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New Aspects for Modeling Supramolecular Interactions in Vanadium Haloperoxidases: β-Cyclodextrin Inclusion Compounds of *cis*-Dioxovanadium(V) Complexes

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The reaction of potassium vanadate and the hydrazone ligand derived from Schiff base condensation of salicylaldehyde and biphenyl-4-carboxylic acid hydrazide (H_2salhybiph) in the presence of β-cyclodextrin (β-CD) in water yields the 1:1 inclusion compound K[VO_2(salhybiph)@β-CD]. The characterization in solution confirmed the integrity of the inclusion compound in different polar solvents such as DMSO and water. The inclusion compound crystallizes with additional water molecules in the triclinic space group *P*1. The supramolecular aggregation of the inclusion compound in the solid state is established through hydrogen bonding interactions between adjacent β-CD hosts and the π–π stacking ability of the ligand side chain of the guest complexes.

Introduction

Vanadium haloperoxidases (V-HPO) are enzymes that catalyze the oxidation of halides to the corresponding hypohalous acids. These oxidized intermediates then readily halogenate organic substrates or convert hydrogen peroxide to singlet oxygen.[1] In addition, these enzymes can also catalyze the oxidation of organic sulfides to sulfoxides.[2] The active site of this class of enzymes consists of a vanadate moiety with a proposed trigonal bipyramidal geometry covalently bound to a histidine residue and held within the protein by strong hydrogen-bonding interactions with several amino acid residues.[3] Furthermore, this active site architecture is also found for certain acid phosphatases,[4] but with subtle distinctions concerning the relative positions of the amino acid residues.[5] The catalytic activity of V-HPO enzymes is proposed to be driven by this hydrogen-bonding network.[6] Therefore, V-HPO model systems need to be designed that provide a polar protic surrounding in order to offer the possibility for such relevant hydrogen-bonding interactions. Examples for such vanadium complexes derived from *N*-salicylidene hydrazides with a hydroxy substituted side chain have recently been reported.[7,8]

An alternative method to provide such an environment for the complex moieties can be through their interaction with appropriate host molecules, which would generate host–guest assemblies. Cyclodextrins (CDs) represent hosts with hydrophobic cavities and hydrophilic outer walls and generate inclusion complexes with various apolar groups that are included partially or completely in the cavity.[9] CDs are well known to form a variety of hydrogen bonds because of their free OH-groups. Parts of the guest protruding out of the CD ring opening could take part in this hydrogen bonding system. CDs and their substituted derivatives could be considered artificial enzymes as a result of their ability to react as catalysts for several asymmetric reactions, such as oxidation reactions, hydrolyses, and racemate separation.[10] Moreover, CDs are known to bind organometallic complexes containing aromatic constituents and such encapsulated complexes often exhibit markedly different physical and chemical properties.[11] Nevertheless, only very few examples of such inclusion complexes reported in the literature have been successfully characterized by single-crystal X-ray diffraction.[12]

We have recently reported the application of the *N*-salicylidene hydrazide ligand system for generating vanadium(V) complexes with a variety of functional groups attached to the ligand core.[7,8,13,14] Extending this approach, we report herein the synthesis and structure of a *cis*-dioxovanadium(V) complex containing an appropriate apolar biphenyl group in the ligand side chain, and its inclusion compound with β-CD.

Results and Discussion

The *N*-salicylidene hydrazide ligand with apolar side chain used in this study is derived from Schiff base condensation of salicylaldehyde and biphenyl-4-carboxylic acid hydrazide (H_2salhybiph; Figure 1). Reaction of potassium

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vanadate with the H_2salhybiph ligand in a methanol/acetone solution leads to the potassium salt of the corresponding *cis*-dioxovanadium(V) complex K[VO_2(salhybiph)]. The addition of acetone to the reaction solution is required owing to the very poor solubility of the H_2salhybiph ligand system in methanol. After a reaction time of 2 d, K[VO_2-(salhybiph)] can be isolated as a yellow crystalline solid material. Notably, the analogous reaction for ammonium vanadate affords the neutral *cis*-dioxovanadium(V) complex [VO_2(Hsalhybiph)] as the isolated product in a much lower yield. This is due to the fact that the ligand system under study is prone to variable protonation states at the amide group, which along with the presence of the protolytically active ammonium ions allows the generation of various complex species.[13] Therefore, the potassium vanadate route seems to be more promising for the generation of the relevant inclusion compounds.

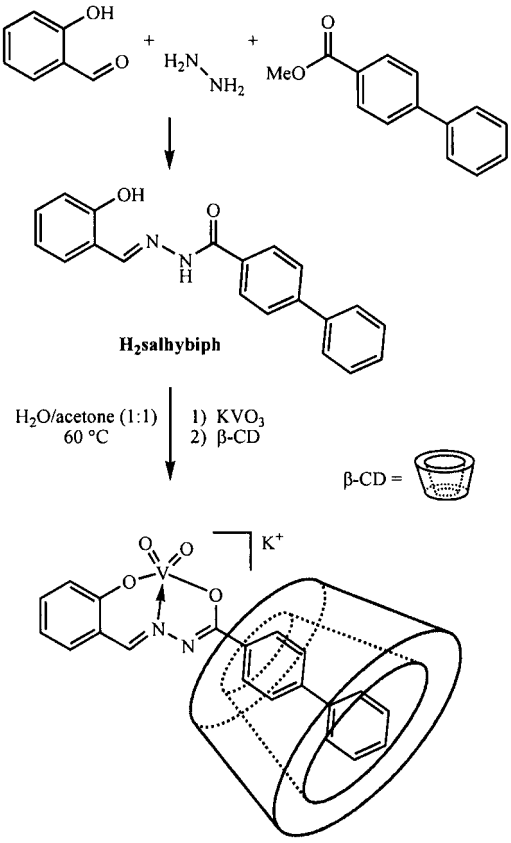

Figure 1. Synthesis of the inclusion compound K[VO_2(salhybiph)@β-CD].

The inclusion compound K[VO_2(salhybiph)@β-CD] was synthesized by a one-pot reaction of potassium vanadate with the H_2salhybiph ligand and β-CD in a water/acetone solution (Figure 1). The presence of β-CD results in a considerably shorter reaction time of about 2 h, and the reaction can be visually followed by the dissolution of the ligand. The 1:1 inclusion compound K[VO_2(salhybiph)@β-CD] can be isolated as yellow crystals, which have been fully characterized in solution and in the solid state.

The solution structure of the inclusion compound K[VO_2(salhybiph)@β-CD] can be unambiguously established by ^{1}H NMR spectroscopy. Proton diffusion-ordered NMR spectroscopy (DOSY) clearly proves the integrity of the inclusion compound in solution, as only one species can be detected. The NOESY NMR spectra exhibit cross-peaks between the proton signals of the biphenyl side chain of the vanadium complex and those of the β-CD host (Figure 2). In particular for the 3-H and 5-H protons of the β-CD that extend into the β-CD host cavity, strong interactions with the aromatic protons of the biphenyl side chain of the guest are observed. The absence of cross-peaks between the 5-H protons of the β-CD and the Hbp7 and Hbp8 protons of the biphenyl group of the guest complex strongly suggests that the guest penetrates into the β-CD cavity from the primary hydroxy side. This is confirmed by the intense cross-peaks that are observed between the 6-H protons of the β-CD host and the Hbp2 and Hbp3 protons of the biphenyl side chain of the guest complex. Moreover, the lack of cross-peaks between the aromatic protons of the salicylidene moiety and the β-CD host proves that this part of the guest complex is distant from the β-CD. This also corroborates the presence of a 1:1 inclusion compound with a clear

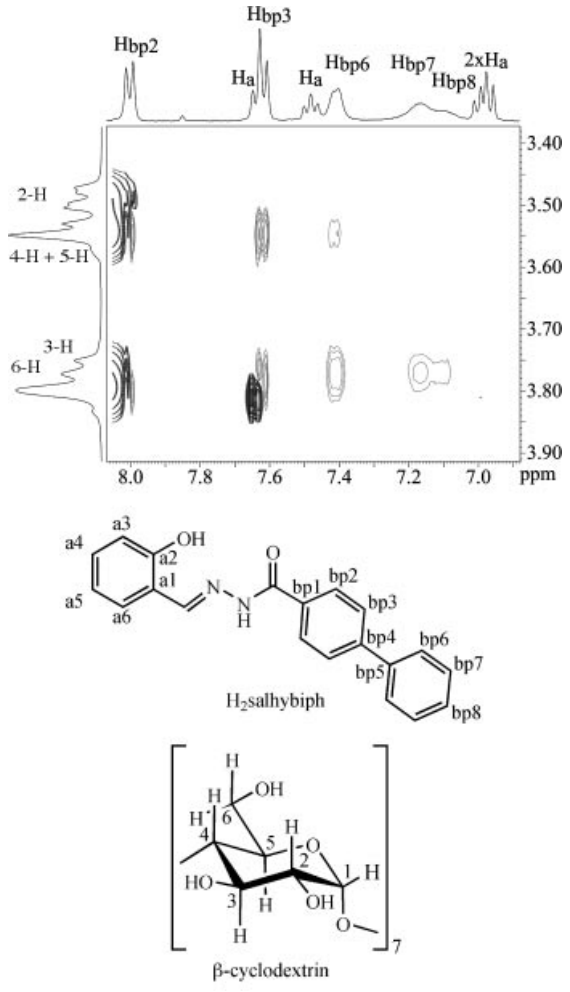

Figure 2. NOESY spectrum of K[VO_2(salhybiph)@β-CD] in D_2O and labeling schemes for host and guest.

preference for the interaction of the biphenyl side chain with the β-CD host cavity.

For the solid state characterization of the inclusion compound K[VO_2(salhybiph)@β-CD], crystals suitable for X-ray analysis were grown by slowly cooling a hot aqueous solution of the inclusion compound. For different batches, a considerable variation in the water content was found. Thermogravimetric analysis (TGA) of these materials reveals a weight loss of about 6.5% (16.6%) in the temperature range form room temperature up to 140 °C, assigned to the removal of water molecules in the interstices between the inclusion compounds. In agreement with the elemental analysis, this indicates anywhere between 6.5 and 18 water molecules of crystallization per host–guest unit in the solid state. Above 200 °C, the inclusion compound starts to decompose. This temperature is somewhat lower than that observed for plain β-CD hydrate which starts to decompose at around 270 °C.[15] This difference can be attributed to the promoting effect of the metal complex host on the decomposition of the β-CD, and this provides further evidence for significant host–guest interaction in the inclusion compound. The final residual masses at 750 °C of 8.8 and 7.1% observed for different batches correspond very well to the values calculated for the formation of potassium orthovanadate, KVO_3 (8.1 and 7.3%, respectively; cf. Experimental Section).[16]

Crystallographic investigation shows that this inclusion compound crystallizes in the triclinic space group *P*1. The asymmetric unit contains two inclusion compounds together with the solvent water molecules, with the latter as well as the potassium cations disordered over several crystallographic positions. The molecular structure of the inclusion compound is shown in Figure 3. As expected from the solution NMR spectra, the *cis*-dioxovanadium(V) complex intrudes only partially into the β-CD cavity. Only the biphenyl side chain is located within the hydrophobic cavity of the host, whereas the remaining polar part of the complex is situated outside the primary hydroxy side of the β-CD host.

The vanadium atom of the guest complex exhibits an almost ideal square pyramidal environment with the coordinated H_2salhybiph ligand in its dianionic form, which is characterized by τ values lower than 0.10 (τ = 0 for ideal tetragonal pyramid; τ = 1 for ideal trigonal bipyramid). The basal plane of the square pyramid is given by atoms N*i*1, O*i*3, and O*i*4 (*i* = 1, 2) of the ligand and the oxo group O*i*2; the apical position is occupied by the oxo group O*i*1. Relative to the mean plane given by the donor atoms of the chelate ligand system, the vanadium atom is displaced towards the apical oxo group O*i*1 by about 40 pm, whereas the oxo group O*i*2 is slightly tilted towards the opposite side of the ligand plane with a deviation by about 15 pm from that plane. The structural parameters are consistent with those observed for other vanadium(V) complexes containing similar *N*-salicylidene hydrazide ligands, in particular the V=O (O*i*1 and O*i*2) as well as the V–N (N*i*1) and V–O (O*i*3 and O*i*4) bond lengths are within the expected range for such *cis*-dioxovanadium(V) complexes.[8,13]

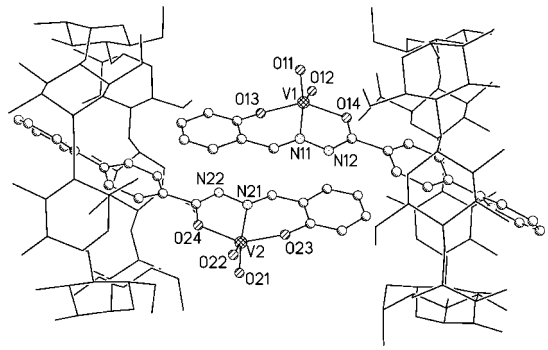

Figure 3. Representation of the molecular structure of the inclusion compound K[VO_2(salhybiph)@β-CD] that shows the two independent host–guest assemblies in the asymmetric unit. Selected bond lengths [pm] and angles [°]: V1–O11 159.6(9), V1–O12 159.8(8), V1–O13 189.3(7), V1–O14 196.7(6), V1–N11 215.5(7), N11–N12 139.3(9), O14–C18 127.8(10), N12–C18 129.7(11), O11–V1–O12 106.0(7), O11–V1–O13 102.4(4), O11–V1–O14 104.0(4), O12–V1–O13 98.5(4), O12–V1–O14 94.0(4), O13–V1–O14 146.3(3), O11–V1–N11 99.8(5), O12–V1–N11 153.4(5), O13–V1–N11 82.2(3), O14–V1–N11 73.0(3).

In the solid state, the inclusion compound K[VO_2-(salhybiph)@β-CD] forms head-to-head dimers with the secondary hydroxy sides of both β-CD hosts linked by hydrogen bonds as depicted in Figure 4. This arrangement leads to a π–π interaction of the biphenyl side chains of the corresponding guest molecules at a distance of 363 pm. The *cis*-dioxovanadium moieties of the guest molecules protrude from their hosts on the primary hydroxy group side and thereby generate a gap with a distance of about 910 pm between the adjacent head-to-head dimers. The protruding complex fragments of the adjacent dimers possess a staggered arrangement with a nearly coplanar orientation of their ligand planes (defined by N*i*1, O*i*3, and O*i*4 with *i* = 1, 2), which are about 340 pm apart. The overall packing of the head-to-head dimers can be described as a so-called "channel-type" arrangement[17] which is built from host guest dimers that are stringed together. These channels are oriented along the [001] direction and linked through hydrogen bonds between primary hydroxy groups (C-6) of neighboring β-CDs as depicted in Figure 5.

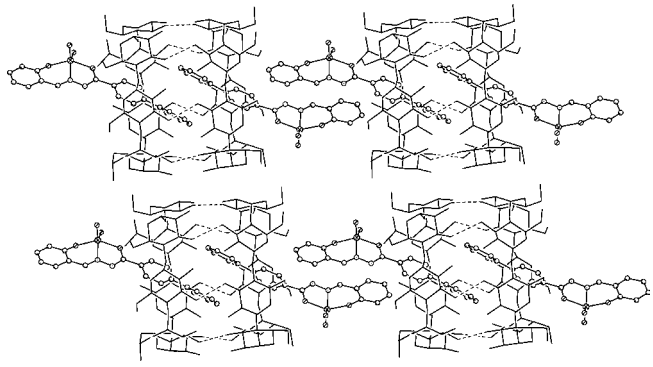

Figure 4. Packing of the inclusion compound K[VO_2(salhybiph)@β-CD] viewed approximately perpendicular to the [001] direction of the β-CD channel alignment. Hydrogen bonds between neighboring β-CDs are drawn as broken lines.

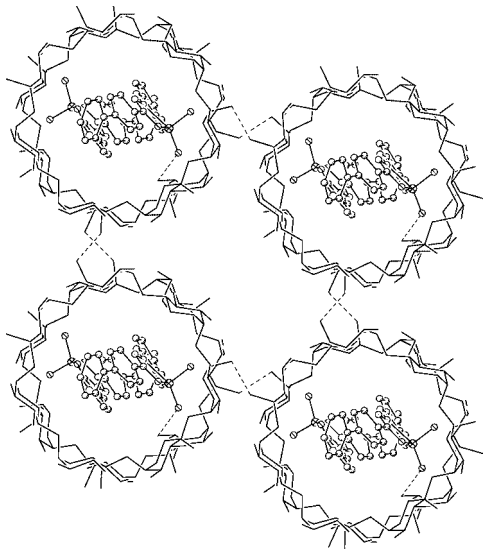

Figure 5. View of the crystal packing along the β-CD channels in the [001] direction. Hydrogen bonds between neighboring β-CDs are drawn as broken lines.

Conclusions

We present the first supramolecular inclusion compound of a *cis*-dioxovanadium(V) complex with cyclodextrins. To facilitate this, a new vanadium complex derived from *N*-salicylidene hydrazide containing a hydrophobic biphenyl side chain matching the β-CD host cavity was synthesized. The integrity of the isolated inclusion compound K[VO_2-(salhybiph)@β-CD] in solution was confirmed by NMR spectroscopy. The solid-state structure reveals a channel-type packing of the head-to-head β-CD dimers which is cross-linked through hydrogen bonds and intercalated potassium cations. Through modification of the CD-host, it should be possible to utilize this concept for the generation of novel systems in oxidation catalysis, including the potential influence of the sugar backbone on chiral induction of vanadium-catalyzed oxidation reactions.

Experimental Section

General Remarks: The synthesis of the ligand biphenyl-4-carboxylic acid salicylidene hydrazide (H_2salhybiph) and its neutral *cis*-dioxovanadium(V) complex [VO_2(Hsalhybiph)] is described in the Supporting Information. ^{1}H, ^{13}C and ^{51}V as well as NOESY and DOSY NMR spectra were recorded with a 400 MHz Bruker AVANCE spectrometer. For notation used in the assignment of the atoms, see Figure 2. The chemical shift values for the ^{51}V NMR spectra are reported relative to $VOCl_3$ as an external standard. Elemental analyses (C, H, N) were carried out with a Leco CHNS-932 elemental analyzer. Mass spectra were measured with a MAT95XL Finnigan instrument utilizing electron spray ionization and observation in the negative mode. IR spectra were recorded with a Bruker IFS55/Equinox spectrometer on samples prepared as KBr pellets. Thermogravimetric analysis (TGA) for powdered samples was performed with a Netzsch STA409PC Luxx apparatus under a constant flow of air ranging from room temperature up to 1000 °C with a heating rate of 5 °C/min. Atomic absorption spectrometry (AAS) was performed with an AA-6800 from Shimadzu.

K[VO_2(salhybiph)]: A suspension of biphenyl-4-carboxylic acid salicylidene hydrazide (0.200 g, 0.63 mmol) in an acetone/methanol mixture (30:5, 35 mL) was heated to 60 °C. After the addition of KVO_3 (0.087 g, 0.63 mmol), the suspension turned yellow–orange, and after 2 d of continuous stirring a clear solution was obtained. Upon removal of the solvent, the crude product was redissolved in hot methanol (30 mL), filtered, and kept for crystallization. Yield: 0.170 g (62%). ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 6.78 (t, J = 7.3 Hz, 1 H, H_{a5}), 6.80 (d, J = 8.4 Hz, 1 H, H_{a3}), 7.35 (t, J = 7.8 Hz, 1 H, H_{a4}), 7.39 (tt, J = 7.4 and 2.1 Hz, 1 H, H_{bp8}), 7.48 (t, J = 7.5 Hz, 2 H, H_{bp7}), 7.57 (d, J = 6.8 Hz, 1 H, H_{a6}), 7.52 (d, J = 8.2 Hz, 2 H, H_{bp3}), 7.75 (t, J = 8.9 Hz, 2 H, H_{bp6}), 8.10 (d, J = 8.3 Hz, 2 H, H_{bp2}), 9.00 (s, 1 H, CH=N) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 116.65 (HC_{a5}), 119.45, 119.86 (HC_{a3} and C_{a1}), 126.34, 126.65 (HC_{bp3} and HC_{bp6}), 127.78 (HC_{bp8}), 128.29 (HC_{bp2}), 128.93 (HC_{bp7}), 131.85 (C_{bp1}), 132.47 (HC_{a6}), 133.03 (HC_{a4}), 139.33 (C_{bp4}), 141.91 (C_{bp5}), 155.51 (C=N), 164.59 (C_{a2}), 169.48 (C=O) ppm. ^{51}V NMR (105 MHz, [D_6]DMSO): δ = –532 ($\nu_{1/2}$ = 1122 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3447 (s), 3055 (w), 3028 (w), 2929 (w), 1615 (vs), 1550 (m), 1513 (m), 1476 (w), 1446 (m), 1383 (w), 1344 (s), 1278 (m), 1204 (w), 1157 (w), 950 (s), 904 (s), 875 (s), 760 (m), 740 (s), 696 (m) cm^{-1}. MS (ESI–, MeOH): m/z (%) = 397 (100) [VO_2(salhybiph)]$^-$.$C_{20}H_{14}KN_2O_4V$ (436.38): calcd. C 55.05, H 3.23, N 6.42; found C 55.05, H 3.25, N 6.28.

K[VO_2(salhybiph)@β-Cyclodextrin]·$x$$H_2O$: Biphenyl-4-carboxylic acid salicylidene hydrazide (0.100 g, 0.32 mmol) was suspended in a solution of β-cyclodextrin (0.359 g, 0.32 mmol) in water (15 mL) at 60 °C. Acetone (15 mL) was added for better solubility of the ligand. Upon addition of KVO_3 (0.044 g, 0.32 mmol), the suspension turned yellow and, after stirring for 2 h at 60 °C, became a clear solution. The hot solution was filtered, and acetone was removed under reduced pressure. The solution was heated to 70 °C, allowed to slowly cool to room temperature, and the product precipitated as pale yellow cubic crystals. The water content of the isolated crystalline material varies considerably for different synthetic batches. Yield: 0.29 g (50%). Batch 1: $C_{62}H_{84}KN_2O_{39}V$·6.5H_2O (1697.47): calcd. C 44.10, H 5.79, N 1.67; found C 44.04, H 5.94, N 1.39. TGA: Weight loss up to 140 °C of 6.5% (calcd. 6.9%), residual mass at 750 °C of 8.8% (calcd. 8.1% for KVO_3). Batch 2: $C_{62}H_{84}KN_2O_{39}V$·18H_2O (1895.64): calcd. C 39.28, H 6.38, N 1.48, K 2.06; found C 39.79, H 6.39, N 1.21, K 1.2–2.3. TGA: Weight loss up to 140 °C of 16.6% (calcd. 17.1%), residual mass at 750 °C of 7.1% (calcd. 7.3% for KVO_3). ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 3.25–3.40 (m, 2 H, 2-H and 4-H), 3.50–3.70 (m, 4 H, 3-H, 5-H, and 6-H), 4.44 (t, J = 5.5 Hz, 1 H, C6-OH), 4.82 (d, J = 3.3 Hz, 1 H, 1-H), 5.66 (d, J = 2.2 Hz, 1 H, C3-OH), 5.71 (d, J = 6.9 Hz, 1 H, C2-OH), 6.77 (t, J = 7.2 Hz, 1 H, H_{a5}), 6.78 (d, J = 7.4 Hz, 1 H, H_{a3}), 7.34 (dt, J = 7.7 and 2.0 Hz, 1 H, H_{a4}), 7.38 (tt, J = 7.5 Hz and 1.2 Hz, 1 H, H_{bp8}), 7.48 (t, J = 7.6 Hz, 2 H, H_{bp7}), 7.56 (dd, J = 8.1 and 1.8 Hz, 1 H, H_{a6}), 7.75 (t, J = 8.2 Hz, 4 H, H_{bp3} and H_{bp6}), 8.08 (d, J = 8.4 Hz, 2 H, H_{bp2}), 8.98 (s, 1 H, CH = N) ppm. ^{1}H NMR (400 MHz, D_2O): δ = 3.43 (dd, J = 9.9 Hz and 3.4 Hz, 1 H, 2-H), 3.45–3.50 (m, 2 H, 4-H and 5-H), 3.70–3.80 (m, 3 H, 3-H and 6-H), 4.90 (d, J = 3.5 Hz, 1 H, 1-H), 6.91 (d, J = 8.4 Hz, 1 H, H_{a3}), 6.94 (t, J = 7.6 Hz, 1 H, H_{a5}), 7.04 (br. s, 1 H, H_{bp8}), 7.11 (s, 2 H, H_{bp7}), 7.35 (d, J = 6.2 Hz, 2 H, H_{bp6}), 7.42 (t, J = 8.0 Hz, 1 H, H_{a4}), 7.57 (t, J = 8.0 Hz, 2 H, H_{bp3}), 7.57 (t, J = 8.0 Hz, 1 H, H_{a6}), 7.95 (d, J = 8.0 Hz, 2 H, H_{bp2}), 8.89 (s, 1 H, CH=N) ppm.^{13}C NMR (100 MHz, [D_6]DMSO): δ = 59.92 (C-6), 72.04 (C-5), 72.41 (C-2), 73.05 (C-3), 81.54 (C-4), 101.93 (C-1), 116.70 (HC_{a5}), 119.51, 119.92 (HC_{a3} and C_{a1}),

126.43, 126.72 (HC_{bp3} and HC_{bp6}), 127.85 (HC_{bp8}), 128.33 (HC_{bp2}), 129.00 (HC_{bp7}), 131.78 (C_{bp1}), 132.51 (HC_{a6}), 133.11 (HC_{a4}), 139.43 (C_{bp4}), 141.94 (C_{bp5}), 155.60 (C=N), 164.69 (C_{a2}), 169.51 (C=O) ppm. ^{51}V NMR (105 MHz, [D$_6$]DMSO): δ = –532 ppm ($\nu_{1/2}$ = 1067 Hz). ^{51}V NMR (105 MHz, D_2O): δ = –533 ppm. IR (KBr): $\tilde{\nu}$ = 3392 (vs), 2929 (m), 1612 (m), 1550 (w), 1509 (w), 1490 (w), 1448 (w), 1388 (w), 1156 (m), 1079 (m), 1028 (s), 945 (m), 906 (m), 759 (w) cm^{-1}. MS (ESI–, MeOH): *m*/*z* (%) = 2667 (8) {[VO_2(salhybiph)] +2β-CD}$^-$, 1532 (42) {[VO_2(salhybiph)] + β-CD}$^-$, 1134 (30) [β-CD – H]$^+$, 397 (100) [VO_2(salhybiph)]$^-$.

X-ray Crystallographic Study of K[VO_2(salhybiph)@β-Cyclodextrin]·*x*H_2O: Crystals suitable for X-ray analysis were grown by slow cooling of a hot water solution of the inclusion compound. $C_{62}H_{84}KN_2O_{39}V(\cdot 8H_2O)$, M_r = 1715.48 g mol^{-1}, triclinic, space group *P*1, *a* = 1535.37(5), *b* = 1545.54(7), *c* = 2146.64(8) pm, *α* = 94.710(2), β = 98.484(2), *γ* = 102.994(2)°, *V* = 4873.9(3) × 10^6 pm^3, *Z* = 2, μ(Mo-K_α) = 0.229 mm^{-1}, 32730 reflections measured with a Nonius KappaCCD diffractometer at 183(2) K in the 2.49 to 27.50° *Θ* range. The structure was solved by direct methods and subsequently refined against F^2 with the SHELXL-97 program,[18] which converged at R_1 = 0.1126 for 20029 observed reflections with $I > 2\sigma(I)$ and wR_2 = 0.3385 for all unique reflections with a goodness-of-fit on F^2 of 1.165. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to carbon atoms were introduced in theoretical positions but not refined. As known from the analytical data of different batches the content of water molecules is varying. For the measured crystals an overall content of eight water molecules could be assigned. The potassium cations and the water molecules were found to be disordered over several crystallographic positions and refined with partial occupancy factors. The discrimination between potassium and water sites is made on the basis of the potential coordination numbers and hydrogen bonding interactions. For the water molecules, no attached hydrogen atoms were considered. Additional disorder was found for one of the included anionic vanadium complexes (V2) which was refined with a relative ratio of about 1:2. The largest positive and negative residual Fourier peaks after the refinement were equal to 0.82 and –0.51, respectively. CCDC-629924 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental details for the synthesis of the H_2salhybiph ligand and the [VO_2H(salhybiph)] complex.

Acknowledgments

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