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Journal of Molecular Structure 833 (2007) 133–144
Journal of MOLECULAR STRUCTURE
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Neutral dioxovanadium(V) complexes of biomimetic hydrazones *ONO* donor ligands of bioinorganic and medicinal relevance: Synthesis via air oxidation of bis(acetylaceto-nato)oxovanadium(IV), characterization, biological activity and 3D molecular modeling

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Received 13 July 2006; accepted 12 September 2006
Available online 13 November 2006

Abstract

The interaction of bis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2]$ with biomimetic hydrazone ONO donor ligands HL in 1:1 mole ratio [where, HL = *N*-(4′-benzoylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (bmphp-inH, **I**), *N*-(4′-butyrylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (bumphp-inH, **II**), *N*-(4′-acetylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (amphp-inH, **III**), *N*-(3′-methyl-1′-phenyl-4′-propionylidene-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (mphpp-inH, **IV**) and *N*-(4′-*iso*-butyrylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (*iso*-bumphp-inH, **V**)] in a mixed solvent (ethanol–methanol, 1:10) via aerial oxidation for 2–3 days yield dioxovanadium(V) complexes of composition $[VO_2(L)(H_2O)] \cdot H_2O$. The compounds so obtained were characterized on the basis of elemental analyses, thermogravimetry, vanadium determination, IR, Electronic, ^{51}V NMR, ^{1}H NMR and mass spectral studies. The 3D molecular modeling and analysis for bond lengths and bond angles have also been carried out for one of the representative compounds, $[VO_2(ampph\text{-}in)(H_2O)]$ (**3**).

Keywords: Neutral dioxovanadium(V) complexes; Biomimetic hydrazones; Bioinorganic; Medicinal relevance; 3D molecular modeling

1. Introduction

Vanadium is normally present at very low concentrations ($<10^{-8}$ M) in virtually all cells in plants and animals. Vanadium in oxidation states III, IV and V readily forms V–O bonds and comfortably binds N and S as well, forming chemically robust, coordination compounds. Vanadium(V) in particular, in stereochemically flexible-coordination geometries ranging from tetrahedral and octahedral to trigonal pyramidal and pentagonal bipyramidal is thermodynamically plausible [1]. The potential for redox interplay, whether V(V)/V(IV) or V(IV)/V(III), increases the versatility of these element in the biological milieu [2]. Vanadium may or may not play an essential role in normal mammalian metabolism [3], however, at pharmacological concentrations, as a potential therapeutic agent, it is attracting increasing attention [4,5].

The coordination chemistry of vanadium with multidentate ligands has achieved a special status in the last decade because of its catalytic [6,7] and medicinal [8–11] input. Structural and/or functional models for vanadate-dependent haloperoxidases, for vanadium nitrogenases and other biologically active vanadium compounds have further stimulated vanadium coordination chemistry [12–15]. The active site structures of the vanadate-dependent haloperoxidases have been revealed by X-ray diffraction studies.

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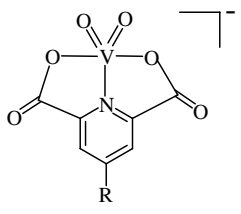
doi:10.1016/j.molstruc.2006.09.022

Accordingly, the vanadate ion is distorted towards a trigonal pyramid, thus providing a fifth coordination site which is occupied by N of a histidine, covalently linking the vanadate ion to the protein [16–18]. These enzymes lose their activity upon reduction or removal of vanadate. Re-oxidation, or reconstitution of the apo-enzymes with vanadate, fully restores their activity [12], demonstrating that vanadium(V) (VO^{3+} or VO_2^+) is essential for the catalytic activity. Different kinds of oxovanadium(V) complexes have been studied [19–55] in this context.

Dioxovanadium(V) complexes are commonly synthesized (i) by the reaction of vanadates with *ONO*-functional ligands in aqueous solution [20, 43–47] (ii) by the reaction of $[VO(OEt)_3]$ with appropriate ligands [51] or (iii) by oxidation of oxovanadium(IV) complexes with KNO_2 in H_2O/MeOH [52] and (iv) by the reaction of $[VO(acac)_2]$ (acacH = acetylacetone) or $VOSO_4$ with the ligands in non-aqueous or mixed solvent media followed by oxidation with O_2 [48–50,56].

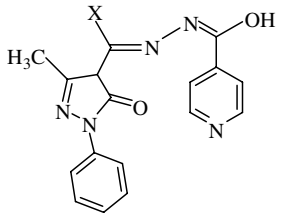
A wide range of vanadium complexes have been shown to have insulin mimetic properties in animal model systems and cell culture. Although most known insulin-like complexes contain vanadium in oxidation state IV, two classes of vanadium(V) compounds, (i) monoperoxovanadates $[VO(O_2)(H_2O)_2(L–L)]^{n-}$ $(n = 0, 1)$ [3] and diperoxovanadates $[VO(O_2)_2((L– L)]^{n-}$ $(n = 1, 2, 3)$ [3] and (ii) dioxovanadium(V) complexes [57–61], have recently been found to have insulin-like properties. The (pyridine-2,6-dicarboxylato)oxovanadate(V) and (4-hydroxypyridine-2,6-dicarboxylato)oxovanadate(V) are recently introduced by Crans et al. [55]. Oral administration of these compound is found to be effective in lowering both the hyperglycemia and hyperlipidemia in rats with streptozotocin (STZ)-induced diabetes (see Fig. 1).

In view of importance of vanadium compounds, and also extending the search for more efficacious compounds of vanadium with neutral charge (one of the desirable qualities of vanadium compounds to be useful as biomimetic drugs include neutral charge [4]), we present here the first synthesis and characterization of VO_2^+ complexes of aroylhydrazones, *N*-(4′-benzoylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (bmphp-inH), *N*-(4′-butyrylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (bumphp-inH), *N*-(4′-acetylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide



R = H(Pyridine-2,6-dicaboxylato)oxovanadate(V)
R = OH(4-hydroxypyridine-2,6-dicaboxylato)oxovanadate(V)

Fig. 1. Structures of (pyridine/4-hydroxypyridine-2,6-dicarboxylato)-oxovanadate(V).



X= -C_6H_5 (bmphp-inH)
-C_3H_7 (bumphp-inH)
-CH_3 (amphp-inH)
-C_2H_5 (mphpp-inH)
-*iso*-C_3H_7 (*iso*-bumphp-inH)

Fig. 2. Structures of aroylhydrazones.

(amphp-inH), *N*-(3′-methyl-1′-phenyl-4′-propionylidene-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (mphpp-inH) and *N*-(4′-*iso*-butyrylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide (*iso*-bumphp-inH) (Fig. 2). Spectral and structural aspects, biological activity of the compounds, 3D molecular modeling and analysis of bond lengths and bond angles for a representative compound are reported here.

2. Experimental

2.1. Materials

3-Methyl-1-phenyl-2-pyrazolin-5-one and vanadyl sulphate pentahydrate (Lancaster, UK), benzoyl chloride, acetyl chloride and propionyl chloride and acetylacetone (Thomas Baker Chemicals Limited, Mumbai), butyryl chloride (S.D. fine-Chem Limited, Mumbai), iso-butyryl chloride (E. Merck, Germany) and isonicotinic acid hydrazide (Aldrich chemical Co, USA), were used as supplied. All other chemicals used were of analytical reagent grade. $[VO(acac)_2]$ was prepared by the method of K.S. Patel [62].

2.2. Preparation of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one

4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (bmphp) was prepared by the interaction of 3-methyl-1-phenyl-2-pyrozoline-5-one in dioxane with calcium hydroxide and benzoyl chloride by the procedure reported by Jensen [63]. Following the same procedure, 4-butyryl-3-methyl-1-phenyl-2-pyrazolin-5-one (bumphp), 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one (amphp), 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one (mphpp), and 4-*iso*-butyryl-3-methyl-1-phenyl-4-pyrazolin-5-one (*iso*-bumphp) were prepared using butyryl chloride, acetyl chloride, propionyl chloride, and *iso*-butyryl chloride, respectively.

2.3. Synthesis of aroylhydrazones

The aroylhydrazones of isonicotinic acid hydrazide were prepared as follows: An ethanolic solution (25 mL) of isonicotinic acid hydrazide (0.685 g, 5 mmol) was added to the solution (~25 mL) of bmphp (1.390 g, 5 mmol), bumphp (1.220 g, 5 mmol), amphp (1.080 g, 5 mmol), mphpp (1.150 g, 5 mmol) or *iso*-bumpph (1.220 g, 5 mmol) in ethanol. The resulting mixture was refluxed with stirring for 3 h. A bright orange coloured precipitate was formed while

refluxing. It was filtered and washed several times with ethanol and dried in a desiccator over anhydrous $CaCl_2$.

2.4. Synthesis of dioxovanadium(V) complexes

A hot methanolic solution (25 mL) of $[VO(acac)_2]$ (0.265 g, 1 mmol) was added to the methanolic solution (~25 mL) of the respective Schiff base, bmphp-inH (0.397 g, 1 mmol), bumphp-inH (0.363 g, 1 mmol), amphp-inH (0.335 g, 1 mmol), mphpp-inH (0.349, 1 mmol) or *iso*-bumphp-inH (0.363, 1 mmol). The resulting solution was refluxed for 4 h. It was cooled and filtered. The filtrate was collected and the residue was dissolved in ethanol–methanol (1:10) and again filtered. The filtrate thus obtained is again added to the above filtrate which is then kept for air oxidation at room temperature for 3–4 days, with occasional shaking. The resulting compound is collected and recrystallized from methanol.

2.5. Analysis

Carbon, hydrogen and nitrogen were determined microanalytically at RSIC, IIT, Bombay. The vanadium content of the synthesized compounds was determined by the following method.

A 100 mg sample of the compound was placed in a silica crucible, decomposed by gentle heating and then adding 1–2 mL of concentrated HNO_3, 2–3 times. An orange coloured mass (V_2O_5) was obtained after decomposition and complete drying. It was dissolved in the minimum amount of dilute H_2SO_4, and the solution so obtained was diluted with distilled water to 100 mL in a measuring flask. The vanadium content of each of the complexes was determined volumetrically [64] using 0.02 M $KMnO_4$ solution as an oxidizing agent in the presence of sulfurous acid. Based on the following redox reactions, the amount of vanadium in the sample solution was calculated using the standard [64] relationship: 1 mL of 0.02 M $KMnO_4 = 0.0051$ g vanadium.

$$2VO_3^{-*} + H_2SO_4 + 4H^+ \rightarrow 2VO^{2+} + SO_4^{2-} + 3H_2O$$

$$MnO_4^- + 5VO^{2+} + 6H_2O \rightarrow 5\ VO_3^- + Mn^{2+} + 12H^+$$

*In aqueous solution V_2O_5 exists as vanadate (VO_3^-) [64].

2.6. Molecular modeling studies

The 3 D molecular modeling of one synthesized compound was carried out on CS Chem 3D Ultra Molecular Modeling and Analysis Programme [65]. It is an interactive graphics programme that allows rapid structure building, geometry optimization and molecular display. It has the ability to handle transition metal compounds.

2.7. Physical methods

The following physical methods were used to determine the structure of the ligand and their resulting dioxovanadium(V) complexes. Solid states IR spectra were recorded in KBr pellets using Perkin–Elmer model 1620 FT-IR spectrophotometer. Electronic spectra were recorded using ATI Unicam UV-2-100 UV/visible spectrophotometer. Thermogravimetric analysis of the complexes was performed on a Perkin–Elmer (Pyris Diamond) Thermoanalyser. C, H and N were determined using Heraeus Carlo Erba 1108 elemental analyser. The ^{51}V NMR spectra were recorded in DMSO on a Bruker Mass Spectrometer. The ^1H NMR in $CDCl_3$ was recorded on a Bruker DRX-300, 300 MHz FT NMR, while mass spectrum was recorded over Jeol SX-102 (FAB). The biological activity test was performed at Yeast Biotechnology Laboratory in our University.

3. Results and discussion

The dioxovanadium(V) complexes in the present investigation were prepared according to the following equations:

$$[VO(acac)_2] + LH \xrightarrow[\text{Reflux}]{\text{Methanol}} [VO(L)(acac)] + acacH$$

$$[VO(L)(acac)] \xrightarrow[\text{Aerial oxidation}]{\text{Ethanol-Methanol(1:10)}} [VO(L)(H_2O)(acac)]\cdot H_2O + acac^-$$

where LH = bmphp-inH, bumphp-inH, amphp-inH, mphpp-inH or *iso*-bumphp-inH and acacH = acetylacetone.

These complexes are found to be air stable. They are thermally stable and their decomposition temperatures are given in Table 4. These are insoluble in most of the common organic solvents but are fairly soluble in DMF, DMSO and acetonitrile. The formulations of these complexes are based on their elemental analysis, infrared spectra, magnetic measurements, ESR, thermogravimetric analysis and electronic spectral studies.

3.1. Infrared spectral studies

The important infrared spectral bands of the ligands as well as complexes, and their tentative assignments are given in Tables 1 and 3, respectively. The aroylhydrazones used in the present investigation may exist in four keto/enol forms (Fig. 3). The infrared spectra of all the aroylhydrazones exhibit a weak broad band centered at 3400–3550 cm^{-1} for ν(OH), a medium band at 1632–1640 cm^{-1} for ν(C=O) (pyrazolone skeleton) and a strong band due to ν(C=N) (azomethine) at 1590–1614 cm^{-1}. Moreover, the absence of ν(NH) and ν(C=O) due to isonicotinic acid hydrazide part of the ligand was observed in the IR spectra of all the ligands. These two observations suggest that the ligands under the present investigation exist in the enol form (I) in the solid state (Fig. 3).

These hydrazones possess seven potential donor sites: (i) The ring nitrogen N^1, (ii) the ring nitrogen N^2, (iii) the cyclic carbonyl oxygen (pyrazolone skeleton) (iv) the enolic (OH) oxygen (v) the azomethine nitrogen, (vi) the hydrazide nitrogen, and (vii) pyridine ring nitrogen. The coordination of the ring nitrogen N^1 is unlikely due to possible

Table 1
Analytical data, colours, melting points, and important IR spectral bands (cm^{-1}) and their assignments

S. no.	Aroylhydrazone (Empirical Formula) (M. W.)	Analysis, Found (Calc. %)			Colour	M. P.	ν(C=O) (pyrazo. skeleton)	ν(C=N) (azometh.)	ν(–OH)	ν(N–N) (amide)	ν(C=N) (pyrazol.) skeleton)
		C	H	N							
1	bmphp-inH ($C_{23}H_{19}N_5O_2$)(397)	69.30 (69.52)	4.71 (4.79)	17.55 (17.63)	Tractor orange	210	1638	1607	3450	1002	1580
2	bumphp-inH ($C_{20}H_{21}N_5O_2$)(363)	66.60 (66.12)	5.66 (5.79)	19.16 (19.28)	Tractor orange	240	1637	1614	3540	1006	1580
3	amphp-inH ($C_{18}H_{17}N_5O_2$)(335)	64.60 (64.48)	5.05 (5.07)	20.46 (20.90)	Tractor orange	258	1637	1608	3412	1020	1583
4	mphpp-inH ($C_{19}H_{19}N_5O_2$)(349)	64.97 (65.33)	5.36 (5.44)	20.12 (20.06)	Tractor orange	200	1640	1606	3400	1046	1580
5	*iso*-bumphp-inH ($C_{20}H_{21}N_5O_2$)(363)	66.35 (66.12)	5.70 (5.78)	19.23 (19.28)	Bright orange	140	1632	1590	3432	1010	1585

Table 2
Analytical data and some physical properties of the synthesized complexes

S. no.	Complex (Empirical Formula)(M.W.)	Found/calculated (%)				Colour	Decomposition temperature (°C)	Λ_M (ohm^{-1} cm^2 mol^{-1}) (in DMF)	Yield (%)
		C	H	N	V				
1	$[VO_2(bmphp\text{-}in)(H_2O)]\cdot H_2O$ ($C_{23}H_{22}N_5O_6V$) (514.94)	53.31 (53.60)	4.19 (4.27)	13.35 (13.59)	9.96 (9.89)	Middle buff	220	13	45
2	$[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O$ ($C_{20}H_{24}N_5O_6V$) (480.94)	49.78 (49.90)	4.86 (4.99)	14.24 (14.55)	10.76 (10.59)	Golden brown	200	12.5	48
3	$[VO_2(amphp\text{-}in)(H_2O)]\cdot H_2O$ ($C_{18}H_{20}N_5O_6V$) (452.94)	47.46 (47.69)	4.26 (4.42)	15.35 (15.45)	11.50 (11.25)	Tractor orange	225	17	38
4	$[VO_2(mphpp\text{-}in)(H_2O)]\cdot H_2O$ ($C_{19}H_{22}N_5O_6V$) (466.94)	48.55 (48.83)	4.64 (4.71)	14.67 (14.99)	10.42 (10.91)	Middle buff	218	18.8	40
5	$[VO_2(iso\text{-}bumphp\text{-}in)(H_2O)]\cdot H_2O$ ($C_{20}H_{24}N_5O_6V$) (480.94)	49.59 (49.90)	4.85 (4.99)	14.37 (14.55)	10.88 (10.59)	Golden yellow	205	20	40

Table 3
Some important IR spectral bands (cm^{-1}) of the synthesized complexes

S. no.	Complex	$\nu_s(VO_2)$	$\nu_{as}(VO_2)$	ν(C=O) (cyclic carbonyl)	ν(C=N) (azomethine)	$\delta(H_2O)$	ν(N–N)	ν(–OH)
1	$[VO_2(bmphp\text{-}in)(H_2O)]\cdot H_2O$	944	883	1560	1586	1629	1026	3440, 3460
2	$[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O$	948	892	1570	1592	–	1020	3400–3500
3	$[VO_2(amphp\text{-}in)(H_2O)]\cdot H_2O$	939	895	1565	1579	–	1023	3383
4	$[VO_2(mphpp\text{-}in)(H_2O)]\cdot H_2O$	972	826	1576	1590	1630	1061	3400
5	$[VO_2(iso\text{-}bumphp\text{-}in)(H_2O)]\cdot H_2O$	911	829	1560	1576	1632	1023	3300–3500

zwitterion [66] formation due to cyclic amide which reduces the election density on N^1. Further, this process increases the electron density of the cyclic carbonyl oxygen. Coordination of N^1 is also unfavourable because of the greater steric demand of the phenyl ring.

The ring nitrogen N^2 in this ligand is found to be inert towards coordination to vanadium as revealed by the appearance of the $\nu(C{=}N^2)$ (cyclic) mode at almost the same position [here merged with ν(C=N) (azomethine)] compared with the $\nu(C{=}N^2)$ (cyclic) at 1580–1585 cm^{-1} of the uncoordinated ligand, after complexation. The band due to ν(C=O) (hydrazide moiety) at approximately 1670 cm^{-1} is absent in all the complexes indicating the enolization of the carbonyl group. Instead, a new band appears at 1106–1163 cm^{-1} due to coordination of ν(C–O enolic).

The ν(C=O) mode of the cyclic carbonyl group observed at 1632–1640 cm^{-1} in the ligands is shifted to lower wave numbers and appears at 1560–1576 cm^{-1} in these complexes. This suggests the bonding of the cyclic carbonyl oxygen [67] to vanadium in all these complexes. The aroylhydrazones under discussion display a sharp and strong band due to ν(C=N) of the azomethine group at 1590–1614 cm^{-1}. The observed low energy shift of this band in the complexes at 1576–1592 cm^{-1} suggests the coordination of the azomethine nitrogen to vanadium. This is further supported by shifting [68,69] of the ν(N–N) from 1002–1046 cm^{-1} to 1020–1061 cm^{-1} in the complexes. The coordination of azomethine nitrogen, cyclic ring carbonyl oxygen and enolic oxygen as concluded from the above discussions is favourable in the light of one 5-membered and one 6-membered chelate rings with the central

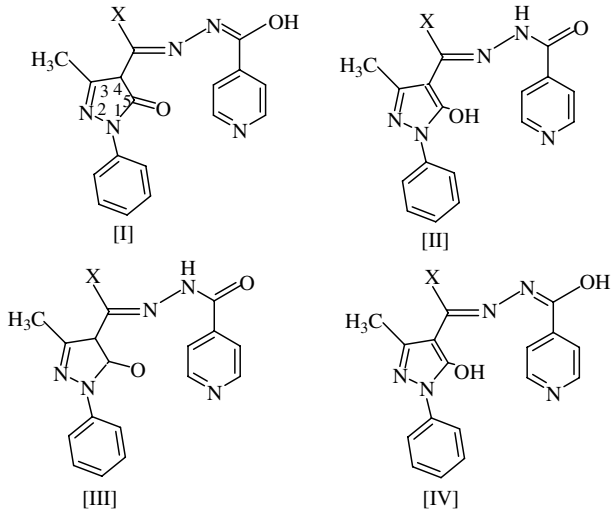


Fig. 3. Different keto-enol forms of the aroylhydrazones.

metal vanadium. In view of this, the coordination of hydrazide nitrogen and pyridine ring nitrogen is ruled out. The overall IR spectral studies conclude that the aroylhydrazones used in the present study behave as monobasic tridentate ONO-ligands.

The metal complexes also show two medium bands or one broad band (see Table 2) due to ν(OH) because of the presence of lattice/coordinated water in them.

3.2. Conductance measurements

The observed molar conductances (12.5–20 $ohm^{-1}\,cm^2\,mol^{-1}$) in 10^{-3} molar DMF solutions of these complexes are given in Table 2, and are consistent with the non-electrolytic nature of the complexes. Such a non-zero molar conductance value for each of the complex in the present study is most probably due to the strong donor capacity of DMF, which may lead to the displacement of anionic ligand and change of electrolyte [70] type.

3.3. ^{51}V NMR spectra

The ^{51}V NMR spectra of two representative compounds $[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O$ and $[VO_2(bmphp\text{-}in)(H_2O)]$ (Figs. 4 and 5) were recorded in DMSO-d_6. The complexes exhibit a strong resonance at ca. −508.81 and −508.96, respectively, as expected for the dioxovanadium(V) complexes having a mixed O/N donor set [12].

3.4. ^{1}H NMR spectra

Proton NMR spectrum of one representative compound, $[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O$ was recorded in $CDCl_3$. The absence of the enolic (–OH) proton signals at approximately 12 ppm and the hydrazone (–NH) proton signal at approximately 11 ppm in the complex indicates the coordination of enolic oxygen to the metal ion after deprotonation. The

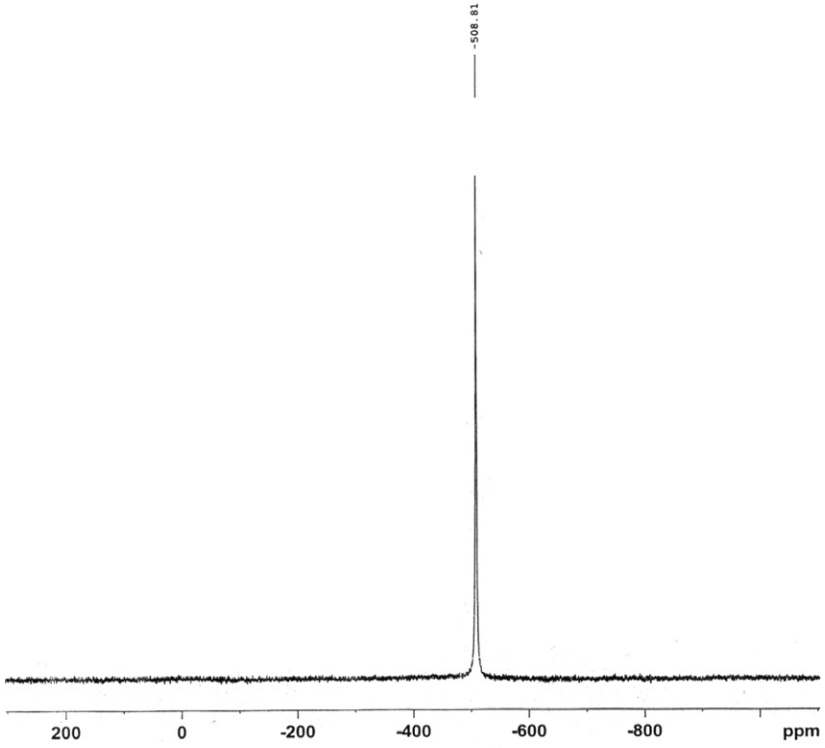


Fig. 4. ^{51}V NMR spectrum of compound $[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O$.

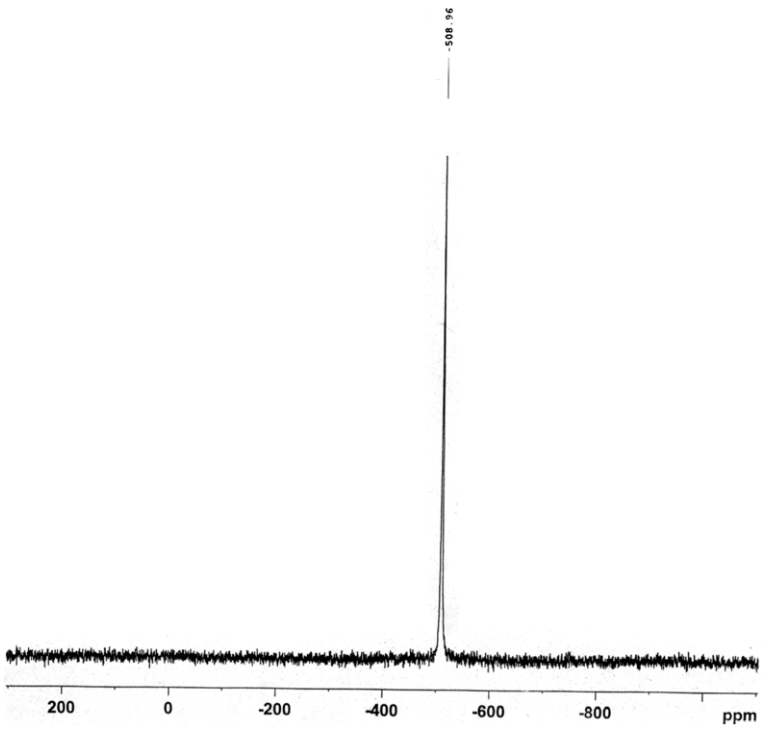


Fig. 5. ^{51}V NMR spectrum of compound $[VO_2(bmphp\text{-}in)(H_2O)] \cdot H_2O$.

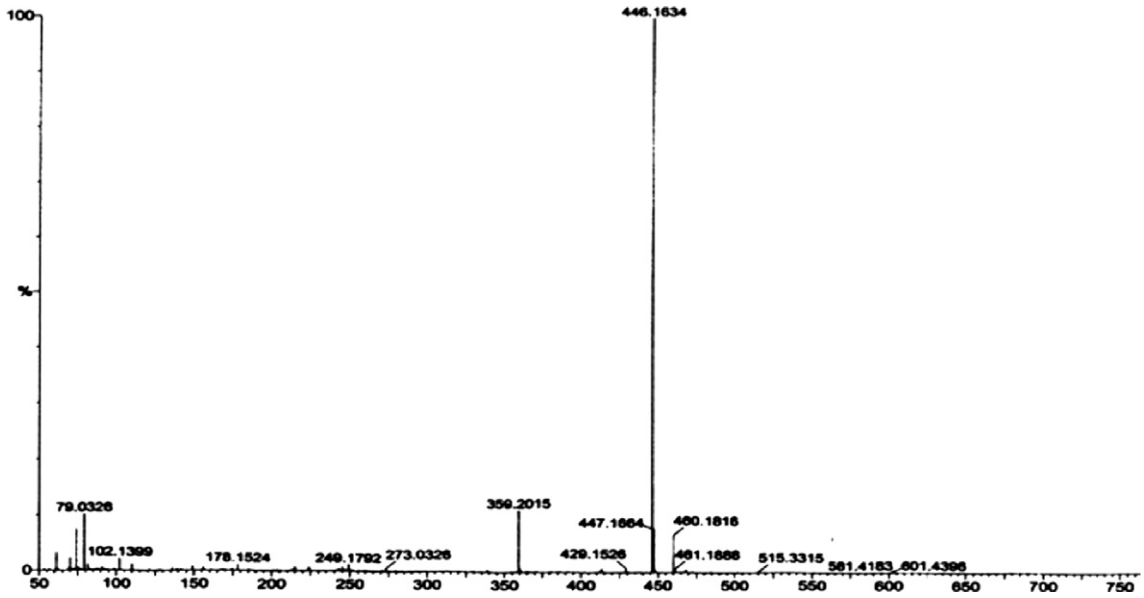


Fig. 6. Mass spectrum of $[VO_2(bumphp\text{-}in)(H_2O)] \cdot H_2O$.

proton signals due to aromatic protons of the ligand in the complex compound appeared at 7.2–7.9 ppm. The two proton signals at 1.5–1.6 ppm and 2.4 ppm may be due to butyryl and methyl group, respectively, present in the ligand.

3.5. Mass spectral studies

The mass spectrum (Fig. 6) of one representative compound, $[VO_2(bumphp\text{-}in)\text{-}(H_2O)] \cdot H_2O$ was recorded. The appearance of a molecular ion peak at 446.1634 m/z is consistent with the molecular mass of the present compound excluding two water molecules present therein, which are supposed to be lost before ionization. This confirms the formula weight, and hence the molecular composition of the synthesized compound.

3.6. Electronic spectral studies

The electronic spectra of 4 compounds, namely, 1, 2, 3 and 4 were recorded in 10^{-4} M DMF solution and their

Table 4
Electronic spectral data of the synthesized complexes

Compound no.	Compound	λ_{Max} (nm)	ν (cm^{-1})	(ε, L cm^{-1} mol^{-1})	Peak assignment
1	$[VO_2(bmphp\text{-}in)(H_2O)]\cdot H_2O$	293	34,129	34,700	Intra-ligand transitions
		310	32,258	34,370	
		357	28,011	36,460	
		365	27,397	36,290	
		415	24,096	28,980	LMCT
2	$[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O$	255	39,215	9900	Intra-ligand transitions
		278	35,971	33,090	
		365	27,397	35,870	
		399	25,062	27,760	LMCT
3	$[VO_2(amphp\text{-}in)(H_2O)]\cdot H_2O$	254	39,370	9460	Intra-ligand transitions
		274	36,496	28,540	
		368	27,174	23,900	
		390	25,641	24,590	LMCT
4	$[VO_2(mphpp\text{-}in)(H_2O)]\cdot H_2O$	256	39,062	9910	Intra-ligand transitions
		286	34,965	33,490	
		354	28,248	35,380	
		365	27,397	35,600	
		415	24,096	28,200	LMCT
Ref. [68]	$[VO_2(acpy\text{-}bhz)(DMF)]$	236	42,372	4703	Intra-ligand transitions
		274	36,496	18,999	
		392.5	25,477	22,041	LMCT
Ref. [71]	$K[VO_2(Clsal\text{-}iNH)(H_2O]$ (methanol)	235	42,553	20,730	Intra-ligand transitions
		279	35,842	10,085	
		316.5	31,595	9600	
		410.5	24,360	6100	LMCT

results are shown in the Table 4. All the complexes displayed three to four intra-ligand transitions in the UV region, which were present in the ligands at some higher wavelengths. Dioxovanadium(V) complexes have a $3d^0$ configuration, and d–d bands are therefore not expected. The additional one spectral peak at 390–415 nm in all the complexes is due to ligand to metal charge transfer (LMCT) transitions. These results are comparable to the data reported elsewhere [68,71], for dioxovanadium(V) compounds.

3.7. Thermogravimetric analysis

The TG curve of a representative compound $[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O$ (**2**) shows a weight loss of 3.41% at 66 °C corresponding to the loss of one lattice water molecule (calcd. 3.74%) from the complex. The second weight loss at 130 °C was observed to be 3.63% (calcd. 3.89%) corresponding to the elimination of one coordinated water molecule. It shows a final weight loss between 395 and 469 °C leaving to a constant value corresponding to the residual mass of V_2O_5 at 580 °C (40.68%) which matches the theoretical value (40.87%). The following equations represent the above decomposition steps:

$$[VO_2(bumphp\text{-}in)(H_2O)]\cdot H_2O \xrightarrow{66\,^{\circ}C} [VO_2(bumphp\text{-}in)(H_2O)] + H_2O\ (Lattice)$$

$$[VO_2(bumphp\text{-}in)(H_2O)] \xrightarrow{130\,^{\circ}C} [VO_2(bumphp\text{-}in)] + H_2O\ (Coordinated)$$

$$[VO_2(bumphp\text{-}in)] \xrightarrow{580\,^{\circ}C} V_2O_5\ (Residue)$$

3.8. Biological activity

Determination of the biological activity of ligand, bumphp-inH and compound, $[VO_2(bumphp\text{-}in)(H_2O)]$ (**2**) was carried out *in vitro* at 0.2 mmol concentration against fungi *Aspergillus flavus* and yeast *Saccharomyces cerevisiae* in 250 mL conical flasks with 100 mL volumes of a sterile

Table 5(a)
Biological activity against yeast

S. no.	Flask	OD on 5th day (at 660 nm[a])	I% on 5th day	OD on 7th day (at 660 nm[a])	I% on 7th day
1	Control	2.500	0	3.163	0
2	Ligand	2.500	0	0.748	76.35
3	Complex	1.822	27.12	0.269	91.50

[a] λ_{max} for yeast.

Table 5(b)
Biological activity against fungi

S. no.	Flask	Culture weight on 5th day (in g)	I% on 5th day	Culture weight on 7th day (in g)	I% on 7th day
1	Control	0.30	0	0.388	0
2	Ligand	0.22	26.66	0.148	61.85
3	Complex	0.24	20	0.317	18.29

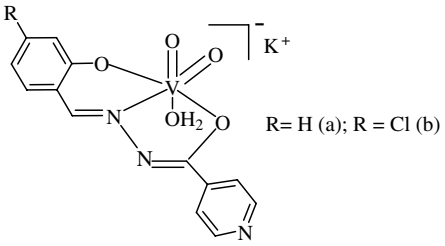


Fig. 7. Structures of $K[VO_2(sal\text{-}iNH)(H_2O)]$ and $K[VO_2(Clsal\text{-}iNH)(H_2O)]$.

NDM [72] medium containing (w/v, %): $(NH_4)_2SO_4$ (0.25), yeast extract (0.25), KH_2PO_4 (0.5), $MgSO_4 \cdot 7H_2O$ (0.05), $CaCl_2 \cdot 2H_2O$ (0.013) and glucose (**2**). The biological activity was enhanced against yeast and reduced against fungi after complexation. The amount of growth inhibition (Tables 5(a) and 5(b)) was determined by the following expression:

$$I\% = (C\text{-}T)/C \times 100$$

where, I, inhibition; C, growth of control plates; T, growth of treated plates.

3.8.1. Yeast

The greater toxicity of the metal complex compared to the free ligand can be explained on the basis of chelation theory. Chelation reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. This increases the lipophilic

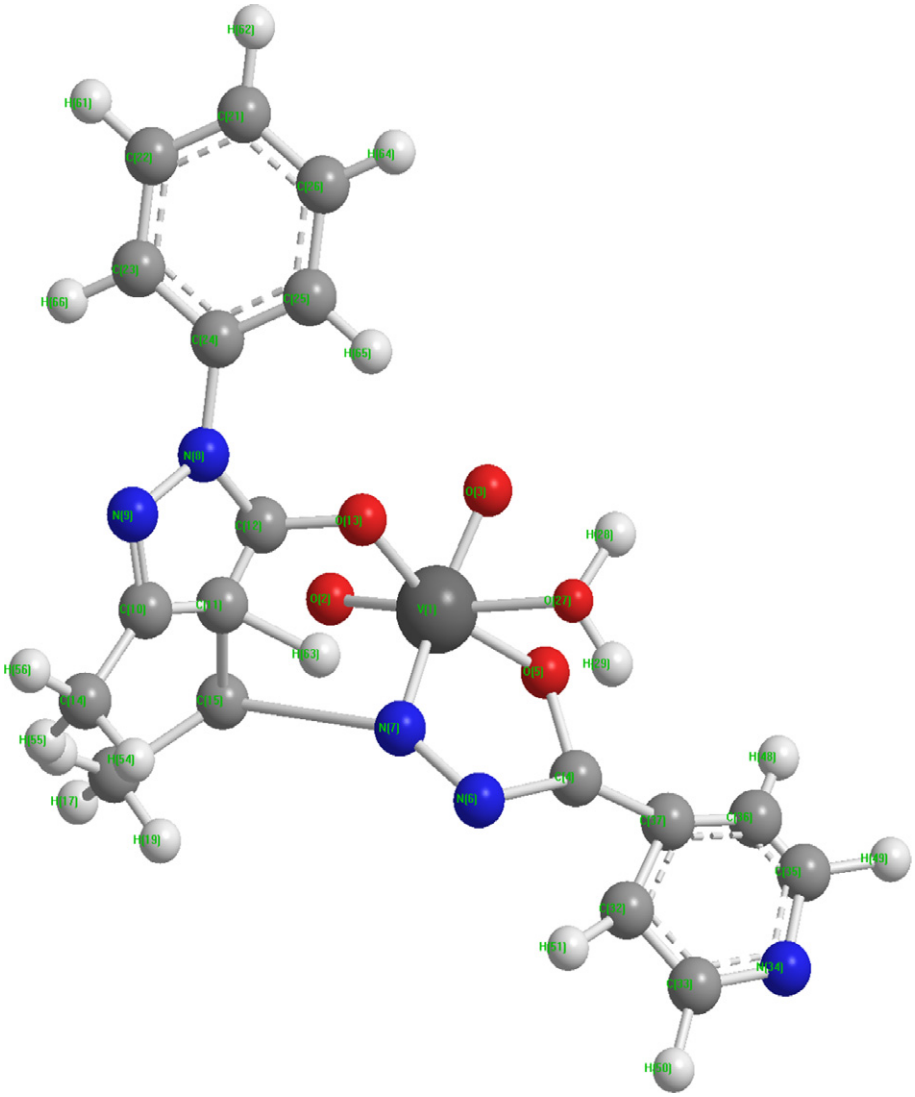


Fig. 8. 3D structure of compound $[VO_2(amphp\text{-}in)(H_2O)] \cdot H_2O$ (**3**).

Table 6
Various bond lengths of compound $[VO_2(amphp\text{-}in)(H_2O)]\cdot H_2O$ (**3**)

S. no.	Atoms	Actual bond length	Optimal bond length
1	V(1)–O(2)	2.013	2.013
2	V(1)–O(3)	1.655	1.655
3	V(1)–O(5)	2.009	2.009
4	V(1)–N(7)	1.906	1.906
5	V(1)–O(13)	1.882	1.882
6	V(1)–O(27)	2.006	2.006
7	C(4)–O(5)	1.505	1.505
8	C(4)–N(6)	2.543	2.543
9	C(4)–C(37)	1.854	1.854
10	N(6)–N(7)	1.496	1.496
11	N(7)–C(15)	2.81	2.81
12	N(8)–N(9)	1.426	1.426
13	N(8)–C(12)	1.47	1.47
14	N(8)–C(24)	1.462	1.462
15	N(9)–C(10)	1.26	1.26
16	C(10)–C(11)	1.409	1.409
17	C(10)–C(14)	1.497	1.497
18	C(11)–C(12)	1.174	1.174
19	C(11)–C(15)	1.866	1.866
20	C(11)–H(63)	1.47	1.47
21	C(12)–O(13)	1.402	1.402
22	C(14)–H(54)	1.113	1.113
23	C(14)–H(55)	1.113	1.113
24	C(14)–H(56)	1.113	1.113
25	C(15)–C(16)	1.751	1.751
26	C(16)–H(17)	1.113	1.113
27	C(16)–H(18)	1.113	1.113
28	C(16)–H(19)	1.113	1.113
29	C(21)–C(22)	1.42	1.42
30	C(21)–C(26)	1.42	1.42
31	C(21)–H(62)	1.1	1.1
32	C(22)–C(23)	1.42	1.42
33	C(22)–H(61)	1.1	1.1
34	C(23)–C(24)	1.42	1.42
35	C(23)–H(66)	1.1	1.1
36	C(24)–C(25)	1.42	1.42
37	C(25)–C(26)	1.42	1.42
38	C(25)–H(65)	1.1	1.1
39	C(26)–H(64)	1.1	1.1
40	O(27)–H(28)	1.078	–
41	O(27)–H(29)	0.952	–
42	C(32)–C(33)	1.316	1.42
43	C(32)–C(37)	1.443	1.42
44	C(32)–H(51)	1.2	1.1
45	C(33)–N(34)	1.531	1.358
46	C(33)–H(50)	1.197	1.1
47	N(34)–C(35)	1.382	1.358
48	C(35)–C(36)	0.943	1.42
49	C(35)–H(49)	1.301	1.1
50	C(36)–C(37)	1.437	1.42
51	C(36)–H(48)	0.921	1.1

character of the metal complex, which subsequently favours its permeation through the lipoid layers of organism cell membrane. Furthermore, the mode of action of compounds may involve the formation of a hydrogen bond through the >C=N (azomethine group) with the active centres of the cell constituents resulting in an interference with the normal cell process.

Table 7
Various bond angles of compound $[VO_2(amphp\text{-}in)(H_2O)]\cdot H_2O$ (**3**)

S. no.	Atoms	Actual bond angles	Optimal bond angles
1	O(2)–V(1)–O(3)	97.842	72.172
2	O(2)–V(1)–O(5)	98.965	124.396
3	O(2)–V(1)–N(7)	105.165	101.719
4	O(2)–V(1)–O(13)	89.782	113.233
5	O(2)–V(1)–O(27)	157.728	124.84
6	O(3)–V(1)–O(5)	87.991	89.322
7	O(3)–V(1)–N(7)	153.078	109.002
8	O(3)–V(1)–O(13)	77.121	109.003
9	O(3)–V(1)–O(27)	68.067	108.818
10	O(5)–V(1)–N(7)	101.803	119.998
11	O(5)–V(1)–O(13)	163.676	119.998
12	O(5)–V(1)–O(27)	64.571	120
13	N(7)–V(1)–O(13)	89.026	120.005
13	N(7)–V(1)–O(27)	93.359	119.996
15	O(13)–V(1)–O(27)	103.009	119.998
16	O(5)–C(4)–N(6)	106.772	120.001
17	O(5)–C(4)–C(37)	99.995	120.003
18	N(6)–C(4)–C(37)	153.213	119.995
19	V(1)–O(5)–C(4)	108.849	120.001
20	C(4)–N(6)–N(7)	89.679	120.003
21	V(1)–N(7)–N(6)	119.209	119.995
22	V(1)–N(7)–C(15)	80.806	120.007
23	N(6)–N(7)–C(15)	149.907	119.996
24	N(9)–N(8)–C(12)	110.997	119.996
25	N(9)–N(8)–C(24)	124.504	119.998
26	C(12)–N(8)–C(24)	124.497	120.005
27	N(8)–N(9)–C(10)	104.501	119.995
28	N(9)–C(10)–C(11)	105.001	112.745
29	N(9)–C(10)–C(14)	122.603	116.651
30	C(11)–C(10)–(14)	132.381	109.524
31	C(10)–C(11)–(12)	123.032	106.536
32	C(10)–C(11)–(15)	119.662	100.145
33	C(10)–C(11)–(63)	123.476	152.281
34	C(12)–C(11)–(15)	110.446	116.994
35	C(12)–C(11)–(63)	89.089	117.772
36	C(15)–C(11)–(63)	79.922	123.845
37	N(8)–C(12)–C(11)	96.458	122.628
38	N(8)–C(12)–O(13)	110.502	120.606
39	C(11)–C(12)–(13)	115.218	117.942
40	V(1)–O(13)–C(12)	110.54	121.446
41	C(10)–C(14)–(54)	109.998	122.329
42	C(10)–C(14)–(55)	109.989	111.609
43	C(10)–C(14)–(56)	109.995	123.95
44	H(54)–C(14)–(55)	109.005	67.357
45	H(54)–C(14)–(56)	109.002	158.646
46	H(55)–C(14)–(56)	108.823	129.027
47	N(7)–C(15)–C(11)	72.172	108.8
48	N(7)–C(15)–C(16)	124.396	108.8
49	C(11)–C(15)–C(16)	101.719	109.51
50	C(15)–C(16)–H(17)	113.233	110
51	C(15)–C(16)–H(18)	124.84	110
52	C(15)–C(16)–H(19)	89.322	110
53	H(17)–C(16)–H(18)	109.002	109
54	H(17)–C(16)–H(19)	109.003	109
55	H(18)–C(16)–H(19)	108.818	109
56	C(22)–C(21)–C(26)	119.998	120
57	C(22)–C(21)–H(62)	119.998	120
58	C(26)–C(21)–H(62)	120	120
59	C(21)–C(22)–C(23)	120.005	120
60	C(21)–C(22)–H(61)	119.996	120
61	C(23)–C(22)–H(61)	119.998	120
62	C(22)–C(23)–C(24)	120.001	120

(*continued on next page*)

Table 7 (*continued*)

S. no.	Atoms	Actual bond angles	Optimal bond angles
63	C(22)–C(23)–H(66)	120.003	120
64	C(24)–C(23)–H(66)	119.995	120
65	N(8)–C(24)–C(23)	120.001	120
66	N(8)–C(24)–C(25)	120.003	120
67	C(23)–C(24)–C(25)	119.995	120
68	C(24)–C(25)–C(26)	120.007	120
69	C(24)–C(25)–H(65)	119.996	120
70	C(26)–C(25)–H(65)	119.996	120
71	C(21)–C(26)–C(25)	119.998	120
72	C(21)–C(26)–H(64)	120.005	120
73	C(25)–C(26)–H(64)	119.995	120
74	V(1)–O(27)–H(28)	112.745	–
75	V(1)–O(27)–H(29)	116.651	–
76	H(28)–O(27)–H(29)	109.524	
77	C(33)–C(32)–C(37)	106.536	120
78	C(33)–C(32)–H(51)	100.145	120
79	C(37)–C(32)–H(51)	152.281	120
80	C(32)–C(33)–N(34)	116.994	123.5
81	C(32)–C(33)–H(50)	117.772	120
82	N(34)–C(33)–H(50)	123.845	116.5
83	C(33)–N(34)–C(35)	122.628	115
84	N(34)–C(35)–C(36)	120.606	123.5
85	N(34)–C(35)–H(49)	117.942	116.5
86	C(36)–C(35)–H(49)	121.446	120
87	C(35)–C(36)–C(37)	122.329	120
88	C(35)–C(36)–H(48)	111.609	120
89	C(37)–C(36)–H(48)	123.95	120
90	C(4)–C(37)–C(32)	67.357	121.4
91	C(4)–C(37)–C(36)	158.646	121.4
92	C(32)–C(37)–C(36)	129.027	120

3.8.2. Fungi

The >C═N groups in the ligand are free and, therefore, the ligand shows higher toxicity as it can easily combine with the fungi cells to check growth. On the other hand, in metal complex, this group is not free to inhibit cell growth, as they are involved in bond formation with the metal ions. Hence, the toxicity of metal complex decreases.

3.9. 3D Molecular modeling and analysis

In view the monomeric hexa-coordination of all the complexes, and also the well established octahedral structure [11] of dioxovanadium(V) complexes, K[VO_2(sal-iNH)(H_2O)] (a) and K[VO_2(Clsal-iNH)(H_2O)] (b) (Fig. 7) involving *N*-isonicotinamido-salicylaldimines (ONO donor) ligand (similar to ONO donor aroylhydrazone ligands in the present investigation), the 3D molecular modeling of one of the representative compounds, viz., [VO_2(amphp-in)(H_2O)] cdot H_2O (**3**), was carried out with the CS Chem 3D Ultra Molecular Modeling and Analysis Programme [65] based on its octahedral structure. The details of bond lengths, bond angles and dihedral angles as per the 3D structure (Fig. 8), are given in Tables 6–8, respectively. For convenience of looking over the different bond lengths and bond angles, the various atoms in the compound in question are numbered in Arabic numerals.

Table 8
Various dihedral angles of compound [VO_2(amphp-in)(H_2O)] · H_2O (**3**)

S. no.	Atoms	Actual bond angles	Optimal bond angles
1	O(2)–V(1)–O(5)–C(4)	−120.71	–
2	O(3)–V(1)–O(5)–C(4)	141.664	–
3	N(7)–V(1)–O(5)–C(4)	−13.041	–
4	O(13)–V(1)–O(5)–C(4)	117.634	–
5	O(27)–V(1)–O(5)–C(4)	75.066	–
6	O(2)–V(1)–N(7)–N(6)	143.044	–
7	O(2)–V(1)–N(7)–C(15)	−12.971	–
8	O(3)–V(1)–N(7)–N(6)	−69.172	–
9	O(3)–V(1)–N(7)–C(15)	134.813	–
10	O(5)–V(1)–N(7)–N(6)	40.244	–
11	O(5)–V(1)–N(7)–C(15)	−15.772	–
12	O(13)–V(1)–N(7)–N(6)	−27.447	–
13	O(13)–V(1)–N(7)–C(15)	76.538	–
14	O(27)–V(1)–N(7)–N(6)	−24.471	–
15	O(27)–V(1)–N(7)–C(15)	179.553	–
16	O(2)–V(1)–O(13)–C(12)	24.49	–
17	O(3)–V(1)–O(13)–C(12)	122.589	–
18	O(5)–V(1)–O(13)–C(12)	147.266	–
19	N(7)–V(1)–O(13)–C(12)	−80.681	–
20	O(27)–V(1)–O(13)–(12)	−73.909	–
21	O(2)–V(1)–O(27)–H(28)	36.707	–
22	O(2)–V(1)–O(27)–H(29)	−91.308	–
23	O(3)–V(1)–O(27)–H(28)	−16.779	–
24	O(3)–V(1)–O(27)–H(29)	−44.796	–
25	O(5)–V(1)–O(27)–H(28)	81.824	–
26	O(5)–V(1)–O(27)–H(29)	−46.193	–
27	N(7)–V(1)–O(27)–H(28)	−76.694	–
28	N(7)–V(1)–O(27)–H(29)	55.285	–
29	O(13)–V(1)–O(27)–(28)	−86.923	–
30	O(13)–V(1)–O(27)–(29)	145.061	–
31	N(6)–C(4)–O(5)–V(1)	−4.555	–
32	C(37)–C(4)–O(5)–V(1)	176.517	–
33	O(5)–C(4)–N(6)–N(7)	25.623	–
34	C(37)–C(4)–N(6)–N(7)	−56.738	–
35	O(5)–C(4)–C(37)–C(32)	−56.969	–
36	O(5)–C(4)–C(37)–C(36)	59.244	–
37	N(6)–C(4)–C(37)–C(32)	25.324	–
38	N(6)–C(4)–C(37)–C(36)	−18.465	–
39	C(4)–N(6)–N(7)–V(1)	−36.612	–
40	C(4)–N(6)–N(7)–C(15)	90.233	–
41	V(1)–N(7)–C(15)–C(11)	−83.254	–
42	V(1)–N(7)–C(15)–C(16)	−75.456	–
43	N(6)–N(7)–C(15)–C(11)	141.785	–
44	N(6)–N(7)–C(15)–C(16)	49.583	–
45	C(12)–N(8)–N(9)–C(10)	0.448	–
46	C(24)–N(8)–N(9)–C(10)	−79.105	–
47	N(9)–N(8)–C(12)–C(11)	0.316	–
48	N(9)–N(8)–C(12)–O(13)	−119.715	–
49	C(24)–N(8)–C(12)–C(11)	179.684	–
50	C(24)–N(8)–C(12)–O(13)	59.775	–
51	N(9)–N(8)–C(24)–C(23)	−60.576	–
52	N(9)–N(8)–C(24)–C(25)	118.844	–
53	C(12)–N(8)–C(24)–C(23)	120.001	–
54	C(12)–N(8)–C(24)–C(25)	−60.576	–
55	N(8)–N(9)–C(10)–C(11)	−0.838	–
56	N(8)–N(9)–C(10)–C(14)	−179.684	–
57	N(9)–C(10)–C(11)–C(12)	1.266	–
58	N(9)–C(10)–C(11)–C(15)	−146.894	–
59	N(9)–C(10)–C(11)–H(63)	115.336	–
60	C(14)–C(10)–C(11)–(12)	180	–
61	C(14)–C(10)–C(11)–(15)	31.767	–
62	C(14)–C(10)–C(11)–(63)	−66.003	–
63	N(9)–C(10)–C(14)–H(54)	−119.998	–

Table 8 (*continued*)

S. no.	Atoms	Actual bond angles	Optimal bond angles
64	N(9)–C(10)–C(14)–H(55)	119.926	–
65	N(9)–C(10)–C(14)–H(56)	0	–
66	C(11)–C(10)–C(14)–(54)	61.536	–
67	C(11)–C(10)–C(14)–(55)	−58.539	–
68	C(11)–C(10)–C(14)–(56)	−178.387	–
69	C(10)–C(11)–C(12)–N(8)	−0.895	–
70	C(10)–C(11)–C(12)–(13)	115.359	–
71	C(15)–C(11)–C(12)–N(8)	149.81	–
72	C(15)–C(11)–C(12)–(13)	−93.898	–
73	H(63)–C(11)–C(12)–N(8)	−131.299	–
74	H(63)–C(11)–C(12)–(13)	−15.009	–
75	C(10)–C(11)–C(15)–N(7)	−121.477	–
76	C(10)–C(11)–C(15)–(16)	1.142	–
77	C(12)–C(11)–C(15)–N(7)	86.657	–
78	C(12)–C(11)–C(15)–(16)	−150.707	–
79	H(63)–C(11)–C(15)–N(7)	1.45	–
80	H(63)–C(11)–C(15)–(16)	124.081	–
81	N(8)–C(12)–O(13)–V(1)	−179	–
82	C(11)–C(12)–O(13)–V(1)	72.171	–
83	N(7)–C(15)–C(16)–H(17)	−135.92	–
84	N(7)–C(15)–C(16)–H(18)	87.155	–
85	N(7)–C(15)–C(16)–H(19)	−25.474	–
86	C(11)–C(15)–C(16)–(17)	147.784	–
87	C(11)–C(15)–C(16)–(18)	10.857	–
88	C(11)–C(15)–C(16)–(19)	−101.771	–
89	C(26)–C(21)–C(22)–(23)	0	–
90	C(26)–C(21)–C(22)–(61)	−179.451	–
91	H(62)–C(21)–C(22)–(23)	−179.451	–
92	H(62)–C(21)–C(22)–(61)	1.142	–
93	C(22)–C(21)–C(26)–(25)	0	–
94	C(22)–C(21)–C(26)–(64)	179.451	–
95	H(62)–C(21)—C(26)–(25)	179.451	–
96	H(62)–C(21)–C(26)–(64)	−1.184	–
97	C(21)–C(22)–C(23)–(24)	0	–
98	C(21)–C(22)–C(23)–(66)	−79.451	–
99	H(61)–C(22)–C(23)–(24)	179.451	–
100	H(61)–C(22)–C(23)–(66)	0	–
101	C(22)–C(23)–C(24)–(8)	179.451	
102	C(22)–C(23)–C(24)–(25)	0	–
103	H(66)–C(23)–C(24)–(8)	−1.184	–
104	H(66)–C(23)–C(24)–(25)	179.451	–
105	N(8)–C(24)–C(25)–(26)	−79.368	–
106	N(8)–C(24)–C(25)–(65)	1.184	–
107	C(23)–C(24)–C(25)–(26)	0	–
108	C(23)–C(24)–C(25)–(65)	−79.368	–
109	C(24)–C(25)–C(26)–(21)	0	–
110	C(24)–C(25)–C(26)–(64)	−79.451	–
111	H(65)–C(25)–C(26)–(21)	179.451	–
112	H(65)–C(25)–C(26)–(64)	0	–
113	C(37)–C(32)–C(33)–(34)	−8.297	–
114	C(37)–C(32)–C(33)–(50)	−175.391	–
115	H(51)–C(32)–C(33)–(34)	179.292	–
116	H(51)–C(32)–C(33)–(50)	12.217	–
117	C(33)–C(32)–C(37)–C(4)	−152.566	–
118	C(33)–C(32)–C(37)–(36)	11.357	–
119	H(51)–C(32)–C(37)–C(4)	11.178	–
120	H(51)–C(32)–C(37)–(36)	175.094	–
121	C(32)–C(33)–N(34)–(35)	8.701	–
122	H(50)–C(33)–N(34)–(35)	174.925	–
123	C(33)–N(34)–C(35)–(36)	−10.764	–
124	C(33)–N(34)–C(35)–(49)	168.516	–
125	N(34)–C(35)–C(36)–(37)	12.526	–
126	N(34)–C(35)–C(36)–(48)	176.575	–
127	H(49)–C(35)–C(36)–(37)	−166.729	–

Table 8 (*continued*)

S. no.	Atoms	Actual bond angles	Optimal bond angles
128	H(49)–C(35)–C(36)–(48)	−2.686	–
129	C(35)–C(36)–C(37)–C(4)	120.699	–
130	C(35)–C(36)–C(37)–(32)	−14.728	–
131	H(48)–C(36)–C(37)–C(4)	−41.374	–
132	H(48)–C(36)–C(37)–(32)	−176.787	

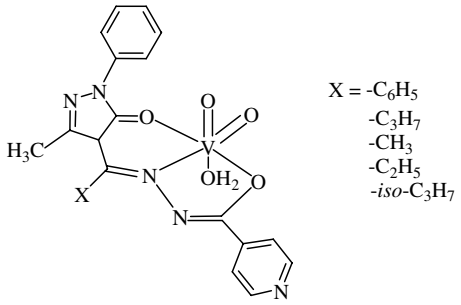


Fig. 9. Proposed structures of the complexes.

In all, 275 measurements of the bond lengths, plus the bond angles including dihedral angles are listed in the tables. Except few cases, optimal values (most favourable) of both the bond lengths and the bond angles are given in the tables along with the actual ones. In most of the cases, the observed bond lengths and bond angles are close to the optimal values, and thus the proposed structure of compound **3** as well as of the others, are acceptable.

4. Conclusion

The satisfactory analytical data coupled with the studies presented above suggest that the dioxovanadium(V) complexes synthesized in this investigation are of the general composition. $[VO_2(L)(H_2O)] \cdot H_2O$, where LH = *N*-(4′-benzoylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide, *N*-(4′-butyrylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide, *N*-(4′-acetylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide, *N*-(3′-methyl-1′-phenyl-4′-propionylidene-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide or *N*-(4′-*iso*-butyrylidene-3′-methyl-1′-phenyl-2′-pyrazolin-5′-one)-isonicotinic acid hydrazide. Keeping in view the monomeric hexa-coordination of all the complexes, and the well established octahedral structure [11] of dioxovanadium(V) complexes, $K[VO_2(sal\text{-}iNH)(H_2O)]$ and $K[VO_2(Clsal\text{-}iNH)(H_2O)]$ involving *N*-isonicotinamido-salicylaldimines (aroylhydrazones) ligand (similar to LH in the present investigation), octahedral structures (Fig. 9) with *cis*-dioxo group have been proposed for these complexes. X-ray crystallographic studies, which might confirm the proposed structures, could not be carried out as suitable crystals were not obtained.

Acknowledgements

The authors are thankful to Dr. S.M. Paul Khurana, Vice-chancellor of this University, for encouragement, and Professor K.K. Verma, Head, Department of Chemistry, for laboratory facilities and helpful discussion. We are grateful to the Department of Science and technology, New Delhi, India, for financial assistance. Analytical facilities provided by the Central Drug Research Institute, Lucknow, India, and the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai and Bombay, India, are gratefully acknowledged.

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