2]^{2+}$ (L = taci or tdci) at a ligand-to-metal ratio = 2:1, total V^{IV} = 4 mM, and $3.5 < pH < 6$ (tdci) or $pH \approx 5.5$ (taci). The EPR spectra of these species (Figure 5a) are very similar to each other. The measured parameters, listed in Table 5, are comparable with those of the mono chelated complex of catechol ($g_{\parallel} = 1.943$, $g_{\perp} =$

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(33) The free tdci ligand is electrochemically active at high pH.

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Table 5. EPR Parameters of the Oxovanadium(IV) and Vanadium(IV) Complexes of taci and tdci in Aqueous Solution[a]

	g_o	A_o	g_x	g_y	g_z	A_x	A_y	A_z
$[VO(taci)(H_2O)_2]^{2+}$	1.965	98	1.978	1.978	1.940	61	61	171
$[VO(tdci)(H_2O)_2]^{2+}$	1.968	100	1.981	1.981	1.941	64	64	171
$[V(taci)_2]^{4+\,b}$	1.935	60	1.902	1.907	1.988	99	97	−16
$[V(tdci)_2]^{4+\,b}$	1.931	59	1.895	1.900	1.988	97	95	−17

[a] A_o, A_x, A_y, and A_z measured in 10^{-4} cm^{-1} units. [b] The EPR spectra of the non-oxo complexes of taci and tdci do not change with increasing pH; thus, the parameters reported are valid also for the deprotonated species $[V^{IV}(taci)_2H_{-x}]^{(4-x)}$ and $[V^{IV}(tdci)_2H_{-x}]^{(4-x)}$ ($1 \leq x \leq 6$).

1.976, $A_{\|} = 170 \times 10^{-4}$, and $A_{\perp} = 63 \times 10^{-4}$ cm^{-1})[35] suggesting that tdci and taci chelate the vanadyl ion through the oxygen atoms by adopting the *basal*−*apical*−*basal* coordination mode (Scheme 2). According to the “additivity rule” proposed by Chasteen,[36] the apical oxygen donor does not contribute to the experimental $A_{\|}$ value. The spectral data are consistent with a complex with a geometry close to the square pyramid, a C_{4v} symmetry and a d_{xy} ground state.

Above pH 6 (tdci) or pH 7 (taci) the EPR spectra change significantly and exhibit the distinctive features of non-oxo vanadium(IV) (Figure 5b). They substantiate the presence of a non-oxo species, with a vanadium(IV) atom coordinated by six deprotonated −OH groups[37] in an arrangement similar to that shown by the crystallographic analysis in the solid state. The EPR spectra of the non-oxo vanadium(IV) complexes of taci and tdci do not change from pH 7 to 13.5, although in this pH range the six $-NH_3^+$ or $-NH(CH_3)_2^+$ groups are stepwise deprotonated with concomitant transformation of $[V^{IV}(taci)_2]^{4+}$ and $[V^{IV}(tdci)_2]^{4+}$ into $[V^{IV}(taci)_2H_{-6}]^{2-}$ and $[V^{IV}(tdci)_2H_{-6}]^{2-}$, respectively. The findings support that the amino and dimethylamino groups in taci and tdci do not participate in the coordination of the metal ion.

Six-coordinate vanadium(IV) complexes can be divided into two groups: those with a d_{xy} ground state, which display $g_z \ll g_x \sim g_y < 2.0023$ and $A_z \gg A_x \sim A_y$ and those with a d_{z^2} ground state which display $g_x \sim g_y \ll g_z \sim 2.0023$ and $A_z \ll A_x \sim A_y$.[38] The geometry of the latter species can be assigned as a distorted octahedron which is strongly shifted toward a trigonal prism.[39]

The first group includes non-oxo complexes such as *trans*-$[V^{IV}Cl_2(salen)_2]$,[40] amavadin,[41] and its models $[V^{IV}(R,S\text{-hidba})_2]^{2-}$ (*R*,*S*-hidba = *meso*-2,2′-(hydroxyimino)dibutyric acid).[42] The second group includes all the tris chelated complexes with a d_{z^2} ground state like $[V^{IV}(catecholato)_3]^{2-}$ [35] and $[V^{IV}(maleonitriledithiolato)_3]^{2-}$,[43] whose parameters are reported in Table S2 (Supporting Information). A more or less evident anisotropy in the *x* and *y* directions can be observed, e.g. in $[V^{IV}(2\text{-mercapto-4-methylphenolato})_3]^{3-}$,[5b] characterized by the EPR parameters $g_z = 2.002$, $g_x = 1.980$, $g_y = 1.958$ and $A_z = 17 \times 10^{-4}$ cm^{-1}, $A_x = 75 \times 10^{-4}$ cm^{-1}, $A_y = 115 \times 10^{-4}$ cm^{-1} (Table S2).

A simulation of the spectra of the non-oxo complexes of taci and tdci (Table 5) indicates that they belong to the second group and are therefore characterized by a d_{z^2} ground state. On the basis of the simulations, the predicted values of A_0, 60×10^{-4} cm^{-1} (taci) and 58×10^{-4} cm^{-1} (tdci), are in good agreement with the experiment (Table 5).

The twist angles Φ observed for the compounds **1**−**3** (56.9, 55.3, and 55.4°) are very close to 60° (Table S1, Supporting Information), and the coordination geometry of these complexes is close to a regular octahedron. Anisotropic EPR parameters reported in the literature for non-oxo complexes, together with the corresponding twist angles Φ which range from ∼0 to 44.5° (Table S2, Supporting Information), show that there is no direct correlation between the *g* and *A* values and the degree of distortion toward the trigonal prism observed in the solid state. In many cases the *g* and *A* values along the *x* and *y* axes are coincident; in other cases, the anisotropy of the g_x, g_y and A_x, A_y values is more evident. As an example, the difference between A_x and A_y of $[V^{IV}(2\text{-mercapto-4-methylphenolato})_2]$ is 30×10^{-4} cm^{-1} and that between g_x and g_y is 0.032.[5b] In our case, $|A_x - A_y|$ is 2×10^{-4} cm^{-1} and $|g_x - g_y|$ is 0.005 for both complexes. The values are consistent with those of several complexes listed in Table S2.

Finally, one must bear in mind that the geometry observed in the crystal structure could be different from that in solution. We cannot exclude that in the solution species the twist angle Φ is considerably smaller. In the structures so far reported for related bis-taci and bis-tdci complexes with a MO_6 coordination, Φ values ranging from 59.4° ($[Al(taci)_2]^{3+}$)[12] to 37.7° ($[Ta(tdci)_2H_{-2}]^{3+}$)[32] were observed (Table S3, Supporting Information), indicating that a distortion toward a trigonal prism is tenable.

The EPR study confirmed the higher stability of the tdci complexes compared with taci. The mono and bis chelated species of tdci exist around pH 3.5 and 5, respectively, whereas the formation of corresponding taci complexes was observed at pH 5 and 7. Moreover, for the taci system, the intensity of the EPR signal decreased around pH 6. We interpret this result by taking into account a dimeric diamagnetic oxovanadium(IV) species which is formed by a hydrolytic condensation process. For the tdci system, the addition of the second ligand occurred at considerably lower pH, which suppressed the formation of such hydrolytic products.

Attempts to obtain a non-oxo vanadium(IV) complex with *all-cis*-1,3,5-cyclohexanetriol were not successful, even in the presence of a very large excess of the ligand (total L:total $V^{IV} \geq 100:1$). This result confirms previous reports, which

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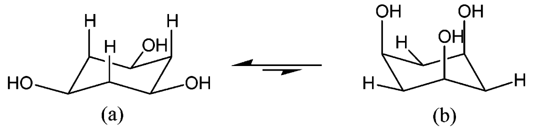
Scheme 3



described the low efficacy of the simple triol as a chelator in aqueous solution.[44] This finding is attributed to the unfavorable conformation (b) with the hydroxy groups in axial position which is required for complex formation (Scheme 3). In taci and, particularly, in tdci, this conformation corresponds to the minimum energy structure. Moreover, taci and tdci are able to generate deprotonated oxygen donors by transferring the protons to the three amino groups. This intramolecular mechanism is in particular responsible for the high effectiveness of these ligands. This report on complex formation with vanadium(IV) further confirms the unique ability of this system to stabilize mononuclear bis complexes of highly charged metal ions.

Decomposition Studies. As anticipated above, the yellow bis complexes $[\mathrm{V^{IV}(taci)_2H_{-x}}]^{(4-x)}$ and $[\mathrm{V^{IV}(tdci)_2H_{-x}}]^{(4-x)}$ ($x \geq 3$) decomposed slowly at high pH, yielding colorless species as the final product. The rate of decomposition strongly increased with increasing pH and increasing temperature. At room temperature and pH 13 the degradation of the yellow species was complete after a few hours, whereas it took several days at pH 10. At higher temperatures (50 °C) the complexes decomposed rather rapidly (few minutes at pH 13). The decomposition of other vanadium(IV) compounds was interpreted previously in terms of an aerobic oxidation to vanadium(V) with formation of tetrahedral $\mathrm{V^V}$−oxo species.[7a,45] However, in our investigation, bubbling a stream of oxygen through the solution did not enhance the formation of the colorless species and, vice versa, the addition of a reducing agent such as $\mathrm{SO_3^{2-}}$ did not suppress the reaction.

The kinetics of the decomposition of $[\mathrm{V^{IV}(tdci)_2H_{-x}}]^{(4-x)}$ in strongly alkaline solution were followed by EPR spectroscopy at three different pH values (12.55, 13.00, and 13.55) (Figure 6).

A transient mononuclear oxovanadium(IV) species was detected in the course of the reaction, with EPR signals superimposed on the spectrum of $[\mathrm{V^{IV}(tdci)_2H_{-x}}]^{(4-x)}$. This new species is characterized by "normal" EPR parameters ($g_z < g_x \sim g_y$ and $A_z > A_x \sim A_y$), $g_z = 1.949$ and $A_z = 161 \times 10^{-4}$ cm^{-1}. The parallel hyperfine coupling constant (A_z or $A_{\|}$) can be calculated as the sum of the contribution of each donor atom in the equatorial plane:[36]

$$A_z = \sum_{i=1}^{4} A_z(i) = A_z(\text{donor 1}) + A_z(\text{donor 2}) + A_z(\text{donor 3}) + A_z(\text{donor 4}) \quad \text{(vii)}$$

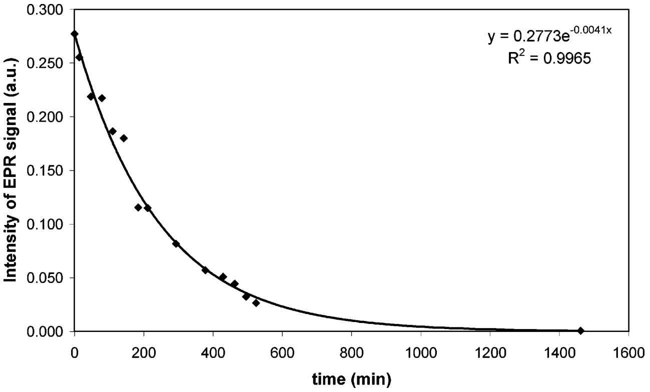


Figure 6. Intensity of the anisotropic EPR signal of $[\mathrm{V^{IV}(tdci)_2H_{-x}}]^{(4-x)}$ as a function of time at pH = 12.55. The vanadium(IV) concentration was 1 mM, and the initial ligand to metal molar ratio was 4. Spectra were recorded at 120 K.

The contribution of an $\mathrm{O^-}$ donor of tdci can be calculated with this formula on the basis of the A_z values of the mono chelated species ($A_z = 171.2 \times 10^{-4}$ cm^{-1}, with two $\mathrm{O^-}$ groups of tdci and two water molecule in the equatorial plane) and of the aqua ion ($A_z = 179.8 \times 10^{-4}$ cm^{-1}). A value of 40.65×10^{-4} cm^{-1} is calculated, corresponding to 162.6×10^{-4} cm^{-1} for four deprotonated oxygen atoms of tdci coordinated in the equatorial plane of oxovanadium(IV) ion and to 158.7×10^{-4} cm^{-1} for the species with two deprotonated oxygens of tdci and two $\mathrm{OH^-}$ ions (the empirical contribution of $\mathrm{OH^-}$ is 38.7×10^{-4} cm^{-1}).[36]

Therefore, either a bis complex $[\mathrm{V^{IV}O(tdci)_2H_{-x+1}}]^{(3-x)}$ ($x = 4-6$) with a tridentate and a bidentate tdci ligand or a mono complex $[\mathrm{V^{IV}O(tdciH_{-x})(OH)_2}]^{x-}$ ($x = 2, 3$) with two additional hydroxo ligands would account for these findings. However, in our previous investigation, a bidentate coordination mode of tdci was never observed and geometrical reasons indicate that such a coordination mode would be rather strained. As a matter of fact in all known cases the coordination behavior of tdci must be described as an all-or-nothing process. We therefore propose the dissociation of one tdci or taci ligand with formation of $[\mathrm{V^{IV}O(LH_{-x})(OH)_2}]^{x-}$ ($x = 2, 3$) as a transient species.

The final product of this reaction was EPR-silent. These findings can be explained either by the oxidation of the oxovanadium(IV) species to a vanadium(V) complex or by the formation of hydroxo-bridged dinuclear oxovanadium(IV) species, e.g. $[\mathrm{(V^{IV}O)_2(tdciH_{-x})_2(OH)_2}]^{(2-2x)}$ ($x = 2, 3$). The observations that (i) $[\mathrm{V^{IV}L_2H_{-x}}]^{(4-x)}$ is rather difficult to oxidize (Figure 4a), (ii) the presence of $\mathrm{O_2}$ does not affect the decomposition rate, and (iii) the EPR signals of $[\mathrm{V^{IV}(tdci)_2H_{-x}}]^{(4-x)}$ are completely restored if the pH is lowered to 7 again are all supportive of the formation of an EPR-silent vanadium(IV) species, whereas the formation of a vanadium(V) complex is less likely.

The decrease in intensity of the EPR signal with elapsing time follows a rate law which is of first order in total vanadium(IV) concentration. The corresponding k_{obs} values depend linearly on the $\mathrm{OH^-}$ concentration (Table 6). The

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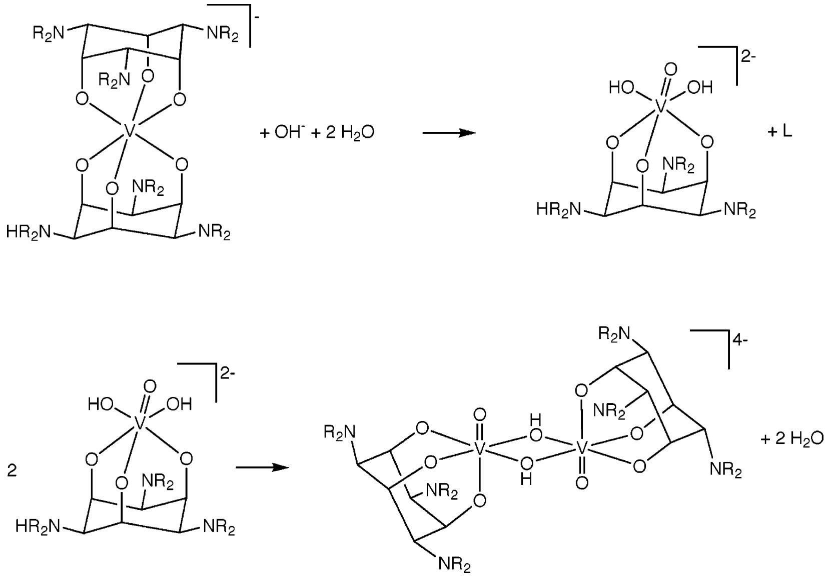
Scheme 4. Decomposition of $[V^{IV}L_2H_{-5}]^{-}$ [a]



[a] The formal charges on the protonated nitrogen (+1) and deprotonated oxygen (−1) atoms are omitted for clarity.

Table 6. Rate Constants of the Decomposition Process

pH	k_{obs}, min^{-1}	k, M^{-1} min^{-1}
12.55	0.0041	0.116
13.00	0.0118	0.118
13.55	0.0419	0.118

reaction rate can thus fit second-order kinetics:

$$-\frac{d[[V^{IV}(tdci)_2H_{-x}]^{(4-x)}]}{dt} = k[OH^-][[V^{IV}(tdci)_2H_{-x}]^{(4-x)}] \quad (viii)$$

$$k = \frac{k_{obs}}{[OH^-]} \quad (ix)$$

The observed kinetics suggest that the rate-determining step of the whole process is the dissociation of one ligand entity from $[V^{IV}L_2H_{-x}]^{(4-x)}$ yielding the intermediate $[V^{IV}O(LH_{-x})(OH)_2]^{x-}$ ($x = 2, 3$, Scheme 4). This process is slow because it involves a significant rearrangement of the complex. Once formed, it may undergo hydrolytic condensation. The final species is an EPR-silent dimeric complex $[(V^{IV}O)_2(LH_{-x})_2(\mu\text{-}OH)_2]^{(2-2x)}$ ($x = 2, 3$), as it usually occurs upon hydrolysis of oxovanadium(IV) species with two accessible adjacent equatorial sites.[46]

Conclusions

The remarkable chelating properties of taci and tdci (=L) have further been demonstrated by the easy formation of a series of vanadium(IV) complexes of composition $[V^{IV}L_2H_{-x}]^{(4-x)}$. The unique properties of the ligands are based on a high degree of preorganization of the donor sets and the presence of an internal base, which greatly facilitates the generation of three negatively charged oxygen donors. The reaction of the oxovanadium(IV) ion with a stoichiometric amount of the ligands resulted in the formation of mononuclear non-oxo species in alkaline solution. This is in marked contrast to other complexing agents such as catechols, for which a 100-fold excess of the ligand is required to replace the vanadium−oxo group and form $[V^{IV}(catecholato)_3]^{2-}$.[35] The $[V^{IV}L_2H_{-x}]^{(4-x)}$ complexes have been fully characterized in the solid state and in aqueous solution. To the best of our knowledge, they represent the first examples of bis chelated non-oxo derivatives of vanadium(IV) with VO_6 geometry.

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Supporting Information Available: Figures showing the molecular structure of the cations in **2** and **3** and the anion in **2**, EPR spectra of taci and tdci non-oxo complexes, and plots of the decomposition kinetics of $[V^{IV}(tdci)_2H_{-x}]^{(4-x)}$ at pH 13.00 and 13.55, tables giving structural parameters for **1**−**3**, experimental EPR parameters for non-oxo vanadium(IV) complexes, and structural parameters of further taci and tdci complexes with an MO_6 structure, and crystallographic data in CIF format for the reported structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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