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CRYSTAL STRUCTURE REDETERMINATION AND ATOMIC CHARGES OF AMMONIUM DECAVANADATE HEXAHYDRATE BASED ON A LOW TEMPERATURE X-RAY EXPERIMENT

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Abstract

The X-ray structure of ammonium decavanadate hexahydrate, $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$, was redetermined at low temperature (100 K) in order to locate the hydrogen sites. A kappa refinement was performed to estimate the experimental atomic charges. Comparisons with previous theoretical calculation results were discussed.

Introduction

The decavanadates belong to wide family of the polyoxometalate complex compounds [1]. Since that vanadium is important in biological systems as a trace element, decavanadates are investigated as potential drugs, for example, in virology [1]. The previous room temperature crystallographic study [2] of ammonium decavanadate hexahydrate, $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$, left open questions with the respect to the hydrogen atom positions and hydrogen bonding system in this compound. Regarding that hydrogen bonds can play very significant role in the intermolecular interactions we performed a low-temperature single-crystal X-ray experiment with a goal to obtain relevant crystallographic results. In this work we report significantly improved crystal structure of ammonium decavanadate hexahydrate and experimental atomic charges in this compound.

Experimental

The title compound was prepared by dissolving NH_4VO_3 (0.4 g, 3.42 mmol) in distilled water (20 ml) as described in reference [3] to obtain decavanadate anions.

Single crystal X-ray data collection was performed at 100 K on a Bruker-SMART three-circle diffractometer equipped with a CCD area detector using monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 42599 reflections were collected in the θ range 1.23 to 38.10°. The Lorentz-polarization correction and the integration of the diffracted intensities were performed using SAINT software package. An empirical absorption correction was applied using the SADABS computer program.

The structure was solved by the heavy atom method and difference Fourier methods and refined on the F^2 by full-matrix least-square method to $R1 = 0.0633$ and $Rw = 0.1166$ for 451 refined parameters and 12342 unique reflections with $I > 2\sigma(I)$. Almost all hydrogen atoms were found from difference Fourier maps. Their positions were refined as a riding and with U_{iso} constrained to U_{eq} of the carrier atom. The rest of H atoms were determined after geometrical consideration and they refined in the same way. Crystallographic data: formula $N_6H_{36}O_{34}V_{10}$, triclinic, space group $P\bar{1}$, $a = 10.1421(2) \text{ \AA}$, $b = 10.2376(2) \text{ \AA}$, $c = 16.6452(3) \text{ \AA}$, $\alpha = 83.817(1)$, $\beta = 87.239(2)$, $\gamma = 71.017(1)^\circ$, $V = 1624.6(2) \text{ \AA}^3$, $Z = 2$, $D_c = 2.399 \text{ g/cm}^3$, $\mu = 2.862 \text{ mm}^{-1}$.

The atomic fractional coordinates were transferred to the input file of the full-matrix least-square MOLLY program [4] allowing both structural and kappa refinements [5]. In this latter model, the atomic electron density is expressed as

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

where ρ_{core} and ρ_{val} are Hartree-Fock free atomic core and valence spherical electron densities, respectively. The refined parameters are the valence population P_{val} yielding the atomic charge and the contraction ($\kappa > 1$) or expansion ($\kappa < 1$) coefficients. During the kappa refinements, the formal charges of $[V_{10}O_{28}]^{6-}$ and $(NH_4)^+$ were always imposed as constraints in the least-squares procedure. The final R(F) residual factor for kappa-refinement was 5.15% [$wR(F) = 4.97\%$].

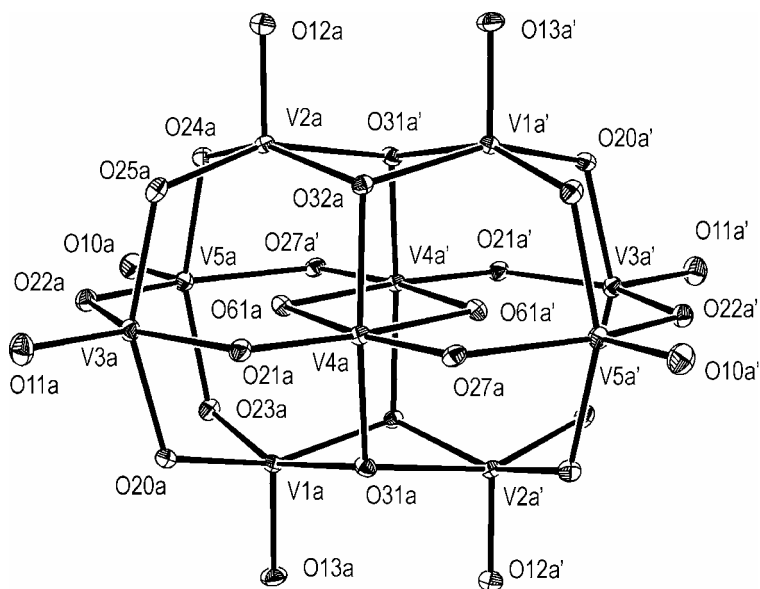


Figure 1. Perspective view of decavanadate polyanion **a** showing the labeling scheme.

Results and Discussion

The title compound crystallizes in $P\bar{1}$ triclinic space group with two independent halves of decavanadate anions (labelled hereafter **a** and **b**), six NH_4^+ cations and six water molecules in the asymmetric unit. The vanadium atoms are in distorted octahedrons where V-O bond lengths are in the range of 1.600(3) to 2.318(2) Å and internal O-V-O angles from 74.3(1) to 106.9(1)°. It was established that three water molecules labelled O91, O93, O95 in the previous X-ray study [2] were in fact ammonium cations. Decavanadate polyanions **a** and **b** are oriented in a such way that 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 anion compact lattice. It is worthy of note that the decavanadate **a** equally interacts with seven NH_4^+ cations and seven water molecules. Conversely, the decavanadate **b** is closely surrounded by eleven counterions and by only two aqua ligands.

The kappa refinement gave an average positive charge for the V atoms of +1.6 *e* and a common κ parameter value of 1.2 (contracted electron density). In the two polyanions, the internal V4**a** and V4**b** (Fig. 1) have the highest charges, +2.0(1) and +1.9(1) *e*, respectively. In 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 [6]. 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**. The Mulliken population analysis for an isolated polyanion restricts, in *ab initio* theoretical calculations, the oxygen atom net charges to the range from -0.7 to -1.3 *e* [6].

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