Synthesis, Reactivity, and Structural Characterization of Dioxovanadium(V) Complexes with Tridentate Schiff Base Ligand: Vanadium Complexes in Supramolecular Networks

Winfried Plass* and Hakan-Peter Yozgatli

Siegen, Anorganische Chemie der Universität

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Abstract. The synthesis, characterization and crystal structure analysis of the ammonium salt of the dioxovanadium(V) complex NH₄[VO₂(salhyph)] with the tridentate Schiff base ligand derived from salicylaldehyde and benzoic acid hydrazide (H₂salhyph) is reported. NH₄[VO₂(salhyph)] crystallizes in the monoclinic space group *Pn* with *a* = 708.8(2), *b* = 1444.3(3), *c* = 717.1(2) pm and β = 101.09(2)°. The vanadium atom of the dioxovanadium(V) moiety has a distorted square-pyramidal coordination geometry. Extensive hydrogen bonding is observed between the ammonium cation and the oxygen atoms coordinated to the vanadium atom yielding to a two-dimensional network, where the complex anions

are arranged in a bilayer. Additional crystal packing within the bilayer appears to be controlled mostly by π stacking between the aromatic rings of the ligand. The reactions of NH₄[VO₂(salhyph)] with several proton acidic compounds including water, methanol, and proton acids lead to neutral monooxovanadium(V) and dioxovanadium(V) complexes ([VO₂(Hsalhyph)], [V₂O₃(salhyph)₂] and [VO(OMe)(salhyph)(HOMe)]).

Keywords: Vanadium; Hydrogen bonding; Salicylidenehydrazides; Schiff base; Crystal structure

Synthese, Reaktionen und Struktur von Dioxovanadium(V)-Komplexen mit dreizähniger Schiffscher Base als Ligand: Vanadiumkomplexe in supramolekularen Netzwerken

Inhaltsübersicht. Für das Ammoniumsalz des Dioxovanadium(V)-Komplexes NH₄[VO₂(salhyph)] mit dem aus Salicylaldehyd und Benzolcarbonsäurehydrazid erhaltenen dreizähnigen Liganden vom Typ der Schiffschen Basen (H₂salhyph) wird die Synthese, Charakterisierung und Kristallstrukturanalyse beschrieben. NH₄[VO₂(salhyph)] kristallisiert in der monoklinen Raumgruppe *Pn* mit *a* = 708.8(2), *b* = 1444.3(3), *c* = 717.1(2) pm und β = 101.09(2)°. Das Vanadiumatom der Dioxovanadium(V)-Einheit besitzt eine verzerrte quadratisch planare Koordinationsumgebung. Zwischen dem Ammoniumkation und den an das Vanadiumatom gebundenen Sauerstoffatomen besteht ein ausgedehntes zweidimensionales Netzwerk von Wasserstoffbrückenbindungen, welches in eine durch die komplexen Anionen gebildete Doppelschicht eingebettet ist. Die weitere Kristallpackung innerhalb der Doppelschichten scheint hauptsächlich durch π -Stapelung zwischen den aromatischen Ringen des Liganden kontrolliert zu werden. Die Reaktionen von NH₄[VO₂(salhyph)] mit verschiedenen H-aziden Verbindungen, wie Wasser, Methanol und Protonensäuren, führt zu neutralen Monooxovanadium(V)- und Dioxovanadium(V)-Komplexen ([VO₂(Hsalhyph)], [V₂O₃(salhyph)₂] und [VO(OMe)(salhyph)(HOMe)]).

Introduction

The interest in coordination chemistry of pentavalent vanadium from a biological and pharmacological perspective is due to the discovery of the insulin-like effect of vanadium compounds and the presence of vanadium in certain haloperoxidases [1, 2]. A key point for the understanding of how vanadium actually functions in biological systems is given by the chemical similarities between vanadate and phosphate [3]. In this context striking similarities are observed for the active site architecture of vanadium haloperoxidases (e.g. *Curvularia inaequalis* [4]) and certain bacterial acid phosphatases (e.g. *Escherichia blattae* [5]). A basic feature of this active site architecture for both enzymatic systems is the extensive hydrogen bonding of the protein environment with either the prosthetic group vanadate or the substrate analog molybdate. The importance of hydrogen bonding in biological systems has been documented to go beyond its well established structural relevance [6–8].

Although various crystal structures of different vanadium haloperoxidases have been reported [4, 9-13], the protonation and the actual structure of the vanadate moiety are still unknown. Mechanisms to account for the haloperoxidase activity of the enzymes as well as a series of model compounds have been proposed, which all include pro-

^{*} Prof. Dr. Winfried Plass Anorganische Chemie Universität Siegen D-57068 Siegen (Germany) Fax: +49 (0)271/740-2555 E-mail: plass@chemie.uni-siegen.de





ton transfer steps at the vanadate moiety [1, 14-16]. Moreover, all model systems known today are either based on cis-dioxovanadium(V) complexes or postulate such a species as intermediate [1, 16]. As structural models for possible intermediates of the catalytic cycle for haloperoxidase activity various oxovanadium(V) and cis-dioxovanadium(V) complexes have been reported [17]. Nevertheless, the knowledge about ligand systems capable of supporting both coordination modes is rather scares. Of particular interest in this context are ligand systems flexible enough to accommodate both an oxovanadium(V) and a *cis*-dioxovanadium(V) unit. In addition, such a ligand system should also support a variable protonation of the obtained complexes. As we have shown previously, N-salicylidenehydrazides are versatile ligand systems that actually feature these desired characteristics [18]. Herein we report on the synthesis, structure and reactivity of the ammonium salt of a cis-dioxovanadium(V) complex of such a Schiff base type ligand system.

Results and Discussion

Synthesis and Reactions

N-Salicylidenehydrazides are tridentate chelate ligands derived from salicylaldehyd and carbonic acid hydrazides. In Scheme 1 the synthesis of H₂salhyph via the Schiff base condensation reaction utilizing benzoic acid hydrazide is depicted. Both tautomers of the ligand system H₂salhyph (see Scheme 1) are capable of coordinating metal ions [19] yielding complexes with either the mono- or dianionic form of the ligand.

Starting from ammonium metavanadate as vanadium source the ammonium salt of the anionic *cis*-dioxovanadi-



Fig. 1 Synthesis and reactions of NH₄[VO₂(salhyph)]: i) DMF, Δ T; ii) MeOH, Δ T; iii) (*t*-BuO)₂PO(OH), THF; iv) H₂O, Δ T; v) liquid NH₃.

um(V) complex NH₄[VO₂(salhyph)] can be isolated, if the synthesis is performed in aprotic solvents like DMF or DMSO. By reacting solutions of NH₄[VO₂(salhyph)] with methanol the complex can be converted to the oxovanadium(V) species [VO(OMe)(salhyph)(HOMe)], which has been described before as an oxidative byproduct in a reaction starting form a vanadium(IV) precursor [20]. With alcohols as reaction media for the complex formation starting from ammonium metavanadate the corresponding oxovanadium(V) complexes are directly accessible (see Fig. 1). This also allows for the synthesis of derivatives with chelating mono deprotonated diols like ethan-1,2-diol (H₂ed), yielding [VO(Hed)(salhyph)] (cf. Ref. [18]). Both oxovanadium(V) complexes, [VO(OMe)(salhyph)(HOMe)] and [VO(Hed)(salhyph)], are dark red-brown crystalline compounds that are soluble in polar organic solvents like DMSO or alcohols.

Treatment of the ammonium salt NH₄[VO₂(salhyph)] with an excess of water leads to the formation of the neutral complex [VO₂(Hsalhyph)] under release of ammonia. [VO₂(Hsalhyph)] is obtained as yellow solid which is only poorly soluble in organic solvents and is insoluble in water. The reconversion to the ammonium salt can be achieved by deprotonation of the neutral complex in liquid ammonia. On the other hand the protonation in absence of water yields the formal anhydrid $[V_2O_3(\text{salhyph})_2]$ as dark brown crystals. By the same synthetic strategy the anhydrid $[V_2O_3]$ (salhyph)₂] is also accessible starting from the oxovanadium(V) complex [VO(OMe)(salhyph)(HOMe)] (see Fig. 1). This anhydride has also been prepared using different synthetic approaches starting from vanadium(IV) precursors [21, 22]. The neutral complex [VO₂(Hsalhyph)], which can be regarded as the tautomer of the corresponding acid, is consequently accessible by hydrolysis of the anhydrid $[V_2O_3(\text{salhyph})_2]$ (see Fig. 1). At this point it has to be noted that in contrast to the N-salicylidenehydrazide ligand system described here, a so-called free acid with an oxohydroxo core, viz [VO(OH)]²⁺, has been reported for a bis(8-quinolinato)vanadium(V) complex [23].

The neutral *cis*-dioxovanadium(V) complex $[VO_2(Hsal-hyph)]$ can be utilized as a general source to synthesize a series of different oxovanadium(V) complexes containing the salhyph²⁻ ligand. Examples are the oxovanadium(V) complexes [VO(OMe)(salhyph)(HOMe)] and [VO(Hed)-(salhyph)] which are obtained by reaction with the appropriate alcohol in nearly quantitative yields (cf. Fig. 1 and Ref. [18]). By hydrolysis with an excess of water both oxovanadium(V) complexes can be reconverted to the neutral *cis*-dioxovanadium(V) complex $[VO_2(Hsalhyph)]$.

The results described above clearly show that *N*-salicylidenehydrazides are tridentate ligands for vanadium(V) complexes that can form both oxo and dioxo species and, moreover, also allow for the variation of the protonation state of the resulting complexes. Consequently for the ammonium salt $NH_4[VO_2(salhyph)]$ a varying solution speciation is observed that is strongly dependent on the solvent and reactants present. In contrast additional speciation for the corresponding potassium salt K[VO_2(salhyph)] is solely observed in the presence of stoichiometric amounts of appropriate acids [18].

Spectroscopic Characterization

The ¹H and ¹³C NMR data for the ammonium salt NH₄[VO₂(salhyph)] summarized in the experimental section is consistent with the formation of a dioxovanadium(V) complex. In particular the deprotonation of both acidic groups of the free ligand H₂salhyph (cf. Scheme 1) upon formation of NH₄[VO₂(salhyph)] is confirmed by the absence of the most downfield ¹H NMR resonances corresponding to the O-H and N-H protons of the phenolate and the amide groups, respectively. The ⁵¹V NMR data for the ammonium salt of the anionic dioxovanadium(V) complex [VO₂(salhyph)]⁻ is somewhat dependent on the solvent, i.e. for DMSO solutions a down-field shift of 7 ppm is observed, as compared to a DMF solution ($\delta = -540$). On the other hand the ⁵¹V NMR resonance of the anionic dioxovanadium(V) complex [VO₂(salhyph)]⁻ is independent of the counter ion present, as the same chemical shifts are observed for the corresponding potassium salt. Unfortunately, for the neutral complex [VO₂(Hsalhyph)] no useful NMR data could be obtained, due to its very poor solubility.

Infrared spectra of the ammonium salt $NH_4[VO_2(salhyph)]$ confirm the deprotonation of the amid functionality in the complex. The free ligand N-H and C=O stretches at 3330 and 1640 cm⁻¹, respectively, are not observed in the complex. Instead a strong band is observed at 1610 cm⁻¹ which can be attributed to the stretching vibration of the conjugate -C=N-N=C- grouping [19]. This band is characteristic for the coordination of the enolate form of the *N*-salicylidenehydrazide ligand to the dioxovanadium(V) moiety. For $NH_4[VO_2(salhyph)]$ two strong bands are observed at 895 and 918 cm⁻¹ assigned to stretching vibrations of the *cis*-VO₂ moiety of the complex. Whereas for the protonated neutral complex [VO₂-



Fig. 2 Molecular structure of the anionic dioxovanadium complex $[VO_2(salhyph)]^-$ in crystals of $NH_4[VO_2(salhyph)]$ (thermal ellipsoids are drawn at the 50 % probability level).

Table 1 Selected bond lengths (in pm) and angles (in °) for $NH_4[VO_2(salhyph)]$.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V-01 V-02 V-03 V-04	162.1(4) 162.7(4) 190.4(4) 196.2(4) 212.0(4)	O4-C8 N1-N2 N1-C7 N2-C8	130.9(7) 139.5(6) 128.4(7) 129.7(8)
	$\begin{array}{c} 01 - V - 02 \\ 01 - V - 03 \\ 01 - V - 04 \\ 02 - V - 03 \\ 02 - V - 04 \end{array}$	$109.9(2) \\103.0(2) \\102.9(2) \\94.5(2) \\91.9(2)$	O3-V-O4 O1-V-N1 O2-V-N1 O4-V-N1 O3-V-N1	149.2(2) 109.0(2) 140.7(2) 74.1(2) 82.1(2)

(Hsalhyph)] a broad strong band at 884 cm^{-1} is attributed to the corresponding stretching vibrations. For the neutral complex [VO₂(Hsalhyph)] an additional band for the N–H stretching vibration of the protonated amide functionality is observed at 2600 cm⁻¹. The site of protonation within the complex is also verified by the synthesis of the corresponding deuterium derivative that shows the expected frequency shift for the relevant band assigned to the N–D stretching vibration which appear at 1980 cm⁻¹ [24].

Molecular Structure of $NH_4[VO_2(salhyph)]$

The molecular structure of the complex anion of the ammonium salt $NH_4[VO_2(salhyph)]$ with the atom numbering scheme is shown in Figure 2 and selected bond lengths and angles are listed in Table 1. The NO_4 coordination sphere around the vanadium atom is defined by the two *cisoid* oxo groups (O1 and O2) as well as the phenolate oxygen atom (O3), the amide oxygen atom (O4) and the imine nitrogen atom of the dibasic tridentate ligand H₂salhyph. The bond lengths N1-N2, N1-C7, N2-C8 and O4-C8 of the coordinated ligand system are consistent with the enolate form of the amide functionality and, moreover, are in good agreement with the data found for the corresponding potassium salt [18]. The most significant parameter for differentiating between the enolate and the keto form of the amide functionality is the O4-C8 bond lengths. For the enolate form of the ammonium and potassium salt a value of 131 and 132 pm, respectively, is found, whereas for the keto form of the neutral complex [VO₂(Hsalhyph)] a O4-C8 bond lengths of 127 pm is observed [18]. The ligand forms a five- and a six-membered chelate ring with bite angles of 74° (O4-V-N1) and 82° (O3-V-N1), respectively. For the vanadium atom a distorted square pyramidal coordination is found with one of the doubly bonded oxo groups (O2), the phenolate (O3) and enolate oxygen atoms (O4) as well as the imine nitrogen atom (N1) forming the tetragonal plane. This tetragonal plane is only twisted by an angle of 7° against the mean plane defined by the tridentate ligand system. With respect to the apical oxo group O1 the vanadium atom lies 39 pm above and the oxo group O2 40 pm below this mean plane of the ligand system. The fact that only slight distortions towards a trigonal bipyramid are present is quantified by a τ parameter of 0.14 ($\tau = 0$ for an ideal tetragonal pyramid; $\tau = 1$ for an ideal trigonal bipyramid). Nevertheless the observed deviation from the ideal square-pyramidal geometry is somewhat larger than that observed for the corresponding potassium salt with a τ parameter of 0.02 [18]. This can be attribute to differences in the crystal packing between the ammonium and the potassium salt (vide infra).

Hydrogen Bonding Network of NH₄[VO₂(salhyph)]

All four oxygen atoms coordinated to the vanadium atom are involved in hydrogen bonding with the ammonium cation as depicted in Figure 3. The shortest hydrogen bonding contacts of the ammonium nitrogen atom are observed towards the oxo group O2 with 279 and 281 pm, whereas the largest distances are found for interactions with the phenolate oxygen atom (O3…N3C 318 pm) and the apical oxo group (O1…N3C 321 pm).

The extensive hydrogen bonding observed leads to the formation of a two-dimensional network oriented along the crystallographic (010) plane which is depicted in Figure 4. The orientation of the oxygen atoms involved in hydrogen bonding towards the layer established by the ammonium cations results in the formation of a bilayer with the hydrophobic part of the complex anions located on the outside. Within the hydrophobic part of the bilayer the crystal packing appears to be controlled mostly by π stacking between the aromatic rings of the ligand. This arrangement leads to the observed distortion of the square-pyramidal coordination around the vanadium atom towards a trigonal bipyramid in order to allow for a better hydrogen bonding interaction with in the established bilayer. As compared to



Fig. 3 Representation of the hydrogen bonding interactions of the anionic dioxovanadium complex $[VO_2(salhyph)]^-$ with the ammonium cations in crystals of NH₄[VO₂(salhyph)] (broken lines represent hydrogen bonds); relevant distances (in pm): O1…N3 296, O1…N3C 321, O2…N3A 281, O2…N3B 279, O3…N3C 318, O4…N3A 306) (symmetry transformations: (A) x - 0.5, 2 - y, 0.5 + z; (B) x, y, 1 + z; (C) 0.5 + x, 2 - y, 0.5 + z).



Fig. 4 Representation of the two-dimensional hydrogen bonding network in crystals of $NH_4[VO_2(salhyph)]$ (view along the negative [001] direction; hydrogen atoms at the anionic dioxovanadium complex are omitted; broken lines represent hydrogen bonding interactions).

the ideal square-pyramidal coordination found for the corresponding potassium salt, this reflects in the decrease of the O2-V-N1 angle from 148° in the potassium salt [18] to 141° in the ammonium salt described here.

Conclusions

The synthesis and reactivity of dioxovanadium(V) complexes with *N*-salicylidenehydrazides presented shows that these are versatile tridentate ligands for vanadium(V) complexes. These ligand systems can stabilize both oxo and dioxo spezies and, moreover, they also allow for a varying protonation state of the resulting complexes. These complexes can be regarded as structural models for the active site in vanadium dependent haloperoxidases. For the ammonium salt NH₄[VO₂(salhyph)] an extensive hydrogen bonding network is observed which leads to the formation of a bilayered arrangement of the complex anions around the ammonium counterions. The protonation of the anionic complex leads to the formation of the neutral compound [VO₂(Hsalhyph)] which contains the amide form of the ligand. This indicates that for the N-salicylidenehydrazide ligand investigated here the amide nitrogen atom is the more basic site compared to the oxo groups at the vanadium atom. As the N-salicylidenehydrazide ligand system can easily be modified, we are currently investigating the effect of additional functional groups in the vicinity of a vanadate moiety.

Experimental Section

Materials: The Schiff base precursor salicylaldehyd-benzoyl-hydrazone (H₂salhyph) was derived form salicylaldehyd and benzole acid hydrazide. All other chemicals were of reaction grade.

Physical Measurements: Elemental analyses (C, H, N) were carried out on a Leco CHNS-932 elemental analyzer. – FT-IR spectra for KBr pellets and Nujol mulls between CsI plates were measured on a Bruker IFS66 spectrometer. – Raman spectra were measured on a Bruker IFS66/FRA106 spectrometer ($\lambda_e = 1064$ nm). – Electronic spectra were recorded on Shimadzu UV-160A (solution transmission) and Beckman Acta MIV (solid state reflection) spectrophotometers. – ¹H and ¹³C NMR spectra were recorded on a Bruker AC250 and the ⁵¹V NMR spectra on a Bruker DRX500 spectrometer. Chemical shifts in ppm are reported as δ downfield from the standards, tetramethylsilane (¹H and ¹³C) and VOCl₃ (⁵¹V).

Synthesis of NH₄[VO₂(salhyph)]: To a solution of H₂salhyph (9.61 g, 40 mmol) in 50 ml DMF was added NH₄VO₃ (4.68 g, 40 mmol). The resulting mixture was heated to 90 °C for 4 h. After cooling to room temperature the mixture was filtrated and the resulting solution reduced in vacuum to about half its original volume. After standing overnight a crystalline material in form of yellow plates can be isolated. Additional material can be obtained by adding toluene (100 ml) to the DMF solution leading to the precipitation of a yellow powder which was collected by filtration. Total yield: 7.70 g (58 %). $C_{14}H_{14}N_{3}O_{4}V$ (339.22): calcd. C 49.57, H 4.16, N 12.39; found C 49.81, H 4.35, N 12.12 %.

¹H NMR ([D₇]DMF): δ = 6.79–6.89 (m, 2H, ph), 7.34–7.51 (m, 4H, ph), 7.60–7.64 (m, 1H, ph), 8.11–8.15 (m, 2H, ph), 9.03 (s, 1H, *HC*=N). – ¹³C NMR ([D₇]DMF): δ = 117.5, 120.2, 121.0, 128.6, 128.7, 131.0, 133.1, 133.7, 133.9, 156.4 (*C*=N), 165.8, 171.1 ppm. – ⁵¹V NMR ([D₇]DMF): δ = -540 ppm. – Selected IR data (cm⁻¹): $\tilde{\nu}$ = 3155 (m, br; N–H), 1610 (s, br; C=N–N=C), 918 (s, VO₂), 895 (s, VO₂). – UV/Vis (solid state reflection, ν_{max} in 10³ cm⁻¹): 35.1, 26.0. – UV/Vis (DMF solution, ν_{max} in 10³ cm⁻¹ (ε in 10⁶ cm² mol⁻¹)): 31.2 (14), 24.8 (14).

Synthesis of [VO(OMe)(salhyph)(HOMe)]: NH_4VO_3 (2.92 g, 25 mmol) was added to a solution of H_2 salhyph (6.01 g, 25 mmol) in 250 ml methanol. The resulting mixture was heated to reflux for ca. 2 h until all solid is dissolved. After reducing the volume of the

Table 2 Crystal and diffraction data for NH₄[VO₂(salhyph)]

formula formula weight	C ₁₄ H ₁₄ N ₃ O ₄ V 339.22
crystal size	$0.50 \times 0.20 \times 0.05 \text{ mm}$
crystal system	monoclinic
space group	Pn
a	708.8(2) pm
b	1444.3(3) pm
С	717.1(2) pm
β	101.09(2)°
V	0.7204(2) nm ³
Ζ	2
Т	293 K
$\rho_{\rm calc}$	1.564 g cm^{-3}
reflection collected	1594
independent reflections	1540
observed reflections	1285
restraints/parameters	12/253
R1 $(I > 2\sigma(I))$	0.039
wR2 (all refl.)	0.091

solution to about 75 ml and cooling to room temperature brown crystals begin to form. A second batch of crystalline material can be obtained after further reduction of the volume of the mother liquor. Total yield: 6.78 g (74 %). $C_{16}H_{17}N_3O_5V$ (368.26): calcd. C 52.18, H 4.65, N 7.61; found C 52.20, H 4.85, N 7.60 %.

¹H NMR (CDCl₃): δ = 3.44 (s, 3H, CH₃OH), 5.25 (s, 3H, VOCH₃), 7.07–7.16 (m, 2H, ph), 7.42–7.61 (m, 5H, ph), 8.11–8.19 (m, 2H, ph), 8.95 (s, 1H, HC=N). – ¹³C NMR (CDCl₃): δ = 50.8 (CH₃OH), 72.3 (VOCH₃), 117.7, 120.2, 121.7, 128.5, 128.7, 130.0, 131.9, 132.3, 135.0, 154.7 (C=N), 164.5, 173.3 ppm. – ⁵¹V NMR (CDCl₃): δ = –547 ppm. – Selected IR data (cm⁻¹): \tilde{v} = 1608 (s, br: C=N–N=C), 969 (s, V=O). – UV/Vis (solid state reflection, v_{max} in 10₃ cm⁻¹): 24.3, 18.5 (sh). – UV/Vis (CHCl₃ solution, v_{max} in 10³ cm⁻¹ (ε in 10⁶ cm² mol⁻¹)): 31.6 (27), 26.2 (13), 19.0 sh (1).

Synthesis of $[V_2O_3(salhyph)_2]$: To a solution of NH₄[VO₂(salhyph)] (1.60 g, 4.7 mmol) in 100 ml THF phosphoric acid dibutylester (1.95 g, 5.0 mmol) was added. The resulting brown solution was stirred at room temperature for additional 5 h. After removing the solvent under reduced pressure the solid residue was washed with dichloromethane yielding a brown powder. Total yield: 1.15 g (78 %). C₂₈H₂₀N₄O₇V₂ (626.38): calcd. C 53.69, H 3.22, N 8.94; found C 53.83, H 3.17, N 8.81 %.

Selected IR data (cm⁻¹): $\tilde{v} = 1605$ (s, br; C=N-N=C), 997 (s, V=O). – UV/Vis (solid state reflection, v_{max} in 10³ cm⁻¹): 24.6, 16.7 (sh). – UV/Vis (CHCl₃ solution, v_{max} in 10³ cm⁻¹ (ε in 10⁶ cm² mol⁻¹)): 31.2 (41), 26.2 (19), 18.5 sh (1).

Synthesis of [VO₂(Hsalhyph)] ([VO₂(Dsalhyph)]): A suspension of [V₂O₃(salhyph)₂] (0.21 g) in 15 ml water was heated to reflux for 2 h. The color of the solid changes from brown to yellow. After cooling to room temperature the insoluble yellow product was isolated by filtration. Total yield: 0.19 g (87 %). The deuterated derivative [VO₂(Dsalhyph)] can be obtained by using D₂O as reaction medium. C₁₄H₁₁N₂O₄V (322.19): calcd. C 52.19, H 3.44, N 8.69; found C 51.86, H 3.44, N 8.61 %.

Selected IR data for [VO₂(Hsalhyph)] (cm⁻¹): $\tilde{\nu} = 2600$ (w, br; N–H at N2 see Figure 1), 884 (s, br; VO₂). – Selected IR data for [VO₂(Dsalhyph)] (cm⁻¹): $\tilde{\nu} = 1980$ (w, br; N–H at N2 see Figure 2), 901 (s, VO₂), 869 (s, VO₂).

X-ray Crystallography: The diffraction data of NH₄[VO₂(salhyph)] were recorded with ω -scan technique in the 2θ range 5–52° with a Siemens R3m/V diffractometer with a graphite monochromator using molybdenum radiation ($\lambda = 71.073$ pm). The crystallographic data for NH₄[VO₂(salhyph)] is summarized in Table 2. The final unit-cell parameters were obtained by least-squares fitting of the setting angles of 30 reflections with 2θ between 17° and 30°. Lo-

rentz and polarization corrections as well as an absorption correction based on azimuthal ψ scans were applied to the diffraction data. The structure was solved by direct methods (SHELXTL) and subsequent full-matrix least square refinement. The refinement afforded a Flack parameter [25] of 0.01(4). All non-hydrogen atoms were refined by using anisotropic thermal parameters. All hydrogen atoms bound to carbon atoms were located from Fourier-difference map and refined including their isotropic displacement parameters. The hydrogen atoms of the ammonium ion were refined with their isotropic displacement parameters fixed at 1.5 times the value of the nitrogen atom attached. In addition the N–H bonds and H···H interatomic distances within the ammonium ion were restricted in order to reproduce a tetrahedral geometry.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-130813. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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