
# Order-disorder phase transition in the peroxidovanadium complex NH4[VO(O2)2(NH3)]

Peter Schwendt, Róbert Gyepes, Jana Chrappová, Ivan Němec, Přemysl Vaněk

PII: S1386-1425(18)30318-4
DOI: doi:10.1016/j.saa.2018.04.019
Reference: SAA 15976

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received date: 30 January 2018
Revised date: 29 March 2018
Accepted date: 9 April 2018

Please cite this article as: Peter Schwendt, Róbert Gyepes, Jana Chrappová, Ivan Němec, Přemysl Vaněk , Order-disorder phase transition in the peroxidovanadium complex NH4[VO(O2)2(NH3)]. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Saa(2017), doi:10.1016/j.saa.2018.04.019

# Order-disorder phase transition in the peroxidovanadium complex $NH_4[VO(O_2)_2(NH_3)]$.

Peter Schwendt,[a] Róbert Gyepes,[b,*] Jana Chrappová,[a] Ivan Němec,[c] Přemysl Vaněk[d]

[a] Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia
[b] Department of Chemistry, Faculty of Education, J. Selye University, Bratislavská 3322, 945 01 Komárno, Slovakia
[c] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, 128 43 Praha 2, Czech Republic
[d] Department of Dielectrics, Institute of Physics ASCR, v.v.i., Na Slovance 2, 182 21, Praha 8, Czech Republic

* Corresponding author, e-mail: gyepesr@ujs.sk

## Abstract

Complex $NH_4[VO(O_2)_2(NH_3)]$ (**1**) undergoes an order-disorder phase transition at $T_c \sim 258$ K. This transition is accompanied by change in the space group of the orthorhombic lattice and also by significant structural rearrangements of the constituent molecules, which are pertinent mostly to their $NH_4^+$ ions and their ammonia ligands. The low-temperature solid state IR and Raman spectra of **1** were corroborated by solid-state computations that employed Gaussian functions as the basis set. Results of these computations yielded excellent agreement with experimental data. On the curves of temperature dependence of vibrational modes, the phase transition is expressed by an abrupt change of the slope above $T_c$.

## Keywords

Vibrational Spectra, Solid-State Computation, Peroxido Complex, Phase Transition, Crystal Structure

## 1. Introduction

The solid-state and molecular structure of $NH_4[VO(O_2)_2(NH_3)]$(**1**) determined at room temperature was published in 1972 as the archetypal example of a peroxidovanadium complex incorporating simultaneously a heteroligand.[1] This structure, composed of $NH_4^+$ cations and $[VO(O_2)_2(NH_3)]^-$ anions already exhibited the characteristic structural features of peroxidovanadium complexes, that were later confirmed in more than hundred sixty examples of such complexes.[2] These important structural features include:

i. The presence of distorted pentagonal pyramidal or pentagonal bipyramidal coordination around the central vanadium atom.
ii. The equatorial position(s) occupied by bidentate peroxide groups.
iii. The presence of a doubly bonded oxygen atom in the axial coordination site.

Methods utilizing peroxidic species for synthesizing zero dimensional species, but also mono-, di-, and tri-dimensional materials are nowadays widespread commonly.[3] After the preparation of such materials they are used in important technological applications, such as electrochemistry, gas sensing, oxidation catalysis and others. Very recently, ammonium peroxidovanadate served as precursor for the preparation of vanadium oxide nanofilm-coated graphene oxide.[4] The thermal treatment of vanadium precursors is of control in the deposition of various vanadium oxides