Low temperature crystal structure, experimental atomic charges and electrostatic potential of ammonium decavanadate hexahydrate (NH$_4$)V$_{10}$O$_{28}$·6H$_2$O

GORAN A. BOGDANOVIĆ[a], NADA BOŠNJAKOVIĆ–PAVLOVIĆ[b], ANNE SPASOJEVIĆ–DE BIRE[c], NOUR EDDINE GHERMANI[c,d] and UBAVKA MIOČ[b*#]

[a]*VINČA Institute of Nuclear Sciences, Laboratory of Theoretical Physicics and Condensed Matters P. O. Box 522, 11001 Belgrade,* [b]*Faculty of Physical Chemistry, University of Belgrade, P. O. Box 137, 11001 Belgrade,* [c]*Laboratoire SPMS UMR CNRS 8580, Ecole Central Paris I, Grande Voie des Vignes, 92295 Châtenay-Malabry, France and* [d]*Laboratoire de Physique Pharmaceutique UMR CNRS 8612, Faculty de Pharmacie 5, Rue Jean-Baptiste Clément, 92296 Châtenay-Malabry cedex, France (e-mail: ubavka@ffh.bg.ac.yu)*

Abstract: The X-ray structure of ammonium decavanadate hexahydrate was redetermined at a low temperature (100 K) in order to locate the hydrogen sites and to study the hydrogen bonds. The hydrogen atoms were assigned to the appropriate atomic group, NH$_4^+$ cations, and water molecules, missing to the best of our knowledge in the literature. A kappa refinement was performed to estimate the experimental atomic charges. These charges were used to generale the electrostatic potential on the molecular surfaces of decavanadate polyanions isolated from the influence of the crystal lattice. Comparisons with previous theoretical (*ab initio*) calculations were made and are also discussed.

Keywords: polyoxometalate, decavanadate, X-ray structure, atomic charges, electrostatic potential.

INTRODUCTION

Polyoxometalate (POM) compounds are of great interest due to a wide variety of their applications in many different fields, such as chemical catalysis, surface sciences and pharmacology.[1–3] In our investigations, the understading of the interactions of POMs in biological media and their putative enzyme inhibition mechanism is of particularly interest. Among these compounds, decavanadates are especially attractive since vanadium is important for biological metabolism (trace element)[4] and plays as essential role in some enzymatic activties.[5–8] Therefore, biochemists have designated decavanadates as potent drugs, for instance, in virology

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* Corresponding author.

\# Serbian Chemical Society member.

(HIV-1).[1,9] Decavanadate is formally a $[V_{10}O_{28}]^{6-}$ polyanion with a cage structure giving rise to fascinating supramolecular architectures in the solid state.[10] However, under physiological conditions, POM decomposition is only prevented by hydrogen bonding and counterion electrostatic interactions.[10] In this context, ammonium decavanadate hexahydrate gives the opportunity to study a sample model of such intereactions between $[V_{10}O_{28}]^{6-}$ anions, $(NH_4)^+$ cations and aqua ligands. Previous room temperature crystallographic and infrared vibration spectroscopic studies of $(NH_4)_6V_{10}O_{28}\cdot6H_2O$ were reported eleven years ago,[11] but neither the positions of the hydrogen atoms were located nor those of the NH_4^+ cations determined exactly.

In the present work, the results derived from low temperature single crystal diffraction data at medium resolution are reported. Contrary to the previous study, the experiment permitted the hydrogen atoms involved in the stability of the crystal lattice to be localized. Also, a kappa refinement based on the Hansen–Coppens electron density multipole model[12,13] was used to estimate the experimental atomic charges of the title compound. The electrostatic potential was computed using the experimental atomic charges in order to depict the topological features of this important physical property. The present results for the electrostatic potential and atomic charge are compared with those of previous theoretical (*ab initio*) calculations, made for an isolated $[V_{10}O_{28})]^{6-}$ anion.

EXPERIMENTAL

Synthesis and crystallization

The title compound was prepared by dissolving NH_4VO_3 (0.4 g, 3.42 mmol) in distilled water (20 ml) as described previously[14] to obtain decavanadate anions. The solution was stirred and heated until complete dissolution of NH_4VO_3 (about 2 h). The pH was adjusted to 5.90 by the dropwise addition of NH_4OH. Orange crystals formed within four days from the solution, kept at room temperature. The crystal samples were washed with ethanol and air-dried at room temperature.

Single crystal X-ray data collection

The 42599 X-ray reflection data were collected at 100 K on a Bruker-SMART three-circle diffractometer equipped with a CCD area detector using MoKα radition ($\lambda = 0.71073$ Å). The Lorentz-polarization and absorption corrections were applied and integration of the diffracted intensities was performed using SAINT software package.[15] The SORTAV program[16] was used for data sorting and averaging, yielding a total of 16219 unique reflections. Table I gives the details of the single crystal experiment.

TABLE I. X-Ray diffraction experiment and refinement details

Chemical formula	$(NH_4)_6V_{10}O_{28}\cdot6H_2O$
Formula weight/g.mol^{-1}	1173.75
Temperature/K	100.0(1)
Wavelength/Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$

TABLE I. Continued

a/Å	10.1421(2)
b/Å	10.2376(2)
c/Å	16.6452(3)
α/°	83.817(1)
β/°	87.239(2)
γ/°	71.017(1)
Volume/Å^3	1624.6(2)
Z	2
Density (calculated)/Mg m^{-3}	2.40
Absorption coefficient μ/mm^{-1}	2.86
Crystal size/mm^3	$0.56 \times 0.12 \times 0.32$
Color	Orange
[$\sin\theta/\lambda$]/Å^{-1}	0.87
Total numbef of reflections	42599
Unique reflections	16219
Unique reflections [$I > 3\sigma(I)$]	10778
R_{int}/%	4.27
Structure refinement	
R(F)/%	5.52
wR(F)/%	6.10
gof(F)	1.84
Kappa refinement	
R(F)/%	5.15
wR(F)/%	4.97
gof(F)	1.50

Structure and kappa refinements

The structure was solved by the heavy atom method and first refined with the SHELXL-97 program of the WINGX software package.[17] The hydrogen atom positions of the six NH_4^+ counterions and of three water molecules were found from the differences in the Fourier maps. The HYDROGEN program[18] was used to locate the hydrogen sites for the remaining three water molecules of the asymmetric unit. The thermal motions of all non-hydrogen atom were refined anisotropically. The atomic fractional coordinates were transferred to the input file of the full-matrix least-square MOLLY program,[12] allowing both structural and kappa refinements.[13] In this latter model, the atomic electron density is expresses as:

$$\rho_{at}(r) = \rho_{core}(r) + P_{val}\,\kappa^3\,\rho_{val}(\kappa r) \tag{1}$$

where ρ_{core} and ρ_{val} are the Hartree–Fock free atomic core and valence spherical electron densities,[19] respectively. The refined parameters are the valence population P_{val}, yielding the atomic charge ($q = P_{val} - N_{val}$, where N_{val} is the valence population of a free atom) and contraction ($\kappa > 1$) or expansion ($\kappa < 1$) coefficients. For vanadium ($3d^34s^2$) atom, the best results were obtained for a starting $V^{2+}(3d^34s^0)$ electron configuration and the P_{val} parameter was assigned to the 3d shell population. During the kappa refinements, the formal charges of $[V_{10}O_{28}]^{6-}$ and $(NH_4)^+$ were always

imposed as constrains in the least-squares procedure. The elctrostatic potential $V(r)$ was computed using the ELECTROS program[20] as:

$$V(r) = \sum_{at}^{molecule} \frac{Z_{at}}{|r - R_{at}|} - \int \frac{\rho_{at}(r')}{|r - R_{at} - r'|} d^3 r' \qquad (2)$$

the sum of the contributions of the positive nuclear charge Z_{at} located at R_{at} and the atomic electron density ρ_{at}.

RESULTS AND DISCUSSION

The title compound crystallizes in P$\bar{1}$ triclinic space group with two independent halves (labeled hereafter **a** and **b**) of decavanadate anions, six NH_4^+ cations and six
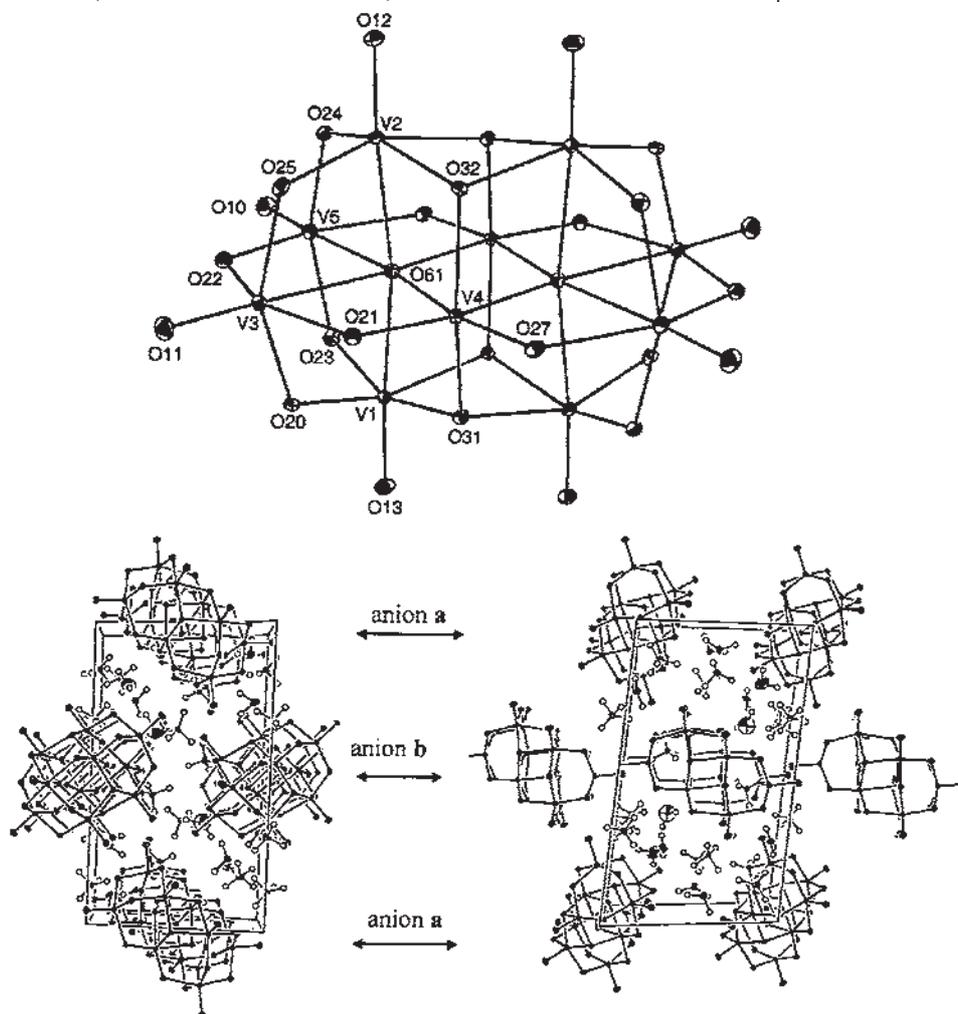
Fig. 1. ORTEP view of the decavanadate anion with the atomic lebelling scheme (top) and crystal lattice packing (bottom) of ammonium decavanadate hexahydrate.

water molecules in the asymmetric unit (Fig. 1). This Figure shows the decavanadate anion cage and the crystal packing of the title compound. The latter displays two inter-penetrated sub-lattices of decavanadate polyanions **a** and **b**. It is also evident, that these decavanadate polyanions **a** and **b** are differently oriented. Therefore, the crystal lattice can be described with a primitive cell of decavanadate **a** having one decavanadate **b** in its center. The NH_4^+ counterions and water molecules are distributed in the empty space of the compact lattice of the anion. The vanadium atoms are in distorted octahedra, in which the V–O bond lengths are in the range from 1.600(3) to 2.318(2) Å and the internal O–V–O angles from 74.3(1) to 106.9(1)°. These results are in good agreement with decavanadate geometries found in previous studies.[11,21] The first structure description of $(NH_4)_6V_{10}O_{28} \cdot 6H_2O$ compound was given on the basis of X-ray data obtained at room temperature, but in comparison with this study,[11] in the present work the hydrogen atoms and hydrogen bonding in this compound were local-ized. Also, it was found that the three water molecules assigned and labeled O91, O93, O95 in the room temperature structure study[11] were in fact ammonium cations. Table II lists the hydrogen bonds between the counterions, water molecules and the decava-nadate anions. It is noteworthy that decavanadate **a** interacts equally with seven NH_4^+ cations and seven water molecules. Conversely, decavanadate **b** is closely surrounded by eleven NH_4^+ counterions and two aqua ligands.

TABLE II. Distances, Å, and angles, °, of the hydrogen bonds in ammonium decavanadate hexahydrate (D donor, A acceptor). Estimated standard deviations are given in parentheses.

D–H···A	d(H···A)	d(D···A)	< DHA
Decavanadate **a**			
N(3)–H(2N3)···O(20**a**)	1.719	2.716(4)	168.6(2)
N(4)–H(1N4)···O(24**a**)	1.830	2.831(4)	170.8(2)
N(5)–H(2N5)···O(25**a**)	1.841	2.740(4)	147.4(2)
N(5)–H(4N5)···O(13**a**)	1.965	2.870(4)	151.8(2)
N(1)–H(2N1)···O(11**a**)	1.997	2.946(4)	160.0(2)
N(4)–H(2N4)···O(25**a**)	1.999	2.900(4)	147.4(2)
N(6)–H(1N6)···O(22**a**)	2.287	3.054(4)	131.8(2)
O(1w)–H(1w1)···O(32**a**)	1.825	2.768(4)	165.7(2)
O(4w)–H(1w4)···O(31**a**)	1.868	2.787(3)	158.3(2)
O(1w)–H(2w1)···O(12**a**)	1.890	2.850(4)	178.-(2)
O(2w)–H(1w2)···O(23**a**)	1.895	2.805(4)	156.3(2)
O(2w)–H(2w2)···O(10**a**)	1.996	2.80(4)	153.4(2)
O(5w)–H(2w5)···O(10**a**)	2.129	3.090(5)	1794(3)
O(3w)–H(1w3)···O(23**a**)	2.243	3.025(4)	137.6(2)
Decavanadate **b**			
N(1)–H(4N1)···O (31**b**)	1.764	2.762(4)	169.3(2)

TABLE II. Continued

D–H···A	d(H···A)	d(D···A)	< DHA
N(3)–H(4N3)···O(23**b**)	1.768	2.773(4)	172.8(2)
N(3)–H(1N3)···O(22**b**)	1.849	2.835(4)	165.2(2)
N(2)–H(3N2)···O(25**b**)	1.866	2.851(4)	164.9(2)
N(1)–H(1N1)···O(20**b**)	1.867	2.853(4)	127,.9(1)
N(1)–H(3N1)···O(10**b**)	1.883	2.890(4)	144.6(1)
N(6)–H(2N6)···O(24**b**)	1.920	2.860(4)	147.0(1)
N(6)–H(2N6)···O(27**b**)	2.020	3.008(4)	165.9(2)
N(5)–H(3N5)···O(11**b**)	2.031	2.987(4)	157.4(2)
N(5)–H(1N5)···O(13**b**)	2.178	2.870(4)	124.2(2)
N(5)–H(1N5)···O(12**b**)	2.204	3.010(4)	135.7(2)
O(6w)-H(2w6)···O(13**b**)	1.847	2.913(9)	171.8(5)
O(4w)-H(2w4)···O(22**b**)	2.237	3.201(4)	179.7(2)

The kappa coefficients and the experimental atomic net charges are listed in Table III. The vanadium atoms have an average positive charge of +1.6 e and a common κ parameter of 1.2 (contracted electron density). In the two polyanions, the internal V4**a** and V4**b** (Fig. 1) have the highest charges of +2.0(1) and +1.9(1) e, respectively. By comparison, a vanadium charge equal to +2.0(1) e was reported for an isolated decavanadate anion (in an ideal D_{2h} symmetry) from theoretical calculations.[22] The decavanadate oxygen atom electron densities are slightly expanded ($\kappa \leq 1.0$). The corresponding experimental charges are found distributed in large intervals: from –0.5(1) to – 1.2(1) e for **a**, and from –0.3(1) to –1.4(1) e for **b**. A Mulliken population analysis of isolated polyanion restricts, in *ab initio* theoretical calculations,[22] gave oxygen atom net charges in the range from –0.7 to –1.3 e. The dispersion magnitude of the oxygen net charges reported here cannot be straightforwardly correlated with the hydrogen bond features given in Table II.

TABLE III. Kappa parameters and experimental net atomic charges (q in e units). Only least-squares significant digits are given

	κ	q		κ	q
V1**a**	1.21(2)	1.6(1)	V1**b**	1.22(2)	1.6(1)
V2**a**	1.21(2)	1.7(1)	V2**b**	1.22(2)	1.6(1)
V3**a**	1.22(3)	1.7(1)	V3**b**	1.25(3)	1.8(1)
V4**a**	1.24(3)	2.0(1)	V4**b**	1.23(3)	1.9(1)
V5**a**	1.22(3)	1.6(1)	V5**b**	1.22(3)	1.6(1)
O10**a**	0.9(1)	–1.2(1)	O10**b**	0.98(1)	–1.0(1)
O11**a**	1.01(1)	–0.5(1)	O11**b**	1.01(1)	–0.4(1)
O12**a**	0.99(1)	–0.7(1)	O12**b**	1.01(1)	–0.3(1)
O13**a**	0.95(1)	–1.1(1)	O13**b**	0.98(1)	–0.8(1)

TABLE III. Continued

	κ	q		κ	q
O20**a**	0.97(1)	−1.0(1)	O20**b**	0.93(1)	−1.4(1)
O21**a**	0.98(1)	−0.8(1)	O21**b**	0.97(1)	−0.9(1)
O22**a**	0.97(1)	−1.0(1)	O22**b**	0.95(1)	−1.4(1)
O24**a**	0.97(1)	−1.2(1)	O23**b**	0.97(1)	−1.0(1)
O25**a**	1.00(1)	−0.6(1)	O24**b**	1.01(1)	−0.4(1)
O27**a**	1.01(1)	−0.5(1)	O25**b**	0.99(1)	−0.9(1)
O31**a**	0.97(1)	−0.9(1)	O27**b**	0.98(1)	−0.9(1)
O32**a**	1.00(1)	−0.6(1)	0.32**b**	1.01(1)	−0.5(1)
O61**a**	1.00(1)	−0.7(1)	O61**b**	0.99(1)	−0.7(1)
N	1.02(1)	−0.82(9)			
H(N)	1.16	0.46(2)			
O(w)	0.99(1)	−0.46(6)			
H(w)	1.16	0.20(3)			

The electrostatic potential distribution on the van der Waals surface for the decavanadate anion is shown in Fig. 2. The electrostatic potential derived from the

Min = -1.33 eÅ⁻¹
Max = -1.06 eÅ⁻¹

Min = -1.38 eÅ⁻¹
Max = -0.93 eÅ⁻¹

Min = -1.52 eÅ⁻¹
Max = -0.90 eÅ⁻¹
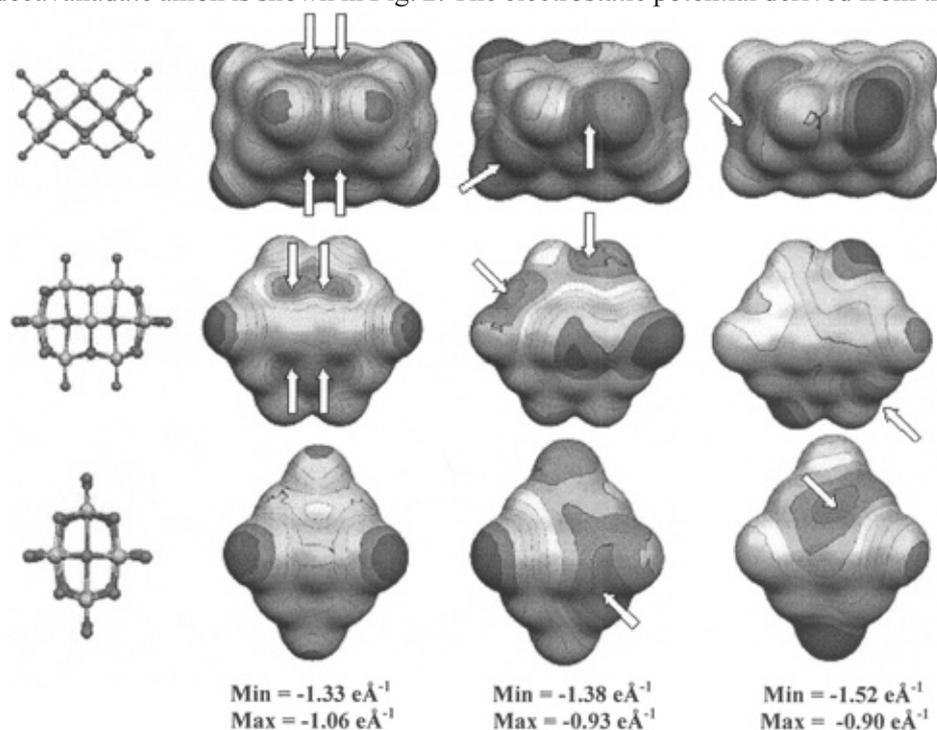
Fig. 2. Three views of the electrostatic potential on the van der Waals surface of the decavanadate polyanion: from Mulliken population analysis (second column, from[22]); from decavanadate **a** experimental charges (third column); from decavanadate **b** experimental charges (fourth column). The arrows indicate the minima of the electrostatic potential and the maximum regions are in black.

Mulliken population analysis[22] is also depicted in Fig. 2 for comparison. Previous theoretical calculations made for the isolated $[V_{10}O_{28}]^{6-}$ anion were used to predict the protonation sites in relation with the relative oxygen atom basicities (minima in Fig. 2). The minimum and the maximum values of the electrostatic potential are in good agreement with those derived from the present experimental charges (see values in Fig. 2). However, the topological features are quite different. The experimental electrostatic potential distribution for both decavanadates **a** and **b** with C_i point symmetry seems to be perturbed by crystal lattice interactions. The minima of the electrostatic potentials are found close to the most negatively charged oxygen atoms of the decavanadate anions (Table III).

CONCLUSION

Redetermination of the crystal structure of ammonium decavanadate hexahydrate $(NH_4)_6V_{10}O_{28}\cdot6H_2O$, was performed using low temperature (100 K) X-ray data. In comparison with the first study, the positions of the hydrogen atoms were localized and the nature of the hydrogen bonding in this compound discussed. Also, the positions of the NH_4^+ cations and water molecules were determined. The atomic net charge and electrostatic potential of this compound was calculated for the first time. The experimental atomic net charges for the vanadium and oxygen atoms are in good agreement with those of previous theoretical (*ab initio*) calculations. The electrostatic potential on the molecular surface was compared for two crystallographicaly different decavanadate polyanions as well for the same polyanion analyzed in previous theoretical calculations. The observed differences in the electrostatic potential distributions are explained by the influence of the number and space distribution of hydrogen bonds between the decavanadate anion, water molecules and NH_4^+ cations. The results demonstrate a strong influence of crystal lattice interactions on the perturbation of the electrostatic potential in decavanadate polyanions.

Supplementary material

Tables of atomic coordinates, thermal displacement parameters, bond distances, and bond angles are available from the authors on request.

И З В О Д

КРИСТАЛНА СТРУКТУРА НА НИСКОЈ ТЕМПЕРАТУРИ, ЕКСПЕРИМЕНТАЛНО ОДРЕЂЕНА НАЕЛЕКТРИСАЊА АТОМА И ЕЛЕКТРОСТАТИЧКИ ПОТЕНЦИЈАЛ АМОНИЈУМ ДЕКАВАНАДАТА ХЕКСАХИДРАТА $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$

ГОРАН А. БОГДАНОВИЋ[а], НАДА БОШЊАКОВИЋ-ПАВЛОВИЋ[б,ц], ANNE SPASOJEVIĆ-DE BIRE[ц], NOUR EDDINE GHERMANI[ц,д] и УБАВКА МИОЧ[б]

[а]Инсūиūуū за нуклеарне науке Винча, Лабораūорија за ūеоријску физику и физику конензоване маūерије, ū. ū. 522, 11001 Беоūрад, [б]Факулūеū за физичку хемију, Универзиūеū у Беоūраду, ū.ū. 137, 11001 Беоūрад, [ц]Laboratoire SPMS UMR CNRS 8580, Ecole Central Paris, 1, Grande Voie des Vignes, 92295 Châtenay-Malabry, France и [д]Laboratoire de Phisique Pharmaceutique UMR CNRS 8612, Faculté de Pharmacie 5, Rue Jean-Baptiste Clément, 92296 Châtenay-Malabry cedex, France

Експериментом дифракције рендгенског зрачења на температури 100 K одређени су положаји атома водоника у кристалној структури амонијум декаванадата хекса-хидрата у циљу проучавања водоничних веза у овој структури. Посебна пажња је посвећена одређивању који од атома водоника припадају NH_4 катјонима, односно моле-кулима воде што није коректно презентовано у претходним литаратурним подацима. Коришћењем такозваног "kappa refinement" одређена су наелектрисања атома која су даље употребљена за израчунавање електростатичког потенцијала на молекулској површини полианјона декаванадата. Ови подаци су упоређени са претходним теориј-ским (*ab initio*) израчунавањима.

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