



## Synthesis and Characterization of Disodium Aquabis(malonato)oxovanadate(IV)

DIPESH GHOSH<sup>1,\*</sup>, DOUGLAS R. POWELL<sup>2</sup> and J. DAVID VAN HORN<sup>3,\*</sup>

<sup>1</sup>Department of Chemistry, Vivekananda Mission Mahavidyalaya, Chaitanyapur, Haldia-721645, India

<sup>2</sup>Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Room 208, Norman, Oklahoma 73019-3051 USA

<sup>3</sup>Department of Chemistry, University of Missouri-Kansas City, 5110 Rockhill Rd., Kansas City, MO 64110-2446, USA

\*Corresponding authors: E-mail: [dipesh105@hotmail.com](mailto:dipesh105@hotmail.com); [vanhornj@umkc.edu](mailto:vanhornj@umkc.edu)

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The complex, disodium aquabis(malonato)oxovanadate(IV) monohydrate, has been synthesized and its structure determined by X-ray diffraction analysis. The geometry around the metal is octahedral and the two malonate ligands are coordinated in a *trans*-arrangement with respect to one another, forming an equatorial plane, with oxo and aqua ligands occupying the axial positions. The V=O bond length is 1.596(2) Å and the four equatorial V–O distances range between 1.995(2) and 2.012(2) Å. An intensive network of weak hydrogen bonds is observed between crystalline water molecules and between oxygen atoms of the anion and sodium cations.

**Keywords:** Vanadium(IV), Oxovanadate(IV) complexes, Malonic acid, X-ray structure, Electron spin resonance.

### INTRODUCTION

Coordination chemistry of oxovanadium(IV) complexes is currently a subject of extensive research due to their increasing the biological importance [1-7]. We are investigating biologically relevant chromium complexes with a number of dicarboxylic acids as ligand and more recently extended these studies to vanadyl(IV) cation with similar ligands [8-11]. The distinct preference of this cation for oxygen donors [4,5,12] has prompted the synthesis of several model vanadium complexes containing such type of ligands. Also, soluble vanadium species have so far received great attention as efficient reagents and catalysts in oxidation of various organic compounds [13-17]. Herein, the synthesis and molecular structure of mononuclear oxovanadium(IV) complex with malonic acid as ligand is reported. The structural information is supported with IR, UV-vis and ESR spectroscopic studies. In addition, the influence of cation on the four other anions containing two malonate and one oxo ligand were compared by Cambridge Structural Database search.

### EXPERIMENTAL

**Synthesis:** An aqueous solution (10 mL) containing vanadium sulfate reacted with a mixture of malonic acid and

sodium carbonate also taken in water (10 mL) (molar ratio 1:2:2) over a water bath. Blue-violet crystals were obtained by slow evaporation of the blue solution at room temperature. Anal. calcd. (found) % for C<sub>6</sub>H<sub>8</sub>Na<sub>2</sub>O<sub>11</sub>V: C, 20.39 (20.65); H, 2.27 (2.08).

**Characterization:** Elemental analyses were performed by Desert Analytics Laboratory, Tucson, USA. Unless stated otherwise all the chemicals used were purchased from the commercial sources and used as received. UV-visible spectra in water solutions were recorded on an Ocean Optics USB2000 fiber optic UV-visible spectrophotometer. The IR spectrum of the title complex was recorded as KBr pellet using a Perkin-Elmer model 2000 FT-IR spectrometer. The X-band ESR spectra in water solution at room temperatures (298K) were recorded on a Bruker model ER200D-SRC spectrometer using a flat quartz cell. ESR measurements at low temperature (LN<sub>2</sub>, 77 K) with a frozen solution were performed using a water/ethylene glycol mixture (3:1 v/v).

**Crystal structure determination:** A blue prism-shaped crystal of dimensions 0.25 mm × 0.20 mm × 0.16 mm was selected for the structural analysis. Intensity data for this compound were collected using a Bruker APEX CCD area detector [18] using graphite-monochromatic Mo K<sub>α</sub> radiation (λ = 0.71073 Å). The sample was cooled to 100 ± 2 K. The

intensity data were measured as a series of  $\omega$  oscillation frames each of  $0.3^\circ$  for 10 sec/frame. Coverage of unique data was 99.7% complete to  $26.00^\circ$  in  $\theta$ . Cell parameters were determined from a non-linear least squares fit of 5714 peaks in the range  $2.56 < \theta < 26.00^\circ$ . A total of 4830 data were measured in the range  $2.57 < \theta < 26.00^\circ$ . The data were corrected for absorption by the semi-empirical method [19] giving minimum and maximum transmission factors of 0.7949 and 0.8612. The data were merged to form a set of 1180 independent data with  $R_{\text{int}} = 0.0367$ .

The orthorhombic space group  $C22_1$  was determined by the systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  [20]. Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the displacement parameters of the bonded atoms. A total of 100 parameters were refined against 1180 data to give  $wR(F^2) = 0.0699$  and  $S = 1.048$  for weights of  $w = 1/[\sigma^2(F^2) + (0.0540 P)^2 + 0.2200 P]$ , where  $P = [F_o^2 + 2F_c^2]/3$ . The final  $R(F)$  was 0.0252 for the 1171 observed,  $[F > 4\sigma(F)]$ , data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.275 and  $-0.320 \text{ e}/\text{\AA}^3$ , respectively. The absolute structure was determined by refinement of the Flack parameter [21]. Final fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table-1.

TABLE-1 CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT FOR COMPLEX 1. $\text{Na}_2[\text{VO}(\text{malonate})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$	
Crystal data	Value
Chemical formula	$\text{C}_6\text{H}_8\text{Na}_2\text{O}_{11}\text{V}$
Formula weight	353.04
Temperature	100(2) K
Wavelength	0.71073 $\text{\AA}$
Crystal system	Orthorhombic
Space group	$C22_1$
Unit cell dimensions	$a = 7.234(1) \text{\AA}$ $b = 15.868(2) \text{\AA}$ $c = 10.366(2) \text{\AA}$
Volume	$1190.0(3) \text{\AA}^3$
Z, Z'	4, 0.5
Absorption coefficient	$0.963 \text{ mm}^{-1}$
$F(000)$	708
Density (calc.)	$1.971 \text{ Mg/m}^3$
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8612 and 0.7949
Theta range for data collection	$2.57$ to $26.00^\circ$
Reflections collected	4830
Independent reflections	1180 [ $R(\text{int}) = 0.0367$ ]
Data/restraints/parameters	1180/0/100
$wR(F^2 \text{ all data})$	$wR2 = 0.0699$
$R(F \text{ obsd data})$	$R1 = 0.0252$
Goodness-of-fit on $F^2$	1.048
Observed data [ $I > 2\sigma(I)$ ]	1171
Absolute structure parameter	0.00(2)
Largest and mean shift/s.u.	0.001 and 0.000
Largest diff. peak and hole	0.275 and $-0.320 \text{ e}/\text{\AA}^3$
$wR2 = \{[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)]\}^{1/2}$ ; $R1 = \sum F_o  -  F_c /\sum F_o $	

**Crystal data:**  $\text{C}_6\text{H}_8\text{Na}_2\text{O}_{11}\text{V}$ ,  $M = 353.04$ , orthorhombic, space group  $C22_1$ ,  $a = 7.2346(12)$ ,  $b = 15.868(2)$ ,  $c = 10.3661(16) \text{\AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 1190.0(3) \text{\AA}^3$ ,  $Z = 4$ ,  $F(000) = 708$ ,  $D_x = 1.971 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.963 \text{ mm}^{-1}$ ,  $(\Delta\rho)_{\text{max}} = 0.275$ ,  $(\Delta\rho)_{\text{min}} = -0.32 \text{ e}/\text{\AA}^3$ .

## RESULTS AND DISCUSSION

**Crystal structure:** The molecular structure of the complex anion is illustrated in Fig. 1 with atom numbering scheme. Table-2 provides a synopsis of selected structure parameters. In the complex anion, vanadium is in a distorted octahedral environment with two bidentate malonate ligands forming the equatorial plane at an average V–O distance of  $2.004 \text{\AA}$ . The apical sites are taken by oxo ligand and by a water molecule. The axial V=O distance,  $d(\text{V}=\text{O}9) = 1.5960(17) \text{\AA}$  is in the expected range. A search of the Cambridge Structural Database [22] reveals the four similar anions [23–28]; three of them possess octahedral geometry and the fourth shows a square–pyramidal geometry around the vanadium; two of these include the sodium cation. A comparison of crystal data and structure refinement parameters for the anion with various cations is summarized in Table-3. The two six membered V-malonate rings have boat conformations in all cases except one in which one ring has a boat and the other has a chair conformation [23]. Average V–O distances are in the range of  $1.964\text{--}2.00 \text{\AA}$  while the double bonded vanadium oxo distances range from  $1.556(3)$  to  $1.589(4) \text{\AA}$ . Intermolecular hydrogen bonds exist between the hydrogen atoms on the coordinated water molecule and O7 [ $d(\text{O}8\text{--H}\cdots\text{O}7\#12) = 2.735(2)$ ] and between the water of crystallization and the malonate oxygen atom O1 [ $d(\text{O}10\text{--H}\cdots\text{O}(1)\#13) = 2.771(2)$ ]. The sodium counterions, coordinated to water molecules, the malonate-O, the oxo groups on vanadium provide interlinkages between the anions and thus a complex supramolecular network *via* intermolecular hydrogen bonding. The hydrogen bonding network is shown in Fig. 2.

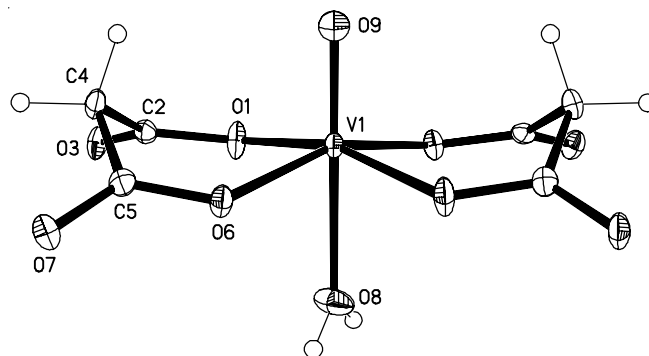


Fig. 1. Molecular structure of  $\text{Na}_2\text{VO}(\text{mal})_2(\text{H}_2\text{O})\cdot\text{H}_2\text{O}$  with atom numbering scheme

**ESR spectra:** The ESR spectrum of the compound in water exhibits the isotropic eight-line pattern [ $\langle g \rangle = 1.957$  and  $\langle A \rangle = 96.45 \times 10^{-4} \text{ cm}^{-1}$ ], typical of  $\text{VO}^{2+}$  complexes [ $S = 1/2$ ,  $I(^{51}\text{V}) = 7/2$ ] (Fig. 3). In the frozen solution, however, the spectrum displays well-resolved axial anisotropy with two sets of eight-line pattern (Fig. 4). Corresponding spin-Hamiltonian

TABLE-2  
SELECTED BOND DISTANCES (Å) AND GEOMETRIES (°) FOR THE TITLE COMPOUND 1

Bond distances (Å)				Geometries (°)	
V(1)–O(9)	1.5960(17)	O(7)–Na(1)#10	2.4851(15)	O(9)–V(1)–O(1)	98.53(4)
V(1)–O(1)	1.9955(14)	Na(2)–O(3)#3	2.4001(16)	O(9)–V(1)–O(1)#1	98.53(4)
V(1)–O(1)#1	1.9955(14)	Na(2)–O(3)#6	2.4001(16)	O(1)–V(1)–O(1)#1	162.95(9)
V(1)–O(6)#1	2.0124(13)	Na(2)–O(7)#7	2.4947(15)	O(9)–V(1)–O(6)#1	100.29(4)
V(1)–O(6)	2.0124(13)	Na(2)–O(7)#4	2.4947(15)	O(1)–V(1)–O(6)#1	88.04(6)
V(1)–O(8)	2.203(2)	Na(2)–O(10)#8	2.6891(5)	O(1)#1–V(1)–O(6)#1	88.93(6)
Na(1)–O(9)	2.264(2)	Na(2)–O(10)	2.6891(5)	O(9)–V(1)–O(6)	100.29(4)
Na(1)–O(10)	2.2953(19)	Na(2)–O(6)#7	2.8156(16)	O(1)–V(1)–O(6)	88.93(6)
Na(1)–O(3)#2	2.3058(13)	Na(2)–O(6)#4	2.8156(16)	O(1)#1–V(1)–O(6)	88.04(6)
Na(1)–O(3)#3	2.3058(13)	O(3)–Na(2)#9	2.4001(16)	O(6)#1–V(1)–O(6)	159.41(8)
Na(1)–O(7)#4	2.4851(15)	O(6)–Na(2)#9	2.8156(16)	O(1)–V(1)–O(8)	81.47(4)
Na(1)–O(7)#5	2.4851(15)	O(7)–Na(2)#10	2.4947(15)	O(1)#1–V(1)–O(8)	81.47(4)
O(3)–Na(1)#9	2.3058(13)			O(6)#1–V(1)–O(8)	79.71(4)
				O(6)–V(1)–O(8)	79.71(4)

Symmetry transformations used to generate equivalent atoms: #1  $-x+2, y, -z+1/2$ ; #2  $x+1/2, -y+3/2, -z+1$ ; #3  $-x+3/2, -y+3/2, z-1/2$ ; #4  $-x+5/2, -y+3/2, z-1/2$ ; #5  $x-1/2, -y+3/2, -z+1$ ; #6  $-x+3/2, y+1/2, -z+1/2$ ; #7  $-x+5/2, y+1/2, -z+1/2$ ; #8  $-x+2, -y+2, z-1/2$ ; #9  $-x+3/2, -y+3/2, z+1/2$ ; #10  $-x+5/2, -y+3/2, z+1/2$ ; #11  $-x+2, -y+2, z+1/2$

TABLE-3  
A COMPARISON OF X-RAY DATA BETWEEN PRESENT COMPOUND AND OTHER REPORTED STRUCTURES

	[Ref. 16]	[Ref. 17]	[Ref. 18]	[Ref. 19]	This work
Compound	(Me <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NHMe <sub>2</sub> )VO(mal) <sub>2</sub> ·2H <sub>2</sub> O	K <sub>2</sub> VO(mal) <sub>2</sub> ·(H <sub>2</sub> O)·3H <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> VO(mal) <sub>2</sub> ·H <sub>2</sub> O	(Bu <sub>4</sub> N) <sub>2</sub> VO(mal) <sub>2</sub>	Na <sub>2</sub> VO(mal) <sub>2</sub> ·(H <sub>2</sub> O)·H <sub>2</sub> O
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>Pnma</i>	<i>P112<sub>1</sub>/b</i>	<i>P2<sub>1</sub>/n</i>	<i>Pbar1</i>	<i>C22<sub>1</sub></i>
a; b; c	11.185(3); 18.512(3); 9.434(4)	21.331(8); 13.793(70); 10.695(4)	7.190(0); 19.252(2); 9.879(2)	9.685(0); 13.312(1); 17.122(1)	7.2346(12); 15.868(2); 10.3661(16)
α; β; γ	α = β = γ = 90°	α = β = 90; γ = 69.16(3)	α = γ = 90; 108.19(1)	92.61(1); 90.30(1); 95.35(1)	α = β = γ = 90
R factor	3.80	4.96	5.32	6.80	2.52
Temperature (K)	295	295	293(2)	223(2)	100(2)
Density (g/cm <sup>3</sup> )	1.507	1.903	1.754	1.144	1.971

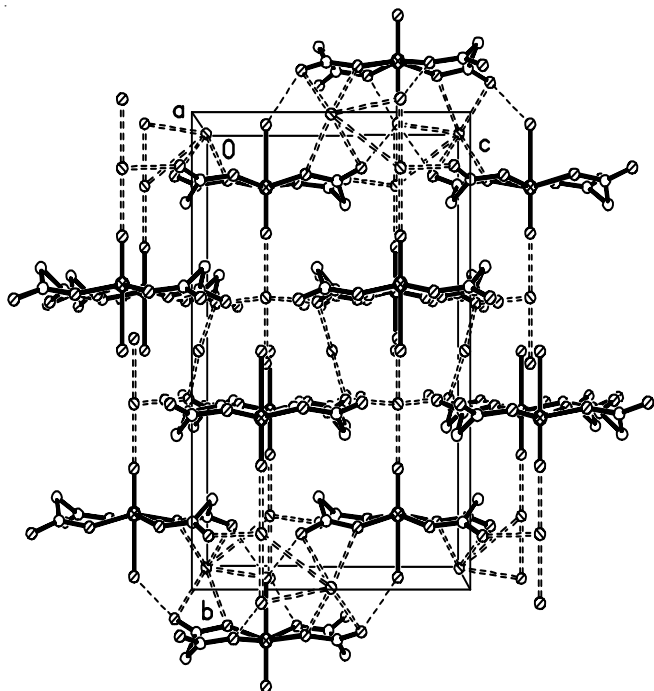


Fig. 2. Hydrogen-bonding supramolecular network of Na<sub>2</sub>VO(mal)<sub>2</sub>(H<sub>2</sub>O)·H<sub>2</sub>O

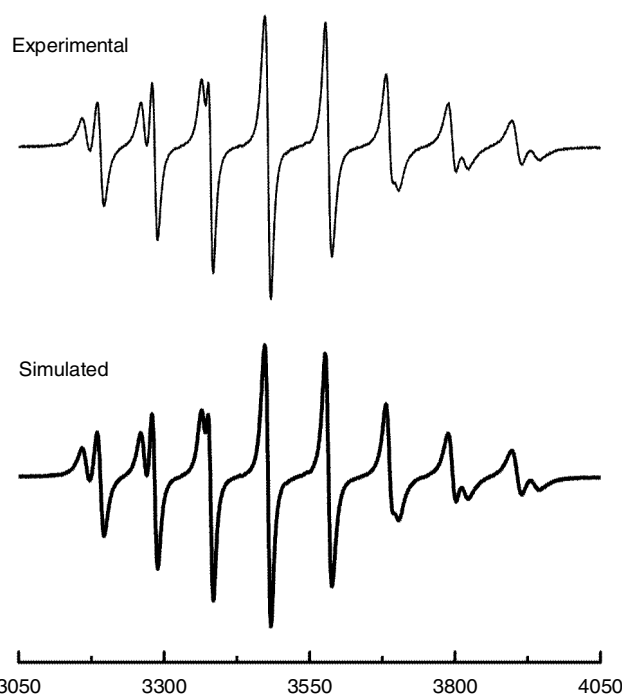


Fig. 3. Experimental and simulated room temperature (298 K) EPR spectra of VO(mal)<sub>2</sub>·H<sub>2</sub>O aqueous solution at 9.74 GHz

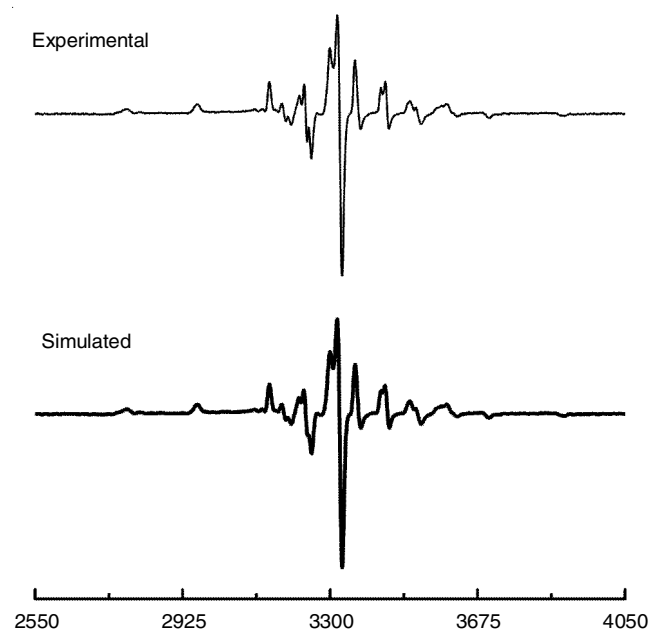


Fig. 4. Experimental and simulated low-temperature (77 K) EPR spectra of  $\text{VO}(\text{mal})_2 \cdot \text{H}_2\text{O}$  at 9.33 GHz

parameters are  $g_{\parallel} = 1.943$  ( $A_{\parallel} = 167.8 \times 10^{-4} \text{ cm}^{-1}$ ) and  $g_{\perp} = 1.97$  ( $A_{\perp} = 63.33 \times 10^{-4} \text{ cm}^{-1}$ ). The order ( $g_{\parallel} < g_{\perp}$  and  $A_{\parallel} \gg A_{\perp}$ ) and magnitude of resonance parameters are consistent with a oxovanadium(IV) site of compressed  $d_{xy}^1$  configuration [29,30].

**IR and electronic spectra:** A strong band associated with the  $\nu(\text{O}-\text{H})$  stretch of water molecules appears at  $3378 \text{ cm}^{-1}$  and a very strong band at  $1585 \text{ cm}^{-1}$  is assignable to  $\nu_{\text{as}}(\text{C}=\text{O})/\text{anionic carboxylate} + \delta(\text{H}_2\text{O})$  stretching frequencies. The characteristic bands with medium intensity of  $[\nu_{\text{s}}(\text{COO}^-) + \delta(\text{CH}_2)]$  were found at  $1416\text{--}1401 \text{ cm}^{-1}$ . A sharp band due to  $\text{V}=\text{O}_i$  stretch was observed at *ca.*  $996 \text{ cm}^{-1}$ . In addition, two bands of medium intensity observed at  $475$  and  $447 \text{ cm}^{-1}$  indicative of  $\text{V}-\text{O}$  stretching vibrations.

The complex displays the two electronic absorptions of moderate intensities ( $\epsilon$ ,  $13\text{--}44 \text{ mol}^{-1} \text{ cm}^2$ ) at  $591(\text{sh})$  and  $800 \text{ nm}$  assignable to the transitions  $d_{xy} \rightarrow d_{xz}$ ,  $d_{yz}$  and  $d_{xy} \rightarrow d_{x^2-y^2}$ , respectively [31]. Two additional bands spectral bands appearing in the UV region originate from intra-ligand transitions.

## Conclusion

Vanadium malonate complex  $\text{Na}_2[\text{VO}(\text{mal})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ , was isolated and characterized by IR, UV-vis, EPR spectroscopy and X-ray diffraction analysis. In this complex, vanadium atom is coordinated by six oxygen atoms in an octahedral geometry. The equatorial plane is occupied by two malonate ligand whereas a terminal  $\text{V}=\text{O}$  and a water molecule occupying the axial positions. At room temperature, the EPR spectra recorded in the aqueous solution exhibit isotropic eight line spectrum characteristic of vanadium(IV) complexes due to the coupling of the unpaired electron ( $n = 1$ ) with the nuclear spin ( $I = 7/2$ ). In aqueous solution at  $77 \text{ K}$ , the spectrum displays two sets of eight hyperfine peaks characteristics of oxovanadium(IV) complexes. The structural parameters of the similar vanadium malonates with four other cations were compared by CCDC search.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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