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# In an attempt to add ligands to the sixth (axial) position of vanadyl bis-acetylacetonate: A unique tetranuclear vanadyl species


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## RESEARCH ARTICLE

## ABSTRACT


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We have explored the interaction of  $[(\text{acac})_2\text{V}=\text{O}]$  (acac = acetylacetonate) with a series of potential ligands which were chosen because of their expected ability to attach themselves onto its sixth (axial) position. Furthermore, some of the species chosen were expected to have the capability of linking pairs of  $[(\text{acac})_2\text{V}=\text{O}]$  molecules, thus creating magnetically coupled substances whose behavior would be interesting to document by magnetic as well as structural methods. Some of the synthetic results were surprising in that unexpected products were obtained which we had not envisioned; specifically, herein we describe a tetranuclear vanadyl cluster (Crystal data for  $\text{C}_{38}\text{H}_{51}\text{N}_4\text{O}_{17}\text{ClV}_4$ : orthorhombic, space group  $Pca2_1$  (no. 29),  $a = 26.4698(3)$  Å,  $b = 13.5167(2)$  Å,  $c = 12.7659(2)$  Å,  $V = 4567.44(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{CuK}\alpha) = 7.842$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.53$  g/cm<sup>3</sup>, 41277 reflections measured ( $6.538^\circ \leq 2\theta \leq 137.892^\circ$ ), 7841 unique ( $R_{\text{int}} = 0.0428$ ,  $R_{\text{sigma}} = 0.0421$ ) which were used in all calculations; the final  $R_1$  was 0.0675 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1641 (all data)), which is unusual in several aspects of its composition as well as its stereochemistry.

## KEYWORDS

 Axial adducts  
 Bridging vanadyls  
 1,3-Diazine ligands  
 Vanadyl acetylacetonate  
 Tetra-nuclear vanadyl compounds  
 5- and 6-Coordinated vanadyl species

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## 1. Introduction

In the past [1-3], we have described studies of  $[(\text{acac})_2\text{V}=\text{O}]$  acting as a substrate for donor ligands capable of attacking the vanadium moiety via the sixth position. In [1], we documented the magnetic and spectroscopic consequences of such interactions for both solids and solutions and suggested that those results could be used as quantitative gauges of the electron-donor acceptor characteristics of such systems. Moreover, it is clear that the subject could be vast since (a) the acac ligands could be modified in an orderly fashion while retaining the potential donor skeleton constant; (b) the ligands could be retained while changing the potential donor; and (c) the solvent can play a role (being able to compete with the potential donor), as in the case of, e.g., pyridine. In the process of carrying out a series of such studies, we discovered tiny black crystals, which are the subject of this report.

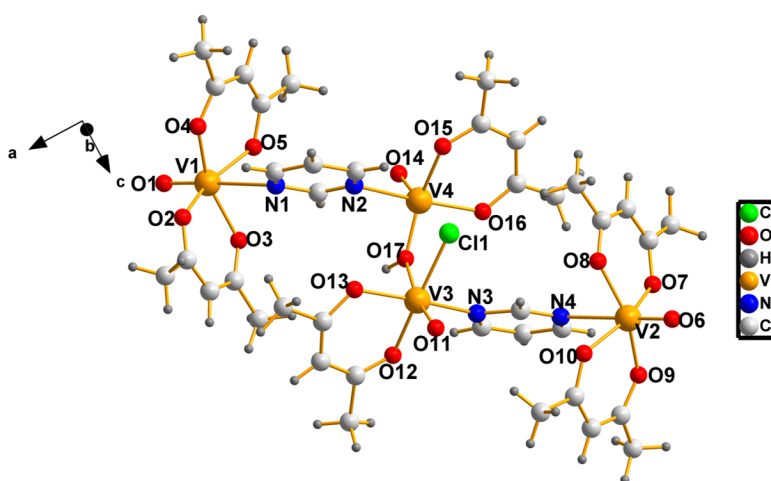
## 2. Experimental

### 2.1. Preparation of bis-acetylacetonato-chlorido-hydroxydo-tetranuclear vanadyl(IV) complex (I)

0.500 g (1.89 mmoles) of vanadyl(acac)<sub>2</sub> (C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>V) and 0.600 g (7.5 mmoles) of pyrimidine (1,3-diazine) (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>) (3.97:1 mole ratio of the 1,3-diazine ligand to vanadyl) and 0.5 mL of 12 M HCl were added to 45 mL of toluene in a sealed glass pressure cell and heated at 130 °C in a silicone oil bath for 1.5 hours with stirring. The mixture was allowed to cool slowly, filtered through a sintered glass funnel, and the filtrate was transferred to three 20 mL vials, whose openings were sealed with parafilm through which was poked a number of small holes. The solutions were allowed to evaporate slowly. After 3-4 days, a small number of black crystals of a vanadyl complex was formed containing four vanadiums, six acac ligands, two 1,3-diazine molecules bridging, a chloride anion and a hydroxide counter anion (which is bridging two of the vanadyls), having composition C<sub>38</sub>H<sub>51</sub>ClN<sub>4</sub>O<sub>17</sub>V<sub>4</sub>, which showed totally unexpected compositional and structural features, as described in what follows. Interestingly, in preparation, the addition of 12 M HCl led to the removal of one acac ligand per vanadyl(acac)<sub>2</sub>(1,3-diazine) fragment and replaced these with one chloride and one OH<sup>-</sup> ion, to take care of the charge compensation; the OH<sup>-</sup> counter anion bridges the two central vanadyl moieties.

**Table 1.** Crystal data and structure refinement for compound **I**.

Empirical formula	C <sub>38</sub> H <sub>51</sub> N <sub>4</sub> O <sub>17</sub> ClV <sub>4</sub>
Formula weight (g/mol)	1075.03
Temperature (K)	100(2)
Crystal system	Orthorhombic
Space group	<i>Pca</i> 2 <sub>1</sub>
<i>a</i> , (Å)	26.4698(3)
<i>b</i> , (Å)	13.5167(2)
<i>c</i> , (Å)	12.7659(2)
Volume (Å <sup>3</sup> )	4567.44(11)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.53
$\mu$ (mm <sup>-1</sup> )	7.842
<i>F</i> (000)	2208.0
Crystal size (mm <sup>3</sup> )	0.21 × 0.144 × 0.127
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54178)
2 $\theta$ range for data collection (°)	6.538 to 137.892
Index ranges	-30 ≤ <i>h</i> ≤ 31, -15 ≤ <i>k</i> ≤ 14, -14 ≤ <i>l</i> ≤ 15
Reflections collected	41277
Independent reflections	7841 [ <i>R</i> <sub>int</sub> = 0.0428, <i>R</i> <sub>sigma</sub> = 0.0421]
Data/restraints/parameters	7841/13/590
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.062
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0675, <i>wR</i> <sub>2</sub> = 0.1512
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0854, <i>wR</i> <sub>2</sub> = 0.1641
Largest diff. peak/hole (e.Å <sup>-3</sup> )	3.23/-1.28
Flack parameter	0.51(2)
CCDC no.	2201346
Programs	SAINT, APEX, SADABS [4-6], SHELXL [8], DIAMOND [11].



**Figure 1.** The tetra-nuclear species incorporates two vanadyls, each with 2 acac ligands, and has a 1,3-diazine in the sixth position. The two central vanadyl moieties, which have only one acac ligand each, are joined to the 'outer' vanadyl fragments via 1,3-diazine linkers. Finally, V3 is bonded exclusively by a Cl<sup>-</sup> counter anion, while V3 and V4 are bridged by the unique OH<sup>-</sup> (O17).

Furthermore, a) no oxidation-reduction reaction was found, and b) HCl merely causes displacement of the acac ligands from the possible dimer, and the resulting fragments are linked to form the tetramer.

## 2.2. X-ray diffraction data collection and processing

A suitable crystal was mounted on a Bruker-AXS SMART APEXII CCD diffractometer at 100(1) K. Cell dimensions and intensities were collected with CuK $\alpha$  radiation ( $\lambda$  = 1.54178 Å). Data processing, Lorentz polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX and SADABS computer programs [4-6]. The structure was solved by direct methods and refined by full-matrix least squares on *F*<sup>2</sup>, using the SHELXTL V6.14 program package [7-9]. Non-H atoms were refined anisotropically. All H atoms were found on electron density difference maps; the methyl H atoms were placed in ideal staggered positions with C-H distances of 0.98 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C); the methine Hs were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C-H distances of 0.95 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The crystal data, intensity data collection, and

structure refinement details are summarized in Table 1. The X-ray data for **I** have been deposited in CCDC #2201346 [10].

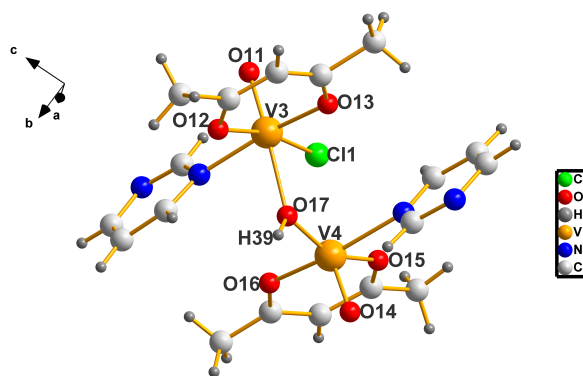
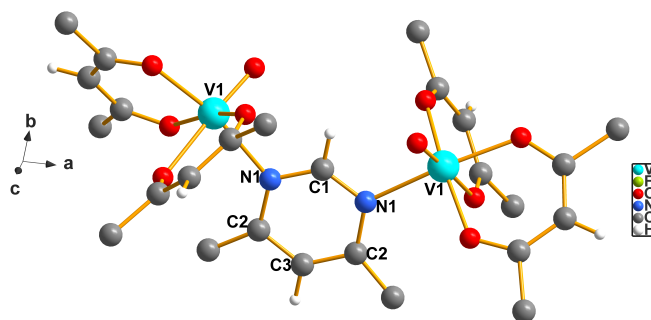
## 3. Results and discussion

The molecule consists of two terminal fragments [(acac)<sub>2</sub>-V=O] whose sixth position (per vanadyl moiety) is filled with 1,3-diazine, as shown below in Figure 1. These two fragments are joined by an asymmetric species consisting of a dinuclear vanadyl cation moiety bridged by a hydroxide (O17) (for more details, see Figure 2); however, the two aforementioned fragments differ in that only V3 has a dangling Cl<sup>-</sup> counter anion. Figure 2 shows the central vanadyl cations with the bridging hydroxide and the single terminal chloride anion.

The distances in structure (*I*) are the following: V3-Cl1 = 2.284(4) Å, V3-O17 = 2.141(8) and V4-O17 = 1.731(8) Å. The distance of V-OH can be compared with 1.968 and 1.959 Å found in the literature [12]. The V-Cl distance from the literature ranges from 2.275 to 2.3031 Å [13]; the V-Cl distance in a bridging Cl (between two vanadyls) is 2.470-2.490 Å [14]. The selected bond distances and angles are given in Table 2.

**Table 2.** Selected bond distances (Å) and angles (°) for compound I.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)		
V3	Cl1	2.284(4)	V2	O9	2.010(9)		
V3	O17	2.141(8)	V2	O10	1.972(8)		
V4	O17	1.731(8)	V2	N4	2.452(12)		
V1	O1	1.602(10)	V3	O11	1.665(10)		
V1	O2	1.990(9)	V3	O12	2.044(10)		
V1	O3	2.012(10)	V3	O13	1.956(9)		
V1	O4	1.985(9)	V3	N3	2.077(11)		
V1	O5	2.027(9)	V4	O14	1.602(12)		
V1	N1	2.477(11)	V4	O15	1.981(10)		
V2	O6	1.592(9)	V4	O16	1.967(9)		
V2	O7	1.994(9)	V4	N2	2.225(11)		
V2	O8	1.977(11)					
Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O1	V1	O2	101.0(4)	O10	V2	O9	89.0(3)
O1	V1	O3	98.5(4)	O10	V2	N4	79.6(4)
O1	V1	O4	103.5(5)	O17	V3	Cl1	82.1(2)
O1	V1	O5	100.7(5)	O11	V3	Cl1	90.2(4)
O1	V1	N1	177.5(5)	O11	V3	O17	169.8(4)
O2	V1	O3	90.2(4)	O11	V3	O12	99.2(5)
O2	V1	O5	158.3(4)	O11	V3	O13	96.8(4)
O2	V1	N1	78.8(4)	O11	V3	N3	93.7(4)
O3	V1	O5	86.8(4)	O12	V3	Cl1	168.3(4)
O3	V1	N1	79.0(4)	O12	V3	O17	87.6(4)
O4	V1	O2	86.0(4)	O12	V3	N3	82.8(4)
O4	V1	O3	157.9(4)	O13	V3	Cl1	97.9(3)
O4	V1	O5	88.8(4)	O13	V3	O17	91.0(4)
O4	V1	N1	79.0(4)	O13	V3	O12	88.0(4)
O5	V1	N1	79.5(4)	O13	V3	N3	167.0(4)
O6	V2	O7	100.9(4)	N3	V3	Cl1	89.7(3)
O6	V2	O8	100.2(5)	N3	V3	O17	79.5(4)
O6	V2	O9	101.4(5)	O17	V4	O15	148.2(4)
O6	V2	O10	100.9(4)	O17	V4	O16	93.3(4)
O6	V2	N4	179.4(5)	O17	V4	N2	89.9(4)
O7	V2	O9	84.5(4)	O14	V4	O17	112.8(5)
O7	V2	N4	78.5(4)	O14	V4	O15	98.3(6)
O8	V2	O7	90.3(4)	O14	V4	O16	100.9(5)
O8	V2	O9	158.4(4)	O14	V4	N2	89.1(5)
O8	V2	N4	80.0(4)	O15	V4	N2	83.6(4)
O9	V2	N4	78.5(4)	O16	V4	O15	87.3(4)
O10	V2	O7	158.0(4)	O16	V4	N2	167.4(4)
O10	V2	O8	88.0(4)				

**Figure 2.** A view of the molecular species with labels for the geometrical factors which form part of the discussion that follows.**Figure 3.** ADAHUI [15] as drawn from the data in the CIF document in the CSD [10]. The 'bare' carbon atoms do not contain substituents because they are disordered CF<sub>3</sub> fragments. Despite the disorder, it is an excellent model for what we envision as the process described above.

Complex (I) may have been obtained as follows: 1,3-diazine attaches itself to the axial position of each of the two [(acac)<sub>2</sub>V=O] molecules (such attachments are illustrated elsewhere [1,3,15]), thereby forming a dimer in which the  $\mu_2$  bridge is the 1,3-diazine, a particularly effective model being that of ADAHUI [15], which, for the convenience of the readers, we have redrawn as Figure 3, below; (b) as for the bridging hydroxide, these are ubiquitous in CCDC [16-18], as examples.

#### 4. Conclusions

The process by which (I) is formed is obviously very complex, involving several displacement and formation steps; our above suggestion is likely to be simplistic, but it is a reasonable description of the process of its formation based on known synthetic and structural studies of vanadyl (see refs. [1] and [3], and references therein). Meanwhile, we are attempting to trap intermediates, such as those suggested above, in an effort to unravel the process of formation of this unique species. Currently we are hindered in making magnetic or any other measurements by the lack of enough material, which, as mentioned above, consisted of only a few, very obviously (black) different, well-defined crystals.

Recently, it has been pointed out [19], and references therein, that there are cases in which the selection of the space group is not straightforward because molecules containing flexible fragments pack better if they undergo relatively small torsional motions that lead to conformational disorder, for example, in [Co(en)<sub>3</sub>]<sub>3</sub>·H<sub>2</sub>O [19], which had previously [21] been assigned the space group *Pbca*, and most recently proven to be a case of kryptoracemic crystallization in which the en ligands' torsional angles required to be enantiomorphic pairs fail to do so. A detailed analysis of this problem is given in [20], where it was shown that lowering the space group from *Pbca* to one of its subgroups, *Pca2<sub>1</sub>*, still resulted in an unacceptable chemical model, while further lowering the symmetry to that of *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* completely cleared the problems encountered previously [20]. Here, we refrain from describing these problems in more detail because they are long and complex and require additional illustrative figures already available in [19], to which the interested readers are directed. When collecting the data set described here, we solved the structure in the *P1* space group and submitted the results to the PLATON program [21], resulting in a recommendation of *Pbca* as the correct space group, which we accepted. However, refinement in that space group resulted in another totally unacceptable model; therefore, we resorted to the previously successful procedure of changing the space group to *Pca2<sub>1</sub>*, (an acceptable subgroup of *Pbca*), producing the model described in Figure 1. The bottom line is that the newly proposed model must make chemical sense and will do so if the appropriate space group is chosen, which, in this case, is *Pca2<sub>1</sub>*.

With respect to the Flack parameter [0.51(2)], it is not surprising that PLATON [21] suggests that the space group is *Pbca*, which we have demonstrated above to be incorrect. The core of the cluster in Figure 2 (and the graphical abstract) suggests that if the bridge were symmetrical (for example, two chlorides or two hydroxides), the resulting fragment would approximately have an inversion center. Additionally, Figure 1, which shows the entire molecule, shares the same characteristics. Therefore, the X-ray scattering power of such an "asymmetric" unit would skew the statistical distribution of x-rays such that the overall lattice would resemble that of a higher symmetry space group, such as suggested by PLATON, which recommended the use of *Pbca*. We have observed this situation on two different occasions in our own work: the above-mentioned [Co(en)<sub>3</sub>]<sub>3</sub>·H<sub>2</sub>O [19], and in our article describing previous work with a Co(III) complex with L and D leucinato as ligands where the (L:D) ratios of the ligands were not (1:1) [22].

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#### Supporting information S

CCDC-2201346 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033. CCDC compound codes: AQAPEP [13]; DECYEQ [14]; ADAHUI [15]; EZEPAA [16]; HOFYAE [17]; PASFIY [18]; ENCOIH [20].

#### Disclosure statement DS

Conflict of interest: The authors have declared that there are no competing interests.  
Ethical approval: All ethical guidelines have been adhered to.

#### CRedit authorship contribution statement CR

Conceptualization: Roger Lalancette, Ivan Bernal; Methodology: Roger Lalancette, Ivan Bernal; Software: Roger Lalancette, Ivan Bernal; Validation: Roger Lalancette, Ivan Bernal; Formal Analysis: Roger Lalancette, Ivan Bernal; Investigation: Roger Lalancette, Ivan Bernal; Resources: Roger Lalancette, Ivan Bernal; Data Curation: Roger Lalancette, Ivan Bernal; Writing - Original Draft: Roger Lalancette, Ivan Bernal; Writing - Review and Editing: Roger Lalancette, Ivan Bernal; Visualization: Roger Lalancette, Ivan Bernal; Supervision: Roger Lalancette; Project Administration: Roger Lalancette, Ivan Bernal.

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