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, K2[(VO)2(NH2O)4(C3H2O4)2]·3H2O, the V(V) centre is bound to a chelating malonate ligand, two bidentate hydroxylamido ligands and one oxo ligand, defining a pentagonal bipyramidal coordination (VO5N2). 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)O7 polyhedron, and the second one is octa-coordinate in an irregular K(2)O8 polyhedron. The K(1)O7/K(2)O8 and VO5N2 polyhedra are closely linked by sharing faces to form V-K dinuclear units KVO9N2 and KVO10N2, respectively. The two close-packed units, KVO9N2 and KVO10N2, are connected by sharing edges to generate a tetrameric unit K2V2O17N4. 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-(ONMe2)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(NH2O)2L]2H2O (L = glycine, serine and glycyglycine), [VO(NH2O)2-imidazole]Cl [4], and [VO(NH2O)(dipic)(H2O)]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 hydroxylamido 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, K2[(VO)2(NH2O)4(C3H2O4)2]·3H2O, 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 K2[(VO)2(NH2O)4(C3H2O4)2]·3H2O may be thought of as made
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$_5$N$_2$) 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$_5$N$_2$, 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$_5$N$_2$) similar to that of V(1)O$_5$N$_2$ (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$_5$N$_2$ and V(2)O$_5$N$_2$ are similar to those reported in the literature [10].

The two crystallographically independent potassium cations exhibit two kinds of coordination environment.
One is seven-coordinated in an irregularly polyhedral environment (denoted K(1)O7) 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)O7 and V(2)O5N2 units are interconnected by sharing faces comprising O(3), O(4) and O(9) to form a K-V dinuclear complex KVO9N2 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)O8) 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)O8 and V(1)O5N2 polyhedra are connected by sharing edges comprising O(1), O(2) and O(7) to form another close-packed unit KVO10N2 (Fig. 1). The KVO9N2 and KVO10N2 units are connected by sharing edges comprising O(3) and O(1) to construct a K-V tetranuclear unit K2V2O17N4 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 KVO9N2 is 1.245(2) Å, while those of O atoms coordinated to V(V) and K ions are

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### Table 3. Hydrogen bond geometry (Å, deg)

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>D–H</th>
<th>H···A</th>
<th>D···A</th>
<th>D–H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–H1B···O8vii</td>
<td>0.90</td>
<td>1.99</td>
<td>2.826(2)</td>
<td>154</td>
</tr>
<tr>
<td>N1–H1A···O11</td>
<td>0.90</td>
<td>2.11</td>
<td>2.999(2)</td>
<td>170</td>
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<tr>
<td>N2–H2B···O11vii</td>
<td>0.90</td>
<td>2.54</td>
<td>3.193(2)</td>
<td>130</td>
</tr>
<tr>
<td>N2–H2B···O12vii</td>
<td>0.90</td>
<td>2.05</td>
<td>2.933(2)</td>
<td>168</td>
</tr>
<tr>
<td>N2–H2A···O15</td>
<td>0.90</td>
<td>2.15</td>
<td>2.883(2)</td>
<td>169</td>
</tr>
<tr>
<td>N3–H3A···O5</td>
<td>0.90</td>
<td>1.94</td>
<td>2.823(2)</td>
<td>169</td>
</tr>
<tr>
<td>N3–H3B···O10vi</td>
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<td>2.866(2)</td>
<td>150</td>
</tr>
<tr>
<td>N4–H4B···O5vi</td>
<td>0.90</td>
<td>2.49</td>
<td>3.223(2)</td>
<td>139</td>
</tr>
<tr>
<td>N4–H4B···O6vi</td>
<td>0.90</td>
<td>2.15</td>
<td>3.002(2)</td>
<td>157</td>
</tr>
<tr>
<td>N4–H4A···O10vi</td>
<td>0.90</td>
<td>2.12</td>
<td>2.989(2)</td>
<td>161</td>
</tr>
<tr>
<td>O15–H15B···O4viii</td>
<td>0.85(2)</td>
<td>2.37(3)</td>
<td>3.016(3)</td>
<td>133(3)</td>
</tr>
<tr>
<td>O15–H15A···O8vii</td>
<td>0.85(2)</td>
<td>1.93(2)</td>
<td>2.771(3)</td>
<td>171(4)</td>
</tr>
<tr>
<td>O16–H16A···O2vi</td>
<td>0.846(10)</td>
<td>2.001(10)</td>
<td>2.844(2)</td>
<td>174(3)</td>
</tr>
<tr>
<td>O16–H16B···O10v</td>
<td>0.841(10)</td>
<td>1.965(14)</td>
<td>2.787(3)</td>
<td>165(4)</td>
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<tr>
<td>O17–H17A···O6vii</td>
<td>0.80(2)</td>
<td>2.01(3)</td>
<td>2.769(3)</td>
<td>156(4)</td>
</tr>
<tr>
<td>O17–H17B···O14vii</td>
<td>0.80(2)</td>
<td>2.23(3)</td>
<td>2.867(3)</td>
<td>137(4)</td>
</tr>
</tbody>
</table>

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*a* Symmetry codes: 

- vix, −y + 2, z − 1/2; 
- vii, x − y + 2, z + 1/2; 
- viii, x, −y + 1, z + 1/2; 
- iix, x − y + 1, y, z; 
- iix, x, y, z + 1; 
- viii, x − y + 1, z + 1/2; 
- x, −y + 1, z − 1/2; 
- x, −y + 1, z − 1/2;
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)O5N2 (or V(2)O5N2), 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 K2[(VO)2(NH2O)4(C3H2O4)2]·3H2O 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 H2O, the bands in the region 3205–3251 cm⁻¹ to νas(NH2) and νs(NH2) 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 νs(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 νs(COO) [16]. The existence of the band multiplicity for νs(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 strong V=O(VO3⁺) stretch at 965 cm⁻¹, in agreement with those observed in other hydroxylamido/amino acid oxovanadium complexes [17].

To investigate the pyrolysis behaviour of K2[(VO)2(NH2O)4(C3H2O4)2]·3H2O, 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, K2[(VO)2(NH2O)4(C3H2O4)2]·3H2O, 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 FT-IR spectrometer in the range 4000 to 400 cm⁻¹. TG analysis was performed on a Netzsch STA 409 PC/PG instrument in N2 with a heating rate of 10 K min⁻¹.

**Synthesis**

NH4VO3 (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. NH2OH·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 MoKα radiation.
Fig. 3. The IR spectra of (a) malonic acid and (b) K$_2$[(VO)$_2$(NH$_2$O)$_4$(C$_3$H$_2$O$_4$)$_2$] · 3H$_2$O.
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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