



Synthesis, structure determination and reactivity of a highly stable vanadium(III) complex

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Abstract—The synthesis, characterization, structure determination and reactivity study of a highly stable vanadium(III) complex of picolinic acid (picH)—a monoacid bidentate chelating donor—is reported. It can be kept in open air for days and can be heated up to 180°C without oxidation. The complex $[V(pic)_3] \cdot H_2O$ crystallizes in the monoclinic system with space group $C2/c$. The V^{III} acceptor centre is in a highly distorted octahedral donor environment. The reason for this exceptional stability of the complex towards oxidation is evident from the analysis of the structural and electrochemical data. © 1997 Elsevier Science Ltd

Keywords: V^{III} complex; N—O donor; exceptional stability; structure determination; reactivity study; electrochemistry.

Vanadium is a versatile element exhibiting formal oxidation states ranging from +5 to -1. Simple vanadium compounds of +3 and lower oxidation states are quite susceptible to oxidation mainly to the +4 or +5 oxidation states. Current revival of interest in vanadium chemistry has been due to its relevance to several biological [1–4] and industrial [5,6] processes. The recent discovery of the presence of trivalent vanadium in several biological systems has excited the interest of chemists and biochemists and focused their attention on V^{III} chemistry. The study and development of V^{III} chemistry has not matched those of its other oxidation states, one contributing factor being the lack of suitable V^{III} containing starting materials that can be handled under normal laboratory conditions. The trivalent state is indeed one of its unstable oxidation states mainly because of its pronounced tendency to oxidize to V^{IV} or V^V and such oxidation reactions taking place in solution are kinetically very fast. We have taken up a programme to synthesize stable V^{III} complexes and to remove the general belief that all trivalent vanadium compounds are unstable under ordinary conditions. The present work reports the synthesis, characterization, chemical

reactivity and structure determination of a complex of the tryptophan metabolite [7] picolinic acid, $[V^{III}(pic)_3]H_2O$, which is highly stable under open laboratory conditions. Although the existence of such a V^{III} complex has been reported by some workers [8,9], no-one else has been able to isolate it, determine its structure or explore its chemical reactivity.

EXPERIMENTAL

All chemicals were of reagent grade and used without further purification. Tetraethylammonium perchlorate (TEAP) used for electrochemical work was prepared as reported in the literature [10]. All operations were performed under purified dinitrogen.

Physical measurements

IR spectra were recorded at room temperature on a Perkin-Elmer 783 spectrometer as KBr pellets. Magnetic moments of solids complexes were determined using a PAR model 155 vibrating sample magnetometer with $Hg[Co(SCN)_4]$ as the calibrant. Electronic spectra were recorded in DMF solution with a Shimadzu Model UV-2100 spectrophotometer and cyclic voltammetric experiments were performed

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using a BAS CV-27 electrochemical analyser and BAS XY recorder at 298° K. The electrodes used were a glassy carbon working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode separated from the working compartment by a salt bridge fitted with a medium glass frit. Electrical conductivity in solution was measured by a Philips PR 9500 conductivity bridge. C, H and N were analysed by a Perkin-Elmer 240 C,H,N analyser.

Synthesis of complex

[V(pic)₃]₂H₂O: VCl₃ (0.43 g, 2.7 mmol) was added to a solution of 1.00 g (8.1 mmol) of picolinic acid in water 30 cm³ and the mixture was stirred for 4 h under nitrogen. The resultant deep red solution deposited shiny red crystals on standing, which were filtered, washed with water and dried in vacuum over fused CaCl₂ (yield 80%). Found: C, 49.3; H, 3.2; N, 9.5. Calc. for [V(pic)₃]₂·H₂O: C, 49.6; H, 3.2; N, 9.6%.

Crystal structure determination

X-ray data were collected in a Enraf-Nonius-CAD-4 diffractometer for a crystal mounted on top of a glass fibre. The unit-cell parameters were determined from a least-squares refinement of 17 high-angle reflections. The three intensity controlled reflections (2,2,0; 8,2,-1; 7,3,3), checked every 2 h, showed no significant variations (+0.5%). The intensities were corrected for Lorentz-polarization and empirical absorption corrections were also made [11]. A total of 5677 reflections gave 3379 unique reflections which contained 2994 reflections with $F_0 > 4\sigma(F_0)$. The structure was solved by direct method using the program SHELXS-96 [12], which revealed the positions of all the non-hydrogen atoms. The program SHELXL-93 [13] was used to refine this structure. The oxygen atom (Ow) of the water of crystallization was located from the difference-Fourier map at the end of the isotropic refinement of the non-hydrogen atoms. Refinement on F using anisotropic displacement parameters for all non-hydrogen atoms were performed. Positions of all the hydrogen atoms were located from the difference-Fourier map. However, hydrogen atoms of the water molecule could not be determined. Hydrogen coordinates and their isotropic temperature factors were refined. The final full-matrix least-square refinement converged at R to 0.056. Crystallographic data and additional details regarding data collection and refinement are given in Table 1.

RESULTS AND DISCUSSION

A [V(pic)₃]₂H₂O core with a V^{III} center is expected to be six-coordinate [14] and it can exist in the four structural modifications (Fig. 1). Only crystal and

molecular structure determination can establish the actual form in which the complex exists in the solid state as well as in solution. The structural data may also be utilized in explaining the exceptional stability of this V^{III} complex, especially towards oxidation. The vanadium(III) acceptor centre is chelated with three ligands; atoms of each of the three ligands are distinguished by the suffices A, B and C, respectively. The compound [V(pic)₃] and one water molecule of crystallization form the asymmetric unit of the structure, which are packed in the C-centred monoclinic $C2/c$ space group with eight molecules in general positions. The bidentate chelating ligand is coordinated through pyridine ring nitrogen and carboxylate oxygen to the vanadium(III) cation generating a highly distorted octahedral geometry.

The distortion of the vanadium chromophore from a regular octahedral geometry is specially indicated by the angles O(2C)—V(1)—N(1C) and O(2B)—V(1)—N(1B), which are 76.48 and 79.18(10)°, instead of 90° and also by the deviation of the angles N(1A)—V(1)—N(1B), O(2A)—V(1)—N(1C) and O(2B)—V(1)—O(2C) from linearity. The nitrogen atoms of the ligand A and B are in the *trans* position, i.e. at the apical position of the octahedron. The distance of the two apical nitrogens N(1A) and N(1B) from the mean plane described by the atoms O(2A), O(2C), N(1C) and O(2B) are 2.098(3) and -2.080(3) Å, respectively. The vanadium atom lies approximately at the middle of this mean plane. The deviation of the vanadium atom from this mean plane is 0.002(1) Å.

The vanadium atom forms three five-membered chelate rings with O(2), C(7), C(2) and N(1) atoms of the three ligands. These three five-membered rings make dihedral angles with each other in the range 80–84°. The dihedral angles made by the distorted square plane O(2A)—O(2C)—N(1C)—O(2B) with each of the following three rings O(2A)—C(7A)—C(2A)—N(1A)—V(1), O(2B)—C(7B)—C(2B)—N(1B)—V(1) and O(2C)—C(7C)—C(2C)—N(1C)—V(1) are 86.20(6), 86.87(8) and 3.48 (15)°, respectively. This indicates that ligand C is almost coplanar with the square plane. Table 2 shows the deviations of some of the atoms from some selected mean planes. The deviations of the atoms C(7A), C(7B) and C(7C) from the mean plane are 1.169(4), -1.168(4) and 0.185(4) Å, respectively, indicating that ligand A lies above and ligand B lies below the square plane, and ligand C is slightly off above the square plane. Further support of this geometry is evidenced from (a) the displacement of the atoms from five membered rings shown in Table 2 and (b) from the lists of some selected torsion angles shown in Table 3b.

The V—N(1C) bond length (2.153 Å) is found to be slightly longer than V—N(1A) (2.122 Å) and V—N(1B) (2.112 Å). The O(2C)—C(7C) distance of 1.277(4) Å is slightly shorter than the corresponding distances O(2A)—C(7A) and O(2B)—C(7B) of 1.299(4) and 1.319(4) Å, respectively (Table 3a). The

Table 1. Crystal data and structure refinement for $[V(2\text{-picolinato})_3] \cdot H_2O$

Empirical formula	$C_{18}H_{14}N_3O_7V$
Formula weight	435.26
Temperature (K)	293(2)
Wavelength (Å)	1.54180
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 30.346(3) \text{ \AA}$, $\alpha = 90^\circ$, $b = 8.5360(10) \text{ \AA}$, $\beta = 94.470(2)^\circ$, $c = 13.973(5) \text{ \AA}$, $\gamma = 90^\circ$
Volume (Å ³)	3608.5(14)
Z	8
Density (calculated) (Mg m ⁻³)	1.602
Absorption coefficient (mm ⁻¹)	5.049
$F(000)$	1776
Crystal size (mm)	$2 \times 1 \times 0.6$
Theta range for data collection (°)	2.92–69.98
Index ranges	$0 \leq h \leq 36$, $0 \leq k \leq 10$, $-16 \leq l \leq 15$
Reflections collected	3439
Independent reflections	3379 [$R_{int} = 0.0354$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3379/0/311
Goodness-of-fit on F^2	0.868
Final R indices [$I > 2\sigma(I)$]	0.0505
R indices (all data)	0.056
Extinction coefficient	0.00061(10)
Largest difference peak and hole (eÅ ⁻³)	0.542 and -0.539

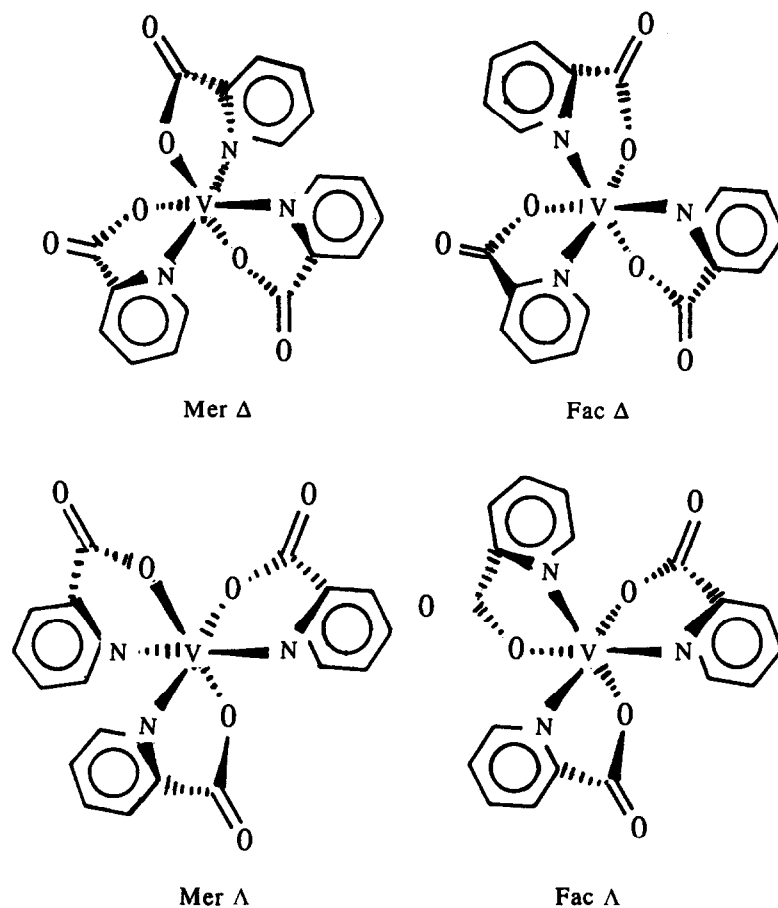


Fig. 1. The four possible isomeric forms of the tris (picolinato) vanadium(III) complex.

Table 2. List of displacements of few atoms from some selected mean planes and the dihedral angles between them

	Atom	Displacement				
Plane 1	O(2A) ^a	0.035(1)				
	O(2C) ^a	0.041(0)				
	N(1C) ^a	0.039(1)				
	O(2B) ^a	0.033(1)				
	N(1A)	2.098(3)				
	N(1B)	-2.080(3)				
	V1	0.002(1)				
	C(7A)	1.169(4)				
	C(7B)	-1.168(4)				
C(7C)	0.185(4)					
Plane 2	O(2A) ^a	-0.058(2)				
	C(7A) ^a	0.031(2)				
	C(2A) ^a	0.029(2)				
	N(1A) ^a	-0.050(2)				
	V1 ^a	0.047(1)				
	O(2B)	-1.837(3)				
	O(2C)	2.011(3)				
	N(1B)	-0.167(4)				
	N(1C)	0.575(4)				
Plane 3	O(2B) ^a	-0.083				
	C(7B) ^a	0.053				
	C(2B) ^a	0.028				
	N(1B) ^a	-0.061				
	V1 ^a	0.063				
	O(2A)	1.986(3)				
	O(2C)	-0.228(4)				
	N(1A)	0.496(4)				
N(1C)	-2.075(3)					
Plane 4	O(2C) ^a	-0.081				
	C(7C) ^a	0.070				
	C(2C) ^a	-0.006(2)				
	N(1C) ^a	-0.028(2)				
	V1 ^a	0.046(1)				
	O(2A)	0.165(4)				
	O(2B)	0.075(28)				
	N(1A)	2.150(3)				
N(1B)	-2.019(3)					
Dihedral angles between planes:						
Planes	1-2	1-3	1-4	2-3	2-4	3-4
Dihedral Angle (°)	86.20(6)	86.87(8)	3.48(15)	80.60(10)	83.69(7)	84.08(9)

^a Atoms marked with asterisks define the plane.

longer O(2B)—C(7B) distance may be due to the participation of the O(2B) atom in hydrogen bonding with the water of crystallization. The water (Ow) molecule shows short contacts with the atoms O(1A){*x,y,-1+z*} and O(2B){*x,y,-1/2+z*} and these short contact distances are 2.820(2) and 2.892(3) Å, respectively. Although the hydrogen of the water molecule has not been determined, these short contacts indicate that the water (Ow) bridges the molecules in the lattice through hydrogen bonding with

O(1A){*x,y,-1+z*} and with O(2B){*x,y,-1/2+z*}. Figure 2 shows the thermal ellipsoid of the molecule, excluding the hydrogen atoms for the clarity of the figure.

Reactivity

[V(pic)₃]·H₂O dissolves in water on heating and can be recrystallized from hot water. During its prep-

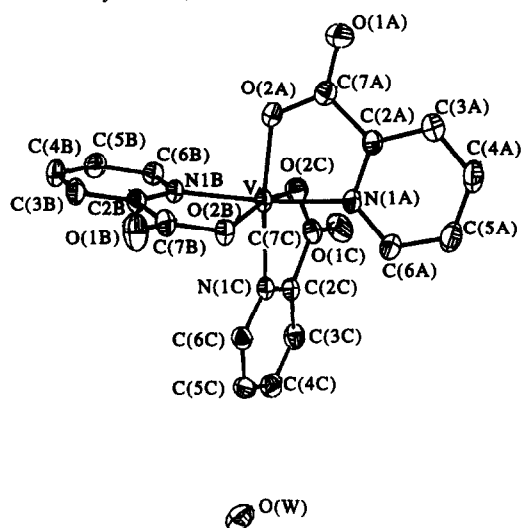
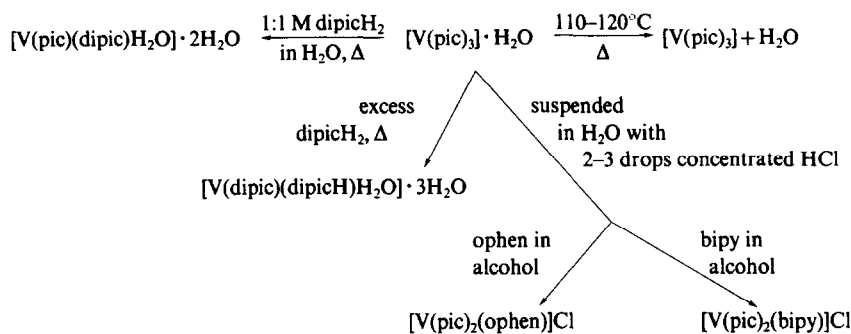


Fig. 2. The thermal ellipsoid of $[\text{V}(\text{pic})_3] \cdot \text{H}_2\text{O}$, excluding the hydrogen atoms.

aration from aqueous solution, after the separation of the crystals by filtration, the mother liquor is still coloured red, indicating that some compound still remains in solution even at room temperature. This solution is fairly stable when kept in open conical flask. Oxidation of the red compound starts slowly after 24 h and after 96 h it is totally converted to $[\text{VO}(\text{pic})_2 \cdot \text{H}_2\text{O}]$, which is deposited as a blue crust. Reactivity of $[\text{V}(\text{pic})_3] \cdot \text{H}_2\text{O}$ is summarized in the following scheme which is self-explanatory:



The complex $[\text{V}^{\text{III}}(\text{pic})_3]\text{H}_2\text{O}$ is insoluble in most common organic solvents, but is moderately soluble in DMF and DMSO. The conductance value in DMF shows that it is a non-electrolyte. Electronic spectra [15] in DMF solution reveal a broad band at $14,000 \text{ cm}^{-1}$ and a sharp one at $26,596 \text{ cm}^{-1}$, which is assigned to the transition ${}^3T_{1g}(\text{F}) \rightarrow {}^3T_{2g}$ and ${}^3T_{1g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$, respectively, and is characteristic of V^{III} in an octahedral environment. The third spin allowed transition ${}^3T_{1g} \rightarrow {}^3A_{2g}$ lies above $34,000 \text{ cm}^{-1}$, but it coincides with the strong charge-transfer band in this region [16]. The magnetic moment of the com-

plex is found to be 2.77 B.M. at room temperature, confirming the +3 state of vanadium (d^2 , $S = 1$).

The IR spectra of the ligand, picolinic acid exhibited the $-\text{COO}$ stretch as a strong absorption band at 1710 cm^{-1} [17]. This band in the complex is shifted towards a lower wave number at 1675 cm^{-1} and is indicative of bonding through the carboxylate moiety. The $\text{C}=\text{N}$ in-plane and out-of-plane deformation modes of the pyridine ring at 640 and 430 cm^{-1} , respectively, are shifted to a higher frequency region by $20-45 \text{ cm}^{-1}$ on coordination through the pyridine ring nitrogen. TG-DTA studies indicate the loss of the lattice water around 120°C and also show that the V^{III} species does not undergo oxidation before 285°C .

The electrochemical behaviour of $[\text{V}(\text{pic})_3] \cdot \text{H}_2\text{O}$ was explored in DMF solution by cyclic voltammetry with 0.1 M TEAP as the supporting electrolyte and a glassy carbon working electrode, the results of which are shown in Table 4. The cyclic voltammogram of $[\text{V}(\text{pic})_3] \cdot \text{H}_2\text{O}$ in the range of $+1.5$ to -1.9 V indicates the presence of a reversible ($\Delta E = 60 \text{ mV}$) one-electron oxidation at $+0.635 \text{ V}$, which is much higher than is usually observed for the $\text{V}^{\text{III}}-\text{V}^{\text{IV}}$ oxidation in several comparable complexes [18-20]. Again the quasireversible ($\Delta E = 90 \text{ mV}$) one-electron reduction of the V^{III} species to V^{II} species is observed at -1.01 V , which is much lower than the value observed in the cases of reduction of V^{III} to V^{II} [21]. These two potentials clearly indicate that $[\text{V}(\text{pic})_3] \cdot \text{H}_2\text{O}$ is neither easily oxidized nor reduced. Such resistance towards both oxidation and reduction is an indication of extensive delocalization of the d -electrons of the

V^{III} centre. Such d -electron delocalization is indicated in the following observations. Lengths of the $\text{C}(7)-\text{O}(2)$ bonds are shortened leading to partial double-bond character in them. The bond lengths of $\text{C}(7)-\text{O}(2)$ vary in the range $1.277-1.319 \text{ \AA}$, which is much shorter than the standard value of a single $\text{C}-\text{O}$ bond length of $1.43(1) \text{ \AA}$ [22]. Shortening is observed in the $\text{C}(7)-\text{O}(1)$ double bond also, the standard value being $1.23(1) \text{ \AA}$. Tangible shortening of the $\text{V}(1)-\text{O}(2)$ and $\text{V}(1)-\text{N}(1)$ bonds are also observed [23-25]. Thus, structure determination of the complex $[\text{V}(\text{pic})_3] \cdot \text{H}_2\text{O}$ has helped us to know the actual struc-

Table 3a. Selected bond angles (Å) and angles (°) of [V(2-picolinato)₃]·H₂O

(a) Bond lengths around Vanadium			
V(1)—O(2A)			1.936(3)
V(1)—O(2B)			1.944(2)
V(1)—O(2C)			1.966(2)
V(1)—N(1B)			2.112(3)
V(1)—N(1A)			2.122(3)
V(1)—N(1C)			2.153(3)
(b) Bond lengths of five membered chelate rings			
	Ligand A	Ligand B	Ligand C
O(2)—C(7)	1.299(4)	1.319(4)	1.277(4)
O(1)—C(7)	1.215(4)	1.199(4)	1.211(4)
C(7)—C(2)	1.500(5)	1.504(5)	1.516(5)
N(1)—C(2)	1.350(4)	1.346(4)	1.347(4)
(c) Distance of water molecules			
OW—O(1A) ^a	= 2.820(2) Å		
OW—O(2B) ^a	= 2.892(3) Å		
(d) Bond angles			
O(2A)—V(1)—O(2B)	100.46(11)		
O(2A)—V(1)—O(2C)	92.31(11)		
O(2B)—V(1)—O(2C)	167.06(11)		
O(2A)—V(1)—N(1B)	92.29(10)		
O(2B)—V(1)—N(1B)	79.18(10)		
O(2C)—V(1)—N(1B)	98.40(10)		
O(2A)—V(1)—N(1A)	80.17(10)		
O(2B)—V(1)—N(1A)	94.20(10)		
O(2C)—V(1)—N(1A)	89.98(11)		
N(1B)—V(1)—N(1A)	168.99(11)		
O(2A)—V(1)—N(1C)	168.58(11)		
O(2B)—V(1)—N(1C)	90.82(10)		
O(2C)—V(1)—N(1C)	76.48(10)		
N(1B)—V(1)—N(1C)	91.55(10)		
N(1A)—V(1)—N(1C)	97.38(10)		

^aSymmetry transformations used to generate atoms: O(1A) {x,y,-1+z}; O(2B) {x,y,-1/2+z}.

Table 3b. List of a few selected torsion angles (°)

C(7A)—O(2A)—V1—N(1A)	= 8.3(3)
C(7A)—O(2A)—V1—N(1B)	= -179.2(3)
C(7A)—O(2A)—V1—O(2B)	= 100.8(3)
C(7A)—O(2A)—V1—O(2C)	= -81.3(3)
C(7C)—O(2C)—V1—N(1A)	= 85.1(3)
C(7C)—O(2C)—V1—N(1B)	= -101.2(3)

ture as well as to explain the stability of this V^{III} complex to oxidation both in the solid state and in aqueous solution.

CONCLUSION

Both the coordinating points (O and N) of the picolinate ligand are hard donors and hence the complex [V(pic)₃]·H₂O, with the hard acceptor V^{III}, is quite stable. This hard-hard interaction along with the uncharged nature of the complex and the extensive delocalization of the *d*-electrons makes it very stable towards oxidation both in the solid state as well as in solution. In fact, it is so stable that it can be left open in the wet working laboratory for days. Its solution in water is also quite stable under open atmospheric conditions.

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Table 4. Experimental results

Compound	Magnetic moments (B.M.)	Electronic spectral data ν_{\max} cm ⁻¹ (ϵ , M ⁻¹ cm ⁻¹)	Cyclic voltammetric data	
			E_{298}^0 , V(ΔE_p , mV) $V^{IV/III}$	$V^{III/II}$
[V(pic) ₃]·H ₂ O	2.77	14,000 26,596(568)	+0.635(60)	-1.01(90)

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