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Tris(3-methylpyridinium) Decavanadate Monohydrate

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Abstract. $[C_6H_8N]_3[V_{10}H_3O_{28}].H_2O$, $M_r = 1260\cdot8$, monoclinic, $P2_1/n$, $a = 7\cdot293$ (3), $b = 21\cdot82$ (2), $c = 23\cdot526$ (8) Å, $\beta = 96\cdot37$ (3)°, $V = 3721$ (4) Å^3, $Z = 4$, $D_m = 2\cdot3$ (1) (by flotation in $CHBr_3/CCl_4$), $D_x = 2\cdot25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1\cdot93$ mm^{-1}, $F(000) = 2480$, room temperature, $R = 0\cdot069$ for 4100 observed reflections. The decavanadate anion is similar to others already described. The severe distortions in the VO_6 octahedra are mainly due to the internal Coulombic repulsion. One molecule of 3-methylpyridine is partially disordered. Intermolecular hydrogen bonding probably exists.

Introduction. As part of a general study of the crystal chemistry of polyanions of organic bases (Arrieta, Gili & Lorente, 1984, and references therein) we have solved the structure of the title compound.

Experimental. Yellow-brown platy crystals have been synthesized from acidic aqueous media following the method described by Arrieta *et al.* (1984). The chemical analysis of V, C, H and N gave the following calculated (experimental) results: V_2O_5 72·06 (71·75), C 17·12 (17·15), H 2·29 (2·28), N 3·33% (3·50%). Vanadium was analysed as V_2O_5 after calcination at 823 K for two hours; data collected from crystal approximately 0·2 × 0·1 × 0·2 mm; cell parameters determined by least squares from the setting angles of 15 reflections ($10 < 2\theta < 25°$); 5503 independent reflections measured; Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω scans up to $2\theta = 47°$; one standard reflection (101) measured every 50 showed only random deviations from mean intensity; Lp corrections applied but no correction for absorption; 4100 reflections $[I \geq 2\cdot5\sigma(I)]$ considered observed and included in refinement; index range $h \pm 7$, k 0–24, l 0–26; structure solved with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), an E map showed the decavanadate anion except for two O atoms. All remaining (non-H) atoms from three ΔF syntheses; refinement by least squares with *SHELX76* (Sheldrick, 1976), unit weights, $\sum(\Delta F)^2$ minimized, completed with anisotropic thermal parameters, the H atoms were not taken into account; final $R = 0\cdot069$; scattering factors from *International Tables for X-ray Crystallography* (1974) and the anomalous-scattering factors from Cromer & Liberman (1970); max. $\Delta/\sigma = 0\cdot90$ [for y, C(64)]; max. and min. electron densities in final difference map + 2·5 and + 1·05 e Å^{-3} (this high value of the residual electron density should be related to the 116 H atoms in the unit cell which we have not considered).

Discussion. Table 1† gives the final atomic parameters with their B_{eq} values. Fig. 1 shows the numbering of the decavanadate anion and the arrangement of different V

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† Lists of structure factors, anisotropic thermal parameters, angles of the decavanadate anion, distances and angles of the disordered organic molecule, intermolecular distances and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44413 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(VI–VIII) and O (O*a*–O*g*) atom types according to Evans (1966). Fig. 2 shows a stereoscopic view of the unit-cell contents. Distances (given in Table 2) and angles* are similar to others previously described for $K_2Zn_2V_{10}O_{28}\cdot16H_2O$ (Evans, 1966), $Ca_3V_{10}O_{28}\cdot17H_2O$ (Swallow, Ahmed & Barnes, 1966), $Y_2V_{10}O_{28}\cdot24H_2O$, $La_2V_{10}O_{28}\cdot20H_2O$ and $Nd_2V_{10}O_{28}\cdot28H_2O$ (Saf'yanov, Kuz'min & Belov, 1979), $Na_6V_{10}O_{28}\cdot18H_2O$ (Durif, Averbuch-Pouchot & Guitel, 1980), $[C_7H_{10}N]_4[V_{10}H_2O_{28}]$ (Debaerdemaeker, Arrieta & Amigó, 1982) and $Er_2V_{10}O_{28}\cdot25H_2O$ (Rivero, Rigotti, Punte & Navaza, 1984). The severe distortions in the VO_6 octahedra are mainly due to the internal Coulombic repulsion (Evans, 1966), and can be interpreted on the grounds put forward by Baur (1970) and by Brown & Shannon (1973). The correlation between distortion (mean-square relative deviation of bond length from the average) and average V—O bond length within each VO_6 octahedron in our compound is similar to that obtained from the data of Evans (1966) and of Rivero *et al.* (1984).

Other parameters of interest, such as intermolecular contacts and the three ideal mean planes corresponding to the symmetry planes, were calculated with *PARST* (Nardelli, 1982). The values of χ^2 [$\chi^2 = \sum(\varDelta/\sigma)^2$, where $\varDelta \equiv$ atomic deviation from the calculated mean plane and $\sigma \equiv$ standard deviation of $\varDelta$] are 1063·9 (18 atoms), 579·1 (12 atoms) and 1·5 (6 atoms), indicating significant deviation from coplanarity in the two former cases. Dihedral angles between these planes are 92·30 (3), 90·0 (1) and 90·1 (1)°.

Table 1. *Atomic coordinates* (× 10⁴) *with e.s.d.'s in parentheses and* B_{eq} *values* (Å²)

The numbers alongside the disordered atoms [N(55), C(56), C(58), N(61), C(62), C(63) and C(64)] are the occupancy factors.

		x	y	z	B_{eq}*
V(1)		9885 (3)	2218 (1)	5636 (1)	1·89
V(2)		7389 (3)	2567 (1)	6655 (1)	1·83
V(3)		6168 (3)	1521 (1)	5761 (1)	2·21
V(4)		11203 (3)	1941 (1)	7007 (1)	2·15
V(5)		9610 (3)	3560 (1)	5246 (1)	2·05
V(6)		7200 (3)	3890 (1)	6209 (1)	2·11
V(7)		7557 (3)	1207 (1)	7025 (1)	2·63
V(8)		11039 (3)	3311 (1)	6596 (1)	1·89
V(9)		9951 (3)	890 (1)	6058 (1)	2·78
V(10)		6026 (3)	2848 (1)	5353 (1)	2·05
O(11)		8797 (10)	1816 (4)	6324 (3)	2·06
O(12)		8618 (9)	2977 (3)	5982 (3)	1·94
O(13)		6591 (10)	3260 (4)	6792 (3)	2·36
O(14)		10611 (10)	2713 (4)	5173 (3)	2·40
O(15)		6291 (12)	4489 (4)	6425 (4)	3·27
O(16)		8431 (10)	4161 (4)	5622 (4)	2·34
O(17)		10521 (11)	3923 (4)	4769 (4)	3·25
O(18)		10754 (10)	1532 (4)	5514 (4)	2·51
O(19)		6735 (10)	2074 (4)	7143 (3)	2·65
O(20)		8871 (11)	625 (4)	6682 (4)	3·30
O(21)		10936 (12)	300 (4)	5847 (4)	3·85
O(22)		6730 (13)	850 (5)	7522 (4)	3·98
O(23)		7749 (11)	897 (4)	5607 (4)	3·08
O(24)		5651 (11)	1183 (4)	6429 (4)	2·98
O(25)		4440 (11)	1363 (4)	5314 (4)	3·22
O(26)		5538 (10)	2349 (4)	6033 (3)	2·28
O(27)		7468 (9)	2085 (4)	5273 (3)	2·16
O(28)		4269 (11)	2693 (4)	4919 (4)	3·02
O(29)		5345 (9)	3539 (4)	5721 (4)	2·44
O(30)		7474 (10)	3263 (4)	4891 (3)	2·36
O(31)		9872 (10)	2703 (4)	7039 (3)	2·17
O(32)		11680 (10)	3625 (4)	5875 (3)	2·27
O(33)		9547 (11)	3905 (4)	6711 (3)	2·42
O(34)		9814 (10)	1522 (4)	7419 (4)	2·68
O(35)		11890 (9)	2452 (4)	6287 (3)	2·01
O(36)		12844 (10)	3456 (4)	7017 (4)	3·04
O(37)		12995 (11)	2079 (4)	7430 (4)	3·25
O(38)		11984 (10)	1232 (4)	6593 (4)	2·89
N(39)		8921 (15)	4969 (5)	3946 (5)	3·61
C(40)		6536 (23)	4072 (8)	3581 (7)	5·11
C(41)		6206 (17)	4417 (6)	4048 (6)	3·24
C(42)		7427 (21)	4864 (7)	4235 (6)	3·87
C(43)		9284 (21)	4649 (7)	3481 (6)	4·03
C(44)		4494 (22)	4305 (8)	4378 (9)	5·84
C(45)		8092 (25)	4177 (8)	3301 (7)	5·14
C(46)		491 (17)	1890 (7)	3109 (6)	3·31
C(47)		1466 (19)	1827 (7)	4124 (6)	3·65
C(48)		1093 (18)	2169 (7)	3632 (6)	3·60
N(49)		338 (15)	1529 (6)	3108 (5)	3·97
C(50)		1288 (22)	1198 (8)	4095 (7)	4·57
C(51)		1265 (24)	2865 (7)	3646 (7)	4·91
C(52)		720 (22)	909 (8)	3593 (8)	4·84
C(53)		5255 (23)	1362 (11)	3125 (8)	5·74
C(54)		6239 (28)	1154 (15)	4087 (8)	6·60
N(55)	0·5	5869 (54)	631 (19)	4107 (22)	9·14
C(56)	0·5	5165 (77)	268 (36)	3644 (34)	9·04
C(57)		6253 (29)	2202 (13)	3794 (11)	8·22
C(58)	0·5	4911 (78)	622 (38)	3072 (23)	7·97
C(59)	0·5	5815 (33)	1591 (13)	3630 (12)	2·94
O*W*(60)		9508 (21)	247 (6)	2453 (6)	7·23
N(61)	0·5	6656 (33)	1650 (18)	4213 (10)	4·85
C(62)	0·5	5600 (44)	2073 (18)	3319 (15)	5·06
C(63)	0·5	5624 (50)	924 (20)	3472 (26)	6·33
C(64)	0·5	5452 (69)	278 (21)	3336 (32)	6·48

* Calculated according to Willis & Pryor (1975).

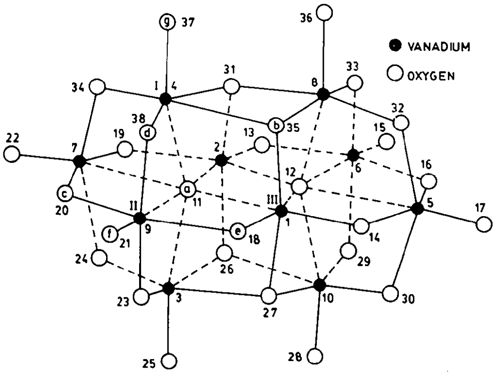

Fig. 1. View of the decavanadate group.

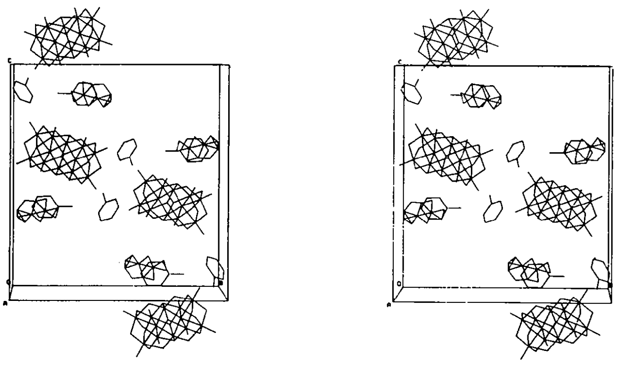

Fig. 2. Stereoscopic view of the molecular packing drawn with *PLUTO* (Motherwell & Clegg, 1978).

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* See deposition footnote.

Table 2. *Molecular geometry*

(*a*) Bond lengths (Å) with e.s.d.'s in parentheses, and the bond numbers *s* of the decavanadate anion

VIII	O*a*	O*a*	O*e*	O*e*	O*b*	O*b*	$\sum s(V)$
V(1)	O(11)	O(12)	O(14)	O(18)	O(27)	O(35)	
	2·076 (8)	2·104 (8)	1·662 (8)	1·662 (8)	1·894 (8)	2·061 (7)	
s	0·47	0·44	1·46	1·46	0·75	0·49	5·07
$\sum s(O)$	2·00	1·99	2·03	1·99	1·92	1·32	
VIII	O*a*	O*a*	O*e*	O*e*	O*b*	O*b*	
V(2)	O(11)	O(12)	O(13)	O(19)	O(26)	O(31)	
	2·127 (8)	2·102 (8)	1·665 (8)	1·681 (9)	1·937 (7)	1·954 (7)	
s	0·42	0·44	1·45	1·38	0·67	0·64	5·00
$\sum s(O)$	2·00	1·99	1·98	1·93	1·83	1·98	
VI	O*a*	O*d*	O*d*	O*g*	O*b*	O*b*	
V(3)	O(11)	O(23)	O(24)	O(25)	O(26)	O(27)	
	2·299 (7)	1·845 (9)	1·814 (9)	1·587 (8)	1·988 (8)	1·993 (8)	
s	0·28	0·86	0·94	1·85	0·59	0·58	5·10
$\sum s(O)$	2·00	1·77	1·76	1·85	1·83	1·92	
VI	O*a*	O*b*	O*d*	O*b*	O*g*	O*d*	
V(4)	O(11)	O(31)	O(34)	O(35)	O(37)	O(38)	
	2·261 (7)	1·930 (8)	1·738 (9)	2·134 (8)	1·580 (8)	1·947 (9)	
s	0·31	0·68	1·17	0·41	1·89	0·66	5·12
$\sum s(O)$	2·00	1·98	1·86	1·32	1·89	1·26	
VII	O*a*	O*e*	O*c*	O*f*	O*d*	O*d*	
V(5)	O(12)	O(14)	O(16)	O(17)	O(30)	O(32)	
	2·328 (8)	2·002 (8)	1·846 (8)	1·580 (9)	1·804 (7)	1·998 (7)	
s	0·26	0·57	0·86	1·89	0·96	0·66	5·20
$\sum s(O)$	1·99	2·03	1·77	1·89	1·84	1·33	
VII	O*a*	O*e*	O*f*	O*c*	O*d*	O*d*	
V(6)	O(12)	O(13)	O(15)	O(16)	O(29)	O(33)	
	2·333 (8)	2·026 (8)	1·575 (3)	1·826 (8)	1·841 (7)	1·969 (7)	
s	0·26	0·53	1·93	0·91	0·87	0·62	5·12
$\sum s(O)$	1·99	1·98	1·93	1·77	1·76	1·81	
VII	O*a*	O*e*	O*c*	O*f*	O*d*	O*d*	
V(7)	O(11)	O(19)	O(20)	O(22)	O(24)	O(34)	
	2·373 (8)	2·013 (9)	1·831 (9)	1·578 (10)	1·862 (8)	1·924 (8)	
s	0·24	0·55	0·89	1·91	0·82	0·69	5·10
$\sum s(O)$	2·00	1·93	1·77	1·91	1·76	1·86	
VI	O*a*	O*b*	O*d*	O*d*	O*b*	O*g*	
V(8)	O(12)	O(31)	O(32)	O(33)	O(35)	O(36)	
	2·274 (7)	1·941 (8)	1·935 (8)	1·731 (8)	2·128 (8)	1·588 (8)	
s	0·30	0·66	0·67	1·19	0·42	1·86	5·10
$\sum s(O)$	1·99	1·98	1·33	1·81	1·32	1·86	
VII	O*a*	O*e*	O*c*	O*f*	O*d*	O*d*	
V(9)	O(11)	O(18)	O(20)	O(21)	O(23)	O(38)	
	2·303 (8)	2·028 (9)	1·836 (10)	1·579 (10)	1·824 (8)	1·982 (8)	
s	0·28	0·53	0·88	1·90	0·91	0·60	5·10
$\sum s(O)$	2·00	1·99	1·77	1·90	1·77	1·26	
VI	O*a*	O*b*	O*b*	O*g*	O*d*	O*d*	
V(10)	O(12)	O(26)	O(27)	O(28)	O(29)	O(30)	
	2·285 (7)	1·999 (8)	1·989 (8)	1·584 (8)	1·833 (8)	1·836 (8)	
s	0·29	0·57	0·59	1·87	0·89	0·88	5·09
$\sum s(O)$	1·99	1·83	1·92	1·87	1·76	1·84	

(*b*) Average bond distances (Å) and ranges in the decavanadate ion; the number of averaged values is given in parentheses

VI –O*g*	1·58	1·580–1·588 (4)
VI –O*a*	2·28	2·261–2·299 (4)
VI –O*b*	2·01	1·930–2·134 (8)
VI –O*d*	1·83	1·731–1·947 (8)
VII –O*f*	1·58	1·575–1·580 (4)
VII –O*a*	2·33	2·303–2·373 (4)
VII –O*c*	1·83	1·826–1·846 (4)
VII –O*d*	1·90	1·804–1·998 (8)
VII –O*e*	2·02	2·002–2·028 (4)
VIII –O*e*	1·67	1·662–1·681 (4)
VIII –O*a*	2·10	2·076–2·127 (4)
VIII –O*b*	1·96	1·894–2·061 (4)

Table 2 (*cont.*)

(*c*) Distances (Å) and angles (°) of the ordered molecules of 3-methylpyridine with e.s.d.'s in parentheses

C(42)–N(39)	1·37 (2)	C(46)–N(49)	1·38 (2)
C(43)–N(39)	1·35 (2)	C(52)–N(49)	1·38 (2)
C(41)–C(40)	1·38 (2)	C(48)–C(46)	1·40 (2)
C(45)–C(40)	1·39 (3)	C(48)–C(47)	1·38 (2)
C(42)–C(41)	1·36 (2)	C(50)–C(47)	1·38 (2)
C(44)–C(41)	1·56 (2)	C(51)–C(48)	1·52 (2)
C(45)–C(43)	1·38 (2)	C(52)–C(50)	1·36 (2)

C(43)–N(35)–C(42)	142 (2)	N(49)–C(46)–C(48)	117 (2)
C(45)–C(40)–C(41)	121 (2)	C(50)–C(47)–C(48)	119 (2)
C(42)–C(41)–C(40)	119 (2)	C(47)–C(48)–C(46)	118 (2)
C(44)–C(41)–C(42)	119 (2)	C(51)–C(48)–C(47)	121 (2)
C(41)–C(42)–N(39)	119 (2)	C(52)–N(49)–C(46)	123 (2)
C(45)–C(43)–N(39)	117 (2)	C(52)–C(50)–C(47)	121 (2)
C(43)–C(45)–C(40)	120 (2)	C(50)–C(52)–N(49)	119 (2)

Table 2(*b*) shows the extreme and average values of the V—O distances for each type of V and O atom. The ranges spanned by each type are a measure of the distortion from *mmm* symmetry (Rivero *et al.*, 1984). These distortions correspond to deviations of no more than 0·05 Å from the distances reported by Evans (1966). Distances and angles of the organic molecules are shown in Table 2(*c*). Other distances of interest are O(17)···N(39) 3·13 (1), O(27)···N(61) 2·67 (3), O(15)···O*W*(60)($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) 2·93 (2), and N(49)···O*W*(60)($1-x,y,z$) 2·72 (2) Å, indicating probable intermolecular hydrogen bonding.

In order to illuminate the controversy (see Klemperer & Shum, 1977; Howarth & Jarrold, 1978) as to which oxygen site would carry the H atoms, Evans & Pope (1984) have used the empirical bond-length/bond-number calculation to try to find valence-deficient O atoms. With the power function $s=(R/1\cdot791)^{-5\cdot1}$ developed by Brown (1981), which relates the V—O distance *R* and the bond number *s*, and data from the $[C_7H_{10}N]_4[V_{10}H_2O_{28}]$ structure (Debaerdemaeker *et al.*, 1982) they obtained strong evidence that the extra proton was attached at a double-linked O*d*-type atom ($\sum s=1\cdot25$). In Table 2(*a*) we give the results of applying the same calculation to our molecule. From the table we can obtain the $\sum s$ values for the O atoms, and all except three are in the range 1·76–2·03. These exceptions are O(32), O(35) and O(38) whose values of $\sum s$ are 1·33, 1·32 and 1·26 respectively, where O(32) and O(38) are doubly linked O*d* atoms and O(35) a triply linked O*b*-type atom. The hypothesis that the acidic protons of the decavanadate ion are attached to these three O atoms is also supported by the distances O(32)···O(29) 2·74 (1), O(35)···O(26) 2·80 (1), and O(38)···O(24) 2·75 (1) Å. These hydrogen bonds are parallel and link three adjacent O atoms in one ion to the corresponding O atoms on its neighbour along the *a* axis. Several other O atoms that are not hydrogen-bonded are brought into close contact, O(36)···O(13) 2·87 (1), O(14)···O(28) 2·80 (1), O(18)···O(25) 2·80 (1), O(37)···O(19) 2·88 (1) Å. [All of the O···O distances cited in this paragraph are of the type O(x,y,z)···O($1+x,y,z$).]

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Structure of Binuclear Hexaaqua-μ-[1,2,4,5-benzenetetracarboxylato(4−)]-bis(ethylenediamine)dinickel(II) Tetrahydrate

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Abstract. $[Ni_2(C_2H_8N_2)_2(C_{10}H_2O_8)(H_2O)_6].4H_2O$, $M_r = 667{\cdot}89$, monoclinic, $P2_1/c$, $a = 9{\cdot}192\,(1)$, $b = 13{\cdot}919\,(2)$, $c = 10{\cdot}754\,(1)$ Å, $\beta = 107{\cdot}70\,(1)°$, $V = 1311\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}69$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}805$ mm^{-1}, $F(000) = 700$, $T = 293$ K, final $R = 0{\cdot}035$ for 1908 independent reflexions having $I \geq 2{\cdot}5\sigma(I)$. The structure consists of binuclear centrosymmetric $[(en)(H_2O)_3Ni\text{-}(pyr)\text{-}Ni(H_2O)_3(en)]$ units [pyr=tetraanion of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid); en=ethylenediamine] and water of hydration. The complex molecules are oriented parallel to the [201] direction. The packing is governed by a three-dimensional network of hydrogen bonds. The Ni atom is octahedrally coordinated, and the pyr anion functions as a bis monodentate ligand. Differences between analogous ternary Ni^{II} and Cu^{II} complexes including the aromatic polycarboxylate ions are discussed. They can be attributed to different coordination geometries, and to a higher degree of hydration found in the Ni complexes.

Introduction. Structures of numerous ternary Ni^{II} and Cu^{II} complexes containing various amines and the phthalate (1,2-benzenedicarboxylate) ion are known (Krstanović, Karanović & Stojaković, 1985; Krstanović, Karanović, Stojaković & Golič, 1982; Poleti,

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