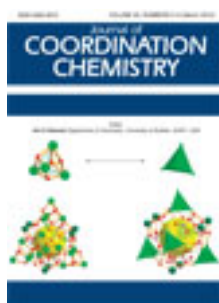


This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:44

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Crystal structure, electrochemistry, and catalytic studies of a series of new oxidovanadium(IV) Schiff-base complexes derived from 1,2-diphenyl-1,2-ethylenediamine

Abolfazl Ghaffari ^a, Mahdi Behzad ^a, Grzegorz Dutkiewicz ^b,
Maciej Kubicki ^b & Mehdi Salehi ^a

^a Department of Chemistry, College of Sciences, The University of Semnan, Semnan, Iran

^b Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

Published online: 21 Feb 2012.

To cite this article: Abolfazl Ghaffari, Mahdi Behzad, Grzegorz Dutkiewicz, Maciej Kubicki & Mehdi Salehi (2012) Crystal structure, electrochemistry, and catalytic studies of a series of new oxidovanadium(IV) Schiff-base complexes derived from 1,2-diphenyl-1,2-ethylenediamine, *Journal of Coordination Chemistry*, 65:5, 840-855, DOI: [10.1080/00958972.2012.662275](https://doi.org/10.1080/00958972.2012.662275)

To link to this article: <http://dx.doi.org/10.1080/00958972.2012.662275>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Crystal structure, electrochemistry, and catalytic studies of a series of new oxidovanadium(IV) Schiff-base complexes derived from 1,2-diphenyl-1,2-ethylenediamine

ABOLFAZL GHAFFARI†, MAHDI BEHZAD*‡, GRZEGORZ DUTKIEWICZ‡, MACIEJ KUBICKI‡ and MEHDI SALEHI†

†Department of Chemistry, College of Sciences, The University of Semnan, Semnan, Iran

‡Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

(Received 3 December 2011; in final form 2 January 2012)

New derivatives of N_2O_2 tetradentate Schiff bases, from condensation of meso-1,2-diphenyl-1,2-ethylenediamine and salicylaldehyde derivatives (X-salicylaldehyde; X = 3-OMe, 4-OMe, 5-OMe, 6-OMe, 5-Cl, 5-Me), and oxidovanadium(IV) complexes were synthesized and characterized by 1H NMR, UV-Vis, IR spectroscopy, and elemental analysis. Crystal structure of 5-OMe; H_2L^3 and two of the complexes (VOL^2 and VOL^3) were also obtained. In the crystals, the molecule of H_2L^3 is C_i symmetrical, as it occupies the special position on the center of symmetry; its conformation is partially determined by classical intramolecular O–H...N hydrogen bonds. The complexes have monomeric structures with a distorted square pyramid of vanadium, with the oxo ligand in the apical position. Cyclic voltammetry studies show quasi-reversible V^{IV}/V^V redox for which the presence of electron-withdrawing groups on salicylaldehyde derivatives shifts the E° to more positive values. The complexes were used as catalysts for selective epoxidation of cyclooctene with *tert*-butylhydroperoxide as oxidant, in various solvents and reaction conditions. High catalytic activities and excellent selectivity was found. The catalytic activity of the complexes increased increasing E° , a consequence of the presence of electronegative substituents. This epoxidation process with the new catalysts was also studied under solvent-free condition and excellent reactivity was observed.

Keywords: Schiff base; Tetradentate; Oxidovanadium(IV); Epoxidation

1. Introduction

The chemistry of vanadium complexes, especially oxidovanadium(IV), has attracted particular interest [1–10] for their biological, medicinal, synthetic, and catalytic activities [11–15]. Vanadium compounds are potential oral drugs for diabetic patients [16] and numerous investigations are carried out in this regard [17, 18]. Due to the disadvantages of the use of inorganic salts of this element in medical treatments, mostly neutral complexes of vanadium ($V^{IV}O$), chelated to organic ligands, have been studied [19, 20]. Another reason for the study of vanadium containing complexes is their ability to catalyze important reactions. Of particular interest is the use of tetradentate

*Corresponding author. Email: mbehzad@semnan.ac.ir

Schiff-base complexes of oxidovanadium(IV) in oxidation catalysis [21–24]. Coordination compounds of vanadium are potential candidates for catalytic purposes thanks to the several oxidation states of this element, as well as a variety of coordination numbers, readily accessible high oxidation states, and a high affinity toward oxygen. The epoxidation of olefinic compounds is an important reaction, since it results in a variety of useful synthetic and industrially important intermediates. Schiff-base complexes of oxidovanadium(IV) are among the most widely employed catalysts for aerobic and non-aerobic alkene epoxidation. Molecular oxygen, hydrogen peroxide, and *tert*-butylhydroperoxide (TBHP) are used in such studies. Molecular oxygen is the greenest but low reaction rates limit its application. Others and we have found that TBHP is a useful oxidizing agent. Hence, and in continuation of our previous studies, we herein report the synthesis, characterization, crystal structure, and catalytic performance of a series of oxidovanadium(IV) complexes of Schiff-base ligands derived from condensation 1,2-diphenyl-1,2-ethylenediamine with salicylaldehyde derivatives. The new complexes were tested as catalysts in the epoxidation of cyclooctene with TBHP under various conditions to find the optimum operating conditions. Our results show that these complexes are highly efficient catalysts with high turnover numbers (TON) and excellent selectivity toward cycloocteneoxide.

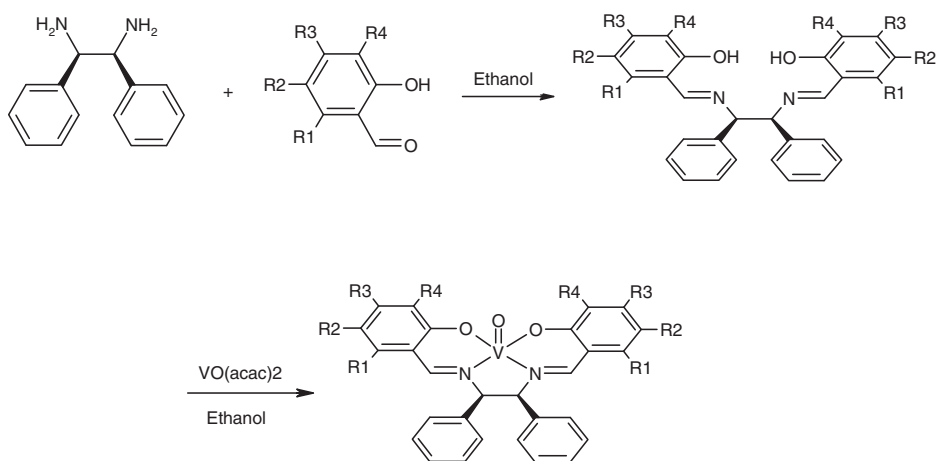
2. Experimental

2.1. Materials and instruments

All chemicals were of the highest purity and used as received. Cyclooctene and cycloocteneoxide were purchased from Aldrich and other chemicals were purchased from Merck. All syntheses and purifications were conducted in aerobic conditions. 1,2-Diphenyl-1,2-ethylenediamine was synthesized following the literature procedure [25]. *N,N'*-bis(salicylidene)-1,2-diphenyl-1,2-ethylenediamine (H_2L^7) was synthesized according to the literature procedure [24]. New tetradentate Schiff bases were synthesized following similar procedure for the synthesis of H_2L^7 . Melting points were obtained on a Thermoscientific 9100 apparatus. 1H NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer using $CDCl_3$ and $DMSO-d_6$; chemical shifts (δ) are given in ppm. Infrared (IR) spectra were obtained as KBr pellets using a Bruker FT-IR instrument and UV-Vis spectra were obtained on a Shimadzu UV-1650PC spectrophotometer. Elemental analyses (C, H, and N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analysesysteme, GmbH, West Germany). A Metrohm 757 VA computerized instrument was employed to obtain cyclic voltammograms in acetonitrile at room temperature (25°C) using 0.1 mol L^{-1} tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) solution as supporting electrolyte. A platinum electrode was used as the auxiliary electrode and an Ag/AgCl electrode as the working electrode. *Gas chromatography* (GC) analyses were carried out on a GC-17A Shimadzu instrument.

2.2. Typical procedure for the synthesis of the ligands

The ligands were synthesized by condensation of 1,2-diphenyl-1,2-ethylenediamine with different salicylaldehyde derivatives in 1:2 ratio in ethanol. In all cases, analytically



Ligand/Complex	R ₁	R ₂	R ₃	R ₄	Ligand/Complex	R ₁	R ₂	R ₃	R ₄
H ₂ L ¹ /VOL ¹	H	H	H	OCH ₃	H ₂ L ⁵ /VOL ⁵	H	Cl	H	H
H ₂ L ² /VOL ²	H	H	OCH ₃	H	H ₂ L ⁶ /VOL ⁶	H	CH ₃	H	H
H ₂ L ³ /VOL ³	H	OCH ₃	H	H	H ₂ L ⁷ /VOL ⁷	H	H	H	H
H ₂ L ⁴ /VOL ⁴	OCH ₃	H	H	H					

Scheme 1. Typical procedure for the synthesis of the ligands and oxidovanadium(IV) complexes.

pure materials were obtained by recrystallization from ethanol. This procedure is shown in scheme 1. The target ligands in all cases were yellow except H₂L⁶ which was white.

2.2.1. Preparation of [*N,N'*-bis(3-methoxysalicylidene)-1,2-diphenyl-1,2-ethylenediamine] (H₂L¹). To a vigorously stirred solution of 1,2-diphenyl-1,2-ethylenediamine (0.32 g, 1.5 mmol) in 15 mL of absolute ethanol was added a solution of 3-methoxysalicylaldehyde (0.46 g, 3 mmol) in 10 mL of ethanol. The reaction mixture was stirred for 30 min and then refluxed for 1 h. The reaction mixture was then cooled to room temperature and left undisturbed overnight. The yellow precipitate was filtered off and washed with 10 mL of ethanol and air dried. Recrystallization from ethanol gave analytically pure material.

Other ligands were synthesized following the same procedure. Spectroscopic and analytical data are collected in table 1 to confirm the synthesis of the ligands.

2.2.2. Typical procedure for the synthesis of the oxidovanadium(IV) complexes. Oxidovanadium(IV) complexes were synthesized by equimolar reaction of bis(acetylacetonato)oxovanadium(IV) with the tetradentate Schiff-base ligands in ethanol. In all cases, green microcrystalline products were collected by filtration and air dried. Recrystallization from DMSO or mixture of DMSO/methanol gave

Table 1. The analytical and spectroscopic data of the ligands.

Ligand (Empirical formula)	m.p. (°C)	Elemental analysis data experimental (Calcd)	¹ H NMR data (ppm)	IR; (ν _{C=N}) cm ⁻¹
H ₂ L ¹ (C ₃₀ H ₂₈ N ₂ O ₄)	212	C, 74.44; H, 5.50; N, 5.92 (C, 74.98; H, 5.87; N, 5.83)	13.74(br, O-H, 2H); 8.08(s, HC=N, 2H); 6.74-7.40(m, H _{Ar} , 16H); 4.8(s, C-H, 2H); 3.9(s, C-H _(CH₃) , 6H)	1627
H ₂ L ² (C ₃₀ H ₂₈ N ₂ O ₄)	216	C, 74.62; H, 5.62; N, 5.70 (C, 74.98; H, 5.87; N, 5.83)	13.4(br, O-H, 2H); 7.98(s, HC=N, 2H); 6.39-7.37(m, H _{Ar} , 16H); 4.76(s, C-H, 2H); 3.8(s, C-H _(CH₃) , 6H)	1620
H ₂ L ³ (C ₃₀ H ₂₈ N ₂ O ₄)	188	C, 74.68; H, 5.70; N, 5.72 (C, 74.98; H, 5.87; N, 5.83)	12.66(br, O-H, 2H); 8.09(s, HC=N, 2H); 6.62-7.36(m, H _{Ar} , 16H); 4.79(s, C-H, 2H); 3.7(s, C-H _(CH₃) , 6H)	1628
H ₂ L ⁴ (C ₃₀ H ₂₈ N ₂ O ₄)	230	C, 74.66; H, 5.56; N, 5.88 (C, 74.98; H, 5.87; N, 5.83)	14.94(br, O-H, 2H); 8.65(s, HC=N, 2H); 6.27-7.38(m, H _{Ar} , 16H); 4.8(s, C-H, 2H); 3.77(s, C-H _(CH₃) , 6H)	1620
H ₂ L ⁵ (C ₂₈ H ₂₂ Cl ₂ N ₂ O ₂)	216	C, 68.50; H, 4.50; N, 5.90 (C, 68.72; H, 4.53; N, 5.72)	8.03(s, HC=N, 2H); 6.9-7.35(m, H _{Ar} , 16H); 4.79(s, C-H, 2H)	1627
H ₂ L ⁶ (C ₃₀ H ₂₈ N ₂ O ₂)	213	C, 80.45; H, 6.55; N, 6.35 (C, 80.33; H, 6.29; N, 6.25)	12.93(br, O-H, 2H); 8.07(s, HC=N, 2H); 6.86-7.35(m, H _{Ar} , 16H); 4.77(s, C-H, 2H); 2.25(s, C-H _(CH₃) , 6H)	1627

analytically pure complexes. Suitable crystals for X-ray crystallography were obtained for VOL² and VOL³ and the crystal structure of these complexes were analyzed. Table 2 contains analytical and spectroscopic data for the complexes.

2.3. X-ray crystallography

Diffraction data were collected at room temperature by the ω -scan technique on an Oxford Diffraction Xcalibur four-circle diffractometer with Eos CCD detector, equipped with graphite-monochromated Mo-K α radiation source ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz polarization as well as for absorption effects [26]. Precise unit-cell parameters were determined by a least-squares fit of 1658 (H₂L³), 2935 ([VOL³]. Sol), and 5171 ([VOL²]. Sol) reflections of highest intensity. The structures were solved with SIR92 [27] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-97 [28]. The scattering factors incorporated in SHELXL-97 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (AP)^2 + BP]$ ($P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). The final values of A and B are listed in table 3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the complexes were inserted in idealized positions and refined riding with the atoms to which they were bonded, while in the ligand they were found in difference Fourier maps and freely refined. Solvent molecules in ([VOL³]. Sol) (CH₃OH) and in ([VOL²]. Sol) (DMSO) experience orientation disorder and were treated accordingly with weak constraints applied to their geometry and thermal parameters. The large residual density in the structure of ([VOL²]. Sol) was interpreted as disordered water, but attempts to find the hydrogen atoms of this molecule gave no results. Relevant crystal data are listed in table 3, together with refinement details.

3. Results and discussion

3.1. Syntheses

The reaction between 1,2-diphenyl-1,2-diaminopropane with different salicylaldehyde derivatives gave the tetradentate N₂O₂ type Schiff bases (H₂L¹⁻⁷) in good yields. Reaction between the ligands with bis(acetylacetonato)oxidovanadium(IV) resulted in the target complexes. The green color of the precipitated complexes indicated that the complexes were in their monomeric form [23]. The procedure for synthesis of the ligands and complexes are summarized in scheme 1.

3.2. Spectroscopic characterization of the ligands and complexes

Common spectroscopic methods such as ¹H NMR, IR, and UV-Vis as well as elemental analyses support the synthesis of the ligands and complexes. Crystal structures of H₂L³, VOL², and VOL³ are also characterized. Cyclic voltammetry further supports the preparation of VO(IV) complexes. In IR spectra of the ligands, the strong band around 1625 cm⁻¹ is indicative of the formation of azomethine (C=N). The disappearance of the C=O stretching bands of the corresponding salicylaldehydes is also a good sign of

Table 2. The analytical and spectroscopic data of the complexes.

Complex (Empirical formula)	Yield (%)	Elemental analysis data experimental (Calcd)	Selected IR bands; ν (cm^{-1})	UV-Vis data; λ nm (ϵ , (mol L^{-1}) $^{-1}$ cm^{-1})
VOL ¹ · H ₂ O (C ₃₀ H ₂₈ N ₂ O ₆ V)	87.6	C, 63.85; H, 4.80; N, 5.10 (C, 63.95; H, 4.97; N, 4.97)	1604($\nu_{\text{C}=\text{N}}$); 987($\nu_{\text{N}=\text{O}}$)	613(149); 390(5580); 300(19,640); 260(21,390)
VOL ² · DMSO (C ₃₂ H ₃₂ N ₂ O ₆ SV)	85.7	C, 61.50; H, 5.05; N, 4.40 (C, 61.58; H, 5.13; N, 4.49)	1589($\nu_{\text{C}=\text{N}}$); 979($\nu_{\text{N}=\text{O}}$)	598(140); 357(17,200); 306(25,600); 259(31,400)
VOL ³ · 0.5(CH ₃ OH)0.5(H ₂ O) (C _{30.5} H ₂₈ N ₂ O ₆ V)	81.6	C, 64.35; H, 4.85; N, 5.10 (C, 64.27; H, 4.92; N, 4.92)	1596($\nu_{\text{C}=\text{N}}$); 979($\nu_{\text{N}=\text{O}}$)	597(93); 405(7000); 283(17,000); 258(33,300)
VOL ⁴ · H ₂ O (C ₃₀ H ₂₈ N ₂ O ₆ V)	86.6	C, 63.90; H, 4.90; N, 5.05 (C, 63.95; H, 4.97; N, 4.97)	1604($\nu_{\text{C}=\text{N}}$); 987($\nu_{\text{N}=\text{O}}$)	613(163); 373(6100); 327(23,700); 257(38,100)
VOL ⁵ (C ₃₀ H ₂₆ N ₂ O ₃ V)	81.9	C, 70.10; H, 5.15; N, 5.40 (C, 70.19; H, 5.07; N, 5.46)	1612($\nu_{\text{C}=\text{N}}$); 987($\nu_{\text{N}=\text{O}}$)	599(146); 258(37,600); 380(10,300)
VOL ⁶ (C ₂₈ H ₂₀ N ₂ Cl ₂ O ₃ V)	88.7	C, 60.55; H, 3.65; N, 5.10 (C, 60.66; H, 3.61; N, 5.06)	1604($\nu_{\text{C}=\text{N}}$); 987($\nu_{\text{N}=\text{O}}$)	607(170); 383(10,000); 284(22,900); 257(43,700)

Table 3. Crystal data, data collection, and structure refinement.

Compound	H ₂ L ³	VOL ³ 0.5(CH ₃ OH) 0.5(H ₂ O)	VOL ² · DMSO
Empirical formula	C ₃₀ H ₂₈ N ₂ O ₄	C _{30.5} H ₂₈ N ₂ O ₆ V	C ₃₂ H ₃₂ N ₂ O ₆ SV
Formula weight	480.54	569.49	623.60
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions (Å, °)			
<i>a</i>	12.5288(12)	8.9728(6)	27.7787(16)
<i>b</i>	5.9928(4)	12.1166(5)	6.5960(3)
<i>c</i>	17.3311(13)	14.3049(6)	17.3846(9)
α	90	72.688(4)	90
β	100.304(10)	80.749(4)	106.362(6)
γ	90	82.076(4)	90
Volume (Å ³), <i>Z</i>	1280.28(18), 2	1458.76(13), 2	3056.4(3), 4
Calculated density (g cm ⁻³)	1.25	1.30	1.35
Absorption coefficient (mm ⁻¹)	0.083	0.384	0.439
<i>F</i> (000)	508	592	1300
θ range for data collection (°)	3.3–28.6	2.9–25.0	3.1–25.0
Limiting indices	–16 ≤ <i>h</i> ≤ 7; –4 ≤ <i>k</i> ≤ 8; –20 ≤ <i>l</i> ≤ 22	–10 ≤ <i>h</i> ≤ 10; –14 ≤ <i>k</i> ≤ 14; –17 ≤ <i>l</i> ≤ 16	–33 ≤ <i>h</i> ≤ 33; –7 ≤ <i>k</i> ≤ 7; –20 ≤ <i>l</i> ≤ 20
Reflections			
Collected	4983	8709	37,790
Unique (<i>R</i> _{int})	2724 (0.013)	5043 (0.019)	5364 (0.065)
With <i>I</i> > 2σ(<i>I</i>)	1916	3933	3898
Number of parameters	209	368	392
Weighting scheme			
<i>A</i>	0.0427	0.0400	0.1037
<i>B</i>	0.1855	1.8950	6.0300
Goodness-of-fit on <i>F</i> ²	1.03	1.18	1.07
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.042, <i>wR</i> ₂ = 0.097	<i>R</i> ₁ = 0.061, <i>wR</i> ₂ = 0.146	<i>R</i> ₁ = 0.080, <i>wR</i> ₂ = 0.201
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.065, <i>wR</i> ₂ = 0.110	<i>R</i> ₁ = 0.078, <i>wR</i> ₂ = 0.153	<i>R</i> ₁ = 0.112, <i>wR</i> ₂ = 0.2183
Largest difference peak and hole (e Å ⁻³)	0.14 and –0.13	0.80 and –0.36	1.04 and –1.17

formation of the iminic bonds. In IR spectra of the VO(IV) complexes, these bands are shifted to lower wavenumbers, indicative of coordination of C=N, through nitrogen. The $\nu_{\text{O-H}}$ of the ligands is also absent in the complexes, indicative of coordination through the phenolic oxygen atoms of the ligands. IR spectra of the monomeric form of VO(IV) Schiff-base complexes contain a band at 960–990 cm⁻¹ due to V=O stretching, while the polymeric form (V=O...V=O...) contains a band at 850–880 cm⁻¹. IR spectra of the complexes in this study contain a band at 980 cm⁻¹ which is a sign of their monomeric form. ¹H NMR data of the ligands and the corresponding assignments are summarized in table 1. The appearance of a broad signal at 13 ppm (phenolic O–H), a sharp band at 9 ppm (HC=N), multiplets at 6–8 ppm (H_{Ar}), and signals due to aliphatic C–H of both diamine and salicylaldehydes confirm the synthesis of the ligands. In the UV-Vis spectra of the complexes, the presence of a band at 600 nm with ϵ of about 150 (mol L⁻¹)⁻¹ cm⁻¹ is due to the d → d transitions in VO(IV) d¹ system.

Table 4. Selected geometrical parameters.

	[VOL ³]. <i>solv</i>	[VOL ²]. <i>solv</i>
V1–O1	1.599(3)	1.595(3)
V1–O12	1.915(3)	1.915(4)
V1–O30	1.919(3)	1.919(3)
V1–N8	2.072(3)	2.043(3)
V1–N26	2.069(3)	2.057(4)
V1–N8–C1–C2	164.1(3)	–91.2(4)
V1–N26–C19–C20	–92.0(3)	139.3(3)

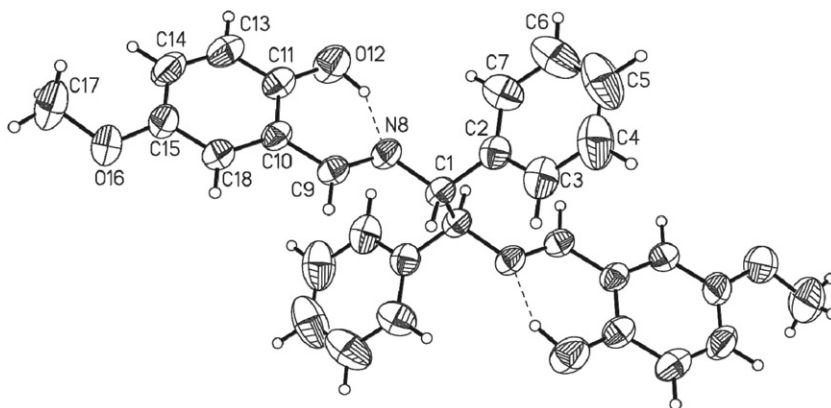


Figure 1. Perspective view of H_2L^3 ; the ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines. The unlabeled half of the molecule is related to the symmetry operation $-x, 2-y, 1-z$.

3.3. Description of the crystal structures

Selected bond lengths and angles for the structures are listed in table 4. Figure 1 shows the perspective view of H_2L^3 . The molecule is C_1 symmetrical, the middle point of the central C–C bond lies at the center of symmetry. There are classical intramolecular N–H \cdots O hydrogen bonds between the hydrogen atoms of OH and nitrogen atoms (figure 1, table 5), and these hydrogen bonds make the plane of the salicylidene phenyl ring almost coplanar with the plane of the C–N=C–C chain; the appropriate dihedral angle is only $2.02(15)^\circ$. The dihedral angle between the planes defined by the rings of the salicylidene fragment and the phenyl substituent in H_2L^3 is $46.38(6)^\circ$, compared to just 23.8 in the *meso* isomer [29]. The molecules are arranged in undulating infinite layers along the *b*-axis by weak intermolecular C–H \cdots O interactions (figure 2). Figures 3 and 4 show perspective views of the structures [VOL³] and [VOL²], respectively. In both complexes the tetradentate Schiff-base ligand coordinates vanadium in four equatorial positions, and the geometry around each vanadium can be described as a distorted square pyramid with the oxo in the apical position. The vanadium is displaced from the N(26)N(8)O(12)O(30) coordination plane toward the apical oxo by $0.580(5)\text{ \AA}$ in [VOL³] and by $0.584(5)\text{ \AA}$ in [VOL²]. The two phenyl groups on C19 and C1 at the N–N

Table 5. Hydrogen-bond data (Å, °).

D-H...A	D-H	H...A	D...A	DHA
[H ₂ L ³]				
O12-H12...N8	1.00(2)	1.71(2)	2.6141(16)	149(2)
[VOL ³]. solv				
C1-H1...O12 ⁱ	0.98	2.40	3.269(5)	147
C25-H25...O1	0.93	2.46	3.236(5)	140
C32-H32...O34 ⁱⁱ	0.93	2.50	3.420(5)	172
[VOL ²]. solv				
C1-H1...O1 ⁱⁱⁱ	0.98	2.56	3.442(5)	150
C7-H7...O1	0.93	2.18	3.071(7)	159
C9-H9...O1 ⁱⁱⁱ	0.93	2.27	3.163(6)	161
C34-H34C...O1S	0.96	2.53	3.418(18)	153
C35-H35...O1 ^{iv}	0.93	2.49	3.305(6)	147

Symmetry codes: ⁱ $-x, -y, 1-z$; ⁱⁱ $-x, -1-y, 2-z$; ⁱⁱⁱ $x, 1+y, z$; ^{iv} $x, -1/2-y, 1/2+z$.

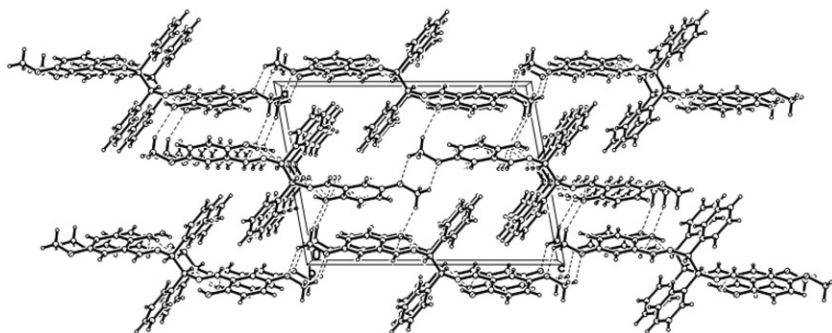


Figure 2. The crystal packing of H₂L³ along the [10] direction. The dashed lines denote hydrogen bonds.

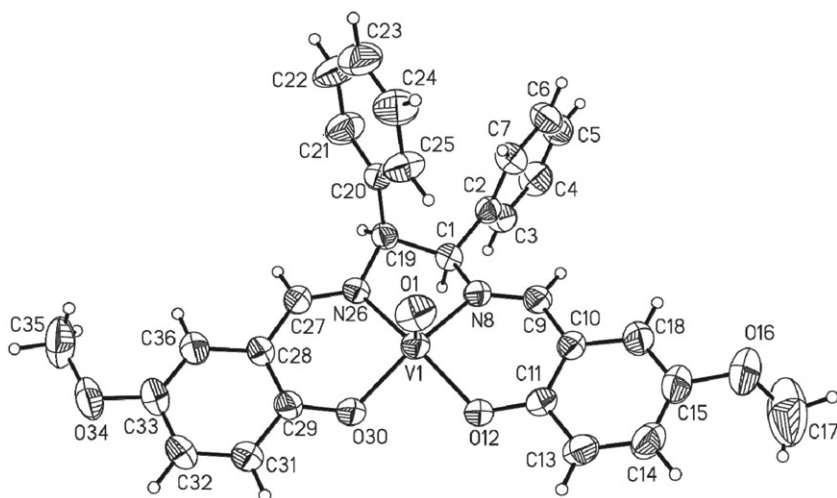


Figure 3. Perspective view of [VOL³]; the ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii. Solvent molecules are omitted for clarity.

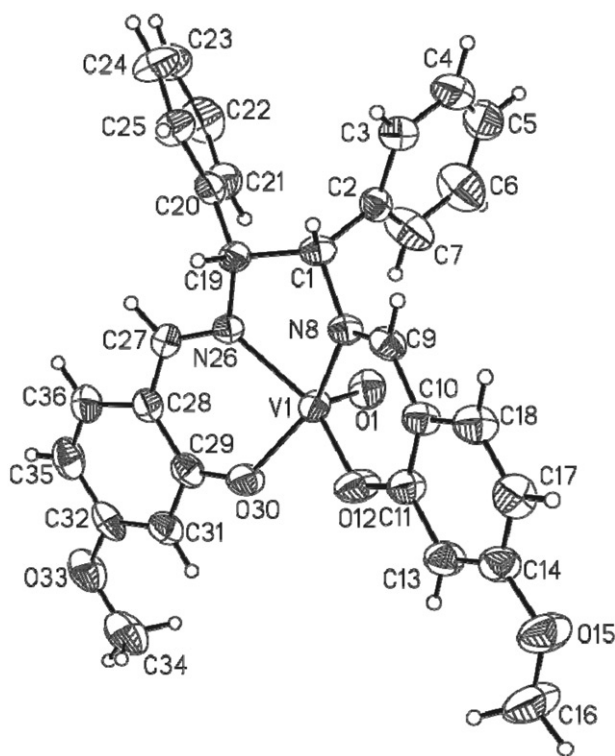


Figure 4. Perspective view of $[\text{VOL}^2]$; the ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii. Solvent molecule is omitted for clarity.

chelate take a different orientation. One phenyl is axial and the other equatorial. The axial group is almost parallel to the apical $\text{V}=\text{O}$ with a slight deviation caused by repulsion with the adjacent equatorial phenyl. The five-membered $\text{N}-\text{N}$ chelate rings adopt a distorted *gauche* conformation with the phenyl groups in axial and equatorial orientations. The $\text{V}-\text{N}-\text{C}$ (phenyl) torsion angles are $164.1(3)^\circ$ and $-92.0(3)^\circ$ in $[\text{VOL}^3]$ and $139.3(3)^\circ$ and $-91.2(4)^\circ$ in $[\text{VOL}^2]$. The average $\text{V}-\text{N}$ and $\text{V}-\text{O}$ bond distances of the complexes are in the range observed for many other vanadium Schiff-base complexes [21, 30, 31]. The VO-complexes are arranged in layers parallel to the (010) planes of their unit cells (figures 5 and 6). Within these layers the complexes are held together by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (cf. table 5), and in the case of $[\text{VOL}^3]$ by weak $\pi-\pi$ -stacking interactions between phenyls (the centroid-to-centroid distances are *ca* 3.95 Å; the interplanar separation is around 3.5 Å).

3.4. Electrochemical studies

Cyclic voltammograms of $10^{-3} \text{ mol L}^{-1}$ solutions of these tetradentate Schiff-base complexes were recorded in DMSO containing 0.1 mol L^{-1} tetra-*n*-butylammonium hexafluorophosphate (TBAHPF) as supporting electrolyte at a platinum working electrode. Figure 7 shows the voltammogram of VOL^3 and other voltammetry data are

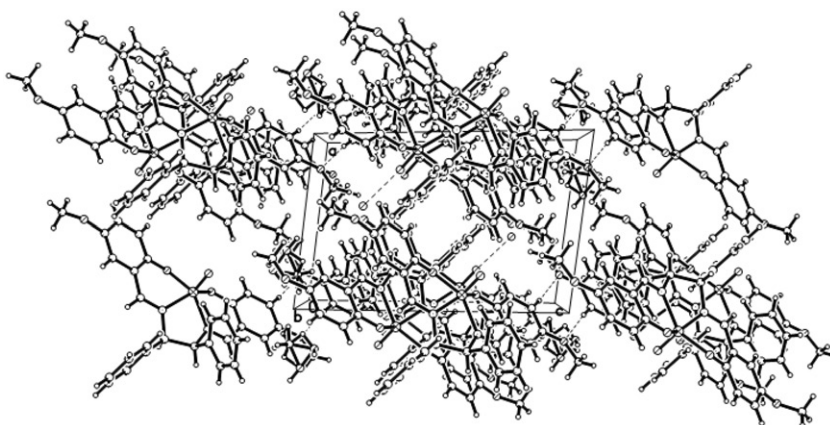


Figure 5. The crystal packing of $[\text{VOL}^3]$ as seen along the $[10]$ direction.

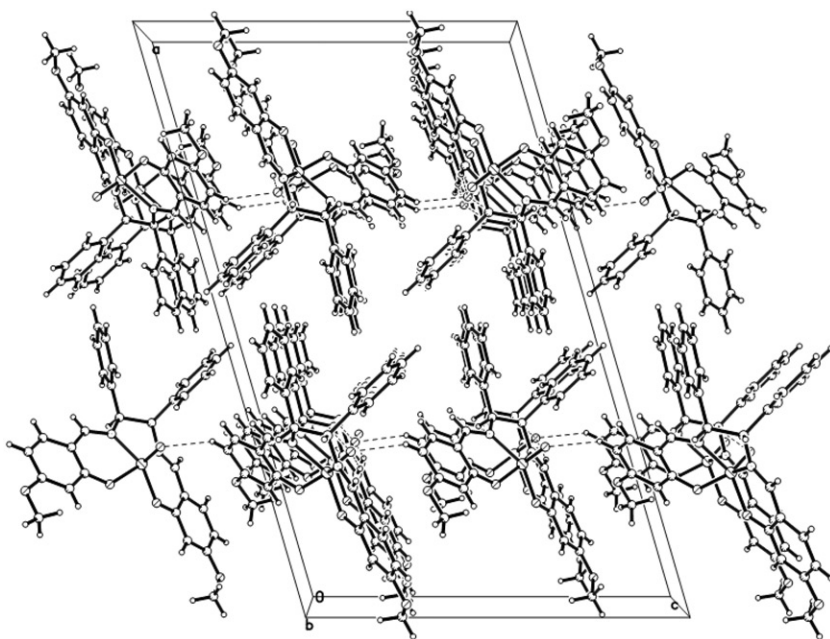


Figure 6. The crystal packing of $[\text{VOL}^2]$ as seen along the $[10]$ direction. The dashed lines denote hydrogen bonds.

collected in table 6. These data are consistent with the quasi-reversible $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ redox process. As the electron-withdrawing nature of the substituents on the ancillary ligand system increases, increase in the $E_{1/2}$ of the $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ redox process is observed. Our previous studies show that the $E_{1/2}$ is a major factor which influences the catalytic activity of oxidovanadium(IV) complexes.

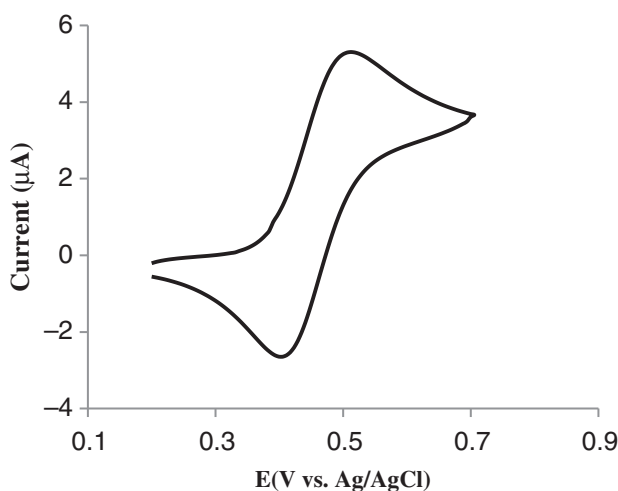


Figure 7. Cyclic voltammogram of $10^{-3} \text{ mol L}^{-1}$ solution of VOL^3 in DMSO containing 0.1 mol L^{-1} TBAHFP and scan rate 50 mV s^{-1} .

Table 6. Electrochemical data for the complexes.

Complex	E_p^a (mV)	E_p^c (mV)	$E_{1/2}$ (mV)	ΔE (mV)
VOL^1	550	390	470	160
VOL^2	568	408	488	160
VOL^3	451	349	401	102
VOL^4	586	432	509	154
VOL^5	626	518	572	108
VOL^6	538	402	470	136

Electrochemical data of $10^{-3} \text{ mol L}^{-1}$ solution of the complexes were obtained using 0.1 mol L^{-1} TBAHFP solution as supporting electrolyte.

3.5. Catalytic studies

These oxidovanadium(IV) Schiff-base complexes were used as catalysts for oxidation of cyclooctene using TBHP as oxidant in different solvents and various reaction conditions. The progress of the reaction was monitored by GC in 30 min intervals. In the absence of the complexes, no or very little oxidation products were observed. Oxidation of cyclooctene gave cycloocteneoxide as the sole product of the reaction. The retention times for the starting materials and the products were determined by comparison with authentic samples. The conversion percent (%) and the TON were calculated by the following equations, in which C_{initial} and C_{final} are initial and final concentration of the substrate, respectively, and $[Q]$ is the concentration of the catalyst.

$$\% \text{Conversion} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100,$$

$$\text{Turnover} = \frac{\% \text{Conversion} \cdot C_{\text{initial}}}{[Q]}.$$

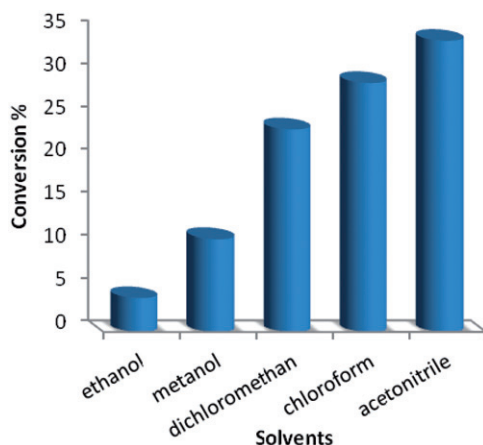


Figure 8. The results of the optimization of solvents for the epoxidation of cyclooctene with VOL⁷.

In a typical experiment, 15 μmol of the oxidovanadium catalyst was dissolved in 20 mL of freshly distilled acetonitrile and then 15 mmol of cyclooctene and 30 mmol of TBHP were added. The reaction mixture was refluxed while being stirred and the reaction progress was monitored at 30 min intervals. Various reaction conditions were optimized. The optimized reaction time was obtained by following the reaction progress at 30 min intervals up to 27 h; 24 h was the optimized reaction time. Figure 8 shows the results of the oxidation of cyclooctene in different solvents at 40°C. Acetonitrile was the best solvent for this study. The reaction was performed in acetonitrile at reaction temperatures ranging from 50°C to 80°C (10°C intervals) and 80°C was found to be the optimized reaction temperature. The amounts of catalysts were also optimized to 15 μmol and the oxidant to substrate ratio was also optimized to 2:1. Figure 9 shows the results of the epoxidation of cyclooctene under optimized conditions for VOL¹⁻⁷; VOL⁵ with electronegative Cl on the Schiff base has the highest conversion percent while the electron donating methyl substituted complex, VOL⁶, has the lowest catalytic activity. It should, of course, be mentioned that the electronegativity of the substituents is not the only factor affecting such catalytic ability and other electronic and steric factors play important roles.

3.6. Solvent-free catalytic studies

To the best of our knowledge, all previous catalytic studies on the epoxidation of alkenes with tetradentate Schiff-base complexes of oxidovanadium(IV) are performed in solvents. Acetonitrile is a common solvent used in such experiments. Our previous studies, as well as the present study, show that the type of the solvent and its amount has great influence on the conversion percent and TON. Therefore, we decided to study the solvent-free oxidation of cyclooctene with these complexes. Typically, a mixture of 15 μmol of the catalysts, 15 mmol of cyclooctene, and 30 mmol of TBHP were refluxed and the progress of the reaction monitored every 20 min by GC. As seen from table 7, cyclooctene was converted in very good yields to cyclooctene epoxide in less than 2 h.

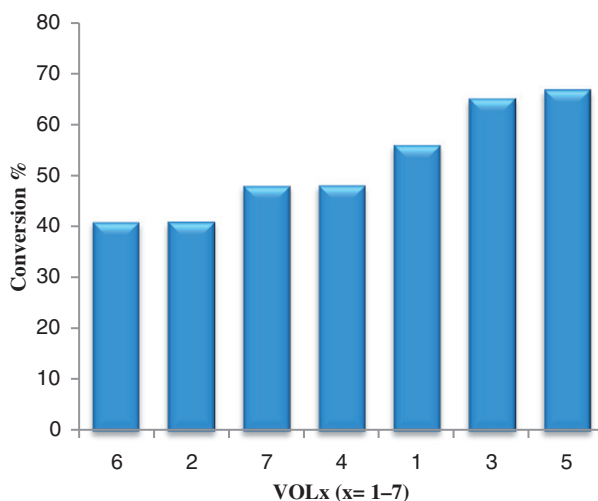
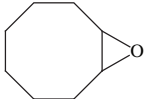
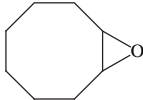


Figure 9. The results of the catalytic epoxidation of cyclooctene with VOL¹⁻⁷.

Table 7. Comparison of the catalytic ability of the VOL¹⁻⁷ complexes in acetonitrile and solvent-free conditions in their optimized conditions.

Complex	Acetonitrile			Solvent free		
	Conversion (%)	Turnover	Product (%)	Conversion (%)	Turnover	Product (%)
						
VOL ¹	56.03	560	100	71.39	714	100
VOL ²	40.97	410	100	63.06	631	100
VOL ³	65.15	652	100	80.58	806	100
VOL ⁴	48.14	481	100	76.79	768	100
VOL ⁵	66.87	669	100	86.40	864	100
VOL ⁶	41.92	419	100	55.87	559	100
VOL ⁷	48.04	480	100	81.63	816	100

These results are comparable with previous studies in organic solvents. Moderate conversion percent and long reaction times are usually among the disadvantages of such experiments. In this study, tetradentate Schiff-base complexes of oxidovanadium(IV) catalyze the epoxidation of cyclooctene in excellent yields and selectivity. The appearance of cycloocteneoxide as the sole product of the reaction is of great importance. Besides, the reaction of epoxidation is almost complete in less than 2h. Energy saving is another strong point in these solvent-free experiments. The reactions are performed at the boiling point of cyclooctene which is less than the reaction temperatures in acetonitrile. The trends in the catalytic ability of the complexes are similar to our solvent based experiments. The results for epoxidation of cyclooctene

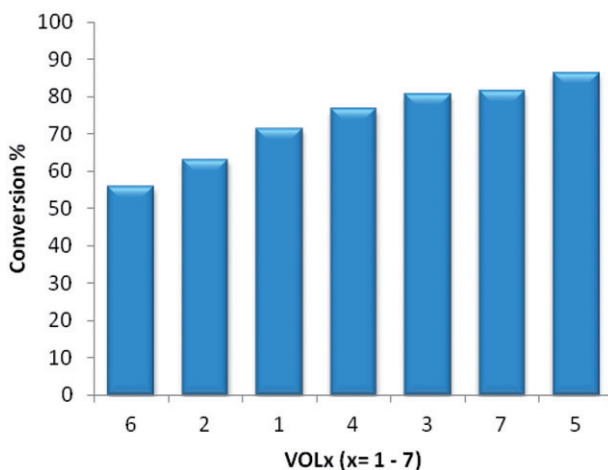


Figure 10. The results for the solvent-free epoxidation of cyclooctene with VOL^x complexes and TBHP.

with VOL¹⁻⁷ are shown in figure 10. A comparison between the ability of the catalysts in both solvent free and with solvent conditions is presented in table 7. The catalysts are more effective in solvent-free conditions. We deliberately obtained the conversion percentages in 2 h. At longer reaction times, all of the catalysts would probably convert cyclooctene to its epoxide quantitatively, and we would not be able to compare the catalysts with each other. VOL⁷ gave more than 95% epoxidation product after 3 h.

Supplementary material

CCDC 854918 (H₂L³), 854919 ([VOL²]. Sol), and 854920 ([VOL³]. Sol) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or E-mail: deposit@ccdc.cam.ac.uk

Acknowledgments

We acknowledge the office of gifted student at the University of Semnan for the financial support.

References

- [1] J.A.L. da Silva, J.J.R.F. da Silva, A.J.L. Pombeiro. *Coord. Chem. Rev.*, **255**, 2232 (2011).
- [2] S. Ramos, R.M. Almeida, J.J.G. Moura, M. Aureliano. *J. Inorg. Biochem.*, **105**, 777 (2011).

- [3] M.R. Maurya, M. Bisht, F. Avecilla. *J. Mol. Catal. A: Chem.*, **344**, 18 (2011).
- [4] T. Jakusch, J.C. Pessoa, T. Kiss. *Coord. Chem. Rev.*, **255**, 2218 (2011).
- [5] C.R. Bhattacharjee, G. Das, P. Mondal, S.K. Prasad, D.S.S. Rao. *Inorg. Chem. Commun.*, **14**, 606 (2011).
- [6] M. Sutradhar, T.R. Barman, G. Mukherjee, M.G.B. Drew, S. Ghosh. *Inorg. Chim. Acta*, **363**, 3376 (2010).
- [7] M. Kojima, H. Taguchi, M. Tsuchimoto, K. Nakajima. *Coord. Chem. Rev.*, **237**, 183 (2003).
- [8] M.R. Maurya, A. Kumar. *J. Mol. Catal. A: Chem.*, **250**, 190 (2006).
- [9] M.R. Maurya, S. Sikarwar. *J. Mol. Catal. A: Chem.*, **263**, 175 (2007).
- [10] S.K. Dutta, S. Samanta, D. Ghosh, R.J. Butcher, M. Chaudhury. *Inorg. Chem.*, **41**, 5555 (2002).
- [11] M.-J. Xie, L. Li, X.-D. Yang, W.-P. Liu, S.-P. Yan, Y.-F. Niu, Z.-H. Meng. *Eur. J. Med. Chem.*, **45**, 2327 (2010).
- [12] M.-J. Xie, G. Xu, L. Li, W.-P. Liu, Y.-F. Niu, S.-P. Yan. *Eur. J. Med. Chem.*, **42**, 817 (2007).
- [13] G. Du, S. Lim, M. Pinault, C. Wang, F. Fang, L. Pfefferle, G.L. Haller. *J. Catal.*, **253**, 74 (2008).
- [14] M.V. Kirillova, M.L. Kuznetsov, V.B. Romakh, L.S. Shul'pina, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, G.B. Shul'pin. *J. Catal.*, **267**, 140 (2009).
- [15] A. Bezaatpour, M. Behzad, D.M. Boghaei. *J. Coord. Chem.*, **62**, 1127 (2009).
- [16] R. Yanardag, T.B. Demirci, B. Ulkuseven, S. Bolkent, S. Tunalı, S. Bolkent. *Eur. J. Med. Chem.*, **44**, 818 (2009).
- [17] T. Rosu, E. Pahontu, C. Maxim, R. Georgescu, N. Stanica, G.L. Almajan, A. Gulea. *Polyhedron*, **29**, 757 (2010).
- [18] T. Rosu, M. Negoiu, S. Pasculescu, E. Pahontu, D. Poirier, A. Gulea. *Eur. J. Med. Chem.*, **45**, 774 (2010).
- [19] L. Leelavathy, S. Anbu, M. Kandaswamy, N. Karthikeyan, N. Mohan. *Polyhedron*, **28**, 903 (2009).
- [20] Z.H. Chohan, S.H. Sumrra, M.H. Youssoufi, T.B. Hadda. *Eur. J. Med. Chem.*, **45**, 2739 (2010).
- [21] J. Rahchamani, M. Behzad, V. Jahed, A. Bezaatpour, G. Dutkiewicz, M. Kubicki, M. Salehi. *Polyhedron*, **30**, 2611 (2011).
- [22] S. Rayati, N. Torabi, A. Ghaemi, S. Mohebbi, A. Wojtczak, A. Kozakiewicz. *Inorg. Chim. Acta*, **361**, 1239 (2008).
- [23] D.M. Boghaei, A. Bezaatpour, M. Behzad. *J. Mol. Catal. A: Chem.*, **245**, 12 (2006).
- [24] D.M. Boghaei, A. Bezaatpour, M. Behzad. *J. Coord. Chem.*, **60**, 973 (2007).
- [25] M.N.H. Irving, R.M. Parkins. *J. Inorg. Nucl. Chem.*, **27**, 270 (1965).
- [26] Oxford Diffraction. *CRYSTALIS PRO (Version 1.171.33.36d)*, Oxford Diffraction Ltd., Yarnton, Oxfordshire (2009).
- [27] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi. *J. Appl. Crystallogr.*, **26**, 343 (1993).
- [28] G.M. Sheldrick. *Acta Crystallogr. Sect. A*, **64**, 112 (2008).
- [29] R. Senn, W. Nowacki. *Z. Kristallogr.*, **145**, 16 (1977).
- [30] K. Nakajima, M. Kojima, S. Azuma, R. Kasahara, M. Tsuchimoto, Y. Kubozono, H. Maeda, S. Kashino, S. Ohba, Y. Yoshikawa, J. Fujita. *Bull. Chem. Soc. Japan*, **69**, 3207 (1996).
- [31] G. Hoshina, M. Tsuchimoto, S. Ohba, K. Nakajima, H. Uekusa, Y. Ohashi, H. Ishida, M. Kojima. *Inorg. Chem.*, **37**, 142 (1998).