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Chiral oxovanadium(V) complexes with a 6-amino-6-deoxyglucopyranoside-based Schiff-base ligand: Catalytic asymmetric sulfoxidation and structural characterization

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ABSTRACT

Two new chiral oxovanadium(V) complexes [VO(OMe)(L)] (**1**) and [VO(Osal)(L)] (**2**) derived from the Schiff-base ligand 6-*N*-[(3,5-di-*tert*-butyl-salicylidene)amino]-6-deoxy-1,2,3-tri-*O*-methyl-α-D-glucopyranose (H_2L) were synthesized via two different routes. The reaction of the Schiff-base ligand H_2L with ammonium metavanadate in hot methanol as well as with tris(isopropoxy)oxovanadium(V) in diethyl ether at room temperature leads to a mixture of complexes **1** and **2**, which can be isolated by means of fractional crystallization. The complexes were characterized with elemental analysis, ^{51}V, ^{1}H and ^{13}C NMR, IR spectroscopy, MS and in case of **1** by X-ray diffraction. Complex **1** crystalizes in the orthorhombic space group $P2_12_12_1$ with a distorted trigonal bipyramidal geometry at the vanadium center ($\tau = 0.58$). Under hydrolytic conditions **1** forms the *cis*-dioxovanadium(V) complex [VO_2(MeOH)(HL)] (**3**) which can be monitored by NMR spectroscopy. Complexes **1** and **2** were tested as catalysts for sulfoxidation of different sulfide substrates PhSR (R = Me, Bz) utilizing hydrogen peroxide or *tert*-butyl hydroperoxide (TBHPO) as oxidant in dichloromethane as solvent. The yield as well as the enantiomeric excess were found to strongly depend on the catalyst, substrate and oxidant used.

1. Introduction

Optically active sulfoxides are an interesting class of compounds widely used in the pharmaceutical industry and academia as chiral auxiliaries in asymmetric syntheses of biologically active compounds [1]. In particular metal catalysts have been employed in the enantioselective oxidation of sulfides to generate chiral sulfoxides. These metal catalysts are mainly based on titanium, vanadium, and manganese complexes [2]. Less is known for metal catalysts based on molybdenum and iron, which have nevertheless proven to efficiently catalyze the oxidation of sulfide substrates by peroxides [3].

A particular focus has been placed on vanadium complexes, not only because of their catalytic properties [4–6], but also because of the fact that vanadium haloperoxidase enzymes facilitate the enantioselective catalytic oxidation of sulfides by hydrogen peroxide [7]. The active site of vanadium haloperoxidases consists of a vanadate moiety with a trigonal bipyramidal geometry covalently bound to a histidine residue [8], with the reactivity attributed to the presence of an extensive hydrogen bonding network [9]. This can be modeled by vanadium(V) complexes with an appropriate ligand [10] or host–guest system based on cyclodextrin [11], where the latter case can provide chiral information through the employed sugar host.

A straightforward approach to generate suitable systems for applications in asymmetric catalysis is the utilization of carbohydrate-based ligands [12]. Over the past two decades an intense exploration has been focused on the functionalization of the sugar backbone with amides, amines, imines, and carboxylic groups to accomplish a stronger metal-ion complexation [13]. In this context particularly Schiff-base ligands have been addressed due to their common availability via condensation of amino sugars with aldehyde moieties [14,15,16]. Vanadium(V) complexes with this type of Schiff-base ligands are rather limited [16,17]. To our knowledge only one case was reported were such a Schiff-base ligand was utilized as a chiral carbohydrate-based auxiliary in vanadium-promoted enantioselective catalysis [18].

In this paper, we report the catalytic properties and characterization of two new oxovanadium(V) complexes derived from 6-amino-6-deoxy-1,2,3-tri-*O*-methyl-α-D-glucopyranoside.

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2. Experimental

2.1. Materials and general procedures

The Schiff-base ligand 6-*N*-[(3,5-di-*tert*-butyl-salicylidene) amino]-6-deoxy-1,2,3-tri-*O*-methyl-α-D-glucopyranose (H_2L) was obtained in a six-step synthesis according to published procedures [15]. All other chemicals and reagents were obtained from commercial sources and used without further purification unless stated otherwise. If required, solvents were further purified by standard methods [19]. Column chromatography was performed using MN silica gel 60 (70–230 mesh) purchased from Macherey-Nagel. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. The IR spectra were measured on a Bruker IFS55/Equinox. Mass spectrometric measurements were carried out on a MAT95XL Finnigan instrument for electron spray ionization (negative and positive mode) and MATSSQ-710 Bruker instrument for FAB measurements. Elemental analyses were made with a LECO CHN/932 elemental analyzer. HPLC measurements were made with a Jasco-MD 1515 instrument equipped with a WHELK-O 1 column and a UV-diode array multiwavelength detector.

2.2. Synthesis of [VO(OMe)(L)] (**1**) and [VO(Osal)(L)] (**2**)

2.2.1. Method A

The Schiff-base ligand H_2L (0.400 g, 0.91 mmol) was dissolved in 15 mL methanol and NH_4VO_3 (0.106 g, 0.91 mmol) was added to this solution. The resulting suspension was stirred at 65 °C. After 6 d one equivalent of ethylene glycol (0.060 mL, 0.97 mmol) was added and after additional stirring for 3 d at 65 °C the resulting clear brown solution was filtered hot and allowed to stand for crystallization at room temperature. Fractional crystallization first yields a very small portion of complex **1** as red crystals (yield <1%) and subsequently dark purple crystals of **2** (0.086 g, 0.12 mmol). Yield: **1** <1%; **2** 13%.

2.2.2. Method B

A suspension of the Schiff-base ligand H_2L 2(0.265 g, 0.61 mmol), NH_4VO_3 (0.071 g, 0.61 mmol), and ethylene glycol (0.037 g, 0.61 mmol) in 10 mL methanol was heated under reflux for 2 d until all metavanadate was dissolved. The brown solution was filtrated hot and allowed to stand at room temperature for crystallization. Fractional crystallization afforded first a first crop of red crystals of complex **1** (0.183 g, 0.34 mmol) and a second crop of dark purple crystals of **2** (0.012 g, 0.02 mmol). Yield: **1** 56%; **2** 3%.

2.2.3. Method C

To a solution of the Schiff-base ligand H_2L (0.440 g, 1.00 mmol) in 15 mL dry diethyl ether VO(O*i*Pr)$_3$ (0.260 g, 1.07 mmol) was slowly added dropwise under an atmosphere of argon. The resulting brown solution was kept with gentle stirring for 3 d. Subsequently the solvent was removed to dryness under reduced pressure. The crude product (0.450 g) was redissolved in 17 mL dry methanol and kept under an atmosphere of argon. After a few days red crystals of complex **1** (0.190 g, 0.36 mmol) could be isolated from this solution. Yield: **1** 36%. Upon exposure of the mother liquor to air for several days a small crop of complex **2** (0.040 g, 0.05 mmol) could be isolated as purple crystals.

2.2.4. Data for [VO(OMe)(L)] (**1**)

Anal. calcd for $C_{25}H_{40}NO_8V$ (533.53): C, 56.28; H, 7.56; N, 2.63. Found: C, 56.38; H, 7.42; N, 2.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9H, C(C*H*$_3$)$_3$), 1.43 (s, 9H, C(C*H*$_3$)$_3$), 3.33–3.37 (m, 2H, H-2 and OC*H*$_3$), 3.42 (s, 3H, OC*H*$_3$), 3.43–3.54 (m, 2H, H-5), 3.55 (s, 3H, OC), 3.64 (s, 3H, OC*H*$_3$), 3.79–3.97 (m, 1H, H-6eq), 4.43 (td, $^2J_{6ax6eq} = {}^3J_{6ax5}$ = 11.4 Hz, $^4J_{6ax4}$ = 1.6 Hz, 1H, H-6ax), 4.86 (d, $^3J_{12}$ = 2.7 Hz, 1H, H-1), 5.02 (s, 3H, VOC*H*$_3$), 5.18–5.29 (m, 1H, H-4), 7.16 (d, ^4J = 2.6 Hz, 1H, Ar), 7.55 (d, ^4J = 2.6 Hz, 1H, Ar), 8.37 (s, 1 H, C*H*=N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.3, 31.0 (2 × C(*C*H$_3$)$_3$), 33.9, 34.8 (2 × *C*(CH$_3$)$_3$), 55.1, 59.2, 60.6 (3 × OCH$_3$), 66.4 (C-6), 68.5 (C-5), 70.4 (VOCH$_3$), 80.8, 82.9 (C-2, C-3), 92.5 (C-4), 98.0 (C-1), 118.6 (Ar-*C*), 127.0 (Ar-*C*H), 130.0 (Ar-*C*H), 138.2 (Ar-*C*), 141.5 (Ar-*C*), 160.7 (Ar-*C*), 165.6 (*C*H=N) ppm. ^{51}V NMR (105 MHz, $CDCl_3$): δ = −535 ppm ($\nu_{1/2}$ = 170 Hz). IR (KBr): 2954 (s), 2907 (m), 2870 (m), 2831 (w), 2798 (w), 1632 (s), 1562 (m), 1466 (m), 1418 (m), 1392 (w), 1363 (w), 1299 (w), 1278 (w), 1199 (m), 1157 (m), 1134 (w), 1065 (s), 1050 (s), 1000 (s), 961 (m), 818 (w), 683 (m), 558 (w) cm^{-1}. MS-FAB (NBA): *m*/*z* (%) = 502 [V(OH)(L)]$^+$ (90), 471 (30), 438 (40), 372 (80), 341 (100).

2.2.5. Data for [VO(Osal)(L)] (**2**)

Anal. calcd for $C_{39}H_{58}NO_9V$ (735.82): C, 63.66; H, 7.94; N, 1.90. Found: C, 64.53; H, 8.05; N, 1.69. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 9H, C(C*H*$_3$)$_3$), 1.24 (s, 9H, C(C*H*$_3$)$_3$), 1.28 (s, 9H, C(C*H*$_3$)$_3$), 1.57 (s, 9H, C(C*H*$_3$)$_3$), 2.92 (s, 3H, OC*H*$_3$), 3.15 (t, $^3J_{31} = {}^3J_{32}$ = 9.0 Hz, 1H, H-3), 3.32 (dd, $^3J_{23}$ = 9.5 Hz, $^3J_{21}$ = 3.7 Hz, 1H, H-2), 3.42 (s, 3H, OC*H*$_3$), 3.48 (s, 3H, OC*H*$_3$), 3.69 (m, 1H, H-5), 3.69 (ddd, $^3J_{56ax}$ = 12.0 Hz, $^3J_{56eq}$ = 4.0 Hz, $^3J_{54}$ = 8.9 Hz, 1H, H-5), 3.94 (dd, $^2J_{6eq6ax}$ = 12.0 Hz, $^3J_{6eq5}$ = 4.0 Hz, 1H, H-6eq), 4.37 (td, $^2J_{6ax6eq} = {}^3J_{6ax5}$ = 12.0 Hz, $^4J_{6ax4}$ = 1.3 Hz, 1H, H-6ax), 4.85 (d, $^3J_{12}$ = 3.6 Hz, 1H, H-1), 5.68 (t, $^3J_{43} = {}^3J_{45}$ = 8.9 Hz, 1H, H-4), 7.14 (d, ^4J = 2.6 Hz, 1H, Ar), 7.21 (d, ^4J = 2.6 Hz, 1H, Ar), 7.42 (d, ^4J = 2.2 Hz, 1H, Ar), 7.59 (d, ^4J = 2.6 Hz, 1H, Ar), 8.41 (s, 1H, C*H*=N), 9.10 (s, 1H, C*H*=O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.4, 29.7, 31.2, 31.4 (4 × C(*C*H$_3$)$_3$), 34.2, 34.3, 35.0, 35.4 (4 × *C*(CH$_3$)$_3$), 55.3, 59.6, 59.8 (3 × OCH$_3$), 66.5 (C-6), 69.0 (C-5), 80.4 (C-2), 83.4 (C-3), 96.6 (C-4), 98.4 (C-1), 120.8 (Ar-*C*), 124.0 (Ar-*C*), 127.2 (Ar-*C*H), 129.4 (Ar-*C*H), 130.6 (Ar-*C*H), 131.9 (Ar-*C*H), 137.1 (Ar-*C*), 138.1 (Ar-*C*), 140.4 (Ar-*C*), 142.3 (Ar-*C*), 161.7 (Ar-*C*), 164.7 (Ar-*C*), 164.9 (*C*H=N), 192.8 (*C*H=O) ppm. ^{51}V NMR (105 MHz, $CDCl_3$): δ = −539 ppm ($\nu_{1/2}$ = 500 Hz). IR (KBr): 2952 (vs), 2905 (s), 2867 (m), 1651 (vs), 1626 (vs), 1558 (m), 1543 (m), 1464 (m), 1438 (m), 1411 (m), 1392 (m), 1363 (m), 1274 (m), 1254 (s), 1170 (w), 1069 (vs), 1053 (vs), 954 (s), 846 (s), 776 (w), 753 (m), 722 (w), 680 (s), 551 (s) cm^{-1}. MS-ESI (MeOH): *m*/*z* (%) = 1494 [2M + Na]$^+$ (20), 758 [M + Na]$^+$ (100), 736 M$^+$ (10).

2.3. NMR data for the hydrolysis product [VO_2(MeOH)(HL)] (**3**)

NMR tube experiments were performed to examine the hydrolytic stability of complexes **1** and **2**. Only complex **1** was found to be susceptible to hydrolysis leading to the complex [VO_2(MeOH)(HL)] (**3**).

^{1}H NMR (400 MHz, DMSO): δ = 1.27 (s, 9H, C(C*H*$_3$)$_3$), 1.42 (s, 9H, C(C*H*$_3$)$_3$), 3.00 (s, 3H, OC*H*$_3$), 3.00–3.07 (m, 2H, H-2 and H-4), 3.16 (d, ^3J = 5.2 Hz, 3H, C*H*$_3$OH → V), 3.21 (t, $^3J_{32} = {}^3J_{34}$ = 9.2 Hz, 1H, H-3), 3.28 (s, 3H, OC*H*$_3$), 3.20–3.30 (m, 1H, H-5), 3.46 (s, 3H, OC*H*$_3$), 3.92 (td, $^2J_{6ax6eq} = {}^3J_{6ax5}$ = 9.8 Hz, $^4J_{6ax4}$ = 2.1 Hz, 1H, H-6ax), 4.06 (q, ^3J = 5.3 Hz, 1H, CH$_3$O*H* → V), 4.29 (dd, $^2J_{6eq6ax}$ = 9.8 Hz, $^3J_{6eq5}$ = 2.1 Hz, 1H, H-6eq), 4.68 (d, $^3J_{12}$ = 3.4 Hz, 1H, H-1), 5.36 (d, ^3J = 6.4 Hz, 1H, O*H* at C-4), 7.25 (d, ^4J = 2.4 Hz, 1H, Ar), 7.44 (d, ^4J = 2.4 Hz, 1H, Ar), 8.34 (s, 1H, C*H*=N) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 29.2, 31.3 (2 × C(*C*H$_3$)$_3$), 33.8, 34.8 (2 × *C*(CH$_3$)$_3$), 48.6 (*C*H$_3$OH → V), 53.9, 57.3, 60.1 (3 × OCH$_3$), 66.2 (C-6), 66.7 (C-6', C-5), 72.3 (C-4), 81.0 (C-2), 82.5 (C-3), 96.2 (C-1), 118.3 (Ar-*C*), 127.8 (Ar-*C*H), 129.0 (Ar-*C*H), 137.9 (Ar-*C*), 138.0 (Ar-*C*), 161.8 (Ar-*C*), 169.1 (*C*H=N) ppm. ^{51}V NMR (105 MHz, DMSO-d_6): δ = −519 ppm.

2.4. Catalysis

The appropriate vanadium(V) complex (0.01 mmol) and alkyl phenyl sulfide (1.0 mmol) were dissolved in dichloromethane