Pyrazolylcyclohexanol Complexes of Vanadium − A Temperature- and Solvent-Dependent Monomer−Dimer Equilibrium

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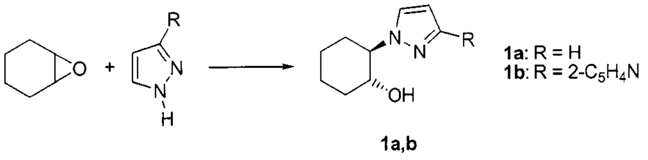
The reaction of $VOCl_3$ with tridentate *rac-trans*-[1-pyrazolyl-3-(2-pyridyl)]cyclohexanol in the presence of K_2CO_3 generates a mononuclear six-coordinate V^V complex. With the bidentate ligand *rac-trans*-2-(pyrazol-1-yl)cyclohexan-1-ol, reduction of V^V to V^{IV} takes place to give a dinuclear complex with bridging alkoxo units; this compound is also accessible starting directly from the V^{IV} precursor $VOSO_4$ and LiCl. Both complexes were characterized spectroscopically and by X-ray diffraction. The dimeric V^{IV} complex is in equilibrium with its monomeric counterpart; this temperature- and solvent-dependent equilibrium was followed by EPR spectroscopy.

Introduction

Vanadium compounds are widely used in catalytic oxidation reactions.[1−3] However, the molecular structures of the actual catalytically active species are often unknown.[4] In a project on vanadium-catalyzed olefin epoxidation, our group has investigated structurally well-defined vanadium(V) complexes bearing bidentate pyrazolylpyridine ligands equipped with alkyl and ester side chains.[5] Owing to this feature, these ligands increase the solubility of the derived metal complexes in nonpolar organic solvents and therefore should allow detailed mechanistic investigations on the oxygen-transfer processes. They are active catalysts for the epoxidation of olefins as well as for the oxidation of aromatic alcohols, giving the corresponding aldehydes in high yield. However, when unfunctionalized olefins are used instead of allylic alcohols, complete conversion of the substrate has never been reached owing to catalyst deactivation, which might be due to ligand dissociation. In the present paper, the synthesis of a V^V complex bearing a tridentate pyrazolylpyridine cyclohexanolato ligand is described. Additionally, the reaction of bidentate pyrazolylcyclohexanol with $VOCl_3$ in the presence of a base was investigated, leading to a new dinuclear V^{IV} complex, which is also accessible by reacting $VOSO_4{\cdot}(H_2O)_3$ with pyrazolylcyclohexanol and LiCl in CH_3CN.

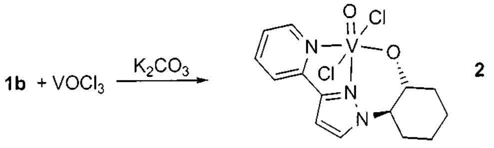
Results and Discussion

Our group has been interested in 1,3-amino alcohols bearing aromatic pyrazolyl N-donor fragments, where both donor sites are attached to a rigid cycloalkane backbone, for some time.[6−9] Such ligands can be obtained by nucleophilic attack of a pyrazole derivative on an epoxycycloalkane, giving the corresponding 1,2-*trans* configured cycloalkanols. Following this procedure, the ligands **1a,b** have been synthesized (Scheme 1, only one of the two stereoisomers is presented, as is the case in the following schemes).[8]



Scheme 1

The V^V oxoalkoxo complex **2** is accessible by reacting racemic *trans*-[1-pyrazolyl-3-(2-pyridyl)]cyclohexanol (**1b**) with $VOCl_3$ in the presence of K_2CO_3 (Scheme 2, only one of the two stereoisomers is shown). Owing to the tridentate ligand, the position of the oxo ligand is fixed *trans* to pyrazole, which is confirmed by a single ^{51}V NMR resonance and one set of resonances in the ^1H NMR spectrum. This is in contrast to the behavior of oxoalkoxo V^V complexes of bidentate pyrazolylpyridines,[5] which exist as mixtures of two isomers differing in the orientation of the oxo and alkoxo ligands relative to the *N*,*N′*-donor.



Scheme 2

As expected, the tridentate ligand enhances the stability of the V^V complex relative to the V^V complexes of bidentate pyrazolylpyridines. Unfunctionalized olefins like cyclooctene are thus efficiently converted into the corresponding epoxides (yield: 80−95%; reaction conditions: **2**/olefin/

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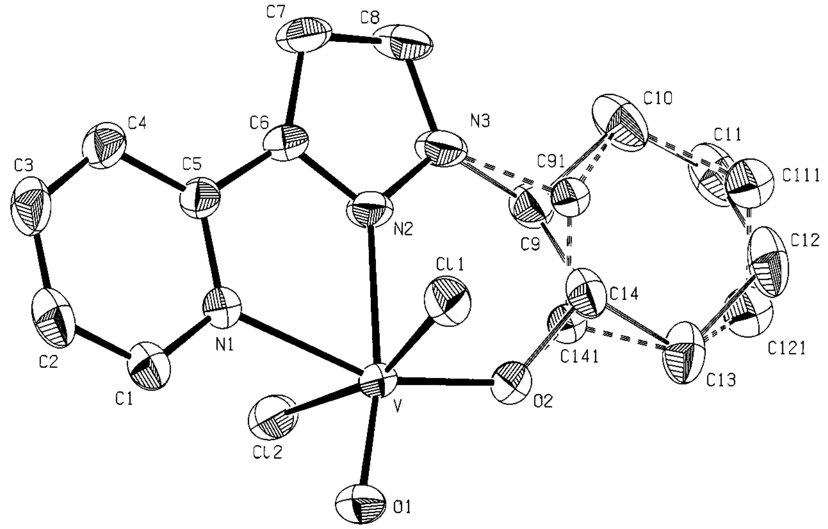


Figure 1. ORTEP[10] drawing of the molecular structure of **2** in the solid state; thermal ellipsoids are at the 50% probability level and hydrogen atoms are omitted for clarity

*t*BuOOH = 0.01:1:1, 24 h at 55 °C, solvent: $CHCl_3$). However, the vanadium complex bearing an enantiomerically pure (1*S*,2*S*)-*trans*-[1-pyrazolyl-3-(2-pyridyl)]cyclohexanol ligand[8] does not induce any enantioselectivity in the epoxidation of prochiral olefins such as 1,2-dihydronaphthalene or allylic and homoallylic alcohols.

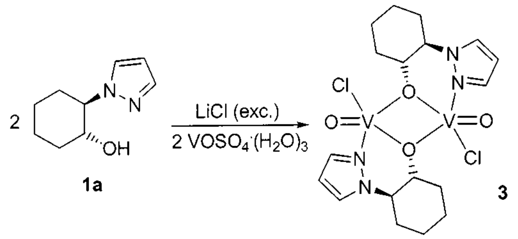
Compound **2** crystallizes from acetone in the centrosymmetric monoclinic space group $P2_1/n$ with 0.5 equiv. of the solvent. Figure 1 shows the molecular structure of **2** in the solid state, and a selection of characteristic bond lengths and angles is given in Table 1.

Table 1. Selected bond distances (Å) and angles (°) for **2**

Bond Distances			
V−Cl1	2.3234(8)	V−O2	1.762(2)
V−Cl2	2.3412(7)	V−N1	2.167(2)
V−O1	1.597(2)	V−N2	2.145(2)
Bond Angles			
Cl1−V−Cl2	163.96(3)	O1−V−O2	105.31(8)
Cl1−V−O1	95.87(7)	O1−V−N1	97.49(8)
Cl1−V−O2	93.40(6)	O1−V−N2	169.51(8)
Cl1−V−N1	81.73(5)	O2−V−N1	157.07(7)
Cl1−V−N2	84.82(6)	O2−V−N2	85.08(8)
Cl2−V−O1	94.02(7)	N1−V−N2	72.21(7)
Cl2−V−O2	96.13(6)	V−O2−C14	132.6(2)
Cl2−V−N1	84.49(5)	O2−C14−C9	115.0(3)
Cl2−V−N2	83.18(6)		

The three ring systems (pyridine, pyrazole, cyclohexane) of the N,N,O ligand and the V=O unit are found in an almost coplanar orientation, while the chloro ligands complete the distorted octahedral coordination geometry at vanadium. Despite the crystallographic disordering in the individual crystal that was used for the structure determination, a satisfactory solution of the structure could be performed. While the V=O [1.597(2) Å] and V−O distances [1.762(2) Å] in **2** are only a few pm longer than the distances found in the isostructural oxoalkoxo vanadium(V) complexes bearing bidentate pyrazolylpyridine ligands [V=O = 1.575(3) and 1.579(2) Å; V−O = 1.740(2) and 1.735(2) Å],[5] the V−N distances in **2** are drastically shortened due to the tridentate ligand system. Usually, the M−N bonds (N = *N*-donor ligand) in the *trans* position to strong σ-donor ligands (e.g. oxo) are found to be about 10−15 pm longer than those in the *trans* position to alkoxo ligands. This is no longer true for **2**: here V−N2 [2.145(2) Å] is slightly shorter than V−N1 [2.167(2) Å], which means that the V−N bond *trans* to the oxo ligand is about 17 pm shorter when a tridentate ligand is coordinated instead of a bidentate ligand [V−N2 = 2.310(3) and 2.338(2) Å] with analogous donor properties.

Since there was no chiral induction in the epoxidation of prochiral olefins with (1*S*,2*S*)-**2**, the reaction of the bidentate ligand *trans*-2-pyrazol-1-ylcyclohexanol (**1a**) with $VOCl_3$ was investigated in order to open up an additional coordination site at the vanadium center for interaction with the substrates. Performing this reaction as for the synthesis described for **2** gives a deep orange-brown solution. However, the primary product is not stable even at −20 °C and decomposes in solution and in the solid state, leading to a black and oily precipitate, which was not investigated further, and a small amount of deep blue crystals. X-ray analysis of these crystals proved that reduction of V^V had taken place, and a dinuclear V^{IV} complex **3**, bearing one chelate, one oxo and one chloro ligand per vanadium center was formed. With this information in mind, a high yield synthesis of **3** starting from *trans*-2-pyrazol-1-ylcyclohexanol (**1a**), $VOSO_4{\cdot}(H_2O)_3$ and LiCl was established (Scheme 3). Among a series of solvents (THF, CH_2Cl_2, $CHCl_3$, MeOH) which were examined for this reaction, acetonitrile proved to be the best.



Scheme 3

Table 2. Selected bond distances (Å) and angles (°) for **3**

Bond Distances			
V1−V2	3.1250(5)		
V1−Cl1	2.3091(6)	V2−Cl2	2.3117(6)
V1−O1	1.581(2)	V2−O3	1.579(1)
V1−O2	1.968(1)	V2−O2	1.980(1)
V1−O4	1.984(1)	V2−O4	1.965(1)
V1−N2	2.087(2)	V2−N4	2.079(2)
O2−C9	1.437(2)	O4−C18	1.439(2)
Bond Angles			
Cl1−V1−O1	106.86(6)	Cl2−V2−O3	107.81(6)
Cl1−V1−O2	144.71(5)	Cl2−V2−O4	144.94(4)
Cl1−V1−O4	90.87(4)	Cl2−V2−O2	90.09(4)
Cl1−V1−N2	89.04(5)	Cl2−V2−N4	87.68(5)
O1−V1−O2	108.37(7)	O3−V2−O4	107.12(7)
O1−V1−O4	110.09(7)	O2−V2−O3	109.94(7)
O1−V1−N2	103.13(7)	O3−V2−N4	106.16(7)
O2−V1−O4	75.14(5)	O2−V2−O4	75.30(5)
O2−V1−N2	85.16(6)	O4−V2−N4	85.52(6)
O4−V1−N2	145.25(6)	O2−V2−N4	142.69(6)
V1−O2−V2	104.69(6)	V1−O4−V2	104.62(6)
V1−O2−C9	129.01(11)	V2−O2−C9	126.07(11)
V1−O4−C18	127.88(11)	V2−O4−C18	127.17(11)
Torsion Angles			
N1−C4−C9−O2	58.4(2)	N3−C13−C18−O4	57.2(2)

Catalytic tests with compound **3** showed that the blue color of the complex vanishes after the addition of *t*BuOOH to give an orange-colored solution, indicating the oxidation of V^{IV} to V^{V}. However, it has not been possible up to now to characterize the V^{V} compound(s) formed here due to rapid decomposition. The catalytic activity of these solutions is about 20% of the activity of compound **2**.

Compound **3** crystallizes from $CHCl_3/Et_2O$ in the centrosymmetric monoclinic space group $P2_1/n$. Figure 2 shows the molecular structure of **3** in the solid state, and a selection of characteristic bond lengths and angles is given in Table 2.

In the solid state structure of **3**, the two V^{IV} centers V1 and V2, which are not equivalent in terms of crystal symmetry, are bridged by the alcoholato moieties of the chelate ligands leading to the formation of a planar V_2O_2 ring with V−O distances of about 2.0 Å. The distance V1···V2 is 3.125(1) Å, which excludes a V−V single bond. The oxo ligands O1 and O3 are found in a *cis* orientation, which has been observed in only a few V^{IV} complexes before.[11−15] Two homochiral chelate ligands are coordinated at the vanadium centers, which leads to a dimeric structure with nearly C_2 symmetry. The square-pyramidal coordination of the V^{IV} centers is completed by the chloro ligands. Complex **3** can be best compared with $[VO(THFfo)Cl]_2$ (THFfo = tetrahydrofurfuryl alcoholate), obtained from $VOCl_2$ and Na(THFfo), wherein the alcoholato moieties are also bridging the two V^{IV} centers.[13] Owing to the five-membered chelate rings formed by the THFfo ligands, the V−O distances in the V_2O_2 ring are shortened, which causes the V−V distance in $[VO(THFfo)Cl]_2$ [3.070(1) Å] to shrink slightly, compared to **3**.

Compound **3** shows an interesting dynamic behavior in solution. When a deep-blue solution of **3** in $CHCl_3$ is treated with MeOH or EtOH, the color turns to green within a few hours at room temp. Decreasing the temperature of the mixture to 0 °C brings back the original blue color. This procedure can be repeated several times, which

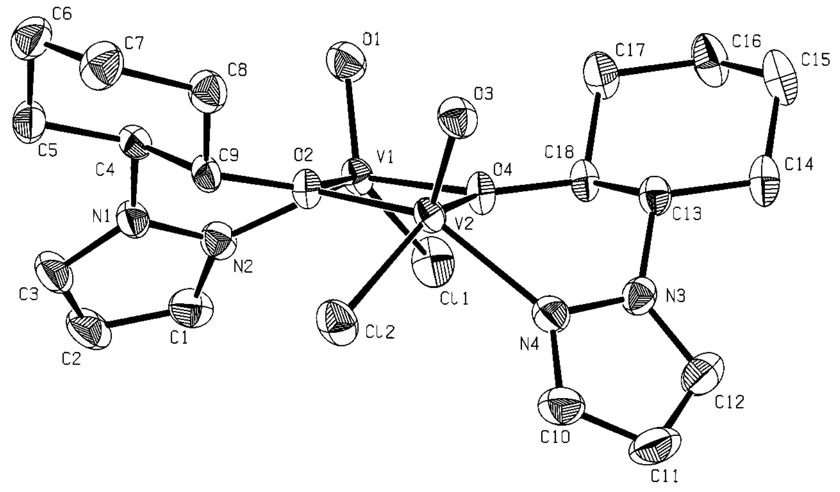


Figure 2. ORTEP[10] drawing of the molecular structure of **3** in the solid state; thermal ellipsoids are at the 50% probability level and hydrogen atoms are omitted for clarity

indicates a reversible reaction, for example a monomer ⇄ dimer equilibrium. When pyridine or THF are added to a solution of **3** in $CHCl_3$, an intense green color is observed, which persists even at low temperatures. However, when the solvents are removed in vacuum, blue microcrystalline **3** is recovered. For a deeper insight into these processes, EPR experiments were carried out.

The monomer ⇄ dimer equilibrium is illustrated in Figure 3 by the EPR spectra of complex **3** in $CHCl_3$ solution with and without addition of pyridine as donor.

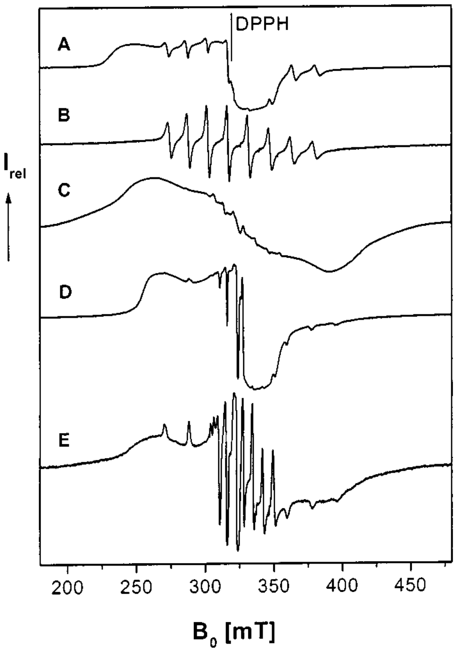
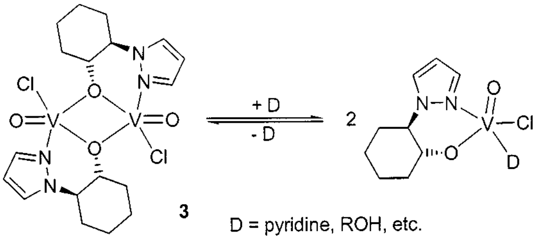


Figure 3. Liquid (A, B; T = 293 K) and frozen (C-E; T = 130 K) solution EPR spectra of the vanadium complex **3** in $CHCl_3$ ($5 \cdot 10^{-3}$ M) before (A and C) and after addition of pyridine (B and E: excess pyridine, D: few drops of pyridine)

The broad sigmoid EPR resonance line at $g \approx 1.97$ (line width $\Delta B_{pp} \approx 130$ mT; Figure 3 A, C−E) results from a weak magnetic interaction of the two unpaired spins in the dimeric vanadium complex (no resonance was observed at "half-field", i.e. no $\Delta M_S = 2$ transition). Similar EPR spectra (partially with better resolution) have been reported in the literature for dinuclear vanadium(IV) complexes.[13,16,17] The vanadium centers of **3** are weakly coupled both at room temperature in solution (Figure 3 A) and in a frozen glass (T = 30 K, Figure 3 C, D). In all cases at least a residual amount of a monomeric vanadium(IV) species is present depending on the temperature. This is reflected by the superposition of a well-resolved line octet which results from the hyperfine interaction of the unpaired electron with the nuclear spin of ^{51}V ($I = 7/2$).

The addition of pyridine at room temperature changed the color of the solution to green. An excess of pyridine provides an EPR spectrum of the monomer only at room temperature [Figure 3 B; $g_0 = 1.974$ (± 0.001); $a_0 = 15.1$ (± 0.03) mT]. Figure 3 C−E illustrate the effect of the stepwise addition of pyridine. Figure 3 E shows a well-resolved frozen solution EPR spectrum of the monomer superimposed on the residual dimeric species. The parameters of the former are typical for a single $S = 1/2$ VO^{2+} complex with a square-pyramidal coordination sphere of mixed donor atoms (N, O, Cl)[13] $g_{\parallel} = 1.952$; $g_{\perp} = 1.983$ (± 0.001); $A_{\parallel}(^{51}V) = 18$ mT; $A_{\perp}(^{51}V) = 6.45$ mT (± 0.05 mT); $B_{pp} = 1.5(_{\perp}) - 2.0(_{\parallel})$ mT. According to the EPR results, a monomer ⇄ dimer equilibrium can be postulated, which is influenced by the addition of donor molecules (D) (as shown in Scheme 4) and also by the variation of the temperature.



D = pyridine, ROH, etc.

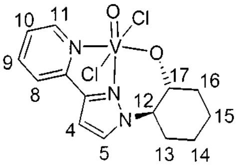
Scheme 4

Conclusion

It could be shown that using a monoanionic tridentate ligand instead of a neutral bidentate ligand enhances the catalytic performance of the V^V catalyst in the olefin epoxidation and in the oxidation of benzylic alcohol due to a reduced tendency for catalyst decomposition. However, this strategy prevents enantioselective epoxidation. Cleaving one of the neutral N-donor sites destabilizes the V^V complex and leads to a formally five-coordinate V^{IV} system, which undergoes dimerization through the alcoholato ligands. This dimerization is a reversible process as shown by EPR spectroscopy.

Experimental Section

All syntheses were performed under an atmosphere of nitrogen; solvents were dried, distilled and degassed before use. The ^1H NMR spectrum of **2** is assigned according to Scheme 5.[18]



Scheme 5

Dichlorooxo{*rac-trans*-[1-pyrazolyl-3-(2-pyridyl)]cyclohexyloxy}-vanadium(V) (2): K_2CO_3 (0.50 g, 3.62 mmol) was dried for 10 min. at 300 °C in a 100 mL flask under vacuum. After cooling to room temperature, a solution of *rac-trans*-[1-pyrazolyl-3-(2-pyridyl)]cyclohexanol[8] (**1b**; 0.30 g, 1.24 mmol) in CH_2Cl_2 (40 mL) was added and the mixture was cooled to 0 °C. A solution of $VOCl_3$ (0.12 mL, 1.24 mmol) in CH_2Cl_2 (10 mL) was added dropwise and the mixture was stirred for 1 h at 0 °C and for 2 h at room temp. The precipitate was removed by filtration, the solvent was removed in vacuum and the orange-red colored residue was dissolved in acetone (20 mL). After 7 days at −18 °C, **2** (0.16 g, 33%) was obtained as dark red crystals, containing 0.5 equiv. of acetone. Concentration of the mother liquor gave rise to further crystallization (0.113 g, 24%). − $(C_{14}H_{16}Cl_2N_3O_2V)_2 \cdot C_3H_6O$ (818.35): calcd. C 45.50, H 4.68, N 10.27; found C 45.20, H 4.78, N 10.13. − IR (KBr): $\tilde{\nu}$ = 1018 vs ($\nu_{V=O}$) cm^{-1}. − ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta = 9.51$ (d, $^3J_{10,11} = 5.5$ Hz, 1 H, 11-H), 8.01 (t, $^3J_{9,10} = 6.5$ Hz, 1 H, 9-H), 7.80 (d, $^3J_{8,9} = 7.5$ Hz, 1 H, 8-H), 7.73 (d, $^3J_{4,5} = 2.5$ Hz, 1 H, 5-H), 7.52 (dd, 1 H, 10-H), 6.83 (d, 1 H, 4-H), 4.34 (ddd, $^3J_{12,17} = 13.0$ Hz, $^3J_{16,17} = 4.5$ Hz, $^3J_{16',17} = 9.0$ Hz, 1 H, 17-H), 2.69 (m, 1 H, 12-H), 2.27 (m, 2 H, CH_2), 1.97−1.24 (m, 6 H, CH_2). − ^{51}V NMR (105.2 MHz, 25 °C, $CDCl_3$): $\delta = -394.9$.

Bis[chlorooxo(*rac-trans*-2-pyrazol-1-ylcyclohexyloxy)vanadium(IV)] (3): $VOSO_4 \cdot (H_2O)_3$ (0.22 g, 1.00 mmol), *rac-trans*-2-(pyrazol-1-yl)-cyclohexan-1-ol[9] (**1a**; 0.17 g, 1.00 mmol) and LiCl (0.06 g, 1.50 mmol) were dissolved in acetonitrile (40 mL) and heated to 60 °C for 4 h. The resulting blue mixture was filtered and the solvent was removed in vacuum. The blue residue was dissolved in $CHCl_3$ (10 mL) and diethyl ether was condensed slowly into the solution. After a few days, deep blue crystals of **3** (0.36 g, 67%) were obtained. − $C_{18}H_{26}Cl_2N_4O_4V_2$ (535.21): calcd. C 40.39, H 4.90; N 10.47; found C 40.18, H 4.88, N 10.40. − IR (KBr): $\tilde{\nu}$ = 1014 s, 1003 vs ($\nu_{V=O}$) cm^{-1}. − EPR: see text.

X-ray Crystal Structure Determination: The complexes were crystallized from acetone (**2**) or by slow diffusion of diethyl ether into a chloroform solution (**3**). The intensity data were obtained with graphite monochromated Mo-K_α radiation on an imaging plate diffraction system (IPDS; STOE & CIE GmbH) equipped with a rotating anode (NONIUS FR591; 50 kV; 60/80 mA; 3.0/4.0 kW). Both structures were solved by a combination of direct methods and difference-Fourier syntheses. Full-matrix least-squares refinements on 307/375 parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at shift/err < 0.001/0.003. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray Crystallography.[19] All calculations were performed on a DEC 3000 AXP workstation and an Intel Pentium II PC with the STRUX-V system,[20] including the programs PLATON,[10] SIR92,[21] and SHELXL-97.[22] Additional crystal data, intensity collection data and refinement parameters are presented in Table 3.

Data Collection, Structure Solution and Refinement for Complex 2: Data collection was performed within the Θ range of 2.84°< Θ < 24.65° with an exposure time of 600 seconds per image (oscillation scan modus from Θ = 0° to 270° with ΔΘ = 1.0°). A total number of 16128 reflections were collected. 273 Systematic absent reflections were rejected from the original data set. Data were corrected for Lorentz, polarization, decay and absorption effects with the DECAY algorithm.[23] Two different modes of disordering had to be included in the refinement process. At first, the positions of the chiral vanadium complex were occupied by the two stereoisomers in a 79:21 ratio. This resulted in a disordering model for the cyclohexan-1,2-diyl units wherein the positions of the carbon atoms 10 and 13 were identical for both six-membered rings. All non-hydrogen atoms of the vanadium complex were refined anisotropically with the exception of the disordered cyclohexandiyl carbon atoms of the minor species. Half an equivalent of acetone is disordered at an inversion center of the crystal system. All acetone non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the major stereoisomer were found in the difference-Fourier map and refined with isotropic thermal displacement parameters. All hydrogen atoms of the minor stereoisomer and of the acetone were calculated in ideal positions (riding model; $U_H = 1.2 \cdot U_C$).

Data Collection, Structure Solution and Refinement for Complex 3: Data collection was performed within the Θ range of 3.15°< Θ < 25.65° with an exposure time of 180 seconds per image (oscillation scan modus from Θ = 0° to 135° with ΔΘ = 1.0°). A total number of 11436 reflections were collected. 460 Systematic absent reflections were rejected from the original data set. Data were corrected for Lorentz, polarization, decay and absorption effects, with the DECAY algorithm.[23] All non-hydrogen atoms of the vana-

Table 3. Crystal data, summary of intensity collection data and structure refinement data of **2** and **3**

	2	**3**
Chem formula	$(C_{14}H_{16}Cl_2N_3O_2V)_2 \cdot C_3H_6O$	$C_{18}H_{26}Cl_2N_4O_4V_2$
Mol. wt.	818.35	535.21
Cryst system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a /Å	7.5926(4)	14.9428(9)
b /Å	18.8462(9)	8.3622(4)
c /Å	12.7320(6)	18.5264(13)
β /deg	105.488(5)	103.527(7)
V /Å^3	1755.7(2)	2250.7(2)
Z	2	4
ρ_{calcd}/g cm^{-3}	1.548	1.579
μ/mm^{-1}	0.885	1.100
T/K	163	193
No. of indep. rflns [$I_o > 2\sigma(I_o)$/all data]	2634/2908	3248/3839
$R1$[a] [$I_o > 2\sigma(I_o)$/all data]	0.0323/0.0364	0.0275/0.0330
$wR2$[b]	0.0788	0.0736
GOF[c]	1.066	0.986
Weights a/b[d]	0.0317/1.7352	0.0561/0.0
$\Delta\rho_{max/min}$ (e Å^{-3})	0.46/−0.52	0.45/−0.37

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. − [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. − [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$. − [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = [\max(0 \text{ or } F_o^2) + 2F_c^2]/3$.

dium complex were refined anisotropically. All hydrogen atoms were found in the difference-Fourier map and refined with isotropic thermal displacement parameters.

Crystallographic data (excluding structure factors) for the structures included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159418 (**2**) and -159419 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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