

# The crystal and molecular structure of ammonium-bis(malonato) oxovanadium(IV) dihydrate

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The title compound,  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ , crystallizes in the monoclinic space group  $\text{P}2_1/n$ , with  $a = 7.1889(7)$ ,  $b = 19.254(2)$ ,  $c = 9.879(2)$  Å,  $\beta = 108.19(1)^\circ$ , and  $Z = 4$ . The  $\text{VO}^{2+}$  cation is five-fold coordinated with two malonate anions acting as bidentate ligands and a water molecule. Infrared and Raman spectra are also reported to attain a wider insight into the compound characteristics.

**KEY WORDS:** Bis(malonato)oxovanadium(IV); crystal structure; IR and Raman spectra.

## Introduction

Increasing interest about the coordination and structural chemistry of oxovanadium(IV) complexes has arisen during the last years, probably due to the increasing evidences of the biological relevance of this cation.<sup>1-5</sup> As part of our model studies related to vanadium metabolism, we have investigated different simple  $\text{VO}^{2+}$  complexes which may be useful as model systems for vanadium biochemistry. As this cation shows a great preference for oxygen donors,<sup>4-6</sup> model complexes with such type of ligands are of special interest.

Some years ago we studied the spectroscopic and thermal behavior of a great number of salts of the complex anion bis(malonato)oxovanadium(IV)<sup>7,8</sup> and more recently we have extended these studies to a number of salts derived from a similar complex containing benzylmalonato as a ligand of the vanadyl(IV) cation.<sup>9</sup> Both systems generate complexes with the biologically relevant  $\text{O} = \text{V}(\text{O})_4$  environment.

Despite the interest in these model systems, no structural information is so far available for any salt

of these complex anions. Therefore, we have examined the crystal and molecular structure of the hydrated ammonium salt of the bis(malonato)oxovanadium(IV) complex anion. The structural information is complemented with spectroscopic data, obtained from infrared and Raman measurements.

## Experimental

### Sample preparation

The investigated salt,  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ , was obtained by reaction between  $\text{NH}_4\text{VO}_3$  with malonic acid in the presence of ammonium carbonate.<sup>7,10</sup> The crude, very soluble, product was recrystallized twice from small portions of water. Finally, the material was dissolved in a greater water volume and left to evaporate slowly at room temperature. In this way, a large number of well formed crystals, with dimensions and characteristics suitable for the crystallographic study, could be obtained.

## Instrumentation

The IR spectra were recorded between 4000 and  $200 \text{ cm}^{-1}$  with a Perkin Elmer 580B spectrophotometer, using the KBr pellet technique. Raman spectra of

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finely powdered samples were obtained with the FRA 106 Raman-attachment of a Bruker FTIR IFS66 spectrometer. The 1064 nm-line of a Nd:YAG solid state laser was used for excitation.

### Crystallographic study

Crystal data, data collection procedures, structure determination methods, and refinement results are summarized in Table 1. The unit cell parameters were obtained by least-squares refinement of  $[\sin \theta/\lambda]^2$  val-

**Table 1.** Crystal data and structure refinement for  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$

Empirical formula	$\text{C}_6\text{H}_{16}\text{N}_2\text{O}_{11}\text{V}$
Formula weight	343.15
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 7.1889(7)$ Å $b = 19.254(2)$ Å $c = 9.879(2)$ Å $\beta = 108.19(1)$ deg.
Volume	$1299.1(4)$ Å <sup>3</sup>
Z	4
Density (calculated)	$1.754$ Mg/m <sup>3</sup>
Absorption coefficient	$0.824$ mm <sup>-1</sup>
F(000)	708
Crystal size	$0.18 \times 0.18 \times 0.35$ mm
Crystal color/shape	Blue/parallelepiped
Diffractometer/scan	Enraf-Nonius CAD-4/ $\omega$ -2 $\theta$
Radiation, graphite monochr.	$\text{MoK}\alpha$ , $\lambda = 0.71069$ Å
Scan width	$0.8 + 0.35 \tan \theta$
Standard reflections	(1, 11, -4); (0, 14, 0)
Decay of standards	$\pm 1.3\%$
$\theta$ range for data collection	2.12 to 29.96 deg.
Index ranges	$-10 \leq h \leq 9$ , $-1 \leq k \leq 27$ , $0 \leq l \leq 13$
Reflections collected	4182
Independent reflections	3773 [R(int) = 0.0499]
Observed reflects. [I > 2 $\sigma$ (I)]	2295
Data reduction and correction and structure solution and Refinement programs	SDP <sup>12</sup> , SHELX-86 <sup>13</sup> , SHELX-93 <sup>14</sup>
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	3755/0/183
Goodness-of-fit on F <sup>2</sup>	1.156
Final R indices <sup>a</sup> [I > 2 $\sigma$ (I)]	$R_1 = 0.0532$ , $wR_2 = 0.1451$
R indices (all data)	$R_1 = 0.1108$ , $wR_2 = 0.2198$
Largest diff. peak and hole	$0.978^b$ and $-0.606$ e.Å <sup>-3</sup>

<sup>a</sup> R indices defined as:  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

<sup>b</sup> Residual hydrogen density of rotationally disordered  $\text{NH}_4^+$  ion (see text).

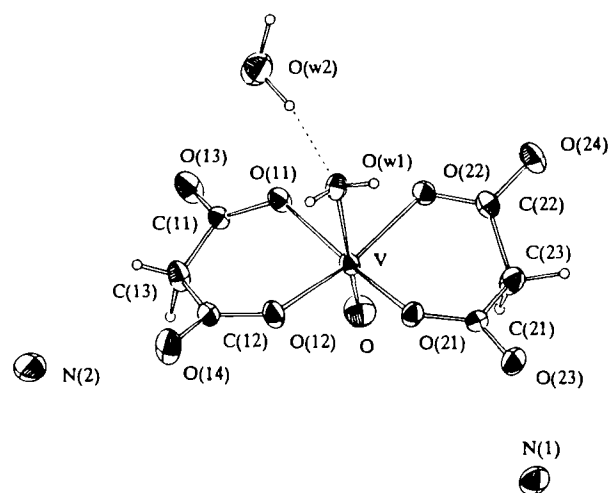
ues for 25 reflections in the  $25.5 < 2\theta < 54.42^\circ$  range. Data were corrected for Lorentz and polarization effects. An absorption correction was not applied to the diffraction data because the transmission factor<sup>11</sup> was practically isotropic and close to one (maximum and minimum values of 0.890 and 0.869).

The structure was solved by Patterson and Fourier methods with neutral atomic scattering factors. The water hydrogen atoms were located in a difference Fourier map and incorporated in the refinement at fixed positions with a common isotropic parameter which, in the final run, converged to  $U = 0.07(1)$  Å<sup>2</sup>. The hydrogen atoms of the malonato ligands were also located in the difference Fourier map. However, they were positioned stereochemically and during the refinement kept riding on the carbon atoms to which they are attached with a common isotropic thermal parameter which converged to  $U = 0.065(9)$  Å<sup>2</sup>. Most of the ammonium hydrogen atoms could not be determined reliably in the final difference Fourier map. This is probably due to rotational disorder of the  $\text{NH}_4^+$  ions, a fact which could be confirmed through the spectroscopic measurements.

## Results and discussion

### 1. Structure of the compound

Figure 1 shows an ORTEP<sup>15</sup> plot of the compound showing the labelling of the non-hydrogen atoms and their vibrational ellipsoids. Atomic fractional coordi-



**Fig. 1.** ORTEP drawing of  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$  showing the atoms labelling and the vibrational ellipsoids

nates and equivalent isotropic temperature parameters are given in Table 2. Bond distances and angles are in Table 3.

The vanadyl cation [ $d(\text{V}=\text{O}) = 1.587(3) \text{ \AA}$ ] is equatorially coordinated by two  $^{-}\text{OOC}-\text{CH}_2-\text{COO}^{-}$  units, which act as bidentate ligands at an average V–O bond distance of  $2.00(1) \text{ \AA}$ . The second axial position around the vanadium atom is occupied by a water molecule, which is bonded to the metal through one of its electron lone pairs [ $d(\text{V}-\text{Ow}) = 2.296(3) \text{ \AA}$ ]. The other lone pair acts as acceptor of a relatively weak hydrogen-bond with the other water molecule [ $d(\text{Ow}\cdots\text{Ow}) = 2.945(5) \text{ \AA}$ ]. The metal-coordinated water molecule acts, in turn, as donor in strong H-bonds with carboxylate oxygens of two other moieties [ $\text{Ow}\cdots\text{O}$  distances of  $2.687(4)$  and  $2.704(4) \text{ \AA}$ ]. H-bonding involving the water molecules are detailed in Table 4.

The observed short  $\text{N}(2)\cdots\text{O}(14)$  contact distance of  $2.714(7) \text{ \AA}$  suggests a strong  $\text{N}-\text{H}\cdots\text{O}$  bond. In fact, the peak of  $0.7 \text{ electron/\AA}^3$  found in the difference Fourier map along the  $\text{N}(2)\cdots\text{O}(14)$  contact can be assigned to one of the corresponding ammonium hydrogens. A discrete rotational disorder of this  $\text{NH}_4^+$  ion mainly around this bond probably accounts for the other peaks found surrounding  $\text{N}(2)$  atom.

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ .  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

Atom	x	y	z	$U(\text{eq})$
V	152(1)	1578(1)	2155(1)	24(1)
O	-363(5)	1279(2)	3492(4)	47(1)
O(11)	-2474(4)	1393(2)	729(3)	30(1)
O(12)	-589(4)	2566(2)	2161(3)	35(1)
O(13)	-5662(4)	1396(2)	218(4)	47(1)
O(14)	-2413(5)	3501(2)	1722(5)	54(1)
C(11)	-4069(5)	1693(2)	688(4)	25(1)
C(12)	-2267(6)	2863(2)	1718(4)	28(1)
C(13)	-4098(6)	2440(2)	1178(5)	36(1)
O(21)	2899(4)	1892(1)	3141(3)	30(1)
O(22)	1239(4)	710(1)	1571(3)	29(1)
O(23)	5904(4)	1716(2)	4579(3)	39(1)
O(24)	3613(5)	-47(2)	1770(4)	42(1)
C(21)	4304(5)	1496(2)	3820(4)	27(1)
C(22)	2881(6)	443(2)	2242(4)	28(1)
C(23)	3987(7)	719(2)	3717(5)	37(1)
O(w1)	827(4)	1911(2)	126(3)	30(1)
O(w2)	-2556(6)	1437(2)	-2243(4)	54(1)
N(1)	2558(6)	173(2)	8653(4)	45(1)
N(2)	-5471(7)	4400(4)	1021(5)	78(2)

**Table 3.** Interatomic bond distances ( $\text{\AA}$ ) and angles (deg) for  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$

Bond distances	
V–O	1.587(3)
V–O(12)	1.975(3)
V–O(11)	2.004(3)
V–O(21)	2.004(3)
V–O(22)	2.006(3)
V–O(w1)	2.296(3)
O(11)–C(11)	1.273(4)
O(12)–C(12)	1.282(5)
O(13)–C(11)	1.233(5)
O(14)–C(12)	1.233(5)
C(11)–C(13)	1.520(5)
C(12)–C(13)	1.498(6)
O(21)–C(21)	1.277(4)
O(22)–C(22)	1.268(5)
O(23)–C(21)	1.236(5)
O(24)–C(22)	1.239(5)
C(21)–C(23)	1.512(6)
C(22)–C(23)	1.521(6)
Bond angles	
O–V–O(12)	102.3(2)
O–V–O(11)	96.2(2)
O(12)–V–O(11)	88.75(12)
O–V–O(21)	98.9(2)
O(12)–V–O(21)	86.19(12)
O(11)–V–O(21)	164.80(12)
O–V–O(22)	98.6(2)
O(12)–V–O(22)	158.96(13)
O(11)–V–O(22)	90.88(11)
O(21)–V–O(22)	88.75(11)
O–V–O(w1)	174.7(2)
O(12)–V–O(w1)	82.21(12)
O(11)–V–O(w1)	81.13(11)
O(21)–V–O(w1)	83.99(11)
O(22)–V–O(w1)	76.95(11)
C(11)–O(11)–V	125.7(2)
C(12)–O(12)–V	130.8(3)
O(13)–C(11)–O(11)	121.6(4)
O(13)–C(11)–C(13)	117.0(3)
O(11)–C(11)–C(13)	121.4(3)
O(14)–C(12)–O(12)	121.0(4)
O(14)–C(12)–C(13)	118.5(4)
O(12)–C(12)–C(13)	120.5(3)
C(12)–C(13)–C(11)	122.0(3)
C(21)–O(21)–V	125.0(2)
C(22)–O(22)–V	124.7(2)
O(23)–C(21)–O(21)	123.3(4)
O(23)–C(21)–C(23)	118.1(3)
O(21)–C(21)–C(23)	118.6(3)
O(24)–C(22)–O(22)	123.1(4)
O(24)–C(22)–C(23)	118.0(4)
O(22)–C(22)–C(23)	118.9(3)
C(22)–C(23)–C(21)	115.6(3)

**Table 4.** Hydrogen bond distances (Å) and angles (deg) for  $(\text{NH}_4)_2[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}^{a,b}$ 

D	H	A	D...A	H...A	<D-H...A	D-H
O(w2)	H(w2)	O(w1)	2.945(5)	1.905(3)	165.5(2)	1.062(4)
O(w1)	H(w1)	O(13 <sup>a</sup> )	2.687(4)	1.866(3)	165.8(2)	0.839(3)
O(w1)	H(w1')	O(23 <sup>b</sup> )	2.702(4)	1.836(3)	174.4(2)	0.869(3)

<sup>a</sup> Donor and acceptor atoms are indicated by D and A, respectively. All H-bond involving water hydrogen atoms with D...A distances up to 3 Å are included.

<sup>b</sup> Symmetry code: (i)  $1 + x, y, z$ ; (ii)  $x - 1/2, 1/2 - y, z - 1/2$ .

N(1)...O contact distances longer than 2.84 Å are observed for the other ammonium ion. This and the constellation of peaks found around N(1) seem to imply that this group is also rotationally disordered.

## 2. Infrared and Raman spectra

The IR-spectrum shows great similarities with those previously obtained for some other salts of the same complex anion.<sup>7</sup> It is additionally complicated by the presence of the typical  $\text{NH}_4^+$  vibrations. The Raman spectrum gave some additional information about the vibrational behavior.

The analysis of the  $\text{NH}_4^+$ -vibrations appears specially interesting to attain complementary information about the behavior of these ions in the crystal lattice. According to Waddington,<sup>16</sup> if the free rotation of the  $\text{NH}_4^+$  ion is hindered in a crystal lattice, then a number of spectroscopic peculiarities may be observed. If the  $\text{NH}_4^+$  ion is involved in hydrogen bonding, one may expect a shift of the IR-active antisymmetric stretching mode,  $\nu_3$ , to lower frequencies in comparison with the value usually found for the "free" ion. In this case, a combination mode ( $\nu_2 + \nu_4$ ) as well as the first overtone of the anti-symmetric bending vibration of this ion ( $2\nu_4$ ) attains sufficient intensity, probably by Fermi resonance with one of the energy-lowered  $\nu_3$ -components. On the other hand, an additional weak band, originated in the interaction of  $\nu_4$  with one torsional oscillation of the  $\text{NH}_4^+$  ion ( $\nu_4 + \nu_6$ ), can also often be observed.

In the present case such peculiarities could be clearly observed, therefore confirming the hindered rotation of at least one of the ammonium ions as suggested by the structural analysis. The combination mode is seen as a weak shoulder at  $3011 \text{ cm}^{-1}$  on the low energy side of a strong IR band centered at  $3160$

$\text{cm}^{-1}$ ; the  $2\nu_4$  overtone also appears as a shoulder on this strong band at  $2865 \text{ cm}^{-1}$ , whereas ( $\nu_4 + \nu_6$ ) is observed as a weak band at  $1949 \text{ cm}^{-1}$ . The expected splittings of  $\nu_3$  and  $\nu_4$ <sup>16</sup> are not evident in our IR spectra due to the fact that these modes become overlapped with other vibrational modes. The  $\nu_3$  region is strongly broadened by the presence of the O-H stretchings of the water molecules; the  $\nu_4$  mode, which is located at  $1407 \text{ cm}^{-1}$ , is overlapped by the  $\nu_s(\text{COO}^-)$  and  $\delta(\text{CH}_2)$  modes of the malonate groups. The  $\nu_6$ -torsional mode appears as a very weak IR band at *ca.*  $505 \text{ cm}^{-1}$ .

Other typical and characteristic IR bands are found at  $1596 \text{ cm}^{-1}$  (very strong and broad), assignable to  $\nu_{\text{as}}(\text{COO}^-) + \delta(\text{H}_2\text{O})$ ;  $1157 \text{ cm}^{-1}$  (medium) and  $935 \text{ cm}^{-1}$  (strong), both assignable to  $\nu(\text{C}-\text{C})$  stretchings and  $743 \text{ cm}^{-1}$  (strong), assignable to  $\delta(\text{OCO})$ . In the Raman spectrum the  $\nu_{\text{as}}$  and  $\nu_s$  modes of the carboxylate groups are found at  $1622$  and  $1414 \text{ cm}^{-1}$ , respectively, both as medium-intensity bands.

The characteristic  $\nu(\text{V}-\text{O})$  stretching is found at  $980 \text{ cm}^{-1}$  in the IR spectrum and at  $978 \text{ cm}^{-1}$  in the Raman spectrum as a very strong and well defined band in both cases. On the other hand, an IR band multiplet of medium intensity, with components at  $470$ ,  $462(\text{sh})$  and  $444 \text{ cm}^{-1}$  ( $468$  and  $436 \text{ cm}^{-1}$  in the Raman spectrum) can be assigned to the V-O-stretching vibrations (cf. also Ref. 9). We could also identify a weak IR band located at  $818 \text{ cm}^{-1}$  ( $817 \text{ cm}^{-1}$  in the Raman spectrum) assignable to a rocking mode of the coordinated water.

Finally, it is worth mentioning that our IR-spectrum resembles that corresponding to a previously reported tetrahydrate of the same salt.<sup>17</sup> In this case, the  $\nu(\text{V}-\text{O})$  stretching was found at  $990 \text{ cm}^{-1}$  and the rocking mode of the coordinated water at  $850 \text{ cm}^{-1}$  whereas no information, neither on the  $\nu(\text{V}-\text{O})$  mode nor on the peculiarities of the  $\text{NH}_4^+$  vibrations were given.

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**Supplementary material.** Crystallographic data (excluding structure factors) for the structure reported in this paper have been

deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5196. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: teched@chemcrs.cam.ac.uk).

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