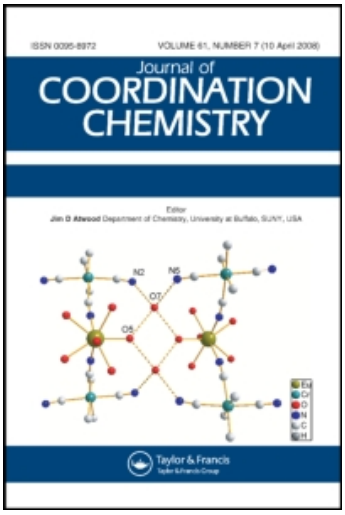

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, characterization, and X-ray crystal structures of two cis-dioxovanadium(V) complexes of pyrazole-derived, Schiff-base ligands

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First published on: 13 July 2010

To cite this Article Roy, Somnath , Mandal, Tarak Nath , Das, Kinsuk , Butcher, Ray J. , Rheingold, Arnold L. and Kumar Kar, Susanta(2010) 'Syntheses, characterization, and X-ray crystal structures of two cis-dioxovanadium(V) complexes of pyrazole-derived, Schiff-base ligands', Journal of Coordination Chemistry, 63: 12, 2146 — 2157, First published on: 13 July 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.499457
URL: http://dx.doi.org/10.1080/00958972.2010.499457

Journal of Coordination Chemistry
Vol. 63, No. 12, 20 June 2010, 2146–2157

Syntheses, characterization, and X-ray crystal structures of two cis-dioxovanadium(V) complexes of pyrazole-derived, Schiff-base ligands

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(*Received 15 October 2009; in final form 30 March 2010*)

Two mononuclear cis-dioxovanadium(V) complexes of pyrazole-derived, Schiff-base ligands have been synthesized and characterized. Single crystal X-ray analyses were performed with *N′*-[(3-methyl-1*H*-pyrazole-5-yl)carbonyl]pyridine-2-carbohadrazonamido cis-dioxovanadium(V), $\{[VO_2(PzOAP)]\cdot H_2O\}$ (**1**), and 5-methyl-*N*-[(1*E*)-1-(pyridin-2-yl)ethylidene]-1*H*-pyrazole-3-carbohydrazonate cis-dioxovanadium(V), $\{[VO_2(PzCAP)]\}$ (**2**). Both complexes crystallize in monoclinic crystal systems with different space groups. Complex **1** crystallizes in the space group *P21/c*, **2** in space group *C2/C*. In each complex, the vanadium sits within a distorted square pyramidal geometry with an N_2O_3 chromophore. The τ parameters of the complexes (0.33 for **1**, 0.22 for **2**) support their square pyramidal geometry. The interesting finding in the work is that the alkoxide oxygen, imino nitrogen, and pyridine nitrogen take part in the coordination process leaving the pyrazole rings inactive in coordination.

Keywords: Vanadium(V) complexes; Syntheses; Spectral properties; Crystal structures

1. Introduction

The coordination chemistry of vanadium is of interest because of its presence in abiotic and biotic systems [1–6]. The element is also present in some sea squirts [1, 2], mushrooms [3, 4], and vanadium-containing enzymes, such as nitrogenase [5] and haloperoxidases [6]. Vanadium(V) complexes are effective inhibitors of various enzymes. Momentum to the coordination chemistry of vanadium in medical applications arises from the ability of vanadium complexes to promote insulin mimetic activity in the pathophysiological state of diabetes mellitus in humans [7–10]. This biological

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.499457

and catalytic relevance of vanadium has prompted the synthesis of numerous vanadium compounds containing O, N donor ligands whose spectroscopic, magnetic, and redox properties have been widely investigated [11–21]. Other vanadium complexes of O, N donor ligands have been reported [22]. Although work on vanadium with heterocyclic thiosemicarbazones and other ligands has been reported [23], little research has been centered on vanadium chemistry with polytopic ligands having pyrazole as the heterocyclic ligand. Considering the broad spectrum of potentially useful biological implications and the catalytic activity of the metal complexes with 5-methylpyrazole-3-carbohydrazide derivatives [15–20], herein we report syntheses, spectroscopic characterization, and X-ray crystallographic characterization of two cis-dioxovanadium(V) complexes with PzOAP and PzCAP. We reported earlier the syntheses and coordinating behaviors of these ligands toward Cu(II) [24, 25]. As an extension, we have used the same ligands to study vanadium chemistry in an NNO donor environment. In our previous work [24, 25], PzOAP and PzCAP formed homoleptic tetranuclear Cu(II) 2×2 square/rectangular grid complexes using alkoxide oxygen as a bridge in 1 : 1 ligand : metal proportion.

2. Experimental

2.1. *Materials*

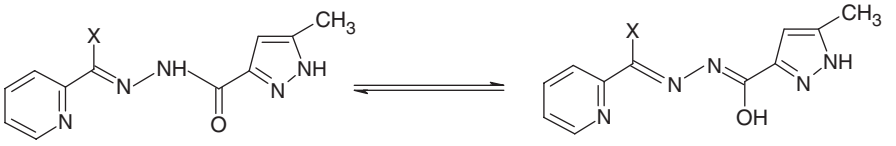
All chemicals were of reagent grade, purchased from commercial sources and used without purification. Ethanol was purified using the established method [26, 27].

2.2. *Purification of ethanol*

A 2 L round bottom flask was washed by chromic acid and then distilled water. The flask was dried in an oven. Approximately 7.5 g magnesium turnings were weighed and very dil. HCl (1 : 50 v/v) was used to clear the magnesium as silver white. The magnesium turnings were again washed 10–15 times by distilled water and alcohol and dried in an oven at ~50°C. Five grams of dry magnesium was taken in the flask in which the alcohol was to be dried; 0.5 g iodine and 50 mL dehydrated alcohol were added to it. The reaction mixture was warmed until vigorous reaction occurred. After complete reaction, the mixture was kept at room temperature. After the formation of magnesium ethoxide as a white cake, 1 L of ethyl alcohol was added and refluxed for 2 h. Finally, the purified ethyl alcohol was distilled off.

2.3. *Physical measurement*

Elemental analyses (carbon, hydrogen, and nitrogen) of the ligands and the metal complexes were determined with a Perkin–Elmer CHN analyzer 2400 at the Indian Association for the Cultivation of Science, Kolkata. Electronic spectra of the complexes in DMF were recorded on a Hitachi model U-3501 spectrophotometer. Infrared (IR) spectra (KBr pellets, 4000–500 cm^{-1}) were recorded on a Perkin–Elmer model 883 IR spectrophotometer. ^{1}H-NMR spectra of the ligands were recorded in d_6-DMSO with a Bruker AM 300L (300 MHz) superconducting FT-NMR.



"Ketoimine" form "Imineol" form

$X = NH_2$; PzOAP
$X = CH_3$; PzCAP

Scheme 1. Tautomeric forms of the ligands.

2.4. *Syntheses and characterization of the ligands*

5-Methylpyrazole-3-carbohydrazide was prepared following established method [28]. The two ligands were synthesized as described below, following the same methods as reported earlier [24, 25]. Schematic representations of the two ligands are shown in scheme 1.

2.4.1. Synthesis of PzOAP ($C_{11}H_{12}N_6O$). The methyl ester of iminopicolinic acid was prepared *in situ* by the reaction of 2-cyanopyridine (5.2 g, 0.05 mol) with sodium methoxide solution, produced by dissolving sodium metal (2.5 g, 0.108 mol) in dry methanol (25 mL). 5-Methylpyrazole-3-carbohydrazide (7 g, 0.05 mol) in 25–30 mL dry methanol was added to the above solution with stirring for 1 h. The mixture was refluxed for 5 h and cooled to room temperature. Excess methanol was removed in a rotary evaporator to leave a red oily sticky liquid. It was then mixed with water (50 mL) and neutralized with AcOH (pH ~ 5) affording a yellow powder. The solid was filtered off, washed thoroughly with methanol, and dried *in vacuo* over fused $CaCl_2$. Yield: 7.32 g, 60%; m.p. 216°C (decomp.); MS (*m*/*z*) 244 (M^+, 100%); IR (cm^{-1}): ν_{NH} 3353; $\nu_{CO/CN}$ 1651(s), 1539(s); ν_{N-Npz} 1057(s); ν_{py} 1004(s). ^{1}H-NMR δ (d_6-DMSO): 2.23 (s, 3H), 6.31 (s, 1H), 6.79 (s, NH_2), 7.43 (m, 1H), 7.82 (m, 1H), 8.12 (d, 1H), 8.54 (d, 1H), 10.03 (s, Pz-NH), 12.96 (b, azo-NH). Anal. Calcd for $C_{11}H_{12}N_6O$: C, 54.09; H, 4.92; N, 34.42. Found: C, 53.95; H, 4.61; N, 34.32%.

2.4.2. Synthesis of PzCAP ($C_{12}H_{13}N_5O$). 5-Methylpyrazole-3-carbohydrazide (1.40 g, 0.01 mol) in 20–25 mL methanol was added dropwise to the methanolic solution (5 mL) of 2-acetyl pyridine (1.21 g, 0.01 mol) with constant stirring. The stirring was continued for 20 min and the mixture was refluxed for 5 h and cooled to room temperature. Excess methanol was removed by rotary evaporator giving a colorless viscous liquid which was kept in an ice bath. After a while, the liquid froze to a microcrystalline white solid. The solid was filtered off, washed thoroughly with cold methanol and dried *in vacuo* over fused $CaCl_2$. Yield: 2.09 g, 80%; m.p. 210°C (decomp.); MS (*m*/*z*) 243 (M^+, 100%); IR (cm^{-1}): ν_{NH} 3325; $\nu_{CO/CN}$ 1661(s), 1534(s); ν_{N-Npz} 1047(s); ν_{py}1020(s). ^{1}H-NMR δ (d_6-DMSO): 2.25 (s, 3H), 2.30 (s, 3H), 6.51 (s, 1H), 7.52 (m, 1H), 7.80 (m, 1H), 8.05 (d, 1H), 8.57 (d, 1H), 10.26 (s, Pz-NH), 13.10 (s, azo-NH). Anal. Calcd (%) for $C_{12}H_{13}N_5O$: C, 59.26; H, 5.35; N, 28.80. Found (%): C, 59.12; H, 5.32; N, 28.78.

2.5. *^{1}H-NMR spectra of the ligands*

^{1}H-NMR spectra (ppm) in d_6-DMSO at 300 MHz of PzOAP and PzCAP give singlets at δ 2.23 (3H) and δ 2.25 (3H) assignable to C_5–CH_3 (ring pz) and singlets at δ 6.31 (1H) and δ 6.51 (1H) due to C_4–H (ring pz). A singlet at δ 6.79 (2H) for PzOAP is ascribed to the terminal C–NH_2 and a singlet at δ 2.30 (3H) for PzCAP is ascribed to terminal C−CH_3. A singlet at δ 10.03 (1H) for PzOAP and a singlet at δ 10.26 (1H) for PzCAP are ascribed to the pyrazolyl –NH proton of the ligands. A broad singlet at δ 12.96 (1H) for PzOAP and a singlet at δ 13.10 (1H) for PzCAP confirm the presence of "ketoimine" –NH protons in the ligands.

2.6. *Preparation of the complexes*

2.6.1. Preparation of *N′*-[(3-methyl-1*H*-pyrazole-5-yl)carbonyl]pyridine-2-carbo-hydrazonamido cis-dioxovanadium(V) {[VO_2(PzOAP)]·H_2O} (1). To a solution of PzOAP (0.447 g, 2.27 mmol) in hot purified ethanol (15 mL) was added $VO(acac)_2$ (0.601 g, 2.27 mmol). The green mixture was refluxed for 3 h turning greenish yellow. This mixture was kept at room temperature for slow evaporation. Yellow crystals suitable for X-ray diffraction so formed were filtered off after 72 h, washed with ethanol : water (1 : 1 v/v) and dried over anhydrous $CaCl_2$. Yield: 0.733 g, 70%. Anal. Calcd for $C_{11}H_{13}N_6O_4V$ (**1**): C, 38.36; H, 3.77; N, 24.40. Found (%): C, 38.38; H, 3.80; N, 24.36. IR (KBr, cm^{-1}): ν_{NH} 3309; $\nu_{CO/CN}$ 1610(s), 1508(s); ν_{N-Npz} 1140(s); ν_{py} 1005(s). ^{1}H-NMR δ (d_6-DMSO): 2.46 (s, 3H), 6.40 (s, 1H), 7.75 (s, NH_2), 8.24 (m, 1H), 8.33 (m, 1H), 8.39 (d, 1H), 8.78 (d, 1H), 10.05 (s, Pz-NH). UV-Vis (CH_3CH_2OH): $\lambda_{max/nm}$: 263, 380.

2.6.2. Preparation of 5-methyl-*N*-[(1*E*)-1-(pyridin-2-yl)ethylidene]-1*H*-pyrazole-3-carbo-hydrazonate cis-dioxovanadium(V), [VO_2(PzCAP)] (2). Complex **2** was prepared using the same procedure and reaction stoichiometry as for **1**. Yield: 0.807 g, 70%. Anal. Calcd (%) for $C_{12}H_{12}N_5O_3V$ (**2**): C, 44.28; H, 3.69; N, 21.52. Found (%): C, 44.31; H, 3.71; N, 21.50. IR (KBr, cm^{-1}): ν_{NH} 3199; $\nu_{CO/CN}$ 1600(s), 1505(s); ν_{N-Npz} 1065(s); ν_{py} 1030(s). ^{1}H-NMR δ (d_6-DMSO): 2.23 (s, 3H), 2.52 (s, 3H), 6.49 (s, 1H), 7.72 (m, 1H), 8.15 (m, 1H), 8.33 (d, 1H), 8.75 (d, 1H), 10.31 (s, Pz-NH). UV-Vis (CH_3CH_2OH): $\lambda_{max/nm}$: 295, 393.

2.7. *Single crystal X-ray crystallography*

Selected crystal data for **1** and **2** are given in table 1 and selected metrical parameters of these complexes are given in table 2. For **1** and **2**, data collections were made using a Bruker SMART CCD area diffractometer and Oxford Diffraction Gemini R equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) fine focus sealed tube source in φ and ω scan mode at 100(2) and 200(2) K, respectively. For **1**, cell parameter refinement and data reduction were carried out using the Bruker SMART [29] and SAINT software [30], and for **2**, these were done by CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.32.15 (release 10-01-2008 CrysAlis171.NET) [31]. The structures were solved by direct methods and refined by full-matrix least squares using F^2 data. SHELXS-97 and SHELXL-97 [32] were used for structure solution and

Table 1. Experimental data of crystallographic analysis for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{11}H_{13}N_6O_4V$	$C_{12}H_{12}N_5O_3V$
Formula weight	344.21	325.21
Temperature (K)	100(2)	200(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P21/c*	*C2/C*
Unit cell dimensions (Å, °)		
a	8.7298(8)	12.5105(3)
b	6.9842(7)	13.2484(3)
c	22.283(2)	16.2139(3)
α	90	90
β	96.232(2)	97.522(2)
γ	90	90
Volume (Å^3), *Z*	1350.6(2), 4	2664.2(1), 8
Calculated density (mg m^{-3})	1.693	1.622
Absorption coefficient (mm^{-1})	0.765	0.763
F(000)	704	1328
Crystal size (mm^3)	$0.30 \times 0.10 \times 0.05$	$0.48 \times 0.41 \times 0.18$
θ range for data collection (°)	2.35 to 28.23	4.50 to 34.91
Index ranges	$-11 \le h \le 11$	$-19 \le h \le 19$
	$-9 \le k \le 8$	$-20 \le k \le 21$
	$-29 \le l \le 29$	$-25 \le l \le 25$
Goodness-of-fit on F^2	1.056	0.979
Completeness to $\theta = 25.00$ (%)	100.0	99.1
Independent reflections	3102 [R(int) = 0.0308]	5541 [R(int) = 0.0268]
Absorption correction	None	Semi-empirical from equivalents
Max. and min. transmission	0.931 and 0.883	1.00000 and 0.92826
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3102/0/219	5541/0/192
Reflections collected	10,997	22,244
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0403$, $wR_2 = 0.1019$	$R_1 = 0.0352$, $wR_2 = 0.0944$
R indices (all data)	$R_1 = 0.0484$, $wR_2 = 0.1071$	$R_1 = 0.0534$, $wR_2 = 0.0999$
Largest difference peak and hole (e Å^{-3})	0.663 and −0.399	0.436 and −0.255

refinement, respectively. For **1** and **2**, absorption corrections were done by multi-scan method using SADABS [33] and CrysAlis RED [31], Oxford Diffraction Ltd., Version 1.171.32.15 (release 10-01-2008 CrysAlis171.NET). Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Positions of some hydrogens are placed in calculated positions and some are determined from dF map. Ortep-3 and Platon programs were used for calculations of geometrical parameters and Diamond 3.1 software was used for drawing the crystal structures of **1** and **2**.

3. Results and discussion

3.1. *Syntheses*

PzOAP and PzCAP are mono-anionic with NNO donors. Complexes **1** and **2** were obtained from the reaction of PzOAP and PzCAP, with $VO(acac)_2$ in 1 : 1 molar ratio in ethanol. Elemental analyses (C, H, and N) and IR spectral data [characteristic bands (cm^{-1}) at 3353–3325 (ν_{NH}), 1534–1539 ($\nu_{CH=N}$), 1057–1047 (ν_{N-Npz}), 1661–1651 (ν_{CO}),

Table 2. Selected bond distances (Å) and angles (°) in **1** and **2**.

1		**2**	
Bond distances (Å)			
V(1)–O(2)	1.625(2)	V(1)–O(1)	1.619(9)
V(1)–O(3)	1.635(2)	V(1)–O(2)	1.62(1)
V(1)–O(4)	1.968(1)	V(1)–O(3)	1.943(9)
V(1)–N(3)	2.036(2)	V(1)–N(2)	2.101(9)
V(1)–N(1)	2.144(2)	V(1)–N(1)	2.104(1)
O(4)–C(5)	1.320(2)	O(3)–C(8)	1.300(1)
N(3)–N(4)	1.392(2)	N(2)–N(3)	1.380(1)
N(4)–C(5)	1.294(3)	N(2)–C(6)	1.291(1)
N(5)–N(6)	1.351(3)	N(3)–C(8)	1.309(1)
N(2)–C(6)	1.324(3)	N(4)–N(5)	1.340(1)
N(3)–C(6)	1.304(3)	C(6)–C(7)	1.483(2)
Bond angles (°)			
O(2)–V(1)–O(3)	110.01(8)	O(1)–V(1)–O(2)	110.29(5)
O(2)–V(1)–O(4)	99.71(8)	O(1)–V(1)–O(3)	100.74(4)
O(3)–V(1)–O(4)	103.33(7)	O(2)–V(1)–O(3)	103.99(5)
O(2)–V(1)–N(3)	121.21(8)	O(1)–V(1)–N(2)	132.32(5)
O(3)–V(1)–N(3)	128.47(8)	O(2)–V(1)–N(2)	117.03(4)
O(4)–V(1)–N(3)	74.58(7)	O(3)–V(1)–N(2)	73.87(4)
O(2)–V(1)–N(1)	95.10(8)	O(1)–V(1)–N(1)	93.76(4)
O(3)–V(1)–N(1)	98.23(7)	O(2)–V(1)–N(1)	99.96(5)
O(4)–V(1)–N(1)	147.69(7)	O(3)–V(1)–N(1)	145.47(4)
N(3)–V(1)–N(1)	73.18(7)	N(2)–V(1)–N(1)	73.21(4)

and 1539–1534 (ν_{CN})] are in good agreement with the structures in scheme 1. The absence of a band in the 3150–3175 cm^{-1} region of the IR spectra of the free ligands suggests the absence of a "imineol" tautomer in the solid state [34, 35]. The elemental analyses, IR, UV-Vis, and NMR spectroscopy are consistent with the proposed mononuclear formulation of **1** and **2**.

3.2. *Description of crystal structures*

The molecular structures of **1** and **2**, including atom labeling diagrams, are shown in figures 1 and 2, respectively. Selected bond lengths and angles are given in table 2. Complex **1** crystallizes in *P21/c* space group while **2** *C2/C* space group. $[VO_2(PzOAP)] \cdot H_2O$ and $[VO_2(PzCAP)]$ are neutral and mononuclear. The asymmetric units of **1** and **2** contain four and eight molecules, respectively. The vanadium in each complex is coordinated to two nitrogens, one alkoxo oxygen, and two terminal oxo groups. PzOAP and PzCAP function as singly deprotonated tridentate ligands. The deprotonation is accompanied by tautomerization to the "iminol" form as shown in scheme 1. The Schiff bases are coordinated meridionally, occupying three equatorial positions. The remaining equatorial position is occupied by one of the two oxo groups (O3 for **1** and O1 for **2**). The apical position has the other oxo (O2 for **1** and **2**). The coordination geometry around vanadium is best described as square pyramidal with a slight distortion (addison parameters (τ) 0.33 for **1** and 0.22 for **2**) toward trigonal bipyramidal. The τ parameters of the complexes (0.33 for **1**, 0.22 for **2**) also support their square pyramidal geometry [36, 37], with **1** showing greater distortion

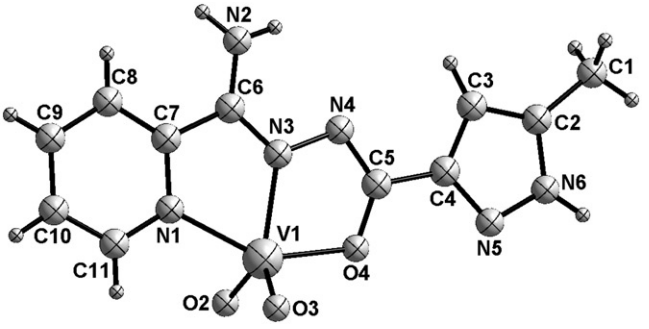


Figure 1. Structural representation and atom-numbering scheme of **1**.

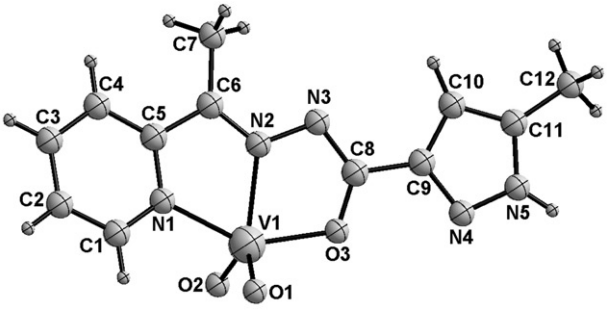


Figure 2. Structural representation and atom-numbering scheme of **2**.

than **2**. All bond angles comprising adjacent donors in the basal plane and V1 as well as any one donor atom, V1 and O3, i.e., O2–V1–O3, O3–V1–O4, N1–V1–O3 (for **1**) and O1–V1–O2, O1–V1–O3 (for **2**) deviate from the ideal value of 90° (table 2) and V1 is shifted from the square plane toward the apical oxygen (O2 for **1** and **2**) by 0.499 Å in **1** and 0.556 Å in **2**. The average V=O distances 1.630 Å in **1** and 1.619 Å in **2**, slightly longer than typical V=O double bond length of 1.595 Å, indicate that this bond length is associated with weak hydrogen-bonding interactions [38]. The V1–N1 and V1–N3 distances 2.144 and 2.037 Å in **1** and V1–N1 and V1–N2 distances 2.104 and 2.101 Å in **2**, respectively, are in accord with the literature values for V–N distances [38, 39]. For **1**, C5, C6, C7, C8, C9, C10, C11, N1, N3, N4, O4 are almost in the same plane (with maximum deviation of 0.069 Å) with the vanadium shifted by 0.021 Å out of that plane toward O3 while for **2**, C1, C2, C3, C4, C5, C6, C8, N1, N2, N3, O3 are also in the same plane (with maximum deviation of 0.109 Å) with vanadium shifted by 0.348 Å out of that plane toward O2 [40]. Hence, for **1**, due to this deviation, the conformation of the five-membered chelate ring containing V1, N3, N4, C5, and O4 is an envelope at V1. Cremer and Pople [41] puckering analysis shows that the other five-membered chelate ring containing V1, N1, N3, C6, and C7 also adopts an envelope conformation but in that case on C6 (with a deviation of 0.056 Å) from the mean plane containing V1, N1, N3, and C7. For **2**, conformation of the five-membered chelate ring containing V1, N2, N3, C8, and O3 is proposed to be an envelope on V1. The other five-membered chelate

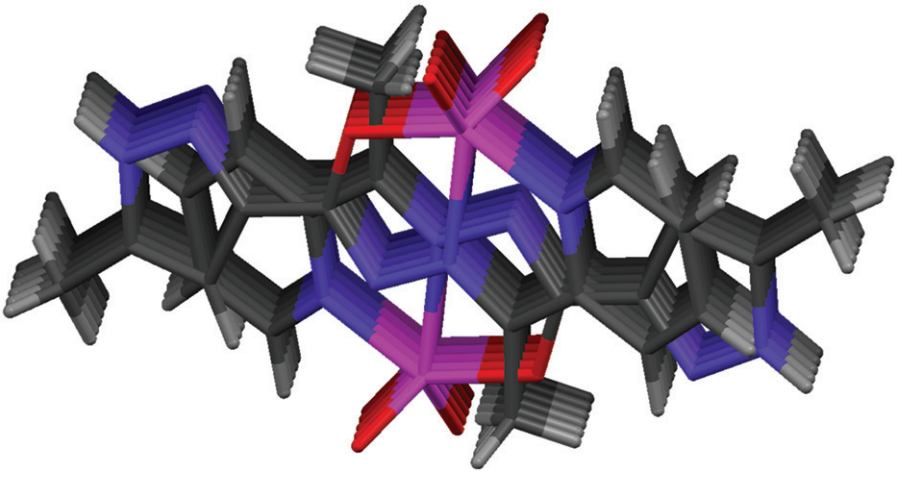


Figure 3. Packing diagram of **2**. View along the *c*-axis.

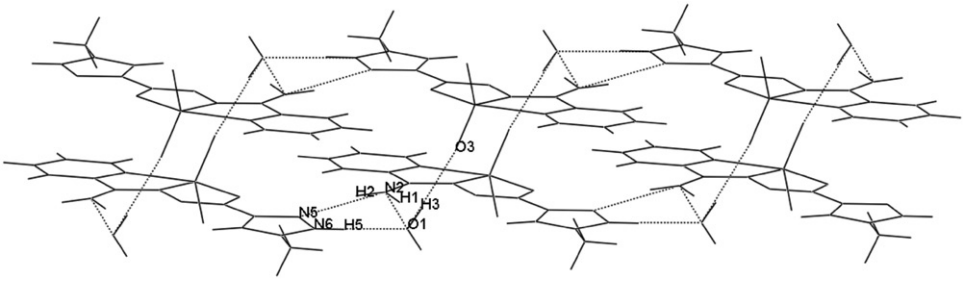


Figure 4. H-bonding pattern in **1**.

ring containing V1, N1, N2, C5, and C6 is also in an envelope conformation on C6 (with a deviation of 0.107 Å) from the mean plane containing V1, N1, N2, and C5. Intermolecular contacts which lead to the observed packing diagram of **2** are shown in figure 3. In the packing of **2**, the molecules are arranged in an opposed fashion, minimizing steric hindrance.

Complex **1** is stabilized through a network of weak H-bond interactions (figure 4). The details are presented in table 3. The H-bond distances between N2 and N5 [2.820 Å], O1 and O3 [2.798 Å], and N6 and O1 [2.817 Å] support a weakly H-bonded structure in **1** (figure 4). Similarly, the H-bond distance between N5 and O2#1 in **2** is 2.872 Å, indicating the presence of weak H-bonding interaction (figure 5).

3.3. *Characterization of the complexes*

The V(V) complexes have been prepared employing a V(IV) starting material, $VO(acac)_2$. Molecular dioxygen from air serves as the oxidant during the reaction. The two complexes gave satisfactory C, H, and N analyses.

Table 3. Details of hydrogen bond distances (Å) and angles (°).

Compounds	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
1	N2–H2···N5	0.88(3)	2.04(3)	2.820(3)	148(3)
	O1–H3···O3	0.78(3)	2.03(4)	2.798(2)	170(3)
	N6–H5···O1	0.89(3)	1.93(3)	2.817(2)	173(3)
	N2–H1···O1	0.88(3)	2.20(3)	3.027(3)	156(3)
2	N(5)–H(5A)···O(2)	0.88(3)	2.03(3)	2.872(3)	159(3)

Symmetry transformations used to generate equivalent atoms: **1**: $-1+x, y, z; -x, 1-y, -z$; **2**: $-x, -y, 1-z$.

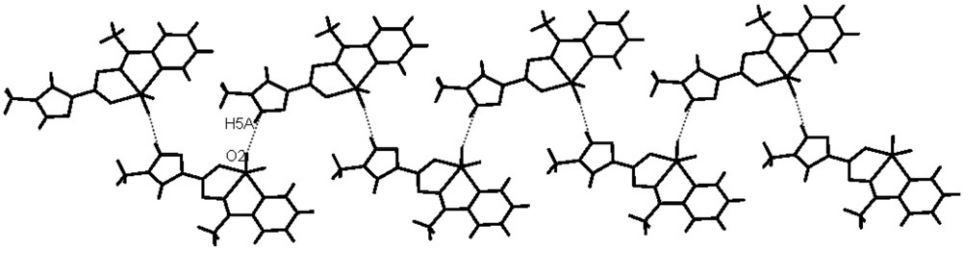


Figure 5. H-bonding pattern in **2**.

3.4. *IR spectra*

A comparative study of the IR spectral data of the reported complexes with those of the uncomplexed ligand gives information regarding bonding sites of the ligand. The complexes show a broad band in the 3400–2900 cm^{-1} region, probably arising from H-bonding between one of the V=O groups with one pyrazole N in **1** and between one of the V=O groups with one water in **2**. The IR band at 1539–1534 cm^{-1} in free PzOAP and PzCAP spectra, ν_{CN} shifts to a lower wavenumber by 31 cm^{-1} in **1** and 29 cm^{-1} for **2**, due to the coordination of azomethine [30]. A strong two-band pattern at 941–818 cm^{-1} is the signature of cis-dioxovanadium(V) [31], assigned to symmetric and asymmetric $\nu_{(O=V=O)}$ vibrations [32]. The same observations were reported in the literature [22]. IR spectra of the two complexes show an intense band at ~1070 cm^{-1}, indicating the presence of ν_{N-Npz} vibration. A strong band at ~1020 cm^{-1} in both complexes may be assigned to coordinated ν_{py}, which is also evident from X-ray crystallographic studies of **1** and **2**. An intense band at *ca* 1656 cm^{-1} characteristic for ν_{CO} in the two ligands shift to a lower wavenumber by *ca* 51 cm^{-1} after complexation, indicating that the oxygen of C=O coordinates in its deprotonated "imineol" form [30].

3.5. *Electronic spectra and DRS of 1 and 2*

The electronic absorption spectra of the complexes were carried out in DMF. The complexes have absorptions at 263 and 380 nm for **1** and 295 and 393 nm for **2**. The intense absorption around 279 nm corresponds to an intraligand transition, whereas the band around 386 nm is assignable to L–V ($d\pi$) LMCT [42, 43]. The diffuse reflectance spectra of the two complexes show one broad band at 410–425 nm.

3.6. *^{1}H-NMR spectra of 1 and 2*

The ^{1}H-NMR spectra (d_H ppm) in d_6-DMSO at 300 MHz of **1** and **2** give singlets at δ 2.46 (3H) and δ 2.23 (3H) assignable to C_5–CH_3 (ring pz) and singlets at δ 6.40 (1H) and δ 6.49 (1H) due to C_4–H (ring pz), respectively. A singlet at δ 7.75 (2H) for **1** and a singlet at δ 2.52 (3H) for **2** are ascribed to the terminal C–NH_2 and C–CH_3, respectively. A singlet at δ 10.05 (1H) for **1** and a singlet at δ 10.31 (1H) for **2** are ascribed to the pyrazolyl –NH proton. The absence of a singlet around δ 12.96 in **1** and δ 13.10 in **2** confirms enolization prior to complexation followed by deprotonation during complexation. This is also evident from the X-ray crystal structure studies.

4. Conclusion

We have prepared two V(V) complexes with pyrazole-derived Schiff-base ligands PzOAP and PzCAP. In complexes, the polytopic ligand in its "imineol" form is a monoanionic ONN donor, where the heterocyclic pyrazole nitrogens remain non-coordinated; the deprotonated "enol" oxygen participates in coordination. In Cu(II) salts, the pyrazole nitrogen takes part in the coordination forming 2×2 grid complexes. To make the alkoxide a donor, the two ligands undergo tautomerization to "imineol" form followed by a deprotonation during complexation with V(V). In the two complexes, V(V) is five-coordinate with alkoxide oxygen, the imine nitrogen, pyridine nitrogen, and two oxo groups. The two similar ligands produce identical coordination environments toward V(V).

Supplementary material

CCDC 743347 and 743348 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version.

Acknowledgments

S. Roy thanks CSIR, New Delhi, India for financial support by awarding senior research fellowship (Sanc. No. 09/028(0698)/2008-EMR-1, dated 14.03.2008). T.N. Mandal also acknowledges University Grants Commission (UGC), New Delhi, India for financial assistance.

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