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X-ray structure analysis, electronic and vibrational circular dichroism of chiral-at-metal dioxidovanadium(V) complexes with amino acids derived Schiff base ligands

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ABSTRACT

Five new chiral dioxidovanadium Schiff base complexes derived from L-valine, L-leucine, L-histidine, L-threonine and D-threonine were synthesized and characterized by elemental analysis, ^{1}H and ^{51}V NMR and IR spectra. The absolute configurations of the complexes were determined by X-ray single crystal analysis in solid state and by electronic and vibrational circular dichroism in CH_3CN solution. The L-threoninato complex, which contains two stereogenic centers in the amino acid site, does not show epimerization of the amino acid, in contrast with the analogical isoleucine-derived complexes reported recently. Conglomerate crystallization was observed in racemic DL-valine- and DL-threonine-derived complexes.

1. Introduction

Vanadium Schiff base complexes have shown catalytic activity in several types of asymmetric oxidations of organic substrates [1–13]. Therefore chiral complexes of vanadium(IV) and (V) are of a great interest and during recent years some diffraction and spectroscopic studies focused on the chirality-at-metal were published. It is assumed that the formation of tetragonally pyramidal and octahedral chiral Schiff base complexes of vanadium is diastereospecific meaning that if there is one stereogenic center in the Schiff base and one stereogenic center is generated on the vanadium atom upon complexation only one stereoisomer instead of two diastereomers is observed in the solid state structure. This assumption is proven by many crystal structures of tetragonally pyramidal [14–24] and octahedral [14,25–34] complexes of vanadium(V) with ONO Schiff base donor set where enantiomerically pure Schiff bases were used. If a racemic Schiff base is used in the synthesis racemic complexes are isolated from the reaction system and the complex formation occurs diastereospecifically again [14,35] although obviously not many syntheses starting from racemic ligands have been performed. This situation clearly illustrates the compound [VO{*N*-(2-oxidobenzylidene)phenylalaninato}(OMe)(HOMe)]: one diastereomer was isolated when L-phenylalanine derivative was used in the synthesis (instead of two possible) [36] while two enantiomers with defined chirality mode on the vanadium atom were present in the crystal structure if DL-phenylalanine was introduced in the synthesis (although four stereoisomers are theoretically possible) [37]. Finally, if a Schiff base without a stereogenic center is applied in the synthesis both possible stereoisomers (enantiomers defined by the stereogenic center at the metal site) are observed, either tetragonally pyramidal [14,38–43] or octahedral [14,29,38,42,44–52].

Although these conclusions are quite straightforward, little is known about the composition of the reaction mixtures, the mother liquors and the solutions of dissolved stereoisomers in respect to chirality-at-metal. It has been shown that despite the crystal structure of [VO{*N*-(2-oxido-1-naphthylmethylene)-L-alaninato}OBu^{S}(HOBu^{S})] carries four centers of chirality (the vanadium atom, the alanine moiety, secondary carbons of coordinated butanol and butanolate), it contains only two stereoisomers (*ASRR* and *CSSS*), and ^{51}V NMR spectrum of the solution of the compound exhibits three signals corresponding to three diastereomers out of eight possible stereoisomers. The situation may be even more complicated due to overlapping signals in ^{51}V NMR spectra, dissociation of ligands and disfavourable formation of specific diastereomers [53].

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Our primary goal was to prepare a new family of chiral dioxido complexes of vanadium(V) derived from amino acids as a low-cost source of chirality. As a continuation of our work on understanding the stereochemistry of chiral vanadium(V) complexes [54–59] we took a closer look at the chirality of the compounds prepared. Recently we have reported on the vanadium catalyzed epimerization of isoleucine and a controlled crystallization of stereoisomers of $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-isoleucinato})]$ [60] together with chiroptical characterization of isolated stereoisomers. The synthetic procedure was utilized to prepare five new chiral dioxido complexes of vanadium(V): $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-valinato})]$ (**VO_2L-val**), $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-leucinato})]$ (**VO_2L-leu**), $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-histidinato})]\cdot 2H_2O$ (**VO_2L-his**), $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-threoninato})]$ (**VO_2L-thr**) and $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-D-threoninato})]$ (**VO_2D-thr**) (Fig. 1). The absolute configuration of the complexes prepared was confirmed not only by X-ray structure analysis, but also by electronic and vibrational circular dichroism which provide comprehensive information on the chirality. Moreover, crystallizations of racemic mixtures of **VO_2DL-val** and **VO_2DL-thr** were examined as well bringing surprising proof of rarely occurring conglomerate crystallization of enantiomers.

2. Experimental

2.1. General information and materials

All reagents and solvents were obtained from commercial sources and used without further purification. V_2O_5 was prepared by thermal decomposition of NH_4VO_3. Elemental analyses (C, H, N) were performed on a Vario MIKRO cube (Elementar). Vanadium(V) was determined volumetrically by titration with $FeSO_4$ using diphenylamine as indicator. Solid state IR spectra were recorded on Thermo Scientific Nicolet 6700 FT IR spectrometer in Nujol mulls and in KBr pellets. The ^{1}H NMR spectra were recorded with a Varian Mercury plus instrument (300 MHz for ^{1}H). Chemical shifts (δ) are given in ppm relative to tetramethylsilane. The ^{51}V NMR spectra of solutions were registered at 278 K on a Varian Mercury Plus 600 MHz spectrometer operating at 157.88 MHz (^{51}V) in 5 mm tubes. Chemical shifts (δ) are given in ppm relative to $VOCl_3$ as external standard (δ = 0 ppm). Solution IR and VCD spectra were recorded on a Bruker Tensor 27 FTIR spectrometer with 4 cm^{-1} resolution equipped with the Bruker PMA 50 VCD sidebench module, using a data collection time of 6 h. CD_3CN solution samples were placed in a 100 μm path length BaF_2 cell. All spectra were corrected for background effects by solvent subtraction. ECD and UV–Vis spectra were recorded on a JASCO J-815 CD spectrometer in CH_3CN solutions with a 1 cm cell.

2.2. X-ray diffraction

Diffraction data were collected using a Kappa Apex II (Bruker) diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems). Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for radiation absorption by methods incorporated in the diffractometer software. The phase problem was solved by direct methods (SHELXS97 [61]) and refined by full-matrix least-squares based on F^2 (SHELXL97 [61]). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined as riding atoms. Geometric data were obtained with a recent version of the PLATON [62] program. Graphics were obtained with DIAMOND [63].

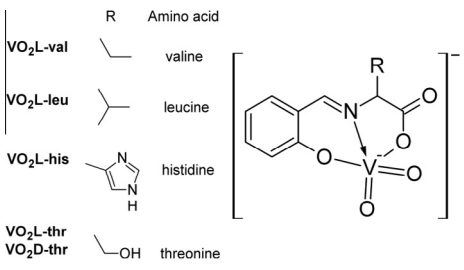

Fig. 1. Structural formulae of vanadium(V) complexes.

2.3. Syntheses

The vanadium(V) complexes reported herein as well as $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-isoleucinato})]$ (**VO_2L-ile**) applied as a reference for designation of absolute configurations were prepared by a modified procedure described previously [60].

2.3.1. $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-valinato})]$ (**VO_2L-val**)

Salicylaldehyde (0.531 mL, 5 mmol) in *tert*-butanol (3 mL) was added to a solution of L-valine (0.580 g, 5 mmol) dissolved in acetone (3 mL) and tetrabutylammonium hydroxide (3.6 mL of 40% *w*/*w* solution, 5 mmol) and the solution was stirred for 1 h. After V_2O_5 (0.45 g, 2,5 mmol) was dissolved in tetrabutylammonium hydroxide (3.6 mL of 40% *w*/*w* solution, 5 mmol) at room temperature the resulting colorless solution was added to the solution of a Schiff base and the solution was stirred for 15 min. To the orange solution 3 mL of distilled water were added. Pale yellow crystals appear on the following day. Yield: 52%. *Anal.* Calc. for $C_{28}H_{49}N_2O_5V$: C, 61.75, H, 9.07, N, 5.14, V, 9.35. Found: C, 61.55; H, 9.18, N, 5.19, V, 9.16%. IR (cm^{-1}): 458, 514, 558, 588, 616, 740, 771, 807, 848, 887, 921, 935, 980, 1005, 1030, 1039, 1059, 1125, 1137, 1148, 1137, 1204, 1307, 1341, 1402, 1544, 1599, 1620, 1670. UV–Vis [λ_{max}, nm]: 227, 260, 370. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.32 (s, 1H), 7.36 (dt, 1H) 7.31 (dd, 1H), 6.98 (d, 1H), 6.74 (t, 1H), 4.11 (d, 1H), 3.49 (broad t, 8H), 2.37 (m, 1H), 1.74 (broad m, 8H), 1.5 (broad m, 8H), 1.13 (d, 3H), 1.08 (d, 3H), 1.00 (t, 12H). ^{51}V NMR (CH_3CN, ppm): −534.

2.3.2. $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-leucinato})]$ (**VO_2L-leu**)

The synthesis of **VO_2L-leu** was similar to the procedure described for **VO_2L-val** except that L-valine was replaced by L-leucine (0.65 g, 5 mmol). Yield: 32%. *Anal.* Calc. for $C_{29}H_{51}N_2O_5V$: C, 62.35, H, 9.20, N, 5.01, V, 9.12. Found: C, 62.45; H, 9.17, N, 4.94, V, 9.21%. IR (cm^{-1}): 455, 476, 540, 557, 574, 615, 687, 740, 771, 811, 873, 895, 916, 938, 958, 1005, 1029, 1079, 1107, 1134, 1147, 1169, 1205, 1224, 1292, 1311, 1340, 1380, 1403, 1426, 1451, 1546, 1599, 1619, 1670. UV–Vis [λ_{max}, nm]: 227, 260, 370. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.31 (s, 1H), 7.37 (dt, 1H) 7.31 (dd, 1H), 6.99 (d, 1H), 6.74 (t, 1H), 4.34 (t, 1H), 3.50 (broad t, 8H), 2.03–1.83 (broad m, 1H + 2H), 1.76 (broad m, 8H), 1.5 (broad m, 8H), 1.03 (d, 6H), 0.99 (t, 12H). ^{51}V NMR (CH_3CN, ppm): −535.

2.3.3. $[N(C_4H_9)_4][VO_2(N\text{-salicylidene-L-histidinato})]\cdot 2H_2O$ (**VO_2L-his**)

The synthesis of **VO_2L-his** was similar to the procedure described for **VO_2L-val** except that L-valine was replaced by L-histidine (0.768 g, 5 mmol). In the final step 5 mL of water and L-histidine (0.768 g, 5 mmol) were added to the solution to precipitate the compound. Yield: 35%. *Anal.* Calc. for $C_{29}H_{51}N_4O_7V$: C, 56.30, H, 8.31, N, 9.06, V, 8.23. Found: C, 56.42; H, 8.39, N, 9.10, V, 8.15%. IR (cm^{-1}): 419, 449, 459, 501, 530, 554, 564, 618, 629, 655, 707, 746, 774, 808, 821, 858, 882, 919, 934, 968, 985, 1030, 1072, 1087, 1108, 1126, 1149, 1176, 1210, 1236, 1276, 1307, 1341, 1361, 1400, 1485, 1538, 1571, 1622, 1653. UV–Vis [λ_{max}, nm]: 227, 260, 370.. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.77 (s, 1H), 7.54 (s, 1H), 7.32 (d, 1H) 7.05 (d, 1H), 6.86 (d, 1H), 6.67 (t, 1H), 4.54 (broad t, 1H), 3.37 (broad t, 8H), 3.12 (broad dd, 2H),