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New dioxido-vanadium(V) complexes containing hydrazone ligands: Syntheses, crystal structure and their catalytic application toward C-H bond functionalization

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Abstract

New dioxido-vanadium(V) complexes derived from hydrazone ligands have been synthesized in good yield. The complexes were characterized by elemental analysis, IR, UV-Visible and ¹H NMR spectroscopies. The structure of both the complexes was established by Single Crystal X-ray crystallography. Complex 1 crystallized in monoclinic P2₁/n space group, with cell parameters a = 8.3725(5) Å, b = 15.0475(17) Å, c = 32.227(3) Å, $\alpha = 90^{\circ}$, $\beta = 91.846(5)^{\circ}$, $\gamma = 90^{\circ}$. Complex 2 crystallized in triclinic P-1 space group, a = 8.1871(7) Å, b = 11.2605(17) Å, c =11.4031(18) Å, $\alpha = 105.961(14)^{\circ}$, $\beta = 110.528(12)^{\circ}$ and $\gamma = 96.387(10)^{\circ}$. Both the complexes act as efficient catalyst which can catalyse the C-H bond functionalization reaction.

Keywords: Crystal structure, C-H activation, Vanadium(V) and DFT

1. Introduction

Vanadium is a trace element and biologically relevant metal which may be beneficial and possibly essential in humans but certainly essential for some living organisms [1-3]. Vanadium ions are found to exist in many oxidation states such as V^{3+} , V^{4+} , and V^{5+} [4-7]. Among these three oxidation states, vanadium(V) compounds have received considerable attention. Moreover, high valence vanadium V(V) and V(IV) complexes are pro-drugs that release active components, such as vanadates or peroxido-vanadates when react with biological media, which then act as potent inhibitors of protein tyrosine phosphatases and altered cell signalling [8, 9]. The research interest on oxidation state of vanadium are very interesting not only due to its ability to exist in three different motifs viz., VO^{3+} , $V_2O_3^{4+}$ and VO_2^+ but also due to its involvement in many catalytic processes. The ability of vanadium to switch easily between +IV and +V oxidation states and their relative stability, depend upon the basicity of the ligands in which it coordinated [10, 11]. The ability of vanadium metal to

possess variable oxidation states which are easily interconvertible, have high affinity for oxygen and the Lewis acidic nature, extends its application in redox and Lewis acid catalyzed reactions [12, 13].

Many vanadium complexes have been synthesized and characterized which act as a catalyst for the oxidation of wide varieties of organic substrates such as oxidative C-H activation, epoxidation, alcohol oxidation reactions, oxidative halogenation and sulfoxidation by utilizing O_2 and H_2O_2 [14-16]. C-H bond functionalization has emerged as a powerful strategy for construction of more useful compound having C-C, C-X (C-F, C-Cl, C-Br and C-I) or C-heteroatom bonds [17]. Due to its low cost and environmentally benign, many vanadium compounds have been extensively used for the synthesis of many organobromines through C-H functionalization [18]. Vanadium compounds utilized O_2 as oxidants in most of these processes, the catalysis vanadate/peroxovanadate catalysts in combination with the reactive peroxides are carried out under strong acidic conditions.

2. Experimental

2.1. Materials and methods

The ligand was prepared as described in the literature [**19**]. All chemical were reagents grade and solvents were reagent grade and used as received. The ¹H NMR and ¹³C NMR were recorded with a Bruker Avance II 400 & 100 MHz in DMSO- d_6 solution using TMS as an internal standard. Infrared spectra in the range 4000 - 200 cm⁻¹ were recorded as KBr discs by using a BX-III/ FTIR Perkin Elmer Spectrophotometer. Electronic spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer.

2.2. X-ray crystallography

Crystallographic data for the compound were measured at 291.8 K, using Xcalibur, Eos, Gemini diffractometer equipped with a monochromated MoK radiation (($\lambda = 0.71073$ Å) source. The CrysAlis PRO; Agilent, 2013 software packages were used for data collection and reduction, respectively [**20**]. In all cases absorption corrections based on multiscan using SADABS software were applied [**21**]. SHELXT-2014 and SHELX-2014 were used for structure solutions and refinements [**22**]. Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Depository number CCDC-1839171, 1854787; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

2.3. Preparation of complexes

Vanadium(V) complex (0.32 g, 1 mmol) was dissolved in 20 mL of methanol. To this solution vanadyl acetyl acetonate (0.265 g, 1 mmol) was added under stirring conditions for

10 minutes. The reaction mixture was refluxed at 70 $^{\circ}$ C for 1 h. The precipitate was then filtered, washed and dried. The resulting solution was then cooled to room temperature which yielded precipitate. Single crystals of the complex were obtained from DMF/water mixture (2:3, v/v) by slow evaporation within a week.

2.4. VO_2L^1

Yield: 87 %. Anal (%), Calcd for $C_{13}H_9BrN_3O_4V$ (MW 400 g/mol) C, 38.80; H, 2.21; N, 10.42. Found: C, 38.81; H, 2.22; N, 10.40. IR data (cm⁻¹ KBr): 1537 (vs) v(N=CO-), 944 (s), 893 (s), v(V=O). ¹H NMR (400 MHz, DMSO-d₆, Me₄Si): δ (ppm): 9.26 (s, 1H, C(H)=N), 8.85-6.85 (m, 7H, Ar-H). Electronic spectrum (λ_{max} , nm): 322, 421.

2.5. VO_2L^2

Yield: 90 %. Anal (%), Calcd for $C_{13}H_9BrN_3O_4V$ (MW 400 g/mol) C, 38.80; H, 2.21; N, 10.42. Found: C, 38.80; H, 2.21; N, 10.40. IR data (cm⁻¹ KBr): 1601 (vs) v(N=CO-), 935 (s), 914 (s), v(V=O). ¹H NMR (400 MHz, DMSO-d₆, Me₄Si): δ (ppm): 8.88, 8.66 (s, 1H, C(H)=N),6.84-7.96 (m, 7H, Ar-H). Electronic spectrum (λ_{max} , nm): 324, 416.

2.6. General experiment for oxidative bromination

In a 50 mL round bottom flask equipped with a magnetic stirring bar, 2hydroxyacetophenone (10 mmol) were added. To this solution, KBr (40 mmol) dissolved in 20 mL water was added and then dissolved by stirring at ambient temperature followed by addition of a 30% H_2O_2 (4 mmol). To this reaction mixture, vanadium(V) complex (0.01 mmol) and 70% $HClO_4$ (4 mmol) were added and the reaction mixture was stirred at 0 °C and then after 10 minutes at room temperature. An additional 4 mmol of 70 % $HClO_4$ was further added in three equal portions after every 10 minutes with continuous stirring. In addition, all the reactions were monitored using thin layer chromatography as a qualitative method. The NMR spectra of bromination products are given in the supporting information.

3. Results and discussion

3.1. Spectroscopic studies



Scheme 1. Structure of ligands used in the present study.

Vanadium(V) complexes was prepared by reaction of hydrazone ligands with vanadium pentoxide in 1:1 molar ratios in methanol. Complex 1 shows three new bands at

945 cm⁻¹, 893 cm⁻¹ and 1537 cm⁻¹, the bands at 945 cm⁻¹ and 893 cm⁻¹ are assigned to V=O stretching vibration and the band at 1537 cm⁻¹ is assigned to newly created -N=CO functional group. Similarly, complex 2 shows three important prominent bands at 1601 cm⁻¹, 935 cm⁻¹ and 914 cm⁻¹, these bands are assigned to -N=CO functional group and V=O stretching vibration [**23**]. The ligand shows resonances at $\delta = 12.20-12.31$ ppm and $\delta = 11.28-11.13$ ppm, these resonances are assigned to -OH and -NH protons respectively (Fig. S1 & S2). The disappearance of these signals during complexation confirmed the ligand coordinate to metal ions in deprotonated form i.e. enol form which are confirmed by IR studies, with the absence of carbonyl stretching frequency (Fig. S3 & S4). The electronic spectrum of the complex shows two absorption bands at 322 nm and 421 nm (complex 1) and 324 nm and 416 nm (complex 2) (Fig. S5 & S6). The band at 322 nm and 324 nm are assigned to intraligand charge transfer whereas the band at 421 nm and 416 nm are assigned to ligand to metal charge transfer transition [**24**].

3.2. X-ray crystallographic studies

The crystal data and structure refinement parameters for the complexes are given in Table 1, whereas the molecular structure of the complex is given in Fig. 1 and Fig. 2, respectively. Selected bond lengths and bond angles of the complex are summarized in Table 2. The ligand coordinates to metal ion in tridentate fashion through -ONO- donors and two oxido ligands forming a penta- coordinated geometry around the metal center in both the complexes.



Fig. 1. Crystal structure of complex 1





Complex 1, crystallized in monoclinic P2₁/n space group. The metal bond lengths in the complex are 1.891(3) Å (V1-O1), 1.967(3) Å (V1-O2), 1.661(3) Å (V1-O3), 1.599(4) Å (V1-O4), 1.980(3) Å (V1-O5), 1.915(3) Å (V1-O6), 1.660(3) Å (V1-O7), 1.601(4) Å (V1-O8), 2.133(4) Å (V1-N1) and 2.165(4) Å (V1-N4), respectively. The geometrical bond angles around vanadium ions are 105.19(18)° (O4-V1-O1), 95.27(16)° (O3-V1-O1), 146.58(16)° (O1-V1-O2), 93.74(15)° (O3-V1-O2), 102.78(16)° (O4-V1-O2), 106.93(19)° (O4-V1-O3), 150.05(14)°, 74.20(14)° (O2-V1-N1), 149.08(18)° (O3-V1-N1), 81.75(15)° (O1-V1-N1), 103.52(17)° and (O4-V1-N1), 73.73(13)°. The trans angle in the complex are 146.58(16)° (O1-V1-O2) and 149.08(18)° (O3-V1-N1) around V1 with $\tau = 0.042$.

Complex 2, crystallized in triclinic P-1 space group. The vanadium-oxygen bond distance in complex are 1.914(3) Å (V1-O1), 1.978(4) Å (V1-O2), 1.607(4) Å (V1-O3), and 1.634(4) Å (V1-O4), whereas the vanadium-nitrogen bond distance is 2.139(5) Å (V1-N1) longer compare to V-O bond length in the complex. The metal-ligand bond angles in the complex are O1-V1-O2 (153.3(17)°, O1-V1-N1 (82.35 (15)°, O2-V1-N1(73.68 (15)°, O4-V1-O1 (97.09 (16)°, O4-V1-O2 (92.86 (17)°, O4-V1-N1 (137.27 (18)°, O3-V1-O1 (101.82 (19)°, O3-V1-O2 (98.31 (19)°, O3-V1-O4 (108.5 (2)° and O3-V1-N1 (113.49 (18)°, respectively. The trans angle in the complex are O1-V1-O2 (153.3(17)° and O4-V1-N1 (137.27 (18)° with $\tau = 0.26$. Hence, vanadium ions adopt a square pyramidal geometry with slight distortion in

complex 1 compared to complex 2. The geometrical bond lengths and bond angles are in good agreement with the literature reports [24].

3.3. Packing diagram of complexes

Molecular packing diagram of the complexes exhibit a weak hydrogen bonding interaction. The molecular packing diagram through crystallographic a-axis is shown in Fig. 3 and Fig. 4.



Fig. 3. Packing diagram of complex 1 along a-axis showing hydrogen bonding

In complex 1, the N--H...O and O--H... N bond distances are 2.774 Å (N(8) --H(8A) ..O(3) and 2.896 Å (O(9) --H(9B) ..N(3) with bond angles of 173° (N(8) --H(8A) ..O(3) and 127° (O(9) --H(9B) ..N(3). The C--H...O bond distances are 3.167(7) Å (C(29) --H(29A) ..O(8), 3.470(10) Å (C(31) --H(31C) ..O(1) and 3.264(8) Å (C(32) --H(32A) ..O(4), with geometrical bond angles 150° (C(29) --H(29A) ..O(8), 152° (C(31) --H(31C) ..O(1) and 129° Å (C(32) --H(32A) ..O(4), respectively.



Fig. 4. Molecular packing diagram of complex 2 along a-axis

The geometrical N--H...O and O--H... N bond distances in complex 2 are 2.722(7) Å (N(4)--H(4A) ..O(4) and 2.756(7) Å (N(4)--H(4B) ..O(5) and 2.803(8) Å (O(5)--H(5B) ..N(3) with their bond angles 167° , 176° and 175° , respectively. The O--H...O bond length and bond angle are 2.967(6) and 169° . The C--H...O bond distances are 3.331(7) Å (C(4)--H(4)..O(4), 3.390(7) Å (C(7)--H(7)..O(3) and 3.425(9) Å (C(15)--H(15C) ..O(5), with bond angles 144° and 153° .

3.4. Computational studies of complexes

Theoretical studies for the electronic structure of the complex in gas phase were performed using density functional theory with hybrid functional B3LYP using GAUSSIAN 09 program [25]. The electronic geometry was calculated using 6-31+G(d,p) basis set for carbon, hydrogen, oxygen, nitrogen and bromine atoms and for vanadium ion LANL2DZ [26] basis set was used. Contour plots of selected molecular orbitals and their energy gap (HOMO-LUMO) are shown in Figs. 5 & 6. The energy different between the HOMO and LUMO in the complexes are 2.89 eV in complex 1 and 3.05 eV in complex 2, which are

lesser compared to that of the corresponding ligands 3.89 eV and 3.72 eV. The compositions of HOMO and LUMO are very useful in order to understand the absorption spectra of the complexes as well as their nature of transition. A large energy gap between HOMO-LUMO corresponds to a high energy required for electron excitation. Hence, energy for electron excitation in the complexes are less compared to that of the ligand due to smaller energy gap. In these two complexes the HOMO is composed of ligand π orbital and whereas the LUMO is mainly composed of ligand π^* orbital and vacant d-orbital of vanadium. The geometrical bond lengths and bond angles optimized in gas phase are in good agreement with the experimental data obtained from single crystal X-ray crystallography. Slight deviation was observed, as a result geometrical optimization is performed in gaseous state in which intermolecular interactions are absent and structure is more extended compared to X-ray crystallography data.



Fig 5. Contour plots for some selected molecular orbitals of complex 1



Fig 6. Contour plots for some selected molecular orbitals of complex 2

3.5. Catalytic studies

The catalytic studies for C-H bond functionalization was tested using stoichiometric amount of the complex with organic substrates such as acetophenone and acetophenone derivatives, 2-hydroxybenzaldehyde in presence of KBr, $HClO_4$ and 15% H_2O_2 .

Table 3. Optimization of reaction conditions for the oxidative bromination catalysed by vanadium(V) complexes.



Entry	Molar ratio			Temperature (°C)	Time (min)	Isolated yield (%)	
	V-comlex: S	S: KBr	Br:H ₂ O ₂	HClO ₄ (mmol)			
1	1:10	1:2	1:1	2	RT	30	64
2	1:10	1:4	1:1	2	RT	30	70
3	1:10	1:4	1:2	2	RT	30	82
4	1:10	1:4	1:4	2	RT	30	79

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5	1:20	1:4	1:4	2	RT	30	56
6	1:05	1:4	1:4	2	RT	30	81
7	1:10	1:4	1:4	2	40	30	73
8	1:10	1:4	1:4	2	55	30	70
9	1:10	1:4	1:4	2	70	30	65
10	1:10	1:4	1:4	4	RT	30	87
11	-	1:4 ^b	_	4	RT	240	7.5

^aAll the reactions were carried out using 0.04 g catalyst (0.1 mmol), 2-hydroxyacetophenone as substrate, KBr as bromide source, $HClO_4$ (4.0 mmol) and H_2O (5 mL) as solvent unless stated.

^bControl reaction: acetophenone (1.0 mmol), catalyst (0.1 mmol), KBr (4.0 mmol), HClO₄ (4.0 mmol) and H₂O (5 mL).



Scheme 1. Substrate scope and isolated yield.

Using our newly synthesized vanadium(V) complexes as catalyst, the reaction was carried out using different molar ratios of complex, acetophenone, KBr and hydrogen peroxide. The reaction mixture first was stirred at low temperature (0 °C) and then after 10 minutes it was raised to room temperature. The effect of solvents was also tested by carrying out the reaction using different solvents and it was found that water gave the best yield. The catalytic studies were carried out using different molar ratios of complex/substrate/KBr and hydrogen peroxide and it was found that 1:10:40:40 molar ratios of complex/substrate/KBr/hydrogen peroxide gave the best yield. The effects of acid for the oxidative bromination reaction were tested and found that 4 molar ratios of HClO₄ gave maximum yield (Table 3, entry 10). Control experiment were also performed using stoichiometric amount of catalyst (0.1 mmol), acetophenone (1.0 mmol), KBr (4.0 mmol), HClO₄ (4.0 mmol) and H₂O (5 mL) in the absence of an oxidant, but it was observed that,

only a trace amount of product was obtained even after a period of 4 hr. The catalytic activity of the complex 2 were also tested using the same reaction condition and it was found that complex 2 can be also used as catalyst for catalytic reaction but its yield is almost similar to complex 1. In the recent past, the bromination of many organic substrates by vanadium-based catalysts has been extensively studied (Table 3). Maurya et al. studied the oxidative bromination of salicylaldehyde using vanadium complexes having $[V^{IV}O_2]^{++}$ and $[V^{V}O_2]^{++}$ cores with binucleating dibasic tetradentate ligands, which show a maximum of 95.7% yield of 5-bromosalicylaldehyde [27]. In their studies they have shown that increase in the hydrogen peroxide concentration improves the conversion of salicylaldehyde. Further, in the absence of catalyst the conversion of product was only 4%. Maurya et al. have also studied the catalytic bromination reaction of salicylaldehyde using polymer-anchored dioxovanadium(V) complexes, which shows a maximum conversion of 85% product (5brompsalicylaldehyde) [28]. In their studies, they also reported that when Chloromethylated polystyrene supported oxo-vanadium(IV) complexes are used as catalysts in the oxidative bromination of salicylaldehyde, the formation of product (5-bromosalicylaldehyde) was 73% and in this case dibrominated product was also formed [29].

Manirul Islam et al. reported the catalytic oxidative bromination of salicylaldehyde using polymer anchored oxovanadium complex (PS-tetaeVO) with 98% yield of 5bromosalicylaldehyde (Table 4). In their studies they showed that hydrogen peroxide plays a very important role in the catalytic oxidative bromination, in the absence of hydrogen peroxide the formation of bromo products was significantly less [**30**].

Catalyst	Yield %	Ref
$Cs_2[CH_2{V^VO_2(sal-bhz)}_2].2H_2O$	95.7	27
polymer-supported-K[VO2(sal-inh)(im)	85	28
polymer-supported-[VO(fsal-ohyba) DMF]	73	29
Polymer anchored oxovanadium complex (PS-tetaeVO)	98	30
Dioxido-vanadium(V) complexes containing hydrazone	90	This study
ligands		

Table 4. Bromination of salicylaldehyde catalyzed by other vanadium-based catalysts

To explore the validity of this method other organic substrates were tested. Some selected results are listed in scheme 1. The bromination reaction of salicylaldehyde gave 90% yield of 5-bromo salicylaldehyde in 40 min. Inspired by these results, we hypothesized that the α -bromoketone could be obtained using vanadium(V) complexes and acetophenone as the substrate. In our study, we found that bromination of acetophenone gave α -

bromoacetophenone as the only product with 80% yield within the time period of 38 min. The bromination reaction of different substituted α -bromoketone was also performed, such as 2-hydroxy acetophenone gave the product α -bromo-2-hydroxy acetophenone with 87% yield within 35 minutes. Bromination reaction of p-methoxy-acetophenone gave the product α -bromo-p-methoxy-acetophenone with 89% yield in 30 min, higher yield is due to the electron donating nature of methoxy group present in the para position of the benzene ring. Other substituted ketones such as 4-methyl-2-hydroxy- acetophenone and 5-methyl-2-hydroxy- acetophenone were also smoothly monobrominated to α -bromoketone in high yields with 85% with the time period of 40 minutes. Hence, the present approach is very simple and efficient method for C-H bond functionalization reaction of many organic substrates and provide an access to α -bromoketones.

3.6. The plausible mechanistic pathway

To explain the observed behaviour, a possible mechanism is shown in Fig 7. In the first step vanadium(V) complexes react with hydrogen peroxide resulting in the formation of peroxo-vanadium species. In the next step, the reaction of peroxo-vanadium with KBr yield bromide species in the presence of an acid. In the last step, α -hydrogen abstraction by monoperoxo vanadium(V) species occur giving rise to a reactive intermediate, which may undergo nucleophilic displacement by the bromide anion yielding α -bromoketones as the product.



Fig 7. Plausible mechanism for C-H bond functionalization catalysed by vanadium(V) complexes

4. Conclusion

Dioxido-vanadium(V) complexes containing mono hydrazone ligands were synthesized in good yield. The complex was synthesized by reaction of the ligand with vanadium pentoxide in 2:1 molar ratio in methanol. Single crystal suitable for Single XRD analysis was obtained from DMF/water mixture in 2:3 (v/v) at room temperature within a week. The complexes obtained adopted a square pyramidal geometry around vanadium ion with slight distortion. The two vanadium(V) complexes can catalyse the peroxidative bromination of organic substrates and can be considered as potential functional models of vanadium halo-peroxidases and their application toward C-H bond functionalization.

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Supplementary data

Supplementary materials may be found online in the supporting information tab for this article.

References

- F. H. Nielsen, E. O. Uthus, In Vanadium in Biological Systems. N. D. Chasteen, Ed. Kluwer Academic Publishers: Boston, (1990).
- [2] K. Kustin, G. C. McLeod, T. R. Gilbert, L. B. R. T. Briggs, Struct. Bonding. 53 (1983) 139.
- [3] R. Wever, K. Kustin, Adv. Inorg. Chem. 35 (1990) 81.
- [4] A. G. J. Ligtenbarg, R. Hage, B. L. Feringa, Coord. Chem. Rev. 237 (2003) 89.
- [5] R. Wever, K. Kustin, Advances in Inorganic Chemistry: Vanadium, a Biologically Relevant Element, ed. A. G. Sykes, Academic Press, New York, 35 (1990) 103.
- [6] (a) D. Rehder, <u>Metallomics.</u> 7 (2015) 730; (b) W. Plass, Coord. Chem. Rev. 255 (2011) 2378.
- [7] B. Mondal, M. G. B. Drew, T. Ghosh, Inorg. Chim. Acta. 363 (2010) 2296.
- [8] (a) A. Levina, A. I. McLeod, A. Pulte, J. B. Aitken, P. A. Lay, Inorg. Chem. 54 (2015) 6707; (b) K. H. Thompson, C. J. Orvig, Inorg. Biochem. 100 (2006) 1925.

- [9] A. K. Srivastava, M. Z. Mehdi, Diabetic Med. 2005, 22, 2. b) M. Zhang, M. Zhou, R. L. Van Etten, C. V. Stauffacher, Biochemistry. 36 (1997) 15.
- [10] (a) C. R. Cornman, J. Kampf, M. Soo Lah, V. L. Pecoraro, Inorg. Chem. 31 (1992) 2035–2043; (b) C. J. Schneider, J. E. Penner-Hahn, V. L. Pecoraro, J. Am. Chem. Soc. 130 (2008) 2712-2713.
- [11] (a) T. Hirao, Chem. Rev. 97 (1997) 2707; (b) S. K. Hanson, T. R. Baker, J. C. Gordon, L, T. D. Scott, Inorg. Chem. 49 (2010) 5611; (c) G. H. Spikes, S. Sproules, E. Bill, T. Weyhermuller, K. Wieghardt, Inorg. Chem. 47 (2008) 10935.
- [12] (a) C. R. Cornman, J. Kampf, M. Soo Lah, V. L. Pecoraro, Inorg. Chem. 31 (1992) 2035; (b) C. J. Schneider, J. E. Penner-Hahn, V. L. Pecoraro, J. Am. Chem. Soc. 130 (2008) 2712.
- [13] (a) T. Hirao, Chem. Rev. 97 (1997) 2707; (b) G. H. Spikes, S. Sproules, E. Bill, T. Weyhermuller, K. Wieghardt, Inorg. Chem. 47 (2008) 10935.
- [14] (a) D. Rehder, Coord. Chem. Rev. 182 (1999) 297; (b) C. R. Cornman, G. J. Colpas,
 J. D. Hoeschele, J. Kampf, V. L. Pecoraro, J. Am. Chem. Soc. 114 (1992) 9925; (c) C.
 J. Schneider, J. E. Penner-Hahn, V. L. Pecoraro, J. Am. Chem. Soc. 130 (2008) 2712.
- [15] (a) G. H. Spikes, S. Sproules, E. Bill, T. Weyhermuller, K. Wieghardt, Inorg. Chem.
 47 (2008) 10935; (b) C. Mukherjee, T. Weyhermuller, E. P. Bothe, Inorg. Chem. 47 (2008) 11620.
- [16] (a) P. B. Chatterjee, K. Bhattacharya, N. Kundu, K. Y. Choi, R. Clrac, M. Chaudhury, Inorg. Chem. 48 (2009) 804; (b) A. G. L. Ligtenbarg, R. Hage, B. L. Feringa, Coord. Chem. Rev. 237 (2003) 89
- [17] (a) X. Chen, K. M. Engle, D. H. Wang, J. Q. Yu, Angew. Chem. Int. Ed. 48 (2009) 5094; (b) F. Kakiuchi, N. Chatani, Adv. Synth. Catal. 345 (2003) 1077-1101.
- [18] D. X. Ren, N. Xing, H. Shan, C. Chen, Y. Z. Cao, Y. H. Xing, Dalton Trans. 42 (2013) 5379–5389.
- [19] S. Sravya, S. Sruthy, a N. Aiswarya, M. Sithambaresanc, M. R. Prathapachandra Kurup, Acta. Cryst. E71 (2015) 734.
- [20] Agilent. CrysAlis PRO. Agilent Technologies, Yarnton, England, (2013).
- [21] R. H. Blessing, Acta. Crystallogr. Sect. A. 51 (1995) 33.

- [22] (a) G. M. Sheldrick, Acta Crystallogr, Sect. A. 64 (2008) 112; (b) G. M. Sheldrick, SHELXL-14: Program for Crystal Structure Refinements; University of Gottingen: Gottingen, Germany (1996).
- [23] (a) S. D. Kurbah, A. Kumar, I. Syiemlieh, R. A. Lal, Inorg. Chem. Commun. 86 (2017) 6; (b) S. D. Kurbah, I. Syiemlieh, R. A. Lal, R. Soc. open sci. 5 (2018) 171471.
- [24] (a) S. D. Kurbah, A. Kumar, I. Syiemlieh, R. A. Lal, Polyhedron. 139 (2018) 80–88;
 (b) S. D. Kurbah, A. Kumar, I. Syiemlieh, R. A. Lal, Inorg. Chem. Commun. 86 (2017) 6.
- [25] M. J. Frisch et al., GAUSSIAN 09, Revision C.01, Gaussian Inc, Walling-ford, CT, 2009.
- [26] S. Y. Ebrahimipour, M. Abaszadeh, J. Castro, M. Seifi, Polyhedron. 79 (2014) 138.
- [27] M. R. Maurya, A. A. Khan, A. Azam, S. Ranjan, N. Mondal, A. Kumar, F. Avecilla, J. C. Pessoa, Dalton Trans. 39 (2010) 1345–1360.
- [28] M. R. Maurya, M. Kumar, A. Arya, Catal. Commun. 10 (2008) 187.
- [29] M. R. Maurya, U. Kumar, P. Manikandan, Dalton Trans. (2006) 3561.

[30] Sk. M. Islam, R. A. Molla, A. S. Roy, K. Ghosh, N. Salam, Md. A. Iqubal, K. Tuhina, J. Organomet. Chem. 761 (2014) 169-178.

	Complex 1	Complex 2
Empirical formula	$C_{34}H_{42}Br_2N_8O_9V_2$	$C_{15}H_{18}BrN_4O_5V$
Formula weight	968.45	465.18
Temperature/K	295.8(3)	292.5(2)
Crystal system	monoclinic	triclinic
Space group	P21/n	P-1
a/Å	8.3725(5)	8.1871(7)
b/Å	15.0475(17)	11.2605(17)
c/Å	32.227(3)	11.4031(18)
α/°	90	105.961(14)
β/°	91.846(5)	110.528(12)
γ/°	90	96.387(10)
Volume/Å3	4058.0(6)	921.0(2)
Z	4	2
pcalcg/cm3	1.585	1.677
μ/mm 1	2.491	1.677
Radiation	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)
Data/restraints/parameters	7098/0/503	3237/0/240
Goodness-of-fit on F2	0.962	1.067
Final R indexes [I>= 2σ (I)]	R1 = 0.0524, wR2 = 0.1363	R1 = 0.0570, wR2 = 0.1308
Final R indexes [all data]	R1 = 0.0935, wR2 = 0.1657	R1 = 0.0809, wR2 = 0.1516

Table 1. Crystal data and structure refinement for complexes 1 & 2

Table 2. Bond Lengths and bond angles for complexes

Atom	Atom	Length	ı/Å
V1	01	1.891(3)
V1	O2	1.967(3)
V1	03	1.661(3)
V1	O4	1.599(4)
V2	O5	1.980(3)
V2	06	1.915(3)
V2	O7	1.660(3)
V2	08	1.601(4)
V2	N4	2.165(4)
V1	N1	2.133(4)
Atom	Atom	Atom	Angle/°
O4	V1	O 1	105.19(18)
03	V1	01	95.27(16)
01	V1	O2	146.58(16)
03	V1	O2	93.74(15)
O4	V1	O2	102.78(16)
O4	V1	O3	106.93(19)
O2	V1	N1	74.20(14)
O3	V1	N1	149.08(18)

01	V1	N1	81.75(15)
O4	V 1	N1	103.52(17)

other the second

Highlights

Dioxovanadium(V) complexes containing simple hydrazone ligands has been synthesized in good yield.

The complexes were characterized by IR, UV-Visible and ¹H NMR spectroscopies.

The structure of complexes has been established by Single Crystal X-ray crystallography.

The complexes act as catalyst which efficiently catalyzed C-H bond activation reaction.