Alkali Metal (Na$^+$ & K$^+$)-Mediated Supramolecular Assembly of Oxovanadium(V) Complexes: Synthesis and Structural Characterization

Rupam Dinda [a, *]**, Paresh Kumar Majhi** [a]**, Parbati Sengupta** [b]**, Sagarika Pasayat** [a]**, Saktiprosad Ghosh** [c, *]**, Larry R. Falvello** [d] **and Thomas C. W. Mak** [e]

[a] *Department of Chemistry, National Institute of Technology, Rourkela 769008, India*

[b] *Department of Chemistry, Fergusson College, S. C. Road, Pune-411004, India*

[c] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India*

[d] *Department of Inorganic Chemistry and Aragon Materials Science Institute, University of Zaragoza, Zaragoza E-50009, Spain*

[e] *Department of Chemistry, Chinese University of Hong Kong , Shatin , New Territories, Hong Kong SAR, People's Republic of China*

Abstract

The syntheses and characterization of alkali metal complexes [{VO$_2$L}M(H$_2$O}$_n$] (**1** & **2**) [M = Na$^+$ (**1**), K$^+$ (**2**)] of anionic cis-dioxovanadium(V) species (LVO$_2^-$) of the Schiff base *2*-hydroxybenzoylhydrazone of *2*-hydroxybenzaldehyde have been reported. The number of coordinated water molecules in [{VO$_2$L}M(H$_2$O}$_n$] decreases as the charge density of the alkali metal ion decreases (n = 5 for Na$^+$ and 1 for K$^+$). These compounds represented M$^+$-mediated supramolecular assembly [{VO$_2$L}M(H$_2$O}$_n$]$_\infty$ with an infinite polymeric structure containing an alternating array of *cis*-dioxo vanadium(V), [VO$_2$L]$^-$, units and aquated metal ion centres, as confirmed by X-ray crystallographic investigation of both. All the compounds are characterized by elemental analysis, IR, UV-Vis and NMR spectroscopy.

Keywords: Tridentate ONO donor ligand / Oxovanadium(V) complexes / X-ray crystal structure / Alkali metal ion mediated supramolecular assembly

*Corresponding author. Tel.: + (91) 661 246 2657; Fax: + (91) 661 246 2999;

E-mail: rupamdinda@yahoo.com

1. Introduction

A new area of research involving the design and synthesis of extended frameworks via supramolecular interactions is growing at a rapid pace. Hydrogen bonding interactions have been particularly explored while dealing with molecular recognition and engineering of molecular solids [1]. So far, numerous studies have focused using monovalent alkali metals as a source of counter ion for the formation of polymeric aggregates, which feature channels or sheets of metal ions, which may have potential to act as ionic conductors [2], charge storage materials, as well as biomimetic models [3]. Chakraborty [4] and Choudhury [5] as well as Schröder [6] and Pan [7] have highlighted the special roles that alkali metal ions can play in influencing the supramolecular assembly. H. Zhu *et*. al [8] have reported some different type of oxovanadium complexes of dialkyldithiocarbamate where all the $[V_2S_2O_2(R_2dtc)_2]^{2-}$ moieties possess very similar structural properties and link each other by the interaction between $V_2O_2(\mu\text{-}S)_2$ units and alkali metal (Na^+, K^+) ion. Very recently Przybylski *et*. al [9] have highlighted the role of the alkali metal ion and hydrogen bonds in $M[VO(O_2)_2bpy].nH_2O$ (M = Li^+, Na^+, K^+ and Rb^+) and $Cs[VO(O_2)_2bpy].H_2O_2$ complexes. In most of these cases the water molecules are present as part of aquated M^+ ions (M = alkali metal), and play a vital role in holding the components of the assembly together through hydrogen bonding network and thereby enhancing its stability through charge neutralization. Collective consideration of all these findings opens up the possibility of obtaining new and novel species with interesting properties under specific and controlled reaction conditions. During last two decades, we have been engaged in studying the chemistry of oxovanadium complexes, using some selected multidentate O/N donor systems [10-14]. In this contribution we report the synthesis and structural characterization of two novel anionic oxovanadium(V) species with a tridentate ONO donor ligand, whose supramolecular structure is controlled by the associated alkali metal counter ion.

2. Experimental

2.1. Materials

[VO(acac)$_2$] was prepared as described in the literature [15]. Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, available commercially and used as received.

2.2. Physical measurements

Elemental analyses were performed on a Perkin-Elmer 240 C, H, N analyzer. IR spectra were recorded on a Perkin-Elmer 783 spectrometer. ^{1}H NMR spectra were recorded with a Bruker AVANCE DPX 300 MHz spectrometer using SiMe$_4$ as the internal standard. Electronic spectra were recorded on a Shimadzu UV/VIS recording spectrophotometer.

2.3. Synthesis of Ligand H$_2$L

Schiff base ligand, *2*-hydroxybenzoylhydrazone of *2*-hydroxybenzoylhydrazine was prepared by the procedure reported in our previous work [16].

2.4. Synthesis of [{VO$_2$L}Na(H$_2$O)$_5$]$_\infty$(1)

A (0.26 g, 1.02 mmol) sample of ligand H$_2$L was dissolved in 20 mL of ethanol and to it HN(CH$_2$CO$_2$Na)$_2$ (0.09 g, 0.52 mmol) dissolved in 3 mL of water was added, when the white suspension turned yellowish. The mixture was refluxed for 5 min to give a clear solution. Thereafter a sample of vanadium (IV) acetylacetonate (0.27 g, 1.02 mmol) was added under stirring condition. After 7 h of stirring the deep yellow solution was filtered and slow evaporation of the filtrate over 10 days produced thin yellow crystals. Yield: 65%. Anal. Calc for C$_{14}$H$_{21}$N$_2$O$_{10}$NaV: C, 37.22; H, 4.69; N, 6.20. Found: C, 37.34; H, 4.32; N, 6.18. ^{1}H NMR (DMSO d$_6$, δ): 7.83 – 6.78 (m, 8H, C$_6$H$_4$), 9.08 (s, 1H, CH), 12.21 (s, 1H, OH).

2.5. Synthesis of [{VO₂L}K(H₂O)] ∝ (2)

A (0.26 g, 1.02 mmol) sample of ligand H_2L was dissolved in 20 mL of ethanol and to it potassium carbonate (0.16 g, 1.16 mmol) dissolved in 3 mL of water was added, when the white suspension turned yellowish. The mixture was refluxed for 5 min to give a clear yellow solution. Thereafter a sample of vanadium (IV) acetylacetonate (0.27g, 1.02 mmol) was added under stirring condition. After 7 h of stirring the deep yellow solution was filtered and slow evaporation of the filtrate over 7 days produced thin yellow crystals. Yield: 67%. Anal. Calc for $C_{14}H_{12}N_2O_6KV$: C, 42.61; H, 3.06; N, 7.10. Found: C, 42.58; H, 3.10; N, 7.06. ^1H NMR (DMSO d₆, δ): 7.85– 6.80 (m, 8H, C_6H_4), 9.10 (s, 1H, CH), 12.23 (s, 1H, OH).

2.6. Crystallography

Suitable single crystal of **1** and **2** were chosen for X-ray diffraction studies. Crystallographic data and details of refinement are given in **Table 1**. These compounds crystallized in the orthorhombic space group Pbca and monoclinic space group $P2_1/c$ respectively. Intensity data for both were collected at 293 K on a Bruker Smart CCD area detector system using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The intensities were corrected for empirical absorption effects using SADABS [17]. The structure was solved by direct method. All non-hydrogen atoms were refined anisotropically by full-matrix least squares, with a riding model for the hydrogen atoms, using the SHELXTL package [18].

3. Results and discussion

3.1. Synthesis

The Schiff base *2*-hydroxybenzoylhydrazone of *2*-hydroxybenzaldehyde has been used as ligand in the present study. The complexes $[\{VO_2L\}M(H_2O)_n]$ (**1 & 2**) were prepared by the reaction of $VO(acac)_2$ with the stoichiometric amount of the ligand H_2L in presence of alkali metal salts, Na- salt of iminodiacetic acid and potassium carbonate respectively in aqueous ethanol (1:9). The products are a M^+-mediated supramolecular assembly $[\{VO_2L\}M(H_2O)_n]_\infty$ with an infinite polymeric structure containing an alternating array of *cis*-dioxo vanadium(V), $[VO_2L]^-$, units and aquated metal ion centres, as confirmed by single crystal X-ray analysis. The cationic and anionic parts of these complexes are held together by the process of self assembly [19, 20] through the simultaneous use of Coulombic interactions and efficient hydrogen bonding. These compounds are highly soluble in protic, viz. water and methanol as well as aprotic solvents, viz. CH_3CN, DMF, or DMSO.

3.2. Spectral Characteristics

Spectral data are presented in experimental section and in **Table 2**. The IR spectra of both contains all the characteristic bands of the coordinated tridentate ligand [16]. The V-O stretching modes [4, 21, 22] of the *cis*-VO_2^+ moiety are observed at 892-929 cm^{-1} region. In the high-frequency region, a medium intensity band at 3428 cm^{-1} (complex **1**) and 3442 cm^{-1} (complex **2**) indicates the presence of coordinated water involved [5] in extensive hydrogen bonding.

The electronic spectra of **1** and **2** in acetonitrile solution consist of four different bands in the region 203- 400 nm. The band at 372-400 nm region is believed to be of the $L \rightarrow V^V$ charge-transfer type and the others are due to intra ligand transition respectively [4, 10].

The ^1H NMR spectrum of the free ligand exhibits two different OH (phenolic) resonance at two different positions (12.02 ppm and 11.76 ppm), CH proton at 8.68 ppm, NH proton at 11.18 ppm

and aromatic protons at 7.85-6.78 ppm, respectively [10, 16]. On coordination, the signal for one OH proton and that of the NH proton disappeared in complexes and only one OH proton signal at 12.21-12.23 ppm region is observed.

3.3. Description of Crystal Structure of [{VO$_2$L}Na(H$_2$O)$_5$]$_\infty$

The preliminary characterization data (microanalytical and spectroscopic) of complex **1** and **2** though gave some idea of their composition, failed to indicate any definite formulation for them. The identities of these complexes were revealed by their structure determination by X-ray crystallography.

The molecular structure of the complex **1** is given in **Fig. 1**. The bonding parameters of the complex are given in **Table 3**. In this complex-anion the vanadium(V) center presents in a highly distorted square pyramidal O$_4$N donor environment. The doubly deprotonated dianionic ligand *2-*hydroxybenzoylhydrazone of *2-*hydroxybenzoylhydrazine (H$_2$L) acts as a tridentate ONO ligand forming five- and six- membered chelate rings at the vanadium(V) center, the bite angles being 74.1(2)^o and 82.0(2)^o respectively. The basal plane consists of three donor points O(4), N(1) and O(3) of the ligand and the vanadyl oxygen O(1). The other vanadyl oxygen O(2) occupies the apical position of the square pyramid and the angles it makes with the basal plane lie in the 101.1(3)^0–110.0(3)^0 range. The angles O(3)-V(1)-O(4) and O(1)-V(1)-N(1) are 150.9(2)^0 and 140.4(3)^0, respectively and indicate that the V(V) centre is shifted (0.4974Å) out of the basal plane towards the apical oxygen atom O(2) [4, 10]. The angle [O(1)-V(1)-O(2)] between the vanadyl groups is 109.0(4)^o, and the V=O distances [1.620(6) and 1.634(6)] are unexceptional [5, 10a, 23]. The V-O distance is significantly shorter than the V-N distance, which has been noted in the cases of some other N-O donor ligands [4, 5, 10a]. This suggests some π- donation leading to partial multiple bond-character, which is a familiar feature of oxygen coordination in vanadium(V) complexes.

On the columns of edge-sharing hexa aqua sodium(I) octahedra, a Na^+ ion is coordinated by aqua ligands O(1W), O(2W), O(3W) and O(4W). Repetition of this five-atom group by a glide symmetry operation generates a grossly octahedral environment about each Na^+ ion (**Fig. 1**). **Fig. 2** shows that the resulting $[Na(H_2O)_6]^+$ octahedra share edges of the type O(1W)…O(2W) to from a column running parallel to the *a* axis, and adjacent columns are connected by bridging water molecules of the type O(5W), giving rise to a hydrogen-bonded layer normal to the *c* axis. The Na^+ ions all lie very close to the plane $z = \frac{1}{4}$, and each $[Na(H_2O)_6]^+$ octahedron forms donor hydrogen bonds with vanadyl complex anions $[VO_2L]^-$ that are located above and below this plane, adding thickness to generate a composite layer. Another similar layer with the Na^+ ions lying near the plane $z = \frac{3}{4}$ is not shown in this figure.

The crystal structure of the polymeric complex $[\{VO_2L\}Na(H_2O)_5]_\infty$ is built of a stacking of previously mentioned composite layers along the *c* axis (**Fig. S1**), and only van der Waals interaction exist between them. The hydrogen-bonding pattern is shown in **Table 4**. In the complex anion $[VO_2L]^-$, the phenoxy oxygen O(5) is involved in intramolecular hydrogen bonding, and the remaining four oxygen atoms O(1) to O(4) form acceptor hydrogen bonds involving all the water molecules. Double columnar packing of the complex along 'b' axis, (**Fig. 3**) which is being held together by H bonding between V=O oxygens (acceptor) and water (O1w), O(2W) and O(4W) molecules coordinated to Na^+. V=O (1) is H-bonded to O1W (bonded to Na^+) and O5W (free water, symmetry code $\frac{1}{2}$ -x, -$\frac{1}{2}$ +y, z , while V=O2 is H- bonded to O2W (1-x, -$\frac{1}{2}$ +y, $\frac{1}{2}$ -z) and O4W (1-x, -$\frac{1}{2}$ +y, $\frac{1}{2}$ -z) (both bonded to Na^+). O5W acts as bridge between parallel double columns situated along 'c' axis. So this structure is a very interesting case where water molecules play a variety of structural roles in the formation and stabilization of a complex polymeric species. Each composite layer may be considered as a two-dimensional supramolecular species. Distance between two vanadium centres belonging to two adjacent layers is 8.277 Å and the distance separating two consecutive vanadium centres of the same layer is 8.347 Å.

3.4. Description of Crystal Structure of [{VO₂L}K(H₂O)]∞

The molecular structure of the complex **2** is given in **Fig. 4,** where the V(V) center is five-coordinate, with O(3) in the apical position of a distorted square pyramid. The bonding parameters of the complex **2** are given in **Table 5**. The vanadium atom lies 0.499(2) Å out of the basal plane formed by O(1), O(2), O(4), and N(1). The distances and angles about the metal atom present no serious anomalies [10], although we note that the V-O distance involving the phenoxy oxygen atom [V(1)-O(2), 1.898(3) Å] is significantly shorter than the distance V(1)-O(1), which is 1.985(2) Å. The five- and six-membered chelate bite angles are 74.37(10) and 82.88(11)º, respectively. An intramolecular hydrogen bond is present in which the hydroxyl group at O(5) donates to the imine nitrogen N(2). The geometric parameters of this interaction have been shown in **Table 6**.

The complexes are stacked in a direction parallel to the b-axis (**Fig. S2**) of the monoclinic cell, and neighbouring stacks related by either the *c*-glide at *y* = ¼ or by the 2_1 screw axis at *(1/2, y, ¼)* have the molecules tilted in different directions. The largely hydrophobic periphery of the ligand *L* points toward the center of the cell, while the oxo ligands point to the cell boundaries, specifically to the *(100)* planes, where the K⁺ ions and water molecules are located (The latter are not rigorously located in the *(100)* planes). The distance between adjacent stacked planes is 3.457(7) Å, although the exact value depends on how the planes are calculated. It should be noted that adjacent molecules are not fully eclipsed, which shows the molecule at *(xyz)* and its neighbour at (x,y-1,z). The potassium ions and the oxygen atoms around them form a puckered sheet that is roughly coincident with the *(100)* crystallographic plane, that is, with the bc-face of the unit cell. Pairs of K⁺ ions are bridged by either two symmetry-related water molecules or by two oxygen atoms that are also coordinated to vanadium, namely O(2) and O(4).

In the center of the cell, in the largely hydrophobic region, the OH group of the ligand *L,* which is the only hydrophilic moiety present, participates in an electrostatic interaction that could perhaps be called a C-H...O hydrogen bond {C(14)-H(14)...O(5)#2} (**Table 6**, **Fig. S3**). This

interaction plays a role in stabilizing the overall structure. A second hydrogen bond is located in the region of the K/O sheet in the hydrophilic region. In this case, the water molecule at O(1W) donates hydrogen H(1W) to an oxo ligand, O(3), of the vanadium complex. The water moiety is involved in a further interaction that could be characterized as a hydrogen bond, in which the ligated oxygen atom O(1) is the acceptor [O(1W)...O(1)#3, 3.033(5) Å, with O(1)#3 at *x, -y+1/2, z+1/2*]. The second hydrogen atom of the unligated water was not located, so not all of the geometric parameters of this interaction are known; however, we assume that the hydrogen atom is located in the vicinity of the line joining O(1W) and O(1)#3.

The packing of the complex along 'a' axis is represented as a beautiful staircase like arrangement (**Fig. 5**) of the vanadium complex units. Each step of the staircase (vanadium complex) is linked with a complex unit below it and above it by V-O2-K,V-O3-K, V-O1-K and V-O4-K bonds. Adjacent staircases are linked to each other by K-O1W-K bonds.

It has been postulated that the most stable structures are formed when all hydrogen bond donors and acceptors are involved in significant interactions. In the present case, we count 10 potential H-bond acceptors – two each for the two oxo ligands, two for the unligated water molecule, and one each for the ligated oxygen atoms O(1) and O(2), the hydroxyl oxygen atom O(5), and the imine nitrogen N(2). There are either 3 or 4 hydrogen-bond donors available – the two water hydrogen atoms, the OH group at O(5), and possibly the C-H moiety at C(14). All of these potential donors are involved in non-covalent interactions, as described above. Although this would appear to leave a deficit of as many as six unfulfilled acceptor sites, in fact the latter are involved in interactions with K^+. So we can conclude that this is a quite stable structure.

4. Conclusion

H-bonds are recognized as one of the most relevant noncovalent interactions in supramolecular chemistry and crystal design [24, 25]. Water is very often involved into such interactions and is present as coordinated or crystallization molecule(s) in a larger number of metal-organic frameworks (MOFs).

In this work we have reported that very subtle modifications in the synthetic condition, actually the use of ethanol or ethanol/water as solvent and slightly different pH medium, generate strongly different MOFs. In the case of **1** & **2** in presence of slight basic medium in aqueous ethanol we are able to generate M^+-mediated supramolecular assembly $[\{VO_2L\}M(H_2O)_n]_\infty$ with an infinite polymeric structure containing an alternating array of *cis*-dioxo vanadium(V), $[VO_2L]^-$, units and aquated metal ion centres, as confirmed by X-ray crystallographic investigation of both . Strong electrostatic and hydrogen bonding interactions play the central role in stabilizing these extended structures in the solid state. Where as in our very recent report we have found that in presence of exactly the same ligand environment in neutral medium in ethanol, the same starting vanadium compound produces the completely different complex, monoalkoxo-bound monooxo-vanadium(V) analogue VOL(OEt). Further studies of polynuclear V(V) complexes are currently in progress in order to generate new supramolecular species and to obtain corresponding host-guest complexes by the incorporation of guest molecules of appropriate dimensions between the adjacent layers.

Appendix A. Supplementary data

CCDC 638401 and 638402 contain the supplementary crystallographic data for Complex **1** and Complex **2** respectively. 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.

The view of the extended crystal structure and the details of the packing for the complex $[\{VO_2L\}Na(H_2O)_5]_\infty$ (**1**), is reported as Supporting Information (**Fig. S1**). Also the view of the extended crystal structure and the details of the packing for the complex $[\{VO_2L\}K(H_2O)]_\infty$ **2**, is reported as Supporting Information (**Fig. S2 and Fig. S3**).

Acknowledgements

References

[1] (a) D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375; (b) D. Braga, F. Grepioni, Coord. Chem. Rev.183 (1999) 19; (c) D. Braga, F. Grepioni, Acc. Chem. Res. 33 (2000) 601.

[2] P.G. Bruce, Solid State Electrochemistry, Cambridge University Press, Cambridge, 1993.

[3] M. J. Pregel, L. Jullien, J.M. Lehn, Angew. Chem., Int. Ed. Engl. 31 (1992) 637.

[4] S. Dutta, P. Basu, A. Chakraborty, Inorg. Chem. 32 (1993) 5343.

[5] (a) S. K. Dutta, S. Samanta, S. Mukhopadhyay, P. Burckel, A. Pinkerton, M. Choudhry, Inorg. Chem. 41 (2002) 2946; (b) S. Samanta, S. Mukhopadhyay, D. Mandal, R. J. Butcher, M. Choudhry, Inorg. Chem. 42 (2003) 6284.

[6] D. M. J. Doble, A. J. Blake, W.S. Li, M. Schröder, J. C. S. Dalton Trans. (2001) 3137.

[7] C. Ling Pan, J. Qing Xu, G. Hua Li, X. Bing Cui, L. Ye and G. Di Yang Dalton Trans. (2003) 517.

[8] H. Zhu, C. Chen, X. Zhang, Q. Liu, D. Liao and L. Li, Inorg. Chim. Acta 328 (2002) 96.

[9] W. Przybylski, R. Grybos´, D. Rehder, M. Ebel, M. Grzywa, W. Łasocha, K. Lewin´ski, J. T. Szklarzewicz, Polyhedron 28 (2009) 1429.

[10] (a) R. Dinda, P. Sengupta, T. C. W. Mak, S. Ghosh, Inorg. Chem. 41 (2002) 1684; (b) M. Sutradhar, G. Mukherjee, M. G. B. Drew, S. Ghosh, Inorg. Chem. 45 (2006) 5150; (c) R. Dinda, P. Sengupta, M. Sutradhar, T. C. W. Mak and S. Ghosh, Inorg. Chem. 47 (2008) 5634.

[11] M. Chatterjee, B. M. Wu, T. C. W. Mak, S. Ghosh, Polyhedron. 17 (1998) 1369.

[12] M. Chatterjee, A. K. Nandi, S. Ghosh, Transition Met. Chem. 24 (1999) 183.

[13] A. Maity, S. Ghosh, J. Inorg. Biochem. 36 (1989) 131.

[14] A. Maity, S. Ghosh. Proc. Indian Acad. Sci. (Chem. Sci.). 104 (1992) 369.

[15] R. A. Rowe, M. M. Jones, Inorg, Synth. 5 (1957) 113.

[16] R. Dinda, S. Ghosh, L. R. Falvello, M. Tomas T. C. W. Polyhedron. 25 (2006) 2375.

[17] G. M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, 1996.

[18] G. M. Sheldrick, SHELXTL 5.10, Structure Determination Software Package, Bruker Analytical X-ray Systems, Madison, WI, 1998.

[19] J. S. Lindsey, New J. Chem. 15 (1991) 153.

[20] D. Philip, J. F. Stoddart, Angew. Chem. Int. Ed. Engl. 35 (1996) 1154.

[21] J. A. Bonadies, C. J. Carrano, J. Am. Chem. Soc. 108 (1986) 4088.

[22] H. Toftlund, S. Larsen, K. S. Murray, Inorg. Chem. 30 (1991) 3964.

[23] X. Li, M. S. Lah, V. L. Pecoraro, Inorg. Chem. 27 (1988) 4657.

[24] G. R. Desiraju, Comprehensive Supramolecular Chemistry; Pergamon Press: Oxford, (1996) Vol. 6.

[25] G. A. Jeffery, J. Mol. Struct. 486 (1999) 293.

Table 1 Crystallographic data and details of refinement of $[\{VO_2L\}Na(H_2O)_5]_\infty$ (**1**) & $[\{VO_2L\}K(H_2O)]_\infty$ (**2**).

Complex	$[\{VO_2L\}Na(H_2O)_5]_\infty$	$[\{VO_2L\}K(H_2O)]_\infty$
Chemical formula	$C_{14}H_{21}N_2O_{10}NaV$	$C_{14}H_{12}N_2O_6KV$
Fw	451.26	394.30
Cryst syst	Orthorhombic	Monoclinic
Space group	Pbca	$P2_1/c$
a, Å	6.9527 (18)	15.628 (3)
b, Å	14.714 (4)	6.6352 (13)
c, Å	36.882 (9)	15.697 (3)
α, β, γ, deg	90, 90, 90	90, 102.45(3), 90
$V, Å^3$	3773.0 (17)	1589.4 (5)
Z	8	4
T, K	293 (2)	293 (2)
λ, Å	0.71073	0.71073
D_c, Mg m^{-3}	1.589	1.648
μ (Mo Kα) mm^{-1}	0.605	0.92
F(000)	1864	800
R1, wR2 [I > 2σ (I)]	0.1163, 0.3083	0.0598, 0.1447
Goodness of fit on F^2	1.031	1.079

Table 2 Characteristics IR[a] bands (cm^{-1}) and electronic spectral[b] data [nm

(dm^3 mol^{-1}cm^{-1})] for the complexes.

_____

Complex	ν (OH)	ν (C=N)	ν (V=O$_t$)	λ_{max} (ε)
[{VO$_2$L}Na(H$_2$O)$_5$]$_\infty$	3428	1610	929, 910	400 (6493); 333 (13997); 212 (22435)
[{VO$_2$L}K(H$_2$O)]$_\infty$	3442	1608	918, 892	372 (8931); 285 (15654); 203 (23709)

[a] In KBr pellet; [b] In CH$_3$CN

_____

Table 3 Selected bond distances (Å) and angles (^{0}) for $[\{VO_2L\}Na(H_2O)_5]_\infty$. The estimated standard deviations are shown in parentheses.

_____

Distances

V(1) – O(1)	1.620(6)	C(1) – O(3)	1.348(10)
V(1) – O(2)	1.634(6)	C(8) – O(4)	1.298(9)
V(1) – O(3)	1.894(6)	C(10) – O(5)	1.354(12)
V(1) – O(4)	1.973(5)	C(8) – N(2)	1.296(10)
V(1) – N(1)	2.113(6)	C(7) – N(1)	1.302(10)

Angles

O(1) – V(1) – O(2)	109.0(4)	O(2) – V(1) – O(4)	100.1(3)
O(1) – V(1) – O(3)	95.6(3)	O(2) – V(1) – N(1)	110.0(3)
O(1) – V(1) – O(4)	92.5(3)	O(3) – V(1) – N(1)	82.0(2)
O(1) – V(1) – N(1)	140.4(3)	O(3) – V(1) – O(4)	150.9(2)
O(2) – V(1) – O(3)	103.5(3)	O(4) – V(1) – N(1)	74.1(2)

Table 4   Scheme of hydrogen bonding of complex $[\{VO_2L\}Na(H_2O)_5]_\infty$

Donor atom D	Acceptor atom A	D…A (Å)	A…D…A' (°)
O1W	O1	2.862	
O1W	O5W#3	2.861	108.1
O2W	O2#4	2.931	
O2W	O5W	2.847	125.5
O3W	O4W#2	2.821	
O3W	O4#5	3.121	104.8
O4W	O2#4	2.802	
O4W	O3#1	2.851	118.6
O5W	O1#5	2.898	
O5W	O3#6	3.217	108.7
N2	O5	2.534	

Symmetry code (the same as that used in the table of bond lengths and angles):
    #1   -1/2 + x, y, 1/2 - z
    #2   1/2 + x, y, 1/2 – z
    #3   1 - x, -1/2 + y, 1/2 – z
    #4   1 - x, 1/2 + y, 1/2 – z
    #5   1/2 - x, 1/2 + y, z

Table 5 Selected bond distances (Å) and angles (^{0}) for [{VO$_2$L}K(H$_2$O)]$_\infty$. The estimated standard deviations are shown in parentheses.

_____

Distances

V(1) – O(1)	1.9845(0.0024)	C(1) – O(1)	1.3087(0.0041)
V(1) – O(2)	1.8982(0.0027)	C(8) – O(2)	1.3398(0.0043)
V(1) – O(3)	1.6277(0.0030)	C(7) – O(5)	1.3602(0.0054)
V(1) – O(4)	1.6331(0.0025)	C(1) – N(2)	1.3073(0.0044)
V(1) – N(1)	2.1225(0.0029)	C(14) – N(1)	1.2922(0.0044)

Angles

O(3) – V(1) – O(4)	109.23(0.15)	O(4) – V(1) – O(1)	91.66(0.11)
O(3) – V(1) – O(2)	103.76(0.15)	O(4) – V(1) – N(1)	142.08(0.14)
O(3) – V(1) – O(1)	100.96(0.14)	O(2) – V(1) – N(1)	82.88(0.11)
O(3) – V(1) – N(1)	107.99(0.14)	O(1) – V(1) – O(2)	150.53(0.12)
O(4) – V(1) – O(2)	95.11(0.13)	O(1) – V(1) – N(1)	74.37(0.10)

Table 6 Scheme of hydrogen bonding of complex [{VO$_2$L}K(H$_2$O)]$_\infty$

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...N(2)	0.86(5)	1.76(5)	2.562(4)	156(5)
O(1W)...O(1)#3			3.033(5)	
O(1W)-H(1W)...O(3)#1	0.79(7)	2.06(7)	2.763(5)	149(8)
C(14)-H(14)...O(5)#2	0.97(4)	2.33(4)	3.263(5)	163(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y+1/2,-z+1/2   #2 -x+1,y-1/2,-z+1/2   #3 x,-y+1/2,z+1/2

Figure Captions

Fig.1. ORTEP diagram (30% probability level) of the asymmetric unit of **1** [{VO$_2$L}Na(H$_2$O)$_5$]$_\infty$, along with atom numbering

Fig. 2. The columns of edge-sharing hexa aqua [Na(H$_2$O)$_6$]$^+$ octahedra of complex **1**, normal to the *c* axis

Fig. 3. Packing diagram of complex **1** along the b axis

Fig. 4. ORTEP diagram (30% probability level) of complex **2**, [{VO$_2$L}K(H$_2$O)]$_\infty$, along with atom numbering scheme of the asymmetric unit.

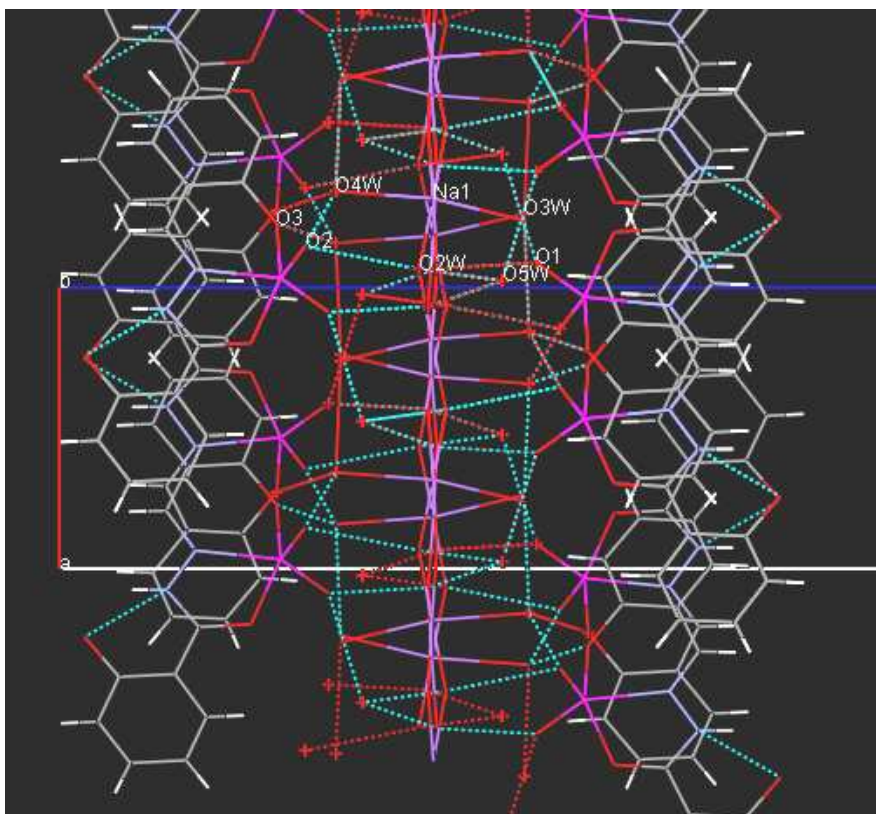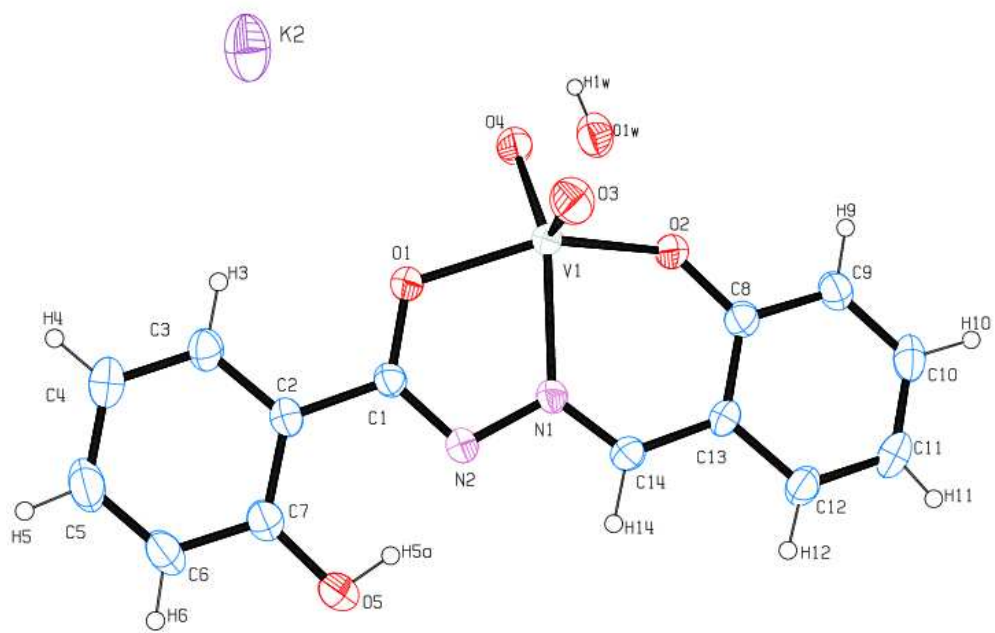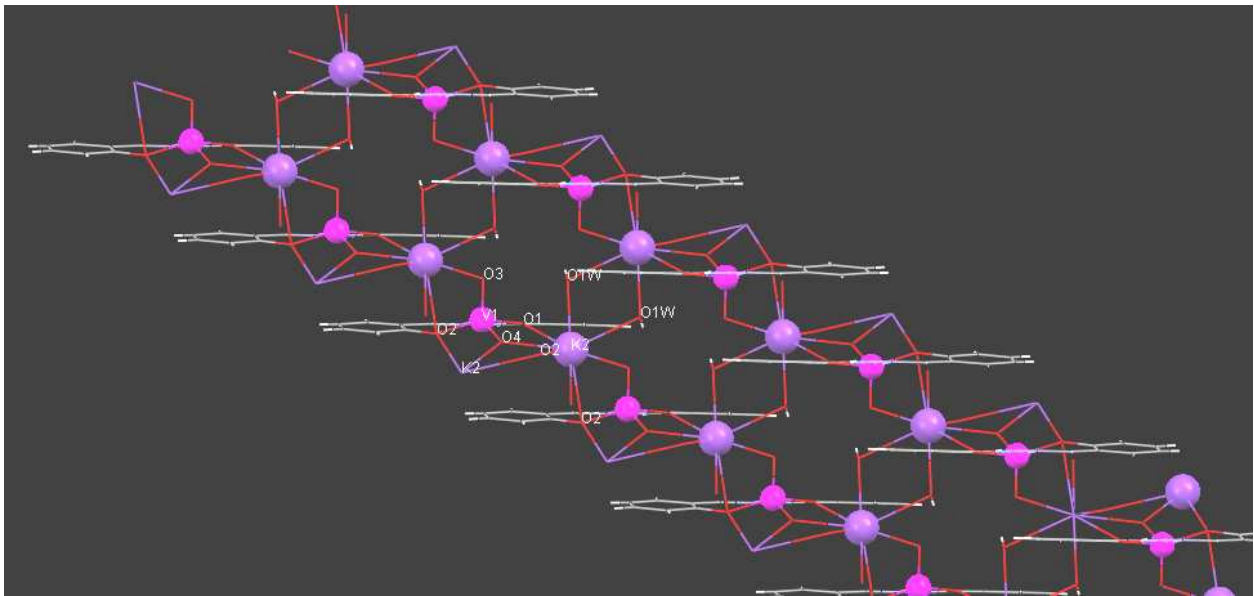**Fig. 5.** Staircase like arrangement of complex **2** along the a axis

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.