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# An oxidovanadium(IV) complex with 4,4'-di-*tert*-butyl-2,2'-bipyridine ligand: synthesis, structure and catalyzed cyclooctene epoxidation

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## Abstract

The interaction of vanadium(III) chloride (VCl<sub>3</sub>) with 4,4'-di-*tert*-butyl-2,2'-bipyridine (dbbpy) in air resulted in the monomeric oxidovanadium(IV) complex [VOCl<sub>2</sub>(dbbpy)(H<sub>2</sub>O)] (**1**) in high yield. The complex was characterized by IR and EPR spectroscopies, by elemental analysis, and by single crystal X-ray diffraction analysis. The vanadium atom has a distorted octahedral coordination environment. The EPR spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> demonstrates an eight-line signal typical of vanadium(IV) with a d<sup>1</sup> electronic configuration. Complex **1** exhibits catalytic activity in the cyclooctene oxidation with *tert*-butyl hydroperoxide (TBHP) in CHCl<sub>3</sub>. Detailed EPR, NMR and GC-MS studies of the reaction revealed a few mechanistic details and the nature of by-products that are generated by involvement of the chloroform solvent.

**Keywords:** oxidovanadium(IV) complexes; 2,2'-bipyridine ligands; crystal structure; EPR spectroscopy; cyclooctene epoxidation.

## 1. Introduction

Oxidovanadium complexes containing the V=O moiety are nearly omnipresent in the chemistry of vanadium [1]. They exhibit high catalytic activity in various organic transformations including alkane oxidation [2–10], olefin epoxidation [11–18], aromatization

of  $\alpha,\beta$ -unsaturated cyclohexanone derivatives [19,20], alcohol oxidation [21–25], C-C bond cleavage of glycols [26–28], naphthol coupling [29] and  $\alpha$ -oxidation of hydroxyl esters and amides [30] etc. The use of oxovanadium complexes in the oxidation reactions of various substrates, in particular saturated and unsaturated hydrocarbons is due to the following factors: (a) the ability of vanadium to adopt different coordination numbers (5 and 6), (b) the stability of vanadium in oxidation states +4 and +5 under aerobic conditions, (c) the Lewis acidic nature of the vanadium centers and (d) the high oxophilicity of vanadium.

Our recent studies have shown that oxovanadium(IV) complexes with redox-active diimine ligands exhibit high catalytic activity towards alkanes and alcohols oxygenation with  $\text{H}_2\text{O}_2$  or *tert*-butyl hydroperoxide in MeCN. In particular, the square-pyramidal oxidovanadium(IV) complex  $[\text{VOCl}_2(\text{dpp-bian})]$  (dpp-bian = bis[N-(2,6-diisopropylphenyl)imino]acenaphthene) [10] and polymeric complexes of general formula  $[\text{VO}(\text{L})\text{X}_2]_n$  (L = bpy, phen and X = Cl, Br) [31] were synthesized and tested as oxidation catalysts. In this framework, we report herein further results on the preparation of a novel octahedral oxidovanadium(IV) complex  $[\text{VOCl}_2(\text{dbbpy})(\text{H}_2\text{O})]$  (**1**), as well as its catalytic properties in the cyclooctene oxidation with *tert*-butyl hydroperoxide in  $\text{CHCl}_3$ , which is another commonly used solvent for catalyzed oxidations. Careful analysis of the reaction products revealed the presence of side reactions that depend on the solvent nature and purity.

## 2. Experimental Section

### 2.1. General procedures

All synthetic manipulations were carried out in air. Catalytic experiments were carried out in argon. Reagent grade chemicals were obtained from Aldrich and used without further purification. All organic solvents were distilled by standard methods before use.

### 2.2. Physical Measurements

The CHN elemental analysis was performed on a Euro EA 3000 analyzer. The FT-IR spectrum in the range of  $4000\text{--}400\text{ cm}^{-1}$  was recorded on a Scimitar FTS 2000 spectrometer. EPR spectra were recorded at the X- and Q- bands at 77 K and 300 K on an E-109 Varian spectrometer equipped with an analog-to-digital signal converter and were analyzed and simulated with the EasySpin (Matlab) software package [32].

### 2.3. X-ray crystallography

Single crystals of  $\mathbf{1}\cdot 1.5\text{CH}_2\text{Cl}_2$  suitable for the X-ray diffraction analysis were obtained by recrystallization from a  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  mixture. The diffraction data for  $\mathbf{1}\cdot 1.5\text{CH}_2\text{Cl}_2$  were collected on a Bruker X8 Apex diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$ ) by doing  $\varphi$

and  $\omega$  scans of narrow ( $0.5^\circ$ ) frames at 150 K. The absorption was empirically corrected using SADABS [33]. Crystallographic data and refinement details for  $1 \cdot 1.5\text{CH}_2\text{Cl}_2$  are given in Table 1. The structure was solved with SHELXT [34] and refined by full-matrix least-squares cycles against  $|F|^2$  in anisotropic approximation with SHELXL 2017/1 [35] in ShelXle program [36]. Hydrogen atoms were refined in geometrically calculated positions. The number of highly disordered  $\text{CH}_2\text{Cl}_2$  molecules was found with the SQUEEZE procedure [37], which gave 63.5 e in a void with a  $154.05 \text{ \AA}^3$  volume. It corresponds to 1.5  $\text{CH}_2\text{Cl}_2$ , which has 42 e and a molecular volume of  $106 \text{ \AA}^3$ . The crystallographic data have been deposited in the Cambridge Crystallographic Data Centre under the deposition code CCDC 1945435.

**Table 1.** Main crystallographic characteristics and X-ray diffraction experimental details for  $1 \cdot 1.5\text{CH}_2\text{Cl}_2$ .

|  | $1 \cdot 1.5\text{CH}_2\text{Cl}_2$                                    |
|--|--|
| Chemical formula   | $\text{C}_{19.5}\text{H}_{29}\text{Cl}_5\text{N}_2\text{O}_2\text{V}$  |
| $M_r$  | 551.65   |
| Crystal system, space group  | Orthorhombic, <i>Cmca</i>  |
| Temperature (K)  | 100  |
| $a, b, c$ ( $\text{\AA}$ )   | 17.8155 (8), 11.4397 (6), 24.1718 (13)                                 |
| $V$ ( $\text{\AA}^3$ )   | 4926.3 (4)   |
| $Z$  | 8  |
| Radiation type   | Mo $K\alpha$   |
| $\mu$ ( $\text{mm}^{-1}$ )   | 0.63   |
| Crystal size (mm)  | $0.22 \times 0.20 \times 0.15$   |
| Diffractometer   | Bruker X8Apex  |
| Absorption correction  | Multi-scan<br>SADABS (Bruker-AXS, 2004)                                |
| $T_{\min}, T_{\max}$   | 0.596, 0.746   |
| No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections | 11345, 2933, 2630  |
| $R_{\text{int}}$   | 0.032  |
| $\theta$ values ( $^\circ$ )   | $\theta_{\max} = 27.6, \theta_{\min} = 3.9$                            |
| $(\sin \theta/\lambda)_{\max}$ ( $\text{\AA}^{-1}$ )                       | 0.652  |
| Range of $h, k, l$   | $-23 \leq h \leq 17, -10 \leq k \leq 14, -26 \leq l \leq 31$           |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$  | 0.056, 0.152, 1.21   |
| No. of reflections, parameters, restraints                                 | 2933, 121, 0   |
| H-atom treatment   | H atoms treated by a mixture of independent and constrained refinement |

|   |   |
|---|---|
| Weighting scheme  | $w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 26.942P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> ) | 0.55, -0.54   |

## 2.4. Synthesis of [V<sup>IV</sup>OCl<sub>2</sub>(dbbpy)(H<sub>2</sub>O)] (1)

To a suspension of VCl<sub>3</sub> (115 mg, 0.7 mmol) in acetonitrile (14 ml) was added 4,4'-di-*tert*-butyl-2,2'-bipyridine (196 mg, 0.7 mmol) and the mixture was refluxed for 4 hours in air. The resulting solution was evaporated to dryness and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (7 ml). Slow diffusion of an Et<sub>2</sub>O layer into the dichloromethane solution produced green crystals of **1**·1.5CH<sub>2</sub>Cl<sub>2</sub>. These crystals readily lost part of the co-crystallized solvent when separated from the mother liquor. Anal. Calc. for C<sub>18</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>V·0.8CH<sub>2</sub>Cl<sub>2</sub>: C, 45.9; H, 5.7; N, 5.7 %. Found: C, 45.7; H, 5.6; N, 5.8 %. Extensive drying **1**·1.5CH<sub>2</sub>Cl<sub>2</sub> under vacuum gave **1**. Anal. Calc. for C<sub>18</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>V: C, 50.9; H, 6.2; N, 6.6 %. Found: C, 50.9; H, 6.4; N, 6.6 %. Yield: 327 mg (95%). IR (KBr) v/cm<sup>-1</sup>: 3440(br.s), 3066(w), 2961(s), 2910(w), 2871(w), 1642(m), 1616(s), 1548(m), 1480(m), 1410(s), 1362(w), 1306(w), 1256(m), 1201(w), 1119(w), 1026(m), 989(s), 901(m), 865(m), 852(m), 746(w), 721(w), 609(m), 560(w).

## 2.5. Procedure for the catalyzed epoxidation reaction

**With GC monitoring.** Cyclooctene (135 mg, 1.2 mmol), complex **1** (10 mg, 0.024 mmol, 2%), trioxane (72 mg, 0.8 mmol) and 4 mL of chloroform were mixed in a Schlenk tube. The mixture was stirred and a first aliquot (0.1 mL) was withdrawn, before adding the TBHP solution (0.43 mL, 5.5 M in decane, 2.4 mmol). A second aliquot (0.1 mL) was then rapidly taken. After that the reaction mixture was warmed to 55°C with stirring for 5 h. Aliquots were analyzed by GC after quenching the residual TBHP by addition of excess PPh<sub>3</sub>. A control experiment with GC and <sup>31</sup>P NMR showed that the reaction between TBHP and PPh<sub>3</sub> is immediate and quantitative to produce *t*BuOH and Ph<sub>3</sub>P=O.

**With <sup>1</sup>H NMR monitoring.** In a Schlenk flask, **1** (10 mg, 0.024 mmol) was dissolved in 4 ml of chloroform. Subsequently, cyclooctene (160 µl, 1.2 mmol) and trioxane (620 µl, 0.8 mmol, internal standard) were added. The mixture was stirred and a first aliquot (0.1 mL) was withdrawn. Then, 0.43 ml of a decane solution of TBHP (5.5 M, 2.4 mmol) were added to the resulting solution. The mixture was stirred at 55°C and 0.1 mL aliquots were periodically withdrawn for the <sup>1</sup>H NMR monitoring. With the exception of the first aliquot which does not contain TBHP, all other aliquots were introduced into an NMR tube containing ca. 63 mg (0.24 mmol) of triphenylphosphine solubilized in CDCl<sub>3</sub> in order to quench the residual TBHP and then directly used for the <sup>1</sup>H and <sup>31</sup>P analyses. A control experiment showed that the reaction

between TBHP and  $\text{PPh}_3$  is immediate and quantitative to produce *t*BuOH and  $\text{Ph}_3\text{P}=\text{O}$  (identified by GC and  $^{31}\text{P}$  NMR). Another control experiment was run in the absence of cyclooctene, in order to make sure that trioxane is not altered under the oxidizing conditions, using the solvent peak as internal standard: integration of the chloroform signal at 7.3 ppm and of the trioxane signal at 5.15 ppm showed a constant intensity ratio over a 21 h period at 55°C.

### **Large-scale epoxidation and isolation of the *trans*-1,2-dichlorocyclooctane product.**

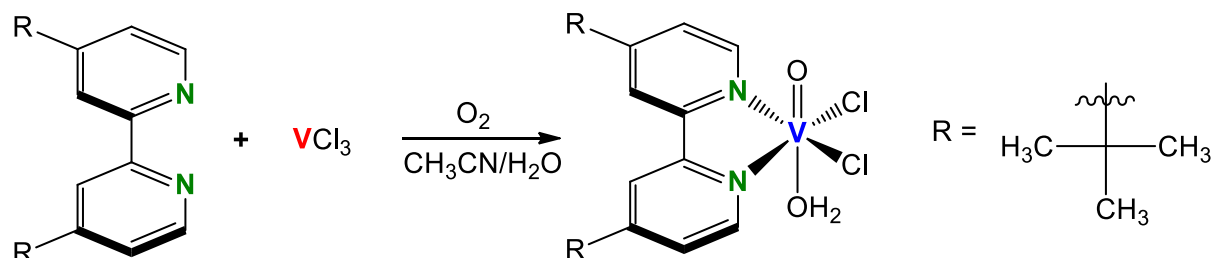
Cyclooctene (2.07 g, 18.8 mmol), complex **1** (80 mg, 0.188 mmol, 1 mol%), and 30 mL of chloroform were mixed in a Schlenk tube under argon. The mixture was stirred and a TBHP solution (6.8 mL, 5.5 M in decane, 37.6 mmol) was added by syringe. The reaction mixture was then warmed to 55°C with stirring for 42 h, with GC monitoring, and evaporated to dryness to give an oily residue, which was redissolved in diethyl ether and filtered on a small patch of silica to remove the catalyst. The resulting solution was evaporated again to dryness yielding a yellow oil, which was dissolved in 4 mL of ethanol. 8 mL of 2 M HCl (16 mmol) were added to this solution and the reaction mixture was stirred for 24 h at room temperature. The organic phase was then extracted by dichloromethane, placed over  $\text{Na}_2\text{CO}_3$ , filtered and evaporated. The oily residue was purified by chromatographic separation on a silica column eluting with pentane. A colorless oily pure compound was obtained (yield: 30 mg, 1%) and characterized as *trans*-1,2-dichlorocyclooctane by NMR analysis. A few other fractions containing *trans*-1,2-dichlorocyclooctane together with other byproducts were also obtained and discarded.

## **3. Results and discussion**

### **3.1. Synthesis and characterization**

The title complex was synthesized from vanadium(III) chloride ( $\text{VCl}_3$ ) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dbbpy), with concomitant oxidation in air to give the  $\{\text{V}=\text{O}\}^{2+}$  moiety, see Scheme 1. The same synthetic procedure was previously used for the preparation of other oxidovanadium(IV) complexes with 2,2'-bipyridine, 1,10-phenanthroline [31], bis(N-(2,6-diisopropylphenyl)-imino)acenaphthene (dpp-bian) [10], dehydrophenanthroline and diazofluorene ligands [42]. The reaction of  $\text{VCl}_3$  with 4,4'-di-*tert*-butyl-2,2'-bipyridine (dbbpy) (1:1 molar ratio) in acetonitrile in air results in  $[\text{VOCl}_2(\text{dbbpy})(\text{H}_2\text{O})]$  (**1**) in high yield (95%). The complex was isolated as a solvate with  $\text{CH}_2\text{Cl}_2$  molecules (**1**·1.5 $\text{CH}_2\text{Cl}_2$ ) as confirmed by the X-ray structure data. The isolated crystals easily lose  $\text{CH}_2\text{Cl}_2$  molecules to give **1**, which is stable in air, both in solution and in the solid state, and is well-soluble in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and other organic solvents. The same complex was recently used by us as a building block to obtain a binuclear complex  $[\text{VO}(\text{dbbpy})\text{Cl}(\text{Ca})\text{Cl}(\text{dbbpy})\text{VO}]$  with bridging chronilate

Ca<sup>2+</sup> [43]. Other previously reported oxidovanadium complexes containing dbbpy ligands are *cis*-[V<sup>IV</sup>O(OH)(dbbpy)]Y (Y = BF<sub>4</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>), *cis*-[V<sup>IV</sup>O(F)(dbbpy)<sub>2</sub>]A (A = BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>), [V<sub>2</sub>O<sub>2</sub>(μ-MeO)<sub>2</sub>(μ-MO<sub>4</sub>)<sub>2</sub>(dbbpy)<sub>2</sub>] (M = Mo, W), [(VO)<sub>2</sub>(μ<sub>2</sub>-SO<sub>4</sub>)<sub>2</sub>(dbbpy)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>] and [(VO)<sub>2</sub>(μ<sub>2</sub>-O)<sub>2</sub>(μ<sub>2</sub>-SO<sub>4</sub>)(dbbpy)<sub>2</sub>] [38–41].

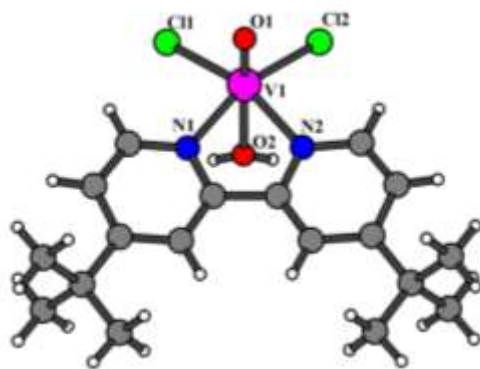


**Scheme 1.** Reaction scheme for the synthesis of **1**

The IR spectrum of **1** shows a strong band at 989 cm<sup>-1</sup>, assigned to a V=O stretching mode in agreement with those reported for other oxidovanadium(IV) complexes [10,44–46]. The broad vibration band at 3440 cm<sup>-1</sup> for the OH group in H<sub>2</sub>O and vibration bands for the CH group (2871–2961 cm<sup>-1</sup>) and for the C=C and C=N groups (1642–1548 cm<sup>-1</sup>) of the dbbpy ligand (Fig. S1, see ESI) were also observed. A band at 901 cm<sup>-1</sup> is assigned to the V-O stretching vibration of the V-H<sub>2</sub>O moiety.

### 3.2. Crystal structure

Crystals of **1**·1.5CH<sub>2</sub>Cl<sub>2</sub> were grown by recrystallization of **1** from a CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O and were studied by single crystal X-ray diffraction analysis. The molecular structure of **1** is represented in Fig. 1. Selected bond distances and angles are given in Table 2. Vanadium(IV) has a distorted octahedral environment. The equatorial plane of the octahedron is defined by two chlorides and two nitrogen atoms of the dbbpy ligand while the oxido and H<sub>2</sub>O ligands occupy the axial positions.



**Fig. 1** Molecular structure of [VOCl<sub>2</sub>(dbbpy)(H<sub>2</sub>O)] in **1**·1.5CH<sub>2</sub>Cl<sub>2</sub>.

**Table 2.** Selected geometric parameters (Å, °) for **1**·1.5CH<sub>2</sub>Cl<sub>2</sub>

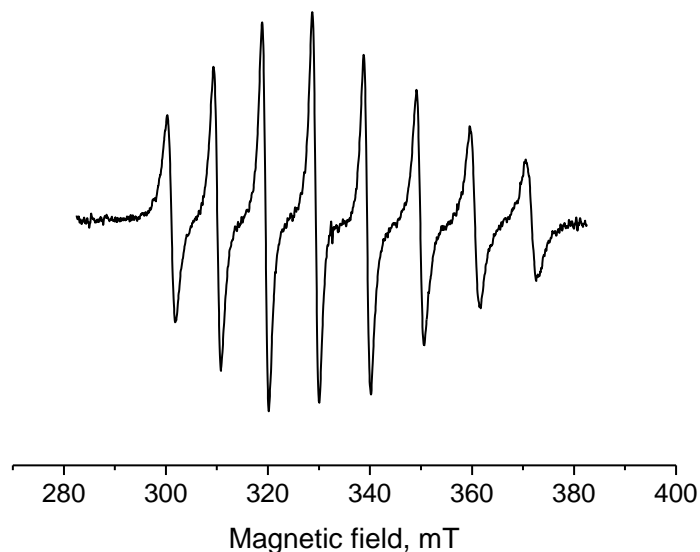
|           | <b>1</b> ·1.5CH <sub>2</sub> Cl <sub>2</sub> |                      | <b>1</b> ·1.5CH <sub>2</sub> Cl <sub>2</sub> |
|-----------|--|----------------------|--|
| V-O(1)    | 1.589 (3)                                    | V-Cl1                | 2.3662 (9)                                   |
| V-O(2)    | 2.259 (3)                                    | V-Cl2                | 2.3663 (9)                                   |
|           |  | V-N                  | 2.128 (3)                                    |
|           |  | <i>Cis</i> -angles   |  |
| O(1)-V-Cl | 98.16 (9)                                    | N(1)-V-N(2)          | 76.14 (13)                                   |
| O(2)-V-Cl | 84.39 (6)                                    | Cl(1)-V-Cl(2)        | 94.58 (4)                                    |
| O(1)-V-N  | 97.74 (12)                                   | N(1)-V-Cl(1)         | 92.42 (7)                                    |
| O(2)-V-N  | 79.30 (10)                                   | N(2)-V-Cl(2)         | 92.42 (7)                                    |
|           |  | <i>Trans</i> -angles |  |
|           |  | O(1)-V-O(2)          | 176.21 (15)                                  |
|           |  | N(1)-V-Cl(2)         | 161.52 (8)                                   |
|           |  | N(2)-V-Cl(1)         | 161.52 (8)                                   |

The V=O distance of 1.5905(1) Å is within the 1.56-1.63 Å range reported for other vanadium(IV) complexes [10,31,47]. The V-Cl (2.3655(1) Å) and V-N (2.1289(1) Å) V-O (2.2589(1) Å) distances are similar to those found elsewhere [10,31,48–50].

### 3.3. EPR spectra

The EPR spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature is shown in Fig. 2. The spectrum shows an eight-line pattern due to hyperfine interaction with the <sup>51</sup>V isotope (I = 7/2, 100%), which is typical for oxidovanadium(IV) complexes [10,51]. The V<sup>4+</sup> ion has a 4d<sup>1</sup> electronic state with S = 1/2 and g = 1.967. The line splitting varies from 8.98 mT to 11.16 mT, and the line half-width varies from 1.28 mT to 2.4 mT, due to the vanadium complex mobility in solution and to an incomplete averaging of the g tensor anisotropy.



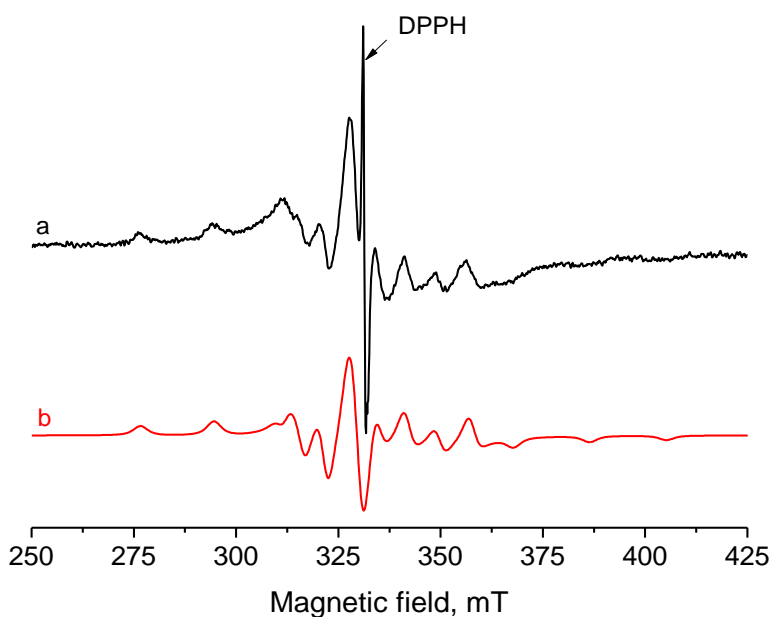


**Fig. 2.** X-Band CW EPR spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> at 298K

The EPR spectrum of the frozen solution of **1** at 77 K is shown in Fig. 3. Simulation shows that the experimental spectrum is described by the spin Hamiltonian:

$$H = g_{xx}\beta H_x S_x + g_{yy}\beta H_y S_y + g_{zz}\beta H_z S_z + A(V)_{xx} S_x I_x + A(V)_{yy} S_y I_y + A(V)_{zz} S_z I_z$$

with the following parameters:  $S = 1/2$ ,  $I = 7/2$ ,  $g_{xx} = g_{yy} = 1.978$ ,  $g_{zz} = 1.945$ ,  $A_{xx} = A_{yy} = 6.5$  mT,  $A_{zz} = 17.86$  mT. Similar values were previously reported for related oxidovanadium(IV) complexes [10,42]. The EPR spectrum of solid **1** reveals a single-line signal with a half-width width ( $\Delta H_{1/2}$ ) of 8.6 mT and  $g = 1.967$  due to the exchange interaction between paramagnetic vanadium ions (Fig. S2, see ESI). The analysis of the hyperfine splitting parameters allowed us to estimate the isotropic and anisotropic contributions to the hyperfine interaction with vanadium:  $A_{iso} = 10.29$  mT and  $A_{aniso} = 3.79$  mT. By using these parameters and assuming a 100% localization on the *s* or *d* orbitals [52], we could estimate the spin density of the unpaired electron on the vanadium atom:  $(3.79/6.246 + 10.29/148.62) \times 100\% = 67.60\%$ .

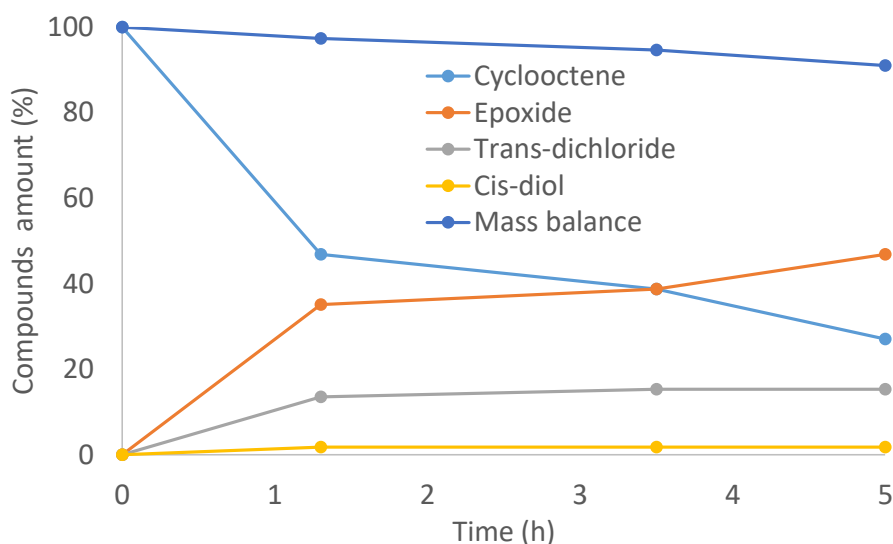


**Fig. 3.** EPR spectra of **1** in  $\text{CH}_2\text{Cl}_2$  at 77 K. DPPH indicates the single EPR resonance of 2,2-diphenyl-1-picrylhydrazyl, which was used as an internal standard, with  $g = 2.0036$ . a – experimental, b – simulated.

### 3.4. Cyclooctene epoxidation

Cyclooctene was chosen as a representative substrate for catalytic studies. It was oxidized by *tert*-butyl hydroperoxide (TBHP) under mild conditions (55° C) in the presence of catalytic amounts of complex **1** in chloroform. The reaction gave, as expected, cyclooctene epoxide as the main product and traces of the *cis*-cyclooctan-1,2-diol, whereas no significant amount of the *trans*-cyclooctan-1,2-diol, which is the expected product of acid-catalyzed epoxide ring opening in the presence of water, was detected. However, a non-negligible amount of a secondary product **2** was also noted. The formation of this product did not depend on the method of quenching for the reaction monitoring (*vide infra*). All products, except for the latter secondary product, were unambiguously identified by the  $^1\text{H}$  NMR resonance of the methyne (CH) proton and by the comparison of the GC retention time with genuine standards. The CH proton of residual cyclooctene yields a multiplet at  $\delta$  5.6, whereas that of cyclooctene epoxide resonates at  $\delta$  2.9 and that of the *cis*-diol at  $\delta$  3.9. The corresponding proton of the *trans*-diol is expected at  $\delta$  3.6 ppm [53], but no significant intensity was observed in this region. The secondary product **2** is characterized by a multiplet at  $\delta$  4.3, the shape of which is quite similar to that of the epoxide product. A representative  $^1\text{H}$ -NMR spectrum, recorded after 3.5 h of

reaction, is shown in Fig. S3 (ESI). The results of the  $^1\text{H}$  NMR monitoring are summarized in Fig. 4 (full data in Table S1). The slight erosion of the mass balance, which is accentuated at longer reaction times (see table S1) indicates that other unknown products are also obtained. The catalyst is presumably deactivated during the reaction, since the residual cyclooctene amount stagnates after 5 h.



**Fig. 4.**  $^1\text{H}$  NMR monitoring of the cyclooctene epoxidation by TBHP in  $\text{CHCl}_3$  at  $55^\circ\text{C}$  catalyzed by compound **1**.

Identification of the significant secondary product **2** was not easy. The GC-MS analysis revealed a molecular ion corresponding to the  $\text{C}_8\text{H}_{14}\text{Cl}^+$  formula that did not match with available library spectra. Unambiguous identification required a large scale catalysis experiment followed by product separation and NMR analysis of the pure product. In this experiment, decane was used as internal standard for a monitoring by GC. The separation was accomplished by quenching the TBHP excess with  $\text{PPh}_3$ , followed by exhaustive hydrolysis of the epoxide product **1** to yield the *trans*-diol, since the epoxide and compound **2** could not be separated in our hands, and by chromatographic separation on a silica column, eluting with pentane, as eluent. Monitoring of the separation step was complicated by the lack of chromophores in both **2** and the decane internal standard, but 30 mg of pure isolated compound could eventually be obtained. The hydrocarbons (decane, residual cyclooctene) were eluted first, followed by the desired compound, while the diols remained trapped on the silicagel. Full  $^1\text{H}$  and  $^{13}\text{C}$  analyses of the recovered product allowed its unambiguous identification as *trans*-1,2-dichlorocyclooctane. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data (see SI, Fig. S4 and S5) were identical to

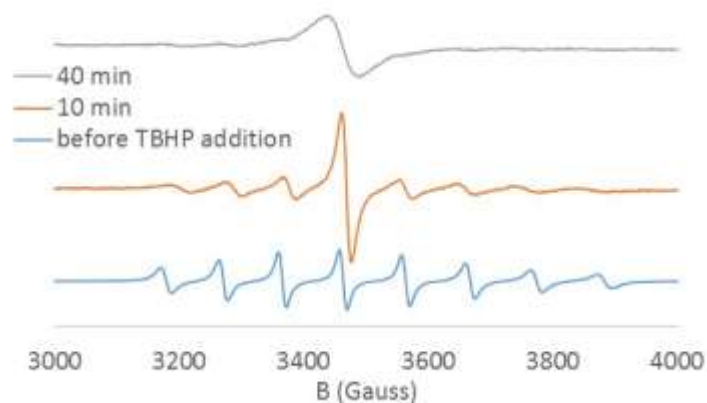
those reported in the literature for this compound [54]. It is worth pointing out that *trans*-1,2-dichlorocyclooctane is the only product of dichlorination. The other isomer, *cis*-1,2-dichlorocyclooctane, with an expected signal at  $\delta$  4.6-4.1ppm [55], was not observed. This perfect stereoselectivity rules out radical dichlorination, which would provide a mixture of diastereoisomers [56]. Because of the *trans* stereoselectivity, we propose that an electrophilic dichlorination is taking place.

Understanding the origin of chlorine for this reaction is of interest. Formation of **2** may be rationalized as the result of 1,2-dichlorination by HCl (a common contaminant of chloroform) under oxidizing conditions. This transformation occurs without need of metal catalysis and is *trans*-selective, presumably via the formation of a chloronium intermediate [57]. In order to check this hypothesis, the catalytic oxidation was repeated in a carefully purified chloroform, and also by adding HCl (as a solution in diethyl ether) but the yield of *trans*-1,2-dichlorocyclooctane were not significantly decreased or improved under these conditions. From these results, we conclude that the source of chlorine is not HCl. The only other possible sources of Cl atoms are compound **1** and chloroform itself. The amount of compound **1** (2%) used in the catalytic reactions is not enough to provide the necessary Cl atoms to produce the observed by-product **2** (23.4% after 72 h, see table S1). We can therefore safely conclude that chloroform (41 equivalents relative to cyclooctene) is the primary source of chlorine atoms. Further studies are necessary to obtain additional insights into the chloroform activation mechanism, but we can tentatively speculate that chloroform may react with TBHP, with or without the intervention of vanadium catalysts, to yield methanol and *t*BuOCl or an ether and hypochloric acid, which are possible sources of electrophilic chloronium [57]. To the best of our knowledge, the formation of this by-product has not been previously mentioned, although chloroform is a rather frequently used as solvent for the catalyzed alkene epoxidations with H<sub>2</sub>O<sub>2</sub> or TBHP [14,16,17].

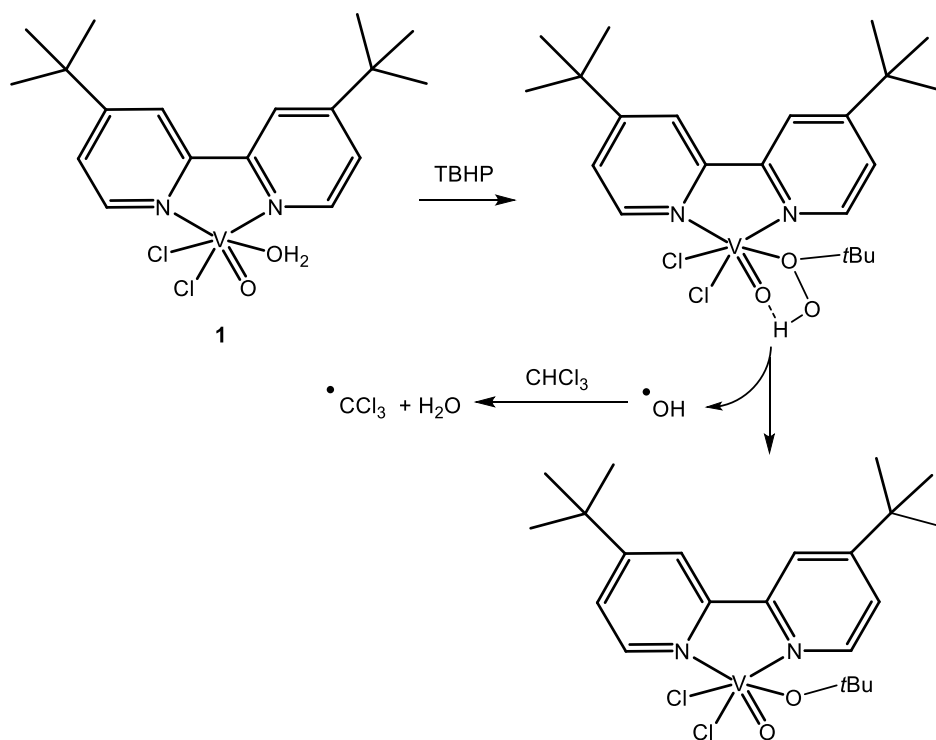
The above mentioned reaction monitoring by <sup>1</sup>H NMR and GC were conducted using PPh<sub>3</sub> to quench the excess TBHP, which rapidly transforms the oxidant to *t*BuOH and generates Ph<sub>3</sub>P=O, as verified by control experiments and <sup>31</sup>P NMR analysis. Preliminary catalytic experiments were also conducted with MnO<sub>2</sub> as reagent to quench the excess TBHP. This procedure led to the same product distribution as with the PPh<sub>3</sub> quench, but substantial amounts of an additional heavy molecular weight product were also observed in the GC trace. This product could only be detected in very small amounts during the experiments run with a PPh<sub>3</sub> quench (see Fig. S6). The GC-MS analysis indicated that this additional product corresponds to 3-trichloromethylcyclooctene. Its formation results from the formal replacement of an allylic hydrogen atom by CCl<sub>3</sub>, suggesting the involvement of CCl<sub>3</sub><sup>•</sup> radicals. This is corroborated by

the parallel observation of  $C_2Cl_6$  in the GC spectrum. The production of a large amount of  $CCl_3\cdot$  radicals during the TBHP quench with  $MnO_2$  can be attributed to the formation of  $HO\cdot$  and/or  $tBuO\cdot$  radicals, followed by H abstraction from the solvent.

Additional investigations were carried out in order to learn more about the catalyst action. When TBHP was added to a solution of complex **1**, which is pale green, the color turned immediately to violet. The EPR spectrum recorded 10 minutes after the addition of TBHP at  $20^\circ C$  shows the overlap of a new 8-line pattern, similar to but different from that of **1** ( $g = 1.990$ ,  $A \sim 94$  G) and a strong single line at  $g = 2.014$ , see Figure 5. The 8-line pattern slowly decreased and completely disappeared, while the second peak still remained after 40 min, and completely disappeared only two days later. In a second similar experiment, carried out at  $55^\circ C$ , the initial spectrum before the addition of TBHP was identical to that recorded at  $20^\circ C$ , showing that the precatalyst is stable at this temperature. Addition of TBHP accelerated the degradation. These experiments suggest an immediate reaction between complex **1** and TBHP at  $20^\circ C$ , with the formation of an intermediate  $V^{IV}$  complex (8-line pattern) and an organic radical (single peak), which then decompose at different rates. The  $V^{IV}$  intermediate is likely the product of  $H_2O$  substitution by TBHP, by analogy with the intermediate proposed in Mo-catalyzed epoxidation [58]. Its decomposition, in the absence of substrate, presumably yields a  $V^V$  product by homolytic O-O cleavage, releasing an  $OH\cdot$  radical (see scheme 2). The latter abstracts the H atom from the solvent and yields the long-lived  $CCl_3\cdot$  radical, which presumably accounts for the second observed product in the EPR spectrum. Indeed, as stated above, the formation of 3-trichloromethylcyclooctene, though in rather small amounts, was also observed in the experiments carried out without a  $MnO_2$  quench. It should be underlined that the reactions leading to disappearance of the  $V^{IV}$  EPR signals are fast at  $55^\circ C$  but, when the substrate is present, the catalytic oxidation at this temperature continues at moderate activity for several hours. Thus, the  $V^V$  species produced by oxidation of the  $V^{IV}$  precatalyst is certainly catalytically active [15]. However, the initially higher catalytic activity may result from either a  $V^V$  or, more likely, a  $V^{IV}$  species.



**Fig. 5.** EPR spectra of the solution of complex **1** in  $\text{CHCl}_3$  before and after TBHP addition at  $20^\circ\text{C}$ . The spectra recorded 10 and 40 min after the TBHP addition have a vertical scale expanded by a factor of 10.



**Scheme 2.** Proposed action of TBHP on compound **1**

#### 4. Conclusion

The octahedral oxidovanadium(IV) complex,  $[\text{VOCl}_2(\text{dbbpy})(\text{H}_2\text{O})]$  (**1**), containing the 4,4'-di-*tert*-butyl-2,2'-bipyridine (dbbpy) ligand was synthesized and characterized using X-ray diffraction, IR and EPR spectroscopies. This complex was tested as a catalyst for

epoxidation of cyclooctene with TBHP in chloroform. A conclusion to be drawn from this study is that one-electron processes occur in the presence of the vanadium(IV) precatalyst, the oxidant and chloroform, generating radical species. In addition, using chloroform in combination with the TBHP oxidant leads to the formation of *trans*-1,2-dichlorocyclooctane as an unwanted side product of 1,2-dichlorination. It therefore seems wise to avoid the use of chloroform as a solvent in catalyzed oxidations with TBHP (and likely also with H<sub>2</sub>O<sub>2</sub>), at least with a vanadium(IV) precatalyst.

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