



## Structural investigation of tetraperoxo complexes of Mo(VI) and W(VI) X-ray and theoretical studies

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### ABSTRACT

The family of very unstable tetraperoxo compounds has been prepared from aqueous solutions containing H<sub>2</sub>O<sub>2</sub> and salts of Mo(VI) or W(VI). The crystal structures of Na<sub>2</sub>[Mo(O<sub>2</sub>)<sub>4</sub>]·4H<sub>2</sub>O and Na<sub>2</sub>[W(O<sub>2</sub>)<sub>4</sub>]·4H<sub>2</sub>O have been determined from single-crystal data, while the crystal structures of Rb<sub>2</sub>[Mo(O<sub>2</sub>)<sub>4</sub>], Cs<sub>2</sub>[Mo(O<sub>2</sub>)<sub>4</sub>], Rb<sub>2</sub>[W(O<sub>2</sub>)<sub>4</sub>] and Cs<sub>2</sub>[W(O<sub>2</sub>)<sub>4</sub>] have been determined from powder X-ray diffraction data. The compounds were also characterised by IR spectroscopy and the number of peroxy groups was determined by titration methods. By means of the density functional theory (DFT) method, the geometry and stability of tetraperoxo complexes have been studied. Even though in all tetraperoxo complexes the central atom Mo(VI), W(VI) or V(V) is surrounded by four peroxy groups and the geometry of the [Me(O<sub>2</sub>)<sub>4</sub>]<sup>n-</sup> anion is essentially the same, the investigated compounds differ in stability and colour and crystallise in different crystallographic systems.

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### 1. Introduction

Hydrogen peroxide readily associates with transition metals such as Mo(VI), W(VI) and V(V), forming a number of peroxy complexes whose nature depends on the pH and relative concentration of the reagents. Interest in peroxy complexes has increased since the 19th century because of their important applications in chemistry and biology. They have been used as both stoichiometric and effective catalytic oxidants of different organic and inorganic substrates [1]. Peroxy compounds generate dioxygen in its first excited singlet state (<sup>1</sup>O<sub>2</sub>), which is a regio- and stereo-selective oxidant [2]. Peroxomolybdates can be used for obtaining selective and efficient non-chlorine oxidising agents, suitable for a closed pulp system in pulp bleaching processes [3]. Peroxo vanadium complexes have been used as extremely efficient insulin-mimetic agents in the treatment of human diabetes [4] and they show antitumor activity in mice [5].

Many peroxy compounds of Mo(VI), W(VI) and V(V) including mono-, di- and tri-peroxy complexes have been prepared and structurally characterised in the laboratories of Stomberg [6–32], Griffith [33–40], Djordjevic [5,41–44] and Einstein [45,46]. The chemistry of peroxy compounds of the transition elements (Cr, Mo, W) and vanadium peroxide complexes was reviewed by

Dickman and Pope [47] and by Butler et al. [48]. In the inorganic crystal structures database ICSD (2007; 100, 243 entries) [49], there are 45 peroxy compounds comprising Mo (19 complexes), W (9 complexes) and V (17 complexes). Among this group there are only five peroxy compounds whose structure is based on the tetraperoxy anion [Me(O<sub>2</sub>)<sub>4</sub>] (Me = transition metal), namely, [Zn(NH<sub>3</sub>)<sub>4</sub>][Mo(O<sub>2</sub>)<sub>4</sub>] [7], K<sub>2</sub>[Mo(O<sub>2</sub>)<sub>4</sub>] [50], K<sub>2</sub>[W(O<sub>2</sub>)<sub>4</sub>] [25], Na<sub>3</sub>[V(O<sub>2</sub>)<sub>4</sub>]·H<sub>2</sub>O<sub>2</sub>·10.5H<sub>2</sub>O and Na<sub>3</sub>[V(O<sub>2</sub>)<sub>4</sub>]·14H<sub>2</sub>O [51]. Such a small number of tetraperoxy complexes results from the great instability of this type of compounds. They decompose within minutes at room temperature, and can even explode when struck.

In earlier investigations in our laboratory we obtained and structurally characterised five tetraperoxy compounds, namely, Li<sub>2</sub>[Mo(O<sub>2</sub>)<sub>4</sub>]·4H<sub>2</sub>O, Li<sub>2</sub>[W(O<sub>2</sub>)<sub>4</sub>]·4H<sub>2</sub>O [52], K<sub>2</sub>[Mo(O<sub>2</sub>)<sub>4</sub>] [50], (NH<sub>4</sub>)<sub>3</sub>[V(O<sub>2</sub>)<sub>4</sub>] and K<sub>3</sub>[V(O<sub>2</sub>)<sub>4</sub>] [53]. In this paper we present the results of crystal structure investigations of six new tetraperoxy complexes of Mo(VI) and W(VI) and also a short review of this type of compounds. Most importantly, the crystal structure studies reported in this paper were performed using both powder diffraction (four complexes) and single crystal methods (two compounds). The results of the crystal structure investigations are correlated with the DFT study of tetraperoxy anions with the aim of explaining the instability of tetraperoxy compounds.

### 2. Experimental

In general, the tetraperoxy complexes of Mo(VI), W(VI) and V(V) were obtained from solutions of molybdates, tungstates and

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vanadates in cold hydrogen peroxide (30%,  $-4^{\circ}\text{C}$ ) with the addition of alcohol to lower solubility. In most cases, under such conditions, only very fine precipitates were obtained. Only in few cases the monocrystals were obtained.

### 2.1. X-ray single crystal study

For X-ray studies, single crystals of the investigated compounds were taken from the mother solutions and very quickly loaded into a glass capillary. The capillary were mounted on the goniometer head and placed in a stream of  $\text{N}_2$  vapor. The temperature of crystals during the diffraction experiment was 258 K.

X-ray data for the single crystal structure determination were collected on a Kappa CCD Bruker–Nonius diffractometer. The crystal data and the refinement details for the

**Table 1**  
Crystal and experimental data for  $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$ .<sup>a</sup>

	(a)	(b)
Compound	$\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$	$\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$
<i>M</i>	341.98	429.89
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (14)	$P2_1/c$ (14)
<i>a</i> (Å)	9.112 (2)	9.118 (2)
<i>b</i> (Å)	8.623 (1)	8.623 (1)
<i>c</i> (Å)	12.396 (2)	12.400 (2)
$\beta$ ( $^{\circ}$ )	93.815 (8)	93.904 (8)
<i>Z</i>	4	4
<i>V</i> (Å <sup>3</sup> )	971.83 (3)	972.68 (3)
Calculated density (Mg/m <sup>3</sup> )	2.337	2.936
<i>F</i> (000)	672	800
Crystal size (mm)	0.25 × 0.15 × 0.15	0.625 × 0.3 × 0.3
Absorption coeff. (mm <sup>-1</sup> ) <sup>a</sup>	1.493	12.019
Theta range for data collection ( $^{\circ}$ )	2.88 to 27.48	2.24 to 27.48
Completeness to theta (%)	99.9	99.9
Data/restraints/parameters	2235/12/169	2236/12/168
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.132	1.372
Reflections collected/unique	2235/2078	2236/2078
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0233, 0.0649	0.0416, 0.1093
<i>R</i> indices (all data) <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0270, 0.0791	0.0462, 0.1151
Largest diff. peak and hole (Å <sup>-3</sup> )	0.469e and -0.686e	1.410e and -5.721e

<sup>a</sup> Special absorption correction technique was not applied except of standard MULTISCAN option in SCALEPACK/DENZO package.

$\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  compounds are listed in Table 1. The structures were solved by direct methods and refined using SHELXS and SHELXL-97 [54] programs, respectively. All non-hydrogen atoms were refined anisotropically. H atoms were located from difference Fourier maps. Absorption corrections were performed using the multiscan procedure of diffractometer software.

### 2.2. Powder diffraction study

For the powder X-ray investigations of the teraperoxo complexes, portions of the wet samples were thoroughly powdered and placed into a sample holder of a low-temperature Anton Paar camera (temperature: 258 K). The XRD measurements were performed by using a Philips X'Pert diffractometer. Radiation type and source: X-ray,  $\text{CuK}\alpha$ , 1.54178 Å. Bragg–Brentano geometry, fixed slits 1/2 $^{\circ}$ .

Experimental and data collection details for the  $\text{Rb}_2[\text{Mo}(\text{O}_2)_4]$ ,  $\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$ ,  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$  and  $\text{Cs}_2[\text{W}(\text{O}_2)_4]$  compounds are listed in Table 2. The lattice parameters and space groups were determined using a PROSZKI package [55]. The crystal structure models were obtained by global optimisation methods (FOX program [56]). Final refinements were performed using XRS-82 [57] or GSAS [58,59] programs, which enabled the use of geometric constraints during the refinement procedure.

### 2.3. Number of O<sub>2</sub> groups

The number of peroxo groups was determined by permanganate  $\text{KMnO}_4$  titration. Taking into account errors and decomposition processes, titration results confirmed the presence of four peroxo groups in each compound, which is particularly important in the case of the powder diffraction study (lower precision). The exact number of  $\text{O}_2$  groups in each compound was found to be equal:  $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$ —3.93, ( $\text{O}_2^{2-}$  found: 36.79%, calculated: 37.44%);  $\text{Rb}_2[\text{Mo}(\text{O}_2)_4]$ —3.90, ( $\text{O}_2^{2-}$  found: 31.60%, calculated: 32.41%);  $\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$ —3.88, ( $\text{O}_2^{2-}$  found: 25.35%, calculated: 26.13%);  $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$ —3.96, ( $\text{O}_2^{2-}$  found: 29.48%, calculated: 29.77%);  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$ —3.90, ( $\text{O}_2^{2-}$  found: 25.85%, calculated: 26.51%);  $\text{Cs}_2[\text{W}(\text{O}_2)_4]$ —3.89, ( $\text{O}_2^{2-}$  found: 21.55%, calculated: 22.16%).

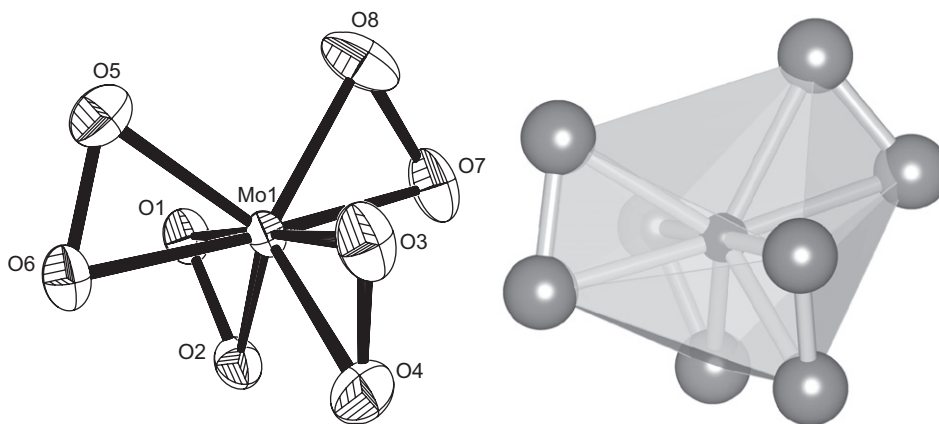
**Table 2**  
Experimental details and data collection of the  $\text{Rb}_2[\text{Mo}(\text{O}_2)_4]$ ,  $\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$ ,  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$  and  $\text{Cs}_2[\text{W}(\text{O}_2)_4]$  compounds.

	(a) $\text{Rb}_2[\text{Mo}(\text{O}_2)_4]$	(b) $\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$	(c) $\text{Rb}_2[\text{W}(\text{O}_2)_4]$	(d) $\text{Cs}_2[\text{W}(\text{O}_2)_4]$
Crystal system	Monoclinic	Monoclinic	Hexagonal/rhombohedral	Monoclinic
Space group	$P2_1/c$ (14)	$P2_1/c$ (14)	$R-3c$ (167)	$P2_1/c$ (14)
<i>Z</i>	4	4	18	4
Measurement range [ $2\theta$ ]	5–80	17–70	5–80	5–80
<i>a</i> (Å)	6.8956 (7)	7.075 (2)	11.9720 (1)	7.0893 (9)
<i>b</i> (Å)	8.6323 (7)	9.017 (2)		8.974 (1)
<i>c</i> (Å)	13.296 (1)	14.681 (3)	25.9873 (6)	13.960 (2)
$\beta$ ( $^{\circ}$ )	116.479 (8)	122.11 (1)		116.853 (9)
<i>V</i> (Å <sup>3</sup> )	708.41 (8)	793.5 (2)	3225.71 (7)	792.36 (2)
<i>M</i> <sub>30</sub>	36.27	15.68	26.77	43.73
<i>F</i> <sub>30</sub>	82.98	35.03	36.87	90.69
Number of observations	3750	2650	3750	3750
Number of reflections	428	332	225	471
Total number of atoms	11	11	11	11
<i>R</i> <sub>wp</sub> (%)	16.9	8.9	11.00	13.0
<i>R</i> <sub>B</sub> (%)	19.0	9.7	10.13	13.1
Crystal model	FOX	FOX	$\text{K}_2[\text{W}(\text{O}_2)_4]$	$\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$
Refinement program	XRS-82	XRS-82	GSAS	XRS-82

**Table 3**  
Significant infrared frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) of the tetraperoxo complexes.

Compound	$\nu_{\text{sym}} [\text{O}-\text{O}]$	$\nu_{\text{sym}} [\text{M}(\text{O}_2)]$	$\nu_{\text{asym}} [\text{M}(\text{O}_2)]$	Other bands
$\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$	836 vs	582 w	557 w	
$\text{Rb}_2[\text{Mo}(\text{O}_2)_4]$	880 m, 858 vs, 831 vs, 817 s	630 vs, 616 vs, 607 vs	551 vs	586 s, 488 m, 463 s
$\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$	843 vs, 828 w	606 m	567 vs, 557 vs, 546 m	485 w, 453 m
$\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$	844 m, 828 vs	596 m	551 s	921 s, 758 s, 471 m, 414 w
$\text{Rb}_2[\text{W}(\text{O}_2)_4]$	830 s	598 m	577 vs, 560 vs, 555 vs	512 m, 495 s
$\text{Cs}_2[\text{W}(\text{O}_2)_4]$	827 s, 812 w	600 m	554 vs	576 w, 539 w, 509 w, 485 m

Abbreviations: vs—very strong; s—strong; m—middle; w—weak.

**Fig. 1.**

## 2.4. IR spectroscopy

The infrared spectra were obtained on a Bruker IFS 48 instrument (KBr pellet technique) across the  $4000\text{--}400\text{ cm}^{-1}$  region. According to the literature data, the stretching modes for peroxy compounds associated with the side-bonded peroxy ligands ( $\nu_{\text{sym}}(\text{O}-\text{O})$ ,  $\nu_{\text{sym}}[\text{M}(\text{O}_2)]$  and  $\nu_{\text{asym}}[\text{M}(\text{O}_2)]$ ) are about 880, 600 and  $530\text{ cm}^{-1}$ , respectively [34]. The obtained results (see Table 3) confirmed the presence of the side-bonded peroxy ligands in the complexes of Mo(VI), W(VI) and V(V).

## 3. Results and discussion

The same type of isolated tetraperoxo anion exists in all investigated compounds. Fig. 1 illustrates a tetraperoxo anion. The  $[\text{Me}(\text{O}_2)_4]^{2-}$  anion ( $\text{Me} = \text{Mo}, \text{W}$ ) has distorted dodecahedral symmetry, approximately  $\bar{4}2m$ .

### 3.1. Crystal structures of $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$ determined from single crystal study

The two sodium salts  $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  are isotopic. The crystals of sodium tetraperoxomolybdate(VI) tetrahydrate consist of sodium cations, tetraperoxomolybdate(VI) anions and molecules of crystallisation water. Similarly, the crystals of sodium tetraperoxotungstate(VI) tetrahydrate consist of sodium cations, tetraperoxotungstate(VI) anions and molecules of water. The fractional atomic coordinates for  $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  are listed in Table 4a and b. Fig. 1 illustrates the tetraperoxo anion, while packing of the molecules in the unit cell for  $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  is presented in Fig. 2a and b. Selected bond distances and angles for the  $[\text{Mo}(\text{O}_2)_4]^{2-}$  and  $[\text{W}(\text{O}_2)_4]^{2-}$  anions are given in Table 5.

**Table 4**Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for (a)  $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$  and (b)  $\text{Na}_2[\text{W}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$ .<sup>a</sup>

Atom	x	y	z	U (eq)
(a)				
Mo	2383 (1)	2308 (1)	6280 (1)	17 (1)
Na1	1857 (1)	−1516 (1)	5166 (1)	28 (1)
Na2	3341 (1)	−1849 (1)	7813 (1)	25 (1)
O1	1211 (2)	4195 (2)	6518 (2)	28 (1)
O2	1672 (2)	3392 (2)	7543 (2)	29 (1)
O3	3602 (2)	462 (2)	6111 (2)	31 (1)
O4	3362 (3)	824 (3)	7259 (2)	38 (1)
O5	3477 (2)	3414 (3)	5217 (2)	31 (1)
O6	4135 (2)	3660 (2)	6329 (2)	28 (1)
O7	599 (2)	1095 (3)	6156 (2)	39 (1)
O8	1051 (2)	1623 (3)	5089 (2)	44 (1)
O10	1130 (2)	−2473 (2)	1823 (2)	25 (1)
O11	1838 (2)	−3962 (2)	4220 (2)	29 (1)
O12	3312 (2)	−706 (2)	3723 (2)	26 (1)
O13	4094 (2)	−2959 (2)	6134 (2)	30 (1)
(b)				
W1	2387 (1)	2315 (1)	6267 (1)	11 (1)
Na1	1834 (3)	−3504 (4)	10161 (2)	22 (1)
Na2	3332 (3)	−1848 (4)	7815 (2)	18 (1)
O1	1223 (6)	4200 (7)	6511 (5)	23 (1)
O2	1676 (6)	3370 (7)	7529 (4)	22 (1)
O3	3600 (6)	451 (6)	6097 (5)	23 (1)
O4	3304 (6)	804 (6)	7251 (5)	30 (1)
O5	6498 (6)	−1567 (7)	9777 (4)	27 (1)
O6	5846 (5)	−1352 (7)	8641 (4)	22 (1)
O7	583 (6)	1095 (8)	6109 (6)	35 (2)
O8	1100 (6)	1700 (8)	5038 (5)	32 (1)
O10	1136 (7)	−2534 (6)	6823 (5)	19 (1)
O11	1835 (6)	−1040 (7)	9228 (4)	23 (1)
O12	3319 (5)	−4302 (6)	8725 (4)	21 (1)
O13	4113 (7)	−2986 (7)	6146 (5)	26 (1)

<sup>a</sup> The full list of anisotropic displacement parameters and atomic coordinates for all atoms have been deposited in ICSD (Fachinformationszentrum, Karlsruhe, Germany).

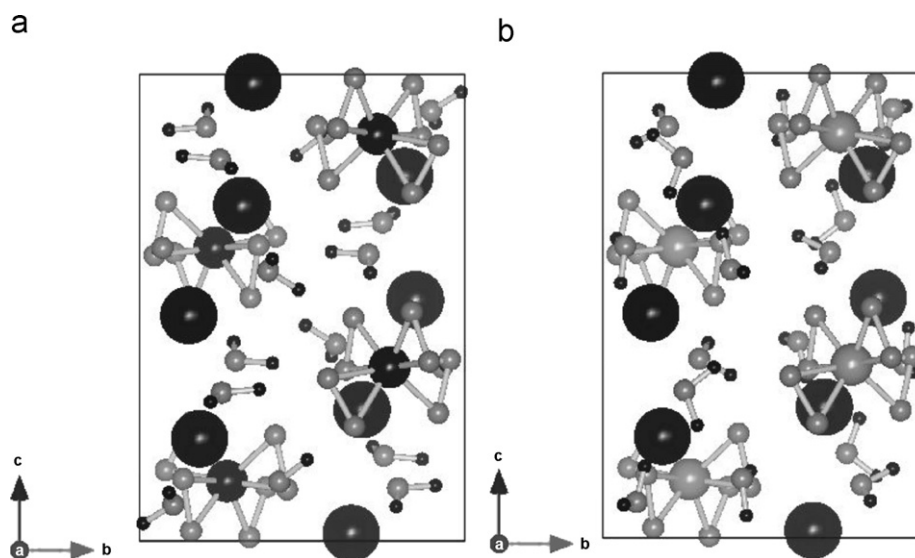


Fig. 2.

Besides ionic bonding, the structures of tetraperoxo complexes are stabilised by moderate hydrogen bonds created by water molecules and oxygen atoms from peroxo groups. Interestingly, some oxygen atoms from  $O_2^{2-}$  groups create bifurcated bonds, while some oxygen atoms do not create hydrogen bonds at all.

In  $Na_2[Mo(O_2)_4] \cdot 4H_2O$  there are two kinds of hydrogen bonds: normal with one acceptor, and bifurcated. The X–H...A bond distances range from 2.814 to 3.484 Å. Among eight oxygen atoms from peroxo groups, two, O7 and O8, do not create H-bonds. Atoms O1, O2 and O5 oxygen are acceptors of more than one H-bond. Atoms H101, H121, H122 and H132 take part in bifurcated H-bonds. A list of H-bonds for the  $Na_2[Mo(O_2)_4] \cdot 4H_2O$  complex is presented in Table 6.

In both compounds there are two kinds of sodium cations. While one is surrounded by the seven nearest oxygen atoms from peroxo groups and water molecules, the other is surrounded by nine oxygen atoms. Oxygen atoms from water molecules are closer to sodium cations than oxygen atoms from peroxo groups.

### 3.2. Crystal structures of $Rb_2[Mo(O_2)_4]$ , $Cs_2[Mo(O_2)_4]$ , $Rb_2[W(O_2)_4]$ and $Cs_2[W(O_2)_4]$ determined from powder diffraction data

#### 3.2.1. Crystal structure of $Rb_2[Mo(O_2)_4]$

A crystal model for  $Rb_2[Mo(O_2)_4]$  was obtained by using global optimisation–parallel tempering methods (FOX program [56]). After 1,000,000 cycles, a weighted profile  $R_{wp}$  factor equalling 9% was achieved. Final refinement was performed using an XRS-82 program [57]. Weak geometric restraints were applied during the refinement procedure. The cell and discrepancy values are reported in Table 2. The Rietveld refinement plot obtained for  $Rb_2[Mo(O_2)_4]$  is presented in Fig. 3.

The crystals consist of tetraperoxomolybdate(VI) ions and  $Rb^+$  ions, held together by ionic forces. No crystallisation water was observed. Rubidium cations are coordinated differently. While the Rb1 atom is surrounded by eleven of the nearest oxygen atoms (2.7(1)–3.20(9) Å), the Rb2 atom is surrounded by seven oxygen atoms (2.84(6)–3.23(9) Å). The atomic parameters and bond lengths for  $Rb_2[Mo(O_2)_4]$  are presented in Tables 7a and 8. Projection of the unit cell is presented in Fig. 4a.

#### 3.2.2. Crystal structure of $Cs_2[Mo(O_2)_4]$

A crystal model for  $Cs_2[Mo(O_2)_4]$  was created by using global optimisation methods–parallel tempering (FOX program [56]).

Table 5

Selected bond distances in  $Na_2[Mo(O_2)_4] \cdot 4H_2O$  and in  $Na_2[W(O_2)_4] \cdot 4H_2O$ .

Mo–O1	1.9795 (19)	W–O1	1.976 (5)
Mo–O2	1.9701 (19)	W–O2	1.958 (5)
Mo–O3	1.9596 (19)	W–O3	1.971 (5)
Mo–O4	1.939 (2)	W–O4	1.936 (5)
Mo–O5	1.953 (2)	W–O5 <sup>a</sup>	1.953 (6)
Mo–O6	1.9743 (19)	W–O6 <sup>a</sup>	1.976 (5)
Mo–O7	1.931 (2)	W–O7	1.952 (5)
Mo–O8	1.940 (2)	W–O8	1.933 (5)
O1–O2	1.483 (3)	O1–O2	1.485 (8)
O3–O4	1.487 (3)	O3–O4	1.505 (8)
O5–O6	1.481 (3)	O5–O6	1.502 (8)
O7–O8	1.484 (4)	O7–O8	1.531 (10)

Symmetry transformations used to generate equivalent atoms.

<sup>a</sup>  $[-x+1, y+1/2, -z+3/2]$ .

Table 6

Hydrogen bonds for  $Na_2[Mo(O_2)_4] \cdot 4H_2O$ .

D–H	<i>d</i> (H..A)	<DHA	<i>d</i> (D..A)	A
O10–H101	1.861	176.23	2.834	O2 <sup>a</sup>
O10–H101	2.564	143.90	3.401	O1 <sup>a</sup>
O10–H102	1.858	175.90	2.854	O1 <sup>b</sup>
O11–H111	1.994	160.81	2.938	O5 <sup>c</sup>
O11–H112	1.888	176.58	2.874	O1 <sup>a</sup>
O12–H121	1.810	175.92	2.814	O3 <sup>d</sup>
O12–H121	2.473	144.38	3.342	O4 <sup>d</sup>
O12–H122	1.856	166.52	2.840	O2 <sup>b</sup>
O12–H122	2.620	144.46	3.484	O1 <sup>b</sup>
O13–H131	1.929	161.07	2.890	O5 <sup>d</sup>
O13–H132	1.962	160.73	2.926	O6 <sup>c</sup>
O13–H132	2.481	146.54	3.362	O5 <sup>c</sup>

Symbols used: D–H, *d*(H..A), *d*(D..A): donor–hydrogen, hydrogen–acceptor and donor–acceptor distances, <DHA—donor–hydrogen–acceptor angle, A—acceptor, a, b, c, d, symmetry codes.

<sup>a</sup>  $[-x, -y, -z+1]$ .

<sup>b</sup>  $[x, -y+1/2, z-1/2]$ .

<sup>c</sup>  $[x, y-1, z]$ .

<sup>d</sup>  $[-x+1, -y, -z+1]$ .

After 500,000 cycles, an  $R_{wp}$  equal to 12% was obtained. The structure was refined by the Rietveld method (XRS-82 program [57]) using weak geometric restraints. The cell and discrepancy values are reported in Table 2. The Rietveld refinement plot obtained for  $Cs_2[Mo(O_2)_4]$  is presented in Fig. 5.



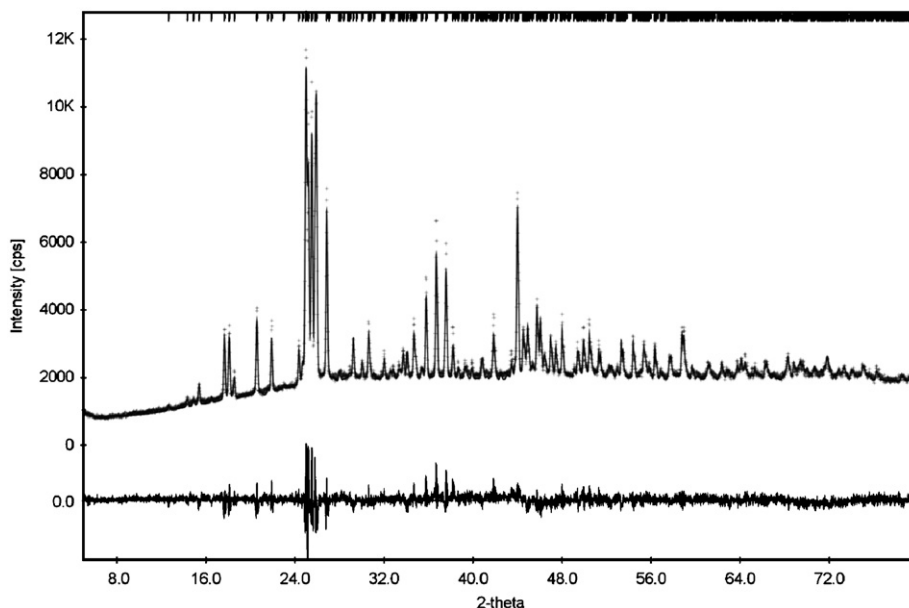


Fig. 3.

The crystals of  $\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$  consist of tetraperoxomolybdate(VI) ions and  $\text{Cs}^+$  ions, held together by ionic forces. No crystallisation water was observed. The coordination sphere of the Cs1 atom is formed by eleven oxygen atoms (2.9(1)–3.36(8) Å), while the Cs2 atom is surrounded by nine oxygen atoms (2.96(9)–3.38(9) Å). The atomic parameters and bond lengths for  $\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$  are presented in Tables 7b and 8. Projection of the unit cell is presented in Fig. 4b.

### 3.2.3. Crystal structure of $\text{Rb}_2[\text{W}(\text{O}_2)_4]$

The obtained  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$  compounds have similar crystal parameters and the same space group as  $\text{K}_2[\text{W}(\text{O}_2)_4]$  [25]. The structure of potassium salt was used as a model for crystal structure refinement. The Rietveld refinement was carried out by using the GSAS program [58,59]. Weak geometric restraints were used during the refinement process.

The cell and discrepancy values for  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$  are reported in Table 2. The Rietveld refinement plot obtained for  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$  is presented in Fig. 6.

The crystals of  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$  consist of tetraperoxotungstate(VI) ions and  $\text{Rb}^+$  ions, held together by ionic forces. No crystallisation water was observed. The coordination sphere of the Rb1 atom is formed by nine oxygen atoms (2.75818(3)–2.96119(3) Å). The Rb2 atom is surrounded by the twelve nearest oxygen atoms (2.84108(3)–3.08348(4) Å), while the Rb3 atom has eight neighbouring oxygen atoms (2.86210(3)–3.21597(3) Å).

The atomic parameters and bond lengths for  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$  are presented in Tables 7c and 8. Projection of the unit cell is presented in Fig. 4c.

### 3.2.4. Crystal structure of $\text{Cs}_2[\text{W}(\text{O}_2)_4]$

The crystal structure of  $\text{Cs}_2[\text{Mo}(\text{O}_2)_4]$  was used as a starting model for the Rietveld refinement for  $\text{Cs}_2[\text{W}(\text{O}_2)_4]$ . The refinement was performed by using the XRS-82 program [57]. In this case also, weak geometric constraints on bond distances were applied. The cell and discrepancy values are reported in Table 2. The Rietveld refinement plot obtained for  $\text{Cs}_2[\text{W}(\text{O}_2)_4]$  is presented in Fig. 7.

The crystals of  $\text{Cs}_2[\text{W}(\text{O}_2)_4]$  consist of tetraperoxotungstate(VI) ions and  $\text{Cs}^+$  ions, held together by ionic forces. In this case also, no crystallisation water was observed. The coordination sphere of the Cs1 atom is formed by eleven oxygen atoms ( $d \leq 3.5$  Å), while the Cs2 atom is surrounded by twelve oxygen atoms ( $d \leq 3.5$  Å). The atomic parameters and bond lengths for  $\text{Cs}_2[\text{W}(\text{O}_2)_4]$  are presented in Tables 7d and 8. Projection of the unit cell is presented in Fig. 4d.

### 3.3. General description of crystal structures of tetraperoxo complexes

In the group of tetraperoxo complexes of Mo(VI) and cations of first group of the periodic table of the elements, four compounds crystallise in the monoclinic system SG. 14 (three are described in  $P2_1/c$ , one in  $P2_1/n$ ). The potassium salts crystallise in the rhombohedral/hexagonal system, space group  $R-3c$  (167). Among tetraperoxotungstates(VI), three complexes crystallise in the monoclinic system SG. 14 (two are described in space group  $P2_1/c$  and one in  $P2_1/n$ ). Two compounds crystallise in the rhombohedral/hexagonal system  $R-3c$  (167). Tetraperoxovanadates(V) crystallise in tetragonal (two compounds) and in triclinic (two compounds) systems, in space groups  $I-42m$  (121) and  $P-1$  (2), respectively. The detailed structural data for tetraperoxo complexes of Mo(VI), W(VI) and V(V) are presented in Table 9.

Compounds with small cations, like  $\text{Li}^+$  and  $\text{Na}^+$ , contain 4 molecules of crystallisation water. Tetraperoxo compounds of  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  are anhydrous.

The O–O bond length in peroxo groups in complexes containing Mo(VI) ranges from 1.477(3) to 1.66(4) Å. The O–O bond length in tetraperoxotungstates(VI) is 1.499(4)–1.512 Å. In tetraperoxovanadates(V), the O–O bond length ranges from 1.42(2) to 1.518. The distance between two oxygen atoms in peroxo groups is marginally greater in compounds of W(VI) than in compounds containing Mo(VI). However, this distance is significantly greater in tetraperoxo complexes of W(VI) than in complexes of V(V). There is no clear relationship in bond lengths between oxygen atoms and the central atom in peroxo

compounds. The bond lengths O–O and distances  $Me-O_{\text{peroxo}}$ , where  $Me$  = transition metal Mo(VI), W(VI) or V(V), are presented in Table 10.

**Table 7**

Atomic parameters for: (a)  $Rb_2[Mo(O_2)_4]$ , (b)  $Cs_2[Mo(O_2)_4]$ , (c)  $Rb_2[W(O_2)_4]$  and (d)  $Cs_2[W(O_2)_4]$ .

Atom	x	y	z	U
(a)				
Mo	0.820 (3)	0.279 (2)	0.087 (2)	0.012 (8)
Rb1	0.497 (5)	0.018 (2)	0.732 (2)	0.000 (6)
Rb2	0.154 (4)	0.192 (2)	0.909 (2)	0.009 (8)
O1	1.08 (1)	0.366 (8)	0.073 (8)	0.01 (1)
O2	1.140 (6)	0.23 (1)	0.153 (8)	0.01 (1)
O3	0.56 (1)	0.192 (9)	0.101 (8)	0.01 (1)
O4	0.77 (1)	0.131 (8)	0.190 (6)	0.01 (1)
O5	0.69 (1)	0.490 (6)	0.078 (7)	0.01 (1)
O6	0.85 (1)	0.454 (8)	0.194 (6)	0.01 (1)
O7	0.65 (1)	0.25 (1)	−0.079 (3)	0.01 (1)
O8	0.81 (2)	0.118 (9)	−0.025 (6)	0.01 (1)
(b)				
Mo	0.354 (4)	0.221 (2)	0.089 (2)	0.016 (9)
Cs1	0.973 (3)	0.016 (1)	0.231 (1)	0.010 (5)
Cs2	0.342 (3)	0.685 (1)	0.092 (2)	0.013 (6)
O1	0.44 (2)	0.011 (5)	0.085 (9)	0.02769
O2	0.54 (2)	0.065 (9)	0.196 (7)	0.02769
O3	0.20 (2)	0.23 (1)	−0.071 (3)	0.02769
O4	0.18 (2)	0.373 (9)	−0.024 (7)	0.02769
O5	0.08 (1)	0.16 (1)	0.09 (1)	0.03 (2)
O6	0.22 (2)	0.27 (1)	0.175 (9)	0.02769
O7	0.59 (1)	0.36 (1)	0.199 (7)	0.02769
O8	0.65 (1)	0.30 (1)	0.122 (8)	0.02769
(c)				
W1	0.3178 (2)	0.0	0.25	0.03 (9)
Rb1	0.0	0.0	0.3347 (8)	0.0 (2)
Rb2	0.0	0.0	0.0	0.0 (4)
Rb3	0.6538 (6)	0.0	0.25	0.0 (2)
O1	0.814 (1)	0.246 (3)	0.5466 (8)	0.1 (7)
O2	0.914 (2)	0.360 (3)	0.5176 (6)	0.2 (5)
O3	0.148 (1)	0.424 (3)	0.6250 (8)	0.1 (5)
O4	0.145 (2)	0.503 (2)	0.581 (1)	0.2 (5)
(d)				
W	0.336 (3)	0.218 (1)	0.086 (1)	0.04 (1)
Cs1	1.009 (6)	0.017 (1)	0.242 (2)	0.001 (6)
Cs2	0.321 (3)	0.688 (2)	0.089 (2)	0.000 (9)
O1	0.29 (2)	0.362 (9)	0.182 (7)	0.00 (2)
O2	0.09 (1)	0.29 (1)	0.107 (8)	0.00 (2)
O3	0.635 (6)	0.24 (1)	0.113 (9)	0.00 (2)
O4	0.55 (1)	0.087 (8)	0.078 (9)	0.00 (2)
O5	0.34 (2)	0.056 (9)	0.186 (6)	0.00 (2)
O6	0.22 (2)	0.012 (5)	0.072 (8)	0.00 (2)
O7	0.19 (2)	0.22 (1)	−0.074 (2)	0.00 (2)
O8	0.29 (2)	0.37 (1)	−0.029 (6)	0.00 (2)

**Table 8**

Bond distances in  $Rb_2[Mo(O_2)_4]$ ,  $Cs_2[Mo(O_2)_4]$ ,  $Rb_2[W(O_2)_4]$  and  $Cs_2[W(O_2)_4]$ .

$Rb_2[Mo(O_2)_4]$		$Cs_2[Mo(O_2)_4]$		$Rb_2[W(O_2)_4]$		$Cs_2[W(O_2)_4]$	
Mo–O1	2.01 (9)	Mo–O1	2.00 (7)	W1–O1	2.006 (2)	W–O1	2.0 (1)
Mo–O2	2.01 (5)	Mo–O2	1.99 (8)	W1–O2	2.0028 (4)	W–O2	2.00 (9)
Mo–O3	2.01 (9)	Mo–O3	2.00 (5)	W1–O3	2.019 (2)	W–O3	1.99 (6)
Mo–O4	2.01 (9)	Mo–O4	2.00 (8)	W1–O4	1.976 (3)	W–O4	1.99 (9)
Mo–O5	2.02 (9)	Mo–O5	2.0 (1)			W–O5	1.99 (9)
Mo–O6	2.02 (8)	Mo–O6	2.0 (1)			W–O6	1.99 (6)
Mo–O7	2.00 (4)	Mo–O7	1.99 (9)			W–O7	1.99 (3)
Mo–O8	2.01 (9)	Mo–O8	1.99 (9)			W–O8	2.00 (6)
O1–O2	1.5 (1)	O1–O2	1.5 (1)	O1–O2	1.490 (2)	O1–O2	1.5 (1)
O3–O4	1.48 (9)	O3–O4	1.5 (1)	O3–O4	1.500 (3)	O3–O4	1.5 (1)
O5–O6	1.48 (9)	O5–O6	1.5 (1)			O5–O6	1.5 (1)
O7–O8	1.5 (1)	O7–O8	1.5 (1)			O7–O8	1.5 (1)

In all the investigated tetraperoxo compounds the same kind of anion is observed. In the anions the central atom—Mo(VI), W(VI) or V(V)—is surrounded by four peroxo groups. In all cases the anion shows distorted dodecahedral symmetry, approximately  $\bar{4}2m$ . The structure of the tetraperoxo anion and coordination polyhedral is presented in Fig. 1. A distortion parameter of polyhedra was calculated according to definition, based on the equation:  $\Delta_1 = \sum_i 1/8 \times [(R_i - R)/R]^2$ , where  $R_i$  is the individual distance between the central atom and an atom in a corner of polyhedra and  $R$  is the average distance between the central atom and an atom in a corner of polyhedral [60]. Generally, the greatest value of the distortion parameter is observed in cases of complexes containing small cations, such as  $Li^+$ ,  $Na^+$  and crystallisation water. This observation is connected with the thermal stability of tetraperoxo complexes. All these compounds are unstable at room temperature. The fastest decomposition (within minutes) is observed in the case of compounds which contain small cations and molecules of water. With an increase in cation size, the distortion parameter decreases and the stability of compounds increases. The distortion parameters for tetraperoxo compounds are presented in Table 11.

In the anion there are two pairs of two peroxo groups lying in the same plane. The planes, perpendicular to each other, are also perpendicular to the equatorial plane created by the Me atom and the O1, O3, O5 and O7 oxygen atoms (see Fig. 1).

Values of O–M–O angles for oxygen atoms lying in the equatorial plane range from  $17X$  to  $180^\circ$ ; O–Me–O angles out of plane range from  $135^\circ$  to  $145^\circ$ . In most cases Me–O distances lying in the equatorial plane are larger than Me–O distances out of plane.

All compounds create packing characteristic of large tetraperoxo groups, which is similar to the densest packing of balls. This packing demonstrates hexagonal symmetry for  $K_2[Mo(O_2)_4]$ ,  $K_2[W(O_2)_4]$  and  $Rb_2[Mo(O_2)_4]$ , while monoclinic symmetry of layers is observable in small cations like  $Li^+$ ,  $Na^+$  and in large cations like  $Cs^+$  or  $Rb^+$  (see Fig. 4a–d).

#### 3.4. Stability of investigated compounds, DFT approach

In all crystal structure presented in this paper, the investigated structures were modeled by their anions of the general formula  $[Me(O_2)_4]^{n-}$  (where  $Me$  = Mo, W, V, and  $n$  = 2, 3). The investigated compounds were studied by means of the Density Functional Theory (DFT) method with the Becke–Perdew functional [61,62] as implemented in the Turbomole package, version 5.7.1 [63]. The Resolution of the Identity approach was applied for computing the electronic Coulomb interaction [64]. Basis sets of TZVP quality were applied for all atoms [65]. The geometric structures of the  $[Me(O_2)_4]^{n-}$  anions were fully optimised and the location of the

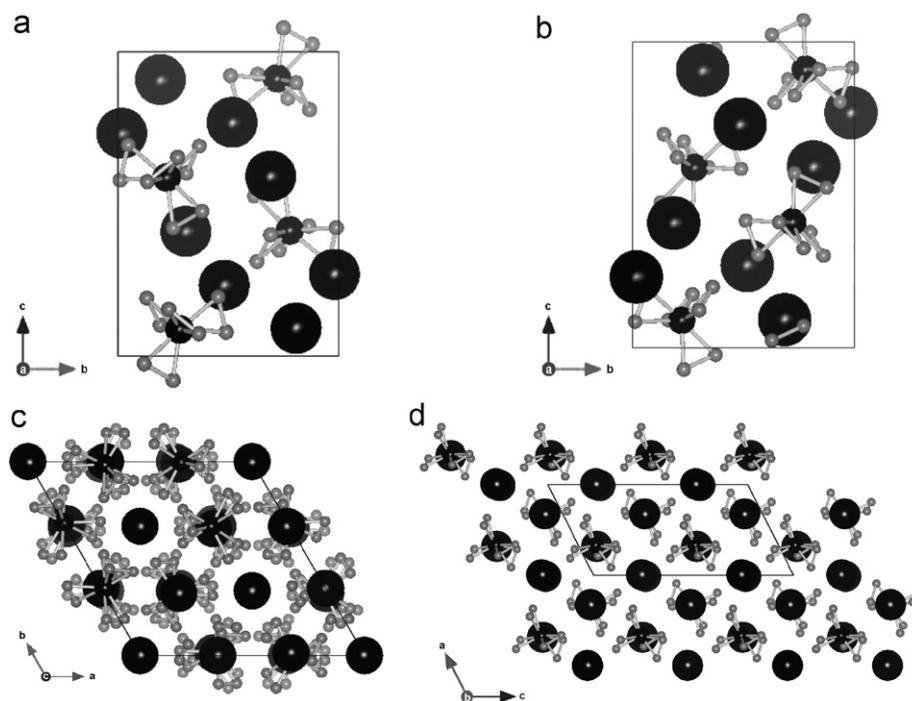


Fig. 4.

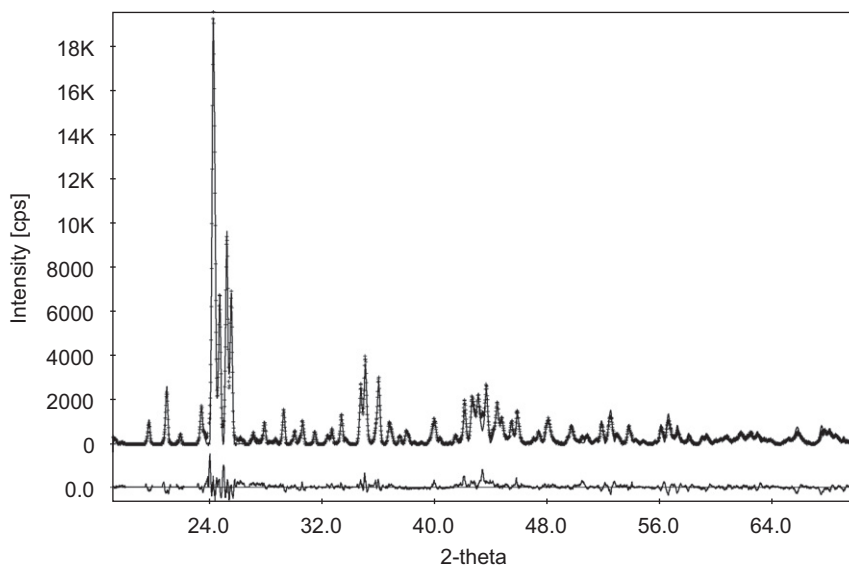


Fig. 5.

minima on the potential energy surface was confirmed by frequency calculations. The theoretical IR spectra were obtained within the harmonic approximation.

Each dioxygen ligand forms two non-equivalent bonds with the central metal ion. In case of the vanadium complex, the shorter V–O bonds (1.966–1.968 Å) lie nearly in the plane defined by four oxygen atoms and the vanadium center (equatorial plane), whereas the longer bonds (2.013–2.017 Å) are formed with the O atoms below and above this plane. A similar orientation of the metal–oxygen bonds is observed in the case of the molybdenum compound. Four oxygen atoms lying in the plane with the Mo atom form shorter bonds with molybdenum (2.006 and 2.007 Å);

the remaining four form the longer Mo–O bonds (2.030–2.031 Å). The converse is found in the tungsten complex, where the “in-plane” W–O bonds are longer (2.024–2.026 Å) than those pointing out of plane (2.020–2.022 Å). However, in the latter complex, the difference in length between shorter and longer bonds is almost negligible. Probably, this phenomenon should be attributed to the increasing radius of the central metal ion.

The internal O–O bonds are of the same length in the studied structures. The O–O distance depends on the type of the central metal and varies with its radius: V (1.476 Å) > Mo (1.483 Å) > W (1.505 Å, 1.506 Å). In the latter case, one O–O bond is slightly longer than the other three, but the difference of 0.001 Å is

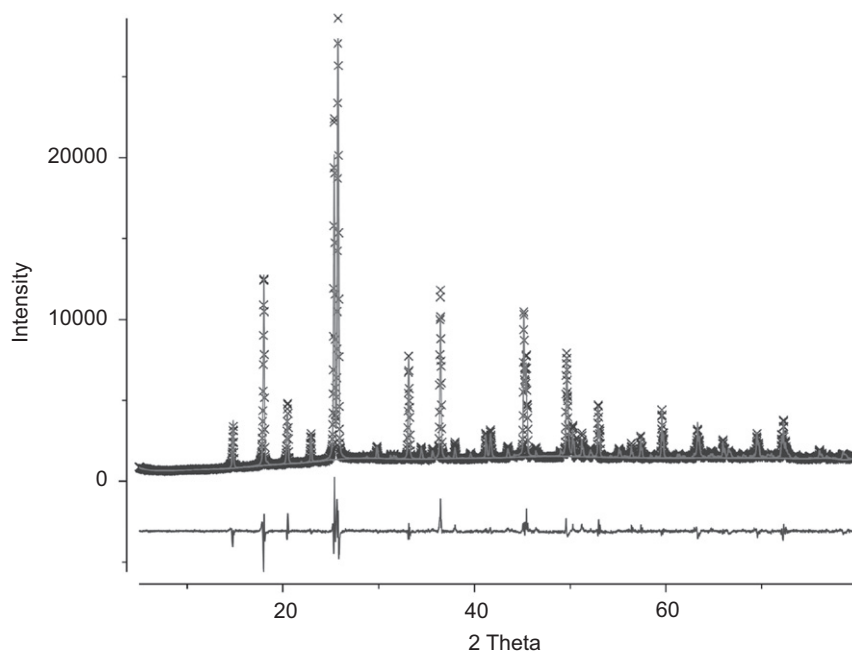


Fig. 6.

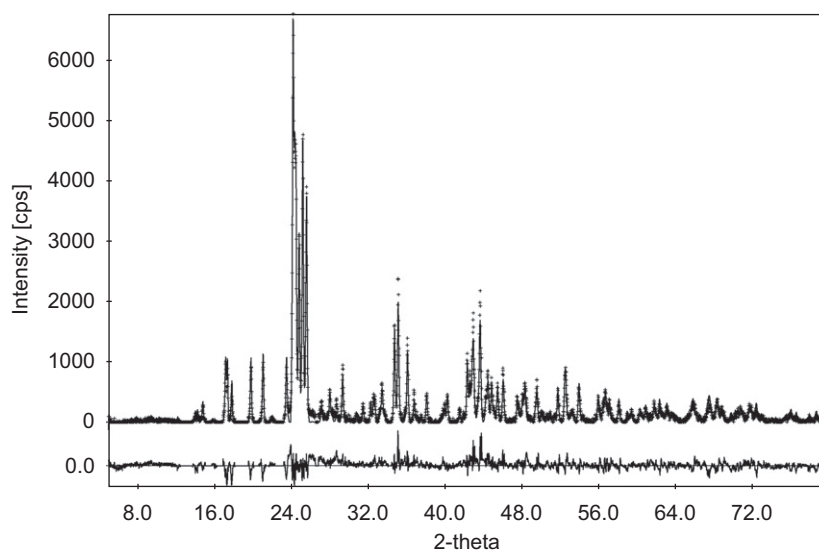


Fig. 7.

considered to be within the accuracy of this type of DFT calculation, therefore the difference seems insignificant. These results are in strong agreement with experimental data (see Table 10). Interestingly, the same sequence is observed in IR results considering the shift of the characteristic strong band for  $\nu_{\text{sym}}(\text{O}-\text{O})$ . This band is observed at ca.  $850\text{ cm}^{-1}$  for tetraperoxovanadates(V), at ca.  $840\text{ cm}^{-1}$  for tetraperoxomolybdates(VI), and at ca.  $830\text{ cm}^{-1}$  for tetraperoxotungstates(VI).

In order to somehow quantify the stability of the investigated structures by the theoretical method, it was decided to compute singlet dioxygen binding energies according to the formula:  $E_{\text{b}}(\text{O}_2) = E([\text{M}(\text{O}_2)_4]^{n-}) - E([\text{M}(\text{O}_2)_3]^{n-}) - E(^1\text{O}_2)$ .

Our results indicate that in all cases the bonds between the  $\text{O}_2$  ligands and the metal centers are thermodynamically stable (negative binding energies). The obtained values, however, enable

us to conclude that the molybdenum complex would be the first to decompose ( $E_{\text{b}}(\text{O}_2) = -10.9\text{ kcal/mol}$ ), followed by the tungsten complex ( $E_{\text{b}}(\text{O}_2) = -14.9\text{ kcal/mol}$ ). The vanadium compound would be the more stable order of magnitude ( $E_{\text{b}}(\text{O}_2) = -133.7\text{ kcal/mol}$ ). This behaviour has been confirmed in experimental work. The results of the DFT calculations are presented in Table 12.

#### 4. Conclusions

In all tetraperoxo compounds isolated  $[\text{Me}(\text{O}_2)_4]^{n-}$  anions are observed. Molybdenum(VI) and tungstate(VI) tetraperoxo compounds are isomorphic; one exception has been observed in the case of  $\text{Rb}_2[\text{Mo}(\text{O}_2)_4]$  and  $\text{Rb}_2[\text{W}(\text{O}_2)_4]$ . The compounds crystallise in monoclinic and rhombohedral/hexagonal symmetry. In the case



**Table 9**

The detailed structural data for tetraperoxo complexes of Mo(VI), W(VI) and V(V).

Compound/color	Crystal system Space group	Lattice parameters <i>a</i> , <i>b</i> , <i>c</i> (Å), $\alpha$ , $\beta$ , $\gamma$ (°)	<i>V</i> (Å <sup>3</sup> ) <i>Z</i>	Sample	Ref.
<i>Tetraperoxomolybdates</i>					
Li <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O; red	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	6.57300 (10) 10.0580(2) 13.2950(3) $\beta$ = 101.8350(9)	860.26 (3) 4	Monocrystal	[52]
Na <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O; red	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>c</i> (14)	9.1120(2) 8.62300(10) 12.3960(2) $\beta$ = 93.8150(8)	971.83 (3) 4	Monocrystal	
K <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]; red	Rhombohedral <i>R</i> -3 <i>c</i> (167) Hexagonal	10.7891(2) $\alpha$ = 64.925(3) 11.5873(7) 25.424(3)	983.6 (4) 6 2956.3 (3)	Powder	[50]
Rb <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]; red	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>c</i> (14)	6.8956(7) 8.6323(7) 13.296(1) $\beta$ = 116.479(8)	708.41 (8) 4	Powder	
Cs <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]; red	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>c</i> (14)	7.075(2) 9.017(2) 14.681(3) $\beta$ = 122.11(1)	793.5 (2) 4	Powder	
<i>Tetraperoxotungstates</i>					
Li <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O; yellow	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	6.5575(3) 10.0440(2) 13.37900(10) $\beta$ = 101.344(3)	863.97 (4) 4	Monocrystal	[52]
Na <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O; yellow	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>c</i> (14)	9.1180 (2) 8.62300 (10) 12.4000 (2) $\beta$ = 93.9040 (8)	972.68 (3) 4	Monocrystal	
K <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]; yellow	Rhombohedral <i>R</i> -3 <i>c</i> (167) Hexagonal	10.784 (4) $\alpha$ = 65.06 (3) 11.598 25.3596	984.73 6 18 2954.22	Monocrystal	[25]
Rb <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]; yellow	Rhombohedral <i>R</i> -3 <i>c</i> (167) Hexagonal	11.0822 $\alpha$ = 65.3881 11.9720 (1) 25.9873 (6)	1075.24 18 3225.71(7)	Powder	
Cs <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]; yellow	Monoclinic <i>P</i> 2 <sub>1</sub> / <i>c</i> (14)	7.0893 (9) 8.974 (1) 13.960 (2) $\beta$ = 116.853 (9)	792.36(2) 4	Powder	
<i>Tetraperoxovanadates</i>					
(NH <sub>4</sub> ) <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ]; blue	Tetragonal <i>I</i> -42 <i>m</i> (121)	6.9769 (5) 8.211 (1)	399.68 (7) 2	Powder	[53]
Na <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ] · 14H <sub>2</sub> O; blue	Triclinic <i>P</i> -1 (2)	8.667 (2) 9.010 (2) 7.520 (2) 98.41 (2) 110.59 (2) 63.99 (2)	494.02 1	Monocrystal	[51]
Na <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ] · H <sub>2</sub> O <sub>2</sub> · 10.5H <sub>2</sub> O; blue	Triclinic <i>P</i> -1 (2)	9.139 (3) 11.774 (3) 9.143 (3) 105.47 (2) 104.58 (2) 71.65 (2)	884.69 2	Monocrystal	[51]
K <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ]; blue	Tetragonal <i>I</i> -42 <i>m</i> (121)	6.6861 (4) 7.708 (2)	344.6 (6) 2	Powder	[53]

of small cations like Li<sup>+</sup> and Na<sup>+</sup>, hydrated compounds are obtained. In the created networks of hydrogen bonds, normal and bifurcated hydrogen bonds are observed. Interestingly, such compounds also exhibit the highest deformation index and are the most unstable.

In the group of tetraperoxovanadates(V), the complexes crystallise in tetragonal and triclinic systems.

Optimised geometry of the anions by the means of DFT methods is in strong agreement with structural investigations. The stability of tetraperoxo complexes is also in strong agreement with the obtained results of singlet dioxygen binding energy calculations. The stability of tetraperoxo compounds decreases from complexes of V(V) through W(VI) to Mo(VI).

**Table 10**  
O–O and Me–O<sub>peroxo</sub> (Me = Mo(VI), W(VI) or V(V)) bond length in tetraperoxo complexes.

Compound	O–O bond length (Å)	Me–O <sub>peroxo</sub> bond length (Å)
[Zn(NH <sub>3</sub> ) <sub>4</sub> ][Mo(O <sub>2</sub> ) <sub>4</sub> ]	1.55 (5)	1.93 (3)–2.00 (2)
Li <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	1.477 (3)–1.486 (2)	1.9307 (19)–1.9895 (19)
Na <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	1.481 (3)–1.487 (3)	1.931 (2)–1.9795 (19)
K <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]	1.63 (4)–1.66 (4)	2.03 (2)–2.14 (2)
Rb <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]	1.48 (9)–1.5 (1)	2.00 (4)–2.02 (9)
Cs <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]	1.5 (1)	1.99 (8)–2.0 (2)
Li <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	1.499 (4)–1.504 (5)	1.934 (3)–1.988 (5)
Na <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	1.484 (8)–1.538 (9)	1.934 (5)–1.977 (5)
K <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]	1.508 (6)–1.512 (6)	1.949 (4)–1.970 (5)
Rb <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]	1.490 (2)–1.500 (3)	1.976 (3)–2.006 (2)
Cs <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]	1.5 (1)	1.99 (3)–2.0 (1)
(NH <sub>4</sub> ) <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ]	1.43 (6)	1.983 (8)–1.99 (3)
Na <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ] · 14H <sub>2</sub> O	1.473–1.518	1.859–1.955
Na <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ] · H <sub>2</sub> O <sub>2</sub> · 10.5H <sub>2</sub> O	1.468–1.473	1.905–1.934
K <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ]	1.42 (2)	1.978 (8)–1.996 (6)

**Table 11**  
Distortion parameter of Me(O<sub>2</sub>)<sub>4</sub> polyhedra in tetraperoxo compounds (distortion: · 10<sup>-6</sup>).

Compound	Single crystal	Powder data
Li <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	96.3	
Na <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	74.4	
K <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]		46.7
Rb <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]		8.88
Cs <sub>2</sub> [Mo(O <sub>2</sub> ) <sub>4</sub> ]		5.88
Li <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	65.1	
Na <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ] · 4H <sub>2</sub> O	63.6	
K <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]	17	
Rb <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]		61.0
Cs <sub>2</sub> [W(O <sub>2</sub> ) <sub>4</sub> ]		5.9
Na <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ] · H <sub>2</sub> O <sub>2</sub> · 10.5H <sub>2</sub> O	28.5	
Na <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ] · 14H <sub>2</sub> O	27.1	
(NH <sub>4</sub> ) <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ]		20.5
K <sub>3</sub> [V(O <sub>2</sub> ) <sub>4</sub> ]		3.1

**Table 12**  
Results of the DFT calculations.

Anion	[Mo(O <sub>2</sub> ) <sub>4</sub> ] <sup>2-</sup>	[W(O <sub>2</sub> ) <sub>4</sub> ] <sup>2-</sup>	[V(O <sub>2</sub> ) <sub>4</sub> ] <sup>3-</sup>
E+ΔZPVE	-670.1836	-669.1167	-1545.7734
Me–O distance (Å)	(2.006, 2.032)	(2.025, 2.022)	(2.016, 1.966)
	(2.006, 2.031)	(2.024, 2.022)	(2.015, 1.968)
	(2.006, 2.031)	(2.024, 2.021)	(2.013, 1.968)
	(2.007, 2.030)	(2.026, 2.020)	(2.017, 1.966)
O–O distance (Å)	1.483	1.505 (3x), 1.506	1.476
IR—main bands	495, 517, 518, 860	492, 506, 837	443, 485, 486, 851
Eb O <sub>2</sub> (kcal/mol)	-10.9	-14.9	-133.7

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