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Dinucleating role of a strong hydrogen bond in crystal structure of $[N(C_4H_9)_4]\{[VO(HO_2)(O_2)(phen)][VO(O_2)_2(phen)]\}\cdot 3H_2O_2\cdot H_2O$

Mária Šimuneková [a], Ján Šimunek [a,*], Jana Chrappová [a,**], Peter Schwendt [a],
Zdirad Žák [b], František Pavelčík [c]

[a] Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15, Bratislava 4, Slovak Republic
[b] Faculty of Natural Sciences, Masaryk University, Kamenice 753/5, 625 00 Brno, Czech Republic
[c] Department of Chemical Drugs, Faculty of Pharmacy, University of Veterinary and Pharmaceutical Sciences Brno, Palackého 1-3, 612 42 Brno, Czech Republic

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ABSTRACT

Diperoxidovanadium complex with 1,10-phenanthroline, $[N(C_4H_9)_4]\{[VO(HO_2)(O_2)(phen)][VO(O_2)_2(phen)]\}\cdot 3H_2O_2\cdot H_2O$ (**1**), has been prepared and characterized by infrared, Raman and ^{51}V NMR spectra. X-ray structure analysis revealed the presence of dinuclear anion in **1** in which the $[VO(HO_2)(O_2)(phen)]$ and $[VO(O_2)_2(phen)]^-$ entities are connected via a short, strong hydrogen bond formed between hydrogenperoxido (HO_2^-) and peroxido groups. Moreover, the crystal structure is stabilized by the stacking interactions between 1,10-phenanthroline ligands. We have attempted to estimate the binding energy of hydrogen bond in the dinuclear anion as well as the binding energy between stacked complex entities based on gas-phase quantum chemistry calculations.

Peroxidovanadium complexes attracted attention during the last years because of their potential application as catalysts in oxidation reactions of organic compounds [1] and biological relevance (insulin enhancement activity [2,3], structural and functional models of vanadium haloperoxidases [4,5]). Intra- and intermolecular hydrogen bonds in the structure of vanadium(V) oxido peroxido complexes have been intensively studied in connection with modeling the catalytic site of vanadium haloperoxidases [6–8]. Oxidation of halides (Cl^-, Br^-) is facilitated by an increase of the electrophilicity at the reaction site by formation of a hydrogenperoxido complex [6].

Several monoperoxidovanadium complexes with 1,10-phenanthroline, e.g. $[VO(O_2)(phen)_2]ClO_4$ [9] and $[VO(O_2)(phen)(H_2O)_2]Cl\cdot 0.38H_2O$ [10], or mixed-heteroligand complexes, e.g. $[N(C_3H_7)_4][VO(O_2)(ox)(phen)]$ [11] and $[VO(O_2)(pca)(phen)]$ (*pca* = pyrazine-2-carboxylate(1−)) [12] have been structurally characterized. Although a number of diperoxidovanadium complexes with 1,10-phenanthroline were reported, e.g. $M[VO(O_2)_2(phen)]\cdot nH_2O$ (M = K, Na, NH_4) [13] and $(NH_4)[VO(O_2)_2(phen)]\cdot 2H_2O$ [14], no complex of this type has been structurally characterized so far.

We present here the synthesis, spectral characterization and X-ray crystal structure of $[N(C_4H_9)_4]\{[VO(HO_2)(O_2)(phen)][VO(O_2)_2(phen)]\}\cdot 3H_2O_2\cdot H_2O$. The compound is the first structurally characterized hydrogenperoxido complex of vanadium(V).

Orange crystals of $[N(C_4H_9)_4]\{[VO(HO_2)(O_2)(phen)][VO(O_2)_2(phen)]\}\cdot 3H_2O_2\cdot H_2O$ have been obtained by the described procedure [15]. Interestingly, the synthesis necessitates the presence of hydrogen fluoride in the reaction mixture, the role of which is unclear. We did not obtained the title compound using other acids (HNO_3, HCl, $HClO_4$).

The infrared spectrum [16] of **1** contains characteristic bands of $[N(C_4H_9)_4]^+$, 1,10-phenanthroline and $VO(O_2)_2$ groups [17]. The Raman spectrum [18, Fig. 1] of **1** exhibits characteristic bands of the $[N(C_4H_9)_4]^+$ cation and 1,10-phenanthroline ligand. Typical bands corresponding to the $VO(O_2)_2$ group [19,20] were observed at 935 cm^{-1} [$\nu(V{=}O)$] and 889 and 865 cm^{-1} [$\nu(O_p-O_p)$, O_p-peroxide oxygen atom]. The bands assigned to [$\nu(V-O_p)$] vibrations in the range 650–450 cm^{-1} are splitted more than usually due to the asymmetry of the $V-O_p$ bonds.

The ^{51}V NMR spectrum [21, Fig. 2] of **1** in formamide showed that the complex is partially decomposed in solution. Besides the dominant signal at −715 ppm, corresponding to the parent $[VO(O_2)_2(phen)]^-$ ion (or $[VO(HO_2)(O_2)(phen)]$ species), other signal was observed at −688 ppm. We assigned this signal, on the basis of our previous study [20], to the $[VO(O_2)_2(HCONH_2)]^-$ ion.

The crystal structure of the title compound [22] consists of the $[N(C_4H_9)_4]^+$ and $[VO(O_2)_2(phen)]^-$ ions, neutral $[VO(HO_2)(O_2)(phen)]$ complexes, water and hydrogen peroxide of crystallization, which are held together by ionic forces, hydrogen bonds (Fig. 3, Figure S1) and stacking interactions (Fig. 4).

The coordination geometry of the vanadium atoms is distorted pentagonal bipyramidal (Fig. 3). The pentagonal planes of both bipyramids with the V1 and V2 centers consist of four oxygen atoms from the

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* Corresponding author.
** Corresponding author. Tel.: +421 260296497; fax: +421 260296273.
E-mail addresses: simunek@fns.uniba.sk (J. Šimunek), chrappova@fns.uniba.sk (J. Chrappová).

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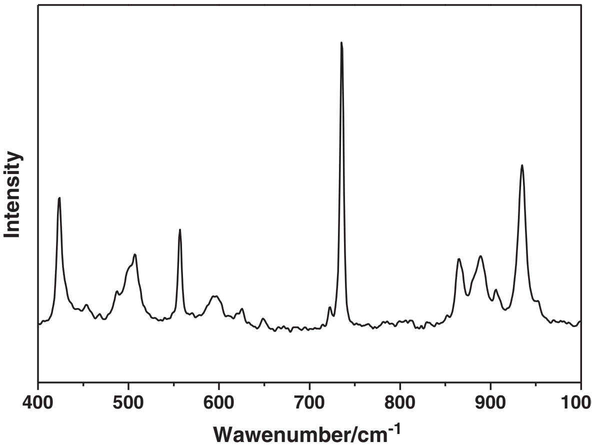

Fig. 1. Raman spectrum of $[N(C_4H_9)_4]\{[VO(HO_2)(O_2)(phen)][VO(O_2)_2(phen)]\}\cdot 3H_2O_2\cdot H_2O$.

peroxide groups and nitrogen atoms from the phenanthroline ligand. In both polyhedra one of two apical positions is occupied by the oxygen atom (O11 resp. O12) bonded to the central vanadium atom by double bond, and the second apical position is occupied by nitrogen atom (N11 or N12) of the phenanthroline ligands. The vanadium atoms are displaced (V1: 0.3341 Å and V2: 0.3373 Å) from the equatorial plane towards the vanadyl oxygen atoms (O11 resp. O12).

Bond distances and bond angles in the $VO(O_2)_2$ groups (Table S2) are comparable to those observed in other diperoxido complexes of vanadium [1,23,24].

A remarkable feature of the structure is the dinucleating role of the hydrogen bond. The hydrogen atom (HP) between the two diperoxido complexes was localized by X-ray diffraction (Fig. 3) and can be considered as covalently bonded to one peroxide group ($d(O42-HP) = 1.151$ Å), and forming a hydrogen bond to another peroxide group. The geometrical parameters: $d(O42\cdots O51) = 2.438$ Å, $d(O51\cdots HP) = 1.293$ Å and angle $O42-H\cdots O51 = 172.26°$ indicate the existence of a very strong hydrogen bond [25]. A similar type of hydrogen bonding was observed by H. Szentivanyi and R. Stomberg [26] in (H*bipy*)[H{$VO(O_2)_2$*bipy*}$_2$], but in this case the central hydrogen atom was not localized by X-ray diffraction. It must be emphasized that data on well characterized transition metal hydrogenperoxido complexes are extremely rare. There are some data on Cu(II) [27] and Fe(III) hydrogenperoxido complexes [28,29], but to our knowledge no reliable data have been published so far on solid vanadium hydrogenperoxido complexes.

Bonding of the hydrogen atom to the peroxide groups (both by covalent and H-bonds) causes a profound asymmetry of the $V-O_p$ bonds ($d(V-O_p(H)) = 1.999$ and 1.956 Å vs. remaining $d(V-O_p)$ bond lengths lying between 1.843 and 1.889 Å). Although the O_p-O_p bond lengths are influenced to a lesser extent, the difference is significant also in this case: $d(O_p-O_p) = 1.470$ and 1.480 Å (with hydrogen), $d(O_p-O_p) = 1.444$ and 1.455 Å (without hydrogen).

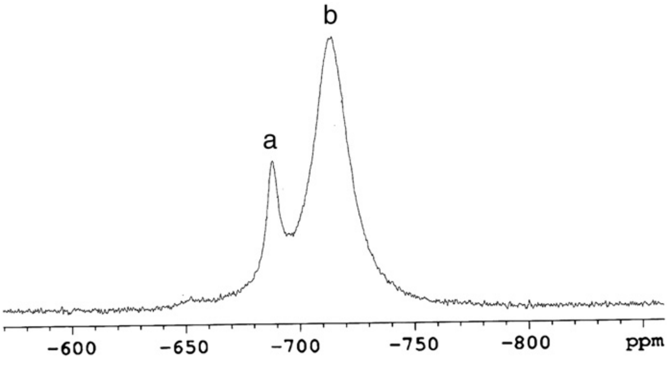

Fig. 2. ^{51}V NMR spectrum of $[N(C_4H_9)_4]\{[VO(HO_2)(O_2)(phen)][VO(O_2)_2(phen)]\}\cdot 3H_2O_2\cdot H_2O$ in formamide: $[VO(O_2)_2(HCONH_2)]^-$ (a), complex **1** (b); $c(V) = 10^{-2}$ mol/dm^3; $T = 278$ K.

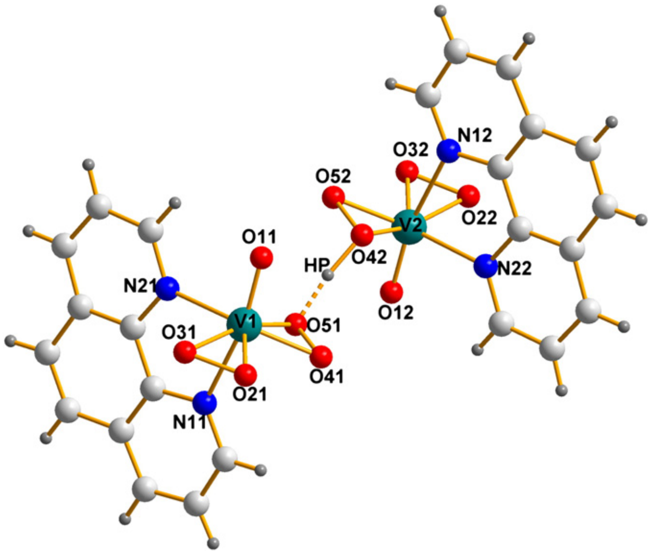

Fig. 3. A diamond presentation of the structure of $\{[VO(HO_2)(O_2)(phen)][VO(O_2)_2(phen)]\}^-$. Selected interatomic distances (Å) and angles (°) for hydrogen bond: O(51)–HP 1.293(3), O(42)–HP 1.151(3), O(51)–HP–O(42) 172.3(2), O(41)–O(51)–HP 104.1(3), HP–O(51)–V(1) 110.9(2), V(2)–O(42)–HP 116.3(2), HP–O(42)–O(52) 100.0(2).

To understand the role of stacking and hydrogen bonding interactions in stabilization of the crystal structure (Fig. 5), we employed quantum chemistry calculations in gas phase to determine binding energies for the given complexes (Table 1). Large variety of different methods suitable for calculation of noncovalent interactions have been introduced into quantum chemistry during last years [30]. In our work we used MP2.5 method in conjunction with proper basis set [31], which has been recently proposed by Pitoňák and coworkers [32]. The robustness and efficiency of this method were furthermore proved by extensive comparison of calculated geometries and binding energies for noncovalent complexes with benchmark data [33].

As demonstrated in Table 1, the binding energies for hydrogen-bonded complexes are already qualitatively described by lower level methods, because hydrogen bond interaction is mostly dominated

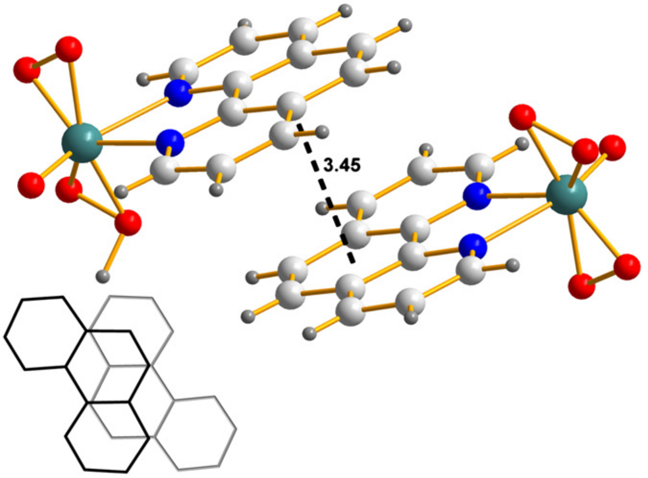

Fig. 4. Upper projection is presenting the stacking interaction between $[VO(HO_2)(O_2)(phen)]$ and $[VO(O_2)_2(phen)]^-$ complex entities in the crystal structure. Approximate distance between phenanthroline planes is 3.45 Å. Lower projection represents more closely mutual displacement of the two interacting 1,10-phenanthroline ligands.