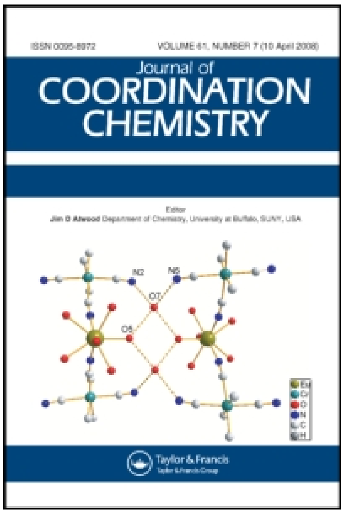

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A New Insulin-Like Vanadyl Complex: Synthesis and Structure of V(IV)O(H_2O)$_2$ (2,6-PyridineDicarboxylate)*E*2H_2O

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A NEW INSULIN-LIKE VANADYL COMPLEX: SYNTHESIS AND STRUCTURE OF $V(IV)O(H_2O)_2$ (2,6-PYRIDINEDICARBOXYLATE)·$2H_2O$

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$V(IV)O(H_2O)_2$(2,6-pyridinedicarboxylate)·$2H_2O$ (**1**) was obtained by the reaction of $VO(acac)_2$ with 2,6-pyridine dicarboxylic acid in MeOH and water. Complex (**1**) was characterized by IR spectroscopy, element analysis and X-ray diffraction. It crystallizes in space group $P\bar{1}$. X-ray structure analysis has shown that complex (**1**) is a monomeric neutral complex containing vanadyl ion, 2,6-pyridinedicarboxylate ligand and coordinated water, possessing distorted octahedral geometry. Complex (**1**) is constructed from mononuclear vanadium, $V(IV)O(H_2O)_2$(2,6-pyridinedicarboxylate) units and crystallization water molecules held together in an extensive two-dimensional network via O–H···O hydrogen bonds, π–π stacking interactions between parallel aromatic pyridines, and face-to-face stacking interactions between parallel carbonyl groups of 2,6-pyridine dicarboxylic acid ligands along the plane formed by the x, z axis of the unit cell.

Keywords: Vanadium complex; 2,6-Pyridine dicarboxylic acid; Synthesis; Crystal structure

INTRODUCTION

Vanadium is an important trace transition metal with biological activity, especially in insulin-like bioactivity [1–4]. For instance, it can pharmacologically lower the glucose level in the blood of diabetic animals and patients [5]; it also serves as an electron acceptor which could stimulate enzymatic [5] and non-enzymatic oxidation of NADH (β-nicotinamide adenine dinucleotide) and NADPH (β-nicotinamide adenine dinucleotide phosphate) into their oxidized forms NAD^+ and $NADP^+$ [6]; its bisperoxovanadium complexes, such as $NH_4[VO(O_2)_2$-(1,10-phenanthroline)], possess bioactivity for cleavage of DNA [7], etc. Vanadium has various oxidation states, e.g., +3, +4, +5, etc., all of which can interact with biomolecules containing negatively charged oxygen donors such as carboxylate, phenolate, phosphate, phosphonate, catecholate and hydroxamate groups [8–11]. Pyridinecarboxylic acids and their ring-substituted derivatives exist in many natural products and have proven biophysiological properties;

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vanadium complexes of pyridinecarboxylic acid are particularly interesting molecular model systems, because they are potential agents for treating insulin-dependent diabetes mellitus (IDDM) in rats by daily intraperitoneal (i.p.) injection or oral administration [12]. Until very recently, although a number of vanadium complexes containing different pyridine derivatives had been reported, including their synthesis, properties and bioactivities, we still could not understand the relationship between the structures of the vanadium complexes and their bioactivities. Furthermore, crystal structures are very rare. The aim is to explore a new family of vanadium(IV) and (V) complexes with desirable qualities for pharmaceutical agents including neutral charge, low molecular weight, thermodynamic and hydrolytic stability, oral bioactivity and, where possible, bifunctional capability. The family of compounds of pyridinedicarboxylate or their derivatives coordinated to vanadium(III), (IV) or (V) ions are of special interest and could form many model complexes with various coordination modes.

The interactions of vanadium (IV) with pyridinecarboxylic acids or their derivatives were studied earlier by various experimental means, and some coordination modes of their complexes were proposed. For example, bis(picolinato)oxovanadium (VO-PA), bis(6-methylpicolinato)oxovanadium (VO-6MPA) [5], bis(3-methylpicolinato)-oxovanadium (VO-3MPA) [5], bis(3-hydroxylpicolinato)oxovanadium (VO-3HPA), bis(6-hydroxylpicolinato)oxovanadium (VO-6HPA) [9], bis(3-hydroxylpicolinato)-oxovanadium (VO-3HPA) [9], bis(5-iodopicolinato)oxovanadium (VO-5IPA) [13], bis(6-ethylpicolinato)oxovanadium (VO-6EPA) [14], have been reported. Among these complexes, we found that substituted groups in the pyridine ring of the picolinate ligand fall into two types: electron-donating groups (Me–, Et–) and electron-withdrawing groups (–OH, –I). To our knowledge, there is no crystal structural data for the vanadium complexes mentioned above except for bis(6-ethylpicolinato)oxovanadium (VO-6EPA) [14]. In order to examine the effect of groups on the pyridine ring on the structures and bioactivity of the corresponding vanadium complexes, in this article, we report a new $V(IV)O(H_2O)_2$(2,6-pyridinedicarboxylate)$\cdot 2H_2O$ complex with a new coordination mode, including its synthesis and characterization.

EXPERIMENTAL

Methods and Materials

The reactions were carried out at room temperature. Solvent and reactants were used as purchased from Wako Pure Chemical Industries, Ltd, Japan. IR spectra were recorded from KBr pellets on a JEOL JIR-7000 spectrophotometer in the range 4000–400 cm^{-1}. Carbon, hydrogen and nitrogen analyses were performed on a Yanaco CHN CORDER MT-6 instrument. Differential scanning calorimetry was conducted using a Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10°C/min under nitrogen.

Synthesis of $V(IV)O(H_2O)_2$(2,6-pyridinedicarboxylate)$\cdot 2H_2O$ (1)

To a solution of $VO(acac)_2$ (0.265 g, 1 mmol) in 5 cm^3 of dry MeOH was added a solution of 2,6-pyridinedicarboxylic acid (0.167 g, 1 mmol) in 10 cm^3 of MeOH and 3 cm^3 of water. The mixture was stirred for 4 h and a green solution was obtained, accompanied by a small amount of green precipitate. The precipitate was filtered and the solution was evaporated under vacuum. The residue was washed extensively with MeOH and dried under vacuum. Analysis shows that both the green precipitate and the solid obtained by evaporation are the same product (by IR), yield, 0.19 g, 60.67% (based on V), d.p. 178.5°C. Crystals of the green solid could be obtained by recrystallizing from MeOH. Anal. Calcd. for $C_7H_{11}NO_9V$% (FW 313.17)(%); C, 26.82; H, 3.51; N, 4.47. Found: C, 27.10; H, 3.40; N, 4.42. IR (KBr, ν cm^{-1}): 3257vw, 1652vs, 1361s, 1180s, 1074w, 1050m, 970s, 927m, 754w, 682w.

Determination of X-ray Structure of (1)

A green plate-shaped crystal of (**1**) was selected. The diffraction measurement was performed by standard techniques at room temperature on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) using an 18-kW rotating generator, and an ω–2θ scan mode. The crystal data, data collection and refinement details are summarized in Table I. A total of 2991 reflections, 2689 unique, were collected up to $2\theta_{\max} = 55°$. Absorption corrections were applied by measuring three ψ-scans. The structure was solved by direct methods using the SHELXS [15] program and refined by full-matrix least-squares methods using the SHELXL-97 [16] program. All the non-hydrogen atoms were refined anisotropically and the contributions of the hydrogen atoms on carbon were included in the calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. The O–H hydrogen atoms in the coordinated water and the lattice water (O_{w1}) were found in the electron maps, inserted at these positions and not further refined. Hydrogen atoms on the disordered water molecule (O_{w2}) were not included. Atomic scattering factors and anomalous dispersion terms were as in the SHELXL-97 program. Structures were drawn using ORTEP32 [17], and all calculations were performed on a Diamondtron

TABLE I Crystallographic data for (**1**)

Formula	$C_7H_{11}NO_9V$
M (g mol^{-1})	313.17
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.129(14)
b (Å)	10.751(16)
c (Å)	6.568(7)
α (°)	100.15(15)
β (°)	94.68(12)
γ (°)	111.47(10)
V (Å^3)	583.0(14)
Z	2
D_{calc}	1.784
Crystal size (mm)	0.70 × 0.50 × 0.10
F(000)	310
μ(Mo Kα) (cm^{-1})	1.003
2θ (°)	5.0–55.0
Reflections collected	2991
Independent reflections ($I > 2\sigma(I)$)	2407
Parameters	299
$\Delta(\rho)$ (e Å^{-3})	1.539 and −1.134
Goodness-of-fit	0.908
R^a	0.0612 (0.0657)^b
wR_2^a	0.1546 (0.1613)^b

$^aR = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/[\Sigma(w(F_o^2)^2)]^{1/2}$; $[F_o > 4\alpha(F_o)]$. ^{b}Based on all data.

TABLE II Atomic coordinates (× 10^4 Å) and equivalent isotropic displacement parameters (×10^3Å) for (**1**)

Atom	*x*	*y*	*z*	*U(eq)*
V	5109(1)	2241(1)	1810(1)	26(1)
O(1)	6894(2)	2376(3)	2413(4)	49(1)
O(2)	5611(3)	4019(2)	871(4)	36(1)
O(3)	4060(3)	376(2)	2594(4)	34(1)
O(4)	4528(2)	3140(2)	4425(3)	31(1)
O(5)	4402(2)	1248(2)	−1286(3)	29(1)
O(6)	2508(2)	394(2)	−4134(3)	35(1)
O(7)	2722(2)	3680(2)	6075(3)	38(1)
N	2655(2)	1987(2)	1008(3)	24(1)
C(2)	1924(3)	1417(2)	−946(4)	26(1)
C(3)	377(3)	1288(3)	−1556(4)	33(1)
C(4)	−377(3)	1768(3)	−11(5)	39(1)
C(5)	415(3)	2361(3)	2038(4)	35(1)
C(6)	1969(3)	2472(2)	2481(4)	26(1)
C(7)	2990(3)	966(2)	−2280(4)	27(1)
C(8)	3129(3)	3157(2)	4514(4)	28(1)
O_{W1}	7108(4)	4330(4)	−2282(4)	67(1)
O_{W2}	9753(5)	5400(5)	2741(8)	109(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE III The selected bond lengths (Å) and angles (°) for (**1**)

V–O(1)	1.592(3)	V–O(2)	2.016(4)
V–O(4)	2.026(3)	V–O(5)	2.051(4)
V–O(3)	2.059(4)	V–N	2.163(4)
O(6)–C(7)	1.227(4)	O(7)–C(8)	1.232(3)
O(5)–C(7)	1.298(4)	O(4)–C(8)	1.289(4)
N–C(2)	1.324(4)	N–C(6)	1.326(3)
O(1)–V–O(2)	97.78(15)	O(1)–V–O(4)	106.48(17)
O(2)–V–O(4)	87.34(16)	O(1)–V–O(5)	106.43(16)
O(2)–V–O(5)	87.77(17)	O(4)–V–O(5)	147.09(10)
O(1)–V–O(3)	95.46(16)	O(2)–V–O(3)	166.76(10)
O(4)–V–O(3)	88.91(17)	O(5)–V–O(3)	88.51(18)
O(1)–V–N	178.04(11)	O(2)–V–N	84.16(13)
O(4)–V–N	73.80(15)	O(5)–V–N	73.33(15)
O(3)–V–N	82.60(14)	C(7)–O(5)–V	122.46(19)
C(8)–O(4)–V	122.8(2)	V–O(2)–H(1′)	115(3)
C(2)–N–C(6)	122.7(2)	C(2)–N–V	118.96(19)
C(6)–N–V	118.3(2)	N–C(2)–C(3)	121.1(2)
N–C(2)–C(7)	111.2(2)	O(5)–C(7)–C(2)	114.0(2)
O(7)–C(8)–O(4)	125.0(3)	O(7)–C(8)–C(6)	120.8(3)
O(4)–C(8)–C(6)	114.2(2)		

RD17GR computer. Final residuals are $R = 0.0612$, $wR_2 = 0.1546$ for 2407 reflections; $R = 0.0657$, $wR_2 = 0.1613$ for all data. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table II. Selected bond distances and angles for (**1**) are given in Table III. An ORTEP view of (**1**) is shown in Fig. 1.

RESULTS AND DISCUSSION

Syntheses

Vanadyl sulfate reacts with 2,6-pyridinedicarboxylic acid to form a (dipicolinato)oxovanadium complex, $VO(H_2O)_2$(2,6-pyridinedicarboxylate) · $1/2SO_4$, [5] (see Scheme 1).

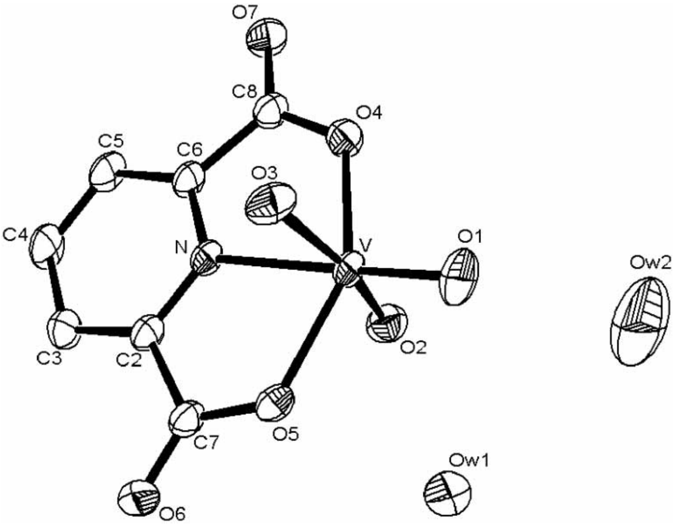
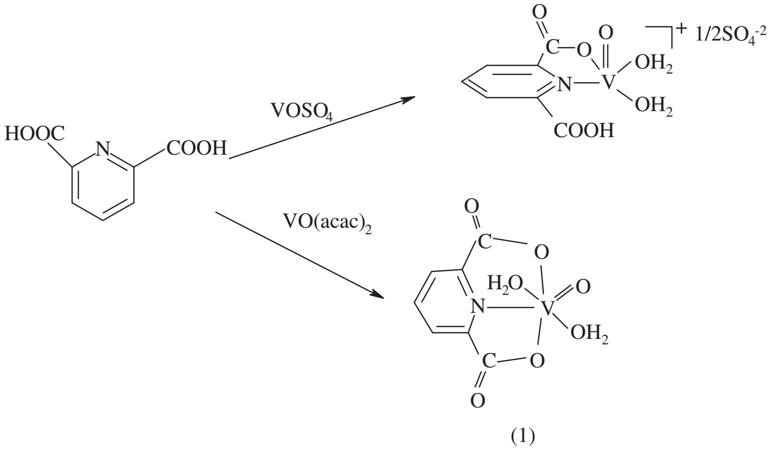


FIGURE 1 An ORTEP drawing of V(IV)O(H_2O)$_2$(2,6-pyridinedicarboxylate) · $2H_2O$ (**1**), showing the atom numbering scheme.



SCHEME 1

The reaction route and the coordination mode are different from the title complex, indicating variety in coordination of 2,6-pyridinedicarboxylic acid to vanadium. The title complex was obtained by the reaction of VO(acac)$_2$ and 2,6-pyridinedicarboxylic acid in methanol and water solution with molar ratios ranging from 1 : 1 to 1 : 2; addition of water should be as small as possible. Green crystals of (**1**) were obtained by recrystallization from MeOH after seven days. Its structure was determined by X-ray diffraction showing that 2,6-pyridinedicarboxylic acid and water participate in the reaction, the first example of a vanadium complex with a pyridinedicarboxylate ligand. The crystals of complex (**1**) isolated from the solution were stable in air for long periods of time. Complex (**1**) was slightly soluble in water, soluble in methanol, and insoluble in CH_2Cl_2, CH_3CN and THF. Attempts to obtain complexes similar to VO(H_2O)$_2$(2,4-pyridinedicarboxylate) · $2H_2O$ from a procedure similar to that for VO_2(acac)(2,6-pyridinedicarboxylate) · $2H_2O$ failed, perhaps because of steric constraints.

Description of the Crystal Structure and Discussion

The X-ray three-dimensional structural determination of complex (**1**) reveals that it crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell, and consists of $VO(H_2O)_2$(2,6-pyridinedicarboxylate) and two lattice water molecules. As illustrated in Fig. 1, the geometry is a disordered octahedron with vanadium coordinated by two oxygen atoms from water, two carboxyl oxygen atoms (COO) and one nitrogen atom from a 2,6-pyridinedicarboxylic ligand and one terminal oxo. The 2,6-pyridinedicarboxylate ligand (COO, COO, N) chelates one vanadium atom to form two five-membered rings. This is a new example of a vanadium(IV) complex with 2,6-pyridinedicarboxylate, different from other related vanadium complexes, e.g., potassium oxodiperoxo(pyridine-2-carboxylate)vanadate(V), $K_2[VO(O_2)_2(PA)]\cdot 2H_2O$ [18]; potassium oxodiperoxo (3-hydroxypyridine-2-carboxylate)vanadate(V), $K_2[VO(O_2)_2$ $(3HPA)]\cdot 3H_2O$ [18]; $K_3[VO(O_2)_2$(2,4-pyridinedicarboxylate)$]\cdot 2H_2O$ [19]; bpV(2,4-pdc); $K_3[VO(O_2)_2$(3-acetatoxypicolinate)$]\cdot 2H_2O$, bpV(3-acetpic) [19,20]; $[VO(3HPA)(H_2O)]_4\cdot 9H_2O$ [20], $V(pic)_3\cdot H_2O$ [21] and $[VO(6epa)_2(H_2O)]\cdot 4H_2O$ [22]. For complex (**1**), the V–O(1) bond length [1.594(3) Å] is shorter than those in $K_2[VO(O_2)_2(PA)]\cdot 2H_2O$, $K_2[VO(O_2)_2(3HPA)]\cdot 3H_2O$, bpV(2,4-pdc), bpV(3-acetpic), $[VO(3HPA)(H_2O)]_4\cdot 9H_2O$, $V(pic)_3\cdot H_2O$ and $[VO(6epa)_2(H_2O)]\cdot 4H_2O$, while the V–N bond length [2.163(4) Å] is slightly longer than those in the corresponding complexes above. The $V–O_{carb}$ distances in complex (**1**) are shorter those of $K_2[VO(O_2)_2$ $(PA)]\cdot 2H_2O$, $K_2[VO(O_2)_2$ $(3HPA)]\cdot 3H_2O$, bpV(2,4-pdc) and pbV(3-acetpic), close to that of $[VO(3HPA)$ $(H_2O)]_4\cdot 9H_2O$ and longer than those in $V(pic)_3\cdot H_2O$ and $[VO(6epa)_2(H_2O)]\cdot 4H_2O$. However, it is surprising that the $V–O_{water}$ distances [2.016(4), 2.059(4) Å] are much shorter than those in the corresponding complexes. The O=V–N and $O{=}V–O_{carb}$ angles are 178.04(11)° and 106.43(16)° in complex (**1**), respectively. Both angles are different from those in related vanadium complexes, perhaps because coordinated nitrogen is *trans* to a terminal oxygen atom in complex (**1**), while, for other corresponding vanadium complexes, the coordinated O (COO) atom is *trans* to the terminal oxygen atom. The $N–V–O_{carb}$ angle is close to those found in other vanadium complexes. Comparisons of the detailed bond distances and angles related to vanadium complexes are given in Tables IV and V, respectively.

It is worth noting that C(8)–O(7) and C(8)–O(4), and C(7)–O(5) and C(7)–O(6) are shortened, indicating partial double bond character. C(8)–O(7) and C(8)–O(4) are 1.232(3) and 1.289(4) Å, respectively; while C(7)–O(5) and C(7)–O(6) are 1.298(4) and 1.227(4) Å, respectively, indicating more electron delocalization in complex (**1**) than in $V(pic)_3\cdot H_2O$ [21] (Table VI).

In addition, complex (**1**) contains some hydrogen bonds, primarily $O_{ligand(H_2O)}–H\cdots O_{uncoordinated\ carbonyl}$, $O_{ligand(H_2O)}\cdots H–O_w$ and $O_w–H\cdots O_{coordinated\ carbonyl}$. Hydrogen bond data are given in Table VII. Molecules are linked by two types of hydrogen bond. One is between coordinated oxygen atoms from the water and uncoordinated carbonyl oxygen atoms from pyridinedicarboxylate ligands, the others are bridging hydrogen bonds formed between coordinated oxygen atoms from the water and coordinated carboxyl oxygen atoms from pyridinedicarboxylate ligands by lattice water (O_{w1}) being bridged, namely O_{oxo} [O(2)]–H$\cdots O_w$(1)–H$\cdots O_{coordinated\ carbonyl}$ [O(4)]. The molecular packing of complex (**1**) is shown in Fig. 2. Mononuclear vanadium $V(IV)O(H_2O)_2$(2,6-pyridinedicarboxylate)$\cdot 2H_2O$ units and crystallization water molecules are held together in an extensive two-dimensional network via O–H$\cdots$O

TABLE IV Comparison of the bond lengths (Å) in related complexes

Complex	*V=O*	*V–N*	*V–O$_{carb}$*	*V–O$_{water}$*	*Ref.*
V(IV)O$(H_2O)_2$(2,6-pyridine-dicarboxylate)$\cdot 2H_2O$	1.594(3)	2.163(4)	2.026(3)–2.051(4)	2.016(4)–2.059(4)	This work
$K_2[VO(O_2)_2(PA)]$	1.599(4)	2.123(5)	2.290(4)		[17]
$K_2[VO(O_2)_2(3HPA)]\cdot 3H_2O$	1.606(2)	2.137(2)	2.314(2)		[17]
bpV(2,4-pdc)	1.622(9)	2.144(11)	2.299(8)		[18]
bpV(3-acetpic)	1.621(3)	2.179(4)	2.190(6)		[18]
$[VO(3HPA)(H_2O)]_4\cdot 9H_2O$	1.584–1.608	2.124–2.152	1.963–2.154	2.034–2.073	[19]
$V(pic)_3\cdot H_2O$		2.112(3)–2.153(3)	1.936(3)–1.966(2)		[20]
$[VO(6epa)_2(H_2O)]\cdot 4H_2O$	1.572(6)–1.596(6)	2.118(5)–2.153(5)	1.956(5)–2.002	2.219(5)–2.283(5)	[21]

TABLE V Comparison of the angles (°) in related complexes

Complex	*N–V=O*	*O=V–O$_{carb1}$*	*O=V–O$_{carb2}$*	*N–V–O$_{carb}$*	*Ref.*
V(IV)O$(H_2O)_2$(2,6-pyridine-dicarboxylate)$\cdot 2H_2O$	178.07(11)	106.40(17)	87.27(16)	73.39(15)–73.75(15)	This work
$K_2[VO(O_2)_2(PA)]$	93.6(2)	166.7(2)		73.1(2)	[17]
$K_2[VO(O_2)_2(3HPA)]\cdot 3H_2O$	94.92(7)	168.73(7)		73.0(6)	[17]
bpV(2,4-pdc)	93.1(4)	166.3(4)		73.7(6)	[18]
bpV(3-acetpic)	93.39(16)	166.04(15)		72.7(4)	[18]
$[VO(3HPA)(H_2O)]_4\cdot 9H_2O$	91.9–95.9	158.2–160.7	96.7–98.4	73.3–90.1	[19]
$V(pic)_3\cdot H_2O$				76.48(10)–168.58(10)	[20]

TABLE VI Comparison of the bond lengths (Å) between the C=O and C–O bonds in complexes of (**1**) and $VO(pic)_3\cdot H_2O$*

	*Complex (**1**)*	*$VO(pic)_3\cdot H_2O$ [21]*		
		Ligand A	*Ligand B*	*Ligand C*
C–O$_{coordination}$	1.289, 1.298	1.299(4)	1.319(4)	2.277(4)
C–O$_{uncoordination}$	1.227, 1.232	1.215(4)	1.199(4)	1.211(4)

* All ligands A, B and C are picolinic acid.

TABLE VII Hydrogen bonds (Å, °) in complex (**1**)*

Donor–H···acceptor	*D–H*	*H···A*	*D···A*	*D–H···A*
$O_w(1)–H\cdots O(4)^{\#1}$	0.94(5)	1.93(4)	2.802(6)	153(5)
$O(2)–H(2)'\cdots OW(1)$	0.68(5)	1.89(5)	2.577(5)	178(5)
$O(3)–H(4)'\cdots O(6)^{\#2}$	0.60(5)	2.10(5)	2.670(4)	158(6)

* $^{\#1}x, y, z-1$; $^{\#2}x, y, z+1$.

hydrogen bonds, π–π stacking interactions between parallel aromatic pyridines, and face-to-face stacking interactions between parallel carboxylate groups of 2,6-pyridine-dicarboxylate along the plane formed by the x, z axis of the unit cell. The V–V distances between molecules along the z axis is 6.568 Å; along the x axis it is 9.129 Å.

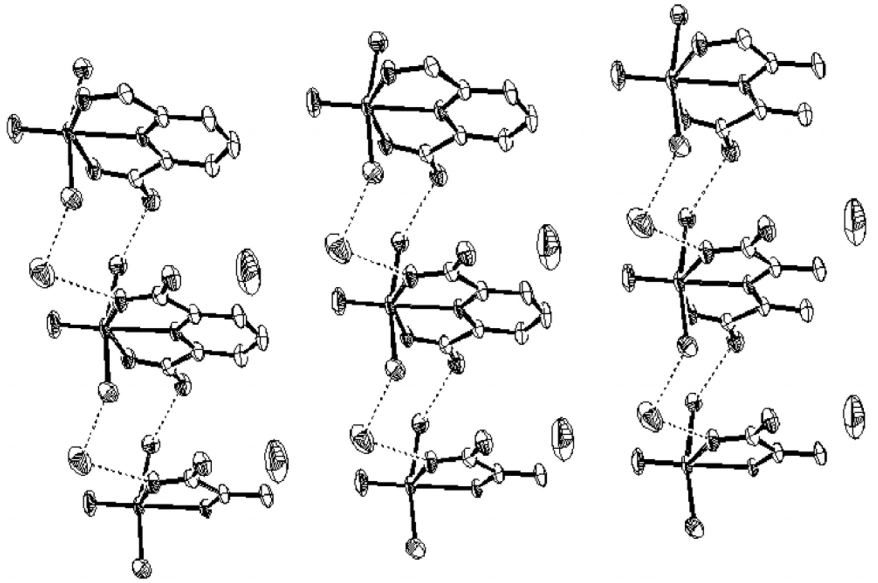


FIGURE 2 A view of the molecular packing of V(IV)O$(H_2O)_2$(2,6-pyridinedicarboxylate) · $2H_2O$ (**1**) along the plane formed by the *x* and *z* axis.

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Supplementary Data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 207745. Copies of this information may be obtained free of charge from the Director, 12 Union Road, Cambridge, CB2 1EZ, UK (deposit@ccdc.cam.ac.uk).

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