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Studies of V(III) complexes with selected α-N-heterocyclic carboxylato NO donor ligands: structure of a new seven-coordinated pentagonal bipyramidal complex containing picolinato ligands

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Some highly stable V(III) complexes involving the biologically important and chemically interesting ONO donor ligand pyridine-2,6-dicarboxylic acid (dipicolinic acid, DPAH$_2$) are reported. They include both homo- and hetero-chelates involving DPAH$_2$ and some other bidentate chelating ligands and one of them is a new highly stable seven-coordinated mononuclear V(III) complex, [V(DPA)(PA)(H$_2$O)$_2$]·H$_2$O **4** (PA = picolinate anion). The complex **4** containing two different α-N-heterocyclic carboxylates has a pentagonal bipyramidal structure with the equatorial plane accommodating the ONO and NO donor points while the two water molecules occupy the axial positions.

Pyridine-2,6-dicarboxylic acid (dipicolinic acid) is a versatile N–O donor capable of forming stable chelates[1] with various metal ions and can exhibit diverse coordination modes such as bidentate,[2] tridentate, meridian[3] or bridging.[4] It can stabilise unusual oxidation states[5] and has proved to be useful in analytical chemistry,[6] in corrosion inhibition[7] and decontamination of nuclear reactors.[8] Another interesting property of this ligand is its diverse biological activity.[9] Along with its 2,4- and 2,5-isomers, pyridine-2,6-dicarboxylic acid (DPAH$_2$) acts as an inhibitor of the enzyme GA 2β-hydroxylase and is also found to inhibit the mechanistically related enzyme proline 4-hydroxylase.[10] Iron complexes of this acid have been utilized as electron carriers in some model biological systems[11] and as specific molecular tools in DNA cleavage.[12] DPAH$_2$ is found to be present in many gram-positive eubacteria during their sporulation and as its calcium salt is thought to be responsible for the heat-resistant property of the spores.[13]

Though the ligational behaviour of DPAH$_2$ towards oxovanadium(IV)[14] and vanadium(V)[15] has been examined earlier, complexation of DPAH$_2$ with V(III) has not been studied. This work explores the ligational behaviour of the biologically important and chemically interesting ONO donor dipicolinic acid towards vanadium(III). Both 1 : 1 and 1 : 2 metal–ligand complexes are isolated along with several interesting mixed ligand complexes involving bidentate N–O and N–N donors including one seven-coordinated monomeric complex [V(DPA)(PA)(H$_2$O)$_2$]·H$_2$O containing two different α-N-heterocyclic carboxylate donors around a V(III) acceptor centre. All the compounds are adequately characterised by elemental analysis, magnetic susceptibility study at room temperature and by various spectroscopic (UV/VIS, IR) techniques. Electrochemical behaviour of the complexes was studied by cyclic voltammetry.

The majority of vanadium complexes are six-coordinated with an octahedral environment. Seven-coordinated vanadium complexes[16,17] are generally not so common and seven-coordinated vanadium(III) complexes[18–20] in particular are rather scarce, most of them being complexes of edta-like ligands.[21–25] In this paper we report the first seven-coordinated mononuclear pentagonal bipyramidal vanadium(III) complex of α-N-heterocyclic carboxylic acids with N–O donor sites which was structurally characterised by a single crystal X-ray diffraction study.

Experimental

Elemental analyses were performed with a Perkin-Elmer 240 CHNS/O analyser. IR and electronic spectra were recorded on a Perkin-Elmer 783 spectrophotometer (as KBr pellets) and on a Shimadzu UV/VIS recording spectrophotometer, respectively. Solution conductance was measured on a Systronics direct reading conductivity meter (Model 304) and magnetic susceptibility was measured with a PAR vibrating sample magnetometer using Hg[Co(SCN)$_4$] as the calibrant. Electrochemical data were collected with a BAS CV-27 electrochemical analyser and a BAS Model X-Y recorder at 298K. Cyclic voltammetry experiments were carried out with a glassy carbon working electrode, platinum auxiliary electrode and Ag–AgCl reference electrode.

Synthesis of complexes

All chemicals were of reagent grade and used without further purification. All operations were performed under purified dinitrogen. Since the starting material (*e.g.* VCl$_3$) is subject to hydrolysis in water, the sequence in which the reagents are added is important.

[V(DPA)(H$_2$O)$_2$F]·1.5H$_2$O 1. To 1.67 g (0.01 mol) of DPAH$_2$ in 50 cm^3 of water was added 2.82 g (0.01 mol) of K$_3$VF$_6$ and the mixture stirred for 3 h. The bright yellow compound formed was filtered off, washed with water and dried over fused CaCl$_2$. Yield 1.93 g, 65% (Found: C, 28.05; H, 3.30; N, 4.09. Calc. for VC$_7$H$_{10}$NO$_{7.5}$F: C, 28.37; H, 3.37; N, 4.72%). IR (KBr pellet, cm^{-1}): 3350 (br), 1650 (br), 1430, 1400, 1280, 1200, 1150, 1080, 1040, 940, 770, 750, 680, 500, 480. Conductance in DMF Λ_M, 17.06 Ω^{-1} cm^2 mol^{-1} (κ, 10.08 × 10^{-6} S cm^{-1}). μ, 2.64 μ_B.

[V(DPA)(DPAH)(H$_2$O)]·3H$_2$O 2. The 1 : 2 metal–ligand complex is easily prepared by adding 0.15 g (9.52 × 10^{-3} mol) of VCl$_3$ to a 30 cm^3 aqueous solution of 0.32 g (1.90 × 10^{-3} mol) of $DPAH_2$. On stirring for 2 h a greenish yellow compound settles at the bottom of the flask and this was filtered off and washed thoroughly with water and dried over fused $CaCl_2$. It has been noted that irrespective of whether the metal–ligand ratio is 1 : 1, 1 : 2, 2 : 1 or even 4 : 1 the product is always complex **2**. The same compound can also be prepared by stirring an aqueous solution of a 1 : 2 molar ratio of K_3VF_6 and $DPAH_2$ or by the addition of $DPAH_2$ to **1**. Yield 0.34 g, 80% (Found: C, 37.31; H, 3.26; N, 6.19. Calc. for $VC_{14}H_{15}N_2O_{12}$: C, 37.31; H, 3.33; N, 6.22%). IR (KBr pellet, cm^{-1}): 3500, 3300 (br), 1710, 1670, 1540, 1490, 1430, 1380, 1360, 1325, 1265, 1195, 1085, 1010, 945, 930, 820, 785, 770, 695, 670, 500, 465, 370. Conductance in DMF Λ_M, 19.81 Ω^{-1} cm^2 mol^{-1} (κ, 11.03 × 10^{-6} S cm^{-1}). μ, 2.72 μ_B.

[V(DPA)(oxin)(H_2O)] 3. Compound **1** (0.23 g, 0.78 × 10^{-3} mol) was dissolved in 70 cm^3 of water by refluxing followed by the addition of a 30 cm^3 ethanolic solution of 0.12 g (0.80 × 10^{-3} mol) of 8-hydroxyquinoline (oxinH) drop by drop. The orange solution gradually turned brown and on complete addition a brown compound settled out. After refluxing for 2 h the solid was filtered off, washed with water and alcohol and dried over $CaCl_2$. Yield 0.24g, 75% (Found: C, 45.62; H, 3.54; N, 6.21. Calc. for $VC_{16}H_{11}N_2O_6$: C, 46.48; H, 3.63; N, 6.77%). IR (KBr pellet, cm^{-1}): 3100 (br), 1640, 1600, 1570, 1495, 1460, 1375, 1320, 1275, 1225, 1200, 1150, 1110, 1080, 1040, 940, 830, 775, 750, 640, 540, 505, 460, 410, 350. Conductance in DMF Λ_M, 21.36 Ω^{-1} cm^2 mol^{-1} (κ, 9.24 × 10^{-6} S cm^{-1}). μ, 2.75 μ_B.

[V(DPA)(PA)(H_2O)$_2$]·H_2O 4. This was prepared by three different routes: (i) [V(DPA)(H_2O)$_2$F]·1.5H_2O **1** + PAH (1 : 1) $\longrightarrow$ **4**; (ii) [V(PA)$_3$]·3H_2O[26] + $DPAH_2$ (1 : 1) $\longrightarrow$ **4**; (iii) [V(DPA)(H_2O)$_2$F]·1.5H_2O **1** + [V(PA)$_3$]·3H_2O + $DPAH_2$ (1 : 1 : 1) $\longrightarrow$ **4** (PAH = pyridine-2-carboxylic acid, picolinic acid). All of these methods involve refluxing the reactants in aqueous medium. When 0.25 g (0.82 × 10^{-3} mol) of **1** suspended in 75 cm^3 of water was refluxed with 0.12 g (0.9 × 10^{-3} mol) of PAH for 3 h, a clear orange-yellow solution was obtained. Shiny yellow crystals of **4** separated out on cooling. The crystals were filtered, washed with water and dried over fused $CaCl_2$. Yield 0.20g, 65% (Found: C, 39.96; H, 3.32; N, 7.05. Calc. for $VC_{13}H_{13}N_2O_9$: C, 40.00; H, 3.33; N, 7.17%). IR (KBr pellet, cm^{-1}): 3200 (br), 1640, 1610, 1390, 1300, 1080, 1060, 1030, 1020, 940, 880, 770, 720, 690, 680, 650, 500, 470, 410, 380. Conductance in DMF Λ_M, 19.10 Ω^{-1} cm^2 mol^{-1} (κ, 7.06 × 10^{-6} S cm^{-1}). μ, 3.02 μ_B.

[V(DPA)(SA)(H_2O)]·2H_2O 5. Compound **1** (0.24 g, 0.80 × 10^{-3} mol) was suspended in 25 cm^3 water and refluxed with 0.13 g (0.97 × 10^{-3} mol) of salicylic acid (SAH_2) for 3 h. The greenish yellow precipitate was filtered off, washed with water and dried over fused $CaCl_2$. Yield 0.24 g, 75% (Found: C, 40.90; H, 3.43; N, 3.46. Calc. for $VC_{14}H_{14}NO_{10}$: C, 41.48; H, 3.45; N, 3.45%). IR (KBr pellet, cm^{-1}): 3300 (br), 1665 (br), 1620, 1590, 1530, 1490, 1470, 1360, 1250, 1190, 1085, 1040, 940, 890, 835, 770, 680, 490, 460, 425, 375. Conductance in DMF Λ_M, 16.51 Ω^{-1} cm^2 mol^{-1} (κ, 5.79 × 10^{-6} S cm^{-1}). μ, 2.78 μ_B.

When **1** is refluxed with phen or 2,2′-bipy in ethanol and then cooled, deep brown crystals of oxovanadium(IV) complexes [VO(DPA)(phen)]·3H_2O[27] or [VO(DPA)(bipy)]·H_2O are isolated even when the entire operation is conducted under dry N_2.

Crystallography

A yellow prismatic crystal of **4** (0.20 × 0.48 × 0.40 mm) was chosen for the X-ray diffraction study. The compound crystallised in the triclinic space group $P\bar{1}$. Crystal data are listed in Table 1. Intensity data were collected on a MSC/Rigaku Raxis-IIc imaging data[28] diffractometer using graphite-monochromatised Mo-Kα radiation (λ = 0.71073 Å) from a rotating anode generator powered at 60 kV and 90 mA. A total of 2841 reflections were collected, all of them being independent reflections (R_{int} 0.00), covering indices $-10 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 0$, $-12 \leqslant l \leqslant 12$, by oscillation photographs (30 frames in total), with φ = 0–180°, $\Delta\varphi$ = 6.0° at a scan rate of 8 min per frame.[29,30] The intensities were corrected for Lorentz and polarization effects and for absorption using the ABSCOR program.[31] The structure was solved by Patterson methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares, with a riding model for hydrogen atoms, using the SHELXTL PLUS-PC version.[32] The weighting scheme was $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ and goodness of fit, S = 1.30.

CCDC reference number 186/1149.

Table 1 Crystal data, data collection, solution and refinement for [V(DPA)(PA)(H_2O)$_2$]·H_2O **4**

Empirical formula	$C_{13}H_{13}N_2O_9V$
M	392.2
Crystal system	Triclinic
a/Å	8.357(2)
b/Å	9.233(2)
c/Å	10.639(2)
α/°	82.28(3)
β/°	72.37(3)
γ/°	71.91(3)
U/Å^3	742.9(4)
T/K	294
Space group	$P\bar{1}$
Z	2
μ(Mo-Kα)/mm^{-1}	0.724
Reflections collected	2841
Independent reflections	2841
Final R indices (obs. data) R, R'	0.055, 0.081
R Indices (all data) R, R'	0.0599, 0.098

Results and discussion

The dipicolinate anion with its two carboxylate groups in *ortho* positions with respect to the pyridine nitrogen is potentially tridentate. The ligand can thus exist as DPA^{2-}, $DPAH^-$ or $DPAH_2$. The acidity constants of $DPAH_2$[11] are pK_{a1} = 2.10 and pK_{a2} = 4.68. The principle underlying the design of the six-coordinated precursor complex reported in this study is to put a strong tridentate chelating ligand in the first coordination sphere of V(III) keeping the other three positions occupied by weak monodentate donors which can act as the binding sites of selected bi- and tri-dentate chelating ligands. The complex [V(DPA)(H_2O)$_2$F]·1.5H_2O **1** is isolated from the reaction of $DPAH_2$ and K_3VF_6 in aqueous medium. Complex **1**, owing to the presence of three labile sites in the form of the monodentate donors H_2O and F^-, holds the possibility of acting as a precursor of a host of mixed ligand complexes in which the three monodentate donors present in the first coordination sphere of V(III) can be fully replaced by a tridentate or partly replaced by a bidentate ligand. Depending on the actual nature of the secondary ligands used, various types of complexes can be prepared. The following types of ligands were tried: (1) neutral tridentate (terpy), (2) diacid tridentate ($DPAH_2$), (3) neutral bidentate (phen, bipy), (4) monoacid bidentate (PAH, oxinH), (5) diacid bidentate (SAH_2). When ligands of type (1) and (3) are reacted with **1** the product is always a VO^{2+} complex, obviously the oxidation product of the precursor V(III) complex. The V(III) complexes representing each of the other classes were isolated in the solid state.

The complex **2** is easily prepared by the reaction of $DPAH_2$ with VCl_3 in water irrespective of whether the ligand–metal ratio is 1 : 1, 1 : 2 or even 1 : 4. The compound was also prepared by reacting one mol of K_3VF_6 with two or more mol of $DPAH_2$. All attempts to prepare a 1 : 1 metal–ligand complex from VCl_3 failed. Even if VCl_3 is kept in large excess and the solution of $DPAH_2$ is added to it slowly drop by drop, the product is always

Table 2 UV/VIS spectral data

Complex	λ_{max}/nm (10^{-3} ε/M^{-1} cm^{-1})
[V(DPA)(H_2O)$_2$F]·1.5H_2O **1**	414 (0.295); 299 (0.550); 273 (1.755)
[V(DPA)(DPAH)(H_2O)]·3H_2O **2**	635 (0.032); 425 (0.567); 200 (3.050)
[V(DPA)(oxin)(H_2O)] **3**	585 (0.251); 415 (3.702); 273 (6.251)
[V(DPA)(PA)(H_2O)$_2$]·H_2O **4**	742 (0.024); 580 (0.205); 394 (0.260); 269 (4.970)
[V(DPA)(SA)(H_2O)]·2H_2O **5**	416 (0.847); 302 (1.918); 271 (2.994)

the 1 : 2 complex **2**. It is well known that the V(III) state is quite susceptible to oxidation to the V(IV) state, mainly to the VO^{2+} species. Again, from the discussion on the synthetic methods adopted it is noted that the secondary ligands (*e.g.* bipyridine, *o*-phenanthroline or terpyridine) which failed to produce the V(III) heterochelates and caused their oxidation to the VO^{2+} state are of rather strongly basic character. In these cases water present in **1** appears to provide both the oxo group and the oxidising agent. It also appears that the secondary ligands, in which the acid function(s) predominates over the basic function(s), or both of them are more or less balanced, are capable of keeping the starting material in the V(III) oxidation state.

The elemental analysis of the complexes corresponds well with the calculated stoichiometry. The magnetic moment of the complexes at room temperature is approximately 2.8 μ_B confirming the presence of two unpaired 'd' electrons.[33] Conductance values in DMF indicate all the complexes are non-electrolytes.

The free ligand DPAH$_2$ exhibits a $\nu_{C=O}$ stretch[34] typical of a free carboxylic group around 1700 cm^{-1} and the presence of intramolecularly hydrogen bonded CO_2H groups is indicated by a very broad and irregular shaped band spanning 3300–2500 cm^{-1}. The broad band in the 3500–3100 cm^{-1} region in the complexes is indicative of the presence of hydrogen bonded lattice water, the presence of which is proved by the crystal structure analysis of **4**. From the IR spectra of the complexes it is indicated that the dipicolinic anion (DPA) acts as a tridentate chelating ligand being bonded to the V(III) acceptor centre *via* the two deprotonated oxygen atoms of the carboxylate moieties ($\nu_{C=O} \approx 1660$ cm^{-1}) and the heterocyclic nitrogen.[35] The $\nu_{C=O}$ of the free carboxylic acid[36] is found to be lowered by 30–40 cm^{-1} due to coordination in all the complexes. The IR spectrum of **2** reveals an extra intense band at 1710 cm^{-1} due to a free carboxylic acid $\nu_{C=O}$ vibration. In the spectrum of **3** an additional band is observed at 1570 cm^{-1} which may be due to the $\nu_{C=N}$ mode of the quinoline ring coordinated to the V(III) centre through the nitrogen atom. Participation of the heterocyclic ring nitrogen in all the complexes is indicated by a 20–50 cm^{-1} red shift of the in-plane and out-of-plane deformation modes[37] of the pyridine ring observed in the free ligand around 640 and 430 cm^{-1} respectively. In the spectrum of complex **1** the presence of a V–F bond is indicated by the strong ν_{V-F} band[38] at 480 cm^{-1}.

The complexes dissolve in DMF to give bright orange-yellow solutions. Spectra of the solutions are recorded immediately over the range 900–250 nm[39] (Table 2). Complexes **1**, **2**, **3** and **5** exhibit a shoulder in the 635–414 nm region and a rather broad band in the 425–299 nm region assigned to $^3T_{1g}(F) \longrightarrow {}^3T_{2g}$ and $^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ respectively which are characteristic of V(III) in an octahedral donor environment. The very sharp and intense band ($\varepsilon = 1.7 \times 10^3$–$6.2 \times 10^3$ M^{-1} cm^{-1}) in the 273–200 nm range is due to intraligand $\pi \longrightarrow \pi^*$ transitions. The third spin-allowed transition [$^3T_{1g}(F) \longrightarrow {}^3A_{2g}$] could not be located as it lies below 300 nm and thus remains buried under the high energy tail of the intense charge transfer band in this region. The spectrum of compound [V(DPA)(PA)(H_2O)$_2$]·H_2O **4** exhibits an additional band in the long wavelength region (742 nm). This band is reported to be diagnostic of seven-coordinated V(III) species[22,36] in solution. This prompted us to prepare good single crystals of **4** and to determine its structure which unambiguously established the seven-coordinated pentagonal bipyramid structure of [V(DPA)(PA)(H_2O)$_2$]·H_2O.

Table 3 Cyclic voltammetric results at 298 K

	$E_{\frac{1}{2}}{}^{a}$/V (ΔE_p/mV)	
Complexes	Reduction	Oxidation
[V(DPA)(H_2O)$_2$F]·1.5H_2O **1**	−1.26(75), −1.57(140)	0.56(E_{pa}), 1.09(E_{pa})
[V(DPA)(DPAH)(H_2O)]·3H_2O **2**	−0.88(85), −1.72(100)	0.89(E_{pa}), 1.05(E_{pa})
[V(DPA)(oxin)(H_2O)] **3**	−1.31(70), −1.92(100)	0.70(E_{pa}), 1.08(E_{pa})
[V(DPA)(PA)(H_2O)$_2$]·H_2O **4**	−1.09(80), −1.58(150)	0.68(E_{pa}), 1.05(E_{pa})
[V(DPA)(SA)(H_2O)]·2H_2O **5**	−1.48(80), −1.92(90)	0.66(E_{pa}), 1.05(E_{pa})

[a] Solute concentration, 10^{-3} M; $E_{\frac{1}{2}}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potential; $\Delta E_p = E_{pa} - E_{pc}$; $I_{pc}/I_{pa} = 1$ and scan rate = 50 mV s^{-1}.

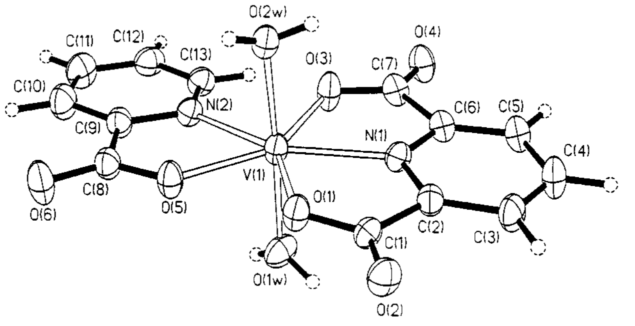

Fig. 1 An ORTEP plot of [V(DPA)(PA)(H_2O)$_2$]·H_2O **4**.

The electron transfer reactions of the complexes were examined by cyclic voltammetry in the −1.9 to +1.7 V range using DMF as solvent and NEt$_4$ClO$_4$ as supporting electrolyte. The results are given in Table 3. Cyclic voltammograms of all the V(III) complexes exhibit a reversible V(III)/V(II) couple[40] around −0.88 to −1.48 V. The quasi-reversible to irreversible couples above −1.58 V are probably due to ligand reduction as the Zn–DPA complex exhibits a couple in the same region. The two irreversible oxidation peaks[41] observed in the ranges +0.56 to +0.89 V and +1.05 to +1.09 V are assigned to the V(III)/V(IV) and V(IV)/V(V) couples respectively. From the $E_{\frac{1}{2}}$ value for complex **1** the V(III)/V(IV) oxidation step appears to be easier in comparison to the corresponding oxidation step of the other complexes. This is expected as **1** contains the highly electronegative F$^-$ ion which has a tendency to stabilise higher oxidation states.

Crystal structure of [V(DPA)(PA)(H_2O)$_2$]·H_2O 4

The geometry around the V(III) centre is a slightly distorted pentagonal bipyramid with dipicolinate and picolinate ligands occupying the pentagonal equatorial plane and the two coordinated water molecules filling up the two axial sites. The dianionic tridentate dipicolinate[42] and monoanionic bidentate picolinate are found to remain chelated to the V(III) centre through their arene N-atoms and carboxylate O-atoms. Fig. 1 shows the ORTEP[43] plot of **4** and selected bond lengths and bond angles are given in Table 4. The bite angles around the vanadium atom range from 71.1(1) to 73.4(1)° summing up the in-plane angles to be 360.3°. This shows the high planarity of these five atoms. The bond angle involving the axial atoms, O(1w)–V(1)–O(2w) is 177.1(1)° giving a more or less symmetric pentagonal bipyramid structure. Atom V(1) is displaced 0.2910 Å above the pentagonal plane defined by O(1), N(1), O(3), N(2) and O(5). Of the two V–O bonds generated by the coordinated

Table 4 Bond lengths (Å) and angles (°) for complex **4**

V(1)–O(1)	2.101(2)	V(1)–O(3)	2.040(2)
V(1)–N(1)	2.162(3)	V(1)–O(5)	2.021(2)
V(1)–N(2)	2.265(3)	V(1)–O(1w)	2.062(2)
V(1)–O(2w)	2.038(2)	O(1)–C(1)	1.284(4)
O(2)–C(1)	1.239(4)	O(3)–C(7)	1.273(5)
O(4)–C(7)	1.228(4)	N(1)–C(2)	1.336(4)
N(1)–C(6)	1.344(4)	O(5)–C(8)	1.268(5)
O(6)–C(8)	1.231(4)	N(2)–C(9)	1.337(4)
N(2)–C(13)	1.341(4)		
O(1)–V(1)–O(3)	142.1(1)	O(1)–V(1)–N(1)	71.1(1)
O(3)–V(1)–N(1)	71.2(1)	O(1)–V(1)–O(5)	72.1(1)
O(3)–V(1)–O(5)	145.5(1)	N(1)–V(1)–O(5)	143.2(1)
O(1)–V(1)–N(2)	144.5(1)	O(3)–V(1)–N(2)	73.4(1)
N(1)–V(1)–N(2)	144.2(1)	O(5)–V(1)–N(2)	72.5(1)
O(1)–V(1)–O(1w)	90.2(1)	O(3)–V(1)–O(1w)	93.1(1)
N(1)–V(1)–O(1w)	89.2(1)	O(5)–V(1)–O(1w)	90.8(1)
N(2)–V(1)–O(1w)	87.5(1)	O(1)–V(1)–O(2w)	89.5(1)
O(3)–V(1)–O(2w)	88.9(1)	N(1)–V(1)–O(2w)	93.4(1)
O(5)–V(1)–O(2w)	86.4(1)	N(2)–V(1)–O(2w)	91.1(1)
O(1w)–V(1)–O(2w)	177.1(1)	V(1)–O(1)–C(1)	123.9(2)

Hydrogen bonds

O(1w) ··· O(2a)	2.666	O(1w) ··· O(4b)	2.716
O(2w) ··· O(1c)	2.813	O(2w) ··· O(3d)	2.610
O(3w) ··· O(6)	2.729	O(3w) ··· O(6e)	2.774

Symmetry transformations: a $1 - x, -y, 1 - z$; b $1 - x, -y, -z$; c $-x, -y, 1 - z$; d $x, 1 + y, z$; e $-x, -y - 1, 1 - z$.

carboxylate oxygens O(1) and O(3) of the dipicolinate moiety, V–O(1) is slightly longer. The V–O(5) bond formed by the coordinated carboxylate of the picolinate is a little shorter than both the V–O bonds of the coordinated dipicolinate. The two bonds V(1)–N(1) and V(1)–N(2) differ considerably in length, the V(1)–N(2) bond formed by the ring nitrogen of picolinic acid being the longer of the two. The average V–O and V–N distances[36] for seven-coordinate V(III) complexes are 2.054–2.061 and 2.222–2.246 Å respectively. This may indicate stronger binding of the dipicolinate–nitrogen N(1) compared to that of the picolinate–nitrogen N(2) which is quite logical because of the enhanced electron density on N(1) due to the presence of two electron-releasing carboxylate groups in the two *ortho* positions. Three types of hydrogen bonding are present as seen in the packing diagram (Fig. 2). One axially coordinated H_2O is found to form hydrogen bonds with two carbonyl oxygens of the two coordinated dipicolinate moieties belonging to two different $[V(DPA)(PA)(H_2O)_2]\cdot H_2O$ units. The other axial water molecule is involved in hydrogen bonding with the two carboxylate oxygens of a coordinated dipicolinate moiety of an adjacent $[V(DPA)(PA)(H_2O)_2]\cdot H_2O$ unit. The third type of hydrogen bonding involves the two lattice water molecules. Each of them participate in two hydrogen bonds with the carbonyl oxygen of two coordinated picolinate moieties belonging to two different units and thus these two water molecules are stabilised within the crystal lattice. All the three types of hydrogen bonding observed leads to the stabilisation of the crystal packing pattern.

Concluding remarks

When the DPA moiety acts in a dianionic tridentate manner, all its three donor points (the pyridine nitrogen and the two carboxylate oxygens) lie in one plane. Synthesis of **4** by route (i) indicates that in the presence of the DPA unit coordinated to the V(III) centre, the incoming bidentate PA moiety is coerced into occupying two coordination positions in the same plane generating a pentagonal planar coordination around V(III). When route (ii) is followed, the incoming tridentate DPA moiety dislodges two of the three coordinated PA units, the PA unit left undisturbed by DPA being the one which is present in the same plane spanned by the incoming DPA moiety. The two vacant axial positions are quite naturally occupied by two water molecules as the reaction is carried out in aqueous medium. The unique combination of DPA and PA led to the formation of the seven-coordinated complex **4**.

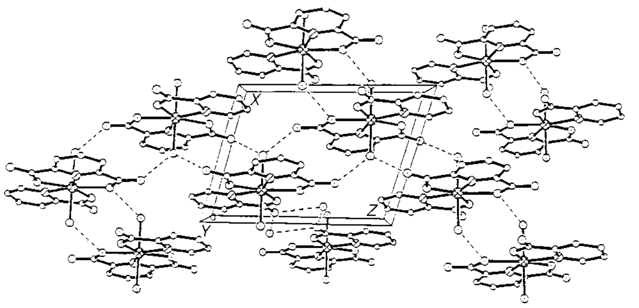

Fig. 2 Packing diagram of $[V(DPA)(PA)(H_2O)_2]\cdot H_2O$ **4**.

This is a rare example of the synthesis of a stable mononuclear seven-coordinated pentagonal bipyramidal vanadium(III) complex from highly stable six-coordinated precursors $[V(DPA)(H_2O)_2F]\cdot 1.5H_2O$ or $[V(PA)_3]\cdot 3H_2O$, the latter being exceptionally stable. A very interesting feature of this complex is that it contains two different α-N-heterocyclic acid donors and both of them are present in the equatorial plane. The high stability of the seven-coordinated complex can be attributed to its neutral nature, symmetric structure as well as to the hard–hard interaction between the hard donor sites (N,O) and the fairly hard V(III) acceptor centre.

Compound **4** holds the possibility of functioning as the parent for a host of seven-coordinated vanadium(III) complexes maintaining the same five point equatorial planar occupation by the dipicolinate and picolinate moieties but replacing the two axial water molecules, wholly or partly, by other suitable monodentate Lewis bases.

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