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Potassium (4-carboxypyridine-2,6-dicarboxylato)dioxidovanadate(V) monohydrate

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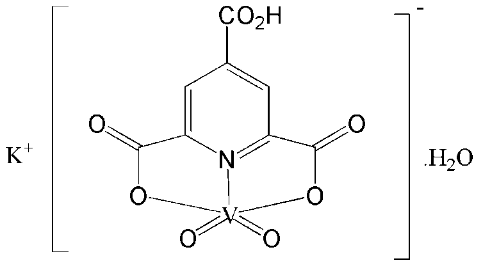
Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.079; data-to-parameter ratio = 11.0.

The title complex, $K[V(C_8H_3NO_6)O_2]\cdot H_2O$, was synthesized by reacting 4-carboxypyridine-2,6-dicarboxylic acid (contaminated as a potassium salt) with NH_4VO_3 in aqueous solution. The title complex, with a vanadium(V) metal center, is a distorted square-based pyramid. Its structure consists of chains of the anionic complexes in the direction of the b axis connected by potassium–oxygen interactions which range from 2.5981 (18) to 3.0909 (18) Å. These chains are linked to each other by hydrogen bonding between the O atoms of the complex and the water molecules.

Related literature

For related literature, see: Cassellato & Vigato (1978); Cingi *et al.* (1971); Crans *et al.* (2000); Crans, Mahroof-Tahir *et al.* (2003); Crans, Yang *et al.* (2003); D'Ascenzo *et al.* (1978); Drew *et al.* (1970); Dutta & Ghosh (1967); Furst *et al.* (1978); Gaw *et al.* (1971); Ghosh *et al.* (1978); Lukes & Jurecek (1948); Murtha & Walton (1973); Payne *et al.* (2007); Syper *et al.* (1980); Yang *et al.* (2002).



Experimental

Crystal data

$K[V(C_8H_3NO_6)O_2]\cdot H_2O$	V = 2337.2 (8) Å^3
M_r = 349.17	Z = 8
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
a = 7.8086 (16) Å	μ = 1.25 mm^{-1}
b = 16.342 (3) Å	T = 153 (2) K
c = 18.316 (4) Å	0.50 × 0.50 × 0.12 mm

Data collection

Rigaku Mercury CCD diffractometer	17213 measured reflections
Absorption correction: multi-scan (*REQAB*; Rigaku/MSC, 1999)	2099 independent reflections
$T_{\min}$ = 0.573, $T_{\max}$ = 0.864	1951 reflections with $I > 2\sigma(I)$
	$R_{\rm int}$ = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.079	$\Delta\rho_{\max}$ = 0.38 e Å^{-3}
S = 1.15	$\Delta\rho_{\min}$ = −0.42 e Å^{-3}
2099 reflections	
190 parameters	

Table 1
Selected bond lengths (Å).

V1—O6	1.6187 (17)	V1—O1	2.0091 (17)
V1—O5	1.6287 (17)	V1—N1	2.086 (2)
V1—O2	1.9949 (17)		

Data collection: *CrystalClear* (Rigaku/MSC, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

AAH thanks the University of Southern Mississippi for a startup grant (No. DE00977), which was very valuable in making this structural elucidation viable. AAH also thanks Dr William Jarrett for acquiring the ^{51}V NMR spectrum.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2108).

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supplementary materials

Acta Cryst. (2007). E**63**, m2051-m2052 [**doi:10.1107/S1600536807031418**]

Potassium (4-carboxypyridine-2,6-dicarboxylato)dioxidovanadate(V) monohydrate

A. A. Holder and **D. VanDerveer**

Comment

Pyridine-2,6-dicarboxylic acid (dipicolinic acid, abbreviated as H_2dipic) has been found to be an interesting and versatile ligand for several reasons: (1) it can function as a tridentate ligand; (2) the carboxylate groups sometimes bridge two metal atoms (Cingi *et al.*, 1971); (3) coordination to a metal atom can occur through dianionic (dipic^{2-}) (Lukes & Jurecek, 1948, Dutta & Ghosh, 1967, Drew *et al.*, 1970), monoanionic (Hdipic^{-}) (Murtha & Walton, 1973, Gaw *et al.*, 1971), or neutral (H2dipic) forms of this ligand (Drew *et al.*, 1970). Based on these facts, a large number of divalent or trivalent transition metal and lanthanide(III) complexes of dipicolinic acid have been studied (Payne *et al.*, 2007, Cassellato & Vigato, 1978, D'Ascenzo *et al.*, 1978, Ghosh *et al.*, 1978, Furst *et al.*, 1978). Recently, a number of cobalt- and vanadium-containing complexes with either 4-hydroxypyridine-2,6-dicarboxylic acid or dipicolinic acid as ligand, were reported to be insulin-like in nature (Crans, Mahroof-Tahir *et al.*, 2003, Crans, Yang *et al.*, 2003, Crans *et al.*, 2000, Yang *et al.*, 2002)·As part of our interest in the coordination chemistry of analogues of dipicolinic acid, we now extend this chemistry to include the structural elucidation of the $[VO_2(\text{dipic-}CO_2H]^{-}$ anion. The title complex, with a vanadium(V) metal centre, is a distorted square-based pyramid.

Experimental

H_2dipic-CO_2H was synthesized by the literature procedure (Syper *et al.*, 1980). Deionized water (20 cm^3) was added to a mixture of H_2dipic-CO_2H (3.15 g, 14.8 mmol) and NH_4VO_3 (1.74 g, 14.9 mmol) in a 50 cm^3 beaker. The mixture was then heated to 353–363 K until the solution became clear yellow; while hot, the pH of the solution was reduced to 1.1 with 2 *M* HCl. The mixture was then heated for an additional 15 minutes and filtered to give a bright yellow-orange solution. Upon standing, a yellowish-white solid was formed. The crude product was filtered off and recrystallized from a minimum of hot water to give a solid, which was found to be the potassium salt, $K[VO_2(\text{dipic-}CO_2H]\cdot H_2O$, as confirmed by X-ray crystallography.

FT IR (cm^{-1}): 3470 (br, ν (OH)), 1682 (*versus*, $\nu_{as}(CO_2^{-})$), and 928 (*versus*, ν (V=O)). ^{51}V NMR (H_2O): $\delta = -533$ p.p.m.

Refinement

Positions of the water H atoms were determined from a difference Fourier map and their coordinates were refined freely. All remaining H atoms were geometrically positioned and allowed to ride on the corresponding non-H atom with C—H = 0.96 Å, O—H = 0.83 Å, and $U_{iso}(H) = 1.2U_{eq}(C,O)$.

Figures

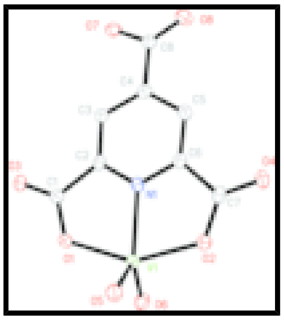

Fig. 1. Displacement ellipsoid drawing (50% probability level) of the vanadate complex.

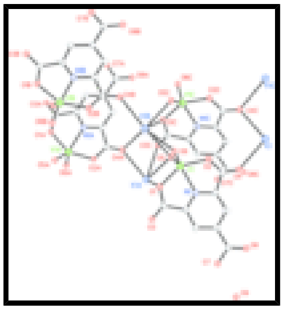

Fig. 2. The complex-potassium network. [Symmetry codes: (A) −*x*, 1/2 + *y*, 1/2 − *z*; (B) −1/2 + *x*, 1/2 + *y*, *z*; (C) 1/2 + *x*, 1/2 + *y*, *z*.]

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Crystal data

$K[V(C_8H_3NO_6)O_2]\cdot H_2O$

$M_r = 349.17$

Orthorhombic, *Pbca*

$a = 7.8086\ (16)$ Å

$b = 16.342\ (3)$ Å

$c = 18.316\ (4)$ Å

$V = 2337.2\ (8)$ Å^3

$Z = 8$

$F_{000} = 1392$

$D_x = 1.985$ Mg m^{-3}

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 8517 reflections

θ = 3.1–26.4°

$\mu = 1.25$ mm^{-1}

$T = 153\ (2)$ K

Plate, colorless

0.50 × 0.50 × 0.12 mm

Data collection

Rigaku Mercury CCD diffractometer

Radiation source: Sealed Tube

Monochromator: Graphite Monochromator

Detector resolution: 14.6306 pixels mm^{-1}

$T = 153(2)$ K

ω scans

Absorption correction: multi-scan (REQAB; Rigaku/MSC, 1999)

$T_{\min} = 0.573$, $T_{\max} = 0.864$

2099 independent reflections

1951 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 25.2°$

$\theta_{\min} = 3.1°$

$h = -9 \rightarrow 9$

$k = -19 \rightarrow 19$

$l = -21 \rightarrow 21$

17213 measured reflections

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.079$	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 2.9965P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{\max} = 0.001$
2099 reflections	$\Delta\rho_{\max} = 0.38$ e Å^{-3}
190 parameters	$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
V1	0.01940 (5)	0.56611 (2)	0.17052 (2)	0.01377 (14)
K1	−0.20989 (6)	0.21723 (3)	0.20644 (3)	0.02000 (16)
O1	0.1877 (2)	0.65071 (9)	0.13611 (9)	0.0165 (3)
O2	−0.0321 (2)	0.45032 (10)	0.19712 (9)	0.0187 (4)
O3	0.4445 (2)	0.67819 (10)	0.08618 (9)	0.0192 (4)
O4	0.0627 (2)	0.32230 (10)	0.21357 (9)	0.0203 (4)
O5	−0.0230 (2)	0.60987 (10)	0.24834 (9)	0.0192 (4)
O6	−0.1336 (2)	0.58848 (10)	0.11431 (9)	0.0207 (4)
O7	0.7845 (2)	0.40826 (10)	0.03885 (9)	0.0199 (4)
H7	0.8721	0.3804	0.0325	0.024*
O8	0.6847 (2)	0.29294 (10)	0.09009 (9)	0.0219 (4)
O9	1.0655 (2)	0.33250 (12)	0.02454 (11)	0.0209 (4)
H9A	1.067 (5)	0.288 (2)	0.0436 (19)	0.038 (10)*
H9B	1.104 (5)	0.333 (2)	−0.017 (2)	0.058 (13)*
N1	0.2394 (2)	0.50057 (11)	0.14296 (10)	0.0138 (4)
C1	0.3378 (3)	0.63102 (14)	0.11050 (12)	0.0153 (5)

C2	0.3713 (3)	0.54026 (14)	0.11337 (12)	0.0145 (5)
C3	0.5159 (3)	0.49909 (14)	0.09037 (12)	0.0146 (5)
H3	0.6112	0.5277	0.0694	0.018*
C4	0.5181 (3)	0.41440 (15)	0.09881 (12)	0.0157 (5)
C5	0.3811 (3)	0.37328 (14)	0.13113 (12)	0.0162 (5)
H5	0.3828	0.3150	0.1377	0.019*
C6	0.2425 (3)	0.42000 (14)	0.15330 (12)	0.0151 (5)
C7	0.0808 (3)	0.39222 (14)	0.19098 (13)	0.0173 (5)
C8	0.6716 (3)	0.36540 (14)	0.07538 (12)	0.0169 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0131 (2)	0.0131 (2)	0.0151 (2)	0.00022 (14)	0.00020 (15)	−0.00044 (15)
K1	0.0174 (3)	0.0170 (3)	0.0256 (3)	−0.00151 (19)	−0.0029 (2)	0.0042 (2)
O1	0.0159 (8)	0.0123 (8)	0.0212 (8)	0.0005 (6)	0.0008 (7)	0.0006 (7)
O2	0.0163 (8)	0.0155 (8)	0.0244 (9)	0.0001 (7)	0.0035 (7)	0.0029 (7)
O3	0.0183 (8)	0.0152 (8)	0.0242 (9)	−0.0039 (7)	0.0023 (7)	0.0025 (7)
O4	0.0220 (9)	0.0129 (9)	0.0260 (9)	−0.0027 (7)	0.0025 (7)	0.0023 (7)
O5	0.0211 (9)	0.0174 (9)	0.0191 (8)	−0.0023 (7)	0.0032 (7)	−0.0016 (7)
O6	0.0182 (8)	0.0208 (9)	0.0230 (9)	−0.0033 (7)	−0.0042 (7)	0.0044 (7)
O7	0.0165 (8)	0.0204 (9)	0.0228 (9)	0.0025 (7)	0.0029 (7)	0.0001 (7)
O8	0.0241 (9)	0.0184 (9)	0.0231 (9)	0.0042 (7)	0.0006 (7)	0.0025 (7)
O9	0.0223 (9)	0.0196 (10)	0.0208 (10)	0.0035 (7)	0.0036 (7)	0.0025 (8)
N1	0.0158 (9)	0.0128 (10)	0.0128 (9)	−0.0006 (7)	−0.0003 (8)	−0.0010 (7)
C1	0.0163 (11)	0.0156 (12)	0.0139 (11)	0.0007 (9)	−0.0012 (9)	−0.0004 (9)
C2	0.0158 (11)	0.0157 (11)	0.0120 (11)	−0.0031 (9)	−0.0027 (9)	−0.0003 (9)
C3	0.0156 (11)	0.0156 (12)	0.0127 (11)	−0.0007 (9)	−0.0008 (9)	0.0002 (9)
C4	0.0167 (11)	0.0197 (12)	0.0106 (11)	−0.0002 (9)	−0.0032 (9)	−0.0014 (9)
C5	0.0195 (12)	0.0148 (11)	0.0144 (11)	−0.0002 (9)	−0.0041 (9)	0.0003 (9)
C6	0.0167 (11)	0.0163 (12)	0.0124 (10)	−0.0023 (9)	−0.0024 (9)	0.0005 (9)
C7	0.0177 (11)	0.0174 (13)	0.0167 (11)	−0.0037 (9)	−0.0015 (9)	−0.0008 (9)
C8	0.0167 (11)	0.0190 (13)	0.0148 (11)	0.0014 (9)	−0.0018 (9)	−0.0010 (9)

Geometric parameters (Å, °)

V1—O6	1.6187 (17)	O5—K1^{vi}	2.6593 (17)
V1—O5	1.6287 (17)	O5—K1^{ix}	2.8313 (18)
V1—O2	1.9949 (17)	O6—K1^{ix}	2.9612 (19)
V1—O1	2.0091 (17)	O7—C8	1.310 (3)
V1—N1	2.086 (2)	O7—H7	0.830
K1—O8^{i}	2.5981 (18)	O8—C8	1.219 (3)
K1—O5^{ii}	2.6593 (17)	O8—K1^{x}	2.5981 (18)
K1—O4	2.7377 (18)	O9—H9A	0.81 (4)
K1—O5^{iii}	2.8313 (18)	O9—H9B	0.81 (4)
K1—O4^{iv}	2.8721 (18)	N1—C6	1.330 (3)
K1—O6^{iii}	2.9612 (19)	N1—C2	1.332 (3)

K1—O1^{ii}	3.0867 (18)	C1—C2	1.507 (3)
K1—O3^{v}	3.0909 (18)	C2—C3	1.380 (3)
O1—C1	1.303 (3)	C3—C4	1.393 (3)
O1—K1^{vi}	3.0867 (18)	C3—H3	0.960
O2—C7	1.301 (3)	C4—C5	1.395 (3)
O3—C1	1.219 (3)	C4—C8	1.504 (3)
O3—K1^{vii}	3.0909 (18)	C5—C6	1.385 (3)
O4—C7	1.224 (3)	C5—H5	0.960
O4—K1^{viii}	2.8721 (18)	C6—C7	1.509 (3)

O6—V1—O5	107.90 (9)	V1—O1—K1^{vi}	89.19 (6)
O6—V1—O2	102.76 (8)	C7—O2—V1	122.32 (15)
O5—V1—O2	99.31 (8)	C1—O3—K1^{vii}	109.16 (14)
O6—V1—O1	97.34 (8)	C7—O4—K1	131.29 (15)
O5—V1—O1	96.06 (8)	C7—O4—K1^{viii}	131.23 (15)
O2—V1—O1	149.45 (7)	K1—O4—K1^{viii}	97.47 (5)
O6—V1—N1	124.72 (8)	V1—O5—K1^{vi}	115.03 (8)
O5—V1—N1	127.20 (8)	V1—O5—K1^{ix}	100.65 (8)
O2—V1—N1	74.81 (7)	K1^{vi}—O5—K1^{ix}	100.33 (6)
O1—V1—N1	74.85 (7)	V1—O6—K1^{ix}	95.89 (7)
O8^{i}—K1—O5^{ii}	141.84 (6)	C8—O7—H7	109.5
O8^{i}—K1—O4	89.24 (6)	C8—O8—K1^{x}	132.11 (15)
O5^{ii}—K1—O4	82.37 (5)	H9A—O9—H9B	114 (4)
O8^{i}—K1—O5^{iii}	106.51 (6)	C6—N1—C2	121.7 (2)
O5^{ii}—K1—O5^{iii}	90.61 (5)	C6—N1—V1	119.25 (16)
O4—K1—O5^{iii}	161.50 (5)	C2—N1—V1	119.01 (15)
O8^{i}—K1—O4^{iv}	86.43 (5)	O3—C1—O1	126.2 (2)
O5^{ii}—K1—O4^{iv}	131.19 (5)	O3—C1—C2	121.1 (2)
O4—K1—O4^{iv}	94.67 (5)	O1—C1—C2	112.74 (19)
O5^{iii}—K1—O4^{iv}	77.10 (5)	N1—C2—C3	121.3 (2)
O8^{i}—K1—O6^{iii}	74.94 (5)	N1—C2—C1	111.1 (2)
O5^{ii}—K1—O6^{iii}	89.49 (5)	C3—C2—C1	127.7 (2)
O4—K1—O6^{iii}	142.54 (5)	C2—C3—C4	117.4 (2)
O5^{iii}—K1—O6^{iii}	53.85 (5)	C2—C3—H3	121.3
O4^{iv}—K1—O6^{iii}	117.40 (5)	C4—C3—H3	121.3
O8^{i}—K1—O1^{ii}	162.14 (5)	C3—C4—C5	121.1 (2)
O5^{ii}—K1—O1^{ii}	55.83 (5)	C3—C4—C8	120.5 (2)
O4—K1—O1^{ii}	97.63 (5)	C5—C4—C8	118.4 (2)
O5^{iii}—K1—O1^{ii}	64.52 (5)	C6—C5—C4	117.3 (2)
O4^{iv}—K1—O1^{ii}	76.63 (5)	C6—C5—H5	121.4
O6^{iii}—K1—O1^{ii}	107.78 (5)	C4—C5—H5	121.4
O8^{i}—K1—O3^{v}	74.10 (5)	N1—C6—C5	121.2 (2)

O5^{ii}—K1—O3^{v}	68.11 (5)	N1—C6—C7	110.3 (2)
O4—K1—O3^{v}	69.04 (5)	C5—C6—C7	128.5 (2)
O5^{iii}—K1—O3^{v}	123.99 (5)	O4—C7—O2	125.0 (2)
O4^{iv}—K1—O3^{v}	154.36 (5)	O4—C7—C6	122.2 (2)
O6^{iii}—K1—O3^{v}	73.98 (5)	O2—C7—C6	112.8 (2)
O1^{ii}—K1—O3^{v}	123.75 (5)	O8—C8—O7	125.2 (2)
C1—O1—V1	122.11 (14)	O8—C8—C4	121.4 (2)
C1—O1—K1^{vi}	111.89 (13)	O7—C8—C4	113.4 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, y-1/2, -z+1/2$; (iii) $-x-1/2, y-1/2, z$; (iv) $x-1/2, y, -z+1/2$; (v) $-x+1/2, y-1/2, z$; (vi) $-x, y+1/2, -z+1/2$; (vii) $-x+1/2, y+1/2, z$; (viii) $x+1/2, y, -z+1/2$; (ix) $-x-1/2, y+1/2, z$; (x) $x+1, y, z$.

Fig. 1

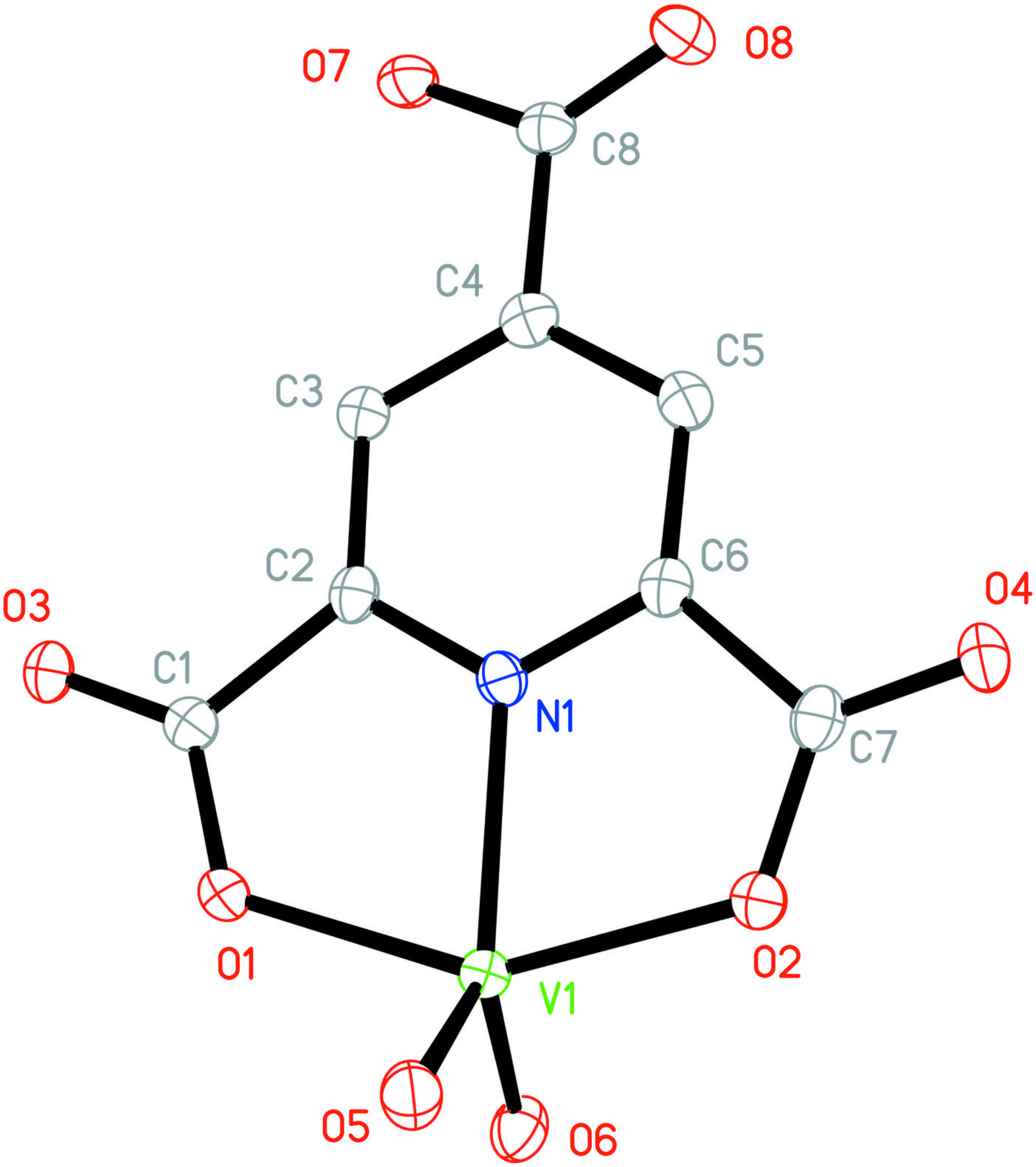
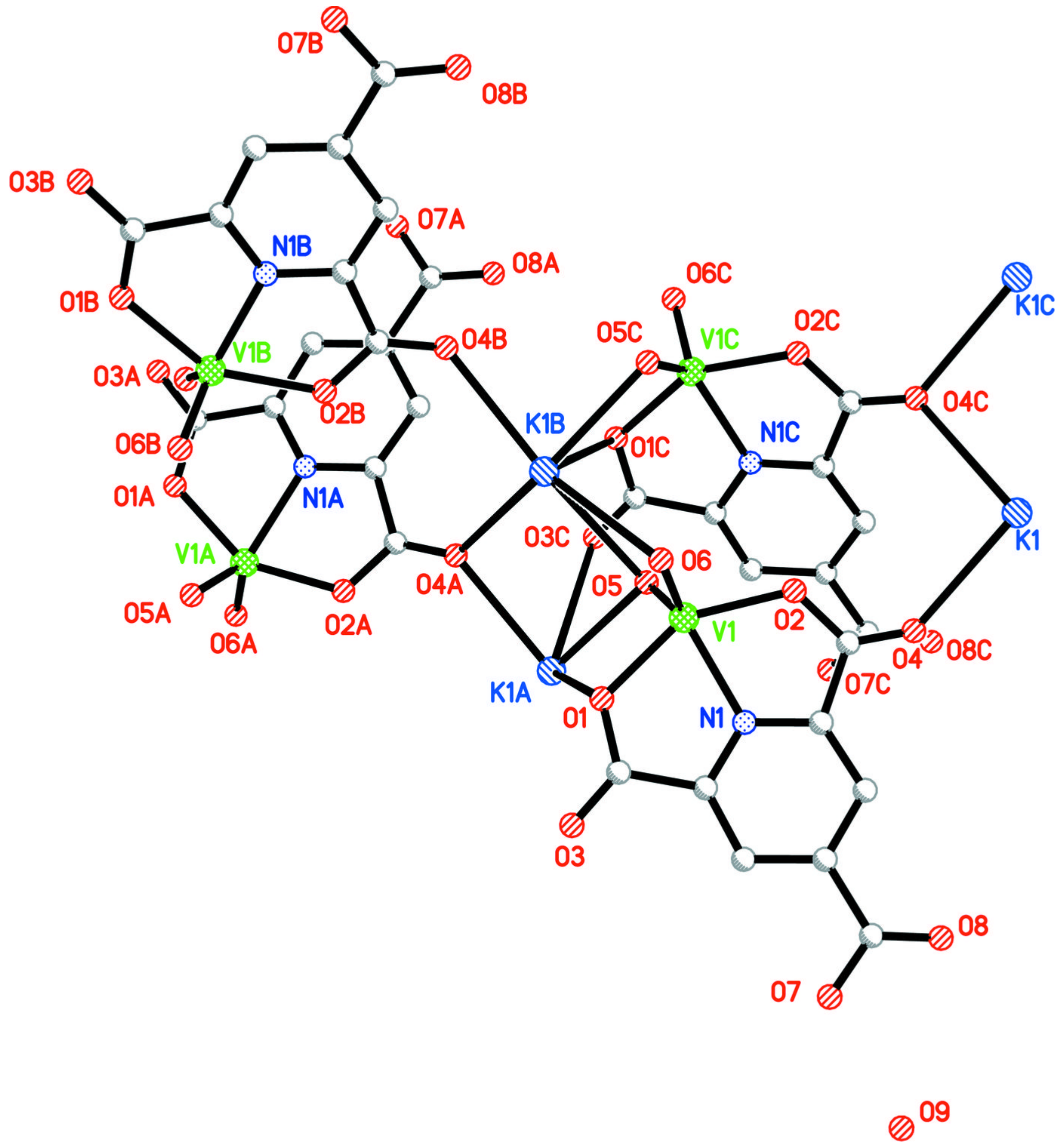


Fig. 2


O7B
O8B
O3B
O7A
N1B
O8A
O1B
O6C
O4B
O5C
V1C
O2C
K1C
O3A
V1B
O2B
O4C
K1B
O6B
O1C
N1C
O1A
N1A
O3C
K1
V1A
O6
O5
O4A
O2
V1
O5A
O6A
O2A
O4
O8C
O7C
K1A
O1
N1
O3
O8
O7
O9