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Vanadyl(acetylacetonate)₂ mediated hydrolytic splitting of 1,3,5-triazine in a solution of toluene at 130 °C: The crystal structure of its axial formamide adduct

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RESEARCH ARTICLE

ABSTRACT



A toluene reaction of vanadyl bis(acetylacetonate) with 1,3,5-triazine produces a symmetrical three-fold hydrolytic cleavage of the triazine, and these three formamide moieties are found in the crystal structure. One of the resulting formamides attaches itself to the sixth (axial) position of the vanadyl complex, producing materials in which the remaining two formamides are trapped in the resulting lattice. Those crystals belong in space group *Pca*2₁, *Z* = 4 and the final *R*-factor = 0.030 for 3213 data collected at 100 K.

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1. Introduction

Spectroscopic studies such as UV-Vis, electron spin resonance (ESR), *etc.* [1] have shown that good electron donor molecules (bases) such as pyridines, ketones, *etc.*, can act as donors to vanadyl bis-acetyl acetonates, thereby perturbing its energy level sufficiently to serve as a useful measurement of the basicity of the donor molecules. Moreover, those studies also demonstrated that the phenomenon is solvent and temperature dependent in a measurable manner. Finally, since frequently the perturbing bases attach themselves permanently to the vanadyl moiety [1], they can be isolated in crystalline form and studied by X-ray diffraction.

Guided by such observations, we decided to determine whether potential multiple donors would link together more than one vanadyl molecule in samples such as [(V=O)AcAc]₂ Donor[(V=O)AcAc]₂, *etc.*, and found that, indeed, such a possibility already existed, as in (μ₂-pyrimidine)-bis(bis(1, 1, 1, 5, 5, 5-hexafluoropentane-2,4-dionato)-oxo-vanadium(IV)) ADAHOC [2] and in (μ₂-4-methylpyrimidine)-bis(bis(1, 1, 1, 5, 5, 5-hexafluoropentane-2,4-dionato)-oxo-vanadium(IV)) ADAHUI [2], both of which used pyrimidines as the linker. Therefore, we decided to use 1,3,5-triazine as the bridge to ascertain whether

such a linker could produce ternary vanadyl moieties. Unexpectedly, the procedure described below caused the symmetrical hydrolytic splitting of the triazine molecule, converting it into three formamide moieties, which, in turn, became (a) an axial ligand to the sixth position of the vanadyl moiety and (b) two cocrystallizing fragments in the isolated crystals, one of which was disordered over two positions.

2. Experimental

2.1. Materials

Vanadyl(AcAc)₂ and 1,3,5-triazine were purchased from Alfa-Aesar and were used without further purification.

2.2. Synthetic procedure and crystal growth

We followed the preparation of the vanadyl(acac)₂ complex given by Rowe and Jones [3], as follows: 0.500 g (1.89 mmoles) of vanadyl(AcAc)₂ and 0.308 g (3.8 mmoles) of 1,3,5-triazine (2:1 mole ratio of ligand to vanadyl) 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.

Table 1. Crystal data and details of the structure refinement for compound I.

Crystal data	
Chemical formula	C ₁₁ H ₁₇ NO ₆ V · 2(CH ₃ NO)
<i>M_r</i>	400.28
Crystal system, space group	Orthorhombic, <i>Pca</i> 2 ₁
Temperature(K)	100(2)
a, b, c (Å)	8.5017(2), 13.1292(3), 16.8795(4)
<i>V</i> (Å ³)	1884.10 (8)
<i>Z</i>	4
Radiation	Cu Kα
μ (mm ⁻¹)	4.805
Crystal size (mm)	0.13 × 0.18 × 0.45
Data Collection	
Diffractometer	Bruker APEX2 diffractometer
Absorption correction	numerical
<i>T</i> _{min} , <i>T</i> _{max}	0.317, 0.650
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	16435, 3213, 3197
<i>R</i> _{int}	0.030
(sin θ/λ) _{max} (Å ⁻¹)	0.605
Refinement	
<i>R</i> [<i>F</i> > 2σ(<i>F</i>)], <i>wR</i> (<i>F</i>), <i>S</i>	0.037, 0.088, 1.19
No. of reflections	3213
No. of parameters	241
No. of restraints	3
H-atom treatment	Treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.36, -0.37
Flack parameter	0.476(11)
CCDC number	1557705
Computer programs: DIAMOND [6], SAINT [7], SADABS [7], APEX [8], SHELXT [10], SHELXL [11].	

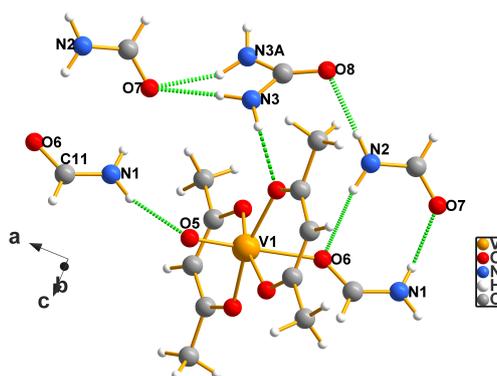


Figure 1. The formamide (N207) of crystallization (middle right) forms a strong cyclic dimer with the new axial formamide adduct (N106) to vanadium. In turn, its hydrogen bond to the disordered formamide (N308), ad infinitum, since (N106, middle left) begins a similar chain at left; this justifies the disorder of the N3 and N3A formamides, given that the hydrogen bonded propagation (up) by N3A hydrogens would otherwise disappear.

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 a few days, the complex containing one formamide bound to the sixth site of the vanadyl complex and two formamides of crystallization was formed [C₁₁H₁₇NO₆V · 2(CH₃NO)]. At this stage, we do not know the mechanism whereby the three formamides were generated; however, since neither VO(AcAc)₂ nor the toluene solvent contain nitrogen and the triazine was not protected from air and moisture, we speculate that water reacted with the 1,3,5-triazine at 130 °C and that was the source of the formamide molecule complexed to the vanadyl as well as those trapped as molecules of crystallization.

2.3. X-ray diffraction study, solution, and refinement of the data

Crystals were taken directly from their mother liquor and immediately mounted on a Bruker-AXS SMART APEXII CCD diffractometer in a stream of nitrogen cooled to 100(1) K. The cell dimensions and the intensities were collected with Cu-Kα radiation (λ = 1.54178 Å). Data processing, Lorentz polarization, and face-indexed numerical absorption corrections

were performed using SAINT, APEX, and SADABS computer programs [4-8]. After acquiring the 100 K datasets, the temperature of the crystal was slowly allowed to warm to room temperature, and the cell dimensions were the same as the 100 K cell, except for very slight elongations due to the higher temperatures. Crystal data and details of the structure refinement for the compound are given in Table 1.

The following programs were used in this document and assigned reference numbers: (a) Cambridge Crystallographic Database, CCDC [4], (b) Mercury [5], (c) Diamond [6], (d) X-ray data collection, processing and refinement programs [7-11]. For convenience of the reader, henceforth we will refer to our compound by a six-character acronym used by the CCDC [4], such as ABCDEF, which can be used for direct access to the information contained in that database.

3. Results and discussion

The contents of the asymmetric unit of the complex were not as predicted: a formamide molecule appeared as an axial ligand to the unchanged vanadyl reagent, and, whereas we had expected 1,3,5-triazine to bind 2 or even three vanadyl moieties together, we found instead that triazine had been hydrolytically cleaved symmetrically.

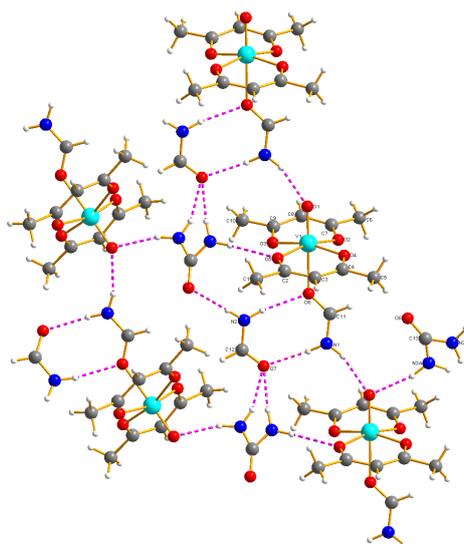


Figure 2. Hydrogen-bonded network.

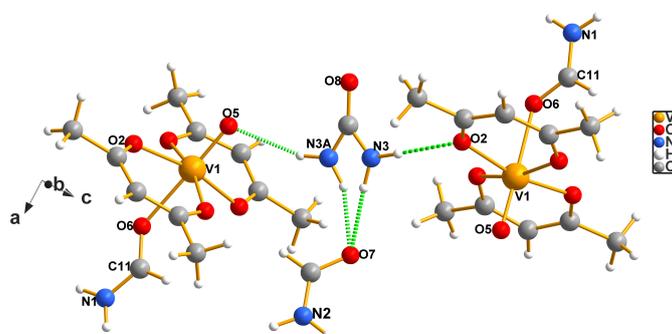


Figure 3. The disorder of one formamide molecule, characterized by N3 and N3A.

Of the three resulting formamides, one was bound to the vanadyl moiety and two appeared as crystallization molecules in the lattice. Figure 1 shows a useful fragment of the unit cell present in the compound.

Figure 2 displays a larger portion of the crystalline lattice to illustrate the profusely hydrogen-bonded network created by the original vanadyl species, its formamide adduct, and the two formamides of crystallization. This network is obviously more extensive, since the depiction is only 2D; moreover, to avoid an unnecessary mess, we have not drawn all possible hydrogen bonds present in that fragment. The disorder of one formamide molecule is displayed in Figure 3. N3 and N3A illustrate the two-fold disorder at the C13-O8 formamide molecule of crystallization. By acting as a bridge between vanadyl O5 with the AcAc ligand O2, the entire lattice becomes infinitely hydrogen bonded, aided by additional hydrogen bonds provided by N1 and N2 hydrogens.

We believe that the driving force for the disorder in the bridging formamide is the opportunity to form additional hydrogen bonds with adjacent vanadyl species. Note that the entire ensemble is asymmetric in that: (a) a hydrogen on N3 forms a hydrogen bond with O2 of the AcAc ligand; (b) another H on N3A forms a bond with the axial vanadyl V=O (O5).

Several examples of formamide binding transition metal complexes are given in Supplementary Part I. Examples of the importance of triazine in a wide variety of fields are given in Supplementary Part II. Bond lengths and angles are given in Tables 4 and 5 in Supplementary Part III, and the H-atom positions are given in Table 6 in Part III as well.

4. Conclusions

(a) Symmetrical cleavage of 1,3,5-triazine occurred while trying to prepare its vanadyl bis(acetylacetonate) triadduct in a toluene medium in a sealed container at 130 °C. The resulting species was unknown to date and contained a formamide in the axial position of (VO)(AcAc)₂; (b) a method of evaluating the basicity of an organic donor (base) molecule can be obtained by ESR measurements of the displacement of the g-factor (and/or of the values of the hyperfine splitting constant, or both) of (VO)(AcAc)₂ molecules in a “standard” solvent such as benzene or hexane which are nondonors (bases). Then, an useful scale of relative basicity of organic ligands may be obtained that way since ESR data yield highly precise values of both those quantities and the test requires only a few minutes (as long as they can enter the sphere of the vanadyl(AcAc)₂ complex and perturb that system).

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Supporting information

CCDC-1557705 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing 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. The online version of this article contains supplementary material, which is available to authorized users. The reader can find (i) some particularly

attractive examples of formamides acting as ligands to various metals in Part I, and (ii) historic records for triazine compounds in Part II.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.

ORCID authorship contribution statement

Conceptualization: Evrim Arslan, Ivan Bernal, Roger Lalancette; Methodology: Evrim Arslan, Ivan Bernal, Roger Lalancette; Writing - Original Draft: Evrim Arslan, Ivan Bernal, Roger Lalancette; Writing - Review and Editing: Evrim Arslan, Ivan Bernal, Roger Lalancette; Visualization: Evrim Arslan, Ivan Bernal, Roger Lalancette.

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