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Cyclodextrin inclusion compounds of vanadium complexes: Structural characterization and catalytic sulfoxidation

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ABSTRACT

Reaction of potassium vanadate with the hydrazone ligand derived from Schiff-base condensation of salicylaldehyde and biphenyl-4-carboxylic acid hydrazide (H_2salhybiph) in the presence of two equivalents α-cyclodextrin (α-CD) in water yields the 1:2 inclusion compound K[VO_2(salhybiph)@(α-CD)$_2$]. Characterization in solution confirmed the integrity of the inclusion compound in the polar solvent water. The inclusion compound crystallizes together with additional water molecules as K[VO_2(salhybiph)@(α-CD)$_2$] · 18H_2O in the monoclinic space group *P*2(1). Two α-CD rings forming a hydrogen bonded head to head dimer are hosting the hydrophobic biphenyl side chain of the complex K[VO_2(salhybiph)]. The supramolecular aggregation of the inclusion compound in the solid state is established through hydrogen bonding interactions among adjacent α-CD hosts and with vanadate moieties of the guest complexes as well as ionic interactions with the potassium counterions. In contrast the supramolecular structure of the guest complex K[VO_2(salhybiph)] without the presence of CD host molecules is governed by π–π-stacking interactions and additional CH/π interactions. The new inclusion complex K[VO_2(salhybiph)@(α-CD)$_2$] and the analogous 1:1 inclusion compound with *β*-CD were tested as catalyst in the oxidation of methyl phenyl sulfide (thioanisol) using hydrogen peroxide as oxidant in a water/ethanol mixture, under neutral as well as acidic conditions.

1. Introduction

There is continuous interest in the chemistry of vanadium complexes due to their biological relevance and catalytic properties [1–9]. This is particularly related with the discoveries of the insulin-like effect of vanadium compounds, and the presence of vanadium in the prosthetic group of certain haloperoxidases and nitrogenases. Vanadium haloperoxidases are enzymes that catalyze different oxidation reactions like the oxidation of halides to corresponding hypohalous acids [10] and the oxidation of organic sulfides to sulfoxides [11–14]. The latter reaction is of considerable current interest, as sulfoxides are valuable products in synthetic organic chemistry [15–17], which are known to be accessible through catalysis promoted by various transition metals [18–23]. In this class of enzymes the active species is a vanadate moiety with proposed trigonal-bipyramidal geometry which is covalently linked to a histidine residue [10]. Nevertheless, their reactivity is attributed to the presence of an extensive hydrogen-bonding network [24], which seems to be a more general feature in the understanding of the biological and catalytic action of vanadium compounds [25]. Such supramolecular interactions can be modeled by vanadium(V) complexes with appropriate ligand systems [26,27]. To generate such model complexes we have recently utilized *N*-salicylidene hydrazide ligands with a variety of functional groups attached to the ligand core [28–31], which for a hydroxy substituted side chain leads to intramolecular assemblies [32–34].

Host–guest systems are attractive alternatives to generate supramolecular environments for relevant complex moieties. Utilizing cyclodextrins (CDs), with their hydrophobic cavities and hydrophilic outer walls as hosts, it is possible to generate inclusion compounds with various apolar groups, that are included partially or completely in the cavity [35–37]. On the other hand, CDs are well-known to form hydrogen bonds due to their free hydroxy groups. In particular parts of the guest protruding out of the CD ring opening could be involved in this hydrogen-bonding system as we have recently been able to show [38]. Moreover, CDs as well as their substituted derivatives are attractive components of artificial enzymes due to their ability to act as catalysts for several asymmetric reactions, like oxidation reactions, hydrolysis and racemate separation [39–41]. Although, CDs are known to encapsulate metallo-organic complexes containing aromatic constituents and such assemblies often exhibit markedly different physical and chemical properties [42,43], only very few examples of such inclusion compounds with metal complexes reported in the literature have been successfully characterized by single-crystal X-ray diffraction [38,44–49].

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We have recently reported the synthesis and structure of a 1:1 inclusion compound of a *cis*-dioxovanadium(V) complex derived from a Schiff-base ligand containing an appropriate apolar biphenyl group in the ligand side chain with β-CD [38]. Extending this approach, we report herein the synthesis and structure of this vanadium complex and its 1:2 inclusion compound with α-CD. The solid state and solution structure of the host–guest compound will be discussed and compared with the analogous 1:1 compound with β-CD. In addition the complex and its inclusion compounds were tested as catalyst for the peroxidic oxidation of sulfides.

2. Experimental

2.1. Materials and methods

The ligand biphenyl-4-carboxylic acid salicylidene hydrazide (H_2salhybiph), its potassium complex K[VO_2(salhybiph)] and its 1:1 inclusion compound with β-CD K[VO_2(salhybiph)@β-CD] were prepared according to published procedures [38]. Crystals of K[VO_2(salhybiph)] · $4H_2O$ suitable for X-ray analysis were grown from a water/acetone mixture via slow evaporation over a period of several days.

^{1}H, ^{13}C and ^{51}V as well as NOESY, ROESY, and DOSY NMR spectra were recorded on a 400 MHz Bruker AVANCE spectrometer. The splitting of proton resonances in the reported ^{1}H NMR spectra are defined as s = singlet, d = doublet, t = triplet, br = broad, and m = multiplet. The chemical shift values for ^{51}V are reported relative to $VOCl_3$ as external standard. Elemental analyses (C, H, N) were carried out on a Leco CHNS-932 elemental analyzer. Mass spectroscopic measurements were performed on a MAT95XL Finnigan instrument utilizing electron spray ionization with observation in negative and positive mode. IR spectra were recorded on a Bruker IFS55/Equinox spectrometer on samples prepared as KBr pellets. The intensity of reported IR bands are defines as s = strong, m = medium, and w = weak. Thermogravimetric analysis (TGA) for powdered samples were performed with a Netzsch STA409PC Luxx apparatus under a constant flow of air ranging from room temperature up to 800 °C with a heating rate of 5 °C/min. HPLC measurements were carried out with a Jasco-MD 1515 instrument equipped with a WHELK-O 1 column and a UV-diode array multiwavelength detector.

2.2. Synthesis of K[VO_2(salhybiph)@(α-CD)$_2$]

α-CD (1.229 g, 1.26 mmol) and KVO_3 (0.087 g, 0.63 mmol) were added to a suspension of H_2salhybiph (0.200 g, 0.63 mmol) in water (50 mL) at 70 °C. Acetone (15 mL) was added for better solubility of the ligand. Upon addition of KVO_3 the suspension turns yellow and after stirring for several hours at 70 °C became a clear solution. It was filtered hot, the acetone removed under reduced pressure and the solution kept at room temperature for crystallization. The product precipitates as pale yellow cubic crystals after slow evaporation of solvent at room temperature (yield: 49%, 0.839 g, 0.31 mmol). Anal. data for $C_{92}H_{134}N_2O_{64}VK \cdot 18H_2O$ (2706.3): Calc.: C, 40.90; H, 6.32; N, 1.04%. Found: C, 40.21; H, 6.27; N, 0.98%. TGA: Weight loss up to 160 °C: 11.5% (calc. for $18H_2O$ 11.8%), residual mass at 800 °C: 5.7% (calc. 5.1% for KVO_3). ^{1}H NMR (400 MHz, D_2O): δ = 3.43 (dd, ^3J = 9.8 Hz and ^3J = 2.8 Hz, 1 H, H-2), 3.50 (t, ^3J = 9.4 Hz, 1 H, H-4), 3.76 (t, ^3J = 9.4 Hz, 1 H, H-3), 3.79 – 3.95 (m, 3 H, H-5 and H-6), 4.92 (d, ^3J = 2.4 Hz, 1 H, H-1), 6.99 (d, ^3J = 8.4 Hz, 1 H, H_{a3}), 7.03 (t, ^3J = 7.2 Hz, 1 H, H_{a5}), 7.52 (t, ^3J = 7.2 Hz, 1 H, H_{a4}), 7.57 (t, ^3J = 7 Hz, 1 H, H_{bp8}), 7.58–7.64 (m, 3 H, H_{bp6} and H_{a6}), 7.66 (d, ^3J = 8.0 Hz, 2 H, H_{bp3}), 7.11 (t, ^3J = 8.0 Hz, 2 H, H_{bp7}), 8.54 (d, ^3J = 7.6 Hz, 2 H, H_{bp2}), 9.10 (s, 1 H, CH=N) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 60.46 (C-6), 71.99 (C-5), 72.28 (C-2), 73.48 (C-3), 81.22 (C-4), 102.22 (C-1), 118.55 (HC_{a3}), 119.93 (HC_{a5} and C_{a1}), 125.47, 125.92 (HC_{bp3} and HC_{bp6}), 127.25 (HC_{bp8}), 129.82 (HC_{bp7}), 130.56 (HC_{bp2} and C_{bp1}), 132.67 (HC_{a6}), 136.00 (HC_{a4}), not detectable C_{bp4} and C_{bp5}, 156.53 (C=N), 163.42 (C_{a2}), 170.72 (C=O) ppm. ^{51}V NMR (105 MHz, D_2O): δ = −534 ($\nu_{1/2}$ = 1635 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3369 s, 2931 m, 1614 m, 1570 w, 1550 w, 1507 w, 1491 w, 1447 m, 1406 m, 1383 m, 1363 m, 1349 m, 1295 w, 1242 w, 1154 s, 1078 s, 1029 vs, 949 m, 937 m, 903 m, 852 w, 758 m, 745 m, 701 m, 573 m cm^{-1}. ESI-MS (negative mode, MeOH): *m*/*z* = 2342.4 (1%, [VO_2L]$^-$@(α-CD)$_2$), 1943 (2%, (α-CD)$_2$-H$^+$), 1369 (8%, [VO_2L]$^-$@α-CD), 971 (12%, α-CD-H$^+$) 397 (100%, [VO_2L]$^-$). ESI-MS (positive mode, MeOH) : *m*/*z* = 2388 (1%, [VO_2L]$^-$@(α-CD)$_2$ + 2Na$^+$), 1967.6 (3%, (α-CD)$_2$ + Na$^+$), 1415.4 (5%, [VO_2L]$^-$@α-CD + 2Na$^+$), 1011 (84%, α-CD + K$^+$), 995 (100%, α-CD + Na$^+$).

2.3. Catalysis

The vanadium(V) compound (0.001 M) and thioanisol (0.01 M) were dissolved in the appropriate solvent (20 mL) with 1,3,5-trimethoxybenzene (0.01 M) as internal standard. In case of the complex K[VO_2(salhybiph)] a methanol/dichloromethane (3/7) mixture and in cases of the inclusion compounds a water/ethanol (53.4/46.6) mixture was used. To this solution the oxidant hydrogen peroxide (0.0125 M, 35% w/w) was added. In case of the acid catalyzed reactions the appropriate amount of $HClO_4$ (0.001 or 0.01 M) was added. The progress of the reaction was monitored by TLC (diethyleter/*n*-hexane = 9/1). After the appropriate reaction time, fractions of 2 mL were quenched with 3 mL sodium sulphite (0.1 M) solution. The resulting aqueous solution was extracted three times with 4 mL dichloromethane. From the combined organic phases all volatiles were removed in vacuo. Conversion and selectivity were determined by ^{1}H NMR spectroscopy of the obtained residual material in $CDCl_3$. After separation of the sulfoxide by column chromatography (silica gel, diethyleter/*n*-hexane = 9/1), the enantiomeric excess value (ee) was determined with HPLC on a chiral column.

Table 1
Crystallographic and refinement data.

	K[VO_2(salhybiph)] · $4H_2O$	K[VO_2(salhybiph)@(α-CD)$_2$] · $18H_2O$
Empirical formula	$C_{20}H_{22}KN_2O_8V$	$C_{92}H_{170}KN_2O_{82}V$
Formula weight	508.44	2706.34
Crystal size (mm)	0.6 × 0.6 × 0.3	0.5 × 0.5 × 0.4
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1$
Unit cell dimensions		
a (pm)	1442.65(11)	1901.8(4)
b (pm)	719.50(5)	1598.7(3)
c (pm)	4289.0(2)	2241.8(5)
β (°)		113.45(3)
V (nm^3)	4.4520(5)	6.253(2)
Z	8	2
T (K)	183(2)	183(2)
ρ_{calc} (g/cm^3)	1.517	1.437
F(000)	2096	2868
μ (mm^{-1})	0.682	0.228
θ range (°)	2.37–27.47	1.98–27.47
Index range	−18 ⩽ h ⩽ 18	−24 ⩽ h ⩽ 19
	−3 ⩽ k ⩽ 9	−20 ⩽ k ⩽ 18
	−49 ⩽ l ⩽ 48	−25 ⩽ l ⩽ 29
Reflections collected	17,503	53,340
Indep. reflections (R_{int})	4825 (0.097)	27,031 (0.030)
Goodness-of-fit on F^2	1.011	1.078
R_1 ($I > 2\sigma(I)$)	0.051	0.057
wR_2 (all data)	0.108	0.162