Synthesis and Structure of a Hexa-coordinated Vanadium(IV) Complex Aquaoxo[*N*-(2-pyridylmethyl)iminodiacetato]vanadium(IV) Dihydrate

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A new complex, aquaoxo[*N*-(2-pyridylmethyl)iminodiacetato]vanadium(IV) dihydrate [VO(pmida)(H_2O)]·$2H_2O$ has been synthesized and its crystal structure determined by the X-ray method. The triclinic crystals obtained from water or aqueous ethanol solution are twinned and contain 2 mol of lattice water. The unit cell contains four formula units and the structure was analyzed on the assumption that the space group is $P\bar{1}$. The positional and thermal parameters were refined to $R=0.115$. The vanadium atom has a distorted octahedral coordination and deviates by 0.39 Å from the equatorial plane, which is composed of two cis carboxylate oxygens, a water molecule and the pyridine nitrogen. Vanadyl oxygen and tertiary nitrogen occupy the axial sites. Absorption spectra indicated that the structure is maintained in an aqueous solution of pH 3.0 to 4.9. This geometrical isomer seems to be formed selectively in an aqueous medium.

Many vanadium(IV) complexes have strong V=O bonds[1] and exhibit characteristic distorted molecular structure. X-Ray crystallography has disclosed that the V=O bond length (1.56 to 1.63 Å)[2–11] is shorter than that of the trans ligand to vanadium (2.18 to 2.51 Å). Sometimes the trans site remains vacant. The vanadium(IV) ion is above the equatorial plane by 0.26 to 0.41 and 0.48 to 0.58 Å in the complexes with coordination numbers 6[2–11] and 5,[12] respectively.

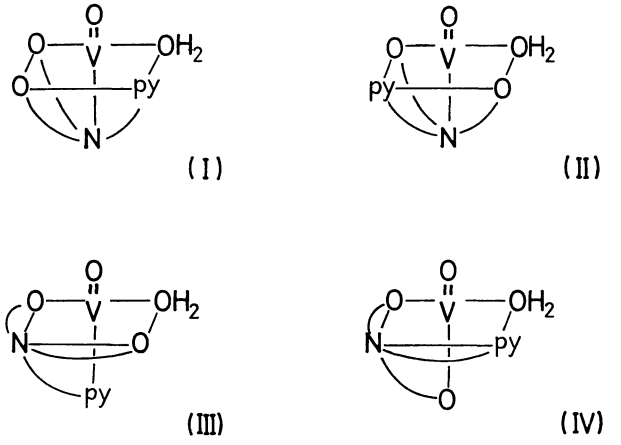

Fig. 1. The possible geometrical isomers of [VO(pmida)(H_2O)].

With a view toward studying the kinetics of direct ligand substitution at the equatorial site,[13] we have synthesized a new complex aquaoxo[*N*-(2-pyridylmethyl)iminodiacetato]vanadium(IV) dihydrate [VO(pmida)(H_2O)]·$2H_2O$. There can be four geometrical isomers depending on the coordination mode of the quadridentate $pmida^{2-}$ ion (Fig. 1). The structure has been determined by the X-ray method, and the properties in aqueous solution have been studied spectroscopically.

Experimental

Materials. The ligand, 2-pyridylmethyliminodiacetic acid H_2pmida,[14] and bis(acetylacetonato)oxovanadium(IV) [$VO(acac)_2$][15] were synthesized by known methods. Equimolar amounts of [$VO(acac)_2$] and H_2pmida (0.01 mol) were heated in acetonitrile (200 cm^3) at 83 °C for 30 min with vigorous stirring. The blue violet precipitate was filtered off, washed with aqueous ethanol and recrystallized by the following two methods. When a large amount of ethanol was added to the aqueous solution of the raw product, a pale violet powder was obtained within a few hours, which was washed with aqueous ethanol (1+1, v/v) and ethanol, and dried *in vacuo* at room temperature. (Yield 60%) Found C, 38.86; H, 4.11; N, 8.98%. Calcd for $C_{10}H_{12}N_2O_6V$: C, 39.10; H, 3.91; N, 9.12%.

When a small amount of ethanol was added to the aqueous solution, blue violet crystals precipitated very slowly (*e.g.* 10 days) with 2 mol of lattice water. Found C, 34.70; H, 4.64; N, 8.12%. Calcd for $C_{10}H_{16}N_2O_8V$: C, 35.00; H, 4.67; N, 8.17%.

The magnetic moment of the dihydrate was 1.7 Bohr magnetons at room temperature. This value is normal to those of VO^{2+} complexes with a $3d^1$ configuration.

Structure Determination. *Crystal Data*: $C_{10}H_{16}N_2O_8V$, $M=343.19$, Triclinic, $a=19.54(2)$, $b=10.846(4)$, $c=6.829(3)$ Å, $\alpha=102.56°(4)$, $\beta=87.64°(8)$, $\gamma=92.84°(9)$, $D_m=1.62$, $D_c=1.62$ g/cm^3, $Z=4$, $\mu(Cu\,K\alpha)=149.9$ cm^{-1}, space group $P\bar{1}$ or P1. The structure analysis was carried out on the basis of the $P\bar{1}$ space group.

The Laue symmetry was determined from the Weissenberg and precession photographs. The unit cell dimensions were obtained by a least-squares analysis of fifteen 2θ values measured on a Philips PW 1100 four circle diffractometer by the use of Cu $K\alpha$ radiation.

The blue violet plate-like crystals of the dihydrate were usually twinned. Recrystallization was repeated in an attempt to obtain single crystals by taking precession photographs, but all the efforts were unsuccessful.

The precession photographs showed clearly the presence of two individuals in twin orientation. Both have a common a* axis and the reciprocal lattice of one crystal of the twin is related to that of the other by a rotation of 180° about the a* axis. This was confirmed by the intensity measurements ($2\theta \leq 40°$) for each constituent in a twinned crystal. The intensities of the corresponding reflections were different from each other in every twin crystal; in the crystal used for X-ray data measurements, the intensity ratio was found to be 6.88: 1.

Data Collection: Intensity data for the major individual of the twin were collected on the diffractometer by use of nickel-filtered Cu $K\alpha$ radiation. A crystal with dimensions $0.07\times0.10\times0.13$ mm^3 was mounted so that the a axis is roughly parallel to ϕ axis. The crystal-to-detector distance and the

detector aperture were 195 mm and 3×3 mm, respectively. The scan rate and the scan width are 0.030° s^{-1} and (0.7+0.2 tan θ)°, respectively. Background counts were measured for (scan time/2)$\sqrt{I_b/I_{int}}$ at each side of the scan range (I_b, mean background intensity obtained from the preliminary background measurements for 5 s at each side of the peak; I_{int} is the total number of counts divided by total scan time). A total of 3080 reflections having $I_t-2\sqrt{I_t}>I_b$ were collected in the $2\theta\leq120°$ range (I_t, intensity at the top of the peak), but 2584 reflections for which $I>2\sigma(I)$ were used in the structure analysis. Intensity data were corrected for the *Lp* factor[16] but not for absorption.

For each reflection no estimation was made of the error derived from the diffraction due to the minor crystal. However, a tentative calculation suggested that under these experimental conditions the intensity from a reciprocal lattice point is liable to suffer from disturbance due to the diffraction from the minor individual; the disturbance is possibly significant unless a reciprocal lattice point of the major is separated from the neighboring point due to the minor by more than 0.013 $Å^{-1}$. Of the 2584 reflections 1027 were under such circumstances but the error induced in the structure amplitude is about 8% on an average.[17] Therefore, all 2584 reflections were used for the structure analysis in the initial stage.

Table 1. Positional and thermal parameters

	x	y	z	B/Å^2
V(1)	0.1605(1)	0.4260(2)	0.3791(3)	2.00(4)
O(1)	0.3681(5)	0.4497(10)	0.3641(14)	3.7(2)
O(2)	0.2575(4)	0.4672(8)	0.4494(12)	2.3(2)
O(3)	0.1589(4)	0.5910(7)	0.2898(11)	1.9(1)
O(4)	0.2502(5)	0.7082(10)	0.0858(15)	4.1(2)
O(5)	0.1785(5)	0.2468(8)	0.3967(13)	2.7(2)
O(6)	0.1148(5)	0.4710(9)	0.5793(13)	2.9(2)
N(1)	0.0832(5)	0.3517(10)	0.1752(15)	2.4(2)
N(2)	0.2176(5)	0.3796(9)	0.0721(14)	2.0(2)
C(1)	0.0171(7)	0.3698(13)	0.2201(20)	2.9(3)
C(2)	−0.0341(8)	0.3318(15)	0.0760(22)	3.8(3)
C(3)	−0.0136(8)	0.2732(15)	−0.1179(22)	3.8(3)
C(4)	0.0549(8)	0.2515(14)	−0.1643(22)	3.4(3)
C(5)	0.1038(7)	0.2912(12)	−0.0161(19)	2.5(2)
C(6)	0.1780(7)	0.2647(13)	−0.0490(20)	2.9(3)
C(7)	0.2900(7)	0.3413(14)	0.1188(21)	3.1(3)
C(8)	0.3068(7)	0.4265(13)	0.3249(19)	2.5(2)
C(9)	0.2197(7)	0.4915(12)	−0.0151(19)	2.4(2)
C(10)	0.1924(6)	0.6041(12)	0.1255(18)	2.1(2)
V′(1)	0.3376(1)	0.9451(2)	0.8745(3)	2.03(4)
O′(1)	0.1292(5)	0.9378(9)	0.9001(14)	3.2(2)
O′(2)	0.2408(4)	0.9751(8)	0.9626(12)	2.1(2)
O′(3)	0.3373(4)	1.1036(8)	0.7673(12)	2.0(2)
O′(4)	0.2914(5)	1.2068(10)	0.5559(15)	4.0(2)
O′(5)	0.3191(5)	0.7663(8)	0.9144(13)	2.7(2)
O′(6)	0.3844(5)	1.0044(9)	1.0622(14)	3.2(2)
N′(1)	0.4139(5)	0.8669(10)	0.6624(15)	2.2(2)
N′(2)	0.2797(5)	0.8759(10)	0.5779(14)	2.0(2)
C′(1)	0.4807(8)	0.8836(14)	0.6961(22)	3.3(3)
C′(2)	0.5310(9)	0.8337(17)	0.5561(26)	5.0(4)
C′(3)	0.5110(9)	0.7595(15)	0.3773(24)	4.3(3)
C′(4)	0.4418(8)	0.7458(14)	0.3344(23)	3.9(3)
C′(5)	0.3937(7)	0.7964(12)	0.4832(19)	2.6(3)
C′(6)	0.3187(7)	0.7646(12)	0.4571(19)	2.5(2)
C′(7)	0.2083(7)	0.8345(12)	0.6466(19)	2.4(2)
C′(8)	0.1902(7)	0.9247(12)	0.8495(19)	2.5(3)
C′(9)	0.2776(7)	0.9848(13)	0.4793(20)	3.0(3)
C′(10)	0.3022(7)	1.1039(12)	0.6083(19)	2.5(2)
O(WA)	0.3886(6)	0.5687(10)	0.7734(17)	4.9(2)
O(WB)	0.0356(6)	0.9014(11)	0.6045(17)	5.1(3)
O(WC)	0.0994(5)	0.0435(9)	0.3022(14)	3.6(2)
O(WD)	0.4787(9)	0.4074(14)	0.1131(22)	8.1(4)

Structure Determination and Refinement: The positions of V atoms were obtained from the Patterson map and those of the remaining nonhydrogen atoms were found from successive Fourier syntheses. The positional and isotropic thermal parameters were refined by the least-squares method. The minimized function was $\sum W(|F_o|-|F_c|)^2$. The weighting scheme was as follows: $W=0.3$ for $F_o<9.8$ and $W=1.0$ for $F_o>9.8$. Several cycles of the least-squares calculations reduced R to 0.109. In the subsequent refinement, zero weight was assigned to the 1027 reflections. The structure converged with $R=0.115$. In the final cycle no parameters were varied by more than 0.3 σ.

Atomic scattering factors of V^0, O, N, and C were taken from Ref. 18. Observed and calculated structure factors are available (Document No. 7902; in the F_o-F_c table those reflections for which zero weight was given in the leasts quares calculation, are marked with asterisks). Table 1 lists final atomic parameters. All computations were carried out on the FACOM 230-60 computer of Osaka City University, by the use of the RSSFR-5, HBLS-IV, and DAPH programs in the UNICS.[19]

Other Measurements. The electronic spectra were recorded with a Hitachi 323 Spectrometer in aqueous solution and by the reflectance method. Infrared spectra were recorded with a JASCO IR-Al Spectrometer in KBr disks. The pH titration was performed with a Metrohm E300B titrator under nitrogen atmosphere. The Magnetic susceptibility was measured by the Gouy method.

Results and Discussion

Crystal Structure. The crystal structure viewed down from the c axis is shown in Fig. 2. Although no H atoms were found in the structure analysis, possible hydrogen bonds are indicated by dotted lines. The unit cell comprises two crystallographically independent complexes which are discerned by atom numberings primed and unprimed. They are very similar in geometry and have virtually equal dimensions, except that they are enantiomeric to each other. Table 2 indicates that chemically equivalent bond lengths and angles are in reasonable agreement with each other. The elevation and projection of the complex are shown in Fig. 3 in which one antipode is depicted. The vanadium ion has a distorted octahedral coordination; the vanadyl oxygen and tertiary amino nitrogen occupy axial positions, while the equatorial plane consists of the pyridine nitrogen, water oxygen and two cis carboxylate oxygen atoms. The bond lengths and angles are listed in Table 2, and the deviation of the atoms from the least-squares plane in Table 3.

The V atom deviates from the equatorial plane by 0.39 Å toward the oxo ligand. This value is comparable with that (0.39 Å) in $Na_2[(VO)_2(ttha)]\cdot10H_2O$[20] ($H_6$ttha, triethylenetetraaminehexaacetic acid), in which the complex has a centrosymmetric dimer structure but is similar to the present complex in the context that each V atom is surrounded octahedrally by 4O and 2N (cis

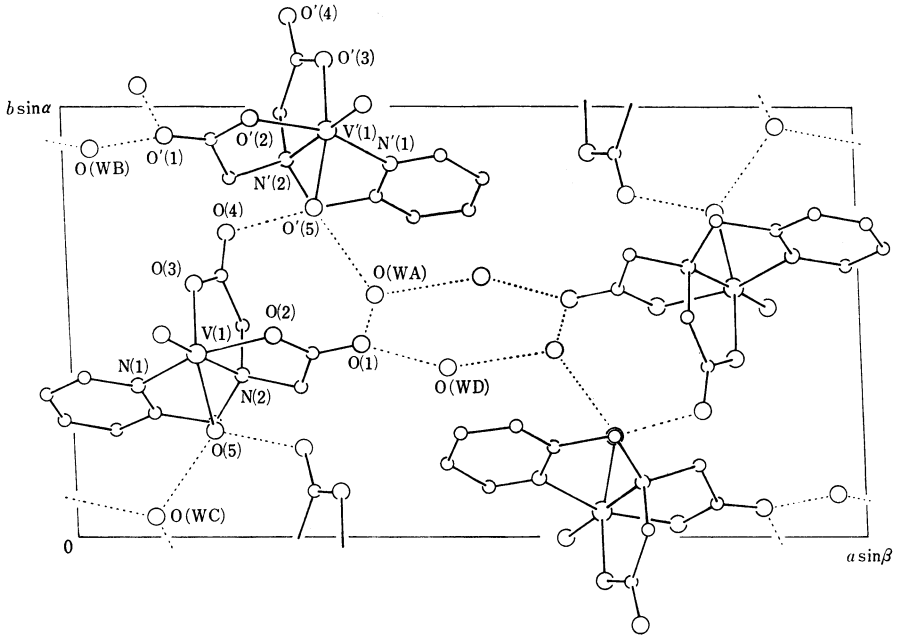

Fig. 2. The crystal structure viewed down the c axis. The dotted lines indicate possible O–H···O hydrogen bonds.

Table 2. Interatomic distances and bond angles

Bond lengths (l/Å)				Bond angles (ϕ/°)			
V–O(2)	1.98(1)	V'–O'(2)	1.98(1)	C(6)–N(2)–C(7)	110(1)	C'(6)–N'(2)–C'(7)	112(1)
V–O(3)	2.02(1)	V'–O'(3)	2.01(1)	C(7)–N(2)–C(9)	113(1)	C'(7)–N'(2)–C'(9)	112(1)
V–O(5)	2.02(1)	V'–O'(5)	2.03(1)	C(6)–N(2)–C(9)	115(1)	C'(6)–N'(2)–C'(9)	114(1)
V–O(6)	1.60(1)	V'–O'(6)	1.60(1)	N(2)–C(6)–C(5)	107(1)	N'(2)–C'(6)–C'(5)	108(1)
V–N(1)	2.11(1)	V'–N'(1)	2.11(1)	C(6)–C(5)–N(1)	117(1)	C'(6)–C'(5)–N'(1)	118(1)
V–N(2)	2.30(1)	V'–N'(2)	2.32(1)	C(5)–N(1)–V	117.5(9)	C'(5)–N'(1)–V'	118.3(9)
N(2)–C(6)	1.53(2)	N'(2)–C'(6)	1.53(2)	N(2)–C(7)–C(8)	105(1)	N'(2)–C'(7)–C'(8)	107(1)
C(6)–C(5)	1.49(2)	C'(6)–C'(5)	1.50(2)	C(7)–C(8)–O(2)	119(1)	C'(7)–C'(8)–O'(2)	118(1)
C(5)–N(1)	1.38(2)	C'(5)–N'(1)	1.36(2)	C(8)–O(2)–V	121.2(8)	C'(8)–O'(2)–V'	121.6(8)
N(2)–C(7)	1.56(2)	N'(2)–C'(7)	1.53(2)	C(7)–C(8)–O(1)	118(1)	C'(7)–C'(8)–O'(1)	118(1)
C(7)–C(8)	1.55(2)	C'(7)–C'(8)	1.55(2)	O(1)–C(8)–O(2)	123(1)	O'(1)–C'(8)–O'(2)	124(1)
C(8)–O(2)	1.29(2)	C'(8)–O'(2)	1.30(2)	N(2)–C(9)–C(10)	113(1)	N'(2)–C'(9)–C'(10)	113(1)
C(8)–O(1)	1.24(2)	C'(8)–O'(1)	1.23(2)	C(9)–C(10)–O(3)	120(1)	C'(9)–C'(10)–O'(3)	121(1)
N(2)–C(9)	1.46(2)	N'(2)–C'(9)	1.49(2)	C(10)–O(3)–V	119.7(8)	C'(10)–O'(3)–V'	119.4(8)
C(9)–C(10)	1.49(2)	C'(9)–C'(10)	1.47(2)	C(9)–C(10)–O(4)	118(1)	C'(9)–C'(10)–O'(4)	118(1)
C(10)–O(3)	1.30(2)	C'(10)–O'(3)	1.31(2)	O(4)–C(10)–O(3)	122(1)	O'(4)–C'(10)–O'(3)	121(1)
C(10)–O(4)	1.23(2)	C'(10)–O'(4)	1.27(2)	N(1)–C(1)–C(2)	122(1)	N'(1)–C'(1)–C'(2)	123(1)
N(1)–C(1)	1.33(2)	N'(1)–C'(1)	1.33(2)	C(1)–C(2)–C(3)	118(1)	C'(1)–C'(2)–C'(3)	118(2)
C(1)–C(2)	1.42(2)	C'(1)–C'(2)	1.39(2)	C(2)–C(3)–C(4)	120(1)	C'(2)–C'(3)–C'(4)	119(2)
C(2)–C(3)	1.39(2)	C'(2)–C'(3)	1.37(3)	C(3)–C(4)–C(5)	120(1)	C'(3)–C'(4)–C'(5)	119(2)
C(3)–C(4)	1.38(2)	C'(3)–C'(4)	1.39(3)	C(4)–C(5)–N(1)	120(1)	C'(4)–C'(5)–N'(1)	121(1)
C(4)–C(5)	1.40(2)	C'(4)–C'(5)	1.40(2)	C(5)–N(1)–C(1)	120(1)	C'(5)–N'(1)–C'(1)	119(1)

Bond angles (ϕ/°)				Possible hydrogen bonds (l/Å)	
O(2)–V–N(1)	152.6(4)	O'(2)–V'–N'(1)	152.4(4)	Symmetry code	
O(3)–V–O(5)	163.7(4)	O'(3)–V'–O'(5)	163.0(4)	I $1-x, 1-y, 1-z$:	II $-x, 1-y, 1-z$;
O(6)–V–O(2)	107.2(4)	O'(6)–V'–O'(2)	107.4(4)	III $x, 1+y, 1+z$;	IV $x, -1+y, z$;
O(6)–V–O(3)	95.4(4)	O'(6)–V'–O'(3)	95.7(4)	V $x, y, 1+z$	
O(6)–V–O(5)	100.9(4)	O'(6)–V'–O'(5)	101.3(5)	O(1)···O(WA)	2.85(2)
O(6)–V–N(1)	100.2(5)	O'(6)–V'–N'(1)	100.1(5)	O(1)···O(WD)	2.70(2)
O(6)–V–N(2)	172.1(4)	O'(6)–V'–N'(2)	172.0(5)	O(5)···O(WC)	2.61(1)
O(2)–V–O(3)	88.5(4)	O'(2)–V'–O'(3)	87.5(4)	O(5)···O'(4^{IV})	2.59(1)
O(3)–V–N(1)	89.2(4)	O'(3)–V'–N'(1)	92.3(4)	O'(1)···O(WB)	2.73(2)
N(1)–V–O(5)	88.1(4)	N'(1)–V'–O'(5)	85.8(4)	O'(1)···O(WC^{III})	2.79(1)
O(5)–V–O(2)	86.6(4)	O'(5)–V'–O'(2)	86.5(4)	O'(5)···O(WA)	2.58(1)
V–N(2)–C(6)	105.1(7)	V'–N'(2)–C'(6)	106.2(7)	O'(5)···O(4^{V})	2.59(1)
V–N(2)–C(7)	104.7(8)	V'–N'(2)–C'(7)	104.0(7)	O(WA)···O(WD^{I})	2.72(2)
V–N(2)–C(9)	108.6(8)	V'–N'(2)–C'(9)	107.4(8)	O(WB)···O(WC^{II})	2.75(2)

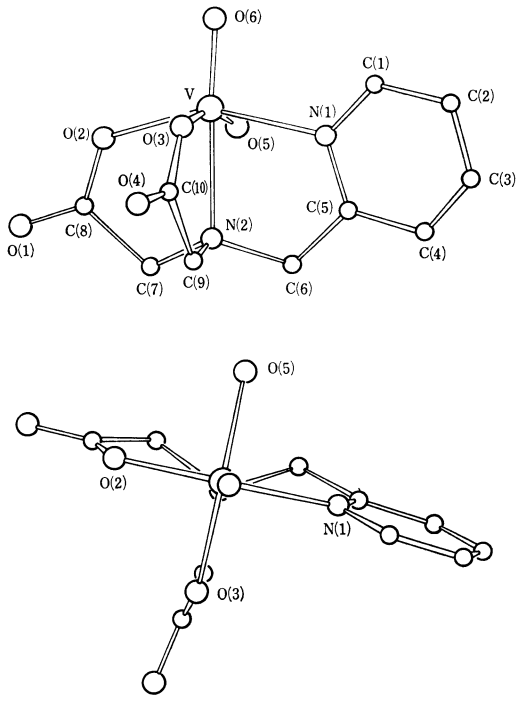

Fig. 3. The elevation and projection of the complex.

Table 3. Deviations (Δd/Å) of atoms from several mean planes

(1)	[N(1), O(2), O(3), O(5)] plane N(1) 0.15, O(2) 0.07, O(3) −0.12, O(5) −0.06, V −0.38
(1′)	[N′(1), O′(2), O′(3), O′(5)] plane N′(1) 0.09, O′(2) 0.10, O′(3) −0.10, O′(5) −0.09, V′ −0.39
(2)	[V, N(1), N(2)] plane C(5) 0.28, C(6) 0.78
(2′)	[V′, N′(1), N′(2)] plane C′(5) −0.26, C′(6) −0.70
(3)	[V, N(2), O(2)] plane C(7) 0.73, C(8) 0.31, O(1) 0.33
(3′)	[V′, N′(2), O′(2)] plane C′(7) −0.69, C′(8) −0.28, O′(1) −0.31
(4)	[V,N(2), O(3)] plane C(9) −0.02, C(10) 0.12, O(4) 0.40
(4′)	[V′, N′(2), O′(3)] plane C′(9) 0.04, C′(10) −0.14, O′(4) −0.37

positions) atoms. In square pyramidal oxovanadium(IV) complexes the deviation of V atom from the equatorial plane ranges from 0.48 to 0.58 Å,[12] whereas in the octahedral complexes this deviation is in the range 0.26—0.41 Å.

The axial ligation thus decreases the deviation, with the O donor giving more marked effect than the N donor. This is in accord with the larger mean L_{eq}–V–L_{eq} angles for *trans*(*O*) than for *trans*(*N*). The V=O bond length (1.60 Å) agrees well with that in the ttha complex.[2] The lengths in the 6-coordinate complexes range from 1.56 to 1.63 Å, differing little from those in the 5-coordinate complexes.[12] The salpn complex [VO(salpn)] (salpn, *N*,*N*′-disalicylidene-1,2-propanediamine) has V=O··· V=O chain in the crystals, and a rather strong intermolecular interaction is expected. Even in this compound the V=O length (1.633(9) Å) is not significantly different from those in the 5-coordinate complexes.

Selbin *et al.* summarized IR frequencies of various oxovanadium(IV) complexes and indicated that the ν(V=O) depends on the variety of ligands.[20] However, there seems to be an overall trend as follows: (1) VO^{2+} complexes with coordination number 5 give ν(V=O) higher than 995 cm^{-1};[21] (2) on the other hand, VO^{2+} complexes with coordination number 6 give lower ν(V=O)'s; *e.g.*, 976, 955,[22] and 854 cm^{-1} for$(NH_4)_2$-[VO(oxalato)$_2$(H_2O)]·H_2O, [VO(acac)$_2$(4-phenylpyridine)] and [VO(salpn)], respectively. The present complex with coordination number 6 gives ν(V=O) at 985 cm^{-1}. It appears as if VO^{2+} complexes with coordination number 5 and 6 have ν(V=O) values higher than and lower than 990 cm^{-1}, respectively, and this figure can serve as a criterion for discriminating the coordination number of VO^{2+} complexes.[23] Correlation could be also expected between the V=O bond length and ν(V=O). However, the variation of the bond length should be very small and a more accurate measurement is desirable.

The axial V–N(2) bond with the tertiary amino nitrogen agrees in length with the corresponding value in $[(VO)_2(ttha)]^{2-}$ but is longer by 0.15 Å than the equatorial V–N(sp^3) bond in the ttha complex. Such a difference is attributed to the trans influence of the oxo ligand.

The 5-membered chelate rings are of the envelope conformation, the ring composed of O(3), C(10), C(9), N(2), and V has relatively planar structure. However, the other two rings are considerably puckered up. Figure 4 shows, as an example, the projection and elevation of the chelate ring which includes the pyridine moiety. The firm disposition of the equatorial bonds may be responsible for such a puckering. Bond lengths and angles in the pmida ligand are normal. The length of the hydrogen bonding (Table 2) range from 2.59 to 2.85 Å, which are normal for lattice waters in coordination compounds.

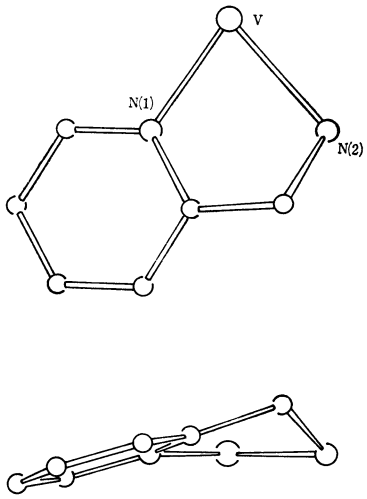

Fig. 4. The projection and elevation of the chelate ring in which pyridine moiety participates.

Table 4. Some structural parameters of 6-coordinate oxovanadium(IV) complexes

	Deviation[b] (d/Å)	L_{eq}–V–L_{eq}[c] (ϕ/°)	V=O (l/Å)	V–O_{eq}[d] (l/Å)	V–N_{eq} (l/Å)	V–L_{ax} (l/Å)
$[VO(pmida)(H_2O)]\cdot 2H_2O$[a]	0.39	157.9	1.60(1)	O(COO⁻) 2.00 O(H_2O) 2.02(1)	2.11(1)(sp^2)	N(sp^3) 2.31(1)
$Na_2[(VO)_2(ttha)]\cdot 10H_2O$[2]	0.39	156.6	1.605(8)	O(COO⁻) 1.933	2.163(5)(sp^3)	N(sp^3) 2.294(7)
[VO(2,6-pyridinedicarboxylato)$(H_2O)_2]\cdot 2H_2O$[3]	0.408	156.6	1.59(1)	O(COO⁻) 2.02(2) O(H_2O) 2.03(1)		N(sp^2) 2.18(1)
$(NH_4)_2VO(NCS)_4\cdot 5H_2O$[4]	0.26	163	1.62(6)		2.04(3)(sp)	O(H_2O) 2.22(5)
$VOSO_4\cdot 5H_2O$[5]	0.281		1.591(5)	O(H_2O) 2.040 O(SO_4) 1.983(5)		O(H_2O) 2.223(5)
$(NH_4)_2[VO(ox)_2(H_2O)]\cdot H_2O$[6]	0.302	161.9	1.594(3)	O(COO⁻) 2.004 O(H_2O) 2.033(3)		O(COO⁻) 2.184(3)
$VOSO_4\cdot 3H_2O$[7]	0.36	159.4	1.559(8)	O(SO_4) 2.017 O(H_2O) 2.065		O(H_2O) 2.284(8)
$VOSO_4$[8]	0.31	162.2	1.59(2)	O(SO_4) 2.03		O(SO_4) 2.28(2)
$VO(acac)_2$(4-Ph-py)[9]	0.22		1.58(1)			
$[VO(acac)_2]_2$(dioxane)[10]			1.62	O(acac) 1.99		O(dioxane) 2.51
VO(salpn)[11]	0.31		1.633(9)	O(C–O⁻) 1.945(9)	2.11(1)(sp^2)	O(V=O) 2.213(9)

a) Present work. b) The deviation of the V atom from the equatorial plane; in every complex four atoms defining the equatorial plane are disposed in a more or less tetrahedral configuration with respect to the plane. The four atoms in the 2,6-pyridinedicarboxylato complex have significant deviations (±0.196 Å), and hence it might be inadequate here to define an "equatorial" plane. However, as is seen in the Table, the "devia tion" of the V atom as well as the L_{eq}–V–L_{eq} value in the 2,6-pyridinedicarboxylato complex have features similar to those of the other complexes with an axial N ligand. c) Mean value of two L_{eq}–V–L_{eq} angles; the two L_{eq}'s denote the ligand atoms which are trans to each other in the equatorial plane. d) In case there are more than two chemically equivalent bonds, the average value of their lengths is listed.

Of the four possible isomers of this complex, the present product seems to involve the least strain, because coordination of the two acetate oxygens in trans positions (II and III in Fig. 1) brings about a larger strain in the chelates. The pyridine ring is parallel to the z-axis. The d^1 electron of VO(2+) is believed to occupy d_{xy} orbital and the delocalization of this electron to the π-orbital of the pyridine moiety should be favorable.

Structure in the Aqueous Solution. The complex gave a pK_a value 6.4 at 25 °C and an ionic strength of 1.0 ($NaClO_4$). Hence, the complex is mostly (>98%) present in the aqua from below pH 4.7. The electronic absorption peaks are at 258, 350, 572, and 765 nm with molar extinction coefficients of 4940, 304, 16, and 27 $cm^{-1}\,M^{-1}$, respectively at pH 3.0 to 4.9. The reflectance spectrum of the solid dihydrate in the range from 340 to 700 nm gave peaks at 354 and 570 nm, suggesting that the complex maintains the same skeletal structure in aqueous solution of pH below 4.7 as in the crystalline state.

Complex formation between the aqueous solution of oxovanadium(IV) sulfate (0.008 M) and $pmida^{2-}$ (0.01 M) is indicated by the visible absorption peaks at 572 and 765 nm with molar extinction coefficients 15 and 26 $cm^{-1}\,M^{-1}$, respectively (*vide supra*) at pH 3.0. The visible peaks are so sensitive to the environment of oxovanadium(IV) ions as to be useful for identifying the complexes.[1] Therefore, it appears as if the present product was formed selectively from among the four possible structures.

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