Synthesis and Crystal Structure of the Novel Three-dimensional Vanadium Coordination Compound Potassium Oxo-bis(hydroxylamido)malonatovanadate(V)

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In the crystal structure of the title complex, $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2] \cdot 3H_2O$, the V(V) centre is bound to a chelating malonate ligand, two bidentate hydroxylamido ligands and one oxo ligand, defining a pentagonal bipyramidal coordination (VO_5N_2). The potassium cations are found to adopt two types of coordination geometry with the malonate ligand, the bidentate hydroxylamido ligand and water molecules: the first one is hepta-coordinate in an irregular $K(1)O_7$ polyhedron, and the second one is octa-coordinate in an irregular $K(2)O_8$ polyhedron. The $K(1)O_7$/$K(2)O_8$ and VO_5N_2 polyhedra are closely linked by sharing faces to form K-V dinuclear units KVO_9N_2 and $KVO_{10}N_2$, respectively. The two close-packed units, KVO_9N_2 and $KVO_{10}N_2$, are connected by sharing edges to generate a tetrameric unit $K_2V_2O_{17}N_4$. Each of these units is joined to four neighbouring units by sharing corners, providing further propagation into a two-dimensional layer. Adjacent layers are connected *via* the carboxylic oxygen atoms of the malonate units to give a three-dimensional framework in the crystals.

Key words: Vanadium Compounds, Hydroxylamine, Insulin Mimics, Malonic Acid

Introduction

Vanadium compounds as insulin mimics have been studied for more than 20 years [1, 2]. A great numbers of organic vanadium compounds were synthesised, including oxovanadium, peroxovanadium [3] and vanadium hydroxylamido compounds [4, 5] in order to seek for promising candidates for the study of insulin-mimetic activity. It has been reported that bis(*N*,*N*-dimethylhydroxylamido)oxovanadate, $[VO(ONMe_2)_2]_2O$ (DMHV), inhibits protein tyrosine phosphatase (PTPase), a group of regulatory enzymes which have significant potential as targets for therapeutic intervention in diabetes [6]. Hence, PTPase inhibitors on the basis of the hydroxylamine motif may lead to effective vanadate-based complexes that have potential as insulin mimics. Several vanadium hydroxylamido complexes such as $[VO(NH_2O)_2L]$ H_2O (L = glycine, serine and glycylglycine), $[VO(NH_2O)_2(\text{imidazole})]Cl$ [4], and $[VO(NH_2O)(\text{dipic})(H_2O)]$ [7] have been synthesised. However, due to the complexity of the vanadium coordination mode, the possible correlation between the biological activity and the coordination structure of the vanadium compounds is still very elusive. Additionally, the coordination chemistry of vanadium hydroxylamine complexes has been rather less studied. These facts prompted us to choose structurally similar molecules that could engage simultaneously in multiple coordination modes, and to use such molecules for the assembly of novel complexes. In this paper, we selected malonic acid as the ancillary ligand to synthesise the vanadium hydroxylamido complex, $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2] \cdot 3H_2O$, and determined the crystal structure of this compound. It may be a promising insulin-mimetic species because experimental results have testified that complexes containing ON multifunctional ligation are superior in insulin-mimetic efficacy to the coordination complexes containing OO, OS and NS donor atom sets, irrespective of the vanadium oxidation state [8], and malonate is an important biomolecule in the metabolism of multi-cellular organisms [9].

Results and Discussion

Structure description

The crystal structure of $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2] \cdot 3H_2O$ may be thought of as made

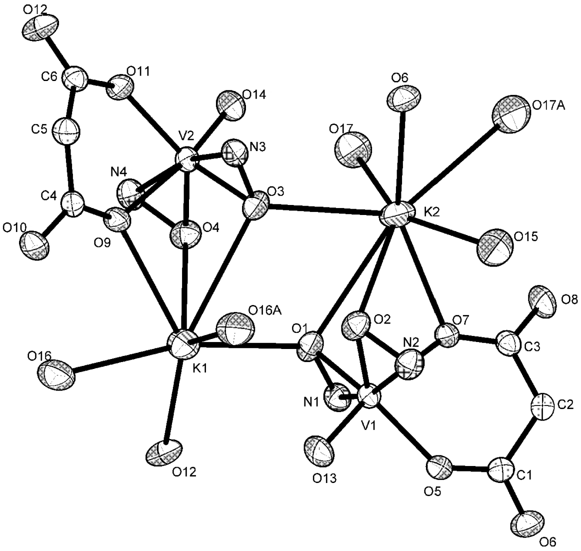

Fig. 1. The coordination environment of the V and K atoms in the tetranuclear K_2V_2 units of $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2]\cdot 3H_2O$.

up of K(I) and V(V) cations, malonate anions, hydroxylamido ligands and water molecules. The two independent vanadium(V) centres are seven-coordinated in a pentagonal bipyramidal geometry (denoted as VO_5N_2) containing two bidentate hydroxylamido ligands, one oxo ligand, and two oxygen atoms of the malonate ligand. The hydroxylamido ligand coordinates in a side-on manner as observed in related structures [4, 7]. The malonate behaves as a chelating ligand to the vanadium atoms. The centroids of the two hydroxylamido ligands and the O(5) (or O(11)) oxygen of the malonate unit define the equatorial plane perpendicular to the V=O bond. The other chelating oxygen O(7) (or O(9)) is in the axial position *trans* to the oxo ligand (see Fig. 1). In the pentagonal bipyramid $V(1)O_5N_2$, the axial angle O(7)–V(1)–O(13) is 169.98°, and the terminal V(1)=O(13) distance is 1.5953(15) Å, leading to the expected *trans* lengthening of the V(1)–O(7) bond (2.1533(14) Å). This distorted coordination environment of the V atom may be due to the steric effect of the chelating malonate group. The seven atoms surrounding V(2) build a distorted pentagonal bipyramid ($V(2)O_5N_2$) similar to that of $V(1)O_5N_2$ (Fig. 1). The O–N, V–O and V–N distances and O–V–N angles related with the hydroxylamine ligands in $V(1)O_5N_2$ and $V(2)O_5N_2$ are similar to those reported in the literature [10].

The two crystallographically independent potassium cations exhibit two kinds of coordination environment.

Table 1. Details of data collection and structure refinement for $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2]\cdot 3H_2O$.

Formula	$C_6H_{18}K_2N_4O_{17}V_2$
Formula weight	598.32
Crystal size, mm^3	$0.33 \times 0.22 \times 0.10$
Crystal system	monoclinic
Space group	Pc
a, Å	9.1118(19)
b, Å	15.513(3)
c, Å	7.3169(15)
β, deg	95.215(2)
V, $Å^3$	1030.04(4)
Z	2
D_{calcd}, $g\,cm^{-3}$	1.92
$\mu(MoK_\alpha)$, mm^{-1}	0.7
$F(000)$, e	600
hkl range	$-10 \le h \le 11$; $-13 \le k \le 19$; $-9 \le l \le 9$
θ range, deg	1.31 – 26.98
Refl. measured / unique / R_{int}	6325 / 4139 / 0.015
Data / restraints / ref. param.	4139 / 3 / 288
$R(F)/wR(F^2)^a$ (all refl.)	0.0226 / 0.0594
x(Flack)	0.181(12)
GoF $(F^2)^a$	1.032
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	0.35 / −0.48

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Table 2. Selected bond lengths (Å) and angles (deg) for $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2]\cdot 3H_2O$ with estimated standard deviations in parentheses[a].

V1–N1	2.0164(17)	$K1^{ii}$–O16	2.8060(2)
V1–N2	2.0223(19)	K1–O16	2.7230(2)
V1–O1	1.9029(15)	K1–$O16^{iii}$	2.8060(2)
V1–O2	1.9046(17)	K2–O1	3.2410(18)
V1–O5	2.0362(15)	K2–O2	2.9005(17)
V1–O7	2.1533(14)	$K2^{i}$–O3	2.9218(16)
V1–O13	1.5953(15)	$K2^{i}$–O6	2.8262(19)
V2–N3	2.0080(18)	K2–O7	2.6483(15)
V2–N4	2.0065(19)	$K2^{iv}$–O17	3.0240(2)
V2–O3	1.9015(15)	K2–$O3^{v}$	2.9218(16)
V2–O4	1.9015(17)	K2–$O6^{v}$	2.8262(19)
V2–O9	2.1724(14)	K2–O15	2.8990(2)
V2–O11	2.0194(15)	K2–O17	2.7310(2)
V2–O14	1.6080(15)	O1–N1	1.3980(2)
K1–O1	2.8444(15)	O2–N2	1.4030(2)
$K1^{i}$–O3	3.1258(17)	O3–N3	1.3950(2)
$K1^{i}$–O4	2.9360(17)	O4–N4	1.3910(2)
N1–V1–N2	161.61(8)	O1–V1–O2	85.96(7)
O2–V1–N2	41.72(7)	O13–V1–O1	100.39(7)
O1–V1–N1	41.67(7)	O1–V1–O5	133.19(7)
O13–V1–N1	97.36(8)	O13–V1–O2	101.07(8)
O1–V1–N2	126.72(8)	O2–V1–N1	126.91(7)
O13–V1–N2	99.38(8)	O13–V1–O5	90.18(7)

[a] Symmetry codes: [i] $x+1, y, z$; [ii] $x, -y+2, z-1/2$; [iii] $x, -y+2, z+1/2$; [iv] $x, -y+1, z-1/2$; [v] $x-1, y, z$.

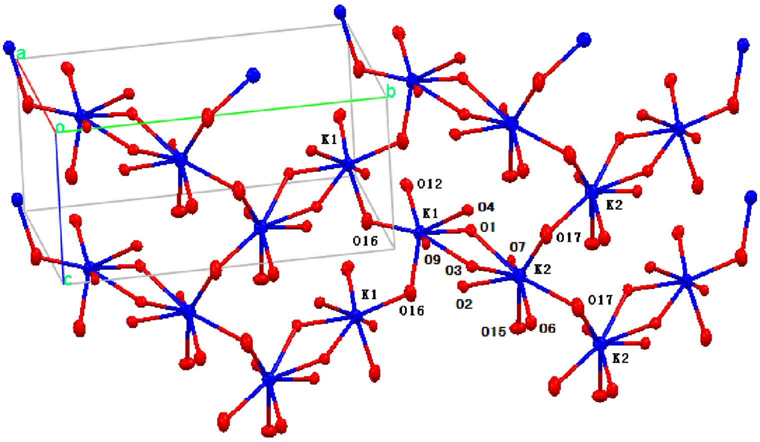

Fig. 2. The two-dimensional layer structure comprising the K–O polyhedra parallel to the crystallographic *bc* plane.

Table 3. Hydrogen bond geometry (Å, deg)[a].

D–H···A	D–H	H···A	D···A	D–H···A
N1–H1B···O8^{iv}	0.90	1.99	2.826(2)	154
N1–H1A···O11	0.90	2.11	2.999(2)	170
N2–H2B···O11^{vi}	0.90	2.54	3.193(2)	130
N2–H2B···O12^{vi}	0.90	2.05	2.933(2)	168
N2–H2A···O15	0.90	2.15	2.883(3)	138
N3–H3A···O5	0.90	1.94	2.823(2)	169
N3–H3B···O10^{iii}	0.90	2.05	2.866(2)	150
N4–H4B···O5^{vii}	0.90	2.49	3.223(2)	139
N4–H4B···O6^{vii}	0.90	2.15	3.002(2)	157
N4–H4A···O10^{ii}	0.90	2.12	2.989(2)	161
O15–H15B···O4^{viii}	0.85(2)	2.37(3)	3.016(3)	133(3)
O15–H15A···O8^{ix}	0.85(2)	1.93(2)	2.771(3)	171(4)
O16–H16A···O2^{ii}	0.846(10)	2.001(10)	2.844(2)	174(3)
O16–H16B···O10^{v}	0.841(10)	1.965(14)	2.787(3)	165(4)
O17–H17A···O6^{x}	0.80(2)	2.01(3)	2.769(3)	156(4)
O17–H17B···O14^{v}	0.80(2)	2.23(3)	2.867(3)	137(4)

[a] Symmetry codes: ^{ii} $x, -y+2, z-1/2$; ^{iii} $x, -y+2, z+1/2$; ^{iv} $x, -y+1, z-1/2$; ^{v} $x-1, y, z$; ^{vi} $x, y, z+1$; ^{vii} $x, y, z-1$; ^{viii} $x-1, y, z+1$; ^{ix} $x, -y+1, z+1/2$; ^{x} $x-1, -y+1, z-1/2$.

One is seven-coordinated in an irregularly polyhedral environment (denoted K(1)O_7) consisting of two water O atoms (O(16), O(16A)), three hydroxylamine O atoms (O(3), O(4), O(1)) and two malonate O atoms (O(9), O(12)) from two different malonate anions. The average O–K distance is 2.859 Å. The K(1)O_7 and V(2)O_5N_2 units are interconnected by sharing faces comprising O(3), O(4) and O(9) to form a K-V dinuclear complex KVO_9N_2 which is, because of the face sharing, referred to as a close-packed unit (Fig. 1). K(2) is octa-coordinated by oxygen atoms in an irregularly polyhedral arrangement (denoted as K(2)O_8) with an average O–K distance of 2.933 Å. Three of these oxygen atoms are hydroxylamine O atoms (O(1), O(2),O(3)), three water O atoms (O(15), O(17), O(17A)), and two malonate O atoms (O(6), O(7)) from two different malonate anions. The K(2)O_8 and V(1)O_5N_2 polyhedra are connected by sharing faces comprising O(1), O(2) and O(7) to form another close-packed unit $KVO_{10}N_2$ (Fig. 1). The KVO_9N_2 and $KVO_{10}N_2$ units are connected by sharing edges comprising O(3) and O(1) to construct a K-V tetranuclear unit $K_2V_2O_{17}N_4$ which is referred to as a close-packed unit because of the edge sharing (Fig. 1). Each close-packed unit is linked to four neighbouring close-packed units by sharing corners (O(16), O(16A), O(17), O(17A)) to lead to the formation of extended two-dimensional layers parallel to the crystallographic *bc* plane (Fig. 2). The adjacent layers are linked by atoms O(6) and O(12) of the malonate ligands to complete the construction of a three-dimensional framework. In this way, the hydroxylamine O atoms are grouped into two types according to the coordination mode. One kind acts as a bridge between the K and V ions in the close-packed unit. The second kind bridges three metal atoms (K(1), K(2) and V atoms) in the close-packed unit (Fig. 1). The malonate anion acts as a tridentate ligand coordinated to two K and one V cations. One O atom (O(8) or (10), unshared) of the malonate anion acts as an acceptor in a hydrogen bond (see Table 3) and is not coordinated to a metal ion. This phenomenon is not found in the vanadium malonate complexes reported as yet [10–15]. The different coordination modes give rise to a diversity of the C–O lengths of the malonate ligand in the title compound. For example, the C–O distance to the unshared O atom of the malonate acting as ligand in the close-packed unit KVO_9N_2 is 1.245(2) Å, while those of O atoms coordinated to V(V) and K ions are

Table 4. V–O, V=O and C–O bond lengths (Å) in vanadium(V) malonate complexes.

Malonate complexes	C–O (coordinated O)	C–O (uncoordinated O)	Ref.
$K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2]\cdot 3H_2O$	1.270(2)		This work
	1.242(3)		
	1.280(2)		
	1.236(3)		
	1.262(2)	1.233(2)	
	1.265(2)	1.245(2)	
$Na[VO(NH_2O)_2(C_3H_2O_4)]\cdot H_2O$	1.2612(16)		[10]
	1.2464(16)		
	1.2952(16)		
	1.2153(17)		
$[VO(acpy\text{-}smdt)(C_3H_2O_4)]$	1.264(3)	1.516(3)	[15]
	1.287(3)	1.513(4)	

1.280(2) and 1.236(3) Å, respectively. The O atom coordinated to V(V) and to K(I) is 1.265(2) Å (see Table 4). Hydrogen bonds, which are generated by the hydroxylamine and carboxylic groups, coordinated water molecules and the terminal oxygen atoms in $V(1)O_5N_2$ (or $V(2)O_5N_2$), connect the layers of close-packed structural units and apparently enhance the stability of the crystal.

IR spectrum and thermal analysis

The IR spectra of malonic acid and $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2]\cdot 3H_2O$ were recorded in the region from 4000 to 400 cm^{-1} (Fig. 3). The assignments of the absorption bands are based on literature data [11, 17]. The band at 3470 cm^{-1} (Fig. 3b) can be assigned to the asymmetric stretching vibration ν(O–H) of H_2O, the bands in the region 3205 – 3251 cm^{-1} to $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ of hydroxylamine. The bands in the range 2800 – 3000 cm^{-1} may be ascribed to ν(C–H) of the malonate ligands. The very strong band at 1586 cm^{-1} is attributed to ν_{as}(COO). The frequency of this band is obviously lower than that (at 1726 cm^{-1}, Fig. 3a) of malonic acid due to coordination. The very strong band with a maximum around 1403 cm^{-1} is attributed to ν_s(COO) [16]. The existence of the band multiplicity for ν_s(COO) could be explained through the diversity of the C–O lengths of the malonate ligand in the title compound. The V=O stretching vibration was observed at 975 cm^{-1}. The hydroxylamido N–O stretching vibration band was found very close to the stong $\nu_s(VO^{3+})$ stretch at 965 cm^{-1}, in agreement with those observed in other hydroxylamido/amino acid oxovanadium complexes [17].

To investigate the pyrolysis behaviour of $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2]\cdot 3H_2O$, a TG analysis was performed (Fig. 4). The water (9.2 %) was lost in the low-temperature region. The 22.0 wt-% weight loss from 195 – 205 °C agrees well with the decomposition of hydroxylamine, and the 30 wt-% weight loss between 250 and 500 °C is mainly due to the decomposition of the malonate ligands. When the sample was further heated above 600 °C, continued weight loss was observed because of the sublimation of a few vanadium oxides produced in the decomposition of the complex.

In summary, the potassium hydroxylamido-malonate-vanadate(V) complex, $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2]\cdot 3H_2O$, with a novel three-dimensional framework structure was synthesised, and its IR spectra and pyrolysis behaviour were investigated.

Experimental Section

General methods and materials

All chemicals were of reagent grade and used without further purification. The infrared spectrum was recorded from a KBr pellet on a Nicolet nexus 670 FI-IR spectrometer in the range 4000 to 400 cm^{-1}. TG analysis was performed on a Netzsch STA 409 PC/PG instrument in N_2 with a heating rate of 10 K min^{-1}.

Synthesis

NH_4VO_3 (1.36 mmol) and malonic acid (2.61 mmol) were dissolved in 10 mL of 1 M KOH at room temperature. The colourless solution was stirred for 0.5 h in an ice bath. $NH_2OH\cdot HCl$ (7.20 mmol) was added in batches to this solution under constant stirring for 0.5 – 1.0 h, and then 5 mL ethanol was added dropwise. The resulting mixture was filtered. Colourless crystals suitable for single crystal X-ray diffraction were obtained after the filtrate was held at 4 °C for 2 d.

Crystal structure determination

Crystallographic measurements were made using a Bruker Smart CCD diffractometer. The intensity data were collected using graphite-monochromatised MoK_α radiation

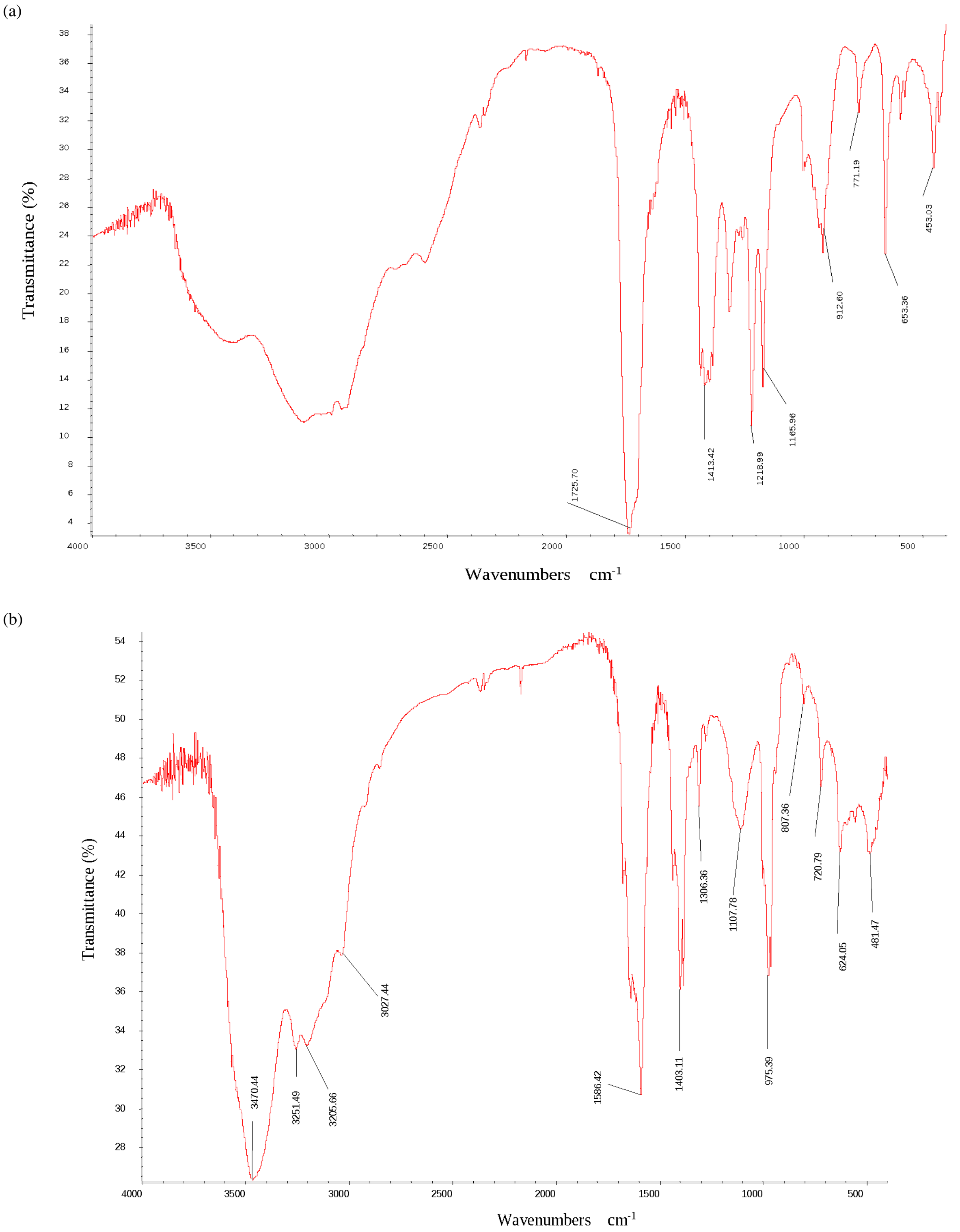

Fig. 3. The IR spectra of (a) malonic acid and (b) $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2] \cdot 3H_2O$.

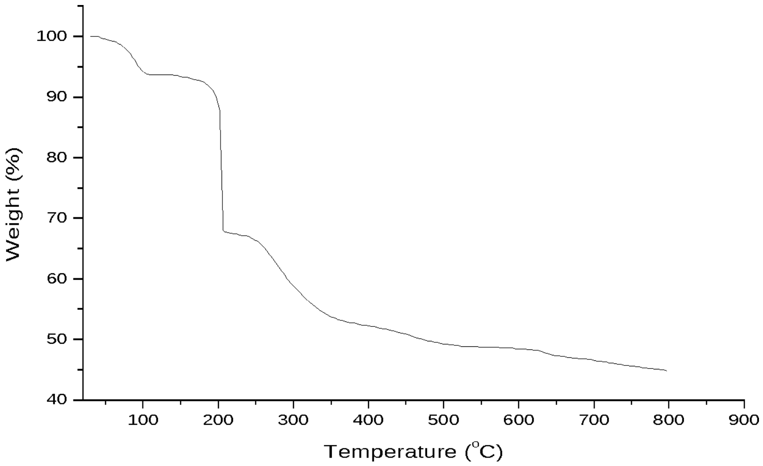

Fig. 4. The TG curve of $K_2[(VO)_2(NH_2O)_4(C_3H_2O_4)_2] \cdot 3H_2O$.

(λ = 0.71073 Å). Accurate unit cell parameters and the orientation matrix were obtained from least-squares refinement using the programs SMART and SAINT, and the data were integrated using SAINT [18]. The structure was solved by Direct Methods (SHELXS-97 [19]) and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 [19]. The H atoms bonded to O15, O16 and O17 were located in a difference map, and their positions were refined with geometric restraints of O–H = 0.85(3) Å and H–H = 1.38(1) Å for the water H atoms. Other H atoms were placed in calculated positions, with N–H = 0.90 Å for amino H atoms, C–H = 0.97 Å for methylene H and refined as riding, with 1.5 U_{eq} (C) for methylene H. Additional details of data collection and structure refinement are listed in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC 704956 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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