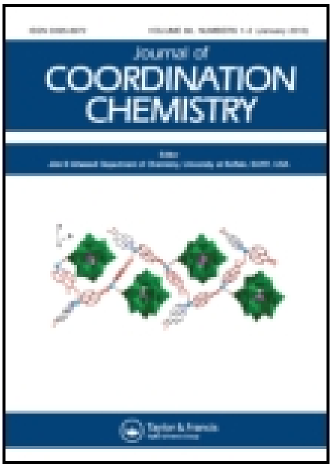


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, characterization, crystal structure, catalytic activity in oxidative bromination, and thermal study of a new oxidovanadium Schiff base complex containing O, N-bidentate Schiff base ligand

Gholamhossein Grivani[a], Vida Tahmasebi[a], Aliakbar Dehno Khalaji[b], Václav Eigner[cd] & Michal Dušek[d]

[a] School of Chemistry, Damghan University, Damghan, Iran

[b] Faculty of Science, Department of Chemistry, Golestan University, Gorgan, Iran

[c] Department of Solid State Chemistry, Institute of Chemical Technology, Prague, Czech Republic

[d] Institute of Physics ASCR, v.v.i., Praha 8, Czech Republic

To cite this article: Gholamhossein Grivani, Vida Tahmasebi, Aliakbar Dehno Khalaji, Václav Eigner & Michal Dušek (2014) Synthesis, characterization, crystal structure, catalytic activity in oxidative bromination, and thermal study of a new oxidovanadium Schiff base complex containing O, N-bidentate Schiff base ligand, Journal of Coordination Chemistry, 67:22, 3664-3677, DOI: 10.1080/00958972.2014.960405

To link to this article: http://dx.doi.org/10.1080/00958972.2014.960405

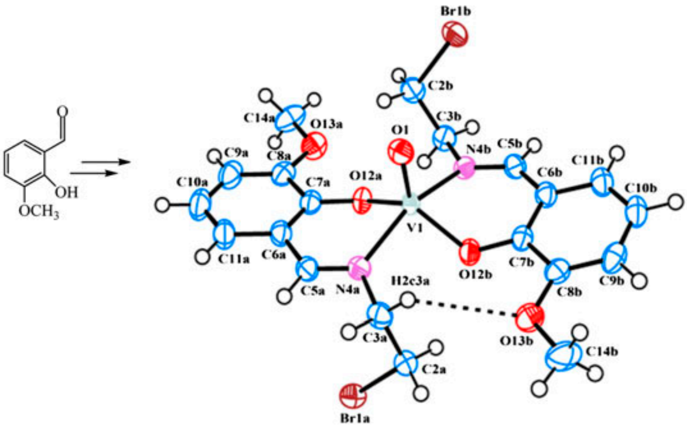
Journal of Coordination Chemistry, 2014
Vol. 67, No. 22, 3664–3677, http://dx.doi.org/10.1080/00958972.2014.960405

Synthesis, characterization, crystal structure, catalytic activity in oxidative bromination, and thermal study of a new oxidovanadium Schiff base complex containing O, N-bidentate Schiff base ligand

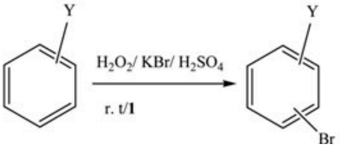
GHOLAMHOSSEIN GRIVANI*†, VIDA TAHMASEBI†,
ALIAKBAR DEHNO KHALAJI‡, VÁCLAV EIGNER§¶ and MICHAL DUŠEK¶

†School of Chemistry, Damghan University, Damghan, Iran
‡Faculty of Science, Department of Chemistry, Golestan University, Gorgan, Iran
§Department of Solid State Chemistry, Institute of Chemical Technology, Prague, Czech Republic
¶Institute of Physics ASCR, v.v.i., Praha 8, Czech Republic

(*Received 15 March 2014; accepted 16 August 2014*)



1



A new oxidovanadium(IV) Schiff base complex, VOL_2 (1), HL = 2-{(E)-[2- (bromoethyl)imino] methyl}-6-methoxy phenol, containing ethyl bromide pendant group was synthesized by direct reaction of HL and $VO(acac)_2$ in the ratio of 2 : 1 in methanol at reflux. The Schiff base ligand and its vanadyl complex were characterized by FT-IR spectra and CHN analysis. Additionally, the Schiff base

---

*Corresponding author. Email: grivani@du.ac.ir

ligand has been characterized by ^1H NMR spectroscopy. The crystal structure of **1** was also determined by single-crystal X-ray analysis, showing the distorted square-pyramidal N_2O_3 coordination around vanadium(IV). The catalytic activity of **1** was studied in the oxidative bromination of 2-nitrophenol as a model substrate, and different reaction parameters were investigated. The oxidative bromination of some organic compounds in the presence of **1** in optimal conditions showed that it was an effective and selective catalyst in those optimal conditions. Thermogravimetric analysis of **1** showed that it decomposed in two stages. **1** was thermally decomposed in air at 660 °C, and the XRD pattern of the obtained solid showed the formation of the V_2O_5 nanoparticles with average size of 34 nm .

Keywords: Oxidovanadium(IV); Schiff base; Single crystal; Oxidative bromination; V_2O_5 nanoparticle

1. Introduction

Schiff base transition metal complexes have been extensively studied because of their potential applications [1–4]. Interest in the coordination chemistry of vanadium complexes has grown enormously due to its structural features [5–7], catalytic applications [8–10], and biological roles in a variety of biochemical processes such as haloperoxidation [11–13], nitrogen fixation [14], phosphorylation [15], glycogen metabolism [16–18], and insulin mimicking [19–22] as well as some biological outcomes such as antimicrobial [23, 24], spermicidal [25], antileukemia [26], and antitumor activities [27]. Halogenated organic compounds are essential substrates because incorporation of halogen on an organic substrate gives suitable properties for different uses such as synthetic intermediates and starting compounds, designer molecules for material science, industrial chemicals, and bioactive compounds [27–29]. Vanadium-dependent haloperoxidases are an important group of halogenating enzymes, and their action was investigated in enzymatic reactions and in biomimetic studies [11–13, 30, 31]. In these enzymes, the vanadium(V) center was surrounded by histidine residue containing O, N donors [32]. Thus, the design and synthesis of vanadyl Schiff base complexes containing O, N donors can be useful as a model compound. In this research, we describe the synthesis, characterization, crystal structure determination, catalytic activity in oxidative bromination, and thermal study of a new oxidovanadium Schiff base complex **1**, derived from 3-methoxy-2-hydroxybenzaldehyde and 2-bromoethyl ammonium hydrobromide.

2. Experimental

2.1. *Materials and physical measurements*

All reagents and solvents for synthesis and analysis were commercially available and purchased from Merck and used as received. FT-IR spectra were recorded from 400 to 4000 cm^{-1} on a Perkin Elmer FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed on a Heraeus CHN–O-rapid analyzer, and results agreed with calculated values. ^1H nuclear magnetic resonance (NMR) spectrum was recorded on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz for HL. All gas liquid chromatography (GLC) yields based on the starting materials were obtained by using Teif Gostar Fraz Co. instrument with silicon-DC 200 column and FID detector. All measurements were taken at 20 psi, 20 psi, and 15 psi for N_2, air, and H_2, respectively, while the temperature of the column was kept at 150 °C. Thermogravimetry (TG) and differential thermoanalysis (DTA) were carried out on a Mettler Toldeo. The measurements were performed in air. The heating rate was kept at 10 °C min^{-1}. XRD pattern of the nanoparticles was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation with nickel beta filter in the range $2\theta = 10–80°$.

2.2. *Synthesis of 2-{(E)-[2- (bromoethyl)imino]methyl}-6-methoxy phenol (HL)*

3-Methoxy-2-hydroxy benzaldehyde (1.52 g, 10 mM), 2-bromoethyl ammonium hydrobromide (2.04 g, 10 mM), and NaOH (0.4 g, 10 mM) were added to 150 mL of methanol, and the mixture was stirred for 4 h. After evaporating the solvent, the yellow precipitate was collected and washed slightly with cooled water and then with 1 : 1 mixture of n-hexane and dichloromethane. Yield: 2.2 g (85%). M.p.: 60 °C. Anal. Calcd for $C_{10}H_{12}BrNO_2$: C, 47.28; H, 4.63; and N, 5.27%. Found: C, 46.53; H, 4.65; and N, 5.42%. IR (KBr pellet, cm^{-1}): 3350–3450 (b, O–H, phenolic), 2782–3000 (w, C–H aliphatic, and aromatic), 1632 (s, C=N), 1436, 1468, 1502, 1581 (m, C=C), 1250 (m, C–O), and 736 (m, C–Br). ^1H NMR ($CDCl_3$, δ(ppm)): 13.39 (s, 1H, –O–H), 8.35 (s, 1H, H–C=N–), 6.95 (d, 1H, phenyl–H:), 6.91 (d, 1H, phenyl–H:), 6.82 (s, 1H, phenyl–H:), 4.01 (t, 2H,–CH_2Br), 3.89 (3H, –OMe), and 3.64 (t, 2H, –N–CH_2–).

2.3. *Synthesis of VOL_2 (1)*

A mixture of HL (1.3 g, 5 mM) and $VO(acac)_2$ (0.66 g, 2.5 mM) was dissolved in methanol (70 mL) and refluxed for 2 h. After evaporating the solvent, the remaining reaction mixture was recrystallized in a solvent mixture of MeOH/$CHCl_3$ (1/1, v/v). The greenish crystals that formed were filtered off, washed with n-hexane and dried in an oven. Yield: 1.2 g (82%). M.p.: 194.2 °C. Anal. Calcd for $C_{20}H_{22}Br_2N_2O_5$ V: C, 40.13; H, 3.74; and N, 4.83. Found: C, 41.32; H, 3.78; and N, 4.82%. IR (KBr pellet, cm^{-1}): 2802–2984 and 3008–3080 (w, C–H aliphatic and aromatic), 1612 (s, C=N), 1444–1550 (m, C=C), 740 (m, C–Br), and 982 (s, V=O).

Table 1. Crystallographic data and structure refinement for **1**.

Empirical formula	$C_{20}H_{22}Br_2N_2O_5V_1$
Formula weight	581.2
Temperature	120
Crystal system	Monoclinic
Space group	*P21/c*
Unit cell dimensions	a = 11.2742(7) Å b = 12.1729(7) Å c = 23.1756(14) Å β = 136.161(9)°
Volume	2203.0(4) $Å^3$
Z	4
Absorption coefficient	8.31 mm^{-1}
Measured reflections	12,060
Independent reflections	3882
Reflections with $I > 3\sigma(I)$	3338
T_{min}	0.152
T_{max}	0.432
$R[F^2 > 2\sigma(F^2)]$	0.025
$wR(F^2)$	0.030
S	1.37
$\Delta\rho_{max}$	0.25 e $Å^{-3}$
$\Delta\rho_{min}$	−0.48 e $Å^{-3}$

2.4. *X-ray structure determination*

Suitable single crystal of dimensions 0.40 mm × 0.23 mm × 0.14 mm of **1** was chosen for X-ray diffraction study. Crystallographic measurements were done at 150 K with a four-circle CCD diffractometer Gemini of Oxford Diffraction, Ltd, with mirrors-collimated Cu-Kα radiation ($\lambda = 1.54184$ Å), using the area detector Atlas. The crystal structure was solved by direct methods with the program SIR2002 [33] and refined with the Jana2006 program package [34] by full-matrix least squares on F^2. The molecular structure plots were prepared by ORTEP III [35]. Hydrogens were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, they were nevertheless kept in ideal positions during the refinement except the ones bonded to nitrogen. The isotropic atomic displacement parameters of all hydrogens were evaluated as $1.2U_{eq}$ of the parent atom. Crystallographic data, details of the data collection and structure solution and refinements are listed in table 1. The synthesized vanadyl complex structure was established on the basis of its spectral analysis: IR, elemental analysis data, and melting point determination.

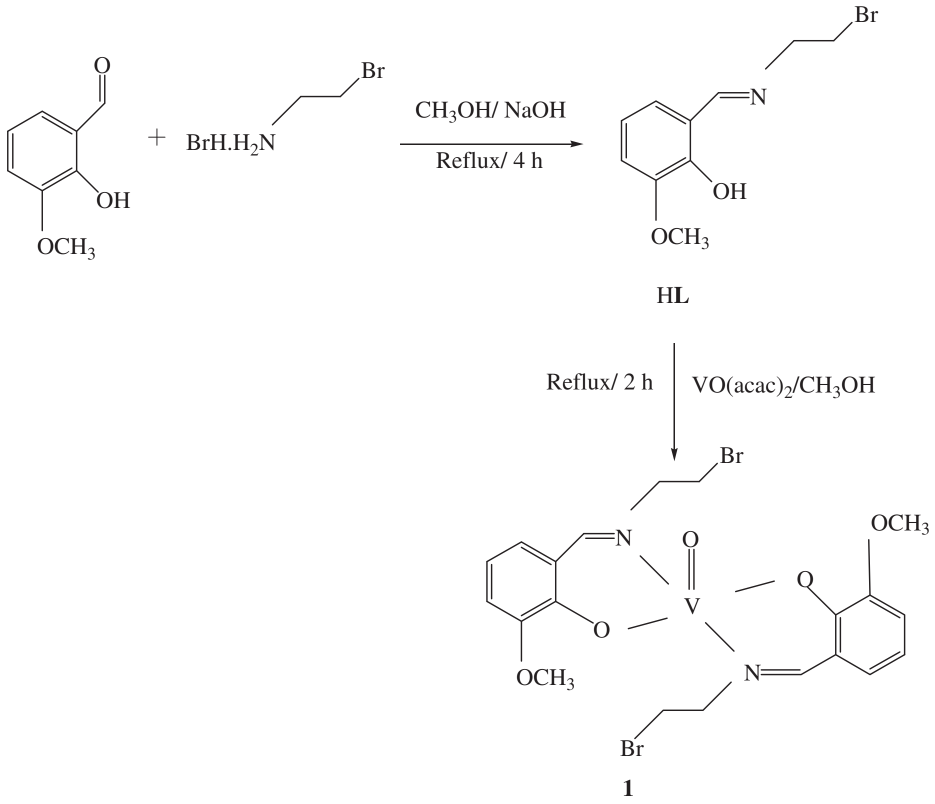
2.5. *General procedure of the oxidative bromination reaction*

In a 10-mL round-bottom flask equipped with a magnetic stirring bar, 1 mM of the 2-nitro phenol was reacted with different amounts of the oxidant, acid, bromide source, and the vanadyl Schiff base complex in 4 mL of solvent. The content was stirred at room temperature. The progress of the reaction was monitored by GLC.

3. Results and discussion

3.1. *Synthesis and characterization*

HL was prepared by the condensation of 3-methoxy-2-hydroxy benzaldehyde and 2-bromoethyl ammonium hydrobromide in methanol, and then, the product was isolated by the evaporation of solvent. The corresponding VO^{2+} complex (1) was synthesized by the reaction of $VO(acac)_2$ and the related Schiff base ligand (HL) in methanol (scheme 1). The ligand and complex are quite air stable as solids and also in solution. They are characterized by FT-IR and ^1H NMR spectra and CHN and X-ray analysis. The CHN analysis of HL and **1** confirms the chemical composition. The ^1H NMR spectrum of HL is given in figure 1. In agreement with the structure of the ligand, eight signals with integration ratios of 1 : 1 : 1 : 1 : 1 : 2 : 3 : 2 were seen in this spectrum related to the protons of a : b : c : d : e : f : h : g (figure 1). The two distinct triplets at 4.00 and 3.63 ppm corresponded to the protons (f and g) of N–CH_2– and –CH_2–Br, respectively. The three peaks at 6.70–7.00 ppm were attributed to the aromatic protons b, c, and d. The signal of the iminic proton (e) was at 8.35 ppm. The methoxy protons (h) appear as singlets at 3.9 ppm. The chemical shift of phenolic proton (H) was strongly shifted downfield at 13.39 ppm. This high chemical shift can be related to the intramolecular hydrogen bonding between nitrogen of imine and hydrogen of phenol [36]. In the FT-IR spectrum of HL, a sharp band appeared at 1632 cm^{-1}, due to $\nu_{(C=N)}$ (azomethine). This band shifted to lower wave number at 1612 cm^{-1} in the FT-IR spectrum of **1**, indicating binding of azomethine nitrogen to vanadium(IV). Complex **1** exhibits a sharp band at 982 cm^{-1} due to $\nu_{V=O}$ that clearly identifies



Scheme 1. The preparation procedures of HL and its vanadyl complex (1).

the vanadium(IV) complex. It has been reported that oxovanadium complexes with coordination number of five (monomeric five-coordinate V=O complexes) have $\nu_{V=O}$ about 980 cm^{-1} and with coordination number of six (with polymeric vanadium–oxygen as ···V=O···V=O··· units) have the $\nu_{V=O}$ lower than 980 cm^{-1}, and this provides an index for discriminating the coordination number of oxovanadium complexes [37–39]. Thus, the sharp band at 982 cm^{-1} was attributed to $\nu_{V=O}$ of five-coordinate **1**. In comparison of the V=O bond length in **1** with those of polymeric forms of vanadyl complexes, it is clear that the length of this bond in **1** is shorter than···V=O···V=O···complexes and lies in the range of the bond lengths of five-coordinate V=O complexes [37–40]. These data are consistent with the crystal structure of 1.

3.2. *Crystal structure of 1*

An ORTEP view of **1** with the atom-numbering scheme is given in figure 2. table 2 lists selected bond lengths and angles. In **1**, the Schiff base ligand is anionic and a bidentate N, O chelate. Vanadium(IV) is coordinated by two oxygens and two nitrogens of two independent ligands in the equatorial plane and the terminal O occupies the axial position [8, 41–44]. The square-pyramidal geometry around V(IV) in **1** is distorted because of the different bond distances and angles. The greatest angular distortion from an ideal square-pyramidal geometry

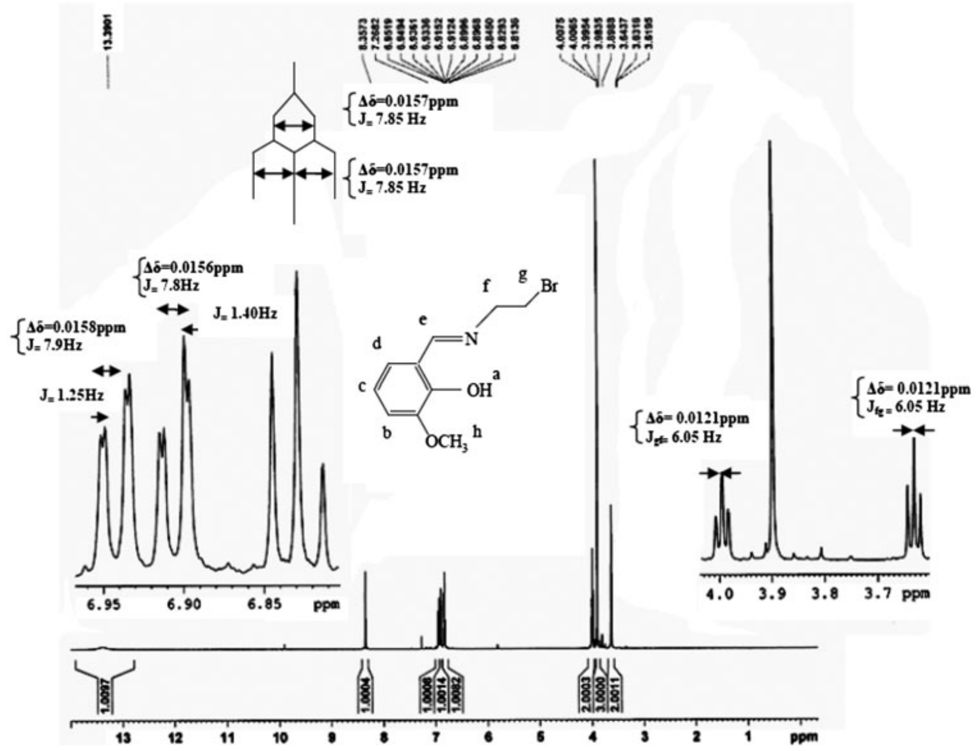


Figure 1. The ^{1}H NMR spectrum of HL.

(109.5°) occurs in the angles O1–V1–O12b [112.63(12)°] and O12b–V1–N4b [85.87(10)°]. The V–N and V–O distances (table 1) are similar to those found in other V(IV) complexes with Schiff base ligands [8, 41–44].

The geometries of the hydrogen bonds in **1** are listed in table 3. As shown in figure 2, there are several intra- and intermolecular hydrogen bonds in **1**, effective in the stabilization of the crystal structure.

3.3. *Catalytic activity*

The oxidative bromination of 2-nitrophenol using hydrogen peroxide, which did not proceed in the absence of catalyst at room temperature, was used as a model reaction. To find the optimum reaction conditions, the influence of different factors that may affect the conversion and selectivity of the reaction was investigated. A systematic examination of the oxidative bromination of 2-nitrophenol in various solvents such as MeOH, MeCN, and $CHCl_3$, and mixture of solvents of H_2O/MeOH, H_2O/MeCN, and $H_2O/CHCl_3$ was carried out in the presence of catalytic amount of **1**. In coordinating solvent mixtures such as H_2O/MeOH, H_2O/MeCN, and $H_2O/CHCl_3$, oxidative bromination of 2-nitrophenol proceeded efficiently. Considering the yield and reaction rate, H_2O/MeOH was the best solvent mixture (figure 3). The typical reaction medium for bromo peroxidases is ocean water [30]. Water, however, is a nucleophile and therefore able to intercept electrophiles, changing

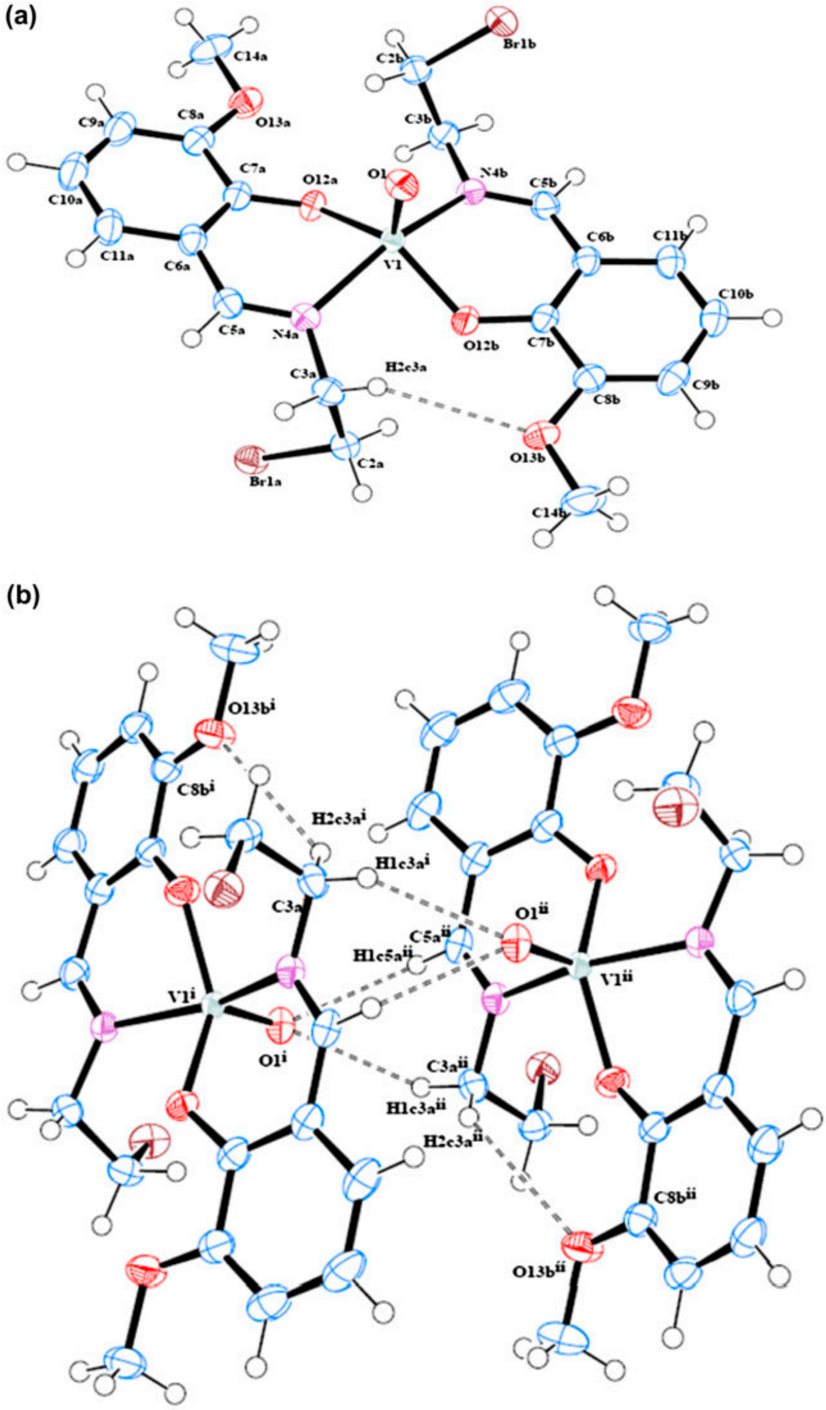


Figure 2. (a) An ORTEP view of 1; atomic displacement parameters are shown at the 50% probability level. (b) Diagram packing of 1 with the atom-numbering scheme. Dashed lines represent hydrogen bonds.

Table 2. Selected bond distances and angles in **1**.

V1–O12b	1.9042(1)	V1–O12a	1.910(2)
V1–N4b	2.101(3)	V1–N4a	2.102(3)
V1–O1	1.598(2)		
O1–V1–N4	102.00(13)	O1–V1–O12a	111.02(10)
O1–V1–N4b	100.64(11)	O1–V1–O12b	112.63(12)
N4a–V1–O12a	85.95(11)	N4a–V1–N4b	157.35(11)
N4a–V1–O12b	85.51(9)	O12a–V1–N4b	85.93(11)
O12a–V1–O12b	136.35(10)	N4b–V1–O12b	85.87(10)

Table 3. Some intra- and intermolecular hydrogen bonds in **1**.

D–H···A	*D*–H	H···A	*D*···A	*D*–H···A
C5–H1c5a···O1	0.960	2.458	3.207	131.857
C3–H1c3a···O1	0.959	2.530	3.364	145.339
C3a–H2c3a···O13b	0.960	2.874	3.549	128.233

selectivity. In order to achieve a good catalytic system for H_2O_2, the formation of the peroxovanadium(IV) and the interaction with hypoacid (HOBr) or Br_3^-, lipophilicity of the solvent should be improved [30]. The effect of bromide salt (bromide source), inorganic acid, and oxidant was also investigated. Based on the yield and reaction rate, among KBr, NaBr, and NH_4Br, KBr was the best bromide source and among the H_2SO_4, HNO_3, and H_3PO_4, H_2SO_4 was the best inorganic acid. H_2O_2 was the best oxidant among H_2O_2, TBHP, and $KHSO_5$ oxidants (table 4). In the presence of homogeneous and enzyme catalysts, liberation

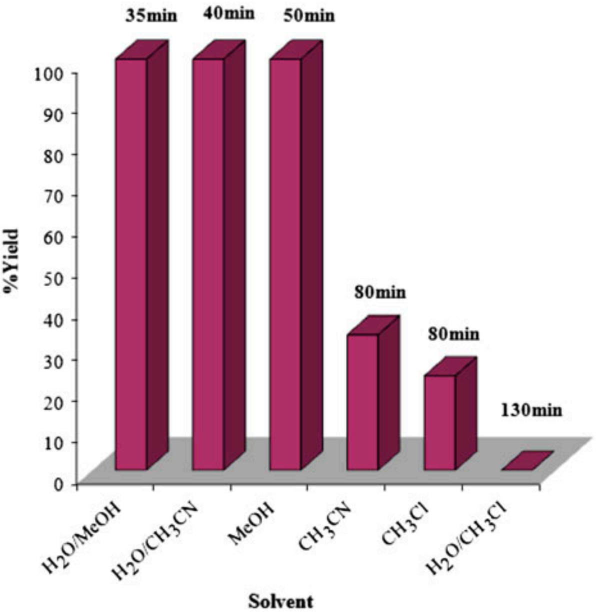


Figure 3. The solvent effect in the oxidative bromination of 2-nitrophenol by **1** in the presence of H_2O_2 as oxidant and KBr as bromide source. Reaction conditions at room temperature: substrate (1 mM), catalyst (0.0073 mM), H_2O_2 (2 mM), H_2SO_4 (2 mM), KBr (4 mM), and solvent (4 mL).

of Br_2 from KBr by H_2O_2 is well known [30, 45, 46]. Thus, it was expected that the same situation may prevail in the present case and could be explained by the proposed mechanism where generation of Br_2 is much easier. For the homogeneous vanadium bromoperoxidase mimics, appreciable catalytic activity is observed in strong acid [45]. Examination of various molar ratios of oxidant/substrate and salt/substrate in the catalytic oxidative bromination of 2-nitrophenol showed that full oxidation of 2-nitrophenol was obtained in 2 : 1 ratio of oxidant/substrate and 4 : 1 ratio of salt/substrate in H_2O/MeOH in the presence of H_2SO_4 and a catalytic amount of **1** (figures 4 and 5). In order to establish the general applicability of the method, various substrates were subjected to the oxidation protocol under the influence of **1** (table 5). In the conversion of 2-nitrophenol, 2-chlorophenol, phenol, 2-hydroxy benzaldehyde, 2-hydroxy-3-methoxy-benzaldehyde, and 2-hydroxy acetophenone, **1** selectively and efficiently converted them to mono-brominated products with full conversion in optimal conditions, while in the case of the benzaldehyde and 2-chloro

Table 4. The effects of oxidant, acid, and bromide salt in the oxidative bromination of 2-nitrophenol by **1**[a,b,c] at room temperature.

Run	Salt[c]	Acid	Oxidant[d]	Time (min)	% Yields
1[e]	KBr	H_2SO_4 2 mM	H_2O_2	100	No reaction
2	KBr	HNO_3 4 mM	H_2O_2	80	100
3	KBr	H_3PO_4 2 mM	H_2O_2	100	45
4	KBr	H_2SO_4 2 mM	H_2O_2	35	100
6	KBr	H_2SO_4 2 mM	TBHP	120	27
7	KBr	H_2SO_4 2 mM	$KHSO_4$	100	No reaction
8	NaBr	H_2SO_4 2 mM	H_2O_2	60	100
9	NH_4Br	H_2SO_4 2 mM	H_2O_2	60	40

[a] 2-Nitrophenol as substrate.
[b] Solvent (4 mL with 1 : 3 ratio of H_2O/MeOH).
[c] Catalyst (0.0073 mM).
[d] 2 mM.
[e] Blank experiment.

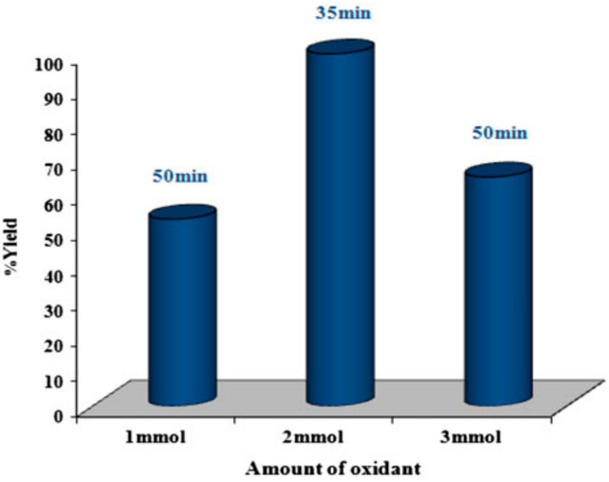


Figure 4. The effect of oxidant amount in the oxidative bromination of 2-nitrophenol by **1** in the presence of H_2SO_4 as an acid source and KBr as a bromide source. Reaction conditions at room temperature: substrate (1 mM), catalyst (0.0073 mM), H_2O_2 (1, 2, and 3 mM), H_2SO_4 (2 mM), KBr (4 mM), and solvent (4 mL).

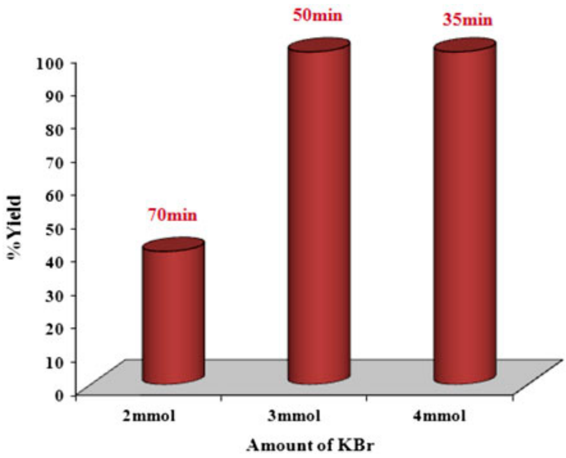


Figure 5. The effect of salt amount in the oxidative bromination of 2-nitrophenol by **1** in the presence of H_2SO_4 as an acid source and H_2O_2 as an oxidant. Reaction conditions at room temperature: substrate (1 mM), catalyst (0.0073 mM), H_2O_2 (2 mM), H_2SO_4 (2 mM), KBr (2, 3, and 4 mM), and solvent (4 mL).

Table 5. The oxidative bromination of organic substrates by catalytic amounts of **1** in optimal conditions[a] at room temperature.

Substrate	Time (min)	Product	Selectivity (%)	% Yields	TOF[b]
2-Nitrophenol	35	4-Bromo-2-nitrophenol	100	100	236
2-Chlorophenol	80	4-Bromo-2-chlorophenol	100	100	103
Phenol	80	4-Bromophenol	100	100	103
Salicylaldehyde	70	5-Bromo-2-hydroxy benzaldehyde	100	100	118
Benzaldehyde	90	4-Bromobenzaldehyde	100	50	50
2-Chloro benzaldehyde	65	4-Bromo-2-chloro benzaldehyde	100	41	52
2-Hydroxy-3-methoxy-benzaldehyde	15	4-Bromo-2-hydroxy-3-methoxy benzaldehyde	100	100	547
2-Hydroxy acetophenone	25	4-Bromo-2-hydroxy acetophenone	100	100	328

[a] Reaction conditions: substrate(1 mM), catalyst (0.0073 mM), H_2O_2 (2 mM), H_2SO_4 (2 mM), and solvent (1 : 3 ratio of H_2O/MeOH, 4 mL).
[b] TOF = M of substrate/M of catalyst × time (h).

benzaldehyde, the catalyst showed lower activity. Comparison of the selectivity and activity (TOF = M of substrate/M of catalyst × time (h)) of recent V(V) and V(IV) complexes [47–51] or other metal mediated catalysts [52, 53] with the selectivity and TOF of the titled vanadyl complex (1) shows high selectivity and activity of **1** in oxidative bromination. Almost all of the organic compounds in table 5 brominated effectively and selectively to mono-brominated compounds only.

3.4. *Thermal analysis and XRD of 1*

Thermal gravimetric analyses were carried out to examine the thermal stability of **1** and the nature of the produced vanadium oxide. The TG/DTA/DTG profiles of **1** in air with a heating rate of 10 °C min^{-1} are shown in figure 6. Based on these profiles, **1** shows two stages of thermal decomposition. The first stage occurs at 422.95–734.5 K with a weight

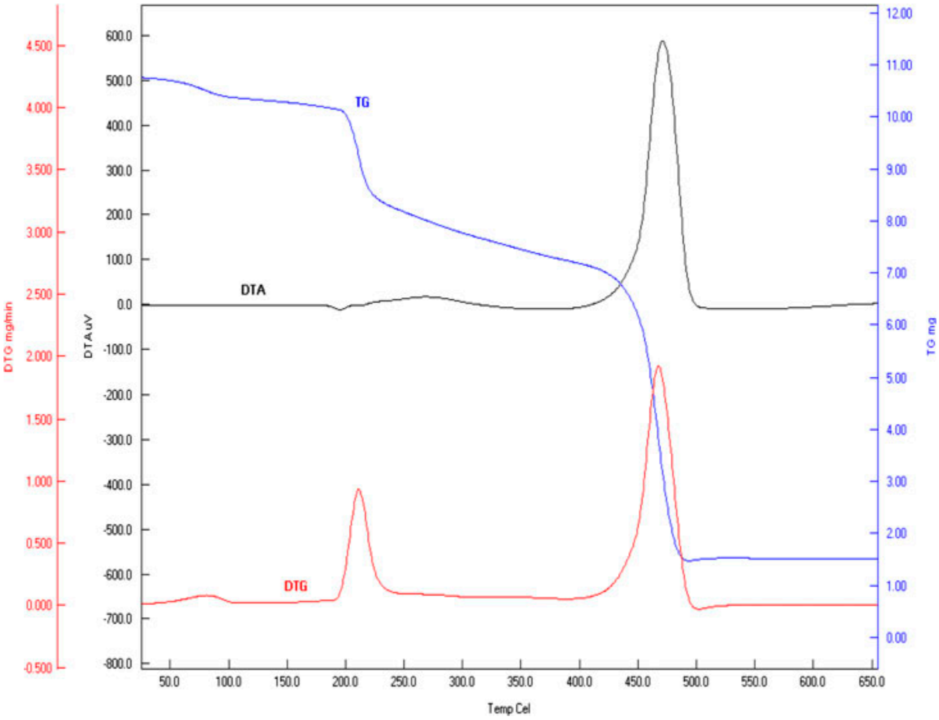


Figure 6. TG/DTA/DTG profiles of **1**.

loss of 35.88%, due to loss of two methoxy and bromines from the Schiff base ligand: **2** (OCH_3), Br (Calcd 38.19%). The second stage from 743.5–923 K is observed with a mass loss of 50.05% due to elimination of organic residue from the remaining Schiff base ligand

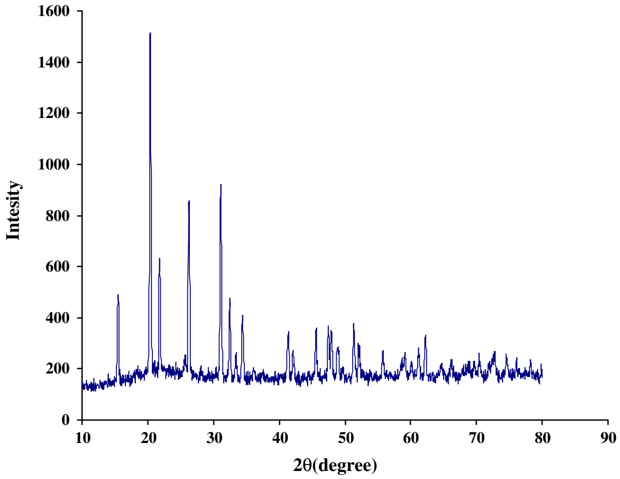


Figure 7. The XRD pattern of the residual powder obtained from thermal decomposition of **1**.

Table 6. Characteristics of the XRD pattern obtained from thermal decomposition of **1**.

Pos. [°2Th.]	Height [cts]	Rel. Int. [%]	*h*	*l*	*k*
15.4946	343.37	25.78	2	0	0
20.3774	1332.03	100	0	0	1
21.7974	408.56	30.67	1	0	1
26.2657	686.72	51.55	1	1	0
31.0929	748.15	56.17	3	0	1
32.5033	300.38	22.55	0	1	1
33.4262	92.64	6.96	1	1	1
34.3972	250.05	18.77	3	1	0
41.4282	148.8	11.17	0	0	2
42.1268	103.09	7.74	1	0	2
45.595	174.56	13.1	1	1	1
47.4554	210.43	15.8	6	0	0
47.9292	188.15	14.12	0	1	2
48.912	121.26	9.1	1	1	2
51.3507	213.1	16	0	2	0
52.1344	111.13	8.34	6	0	1
55.7545	88.5	6.64	0	2	1
59.1332	84.82	6.37	4	1	2
61.2047	96.03	7.21	3	2	1
62.2711	141.42	10.62	7	1	0
64.6822	44.52	3.34	6	0	2
66.212	55.28	4.15	7	1	1
72.6231	73.6	5.53	6	2	0
74.5965	74.47	5.59	3	1	3

(Calcd 48.21%), resulting in the formation of V_2O_5. We also examined a simple route for the preparation of the V_2O_5 nanoparticles. **1** was heated in an oven at 933 K. After cooling to room temperature, the obtained powder was analyzed by X-ray powder diffraction. The XRD of the obtained powder from this thermal decomposition and the obtained results (positions; intensities; and *h*, *k*, and *l*) from this pattern are given in figure 7 and table 6. Based on the resulting XRD pattern, the average crystallite size calculated using Scherrer's formula was 34 nm.

4. Conclusion

We described the synthesis and characterization of a new monomeric oxidovanadium Schiff base complex containing bidentate O, N Schiff base ligand. The complex shows distorted square-pyramidal N_2O_3 coordination sphere around the vanadium(IV) with two N, O coordinations from two Schiff base ligands and one oxido ion in an apical position. The catalytic activity of **1** was investigated in oxidative bromination, and different reaction parameters were optimized in the oxidative bromination of 2-nitrophenol. The results showed that the vanadyl complex was active and selective in the oxidative bromination of substituted phenols and produced mono-bromo products. In addition, thermal decomposition of this vanadyl Schiff base complex showed that the complex was stable to 180 °C and decomposed at two stages and converted to V_2O_5 at the end of decomposition.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article has been deposited with the Cambridge Crystallographic Center, CCDC No. 965176.

Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgments

G. Grivani, V. Tahmasebi, and A.D. Khalaji are grateful to the Damghan University and Golestan University for financial support.

References

[1] L. Canali, D.C. Sherrington. *Chem. Soc. Rev.*, **28**, 85 (1999).
[2] G.J. Kim, J.H. Shin. *Catal. Lett.*, **63**, 83 (1999).
[3] T. Katsuki. *Coord. Chem. Rev.*, **140**, 189 (1995).
[4] K.J. O'Connor, S.J. Wey, C.J. Burrows. *Tetrahedron Lett.*, **33**, 1001 (1992).
[5] N. Chantarasiri, V. Ruangpornvisuti, N. Muangsin, H. Detsen, T. Mananunsap, C. Batiya, N. Chaichit. *J. Mol. Struct.*, **701**, 93 (2004).
[6] R. Ziessel. *Coord. Chem. Rev.*, **216–217**, 195 (2001).
[7] H. Hosseini Monfared, R. Bikas, P. Mayer. *Inorg. Chim. Acta*, **363**, 2574 (2010).
[8] S. Rayati, N. Torabi, A. Ghaemi, S. Mohebbi, A. Wojtczak, A. Kozakiewicz. *Inorg. Chim. Acta*, **361**, 1239 (2008).
[9] R. Ando, H. Ono, T. Yagyu, M. Maeda. *Inorg. Chim. Acta*, **357**, 2237 (2004).
[10] C.J. Schneider, J.E. Penner-Hahn, V.L. Pecoraro. *J. Am. Chem. Soc.*, **130**, 2712 (2008).
[11] C. Wikete, P. Wu, G. Zampetlla, L.D. Gioia, G. Licini, D. Rehder. *Inorg. Chem.*, **46**, 196 (2007).
[12] H. Sakurai, H. Sano, T. Takino, H. Yasui. *J. Inorg. Biochem.*, **80**, 99 (2000).
[13] T.S. Smith, C.A. Root, J.W. Kampf, P.G. Rasmussen, V.L. Pecoraro. *J. Am. Chem. Soc.*, **122**, 767 (2000).
[14] C.R. Cornman, E.P. Zovinka, M.H. Meixner. *Inorg. Chem.*, **34**, 5099 (1995).
[15] D.C. Crans, R.L. Bunch, L.A. Theisen. *J. Am. Chem. Soc.*, **111**, 7597 (1989).
[16] D.C. Crans, J.J. Smee, E. Gaidamauskas, L.Q. Yang. *Chem. Rev.*, **104**, 849 (2004).
[17] J.H. McNeill, V.G. Yuen, H.R. Hoveyda, C. Orvig. *J. Med. Chem.*, **35**, 1489 (1992).
[18] K.H. Thompson, J.H. McNeill, C. Orvig. *Chem. Rev.*, **99**, 2561 (1999).
[19] A.J. Tasiopoulos, A.N. Troganis, A. Evangelou, C.P. Raptopoulou, A. Terzis, Y. Deligiannakis, T.A. Kabanos. *Chem. Eur. J.*, **5**, 910 (1999).
[20] H. Sakurai, Y. Kojitane, Y. Yoshikawa, K. Kawabe, H. Yasui. *Coord. Chem. Rev.*, **226**, 187 (2002).
[21] A. Butler, C.J. Carrano. *Coord. Chem. Rev.*, **109**, 61 (1991).
[22] A.P. Mishra, M. Soni. *Met.-Based Drugs*, **2008**, 1 (2008).
[23] N. Muhammad, S. Ali, S. Shahzadi, A.N. Khan. *Russ. J. Coord. Chem.*, **34**, 448 (2008).
[24] O.J. D'Cruz, Y. Dong, F.M. Uckun. *Biol. Reprod.*, **60**, 435 (1999).
[25] Y. Dong, R.K. Narla, E.F. Sudbeck, M. Uckun. *J. Inorg. Biochem.*, **78**, 321 (2000).
[26] P. Noblia, M. Vieites, B.S. Parajon-Costa, E.J. Baran, H. Cerecetto, P. Draper, M. Gonzalez, O.E. Piro, E.E. Castellano, A. Azqueta, A.L. Cerain, A. Monge-Vega, D. Gambino. *J. Inorg. Biochem.*, **99**, 443 (2005).
[27] M.J. Dagani, H.J. Barda, T.J. Benya, D.C. Sanders. *Ullmann's Encyclopedia of Industrial Chemistry: Bromine Compounds*, Wiley-VCH, Weinheim (2002).
[28] J. Fauvarque. *J. Pure Appl. Chem.*, **68**, 1713 (1996).
[29] S. Stavber, M. Jereb, M. Zupan. *Synthesis*, **10**, 1487 (2008).
[30] D. Wischang, O. Brücher. *Coord. Chem. Rev.*, **255**, 2204 (2011).
[31] W. Plass. *Coord. Chem. Rev.*, **255**, 2378 (2011).
[32] D. Rehder, G. Santoni, G.M. Licini, C. Schulzkec, B. Meier. *Coord. Chem. Rev.*, **237**, 53 (2003).
[33] M.C. Burla, M. Camalli, B. Carrozzini, G. Cascarano, C. Giacovazzo, G. Polidori. *J. Appl. Crystallogr.*, **36**, 1103 (2003).
[34] V. Petricek, M. Dusek, L. Palatinus. *Structure Determination Software Programs*, Praha, Institute of Physics (2008).
[35] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).
[36] G. Grivani, A.D. Khalaji, V. Tahmasebi, K. Gotoh, H. Ishida. *Polyhedron*, **31**, 265 (2012).
[37] R. Ando, H. Ono, T. Yagyu, M. Maeda. *Inorg. Chim. Acta*, **357**, 817 (2004).
[38] R. Ando, S. Mori, M. Hayashi, T. Yagyu, M. Maeda. *Inorg. Chim. Acta*, **357**, 1177 (2004).
[39] C.J. Chang, J.A. Labinger, H.B. Gray. *Inorg. Chem.*, **36**, 5927 (1997).
[40] G. Grivani, S. Delkhosh, K. Fejfarova, M. Dusek, A.D. Khalaji. *Inorg. Chem. Commun.*, **27**, 82 (2013).

[41] J. Rahchamani, M. Behzad, A. Bezaatpour, V. Jahed, G. Dutkiewicz, M. Kubicki, M. Salehi. *Polyhedron*, **30**, 2611 (2011).
[42] S. Rayati, M. Koliaei, F. Ashouri, S. Mohebbi, A. Wojtczak, A. Kozakiewicz. *Appl. Catal., A*, **346**, 65 (2008).
[43] M.P. Weberski Jr, C.C. McLauchlan, C.G. Hamaker. *Polyhedron*, **25**, 119 (2006).
[44] X. Wang, X.M. Zhang, H.X. Liu. *Polyhedron*, **14**, 293 (1995).
[45] B.F. Sels, D.E. DeVos, M. Buntinx, P.A. Jacobs. *J. Catal.*, **216**, 288 (2003).
[46] D. Wischang, J. Hartung. *Tetrahedron*, **68**, 9456 (2012).
[47] M.R. Maurya, H. Saklani, S. Agarwal. *Catal. Commun.*, **5**, 563 (2004).
[48] M.R. Maurya, A. Kumar, P. Manikandan, S. Chand. *Appl. Catal., A*, **277**, 45 (2004).
[49] S.M. Islam, A.S. Roy, P. Mondal, N. Salam. *J. Mol. Catal. A: Chem.*, **358**, 38 (2012).
[50] H.Y. Zhao, Y.H. Zhang, Y.H. Xing, Z.P. Li, Y.Z. Cao, M.F. Ge, X.Q. Zeng, S.Y. Niu. *Inorg. Chim. Acta*, **362**, 4110 (2009).
[51] Y.Z. Cao, H.Y. Zhao, F.Y. Bai, Y.H. Xing, D.M. Wei, S.Y. Niu, Z. Shi. *Inorg. Chim. Acta*, **368**, 223 (2011).
[52] J.J. Boruah, S.P. Das, R. Borah, S.R. Gogoi, N.S. Islam. *Polyhedron*, **52**, 246 (2013).
[53] S.M. Islam, A.S. Roy, P. Mondal, K. Tuhina, M. Mobarak, J. Mondal. *Tetrahedron Lett.*, **53**, 127 (2012).