Probing chirality of oxidovanadium(V) centers in complexes with tridentate sugar Schiff-base ligands: solid-state and solution behavior

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Supplementary Information

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1 Summarized NMR spectral data and assignments for complexes 1–4

Table S1 ^{1}H NMR data for **1** including proton and diastereomer assignments (for atom labeling see Scheme 1 of the main text)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)				
δ (ppm)	Proton #	Proton assignment[a]	Multiplicity	J (Hz)
3.55	1H	H-2(*A*)	dd	$^{3}J_{av}$ = 10.0
3.77	1H	H-4(*A*)	dd	$^{3}J_{4,3}$ = $^{3}J_{4,5}$ = 9.1
3.81–3.98	3H	H-6a(*A*), H-6a(*C*), H-5(*C*)	m	
4.00–4.18	2H	H-4(*C*), H-5(*A*)	m	
4.27–4.41	2H	H-6e(*C*), H-6e(*A*)	m	
4.63	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b}$ = 12.0
4.70	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b}$ = 12.4
4.68–4.76	1H	H-2(*C*)	m	
4.79	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b}$ = 12.0
4.86	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b}$ = 12.2
4.93	3H	V–OCH_3(*C*)	s	
5.17	3H	V–OCH_3(*A*)	s	
5.22	1H	H-3(*C*)	dd	$^{3}J_{3,4}$ = $^{3}J_{3,2}$ = 10.0
5.40	1H	H-1(*C*)	s	
5.44	1H	H-1(*A*)	s	
5.52	1H	H-3(*A*)	dd	$^{3}J_{3,4}$ = $^{3}J_{3,2}$ = 9.8
5.58	1H	H-21(*A*)	s	
5.62	1H	H-21(*C*)	s	
6.80–7.60	28H	Ph(*A*), Ph(*C*)	m	
7.87	2H	H-14(*A*), H-14(*C*)	s	

[a] For each diastereomer of **1** present in $CDCl_3$ solution an individual sets of signals is observed with an integral ratio of 2:1 (**1***A*:**1***C*) (with *A* and *C* denoting the absolute configurations at the vanadium center).

Table S2 ^{13}C NMR data for **1** including carbon and diastereomer assignment (for atom labeling see Scheme 1 in main text)

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)	
δ (ppm)	Carbon assignment
64.5, 64.6	C-5(*A*), C-5(*C*)
68.8, 68.8, 68.9	C-6(*A*), C-7(*A*), C-6(*C*), C-7(*C*)
70.8	V–OCH_3(*C*)
72.8	V–OCH_3(*A*)
73.0	C-2(*A*)
75.0	C-2(*C*)
81.5	C-3(*A*)
84.3	C-4(*A*)
84.5	C-4(*C*)
85.7	C-3(*C*)
94.9	C-1(*C*)
95.1	C-1(*A*)
101.8	C-21(*C*)
101.9	C-21(*A*)
118.2, 118.9, 119.4, 119.7, 120.1, 120.5, 126.4, 126.5, 128.1, 128.2, 128.8, 128.9, 129.0, 129.1, 129.2, 132.6, 132.8, 135.8, 136.1, 137.0, 137.1, 137.2	all Ph(*A*), Ph(*C*)
161.3, 161.8, 163.5, 164.8	C-14(*A*), C-14(*C*), Ph(*A*), Ph(*C*)

Table S3 ^{51}V NMR data for **1** including diastereomer assignment

^{51}V NMR (105 MHz, $CDCl_3$, 25 °C)		
δ (ppm)	$\nu_{1/2}$ (Hz)	Assignment
−507	110	*C*
−537	187	*A*

Table S4 ^{1}H NMR data for **2** including proton and diastereomer assignment (for atom labeling see Scheme 1 in main text)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)				
δ (ppm)	Proton #	Proton assignment[a]	Multiplicity	J (Hz)
1.22	3H	CH_3OH	s	
3.42	1H	CH_3OH	s	
3.61	1H	H-2(*A*)	dd	$^{3}J_{av} = 10.6$
3.77	1H	H-4(*A*)	dd	$^{3}J_{4,3} = {}^{3}J_{4,5} = 9.2$
3.82–4.00	3H	H-6a(*A*), H-6a(*C*), H-5(*C*)	m	
4.04–4.20	2H	H-4(*C*), H-5(*A*)	m	
4.28–4.45	2H	H-6e(*C*), H-6e(*A*)	m	
4.66	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b} = 12.2$
4.71	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b} = 12.3$
4.71–4.78	1H	H-2(*C*)	m	
4.80	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b} = 12.3$
4.87	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b} = 12.2$
5.05	3H	V–OCH_3(*C*)	s	
5.18–5.30	4H	H-3(*C*), V–OCH_3(*A*)	s	
5.43	1H	H-1(*C*)	d	$^{3}J_{1,2} = 2.3$
5.46	1H	H-1(*A*)	d	$^{3}J_{1,2} = 2.9$
5.58	1H	H-21(*A*)	s	
5.60–5.70	2H	H-3(*A*), H-21(*C*)	m	
7.01	1H	H-19(*C*)	d	$^{3}J_{19,18} = 9.2$
7.07	1H	H-19(*A*)	d	$^{3}J_{19,18} = 9.2$
7.26–7.63	20H	Ph(*A*), Ph(*C*)	m	
7.67	1H	H-14(*A*)	s	
7.72	1H	H-14(*C*)	s	
7.89	1H	H-16(*C*)	d	$^{3}J_{16,18} = 2.4$
7.97	1H	H-16(*A*)	d	$^{3}J_{16,18} = 2.7$
8.30	2H	H-18(*A*), H-18(*C*)	dd	$^{3}J_{18,19} = 9.2$ / $^{3}J_{18,16} = 2.6$

[a] For each diastereomer of **2** present in $CDCl_3$ solution an individual sets of signals is observed with an integral ratio of 2:1 (**2***A*:**2***C*) (with *A* and *C* denoting the absolute configurations at the vanadium center).

Table S5 ^{13}C NMR data for **2** including carbon and diastereomer assignment (for atom labeling see Scheme 1 in main text)

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)	
δ (ppm)	Carbon assignment
64.6, 64.7	C-5(*A*), C-5(*C*)
68.7, 68.8, 69.0, 69.1	C-6(*A*), C-7(*A*), C-6(*C*), C-7(*C*)
72.7	V – OCH_3(*C*)
73.4	C-2(*A*)
74.1	V – OCH_3(*A*)
75.3	C-2(*C*)
82.1	C-3(*A*)
84.1	C-4(*A*)
84.3	C-4(*C*)
85.6	C-3(*C*)
94.3	C-1(*C*)
94.6	C-1(*A*)
101.9	C-21(*C*), C-21(*A*)
118.7	C-15(*A*)
119.5	C-15(*C*)
120.4	C-19(*A*)
120.5	C-19(*C*)
126.4, 126.5, 128.2, 128.3, 129.2, 129.3, 129.4, 129.5, 129.6, 129.7	all Ph(*A*), Ph(*C*)
130.1	C-18(*A*)
130.5	C-18(*C*)
135.5, 135.8, 137.0	all Ph(*A*), Ph(*C*)
139.5	C-17(*A*)
139.8	C-17(*C*)
161.1	C-14(*C*)
161.3	C-14(*A*)
167.7	C-20(*C*)
169.0	C-20(*A*)

Table S6 ^{51}V NMR data for **2** including diastereomer assignment

^{51}V NMR (105 MHz, $CDCl_3$, 25 °C)		
δ (ppm)	$\nu_{1/2}$ (Hz)	Assignment
−512	144	*C*
−535	223	*A*

Table S7 ^{1}H NMR data for **3** including proton and diastereomer assignment (for atom labeling see Scheme 1 in main text)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)				
δ (ppm)	Proton #	Proton assignment[a]	Multiplicity	J (Hz)
3.52	1H	H-2(*A*)	dd	$^{3}J_{av}$ = 10.7
3.76	1H	H-4(*A*)	dd	$^{3}J_{4,3}$ = $^{3}J_{4,5}$ = 9.2
3.79, 3.80	6H	3-OCH_3(AC), 3-OCH_3(*C*)	s	
3.82–3.95	3H	H-6a(*A*), H-6a(*C*), H-5(*C*)	m	
3.99–4.20	2H	H-4(*C*), H-5(*A*)	m	
4.20–4.43	2H	H-6e(*C*), H-6e(*A*)	m	
4.64	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b}$ = 12.1
4.70	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b}$ = 12.3
4.67–4.75	1H	H-2(*C*)	m	
4.78	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b}$ = 12.1
4.86	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b}$ = 12.3
4.91	3H	V–OCH_3(*C*)	s	
5.15	3H	V–OCH_3(*A*)	s	
5.21	1H	H-3(*C*)	dd	$^{3}J_{3,4}$ = $^{3}J_{3,2}$ = 9.8
5.40	1H	H-1(*C*)	d	$^{3}J_{1,2}$ = 2.2
5.45	1H	H-1(*A*)	d	$^{3}J_{1,2}$ = 2.8
5.48	1H	H-3(*A*)	dd	$^{3}J_{3,4}$ = $^{3}J_{3,2}$ = 10.0
5.58	1H	H-21(*A*)	s	
5.61	1H	H-21(*C*)	s	
6.46	1H	H-16(*C*)	d	$^{3}J_{16,18}$ = 2.8
6.51	1H	H-16(*A*)	d	$^{3}J_{16,18}$ = 2.8
6.90	1H	H-19(*C*)	d	$^{3}J_{19,18}$ = 9.0
6.99	1H	H-19(*A*)	d	$^{3}J_{19,18}$ = 9.1
7.05–7.19	2H	H-18(*A*), H-18(*C*)	m	
7.20–7.49	16H	Ph(*A*), Ph(*C*)	m	
7.49–7.64	4H	Ph(*A*), Ph(*C*)	m	
7.77	1H	H-14(*A*)	s	
7.79	1H	H-14(*C*)	s	

[a] For each diastereomer of **3** present in $CDCl_3$ solution an individual sets of signals is observed with an integral ratio of 2:1 (**3***A*:**3***C*) (with *A* and *C* denoting the absolute configurations at the vanadium center).

Table S8 ^{13}C NMR data for **3** including carbon and diastereomer assignment (for atom labeling see Scheme 1 in main text)

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)	
δ (ppm)	Carbon assignment
55.9	3-OCH_3(*A*), 3-OCH_3(*C*)
64.5, 64.6	C-5(*A*), C-5(*C*)
68.7, 68.8	C-6(*A*), C-7(*A*), C-6(*C*), C-7(*C*)
70.6	V – OCH_3(*C*)
72.6	V – OCH_3(*A*)
72.8	C-2(*A*)
74.8	C-2(*C*)
81.2	C-3(*A*)
84.3	C-4(*A*)
84.5	C-4(*C*)
85.7	C-3(*C*)
94.9	C-1(*C*)
95.1	C-1(*A*)
101.7	C-21(*C*)
101.8	C-21(*A*)
113.8	C-16(*A*)
114.3	C-16(*C*)
119.4	C-20(*C*)
119.6	C-19(*A*), C-19(*C*)
119.9	C-20(*A*)
124.0	C-18(*C*)
124.1	C-18(*A*)
126.4, 126.5, 128.6, 128.9, 128.9, 129.0, 129.2, 129.3, 135.9, 136.2, 137.1, 137.2	all Ph(*A*), Ph(*C*)
152.6	C-17(*A*)
152.9	C-17(*C*)
158.5	C-15(*C*)
159.6	C-15(*A*)
160.9	C-14(*C*)
161.4	C-14(*A*)

Table S9 ^{51}V NMR data for **3** including diastereomer assignment

^{51}V NMR (105 MHz, $CDCl_3$, 25 °C)		
δ (ppm)	$\nu_{1/2}$ (Hz)	Assignment
−500	150	*C*
−533	266	*A*

Table S10 ^{1}H NMR data for **4** including proton and diastereomer assignment (for atom labeling see Scheme 1 in main text)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)				
δ (ppm)	Proton #	Proton assignment[a]	Multiplicity	J (Hz)
1.22	3H	CH_3OH	s	
1.49	9H	$C(CH_3)_3$(*C*)	s	
1.52	9H	$C(CH_3)_3$(*A*)	s	
3.46	1H	CH_3OH	s	
3.55	1H	H-2(*A*)	dd	$^{3}J_{av}$ = 10.9
3.81	1H	H-4(*A*)	dd	$^{3}J_{4,3}$ = $^{3}J_{4,5}$ = 9.2
3.87–4.00	3H	H-6a(*A*), H-6a(*C*), H-5(*C*)	m	
4.09	1H	H-4(*C*)	dd	$^{3}J_{4,3}$ = $^{3}J_{4,5}$ = 8.9
4.15	1H	H-5(*A*)	dt	J_t = 9.9 / J_d = 4.7
4.36–4.45	2H	H-6e(*C*), H-6e(*A*)	m	
4.69	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b}$ = 12.1
4.75	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b}$ = 12.4
4.69–4.75	1H	H-2(*C*)	m	
4.81	1H	H-7a(*C*) or H-7b(*C*)	d	$^{2}J_{7a,7b}$ = 12.1
4.88	1H	H-7a(*A*) or H-7b(*A*)	d	$^{2}J_{7a,7b}$ = 12.4
4.97	3H	V–OCH_3(*C*)	s	
5.23	3H	V–OCH_3(*A*)	s	
5.27	1H	H-3(*C*)	dd	$^{3}J_{3,4}$ = $^{3}J_{3,2}$ = 9.5
5.44	1H	H-1(*C*)	d	$^{3}J_{1,2}$ = 2.8
5.46	1H	H-1(*A*)	d	$^{3}J_{1,2}$ = 3.0
5.46–5.54	1H	H-3(*A*)	m	
5.63	1H	H-21(*A*)	s	
5.67	2H	H-21(*C*)	s	
6.90–6.97	2H	Ph(*A*), Ph(*C*)	m	
7.22–7.53	18H	Ph(*A*), Ph(*C*)	m	
7.53–7.67	6H	Ph(*A*), Ph(*C*)	m	
7.88	1H	H-14(*A*)	s	
7.91	1H	H-14(*C*)	s	

[a] For each diastereomer of **4** present in $CDCl_3$ solution an individual sets of signals is observed with an integral ratio of 2:1 (**4***A*:**4***C*) (with *A* and *C* denoting the absolute configurations at the vanadium center).

Table S11 ^{13}C NMR data for **4** including carbon and diastereomer assignment (for atom labeling see Scheme 1 in main text)

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)	
δ (ppm)	Carbon assignment
29.6	$C(CH_3)_3$(*A*), $C(CH_3)_3$(*C*)
35.2	$C(CH_3)_3$(*C*)
35.4	$C(CH_3)_3$(*A*)
64.4, 64.6	C-5(*A*), C-5(*C*)
68.5, 68.7	C-6(*A*), C-7(*A*), C-6(*C*), C-7(*C*)
69.7	V – OCH_3(*C*)
72.2	V – OCH_3(*A*)
72.6	C-2(*A*)
74.7	C-2(*C*)
80.8	C-3(*A*)
84.4	C-4(*A*)
84.5	C-4(*C*)
85.7	C-3(*C*)
94.8	C-1(*C*)
95.1	C-1(*A*)
101.6	C-21(*C*)
101.9	C-21(*A*)
119.6, 120.0, 126.4, 126.5, 126.7, 126.9, 128.0, 128.1, 128.6, 128.8, 128.9, 129.0, 129.2, 129.3, 130.7, 131.0, 135.8, 136.1, 137.1, 137.2, 138.3, 138.4, 141.7, 142.4	all Ph(*A*), Ph(*C*)
162.0	C-14(*C*)
162.5	C-14(*A*)

Table S12 ^{51}V NMR data for **4** including diastereomer assignment

^{51}V NMR (105 MHz, $CDCl_3$, 25 °C)		
δ (ppm)	$\nu_{1/2}$ (Hz)	Assignment
−510	221	*C*
−545	371	*A*

2 Additional structural information

Table S13 Selected bond lengths (pm) and angles (°) for **1** and **2**

Bond lengths	**1**	**2**[a]		
		(a)	(b)	(c)
V–O1	159.9(4)	159.8(7)	159.5(6)	158.6(7)
V–O2	188.9(4)	193.5(6)	193.6(6)	192.0(7)
V–O3	182.4(4)	184.9(6)	186.5(6)	184.6(6)
V–O4	177.4(4)	178.0(6)	178.5(6)	177.6(6)
V–N1	214.9(4)	217.2(6)	217.6(6)	216.8(8)
V–O1M		231.7(6)	232.7(6)	236.5(7)
Bond angles				
O1–V–O2	102.81(18)	96.7(3)	96.6(3)	96.7(4)
O1–V–O3	107.89(18)	99.4(3)	100.5(3)	101.0(4)
O1–V–O4	105.54(18)	103.5(3)	103.1(3)	104.5(4)
O1–V–N1	98.36(17)	93.8(3)	94.3(3)	93.4(4)
O2–V–O3	145.39(16)	154.4(3)	154.5(2)	155.0(3)
O2–V–O4	91.48(16)	98.3(3)	98.1(3)	94.0(3)
O2–V–N1	82.32(16)	80.9(3)	81.8(2)	82.1(3)
O3–V–O4	95.29(16)	97.1(2)	96.3(3)	98.5(3)
O3–V–N1	77.85(16)	78.3(2)	78.2(2)	79.3(3)
O4–V–N1	156.09(17)	162.6(3)	162.5(3)	162.0(3)

[a] There are three crystallographically independent molecules present in the crystal structure of **2**.

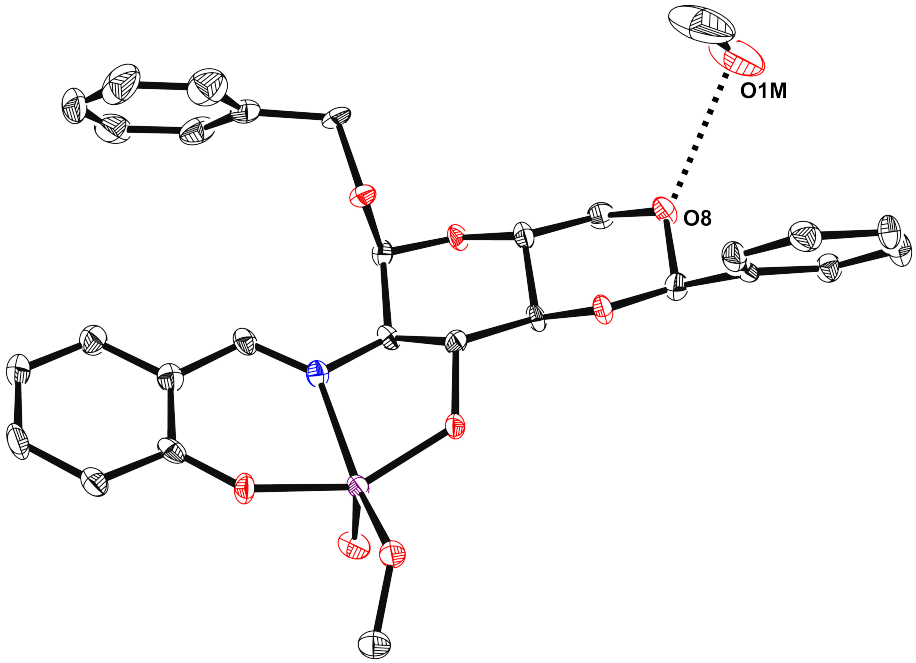

Figure S1 Representation of the hydrogen bonding interaction of the complex molecule in the crystal structure of **1**·MeOH with the co-crystallized methanol molecule (O1M) with the oxygen atom (O8) attached to C-6 of the sugar backbone (O1M···O8, 281.3(7) pm). Hydrogen atoms have been omitted for clarity.