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Oxovanadium(IV) complexes as molecular catalysts in epoxidation: Simple access to pyridylalkoxide derivatives

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Abstract

Reaction of bis(aryl)-2-pyridylmethanol ligands (**1a**–**7a**) with $VO(SO_4) \cdot 5H_2O$ results in the formation of metal-oxo complexes $[VO(N\text{-}O)_2]$ (**1**–**7**), with N-O = bis(aryl)-2-pyridylmethanol. A molecular structure of (**4**) has been determined by single crystals X-ray diffraction study, which showed the expected square planar pyramidal geometry with the pyridine ring nitrogens in *trans*-position to each other. The metal-oxo complexes (**1**–**4**,**6**,**7**) demonstrated the ability to catalyse epoxidation reactions of alkenes with molecular oxygen.

Keywords: Epoxidation; Metal oxides; Pyridyl alcohols; Vanadium

1. Introduction

An application of oxovanadium(IV) compounds as oxidation catalysts was first discovered by Sharpless in the case of the regioselective epoxidation of allylic alcohols [1]. Although these oxovanadium(IV) complexes were studied intensively with *tert*-butylhydrogenperoxide as oxidant [2–4], these complexes have – with one exception: VO-$(acac)_2$ (**8**) – never been employed in oxidation catalysis with molecular oxygen [5]. To investigate the potential of these oxovanadium(IV) compounds in epoxidation catalysis with molecular oxygen, the class of vanadium complexes with bidentate N,O-ligands was synthesized [6]. Pyridyl alcohols, which consist of an aliphatic alkoxy function and an aromatic nitrogen donor atom, were used as N,O-ligands for the syntheses, because it has been shown, that these ligands are perfectly stable in oxidation catalysis with dioxomolybdenum(VI) complexes [7,8].

2. Results and Discussion

The new oxovanadium(IV)-complexes build up a big variety of vanadium(IV)-complexes with a bidentate N,O-ligand, which consist of an aliphatic hydroxy function combined with a nitrogen-donor of a pyridine ring and two phenyl groups at the backbone, bound to a $(VO)^{2+}$-unit. The used ligands were made by nucleophilic attack of 2-lithiumpyridine on various aromatic ketones [9,10]. After hydrolisation the prepared ligands were received pure and in high yields.

The new oxovanadium(IV) catalysts **1**–**7** were synthesized by a simple ligand exchange reaction of the sulphate counter ion of the starting reagent $VO(SO_4) \cdot 5H_2O$ with two equivalents of various pyridyl alcohols **1a**–**7a** (Scheme 1). To deprotonate each equivalent of the chelating alcohol sodium acetate was used. The driving force of this reaction

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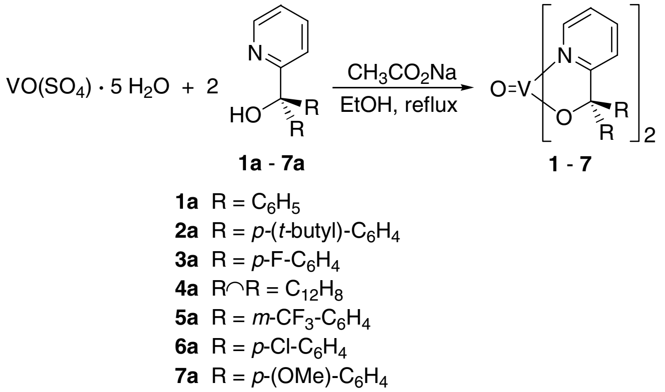

Scheme 1. Synthesis of the complexes **1**–**7**.

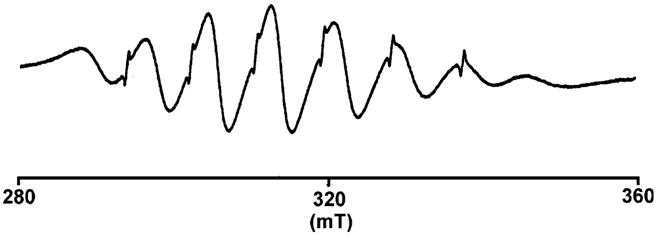

Fig. 1. ESR spectra of complex **2** at 293 K.

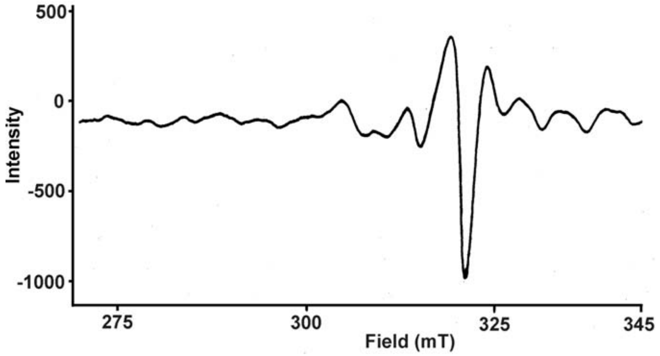

Fig. 2. ESR spectra of complex **2** at 133 K.

is the chelating effect of the two bidentate N,O-ligands. The same reactions were carried out with vanadium acetylacetonate as starting material, but in this case the yields were lower in comparison to the method described above.

The characterization of **1**–**7** is based on infrared spectroscopy. The characteristic oxovanadium stretching frequency was detected in the range between 958 and 982 cm^{-1}, which is in accordance to the literature (970–985 cm^{-1}) [6,11]. Additionally the aromatic stretching frequencies of the pyridine ring indicate the complexation of the oxovanadium-fragment by the ligands. The elemental analyses clearly prove the existence of the resulting complexes. Since vanadium(IV) complexes are known to be paramagnetic systems, ESR methods are applied to prove this. At room temperature, the ESR spectrum of **2** clearly shows 8 lines, as expected for an $I = 7/2$ nucleus (Fig. 1). The low temperature (133 K) ESR spectrum of **2** depicts the anisotropic behaviour, as published by Attanasio et al. for oxovanadium(IV) salen complexes (Fig. 2) [12]. In the case of **1**–**5** a magnetic moment of about 1.8 Bohr magnetons was detected in accordance to published data [13].

Suitable single crystals of the fluorenyl-derivative **4** for X-ray diffraction study were grown from a dichloromethane/*n*-hexane mixture (Fig. 3).

The structure of complex **4** can be described as a square planar pyramid. The nitrogen atoms in the pyridine rings of the ligands are positioned *trans* to each other. This is

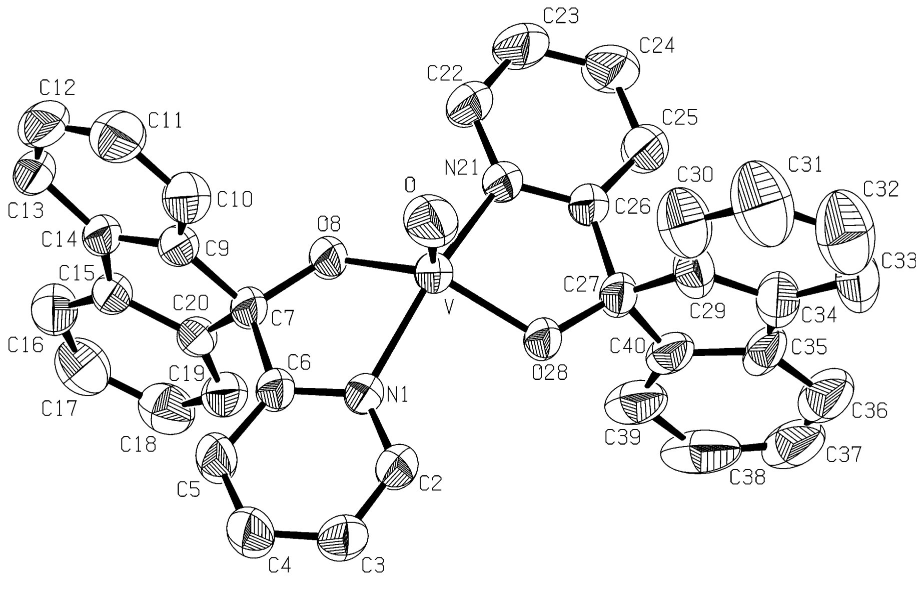

Fig. 3. ORTEP style plot [14f] of the solid state structure of complex **4**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: V–O 1.609(3), V–O8 1.885(2), V–O28 1.893(2), V–N1 2.090(3), V–N21 2.097(4), O8–C7 1.411(4), O28–C27 1.397(4); O–V–O8 114.7(1), O–V–O28 114.3(1), O–V–N1 101.9(1), O–V–N21 104.3(1), O8–V–O28 131.0(1), O8–V–N1 79.22(9), O8–V–N21 88.9(1), O28–V–N1 90.61(9), O28–V–N21 79.63(9), N1–V–N21 153.8(1), V–O8–C7 119.1(2), V–O28–C27 119.8(2).