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Structure of 2,2'-Bipyridyl(iminodiacetato)oxovanadium(IV) Dihydrate, $C_{14}H_{13}N_3O_5V \cdot 2H_2O$

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Abstract. $M_r = 390.2$, monoclinic, $P2_1/a$, $a = 11.878$ (1), $b = 15.698$ (3), $c = 9.027$ (1) Å, $\beta = 100.9$ (5)°, $U = 1653$ (3) Å³, $Z = 4$, $D_x = 1.57$ (1), $D_m = 1.55$ (1) g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 56.7$ cm⁻¹, $F(000) = 804$, $T = 293$ K. Final $R = 0.047$ for 2450 reflections. The V atom is octahedrally coordinated to the vanadyl O, two carboxyl O atoms and one N from the tridentate iminodiacetate ligand, and to two N atoms from the bidentate bipyridyl ligand. The structure consists of individual complexes and two loosely bound molecules of water of crystallization.

Introduction. In the course of their extensive study of the chemistry of the oxovanadium ion, Dutta & Ghosh (1967, especially paper on pp. 306–313) found a general synthetic route to the oxovanadium(IV) heterochelates. The majority of the oxovanadium complexes synthesized so far are of the type [VO(X)(bidentate ligand)₂], a few being of the type [VO(X)(quadridentate ligand)], X being H₂O, some amine molecule or non-existent. The title compound is a rare example where a tridentate ligand is present along with a bidentate one. The determination of the crystal structure of this compound was undertaken to find out the details of the coordination of V in this complex.

Experimental. Very dark prismatic crystals made available to us believed to be the monohydrate. Direction of elongation of crystal arbitrarily named as **c** and from oscillation and Weissenberg photographs space group found to be $P2_1/a$. D_m measured by flotation in benzene/bromoform. Structure solved by

Patterson and successive Fourier syntheses using a set of visually estimated photographic data. Since the reasonable model of the monohydrate structure failed to refine, a fresh set of intensity data was collected using a CAD-4 diffractometer and graphite-monochromated Cu $K\alpha$ radiation, with a specimen of dimensions 0.15 × 0.15 × 0.175 mm. 25 reflections used for measuring lattice parameters. Absorption correction applied, max. 1.940, min. 1.835. $2\theta_{\text{max}} = 120^\circ$. $h - 13 - 13$, $k 0 - 17$, $l 0 - 10$. Three standard reflections, decay corrections: max. = 1.0682, min. = 1.0001, av. 1.0403. Intensities of 2450 independent reflections measured, 263 with $I \leq \sigma(I)$ unobserved.

Using the refined cell parameters obtained by diffractometry, it was found that unless the crystal was assumed to be a dihydrate, a value of D_x consistent with D_m could not be obtained. For verification, a difference Fourier synthesis was made on the basis of structure factors calculated with the contribution from only the 23 atoms of the complex itself. The map distinctly revealed the positions of two water molecules. Thus the compound is a dihydrate.

Complete model subjected to least-squares refinement, using values of form factors for V, O, N, and C as given by Cromer & Waber (1965). Function $w(F_o - F_c)^2$ minimized, where $w = 1/\sigma^2(F)$, the estimation of the standard deviations $\sigma(F)$ being based on counting statistics, $S = 2.77$. Three cycles of full-matrix least-squares refinement with an individual isotropic temperature factor, followed by another three cycles of anisotropic refinement in block-diagonal approximation lowered R to 0.067. At this stage all 17 H atoms located from a difference Fourier synthesis. Thermal parameters for four H atoms belonging to the two water molecules kept fixed, parameters of other 13 H refined isotropically in subsequent cycles. Values

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of form factors used for H as calculated by Stewart, Davidson & Simpson (1965) ($R = 0.049$). V treated as an anomalous scatterer with $f' = 0.035$, $f'' = 2.110$ (Cromer & Liberman, 1970). Final values of R and R_2 0.047 and 0.035 for all 2450 reflections. $(\Delta/\sigma)_{\max} = 0.874$ for H(O22) y coordinate. $\Delta\rho = -0.7-0.1 e \text{ \AA}^{-3}$ at V position, elsewhere min. $-0.2 e \text{ \AA}^{-3}$. No correction for secondary extinction. Programs used from XRAY ARC (*World List of Crystallographic Computer Programs*, 1973), modified for the B6700 computer.

Discussion. The atomic coordinates are given in Table 1; some interatomic distances and angles are presented in Table 2.*

The structure consists of discrete complexes and loosely bound water molecules of crystallization. One asymmetric unit of the structure, projected on a plane normal to the a axis, is shown in Fig. 1. The packing in one unit cell is shown in Fig. 2. The V atom is octahedrally coordinated with the vanadyl O at a distance of 1.596 (2) Å, the two carboxyl O atoms O(11) and O(22) at distances of 1.991 (2) and 2.003 (2) Å respectively, the imino N at a distance of 2.328 (3) Å and the two bipyridyl N atoms N(1) and

N(2) at distances 2.110 (2) and 2.102 (2) Å respectively. The V—O bond was found to make an angle of 1.8 (2)° with the normal to the plane N(1)—N(2)—O(11)—O(22) and is thus practically perpendicular to that plane. Further, the V atom was found to be actually contained in both the mean planes through O—O(11)—N—N(2) and O—O(22)—N—N(1).

The dihedral angle between the mean planes through the two cyclic rings of the bipyridyl ligand is 6.6 (3)°. The axis C(2)—C(5) of one ring makes an angle of 10.1 (3)° with the axis C(6)—C(9) of the other ring.

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Coordination octahedron			
V—O	1.596 (2)	V—N	2.328 (3)
V—O(11)	1.991 (2)	V—N(1)	2.110 (2)
V—O(22)	2.003 (2)	V—N(2)	2.102 (2)
O—V—O(11)	101.08 (9)	O(11)—V—N(2)	156.67 (8)
O—V—O(22)	98.31 (9)	O(22)—V—N	76.51 (9)
O—V—N	173.7 (1)	O(22)—V—N(1)	159.12 (8)
O—V—N(1)	101.30 (9)	O(22)—V—N(2)	92.68 (8)
O—V—N(2)	100.53 (9)	N—V—N(1)	84.30 (9)
O(11)—V—O(22)	92.82 (8)	N—V—N(2)	83.38 (9)
O(11)—V—N	75.90 (9)	N(1)—V—N(2)	76.81 (8)
O(11)—V—N(1)	90.39 (8)		
2,2'-Bipyridyl group			
C(1)—C(2)	1.386 (4)	C(6)—C(7)	1.377 (4)
C(2)—C(3)	1.364 (4)	C(7)—C(8)	1.377 (5)
C(3)—C(4)	1.374 (4)	C(8)—C(9)	1.373 (5)
C(4)—C(5)	1.395 (4)	C(9)—C(10)	1.377 (5)
C(5)—N(1)	1.352 (3)	C(10)—N(2)	1.346 (3)
N(1)—C(1)	1.346 (3)	N(2)—C(6)	1.357 (3)
C(5)—C(6)	1.471 (4)		
C(1)—H(1)	0.94 (2)	C(7)—H(7)	0.96 (3)
C(2)—H(2)	0.93 (3)	C(8)—H(8)	0.93 (3)
C(3)—H(3)	0.96 (3)	C(9)—H(9)	0.98 (3)
C(4)—H(4)	0.96 (3)	C(10)—H(10)	0.93 (3)
C(5)—N(1)—C(1)	118.8 (2)	C(6)—N(2)—C(10)	118.5 (2)
N(1)—C(1)—C(2)	121.9 (3)	N(2)—C(10)—C(9)	122.4 (3)
C(1)—C(2)—C(3)	119.3 (3)	C(10)—C(9)—C(8)	118.6 (3)
C(2)—C(3)—C(4)	119.6 (3)	C(9)—C(8)—C(7)	119.8 (3)
C(3)—C(4)—C(5)	119.2 (3)	C(8)—C(7)—C(6)	119.3 (3)
C(4)—C(5)—N(1)	121.1 (3)	C(7)—C(6)—N(2)	121.3 (3)
N(1)—C(5)—C(6)	115.3 (2)	N(2)—C(6)—C(5)	114.7 (2)
C(4)—C(5)—C(6)	123.5 (3)	C(7)—C(6)—C(5)	123.9 (3)
Iminodiacetate group			
N—C(12)	1.462 (4)	N—C(21)	1.462 (4)
C(12)—C(11)	1.510 (5)	C(21)—C(22)	1.504 (5)
C(11)—O(12)	1.229 (4)	C(22)—O(21)	1.235 (3)
C(11)—O(11)	1.286 (4)	C(22)—O(22)	1.272 (4)
C(12)—H(121)	1.04 (3)	C(21)—H(211)	0.92 (3)
C(12)—H(122)	0.97 (3)	C(21)—H(212)	0.96 (3)
N—H(N)	0.78 (2)		
O(11)—C(11)—O(12)	125.0 (3)	O(22)—C(22)—O(21)	124.2 (3)
O(11)—C(11)—C(12)	117.0 (3)	O(22)—C(22)—C(21)	118.4 (3)
C(12)—C(11)—O(12)	118.0 (3)	O(21)—C(22)—C(21)	117.4 (3)
C(11)—C(12)—N	112.0 (3)	C(22)—C(21)—N	113.0 (3)
C(12)—N—V	106.8 (2)	C(12)—N—C(21)	114.0 (3)
		C(21)—N—V	107.9 (2)
Water molecules			
O(1)—H(O11)	0.79 (3)	O(2)—H(O21)	1.05 (3)
O(1)—H(O12)	0.99 (3)	O(2)—H(O22)	1.02 (3)

Table 1. *Final atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters for the non-H atoms*

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	$B_{\text{eq}} (\text{Å}^2)$
V	0.13916 (4)	0.12777 (3)	-0.17427 (5)	2.15
O	0.0182 (2)	0.1041 (1)	-0.1327 (2)	3.16
O(1)	0.4993 (2)	0.0220 (2)	-0.2810 (3)	8.13
O(2)	0.3892 (2)	0.1337 (2)	-0.5065 (3)	6.90
O(11)	0.1272 (2)	0.2541 (1)	-0.1893 (2)	2.99
O(22)	0.2319 (2)	0.1322 (1)	0.0354 (2)	3.18
O(12)	0.1935 (2)	0.3786 (1)	-0.2554 (2)	4.30
O(21)	0.3977 (2)	0.1499 (2)	0.1924 (2)	4.96
N	0.3195 (2)	0.1709 (2)	-0.2106 (3)	2.59
N(1)	0.1019 (2)	0.1177 (1)	-0.4116 (2)	2.26
N(2)	0.2002 (2)	0.0058 (1)	-0.2139 (2)	2.32
C(1)	0.0443 (2)	0.1761 (2)	-0.5059 (3)	2.89
C(2)	0.0249 (3)	0.1660 (2)	-0.6612 (3)	3.24
C(3)	0.0667 (3)	0.0956 (2)	-0.7209 (3)	3.34
C(4)	0.1255 (3)	0.0352 (2)	-0.6265 (3)	3.07
C(5)	0.1423 (2)	0.0475 (2)	-0.4708 (3)	2.23
C(6)	0.1995 (2)	-0.0149 (2)	-0.3600 (3)	2.39
C(7)	0.2475 (3)	-0.0897 (2)	-0.3980 (3)	3.56
C(8)	0.2918 (3)	-0.1466 (2)	-0.2859 (4)	4.38
C(9)	0.2896 (3)	-0.1274 (2)	-0.1381 (4)	4.02
C(10)	0.2437 (3)	-0.0506 (2)	-0.1059 (3)	3.22
C(11)	0.2022 (3)	0.3013 (2)	-0.2351 (3)	3.01
C(12)	0.3064 (3)	0.2572 (2)	-0.2722 (4)	3.70
C(21)	0.3986 (3)	0.1647 (3)	-0.0658 (4)	4.70
C(22)	0.3387 (3)	0.1486 (2)	0.0642 (3)	3.27

* Lists of anisotropic thermal parameters, structure factors, H-atom coordinates and a table containing equations of some mean planes along with some related distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38680 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

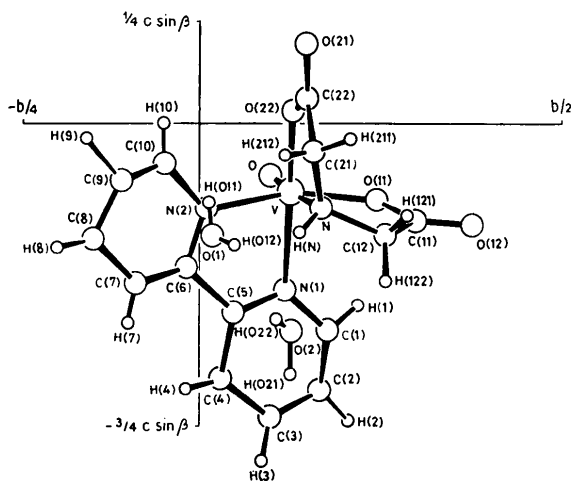


Fig. 1. One asymmetric unit of the structure projected normal to the a axis.

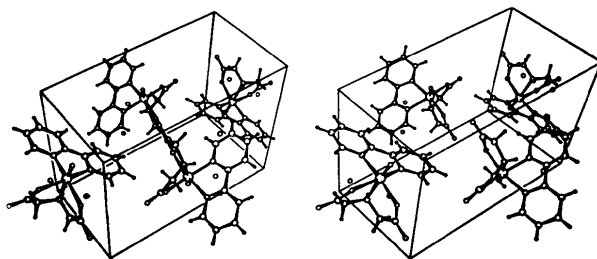


Fig. 2. Stereoscopic view of the packing.

This distortion has the effect of pushing atoms N(1) and N(2) towards the metal atom and the angles N(1)–C(5)–C(6) and N(2)–C(6)–C(5) are $\sim 115^\circ$ while the angles C(4)–C(5)–C(6) and C(5)–C(6)–C(7) are $\sim 124^\circ$. Similar angular configuration is quite common in the bipyridyl ligand (Camus, Marsich & Nardin, 1977; Weakley, 1978; Endres, Keller, Moroni, Nöthe & Dong, 1978; Harrison & Hathaway, 1978) and may be attributed to the steric repulsion between the overcrowded hydrogen pair H(4) and H(7). The non-bonded distance between these two is 2.03 Å. Results derived for biphenyl at 110 K (Charbonneau & Delugeard, 1976) show no such distortion since in that case all the four positions contiguous to the C–C bridge are occupied by C atoms with an H atom attached to each, and steric repulsion between the hydrogen pair on one

side of the bridge is exactly balanced by that between the pair on the other side.

Regarding bond distances in the rings, the average value 1.350 (6) Å for the C–N bond is significantly lower than the average value 1.378 (9) Å obtained for the C–C bond. This latter value is in agreement with the average value 1.392 (4) Å obtained in the case of the C–C bond in crystalline benzene (Cox, Cruickshank & Smith, 1958), showing that in spite of the presence of the heteroatoms N(1) and N(2), the benzene character is still retained by the rings. The central C–C bond [C(5)–C(6) 1.471 (4) Å] is much larger, as expected.

Neither of the two five-membered rings V–N–C–C–O resulting from the tridentate chelation of the iminodiacetate ligand is really planar. Both are puckered in the same way, with the coordinating carboxyl O and the imino N on one side of the mean plane and the other atoms lying on the other side.

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