



HAL
open science

Electronic Properties of a Cytosine Decavanadate: Toward a Better Understanding of Chemical and Biological Properties of Decavanadates

Nada Bošnjaković-Pavlović, Anne Spasojevic - de Biré, Isabel Tomaz, Nouzha Bouhmaida, Fernando Avecilla, Ubavka Mioč, João Costa Pessoa, Nour Eddine Ghermani

► To cite this version:

Nada Bošnjaković-Pavlović, Anne Spasojevic - de Biré, Isabel Tomaz, Nouzha Bouhmaida, Fernando Avecilla, et al.. Electronic Properties of a Cytosine Decavanadate: Toward a Better Understanding of Chemical and Biological Properties of Decavanadates. *Inorganic Chemistry*, 2009, 48 (20), pp.9742-9753. 10.1021/ic9008575 . hal-02298732

HAL Id: hal-02298732

<https://hal.science/hal-02298732v1>

Submitted on 24 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Electron and electrostatic properties of a cytosine decavanadate compound from high resolution X-ray diffraction: toward a better understanding of chemical and biological properties of decavanadates

Journal:	<i>Inorganic Chemistry</i>
Manuscript ID:	draft
Manuscript Type:	Article
Date Submitted by the Author:	
Complete List of Authors:	<p>Bošnjaković-Pavlović, Nada; Ecole Centrale Paris, Laboratoire Structures, Propriétés et Modélisation des Solides (SPMS), UMR CNRS 8580; University of Belgrade, Faculty of Physical Chemistry Spasojevic - de Biré, Anne; Ecole Centrale Paris, Laboratoire Structures, Propriétés et Modélisation des Solides (SPMS), UMR CNRS 8580</p> <p>Tomaz, Isabel; Centro de Química Estrutural, Instituto Superior Técnico, TU Lisbon</p> <p>Bouhaida, Nouzha; Université Cadi Ayyad, Faculté des Sciences Semlalia, Physique</p> <p>Avecilla, Fernando; Universidade da Coruña,, Departamento de Química Fundamental, Facultad de Ciencias</p> <p>Mioč, Ubavka; University of Belgrade, Faculty of Physical Chemistry</p> <p>Pessoa, João; Instituto Superior Técnico, Universidade Técnica de Lisboa</p> <p>Ghermani, Nour Eddine; Université Paris XI, Faculté de Pharmacie; Ecole Centrale Paris, Laboratoire Structures, Propriétés et Modélisation des Solides (SPMS), UMR CNRS 8580</p>



1 Electron and electrostatic properties of a cytosine
2
3 decavanadate compound from high resolution X-ray
4
5
6
7 diffraction: toward a better understanding of chemical and
8
9
10
11 biological properties of decavanadates
12
13
14

15 *Nada Bošnjaković-Pavlović,^{a,b} Anne Spasojević-de Biré*,^a Isabel Tomaz,^c Nouzha Bouhmada,^d*

16
17 *Fernando Avecilla,^e Ubavka B. Mioč,^b João Costa Pessoa,^c and Nour Eddine Ghermani*^{a,f}*

18
19
20
21
22 ^aLaboratoire Structures, Propriétés et Modélisation des Solides (SPMS), UMR CNRS 8580, Ecole

23
24
25 Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry, France

26
27 ^bFaculty of Physical Chemistry, University of Belgrade, P.O. Box 47, 11158 Belgrade, PAC:

28
29
30 105305, Serbia

31
32 ^cCentro de Química Estrutural, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001

33
34 Lisboa, Portugal

35
36 ^dLaboratoire des Sciences des Matériaux (LSM) Université Cadi Ayyad, Faculté des Sciences

37
38 Semlalia, Boulevard Prince Moulay Abdallah, BP 2390, 40000 Marrakech, Morocco

39
40
41 ^eDepartamento de Química Fundamental, Facultad de Ciencias, Universidade

42
43 da Coruña, Campus da Zapateira s/n, 15071 A Coruña, Spain

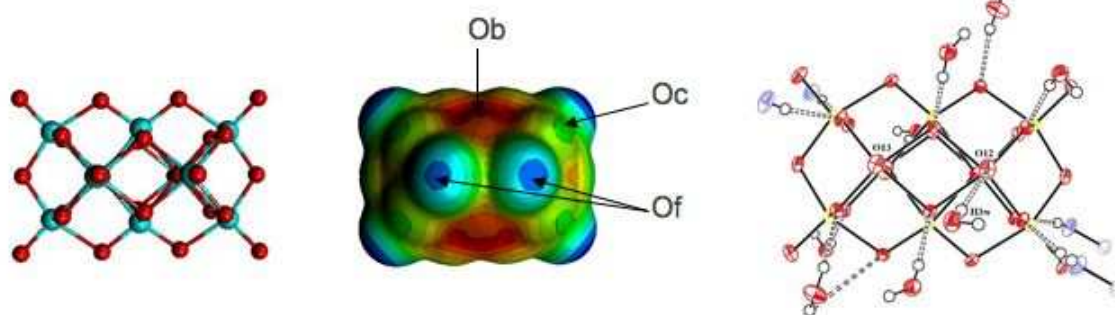
44
45
46 ^fLaboratoire de Physique Pharmaceutique, UMR CNRS 8612, Faculté de Pharmacie, 5 rue Jean-

47
48
49 Baptiste Clément, 92296 Châtenay-Malabry, France

50
51
52
53 email :anne.spasojevic@ecp.fr

54
55
56
57
58 Title running head : Electron and electrostatic properties of a decavanadate
59
60

TABLE OF CONTENTS GRAPHIC



ABSTRACT

1
2
3
4
5
6 Investigation of the interactions of the polyoxometalates with peptides or proteins presents a
7
8 growing interest, since the polyoxometalates have been successfully used as drugs and their
9
10 biological activity has been established. The polyoxovanadates have been found able to interact with
11
12 biomolecules with various and versatile activities (enzyme activator or inhibitor). However, despite
13
14 the fact that such inhibitory or stimulating functions have been extensively studied not much
15
16 information is available at the molecular level. A contribution to the understanding of the
17
18 mechanism involved at the molecular level could be partially reached by a better knowledge of the
19
20 electronic and electrostatic properties of the compound. These properties may be extracted from a
21
22 high resolution X-ray diffraction experiment and derived from charge density studies. Among
23
24 different synthesized polyoxometalates, we have focused our attention on polyoxovanadates due to
25
26 the relative low toxicity in biological media of vanadium and the feasibility of the charge density
27
28 study. In an attempt to increase the knowledge on the biochemical interactions of such polyanions,
29
30 we have synthesized and crystallized a cytosine-decavanadate compound, $\text{Na}_3 [\text{V}_{10}\text{O}_{28}]$
31
32 $(\text{C}_4\text{N}_3\text{OH}_5)_3(\text{C}_4\text{N}_3\text{OH}_6)_3 \cdot 10\text{H}_2\text{O}$. We present the crystal structure, the deformation density maps, the
33
34 atomic net charges and the electrostatic properties of the title compound after a multipole
35
36 refinement. Some conclusions on the properties of the decavanadate (electrostatic properties, net
37
38 atomic charges, hydrogen bond network) are drawn for the evidence of biological activities of this
39
40 particular anion.
41
42
43
44
45
46
47
48
49

KEY WORDS

50
51
52
53
54
55 Electron density, decavanadate, electrostatic potential, AIM, hydrogen bonds
56
57
58
59
60

INTRODUCTION

Polyoxometalates (POM's) are a fascinating class of metal-oxygen cluster compounds with a unique structural variety and interesting properties, which are used in different fields. Among the different synthesized POM's, we have focused on the polyoxovanadates (POV's). The vanadium has been chosen for its relative low toxicity in biological media. Interaction analysis of vanadate and cellular proteins is difficult under physiological conditions because the aqueous vanadate species are pH, temperature, buffer and vanadate concentration dependant.¹ In biological systems, vanadium (V) containing solutions exhibits different oligomeric vanadate species in equilibrium e.g., monomeric, dimeric, tetrameric and decameric, each with different states of protonation and conformation, depending on experimental conditions. It is believed that almost 98% of vanadium in cells is present in the vanadium (IV) oxidation state, the intracellular concentration of vanadium (V) being very low for the formation of vanadate oligomers. This is probably the reason why *in vivo* toxicological studies of vanadate oligomers are scarce. However, it is proposed that once formed, decavanadate (DV) eventually converts to the labile oxovanadates but the rate can be very slow and effectively allows DV to exist for some time under physiological conditions.² V half - life in the intracellular medium has been estimated to be approximately half an hour,³ enough to allow to study its effects not only *in vitro*, but also *in vivo*.^{4,5} However its presence in significant amounts can be explained by the existence of special cell compartments where vanadium can be accumulated and preserved from decomposition (protective "cage"). This can be explained by hydrogen-bonding interactions with surrounding molecules, like proteins or macrocyclic ligands.⁶

Several studies report that DV has a strong inhibitory effect on several enzymes, when compared to other oligomers:⁷⁻⁹ inhibition of Ca²⁺ATPase,¹⁰⁻¹³ Na,K-ATPase,¹⁴ muts ATPase,¹⁵ myosin ATPase,¹⁶⁻²⁰ acid phosphatase A,²¹ methaemoglobin reductase,⁴ hexokinase, adenylate kinase and phosphofructokinase,²² protein kinase,²³ (NADPH) oxidase,²⁴ aldolase,²⁵ ribonuclease,²⁶ nucleotidase,²⁷ phosphorylase.²⁸ It has also been recently reported that DV can act as an insulin

1 mimetic agent.^{29,30} Aureliano et al. have formulated the hypothesis that mitochondria might be a
2 target for DV species.³¹ A complete review of biological activities of DV is given in a recent review
3 of Aureliano et al.²
4
5
6
7
8

9 Investigations of POV's in the presence of enzymes and proteins can provide additional information
10 on their mode of action. This research needs to proceed through combined crystallographic,
11 spectroscopic, and enzymatic studies with mutants as well as with wild-type enzymes.
12 Potentiometric studies have proven to be an adequate means to investigate the vanadate - peptide
13 systems. ⁵¹V NMR spectroscopy was used to determine the rates of oligoanion exchange under the
14 physiological condition. For example, Meicheng et al.³² have observed hydrogen bonding
15 interactions between the 4-ethylpyridinium cation and the DV ion that involves oxygen atoms
16 possessing two or three bonds with vanadium. Crans et al.^{33,34} have extensively investigated POV-
17 enzyme interactions. They have structurally characterized the DV - dipeptide complex. It was found
18 that the dipeptides are connected to DV anions *via* hydrogen bonds. Very weak hydrogen bonding
19 interactions between guanidinium ion and singly and doubly coordinated oxygen atoms in DV
20 anions have also been observed.³⁵ These studies illustrate the importance of the noncovalent
21 interactions between DV and peptides; DV interacts very strongly with positively charged proteins.
22 Therefore, the study of POV containing organic molecules is important, particularly the role of the
23 organic cations in the structure of the DV and understanding the direct interactions of vanadate with
24 cellular proteins and enzymes may be an important key to reveal the physiological functions of
25 vanadium oxoanions. Since the biological properties also result from interactions with viral enzymes
26 or with viral cell envelopes, the understanding of these interactions at a molecular level is essential
27 for the interpretation and the development of potent compounds with selective enzymatic affinity.
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55

56 It has been demonstrated that accurate electron density can give pertinent information concerning the
57 interactions between drug or potent drug and their biological targets.³⁶⁻⁴¹ Experimental X-ray
58 determination of the accurate electron density in compounds containing transition metals has grown
59
60

1 as a major area in the past few years. Most of the progress is due to the recent availability of fast
2 devices like area detectors which provide full and very accurate data sets in short times even for
3 crystals with large unit-cells. The fact that deformation density studies require optimal diffraction
4 data quality and that 3d transition metals present special problems when refining the deformation
5 density, because of the significantly different radial extension of the 3d and 4s valence orbitals,
6 could explain that there is a very few number of papers dealing with experimental deformation
7 density of vanadate compounds.⁴²⁻⁴⁴

8 Besides experimental studies, theoretical calculations have already been performed for an isolated
9 $[V_{10}O_{28}]^{6-}$ anion.⁴⁵⁻⁴⁸ The goal of these calculations is to investigate the electronic structure of the
10 POV anion. As this anion may possess different protonation sites, spectroscopic and structural
11 studies were performed in order to localize the protonation sites of the DV's.^{49,50} In order to get a
12 quantitative determination of the reactivity of the six external sites of oxygen atoms, the theoretical
13 calculations explain and predict the behaviour of those species in case of an attack from protons or
14 cationic groups. The possibility of predicting hydrogen bonds between polyanion and water
15 molecules with their associated interaction energies was established. It was found that the double-
16 linked and triple-linked oxygen atoms are those which are most susceptible of protonation owing to
17 the basicity of these atoms compared with the terminal atoms. The topography of the electrostatic
18 potential (EP) distribution in the accessible region of the molecules is expected to provide
19 information concerning the approach of a reagent, either electrophilic, dipolar, or nucleophilic.

20 We have already studied the crystal structure and the electrostatic properties of the $(NH_4)_6 [V_{10}O_{28}] \cdot$
21 $6H_2O$ derived from a κ -refinement.⁵¹ In this paper, we report the crystal structure and electrostatic
22 properties of $Na_3 [V_{10}O_{28}] (C_4N_3OH_5)_3 (C_4N_3OH_6)_3 \cdot 10H_2O$ in order to have experimental evidence
23 of the electrostatic properties derived from a co-crystal containing DV and an organic moiety, and to
24 relate the properties derived from a charge density study to the DV biological properties observed
25 elsewhere.

METHODOLOGY

1
2
3 The crystal electron density is described as a superposition of aspherical pseudoatoms according to
4
5 the Hansen-Coppens formalism.⁵² The deformation density maps have been clearly defined by
6
7 Coppens.⁵³ A κ -refinement⁵⁴ has been performed: P_{val} and κ parameters for the non-hydrogen atoms
8
9 have been refined. Atomic net charges are derived from the experimental monopole population (P_{val})
10
11 after a κ -refinement and referenced as to the κ charges. A quantitative investigation of the bonding
12
13 can be performed by means of a topological analysis according to the Atoms in Molecules (AIM)
14
15 theory.⁵⁵ Following Bader⁵⁵ and Cremer et al.^{56,57} the atomic interaction may be characterized
16
17 through the values of density $\rho(r_{CP})$, the Laplacian $\nabla^2\rho(r_{cp})$, the kinetic energy density $G(r_{cp})$ and the
18
19 local energy density $E(r_{cp})$ at the (3,-1) bond critical points (BCP). The total energy density $H(r_{cp})$ is
20
21 defined as the sum of a kinetic energy density $G(r_{cp})$ and a potential energy density $V(r_{cp})$.
22
23

24
25
26
27 Abramov⁵⁸ has proposed an empirical formula: $G(r_{cp}) = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3}(r_{cp}) + \frac{1}{6}\nabla^2\rho(r_{cp})$. The

28
29
30
31 Laplacian and the energy density are related by: $2G(r_{cp}) + V(r_{cp}) = \frac{1}{4}\nabla^2\rho(r_{cp})$. The topological

32
33
34 analysis of the electron density has been carried out using the NEWPROP program.^{59,60}

35
36
37 Experimental atomic net charges is derived from results of the topology of the charge density and
38
39 referenced as to the AIM charges.⁵⁵ Further quantitative information on the electronic structures of

40
41
42 metal atoms is obtained by *d*-orbital population analysis. Since the multipole terms in the Hansen-

43
44
45 Coppens model⁵² represent an analytical description of the asphericity of the atomic charge density

46
47
48 distribution, the *d*-orbital populations can be calculated directly from the multipole coefficients, P_{lm}

49
50
51 according to the linear combination reported by Holladay et al.⁶¹ The electrostatic potential (EP)

52
53
54 $\Phi(r)$ is computed using ELECTROS program⁶² as $\Phi(r) = \sum_{atom}^{molecule} \frac{Z_{at}}{|r - R_{at}|} - \int \frac{\rho_{at}(r')}{|r - R_{at} - r'|} d^3r'$ the sum

55
56
57 of the contributions of the positive nuclear charge Z_{at} located at R_{at} and the atomic electron density

58
59
60 ρ_{at} .

EXPERIMENTAL

Synthesis

Heteropoly- and isopoly- anions have been prepared and isolated from both aqueous and non-aqueous solutions.⁶³ The most common preparative method involves acidification of aqueous solutions of simply oxoanion and the necessary heteroatoms; in many cases, it is necessary to control temperature or pH. Isolation of the polyanion from solution is generally achieved by addition of an appropriate counterion, commonly an alkali metal, ammonium or tetraalkyl-ammonium.⁶⁴

Cytosine (0.444 g, 4.00 mmol) was dissolved in ca. 40 mL of water at 50°C. Sodium acetate trihydrate (0.964 g, 7.09 mmol) were added. A solution of salicylaldehyde (0.84 mL, 8 mmol) in 10 mL ethanol was added drop wise and slowly, and the mixture allowed to react for 1 h at 323 K.

A concentrated blue solution of oxidovanadium(IV) sulphate pentahydrate (0.862 g, 3.4 mmol) in 2.5 mL of water was then added drop wise. The reaction mixture became dark brown, and within a few minutes heavy precipitation of a light green solid occurred, which was filtrated from the reaction mixture. This solid was most probably a mixture of the oxidovanadium(IV) bis-complex with salicylaldehyde ($V^{IV}O(\text{Sal})_2$) and the oxidovanadium(IV) Schiff-base complex of salicylaldehyde and cytosine: $[V^{IV}O(\text{Sal-Cyt})X]$; the identity/amount of anion X was not determined.

The filtrate was kept in a closed vessel at 279 K. A few weeks later reddish crystals suitable for X-ray diffraction analysis were separated from the liquid.

Data collection, data reduction and refinements

Crystallographic measurements were carried out at 210 K on a Siemens SMART CCD 1K diffractometer using Mo $K\alpha$ radiation. This temperature was chosen due to the fact that we have observed a phase transition occurring below 200 K from the $P\bar{1}$ (centrosymmetric) to the P1 space group (non-centrosymmetric). Resolution of the structure at 100 K does not allow us to get of a good

1 quality results (localization of the all hydrogen atoms) because, in the P1 space group, the number of
2 parameters is too high. A total of 38 400 frames were recorded with five different exposure time per
3 frame (2, 5, 10, 20, 30 s) depending on the 2θ detector position; 221 309 reflections were collected.
4
5
6
7 The absorption correction was applied using SADABS.⁶⁵ Data were sorted and merged using
8
9
10 SORTAV,⁶⁶ giving 28 757 independent data up to a resolution of $[\sin\theta/\lambda]_{\max} = 1.11$ ($\theta_{\max}=75^\circ$). The
11
12 structure was solved by SIR92.⁶⁷ $\text{Na}_3 [\text{V}_{10}\text{O}_{28}] (\text{C}_4\text{N}_3\text{OH}_5)_3 (\text{C}_4\text{N}_3\text{OH}_6)_3 \cdot 10\text{H}_2\text{O}$ crystallizes in the
13
14
15 centro-symmetric space group $\text{P}\bar{1}$ at temperature > 210 K. All structural calculations were
16
17 performed by using the SHELXL-97,⁶⁸ program of the WINGX software package.⁶⁹ All atoms,
18
19 except the hydrogen ones, were refined by using anisotropic thermal parameters. Thermal ellipsoid
20
21 plots were obtained using the program ORTEP3.⁷⁰ The Hansen-Coppens multipole formalism,⁵²
22
23 implemented in the MOLLY program, was used for multipole and κ refinements.^{54,71} Table 1 gives
24
25 the experimental details of the single crystal experiment.
26
27

28
29 The radial terms used for V atoms were simple Slater functions, $R_{nl}(r) = N r^{nl} \exp(-\xi_l r)$, $n = 4$ and $\xi =$
30
31 5.99 bohr^{-1} (for $l = 1$ to 4). The multipole terms up to hexadecapole are included for the vanadium,
32
33 up to octapole for nitrogen, carbon and oxygen, and up to dipole for hydrogen atom. The local
34
35 atomic frames for multipoles are given in Supplementary Material. The atomic core and valence
36
37 scattering factors were taken from International Tables for X-ray Crystallography.⁷² The core
38
39 electron configuration was assumed to be He core for O, N and C and Ar core for V.
40
41

42
43 It is well established^{71,73-75} that $3d$ transition metals imply some difficulties when refining the
44
45 deformation density because of the significantly different radial extension of the $3d$ and $4s$ valence
46
47 orbitals. In view of these problems, it is a common practice to treat the $4s$ density as "core"
48
49 density.⁷⁶ Therefore, we have tried different models. Models based on the $4s^2 3d^3$ electron
50
51 configuration were initially examined, but gave chemically unrealistic populations; those based on
52
53 the $4s^0 3d^5$ configuration gave significantly high residuals in the density maps. The final model used
54
55 was based on the $4s^0 3d^3$ configuration, where V^{2+} possesses 18 core electrons. In order to conserve
56
57 the electron-neutrality, we have attributed the formal charges as follows: $[\text{Na}_3]^{3+} [\text{V}_{10}\text{O}_{28}]^{6-}$
58
59 $[(\text{C}_4\text{N}_3\text{OH}_5)_3]^0 [(\text{C}_4\text{N}_3\text{OH}_6)_3]^{3+} \cdot 10\text{H}_2\text{O}$. In this approach, we have not authorized a charge transfer
60

1 between the different ions of the compound. In order to minimize the number of refined parameters,
2 we have imposed chemical constraints on water molecules: same populations and κ 's for O and H
3 respectively. Reliability refinement factors are given in Table 1.
4
5
6
7
8

9 10 **RESULTS AND DISCUSSION**

11
12
13
14
15 Selected interatomic distances of covalent and non-covalent interactions and topological analysis
16 features are given in Tables 2, 3 and 4; d orbital populations are reported in Table 5. Net atomic
17 charges and EP are given in Tables 6 and 7. Figure 1 gives the labeling of the different atoms in the
18 crystal structure. After the multipole refinement, the residual deformation electron density maps of
19 the title compound are presented in Figure 2. The absence of significant peaks and holes of residual
20 density indicates that the multipole model refinement is satisfactory. The maximum random errors
21 according to Rees' formulism⁷⁷ is $0.0675 \text{ e.}\text{\AA}^{-3}$. The same trend is observed for the cytosine
22 molecules, which, however, exhibit a significant accumulation of charge density around the N1c,
23 C6c and C2c. This poor quality is due to a local disorder leading to high values of thermal
24 parameters which have been observed for these atoms.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 **Crystal structure**

42
43
44
45
46 The X-ray structural analysis reveals that the asymmetric unit of the title compound is composed of
47 one half of a DV anion, three molecules of cytosine, one and half of sodium and five water
48 molecules. DV is not protonated in the title compound, while in other crystal structures they could
49 be protonated according to the formula $[\text{V}_{10}\text{O}_{28}\text{H}_x]^{(6-)-x}$ where $x = 1-5$.⁷⁸
50
51
52

53 The $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion is formed by ten slightly distorted edge-sharing VO_6 octahedra building a very
54 compact entity. In the title compound, this entity is centrosymmetric and built by only five
55 crystallographically independent VO_6 octahedra with approximate D_{2h} (mmm) symmetry (Figure 1).
56
57
58
59
60

The vanadium atoms are not in the geometric center of the octahedron but they are closer to the

1 vertex occupied by the terminal oxygen atoms. Owing the complexity of the structure, it is necessary
2 to precisely characterize the different environment of oxygen and vanadium atoms. If we classify the
3 oxygen atoms according to their vanadium coordination, four types of oxygen atoms are involved in
4 this compound (Figure 1a). The first type corresponds to oxygen atoms bonded to only one vanadium
5 atom (O1x). The second type corresponds to oxygen atoms shared between two vanadium atoms
6 (O2x). The third type are those shared between three vanadium atoms (O3x). The fourth type of
7 oxygen atoms, have a sixfold coordination with vanadium atoms building an almost regular VO₆
8 octahedron (O6x). Considering now the different vanadium atoms, there are three types of vanadium
9 atoms: the first type (type I), presents two V-O2x, two V-O3x and two V-O6x bonds; the second
10 type of vanadium atoms (type II) presents four V-O2x, one V-O1x and one V-O6x bonds; the third
11 type of vanadium atoms (type III) presents two V-O2x, two V-O3x, one V-O1x and one V-O6x
12 bonds. In order to compare all V-O distance values with those found in literature (experimental and
13 theoretical data), we have classified oxygen atoms in subtypes according to new labels (Figure 1b).
14 Type **a** concerns oxygen atom O6x, type **b** is O3x atoms, type **c** concerns O2x connected to one VII
15 vanadium atom and one VIII vanadium atom, type **d** concerns O2x atoms connected to two VII
16 vanadium atoms, type **e** concerns O2x connected to one VI vanadium atom and one VII vanadium
17 atom, type **f** concerns O1x connected to VIII vanadium atom and type **g** concerns O1x connected to
18 VII vanadium atom.

19 In order to compare the interatomic distances of the title compound with the literature, we have
20 examined the organic / organometallic Cambridge Structural Database (CSD).⁷⁹ We have found 37
21 data for 33 [V₁₀O₂₈]⁶⁻ structures with agreement factor R less than 10%.⁸⁰ A search in the Inorganic
22 Crystal Structure Database (ICSD)⁸¹ has given 44 [V₁₀O₂₈]⁶⁻ structures with agreement factor R less
23 than 10%.⁸² The longest interatomic distance is V-Oa: 2.0781(6) Å < V-O < 2.3324(6) Å. The
24 shortest distance is V-Og: 1.6115(6) Å < V-O < 1.6200(6) Å. Interatomic bond distances and angles
25 observed for the [V₁₀O₂₈]⁶⁻ unit of the title compound exhibit a geometry which is quite similar to
26 those found in previously reported structures of DV salts or co-crystals (Table 2). The interatomic
27 distances V-Of or V-Og observed for the title compound are slightly longer than those observed in

1 the literature. This difference may be due to the crystal packing effect, because the oxygen atom
2 involved in this bond is a mono-coordinated O1x oxygen atom and could be more affected by the
3 hydrogen-bond network. Therefore, one can consider that DV is a very rigid entity for which the
4 interatomic distances are almost independent of the non-covalent interactions.
5
6
7
8

9 The asymmetric unit of the title compound contains three different molecules of cytosine (Figure
10 1c). The cytosine C is not protonated and is neutral. The cytosinium B is protonated, and hydrogen
11 atom H2b is bonded to N3b leading to a charge of +1e for the molecule. The cytosinium A is
12 protonated, a half of hydrogen atom H2a is bonded to N3a, with a charge of +0.5e. This hydrogen
13 lies on the crystallographic center of symmetry. One can remark (Table 3) that some interatomic
14 distances in cytosine C (C2c-O2c, C6c-N1c) deviate significantly from the corresponding distances
15 in cytosinium A and cytosinium B. A poor resolution for the cytosine C is observed, due to high
16 thermal anisotropic Uij values, mainly located on N1c and C6c. We have compared the distances for
17 protonated cytosinium B (with H atom on N3b) with corresponding molecules of cytosinium, and
18 retrieved from CSD bases 18 data extracted from 14 different structures containing cytosinium
19 cations.⁸³ The geometry is quite similar to those found in previously reported structures of cytosine.
20 As was shown in previous studies,⁸⁴⁻⁸⁶ the protonation of the cytosine molecule induces a
21 modification of the bond length. Not unexpectedly, the N3-C bonds of the protonated N3b nitrogen
22 atom are slightly longer than those of the nitrogen atom N3c that acts as a hydrogen acceptor.
23 Accordingly, both N3b-C4b and N3b-C2b bond lengths are longer than those of N3c-C4c and N3c-
24 C2c (1.354(1) *versus* 1.351(1) Å and 1.365(1) Å *versus* 1.357(1) Å, respectively). Furthermore, the
25 C2-N3-C4 angle around the protonated N3b is slightly greater (0.2°) than those of the non-
26 protonated N3c (122.26° *versus* 122.01°). Thus, as expected, the difference between the angle in the
27 protonated (cytosinium) and the non-protonated molecule (cytosine) are sensitive to the protonation
28 ($\Delta_{B-C}(N3-C4-C5)=-1.5^\circ$) and $\Delta_{B-C}(N4-C4-C5)=+1.6^\circ$). All these experimental values exhibit the
29 same trend founded in previous theoretical DFT study⁸⁵ and experimental works.^{84,86}
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

The asymmetric unit also contains two sodium atoms. Both sodium atoms (Na1 and Na2) are in octahedral coordination: Na1 is surrounded by four water molecules and two oxygen atoms

1 belonging to DV (O12) while Na2 is surrounded by four water molecules, one DV oxygen (O13)
2 and one oxygen belonging to cytosine O2a (Figure 1d). The oxygen atom involved in these bonds
3 belongs to different molecules, anions or cations, implying that the influence of environmental atoms
4 and hydrogen-bonds on interatomic distances is different and consequently the Na-O distances are in
5 a wide range. The Na-Ow distances are in the range from 2.3562(7) Å to 2.4031(8) Å while the other
6 Na-O distances belongs to a wider range (2.4489(7) Å to 2.7999(7) Å). The interatomic distances
7 retrieved in the ICSD base for nine compounds⁸⁷ give Na-Ow distance from 2.293 Å to 2.647 Å and
8 Na-O distances (O not belonging to a water molecule) from 2.290 Å to 2.469 Å. The Na-O distances
9 observed for the title compound are slightly longer.

24 **Crystal packing**

25
26
27
28 The crystal structure of the title compound is stabilized by an extensive network of hydrogen bonds
29 which involve the DV anions, the cytosine and the water molecules. Table 4 reports the most
30 significant hydrogen bond features according to the usual criterion ($d(D\cdots A) < 3.5 \text{ \AA}$). Symmetry
31 codes used in the text are defined in caption 4. The structure contains several varieties of
32 intermolecular interactions such as O-H \cdots O, N-H \cdots O, N-H \cdots N, C-H \cdots O and O-H \cdots N. The strongest
33 interaction in DV anion is of Ow-Hw \cdots O type. The O1w'-H1w' \cdots O32 is the shortest interaction
34 (1.6924(5) Å) followed by O2w-H2w' \cdots O20^(v) (1.7049(6) Å) and O4w-H4w' \cdots O31^(x) (1.7583(5) Å).
35 There is a strong hydrogen bonding interactions between bridging oxygen atoms O2x of the DV
36 anion and the N4 atoms of the cytosine. The shortest distance 1.8536(5) Å is found for bond N4b-
37 H4b \cdots O24^(viii), followed by N4a-H4a \cdots O23⁽ⁱ⁾ (1.8678(6) Å) and N4c-H4c \cdots O22⁽ⁱⁱⁱ⁾ (1.8798(5) Å).
38 The water molecules interact with the DV and the cytosine *via* hydrogen bond, as expected.

39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Hydrogen bonds occur naturally between nucleic acid bases of the purine and pyrimidine type
(cytosine) and that is of great biological importance for secondary structures of deoxyribonucleic
acid (DNA) and ribonucleic acid (RNA).⁸⁶ The cytosinium - cytosine dimer [(Cyt)₂H]⁺ (Figure 1c)

1 is the most simple model compound to mimic the hydrogen pattern of cytosine in nucleosides and
2 nucleotides. Two molecules of cytosine A are connected over the three strong hydrogen bonds
3 forming a dimeric cation cytosinium - cytosine, namely two terminal N4-H...O (N4a...O2a⁽ⁱ⁾
4 =2.841(1) Å and N4a-H3a-O2a⁽ⁱ⁾ =177.12(6)°) and a central N3-H...N3 (N3a...N3a⁽ⁱ⁾ =2.838(2) Å and
5 N3a-H2a-N3a⁽ⁱ⁾ =167.72(2)°). In this dimeric cation, the terminal N4a-H3a...O2a hydrogen bonds are
6 identical. The hydrogen atom of the central N3a-H2a-N3a hydrogen bond is disordered over two
7 equally occupied positions related by an inversion center. Two molecules of cytosinium B and C are
8 connected *via* three strong hydrogen bonds. The central hydrogen bond is N3b...N3c (N3b...N3c⁽ⁱⁱ⁾ =
9 2.816(1) Å and N3b-H2b-N3c⁽ⁱⁱ⁾ = 173.39(5)°). The two terminal N4-H3...O2 hydrogen bonds are
10 different, a weaker (N4b...O2c⁽ⁱⁱ⁾ = 2.874(2) Å) and a stronger N4c...O2b⁽ⁱⁱ⁾ = 2.756(1) Å) one. This
11 is expected because protonation implies different bond distances and bond angles (Table 3). We
12 have observed a difference in the hydrogen bonds in cytosine A, B and C, in the N1 - C6 region. The
13 hydrogen bonds which exist in cytosine C (C5c-H5c...O22⁽ⁱⁱⁱ⁾, N1c-H1c...O2w) are longer than those
14 present in cytosinium B and A (2.6819(5) *versus* 2.0702(6) and 2.2430(7) and 2.288(1) *versus*
15 1.7519(7) and 1.7006(7), respectively. Hydrogen bonds which exist in cytosine C (C5c-
16 H5c...O22⁽ⁱⁱⁱ⁾, N1c-H1c...O2w) are longer than in cytosine B and C. The summation of d(H...A)
17 interatomic distances for each cytosine, gives a quantification of the strength of the hydrogen bond
18 network and clearly indicates that cytosine C is not stabilized with strong hydrogen bond
19 ($\Sigma_C [d(H...A)] = 9.267 \text{ \AA}$), compared to the two other cytosine molecules ($\Sigma_A [d(H...A)] = 8.625 \text{ \AA}$,
20 $\Sigma_B [d(H...A)] = 8.352 \text{ \AA}$). This is in agreement with the thermal parameter values which are higher
21 for cytosine C.

22 In order to describe the extensive hydrogen bond network, one can first examine, the connection
23 network built by DV anion to the rest of the structure. The DV anions are connected *via* oxygen-
24 sodium-oxygen chains in the (001) plane (Figure 3). In the crystal packing, Na2 interacts with O13
25 of DV and Na1 interacts with O12 forming a layered structure with O13-Na2-Na2-O13 and O12-
26 Na1-O12 chains. It means that each DV anion is connected to four neighboring DV anions. As it is

1 shown in Figure 3, the DV are located between these layers (Na1-Ow5-Na2-Ow2-Na2-Ow5-Na1
2 chain). The Na2 sodium cations are connected *via* two bridged Ow2 atoms and Na1 and Na2 *via*
3 Ow5 atom. The shortest contact between two different layers corresponds to Na2...Na2^(x) distance
4 (3.5830(8) Å). Then, each layer is bonded to cytosine A *via* Na2 cation. Na2 atoms serve to link
5 adjacent DV clusters to form infinite chains. In an other direction, the anions are connected *via*
6 hydrogen bonds (medium and weak) with cytosine B and cytosine C. DV are located between these
7 organic layers and are connected *via* hydrogen bonds (medium and weak) with cytosine B and
8 cytosine C. The strongest hydrogen bond is N4b-H4b...O24^(viii) with $d_{(H-A)} = 1.8536(5)$ Å and then
9 N4c-H4c...O22⁽ⁱⁱⁱ⁾ with $d_{(H-A)} = 1.8798(5)$ Å. Other hydrogen bonds exhibit distance ($d_{(H-A)}$) greater
10 than 2.0 Å.
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

26 Description of covalent bonds in DV anion

27
28
29
30
31 Static deformation density maps for horizontal and vertical XZ and YZ planes are represented in
32 Figure 4. As expected, there is a significant charge accumulation on the shorter V-O bond. For the
33 longest bond we do not observe any deformation density. The deformation density maps display
34 regions of electron density accumulation around all vanadium atoms. These accumulations are
35 oriented toward the Oa atoms. Since V-Oa distance are the longest V-O bond in the cage (yellow
36 color in Figure 4), the density accumulations can be interpreted as the counterpart of the charge
37 depletion occurring along the opposite and shorter V-O bonds (red color). Differences in static
38 electron density maps in the vicinity of oxygen atoms are well expressed. Around the O22 oxygen
39 atom (Figure 4a) we see, symmetrically distributed, an electron density accumulation in the direction
40 of the bonds while in the vicinity of the O21 and O27 atoms, the electron density is asymmetrically
41 shared. This is an expected result because all the vanadium atoms are not in the same environment.
42 O22 atom is connected to two V atoms (V3 and V5) which are in the same environment, having a V-
43 O distance of 1.8871(6) Å and 1.8795(6) Å, respectively. Therefore, we can observe a symmetrical
44 density accumulation around O22 (Figure 4a). As it is shown in Figure 4a, O27 and O21 atoms are
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1 located between two different types of V atoms; in this case, the charge accumulation is in the
2 direction of the shortest bond (O27-V4 (1.6848(5) Å) and O21-V4 (1.7059(6) Å)). The highest
3 electron density peaks (Figure 4b) are found between V1-O13 followed by those in V2-O12 because
4 the distance V1-O13 (1.6189(6) Å) is shorter than the V2-O12 distance (1.6230(6) Å). We have
5 found for O61 atom (Figure 4a) a practically spherical electron distribution, which is in a good
6 agreement with the theoretical calculation results.^{45,46} The main differences could be attributed to the
7 hydrogen bonding network. The deformation density is symmetrically distributed in the direction of
8 the bonds due to very similar distances (O31-V2 = 2.0040(5) Å and O31-V1 = 2.0205(5) Å; O32-V1
9 = 1.9981(6) Å and O32-V2 = 2.0268(6) Å). Additionally, the lone pairs of the mono-coordinated
10 oxygen atoms (O1x) are clearly visible.

11 Topological parameters of the electron density for the (3,-1) BCP's of DV containing bonds are
12 given in Table 2. All V-O bonds are characterized by a very large positive curvature at the BCP
13 along the direction of the bond path (λ_3). The value of Laplacian $\nabla^2\rho(r_{cp})$ trace is largely dominated
14 by λ_3 and therefore is positive for the whole range of V-O distances. It has been established that the
15 positive values of $\nabla^2\rho(r_{cp})$ are characteristic of "closed-shell" interactions governed by the
16 contraction of the charge density toward each of interacting nuclei.⁸⁸ As it is also shown in table 2,
17 $\rho(r_{cp})$ values range from 0.324 eÅ⁻³ for the longest V-O bond (V3-O61 = 2.3324(5) Å) to the
18 relatively high value of 1.789(6) eÅ⁻³ for V1-O13. The $\nabla^2\rho(r_{cp})$ value ranges from 4.36 to 30.96 eÅ⁻⁵.
19 Correlation between experimental and theoretical data is very good, except $\rho(r_c)$ value for VII-Od.
20 This is not surprising because the distance VII-Od⁴⁶ is 1.831Å compared to our experimental result
21 of 1.8871(6) Å. We observe (Figure 5) that $\rho(r_{cp})$ at the BCP is a decreasing function of the
22 interatomic distances. The topological results fit quite well with the classification of the oxygen
23 types and the vanadium types in the DV anion. The dispersion of the data is very small, leading to a
24 quantitative agreement. Additionally, d_1+d_2 is always very close to the interatomic distance, except
25 for three bonds V3-O20, V3-O22 and V5-O22; the position of the BCP is generally at the middle of
26 the bond, except for the shortest V-O distance where larger discrepancies are observed. The total

1 energy density $H(r_{cp})$ according to the Abramov formula⁵⁸ has also been calculated and presents a
2 quite good behavior leading to significant energy for short V-O bonds.
3

4
5 The analysis of the total density through the existence of the BCP and the analysis to the
6 deformation density lead to similar results and give the first experimental description of V-O bonds
7 in a POV entity.
8
9

10 11 12 13 14 **Description of hydrogen bonds**

15
16
17
18
19 Topological analysis of the charge density is also a very useful tool for the characterization of
20 hydrogen bonds.⁸⁹ It is extremely interesting to compare accurately the results of the topology and
21 the determination of the existence of hydrogen bonds using simple geometrical parameters ($d(D...A)$
22 $< 3.5 \text{ \AA}$) (Table 4). The number of significant hydrogen bonds decreases from 37 to 20. As expected,
23 all hydrogen-bond critical points are of (3,-1) type. Hydrogen bonds are considered as closed-shell
24 interaction, because they display $\nabla^2\rho(r_{cp}) > 0$ and small $\rho(r_{cp})$ values. The O-H...O and N-H...O
25 interactions are found to be the strongest and present higher $\rho(r_{cp})$ value than N-H...N and C-H...O,
26 which are very weak interactions. The O1w-H1w'...O32 and N1a-H1a...O4w are the two shortest
27 hydrogen bonds having the highest $\nabla^2\rho(r_{cp})$. The $\rho(r_{cp})$ values for all types of bonds are in the range
28 of $\rho(r_{cp})$ magnitudes previously reported for this kind of bonds.⁹⁰ $\rho(r_{cp})$ expresses an exponential
29 function of the interatomic distances. The same trend is observed for the $\nabla^2\rho(r_{cp})$ despite the fact that
30 some points are slightly out of the curves. We have observed an exponential behavior of the
31 eigenvalue λ_3 versus $d(H...O)$ in all D-H...O interactions. The correlation between the positive
32 curvature λ_3 and the interatomic distance for our result is especially excellent ($y = 387.2 e^{-2.34x}$, $R^2 =$
33 0.933) and in a quantitative agreement with the results obtained previously)⁹⁰ ($y = 245.7 e^{-2.11x}$, $R^2 =$
34 0.925).
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

The O-H...O hydrogen bond type. We have found BCP's for the eight O-H...O interaction for
which $d(D...A) < 3 \text{ \AA}$ and $D-H...A \text{ angle} > 150^\circ$ (Table 4). For this hydrogen bond type, $D-H...A$

1 angles and $d(D...A)$ distances correspond to a criterion coherent with the existence of the BCP.
2 These Ow-Hw...O bonds exhibit various electron accumulations from strong ($d(H...A) = 1.6924(5)$)
3 to weak bonds ($d(H...A) = 2.9904(6)$ Å). Observation of the static deformation maps indicates that
4 the accumulation (number of contours at the point intersecting the bond) of the lone pair directed
5 toward the hydrogen of the water molecule is clearly a function of the interatomic distance d
6 ($H...A$). The density peak height of the lone pair is in reasonable agreement with the $d(H...A)$
7 (Figure 6a,b). The height of the Ow-Hw deformation density peaks remains in the range of 0.5 to
8 0.6 $e\cdot\text{Å}^{-3}$, while for a same $d(Hw...O)$ the peak height of the static deformation density involved in
9 the interaction could vary within three contours. This clearly indicates that the deformation density
10 of the lone pair is sensitive to other parameters such as the coordination oxygen atom polyhedra
11 (number of vanadium atoms or hydrogen bonds). Nevertheless, the shortest O...H distance
12 ($d_{H1w'...O32} = 1.6924(5)$ Å) exhibits the highest density peak. The lone pair electron density peak
13 height (maximum contour level of the lone pair) is 0.5 $e\cdot\text{Å}^{-3}$ in agreement with the highest $\rho(r_{cp})$ and
14 $\nabla^2\rho(r_{cp})$ values observed at the BCP. In that case, oxygen lone pair is oriented toward the hydrogen
15 bond (Figure 6a). On the contrary, the oxygen lone pair of O25 is shifted between the two O-H...O
16 hydrogen bonds in the case of bifurcated hydrogen bonds (Figure 6b).

17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40 **The N-H...O hydrogen bond type.** We have found BCP's for the eight N-H...O interactions, for
41 which $d(D...A) < 3$ Å and $D-H...A$ angle $> 160^\circ$ (Table 4). These hydrogen bonds only concern the
42 oxygen atoms of coordinence 2 with the vanadium atom. The observation of the electron
43 deformation density maps reveals the following remarks: i) the intensity of the lone pair is less
44 pronounced than in the O-H...O bond for a similar A...H distance, ii) the H-N deformation bond
45 exhibits a more delocalized deformation density cloud than the corresponding one in the Ow-Hw
46 bond (Figure 6c). Oxygen atom O24 is involved in one strong bond, O24^(viii), H4b and N4b, with
47 $d_{H...A} = 1.8536(5)$ Å, but the oxygen lone pair is shifted toward N-H...O hydrogen bonds. O22
48 presents an interesting behavior; the strongest hydrogen bond is N4c-H4c...O22⁽ⁱⁱⁱ⁾, with $d_{H...A}$
49 $= 1.8798(5)$ Å, but the oxygen lone pair is clearly in the direction of the H5c hydrogen. That feature

1 means that the N-H...O interaction is not enough strong to induce a shift of the oxygen lone pair. On
2 the opposite, the O-H...O contacts are exhibiting strong interaction. We can conclude that the O-
3 H...O interaction is stronger than the N-H...O one. Moreover, the lone pair exhibits higher contours
4 measured at the maximum of the lone pair (0.5; 0.3; 0.4 e.A⁻³ for the O-H...O bond) and (0.2; 0.3;
5 0.3 e.A⁻³ for the N-H...O bond).
6
7
8
9
10
11
12
13

14 **The C-H...O hydrogen bond type.** The C-H...O bond belongs to the category of weak or very weak
15 hydrogen bonds.⁹¹ For only three C-H...O hydrogen bonds, we have found a BCP. The $\rho(r_{cp})$ and
16 $\nabla^2\rho(r_{cp})$ values for these bonds are very small and characteristic of weak hydrogen bonding.⁹² It has
17 been already noticed that it is difficult to observe electron density deformation for such a bond. This
18 trend remains verified for the C-H...O bonds in our compound. That observation does not indicate
19 that there is no interaction but this interaction is not detectable using the tool of the static electron
20 deformation density. One can take the example of the O10 (Figure 6e) where two medium hydrogen
21 bonds are represented: C5b-H5b...O10^(vi), with $d_{H...A} = 2.0702(6)$ Å and C5a-H5a...O10⁽ⁱ⁾, with $d_{H...A}$
22 = 2.2430(7) Å. Due to the large space available in the vicinity of these atoms, the number of multi-
23 furcated H-bond is high. The oxygen atom is connected to three C-H...O bonds of short or medium
24 distances. Therefore the lone pair remains almost in the opposite direction of the V-O bond. For the
25 weak hydrogen bond the trend is less pronounced. Nevertheless, the shortest contact C5b-
26 H5b...O10^(vi) is not characterized by a BCP. This is not surprising due to the fact that it possesses a
27 small D-H...A angle (98.22(6)°). The discrepancy between the bonds which present a BCP and
28 those not displaying a BCP is consistent with the increasing interatomic distances, but the separation
29 at $d(H...A) = 2.68$ Å is not straightforward.
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54

55 ***d*-orbital populations of the vanadium atoms**

56
57
58

59 Holladay et al.⁶¹ have demonstrated that a linear combination of the multipole population used in the
60 pseudo-atom model,⁵² depending of the symmetry used in the refinement lead to an experimental

1 determination of the *d*-orbital populations. These determinations could give quite good results, at
2 least a quantitative agreement between experiment and theory. This was, for example, the case of a
3 chromium complex^{93,94} or other metal transition complexes.^{61,95} Nevertheless experimental
4
5
6 determination of the *d*-orbital population is rarely extracted from the multipole refinement and from
7
8 our better knowledge no such experimental determination has never been published concerning a
9
10 vanadate compound. metal coordination are slightly distorted octahedra, therefore we have chosen
11
12 to refine the vanadium in the symmetry 1 leading to P_{lm} parameters ($l=0, 2, 4$) in agreement with
13
14 Holladay et al.⁶¹ For all V atoms, *z* axis is chosen in the direction of the closest atom, and the *x* axis
15
16 toward the second closest atom. We have determined for each vanadium atom the *d*-orbital
17
18 population (Table 5). Total *d*-orbital population analysis is coherent with an oxidation state for the V
19
20 atoms of +2 in the $4s^0d^x$ configuration (*x* varying from 3.03 for VI to 3.20 for VII and VIII). The *d*-
21
22 orbital population analysis is in good agreement with the features observed in the crystal structure,
23
24 deformation density maps and topological analysis. Since a high charge concentration and higher ρ
25
26 value is found on the shorter V-O bond, the highest population value is found in the d_{z^2} orbital for
27
28 VII and VIII atoms. The highest population for $d_{x^2-y^2}$ orbital is found for V1 and V2. For V4, $d_{x^2-y^2}$ in
29
30 the plane O21-V4-O31 and d_{xz} which is along the bond V4-O21 exhibit the highest populations.
31
32
33
34
35
36
37
38
39

40 Atomic net charges

41
42
43
44
45 A κ -refinement has been carried out without charge transfer between cytosine molecules and DV
46
47 anion, therefore only separate and comparative discussions on each entity make sense. A final
48
49 refinement cycle has been performed without restraints on charge transfer leading to similar results.
50
51 Nevertheless, we will only discuss the results without charge transfer. The κ coefficients,
52
53 experimental atomic net charges (derived⁵¹ from different methods on the two available $(\text{NH}_4)_6$
54
55 $[\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ compounds) and data from theoretical calculation^{46,48} of the DV anion are compiled
56
57 in Tables 6 and 7. The values are in good agreement with those determined from a κ -refinement. As
58
59 expected, some differences are found between charges derived from the κ -refinement and from AIM
60

1 analysis of the experimental model density. According to the results of the κ -refinement, the
2 vanadium atom carries an average positive charge of +1.80 e and a common κ parameter value of
3 1.04. The AIM vanadium atom charges are less positive than monopole charge (+1.60 e versus
4 +1.80 e , respectively). In comparison, vanadium κ -charge equal to +1.6(1) e was reported for
5 ammonium-DV and vanadium charge equal to +2.0(1) e was reported for an isolated DV anion (in
6 an ideal D_{2h} symmetry) from theoretical calculations⁴⁶ and a value of +1.80(1) from PACHA
7 theoretical calculation was reported by Henry.⁴⁸ In the polyanions, the internal V4 have the highest
8 charges, whatever the method, which is in good agreement with the results from theoretical
9 calculation.⁴⁶ The DV oxygen atom electron densities are slightly expanded ($\kappa \leq 1.0$). For the
10 oxygen atoms, the AIM charges are less negative than the monopole charges derived from the
11 κ -refinement (from $-0.57 e$ to $-0.92 e$ versus $-0.65(5) e$ to $-1.08(5) e$ respectively). The Mulliken
12 population analysis for an isolated polyanion, deduced from *ab initio* SCF theoretical calculations,
13 indicates that the oxygen atomic net charges are in the range $-0.7 e$ to $-1.3 e$.⁴⁶ The PACHA
14 calculations⁴⁸ give oxygen charges varying from $-0.56 e$ to $-0.87 e$. The negative charge on oxygen
15 atoms consistently increases with the number of connected metal atoms. This trend is both observed
16 in experimental and theoretical studies. Generally, net atomic charges derived from experimental
17 and theoretical densities are in good agreement, despite the fact that the theoretical calculations are
18 based on an isolated molecule. Nevertheless, the AIM analysis gives a more rigorous definition of
19 the charges of the atoms in molecules, thus providing a more reliable framework for comparison
20 between molecules and between experiment and theory.^{95,96}

50 **Electrostatic potential**

51
52
53
54
55 In order to obtain information on the potent reactivity of the compound, it is useful to color with the
56 EP values the reactive surface of the molecule; the most nucleophilic molecular regions correspond
57 to the most negative EP. The experimental EP can be calculated at the final step of the three
58 refinements (the κ -refinement, the multipole refinement and using the AIM charges). The EP values
59
60

1 at the 3D isodensity surface (0.007 eA^{-3}) of the DV anion are shown in Figure 7 (first column) using
2 the maximum color scale for the EP values on the molecular surface; the blue region correspond to
3 -4.9 eA^{-1} and the red value to -8.7 eA^{-1} . In order to have a complete picture of the electrostatic
4 properties of the DV in the vicinity of the oxygen atoms, we have reported in Table 7 the
5 experimental and the theoretical EP projected at the molecular surface of the DV anion in different
6 environments or using different models.
7
8

9
10 The EP on the surface is negative on the whole molecular surface of DV, as it is expected for an
11 anion. Some differences are found between the values from the κ -refinement, from the multipole
12 refinement and from AIM charges. The greatest differences between the two EP determinations are
13 found in the vicinity of the Ob oxygen sites which are involved in strongest hydrogen bond (-8.7
14 eA^{-1} from multipole refinement *versus* -8.2 eA^{-1} from κ -refinement, respectively). The absolute
15 values obtained from the multipole refinement are generally higher than those obtained from the κ -
16 charges. According to the fact that the multipole model is closer to the reality than the κ one, the EP
17 values obtained from the multipole refinement will be only discussed in the following paragraphs.
18
19

20
21 The value of EP found in the vicinity of oxygen atoms are in the following order: Ob (-8.7 eA^{-1}) <
22 Oe (-7.4 eA^{-1}) < Oc (-7.2 eA^{-1}) < Od (-6.9 eA^{-1}) < Of (-6.2 eA^{-1}) < Og (-5.8 eA^{-1}). Previous
23 theoretical calculations on an isolated $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion⁴⁷⁻⁴⁹ were used to predict the protonation sites
24 in relation with the relative oxygen atom basicities. The authors have found that the most negative
25 region on the EP is in the vicinity of the Ob and Oc atoms. It means that Ob and Oc oxygen atoms
26 are more involved in electrostatic interactions and hydrogen bonds. Our experimental EP results
27 confirm the theoretical predictions. These very close values obtained on two different compounds
28 clearly indicate that the properties obtained experimentally at a molecular level are transferable from
29 an anion in a given environment, to an anion in another environment. For the values concerning the
30 vanadium atom, it could be expected that the environment (such as non-covalent interactions) do not
31 affect the vanadium atom, which is not directly at the molecular surface of the anion. Therefore,
32 concerning the vanadium atom in a DV compound, we can note: i) we have experimentally
33 determined the *d*-orbital population, the values could be taken as transferable. Hence, on the one
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1 hand, we have observed from the comparison of the five vanadium that there is a real correlation
2 within the distorted octahedra (in interatomic distances, and consequently in static deformation
3 density and topology analysis), and on the other hand, we have observed that the DV anion remains
4 geometrically almost invariant with respect to non-covalent interactions. ii) We have determined the
5 net atomic charge values from different methods on different species. There is a quantitative
6 agreement between the same partitioning method used for different anions and an agreement
7 between different partitioning method for the same anion. Therefore one can also conclude that for a
8 chosen partitioning method (here a κ -refinement) the values obtained for VI (1.9 e), VII (1.78 e) and
9 VIII (1.76 e) could be also transferable for an other $[V_{10}O_{28}]^{6-}$ in another environment.

10 One can notice than the experimental order based on EP estimates (Ob, Oe, Oc, Od, Of and Og) is
11 slightly different to the theoretical one (Ob, Od, Oc, Oe, Og and Of). This is mainly due to the
12 crystal packing which has an influence on the atomic properties. Henry⁴⁸ has emphasized, from the
13 PACHA charges, the influence of the partial charges applied to the DV anion.

14 When looking at the value of the experimental EP projected on the molecular surface in the vicinity
15 of each oxygen atom (Table 7), one can notice that these values are less sensitive (at least
16 independent on the environment of the anion) than the atomic net charges. This remains true for the
17 EP which has been calculated from the net atomic charges. It implies that the EP found
18 experimentally in the solid state is independent of the crystalline environment. Due to the rigidity of
19 the anion, it could be taken as a characterization of the $[V_{10}O_{28}]^{6-}$ transferable to DV anions in other
20 environment. This result will be very useful for the discussion of the interactions of the DV anion
21 with the biological species for instance.

22 If we compare our experimental characterization of the EP at the molecular surface to those
23 recalculated with the theoretical atomic charges (Mulliken⁴⁶ or PACHA charges⁴⁸), one can observe
24 that the Mulliken determination from an *ab initio* SCF calculation give very similar results to those
25 obtained experimentally. This is clear in Figure 7, but also from the EP values reported in Table 7.
26 On the contrary, the PACHA calculation seems not adequate to describe correctly the EP of the DV
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1 anion. Nevertheless, these calculations give the same trend (Ob possesses the most negative EP)
2
3 according to the linear correlation between the PACHA and the Mulliken charges (Figure 7).
4
5
6

7 **CONCLUDING REMARKS AND FURTHER APPLICATIONS**

8
9

10
11
12
13 In this paper, we have characterized the chemical bonds, the net atomic charges and the electrostatic
14 properties of $\text{Na}_3[\text{V}_{10}\text{O}_{28}](\text{C}_4\text{N}_3\text{OH}_5)_3 (\text{C}_4\text{N}_3\text{OH}_6)_3 \cdot 10\text{H}_2\text{O}$ deduced from a high resolution X-ray
15 diffraction experiment. One of the main results is that the EP found at the molecular surface could be
16 considered as “transferable”, that means independent of its crystalline environment. Since the DV
17 anion is a rigid entity which remains the same in solution,³³ one can make some hypotheses in order
18 to correlate the properties at the molecular level of the DV anion and its interaction with some
19 biological targets. We will focus on the putative mechanisms of interaction / inhibition / activation
20 and the possible better understanding of those mechanism due to our very precise knowledge of the
21 electronic and electrostatic properties of the DV anion. Therefore we will discuss the biological
22 targets for which a crystallographic structure or electron microscopy with the DV anion as a ligand
23 is known, or with the biological targets for which a docking of DV has been performed.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38

39 A large family of ATP-dependent ion pumps, known as P-type ATPases, achieves active transport of
40 cations. The determination of two Ca^{2+} -ATPase structures has been performed by X-ray
41 crystallography.^{97,98} Together with cryoelectron microscopy, several conformations have so far been
42 defined.^{14,99-101} The papers in the middle of the eighties has demonstrated from biological inhibition
43 of ATPase activity that two binding sites exist for the DV anion.^{10,11} The existence of the two sites
44 was confirmed in the 2000 years by Hua et al.¹⁰² All these studies demonstrated that the precise
45 localization of the DV in the different structures of the Ca^{2+} -ATPase could be of great interest for a
46 better understanding of the calcium pump mechanism. Unfortunately the low resolution of the
47 structures concerned has not permitted such a precise determination. Therefore, only new docking
48 modelisation using our experimental EP and hydrogen bond predictions could give new information.
49
50
51
52
53
54
55
56
57
58
59
60

1 Acid phosphatase A is a respiratory burst-inhibiting acid phosphatase from the American Centers for
2 Disease Control and Prevention (Category A bioterrorism agent) *Francisella tularensis* and
3 prototype of a super-family of acid phosphatases and phospholipases C. Felts et al.²¹ has reported
4 the 1.75-Å resolution crystal structure of Acid phosphatase A complexed with the inhibitor
5 orthovanadate, the first published structure for any member of this super-family (**2d1g** code in the
6 Protein Data Bank). The DV anion is linked to the chain B of the asymmetric unit through three
7 histidine and a lysine, to the chain A obtained with a symmetry operation through two asparagine,
8 and to one water molecule. The stronger hydrogen bond interactions between DV and the rest of the
9 protein takes place on the most reactive oxygen atoms (NH...O interactions with a dN...O < 2.70 Å
10 at Ob, Oc, Oe). Therefore, these results show that the hydrogen bond behavior of the DV anion we
11 have observed and described remains the same when the DV anion is bound to a protein.
12
13
14
15
16
17
18
19
20
21
22
23
24
25

26 Tiago et al.²⁰ have performed a docking study using the structure of truncated *Dictyostelium*
27 *discoideum* myosin motor domain (**S1dC** code in the Protein Data Bank). These authors have used
28 the theoretical results⁴⁶ for the modelisation of the DV assuming that Ob and Oc oxygen atoms have
29 a charge of -2 and the other oxygen atoms have a charge of -1, while the charge of the vanadium
30 atom were fixed to +2.4. We have computed the EP at the molecular surface of the decavanadate
31 anion. The values vary from -6.5 e.Å⁻¹ to -9.81 e.Å⁻¹ compared to those determined experimentally
32 or theoretically by Kempf et al.⁴⁶ (Table 7). The approximation chosen by Tiago et al.,²⁰ give
33 significant different EP values at the molecular surface, which could imply some uncertainties in the
34 docking results.
35
36
37
38
39
40
41
42
43
44
45
46

47 Pezza et al.¹⁵ have studied the inhibition of the ATPase activity and the DNA binding capability of
48 bacterial MutS and have shown that the ATPase activity of *Pseudomonas aeruginosa* and *Escheria*
49 *coli* is inhibited by orthovanadate and DV anion. Docking of DV on the ATP-binding region of
50 MutS showed that energetically more favorable interaction of this compound would take place with
51 the complex MutS-ADP-Mg, suggesting that the inhibitory effect could be produced by a steric
52 impediment of the protein ATP/ADP exchange. New docking, using our precise determination of the
53 electronic and electrostatic properties of the DV anion, could improve these results.
54
55
56
57
58
59
60

1 Nilius et al.¹⁰³ has tested the effects of the DV on TRPM4 a Ca²⁺-activated voltage dependent
2 monovalent cation channels, whose activity is potently blocked by intracellular ATP⁴⁻. The DV
3 induces a dramatic shift in the voltage dependence and decreases the voltage sensitivity of TRPM4
4 when applied to the inner side of excised patches. Using an analogy approach, the authors have
5 identified the site of DV action resides in the C-terminus of TRPM4. For this case a docking study
6 using our DV properties could give new insight in the understanding of the mechanism.
7
8
9
10
11
12
13
14
15
16

17 One can divide the examples explored below in two groups; the first group, constituted by
18 Ca²⁺ATPase, ABC-ATPase, myosin and TRPM4, contains biological targets against which DV
19 possesses inhibition properties. The second group contains the acid phosphatase A for which the X-
20 DV anion is not supposed to participate to the inhibition. Therefore one can conclude the following:
21
22
23
24
25

26 i) Due to the potent different types of interaction (strong and weak DH...O bonds, cations...O), DV
27 could definitively try to be used as a crystallization agent. That could be done in the cases where
28 orthovanadate is an inhibitor. The pH conditions have to be carefully controlled. ii) Our hydrogen
29 bond or cation interaction predictions fit well with the only reported high resolution (**2d1g**) structure.
30 It could even help for determining some remaining water molecules in further structures. iii) Our
31 atomic net charges, hydrogen bond and cation interaction predictions could be suitably used in the
32 docking computations and would probably give better results than the common used charges.
33
34
35
36
37
38
39
40
41
42
43
44

45 ACKNOWLEDGEMENTS.

46
47
48
49

50 NB-P, ASdB and UM would thank the French foreign Ministry for a COCOOP support on this
51 project. NB-P and UM would thank the Ministry of Science and Technological Development of the
52 Republic of Serbia (Project 142047). This paper is a part of a join PhD thesis between the University
53 of Belgrade, Faculty of Physical Chemistry and Ecole Centrale Paris. JCP thanks FCT, FEDER,
54 POCI 2010 and PPCDT/QUI/56959/2004.
55
56
57
58
59
60

SUPPORTING INFORMATION.

1
2
3
4
5 Tables of atomic coordinates, thermal displacement parameters, bond lengths and bond angles,
6
7 figures of local coordinates scheme, experimental, dynamic and static deformation maps of different
8
9 planes are deposited as supporting information. They are available free of charge from the JACS
10
11 home page (<http://pubs.acs.org/JACS>).
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

REFERENCES

- 1
2
3
4
5
6 (1) Crans, D.C. *Comments Inorg. Chem.* **1994**, *16*, 1.
7
8 (2) Aureliano, M.; Crans D.C. *J. Inorg. Biochem.* **2009**, *103*, 536.
9
10 (3) Chasteen, N.D.; Grady, J.K.; Hoolway, C.E. *Inorg. Chem* **1986**, *25*, 2754.
11
12 (4) Soares, S.S.; Aureliano, M.; Joaquim, N.; Coucelo, J.M. *J. Inorg. Biochem.* **2003**, *94*, 285.
13
14 (5) Aureliano, M.; Joaquim, N.; Sousa, A.; Martins, H.; Coucelo, J. *J. Inorg. Biochem.* **2002**,
15
16
17
18
19
20
21
22 (6) Farahbakhsh, M.; Schmidt, H.; Rehder, D. *Chem. Ber.* **1997**, *130*, 1123.
23
24 (7) Ramos, S.; Tiago, T.; Duarte, R.; Moura, J.J.G.; Aureliano, M. *6th International Vanadium*
25
26
27
28
29
30 (8) Fraqueza, G.; Rito, E.; Brissos, R.; Tiago, T.; Martins, J.; Duarte, R.O.; Moura, J.J.;
31
32
33
34 Aureliano M. *6th International Vanadium Symposium*, **2008**, 46
35 (9) Brissos, R.; Fontes, F.L.; Martins, H.; Fraqueza, G.; Tiago, T.; Martins, J.; Duarte, R.O.;
36
37
38
39 Moura, J.G.; Aureliano, M. *6th International Vanadium Symposium*, **2008**, P44
40 (10) Csermely, P.; Varga, S.; Martonosi, A. *Eur. J. Biochem.* **1985**, *150*, 455.
41
42 (11) Csermely, P.; Martonos, i A.; Levy, G.C.; Ejchart, A.J. *Biochem. J.* **1985**, *230*, 807.
43
44 (12) Aureliano, M. *J. Inorg. Biochem.* **2000**, *80*, 145.
45
46 (13) Krstić, D.; Čolović, M.; Bosnjaković-Pavlović, N.; Spasojević-de Biré, A.; Vasić, V. *Gen.*
47
48
49
50
51
52
53
54
55
56
57
58
59 (14) Rice, W.J.; Young, H.S.; Martin, D.W.; Sachs, J.R.; Stokes, D.L. *Biophys. J.* **2001**, *80*,
60
2187.
(15) Pezza, R.J.; Villarreal, M.A.; Montich, G.G.; Argarana, C.A. *Nucleic Acids Res.* **2002**,
4700.
(16) Aureliano, M. *J. Inorg. Biochem.* **2000**, *80*, 141.

- 1 (17) Tiago, T.; Aureliano, M.; Duarte, R.O.; Moura, J.J.G. *Inorg. Chim. Acta* **2002**, 339.
2
3 (18) Tiago, T.; Aureliano, M.; Gutierrez-Merino, C.G. *Biochemistry* **2004**, 43, 5551.
4
5
6 (19) Tiago, T.; Aureliano, M.; Moura, J.J. *J. Inorg. Biochem.* **2004**, 98, 1902.
7
8
9 (20) Tiago, T.; Martel, P.; Gutierrez-Merino, C.G.; Aureliano, M. *Bioch. Bioph. Acta* **2007**,
10
11 1774, 474.
12
13
14 (21) Felts, R.L.; Reilly, T.J.; Tanner, J.J. *J. Biol.Chem.* **2006**, 281, 30289.
15
16
17 (22) Boyd, D.W.; Kustin, K.; Niwai, M. *Biochim. Biophys. Acta* **1985**, 827, 472.
18
19
20 (23) Pluskey, S.; Mahroof-Tahir, M.; Crans, D.C.; Lawrance, D.S. *Biochem J.* **1997**, 321, 333.
21
22 (24) Okamura, N.; Sakai, T.; Nishimura, Y.; Araki, S.; Yamaguchi, M.; Ishibashi, S. *Biol.*
23
24 *Pharm. Bull.* **1999**, 22,799.
25
26
27 (25) Crans, D.C.; Sudkahar, K.; Zamborelli, T.J. *Biochemistry* **1992**, 6812.
28
29
30 (26) Messmore, J.M.; Raines, R.T. *Archive Biochem. Biophys.* **2000**, 381, 25.
31
32
33 (27) Hir, M. *Biochem. J.* **1991**, 273, 795.
34
35
36 (28) Soman, G.; Chang, Y.C.; Graves, D.J. *Biochemistry* **1983**, 22, 4994.
37
38
39 (29) Garcia-Vicente, S. et al. *Diabetes* **2007**, 57, 486.
40
41 (30) Yraola, F.; Garcia-Vicente, S.; Marti, L.; Albericio, F.; Zorzano, A.; Royo, M. *Chem. Biol.*
42
43 *Drug Des.* **2007**, 69, 423.
44
45
46 (31) Aureliano, M.; Gandara, R.M.C. *J. Inorg. Biochem.* **2005**, 99, 979.
47
48
49 (32) Meicheng, S.; Lifeng, W.; Youqi, T. *Sci. Sin, Ser B* **1984**, 2, 137.
50
51
52 (33) Crans, D.C. *Comments Inorg. Chem.* **1994**, 16, 35.
53
54 (34) Crans, D.C.; Mahroof-Tahir, M.; Anderson, O.P.; Miller, M.M. *Inorg. Chem.* **1994**, 33,
55
56 5586.
57
58
59 (35) Wang, X.; Liu, H.-X.; You, X.X.; You, X.-Z. *Polyhedron* **1993**, 12, 77.
60

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (36) Spasojević-de Biré, A.; Kremenović, A.; Morgan, G.; Ghermani, N.E. *J. Phys Chem.* **2002**, *A106*, 12170.
- (37) Bouhmaida, N.; Dutheil, M.; Ghermani, N.E.; Becker, P. *J. Chem. Phys.* **2002**, *116*, 14
- (38) Ghermani, N.E.; Spasojević-de Biré, A.; Bouhmaida, N.; Ouharzoune, S.; Bouligand, J.; Layre, A.; Gref, R.; Couvreur, P. *Pharm. Res.* **2004**, *21*, 598.
- (39) Overgard J.; Hibbs D.E. *Acta Crystallogr.* **2004**, *A60*, 480.
- (40) Pizzonero, M.; Keller, L.; Dumas, F.; Ourevitch, M.; Morgan, G.; Ghermani, N. E.; Spasojević-de Biré, A.; Bogdanović, G. A.; d'Angelo, J. *J. Org. Chem.* **2004**, *69*, 4336.
- (41) Firley, D.; Courcot, B.; Gillet, J.M.; Fraisse, B.; Zouhiri, F.; Desmaele, D.; D'Angelo, J.; Ghermani, N.E. *J. Phys. Chem.* **2006**, *B110*, 537.
- (42) Bergstrom, O.; Gustafsson, T.; Thomas, J.O. *Solid State Ionics* **1998**, *110*, 179.
- (43) Claiser, N. DEA report, Université Henri Poincaré, Nancy, **2000**
- (44) Ozerov, R.P.; Streltsov, V.A.; Sobolev, A.N.; Figgis, B.N.; Volkov, V.L. *Acta Crystallogr.* **2001**, *B57*, 244.
- (45) Rohmer, M.M.; Ernenwein, R.; Ulmschneider, M.; Wiest, R.; Benard, M. *Int. J. Quantum Chem.* **1991**, *40*, 723.
- (46) Kempf, J.Y.; Rohmer, M.M.; Poblet, J.M.; Bo, C.; Benard, M. *J. Am. Chem. Soc.* **1992**, *114*, 1136.
- (47) Rohmer, M.M.; Benard, M.; Blaudeau, J.P.; Maestre, J.M.; Poblet, J.M. *Coord. Chem. Rev.* **1998**, *178-180*, 1019
- (48) Henry, M. *J. Cluster Sci.* **2002**, *13*, 437
- (49) Brown, I.D.; Shannon, R.D. *Acta Cryst.* **1973**, *A29*, 266.
- (50) Klemperer, W.G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 3544.
- (51) Bogdanović, G.A.; Bošnjaković-Pavlović, N.; Spasojević-de Biré, A.; Ghermani, N.E.; Mioč, U. *J. Serb. Chem. Soc.* **2007**, *72*, 545.

- 1 (52) Hansen, N.; Coppens, P. *Acta Crystallogr.* **1978**, A34, 909.
- 2
- 3 (53) Coppens, P. in *X-ray charge densities and chemical bonding*. Oxford: International Union
4 of Crystallography/Oxford University Press, 1997.
- 5
- 6
- 7
- 8 (54) Coppens, P.; Guru Row, T.N.; Leung, P.; Stevens, E.D.; Becker, P.; Yang, Y.W. *Acta*
9 *Crystallogr.* **1979**, A35, 63.
- 10
- 11
- 12
- 13 (55) Bader, R.F. in *Atoms in molecules: A Quantum Theory* Int. Series of Monographs in
14 Chemistry 22, Oxford University Press: Oxford, 1990.
- 15
- 16
- 17
- 18 (56) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 627.
- 19
- 20
- 21 (57) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, 57, 1259.
- 22
- 23
- 24 (58) Abramov, Y.A. *Acta Crystallogr.* **1997**, A53, 264.
- 25
- 26 (59) Souhassou, M.; Blessing, B. *J. Appl. Crystallogr.* **1999**, 32, 210.
- 27
- 28
- 29 (60) Souhassou, M. *19th European Crystallographic Meeting*, **2000**, 195
- 30
- 31
- 32 (61) Holladay, A.; Leung, P.; Coppens, P. *Acta Crystallogr.* **1983**, A39, 377.
- 33
- 34 (62) Ghermani, N.E.; Bouhaida, N.; Lecomte, C. *Internal report UMR CNRS 7036, Université*
35 *Henri Poincaré, Nancy1, France and UMR CNRS 8612, Université Paris XI, France,*
36 **1992-2001**
- 37
- 38
- 39
- 40
- 41
- 42 (63) Drechsel, E. *Ber.* **1887**, 20, 1452.
- 43
- 44 (64) Chinea, E.; Dakternieks, D.; Duthie, A.; Ghilardi, C.A.; Gili, P.; Mederos, A.; Midollini,
45 S.; Orlandini, A. *Inorg. Chim. Acta* **2000**, 298, 172.
- 46
- 47
- 48
- 49
- 50 (65) Bruker-AXS, *Analytical X-ray Instruments Inc., Madison* **1998**.
- 51
- 52 (66) Blessing, R.H. *J. Appl. Crystallogr.* **1997**, 30, 421.
- 53
- 54
- 55 (67) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.C.; Polidori, G.;
56 Camalli, M. *J. Appl. Crystallogr.* **1994**, 27, 435.
- 57
- 58
- 59 (68) Sheldrick, G.M. *University of Göttingen, Germany*, **1997**.
- 60 (69) Farrugia, L.J. *Appl. Cryst.* **1999**, 32, 837.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (70) Burnett, M.N.; Johnson, C.K. *Oak Ridge National Laboratory, Tennessee, USA* **1996**.
- (71) Coppens, P. *Coord. Chem. Rev.* **1985**, *65*, 285.
- (72) International Tables for X-ray Crystallography; Kynoch Press: Birmingham, U.K. **1974**, IV pp 103.
- (73) Macchi, P.; Garlaschelli, L.; Martinengo, S.; Sironi, A. *J. Am. Chem. Soc.* **1999**, *121*, 10428.
- (74) Ozerov, R.P.; Streltsov, V.A.; Sobolev, A.N.; Figgis, B.N.; Volkov, V.L. *Acta Crystallogr.* **2001**, *B57*, 244.
- (75) Farrugia, L.J.; Mallinson, P.R.; Stewart, B. *Acta Crystallogr.* **2003**, *B59*, 234.
- (76) Martin, M.; Rees, B.; Mitschler, A. *Acta Crystallogr.* **1982**, *B38*, 6.
- (77) Rees, B. *Acta Crystallogr.* **1976**, *A32*, 483.
- (78) See crystal structure studies references in Table S1, Supplementary Information Material.
- (79) Allen, F.H. *Acta Crystallogr.* **2002**, *B58*, 380.
- (80) See crystal structure studies references in Table S2, Supplementary Information Material.
- (81) ICSD, *Fachinformationszentrum (FIZ) Karlsruhe* **2007**.
- (82) See crystal structure studies references in Table S3, Supplementary Information Material.
- (83) See crystal structure studies references in Table S4, Supplementary Information Material.
- (84) Kruger, T.; Bruhn, C.; Steinborn, D. *Org. Biomol. Chem.* **2004**, *2*, 2513.
- (85) Muller, J.; Freisinger, E. *Acta Crystallogr.* **2005**, *E61*, o320.
- (86) Muller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100*, 143.
- (87) See crystal structure studies references in Table S5, Supplementary Information Material.
- (88) Bader, R.F.; Preston, H.J.T. *Int. J. Quantum Chem* **1969**, *3*, 327.
- (89) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, *285*, 170.
- (90) Espinosa, E.; Souhassou, M.; Lachekar, H.; Lecomte, C. *Acta Crystallogr.* **1999**, *B55*, 563

- 1 (91) Desiraju, G.R.; Steiner, T. in *The Weak Hydrogen Bond in Structural Chemistry and*
2 *Biology*. Oxford Univ. Press, Oxford, 1999
3
4
5 (92) Kubicki, M.; Borowiak, T.; Dutkiewicz, G.; Souhassou, M.; Jelsch, C.; Lecomte, C. *J.*
6 *Phys. Chem* **2002**, *B106*, 3706.
7
8
9
10 (93) Spasojević-de Biré, A.; Nguyen, Q.D.; Becker, P.J.; Benard, M.; Strich, A.; Thieffry, C.;
11 Hansen, N.K.; Lecomte, C. in *Application of charge density research to chemistry and*
12 *drug design*. NATO Asi Series, Jeffrey Ed., Plenum Publisher, New York **1991**, pp 385.
13
14
15
16
17
18 (94) Spasojević-de Biré, A.; Dao, N.Q.; Hansen, N.K.; Fisher, E.O. *Inorg. Chem.* **1993**, *32*,
19 5354.
20
21
22
23 (95) Lee, C.R.; Wang, C.C.; Chen, K.C.; Lee, G.H.; Wang, Y. *J. Phys. Chem.* **1999**, *A103*, 156.
24
25
26 (96) Volkov, A.; Gatti, C.; Abramov, Y.; Coppens, P. *Acta Crystallogr.* **2000**, *A56*, 252.
27
28
29 (97) Toyoshima, C.; Nakasako, M.; Nomura, H.; Ogawa H. *Nature.* **2000**, *405*, 647.
30
31
32 (98) Toyoshima, C.; Nomura, H. *Nature* **2002**, *418*, 605.
33
34
35 (99) Stokes, D.L.; Green, N.M. *Biophys. J.* **2000**, *78*, 1765.
36
37 (100) Xu, C.; Rice, W.J.; He, W.; Stockes, D.L. *J. Mol. Biol.* **2002**, *316*, 201.
38
39 (101) Hinsén, K.; Reuter, N.; Navaza, J.; Stokes, D.L.; Lacapere, J.J. *Biophys. J.* **2005**, *88*, 818.
40
41
42 (102) Hua, S.; Inesi, G. *J. Biol. Chem.* **2000**, *275*, 30546.
43
44
45 (103) Nilius, B.; Prenen, J.; Janssens, A.; Voets, T.; Droogmans, G. *J. Physiol.* **2004**, *560*, 753.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

TABLE CAPTIONS

Table 1. X-ray diffraction experiment and refinement details ^a

^aThe value R_{int} , gof , R_1 and wR_1 are defined as $R_{\text{int}} = \sum_{\text{H}} \left[\frac{N_{\text{H}}}{N_{\text{H}} - 1} \right]^{\frac{1}{2}} \sum_{i=1}^{N_{\text{H}}} |I_i(\text{H}) - I_i^{\text{mean}}(\text{H})| / \sum_{\text{H}} \sum_{i=1}^{N_{\text{H}}} |I_i(\text{H})|$ $I(\text{H})$ is the observed reflection intensity for H vector. $N(\text{H})$ is the number of equivalent and redundant reflections. $R = \sum \|F_{\text{obs}} - F_{\text{calc}}\| / \sum |F_{\text{obs}}|$, $R_w = \left[\sum w(F_{\text{obs}} - F_{\text{calc}})^2 / \sum wF_{\text{obs}}^2 \right]^{\frac{1}{2}}$, $\text{GOF} = \left[\sum w[F_{\text{obs}}^2 - F_{\text{calc}}^2]^2 / (m_{\text{obs}} - n_p) \right]^{\frac{1}{2}}$. The statistical weight is $w = 1/\sigma^2(F_{\text{obs}})$ or $1/\sigma^2(F_{\text{obs}}^2)$ where σ^2 is the variance, m_{obs} and n_p are the number of observations and refined parameters, respectively.

Table 2. Intramolecular distances and topology analysis of the DV anion ^b

^b Different V-O distances (\AA) are reported according to the vanadium and oxygen classification. This work (estimated standard deviations in parentheses), theoretical data from Kempf ⁴⁸ and average values from 37 structures retrieved in CSD bases (second column in italic). Results of the topological analysis of charge density at (3,-1) (BCP) of the DV anion. Our results ($\rho(r_{\text{cp}})$ is the electron density at the BCP ($\text{e}\text{\AA}^{-3}$), $\nabla^2\rho(r_{\text{cp}})$ is Laplacian at the BCP ($\text{e}\text{\AA}^{-5}$), ε is ellipticity, $\lambda_1, \lambda_2, \lambda_3$ are the eigenvalues at the BCP, H is the total energy density (Kcal.mol^{-1}) are compared to the $\rho(r_{\text{cp}})$ and $\nabla^2\rho(r_{\text{cp}})$ theoretical data. ⁴⁵

Table 3. Selected bond lengths (\AA) in cytosine molecules with estimated standard deviations in parentheses**Table 4.** Distances (\AA) and angles ($^\circ$) of the hydrogen bonds (D donor, A acceptor) ^c

^c Estimated standard deviations are given in parentheses. (i) = -x,-y+1,-z+2, (ii) = -x+1,-y+1,-z+2, (iii) = x,+y,+z+1, (iv) = -x+2,-y,-z+1, (v) = x+1,+y,+z, (vi) = -x+1,-y,-z+2, (vii) = -x+1,-y+1,-z+1, (viii) = +x,+y,+z-1, (ix) = x-1,+y,+z, (x) = -x,-y+1,-z+1. Results of the topology analysis are given. Unit are given in Table 2. d_1 and d_2 are BCP-atoms distance (\AA).

1
2
3 **Table 5.** Experimental determination of the *d* orbital (e) populations of the vanadium in the DV
4
5 anion
6
7

8
9 **Table 6.** Experimental and theoretical net atomic charge (e) for vanadium atoms in a DV anion
10
11

12
13 **Table 7.** Experimental and theoretical net atomic charges (e) and EP ($e\text{\AA}^{-1}$) at the molecular surface
14
15 in the vicinity of the oxygen atoms of the DV anion
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

FIGURE CAPTIONS

1
2
3
4
5 **Figure 1.** ORTEP views of the $\text{Na}_3 [\text{V}_{10}\text{O}_{28}] (\text{C}_4\text{N}_3\text{OH}_5)_3 (\text{C}_4\text{N}_3\text{OH}_6)_3 \cdot 10\text{H}_2\text{O}$ structure. a) and b)
6
7 labeling scheme and type of atoms for the SV anion, c) cytosine - cytosinium interactions between
8
9 cytosinium A and A' and d) octahedral environment of sodium atoms.

10
11
12
13
14 **Figure 2.** Residual electron density maps. a) DV-horizontal plane (plane containing O10, O11, O21,
15
16 O27, O22, O61, V3, V4 and V5 atoms), b) DV-vertical-XZ plane (plane containing O12, O13, O22,
17
18 O61, V1 and V2 atoms) c) DV-vertical-YZ (plane containing O31 O32 and V4 atoms). O61 oxygen
19
20 atoms are omitted. Contour intervals are $0.1 \text{ e}\text{\AA}^{-3}$. Negative contours are dashed.

21
22
23
24
25
26 **Figure 3.** Crystal packing. The DV – sodium chains. Cytosine molecules have been omitted.

27
28
29
30
31 **Figure 4.** Static model deformation density. Planes a) and b) and contours as defined in Figure 2. c)
32
33 DV-vertical-YZ (plane containing O31 O32 and V4 atoms). The longest V-O bonds (VI-Oa, VII-Oa,
34
35 VIII-Oa) in the cage are in yellow, the medium bonds are in green (VII-Od) and blue (VII-Oe) color
36
37 and shortest V-O bonds (VI-Oe, VIII-Of, VII-Og) are in red color. The other bonds are in dark color.

38
39
40
41
42 **Figure 5.** Behavior of $\rho(r_{\text{cp}})$ of the V-O bond as a function of the interatomic distance.

43
44
45
46
47 **Figure 6.** Static deformation density of D-H...A hydrogen bonds. Planes containing a) O32, H1w'
48
49 and O1w, b) O25, H4c^(viii) and H5w^(vii), c) O24, H4c^(viii) and H4b^(viii), d) O22, H4c^(viii) and H5c^(viii), e)
50
51 O10, H5a⁽ⁱ⁾ and H5b^(vi), f) Na2, O5w and Na1 atoms. Contours as defined in Figure 2.

52
53
54
55 **Figure 7.** Experimental EP on the molecular surface ($0.007 \text{ e}\text{\AA}^{-3}$) (column 1-4). Column 1-3 Na_3
56
57 $[\text{V}_{10}\text{O}_{28}] (\text{C}_4\text{N}_3\text{OH}_5)_3 (\text{C}_4\text{N}_3\text{OH}_6)_3 \cdot 10\text{H}_2\text{O}$, column 4 $(\text{NH}_4)_6 [\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$. Electrostatic potential
58
59 of the decavanadate isolated from the crystal computed from the multipole refinement (column 1),
60
from the charge determined by the AIM method (column 2), and by a κ refinement (column 3 and

1 4). Theoretical EP (column 5-6) computed from the charge determined by the Mulliken partitioning
2
3 (column 5) and by a PACHA partitioning (column 6).
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 1.

Chemical formula	Na ₃ [V ₁₀ O ₂₈] (C ₄ N ₃ OH ₅) ₃ (C ₄ N ₃ OH ₆) ₃ · 10H ₂ O
Temperature (K)	210(1)
Wavelength (Å)	0.71073
Cell setting, space group	triclinic, P $\bar{1}$
Z	1
Crystal size: (mm) x (mm) x (mm)	0.36 x 0.29 x 0.18
Density (calculated) (Mg/m ³)	2.12
a (Å)	9.8526(1)
b (Å)	12.2227(1)
c (Å)	13.0852(1)
α (°)	85.995(1)
β (°)	80.110(1)
γ (°)	70.954(1)
Volume(Å ³)	1467.25(3)
[sinθ/λ] _{max} (Å ⁻¹)	1.11
Scan width (°) / scan method	0.15° / Δω scan
Crystal-to-detector distance (d) (cm)	4.075
Total frames / time per frame (s)	38400 / 2 to 30
Absorption correction	SADABS
Total measured reflexions	221 309
R _{int} (F ²) before SADABS	0.071
R _{int} (F ²) after SADABS	0.031
Number of reflexions used after SADABS	207 128
R _{int}	0.0276
Number of reflexions used in SHELX : all data / unique (F ₀ > 4σF ₀)	28 757 / 20 587
Spherical refinement : R(%) / R _w (%) / GOF / parameters	2.88 / 3.27 / 1.28 / 28
Number of reflexions used in MOLLY(I>3σ(I))	18 394
κ refinement : R (%) / R _w (%) / GOF / parameters	2.76 / 2.97 / 1.16 / 20
Multipole refinement : R (%) / R _w (%) / GOF / parameters	2.32 / 2.34 / 0.91 / 505

Table 2.

Vanadium atoms	Type of Vanadium bonds	bond	distance		ρ_{cp}		$\nabla^2\rho(r_{cp})$		ε	λ_1	λ_2	λ_3	$H(r_{cp})$
			this work	Kempf ⁴⁶	this work	Kempf ⁴⁶	this work	Kempf ⁴⁶					
V-Oa	VI-Oa 2.113	V4-O61	2.0781(5)	2.116	0.52	0.47	8.87	7.59	0.01	-2.09	-2.08	13.04	-5.71
		V4-O61	2.1583(5)		0.44		6.90		0.05	-1.63	-1.56	10.09	-3.84
	VII-Oa 2.323	V3-O61	2.3324(5)	2.316	0.32	0.28	4.36	5.52	0.03	-0.94	-0.91	6.2	-1.98
		V5-O61	2.2937(5)		0.34		4.72		0.10	-1.02	-0.93	6.68	-2.22
	VIII-Oa 2.244	V1-O61	2.2679(6)	2.243	0.37	0.34	5.17	6.49	0.013	-1.19	-1.18	7.54	-1.94
		V2-O61	2.2414(5)		0.37		5.34		0.06	-1.13	-1.06	7.52	-2.40
V-Ob	VI-Ob 1.928	V4-O31	1.9217(5)	1.927	0.77	0.77	13.66	9.59	0.03	-4.1	-3.98	21.72	-18.09
		V4-O32	1.9427(5)		0.74		12.76		0.03	-3.94	-3.82	20.52	-17.09
	VIII-Ob 2.006	V1-O32	1.9981(6)	2.013	0.65	0.62	11.04	8.60	0.03	-3.25	-3.14	17.43	-12.77
		V1-O31	2.0205(5)		0.58		10.04		0.03	-2.60	-2.52	15.16	-8.37
		V2-O31	2.0040(5)		0.65		10.95		0.03	-3.25	-3.17	17.36	-12.70
		V2-O32	2.0268(6)		0.58		10.02		0.13	-2.76	-2.43	15.21	-8.77
V-Oc	VII-Oc 1.880	V3-O20	1.8504(6)	1.883	0.79	0.84	14.49	10.63	0.03	-4.1	-3.96	22.55	-18.83
		V3-O25	1.8716(5)		0.85		14.99		0.06	-4.91	-4.64	24.54	-24.63
		V5-O23	1.8795(5)		0.86		14.83		0.04	-4.91	-4.72	24.46	-26.38
		V5-O24	1.8911(5)		0.86		14.61		0.07	-5.1	-4.72	24.47	-26.97
	VIII-Oc 1.821	V1-O23	1.8132(6)	1.826	1.06	0.97	17.77	12.41	0.05	-6.88	-6.54	31.19	-44.12
		V1-O20	1.8338(6)		0.97		17.45		0.04	-5.83	-5.59	28.87	-32.89
		V2-O24	1.8141(6)		1.05		17.55		0.02	-6.55	-6.45	30.54	-42.70
		V2-O25	1.8240(6)		1.00		17.70		0.04	-6.07	-5.82	29.54	-36.40
V-Od	VII-Od 1.832	V3-O22	1.8871(6)	1.831	0.94	0.95	16.00	12.19	0.11	-5.76	-5.2	26.96	-32.90
		V5-O22	1.8795(6)		1.03		16.58		0.09	-6.65	-6.12	29.35	-42.65
V-Oe	VI-Oe 1.688	V4-O27	1.6848(5)	1.697	1.42	1.35	24.62	17.42	0.04	-9.55	-9.21	43.39	-80.50
		V4-O21	1.7059(6)		1.29		24.66		0.04	-8.30	-7.98	40.94	-60.71
	VII-Oe 2.049	V3-O21	2.0183(6)	2.032	0.57	0.55	9.88	8.46	0.08	-2.64	-2.43	14.95	-7.80
		V5-O27	2.0697(6)		0.54		8.78		0.05	-2.49	-2.38	13.75	-7.45
V-Of	VIII-Of 1.609	V1-O13	1.6189(6)	1.614	1.79	1.66	29.10	22.48	0.04	-13.67	-13.18	55.96	-133.72
		V2-O12	1.6230(6)		1.61		28.85		0.09	-11.74	-10.76	51.36	-102.93
V-Og	VII-Og 1.603	V3-O11	1.6115(6)	1.605	1.71	1.68	30.96	22.32	0.06	-12.28	-11.54	54.78	-114.57
		V5-O10	1.6120(6)		1.75		30.17		0.11	-13.54	-12.24	55.95	-124.92

Table3.

bond	Cytosinium A	Cytosinium B	Cytosine C
C4-N4	1.325(1)	1.322(1)	1.317(1)
C4-C5	1.430(1)	1.428(1)	1.427(11)
C5-C6	1.360(1)	1.359(1)	1.351(2)
C6-N1	1.357(1)	1.358(1)	1.385(2)
N1-C2	1.372(1)	1.363(1)	1.362(2)
C2-N3	1.372(1)	1.365(1)	1.357(1)
N3-C4	1.351(1)	1.354(1)	1.351(1)
C2-O2	1.242(1)	1.240(1)	1.254(2)

Table 4.

	D-H ...A	d (H-A)	d(D...A)	∠DHA	d ₁	d ₂	ρ(r _{cp})	∇ ² ρ(r _{cp})	ε	λ ₁	λ ₂	λ ₃	H(r _{cp})
O-H...O													
	O1w-H1w'...O32	1.6924(5)	2.6535(8)	174.49(5)	1.692	0.533	0.20	6.39	0.04	-0.95	-0.91	8.25	8.78
	O2w-H2w'...O20^(v)	1.7049(6)	2.672(1)	176.92(6)	1.705	0.547	0.18	5.96	0.02	-0.83	-0.82	7.60	8.72
	O4w-H4w'...O31^(x)	1.7583(5)	2.7201(9)	177.40(5)	1.758	0.570	0.15	5.30	0.02	-0.62	-0.61	6.53	8.28
	O2w-H2w ...O21	1.8311(5)	2.753(1)	159.29(6)	1.831	0.668	0.14	3.49	0.30	-0.75	-0.57	4.82	4.62
	O5w-H5w'...O2b	1.8439(7)	2.777(1)	162.16(5)	1.844	0.662	0.11	3.51	0.31	-0.66	-0.5	4.67	5.54
	O3w-H3w'...O12^(x)	1.8620(6)	2.8132(9)	169.01(5)	1.862	0.654	0.10	3.58	0.29	-0.53	-0.42	4.53	6.03
	O5w-H5w...O25^(vii)	1.8921(6)	2.8356(9)	164.95(5)	1.892	0.647	0.09	3.62	0.22	-0.37	-0.30	4.29	6.46
	O3w-H3w...O2c^(ix)	1.9730(9)	2.841(1)	148.40(6)	1.973	0.769	0.10	2.31	0.33	-0.53	-0.4	3.23	3.39
	O2w-H2w'...O11^(iv)	2.8023(7)	3.306(1)	113.23(5)									
	O4w-H4w...O11^(vii)	2.8271(7)	3.315(1)	112.60(5)									
	O1w-H1w'...O12	2.9091(7)	3.449(1)	115.72(5)									
	O2w-H2w...O11^(iv)	2.9382(7)	3.306(1)	103.95(5)									
	O5w-H5w...O12^(vii)	2.9378(7)	3.302(1)	103.67(5)									
	O3w-H3w'...O13^(x)	2.9904(6)	3.3954(9)	106.75(4)									
N-H...O	D-H ...A												
	N1a-H1a...O4w	1.7006(7)	2.705(1)	173.70(6)	1.701	0.531	0.19	6.26	0.04	-0.96	-0.92	8.14	9.03
	N4c-H3c...O2b⁽ⁱⁱ⁾	1.7475(8)	2.756(1)	173.49(6)	1.748	0.595	0.27	3.74	0.02	-1.56	-1.53	6.84	-0.35
	N1b-H1b...O1w	1.7519(7)	2.757(1)	173.48(6)	1.752	0.597	0.17	4.32	0.26	-0.99	-0.79	6.1	5.52
	N4a-H3a...O2a⁽ⁱ⁾	1.8324(7)	2.841(1)	177.12(6)	1.834	0.641	0.20	3.01	0.03	-1.11	-1.08	5.21	1.40
	N4b-H4b...O24^(viii)	1.8536(5)	2.8603(9)	174.92(5)	1.854	0.632	0.09	3.77	0.52	-0.46	-0.3	4.53	6.78

	N4b-H3b...O2c⁽ⁱⁱ⁾	1.866(1)	2.874(2)	178.47(7)	1.866	0.619	0.09	3.86	0.38	-0.42	-0.31	4.59	7.06
	N4a - H4a...O23⁽ⁱ⁾	1.8678(6)	2.8581(9)	166.44(6)	1.867	0.707	0.12	2.80	0.66	-0.77	-0.47	4.04	3.86
	N4c-H4c...O22⁽ⁱⁱⁱ⁾	1.8798(5)	2.875(1)	169.84(1)	1.879	0.695	0.13	2.53	0.49	-0.66	-0.45	3.64	3.06
	N1c-H1c...O2w	2.288(1)	3.084(2)	155.6(1)									
	N1c-H1c...O20^(v)	2.4963(5)	3.1466(6)	135.8(1)									
	N4c-H4c...O25^(viii)	2.7832(6)	3.373(1)	117.91(6)									
	N4c-H4c...O24^(viii)	2.9210(6)	3.407(1)	110.55(6)									
N-H...N	D-H ...A												
	N3b-H2b...N3c⁽ⁱⁱ⁾	1.8087(9)	2.816(1)	173.39(5)	1.801	0.594	0.39	1.78	0.03	-2.3	-2.22	6.31	-11.72
	N3a-H2a...N3a⁽ⁱ⁾	1.8491(8)	2.838(2)	167.72(2)									
C-H...O	D-H ...A												
	C5b-H5b...O10^(vi)	2.0702(6)	3.150(1)	98.22(6)									
	C5a-H5a...O10⁽ⁱ⁾	2.2430(7)	3.304(1)	165.93(6)	2.242	0.865	0.04	1.25	0.60	-0.16	-0.1	1.52	2.28
	C6c-H6c...O11^(iv)	2.4177(8)	3.222(2)	144.9(1)	2.417	1.016	0.08	0.95	0.08	-0.24	-0.22	1.42	0.84
	C6b-H6b...O10	2.6784(7)	3.292(1)	115.46(6)									
	C5c-H5c...O22⁽ⁱⁱⁱ⁾	2.6819(5)	3.489(1)	130.78(6)									
	C6b-H6b...O23	2.7570(6)	3.147(1)	100.89(6)	2.758	1.281	0.06	0.70	0.29	-0.16	-0.13	0.99	0.75
	C6a-H6a...O11^(vii)	2.8154(7)	3.384(1)	112.86(6)									
	C6c-H6c...O22^(iv)	2.8392(5)	3.390(1)	119.2(1)									

Table 5.

	V(I)	V(II)	V(III)
d_{z^2}	0.57(4)	0.70(5)	0.68(5)
$d_{x^2-y^2}$	0.68(4)	0.61(5)	0.68(5)
d_{xy}	0.60(8)	0.60(9)	0.61(8)
d_{xz}	0.62(4)	0.66(5)	0.57(5)
d_{yz}	0.56(4)	0.64(5)	0.67(5)
d orbital population	3.03(5)	3.20(5)	3.20(5)

Table 6.

		Experimental			Theoretical		
		Na ₃ [V ₁₀ O ₂₈](C ₄ N ₃ OH ₅) ₃ (C ₄ N ₃ OH ₆) ₃ ·10H ₂ O This work			(NH ₄) ₆ V ₁₀ O ₂₈ ·6H ₂ O Bogdanovic et al. ⁵¹	[V ₁₀ O ₂₈] ⁶⁻ Henry ⁴⁸	[V ₁₀ O ₂₈] ⁶⁻ Kempf et al. ⁴⁶
atom	type	Multipole refinement	AIM	κ refinement	κ refinement	PACHA	Mulliken
V4	I	+1.97(5)	+1.688	+1.94(5)	+2.0(1) +1.9(1)	+1.514	+2.13
V3	II	+1.79(5)	+1.540	+1.85(5)	+1.7(1) +1.8(1)	+1.865	+2.04
V5		+1.81(5)	+1.509	+1.71(5)	+1.6(1) +1.6(1)	+1.870	
V1	III	+1.80(5)	+1.533	+1.74(5)	+1.6(1) +1.6(1)	+1.780	+2.05
V2		+1.80(5)	+1.535	+1.78(5)	+1.7(1) +1.6(1)	+1.766	

Table 7.

		Experimental						Theoretical				
		Na ₃ [V ₁₀ O ₂₈] (C ₄ N ₃ OH ₅) ₃ (C ₄ N ₃ OH ₆) ₃ ·10H ₂ O This work			(NH ₄) ₆ V ₁₀ O ₂₈ · 6H ₂ O Bogdanovic et al. ⁵¹			[V ₁₀ O ₂₈] ⁶⁻ Henry ⁴⁸		[V ₁₀ O ₂₈] ⁶⁻ Kempf et al. ⁴⁶		
		Multipole refinement	κ refinement		AIM		κ refinement		PACHA		Mulliken	Ab initio SCF
		EP	charge	EP	charge	EP	charge	EP	charge	EP	charge	EP
O61	a		-0.88(5)		-0.724		-0.7(1)		-0.861		-1.27	
O31	b	-8.7	-0.97(5)	-	-0.873	-	-0.9(1)	-	-0.726	-	-1.04	-8.2
O32			-1.08(5)	8.2	-0.918	8.7	-0.6(1)	8.5	-0.713	7.4		
O24	c		-0.90(5)		-0.857		-1.2(1)					
O25		-7.2	-0.84(5)	-	-0.799	-	-0.6(1)	-	-0.666	-	-0.93	-6.8
O20			-0.81(5)	6.9	-0.808	7.1	-1.0(1)	7.1		6.1		
O23			-0.91(5)		-0.900		-0.7(1)					
O22	d	-6.9	-0.93(5)	-	-0.797	-	-1.0(1)	-	-0.686	-	-0.94	-6.5
				6.6		6.8		6.9		5.8		
O21	e	-7.4	-0.87(5)	-	-0.783	-	-0.8(1)	-	-0.635	-	-0.82	-7.0
O27				-0.92(5)	7.1	-0.733	7.4	-0.5(1)	7.2		6.4	
O13	f	-6.2	-0.63(5)	-	-0.573	-	-1.1(1)	-	-0.555	-	-0.63	-5.9
O12				-0.81(5)	5.9	-0.668	6.2	-0.7(1)	6.4		5.3	
O11	g	-5.8	-0.84(5)	-	-0.717	-	-0.5(1)	-	-0.560	-	-0.66	-5.5
O10				-0.65(5)	5.6	-0.620	5.8	-1.2(1)	5.7		4.9	

Figure 1.

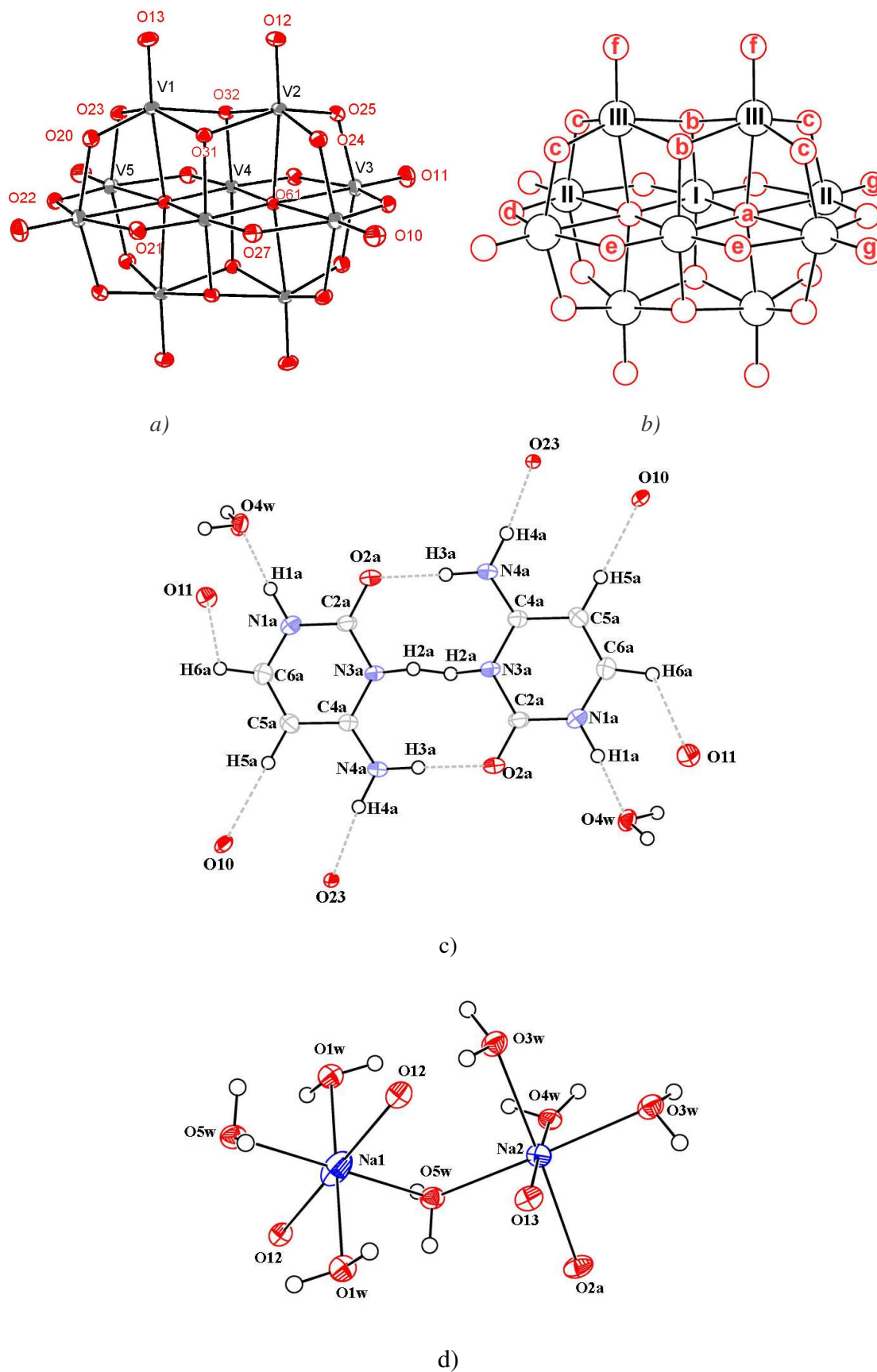
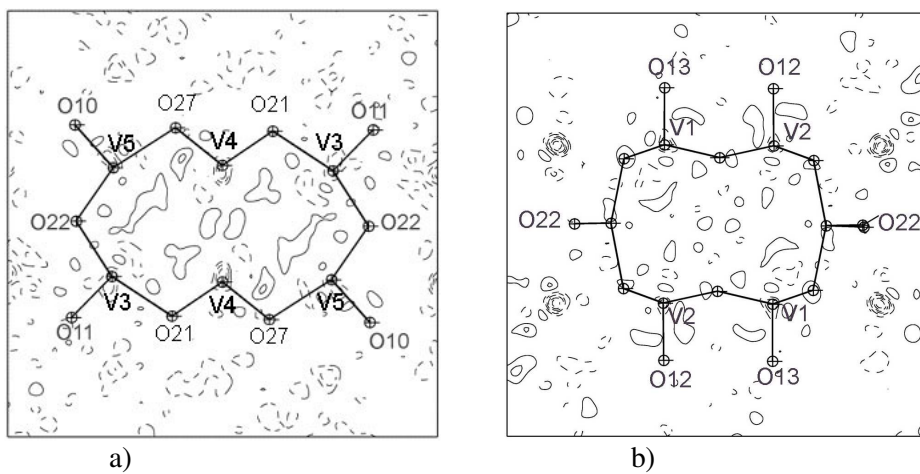


Figure 2



a)

b)

Figure 3.

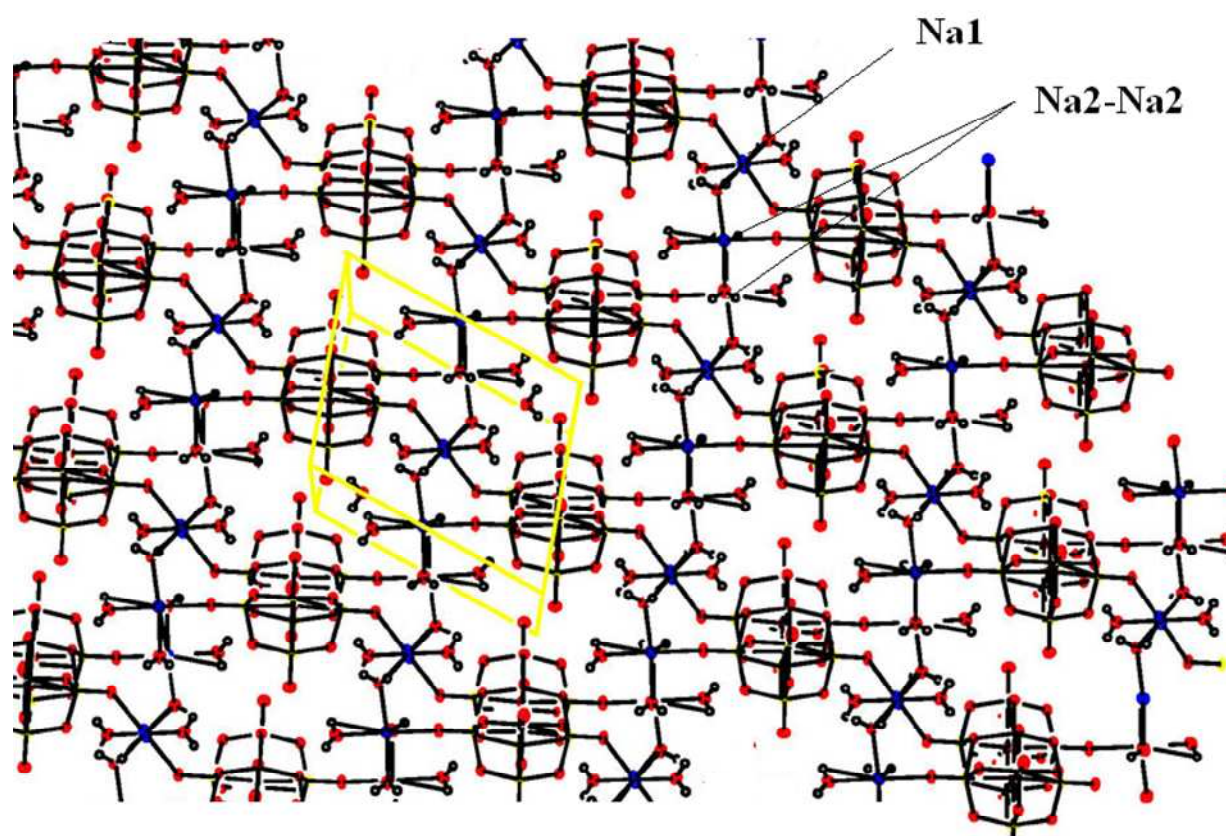


Figure 4.

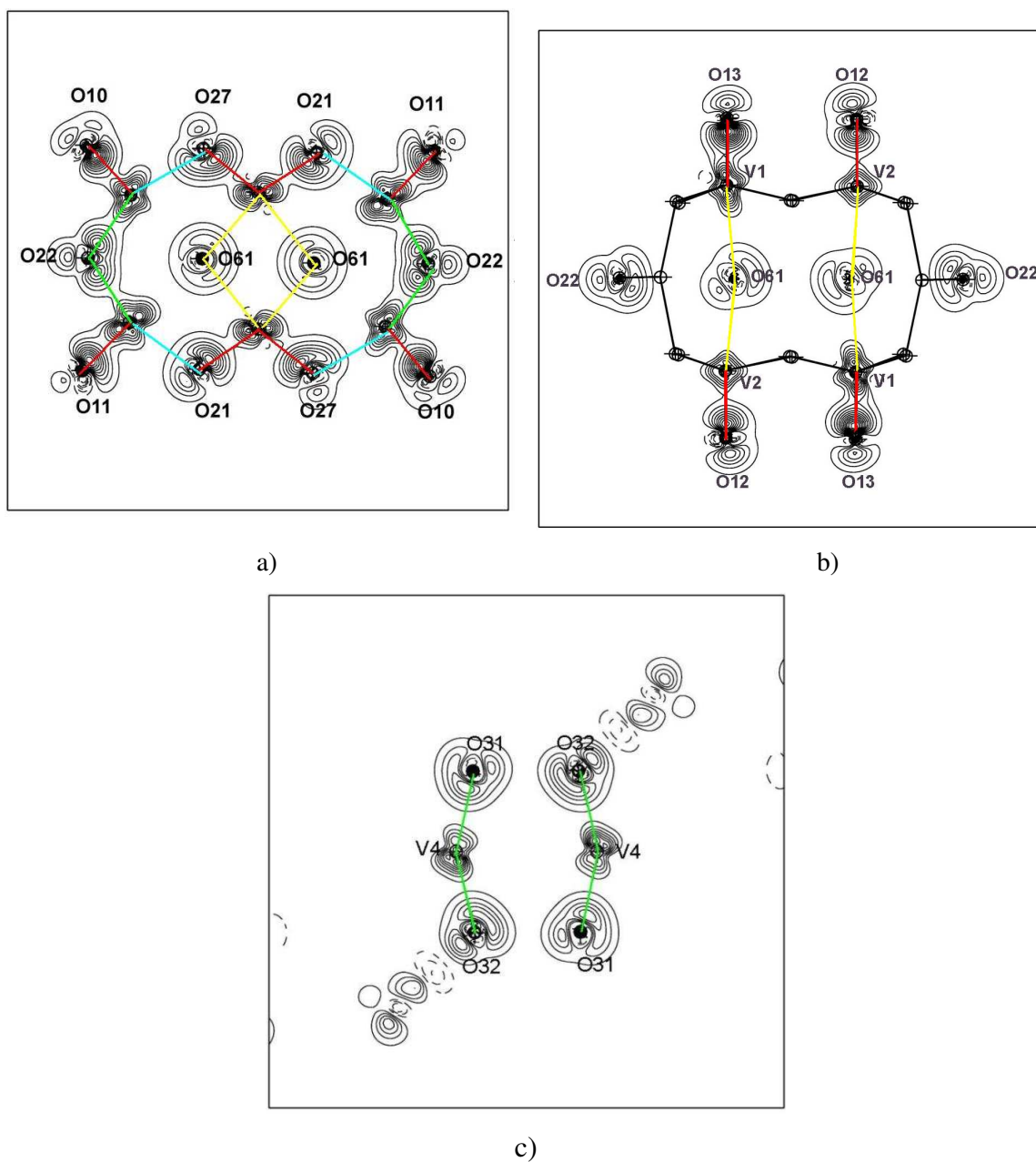


Figure 5.

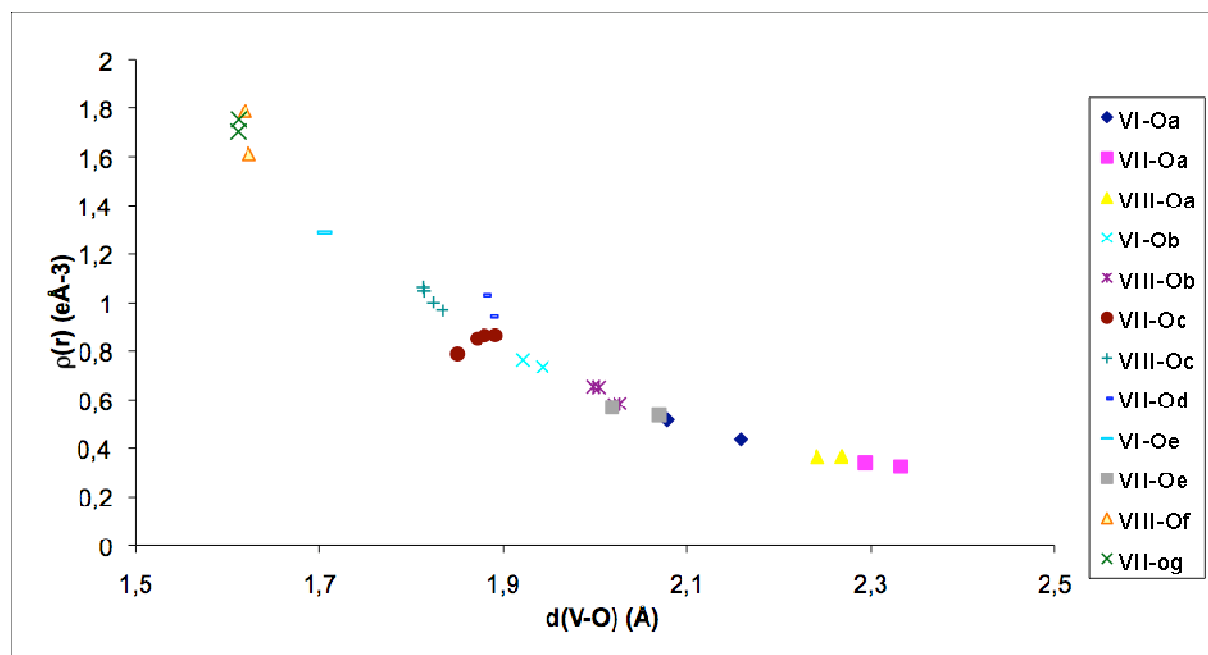


Figure 6.

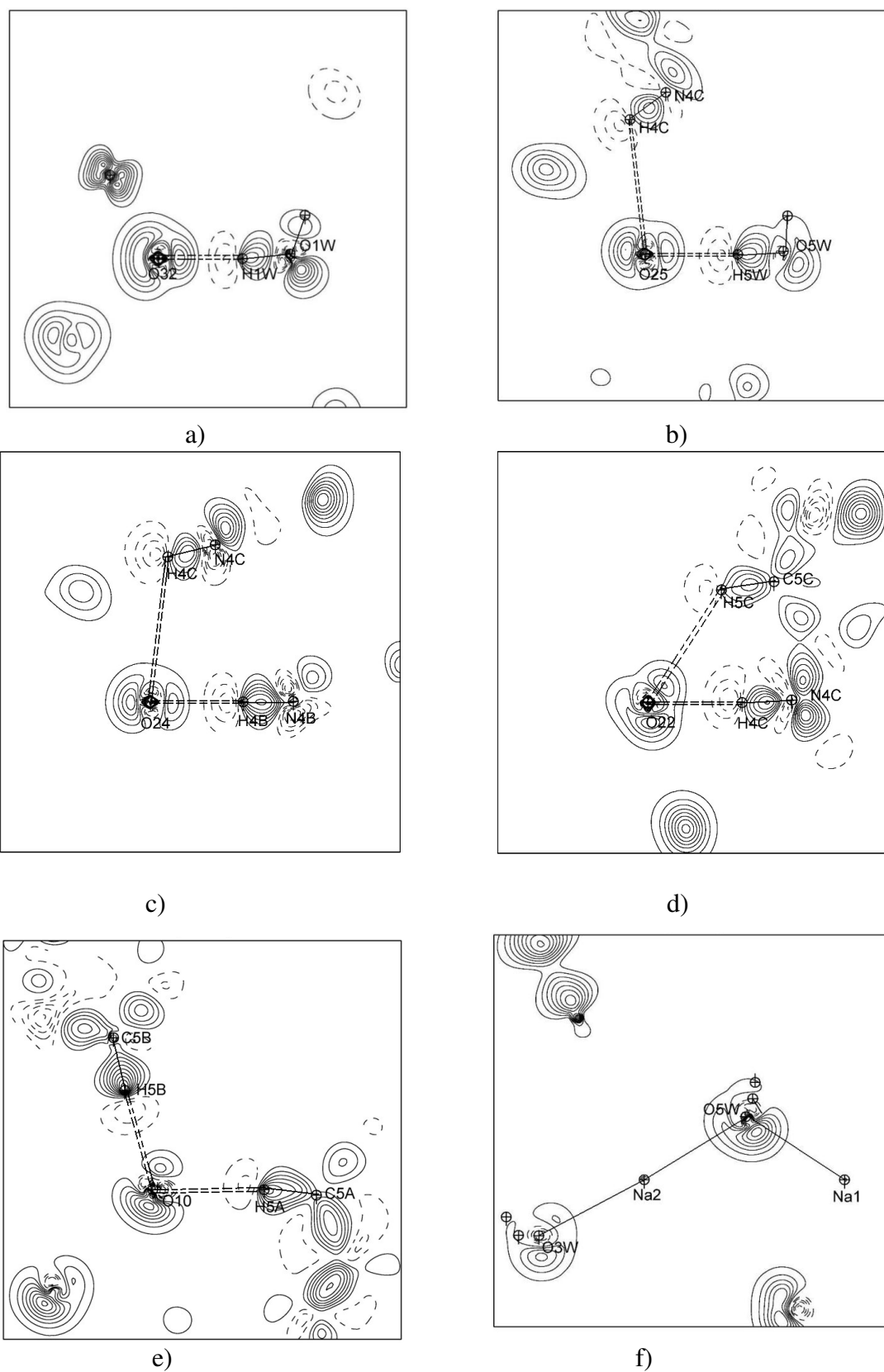


Figure 7.

