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Spectroscopic, magnetic and crystal structure investigation of a new pseudo-Dawson nano-sized polyoxometalate cluster with mixed addenda

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A new nano-sized polyoxometalate cluster was synthesized as a neutral salt. The cluster, which corresponds to the formula $Na_2(NH_4)_6[H_3Sb^{III}V^{IV}W_{17}O_{60}]\cdot 14H_2O$, contains a heteroatom Sb^{III} with an unshared electron pair and mixed addenda, *i.e.,* W and V^{IV}. Structural investigation of the new substance was performed by FT-IR, Raman, UV-Vis-NIR spectroscopy, magnetic susceptibility measurements and by X-ray diffraction. Single-crystal X-ray diffraction analysis showed that the $[H_3Sb^{III}V^{IV}W_{17}O_{60}]^{8-}$ polyoxometalate molecule is made up of two halves, each being of trilacunary Keggin-type, namely *Bα*-$[SbM_9O_{33}]$ and *Bα*-$[H_3M_9O_{33}]$, linked by corners and edges. The Sb^{III} heteroatom is statistically distributed between the two halves. The Sb^{III} heteroatom is tricoordinated, forming an unusual trigonal SbO_3 pyramid in the $[SbM_9O_{33}]$ unit. The paramagnetic V^{IV} metal centre is disordered over all 18 addenda positions. It is proposed that this structure, called initially *non*-Dawson, should be renamed as *pseudo*-Dawson.

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Keywords: Polyoxometalate, Metal cluster, FTIR spectroscopy, Paramagnetism, X-ray structure

1. Introduction

Polyoxometalates, also called metal-oxygen clusters, are the most important representatives of the inorganic molecular nanoclusters. Over the past 10-15 years, polyoxometalates underwent a spectacular development. The continuous diversification of polyoxometalates through the synthesis of an impressive number of new structures, including the largest molecules ever synthesized, yielded substances with interesting electronic structures, high symmetry, unexpected topologies, which undergo electron-transfer processes and remarkable magnetic-exchange interactions. These properties enabled for various applications, especially in catalysis, analysis, medicine, biochemistry and materials science [1-6].

According to a widely used definition, polyoxometalates are polyoxoanions of the early transition elements, especially Mo, W and V, made up by linked MO_n units. The M metal centres, which may belong to one or more atomic species, are called addenda. Polyoxometalates are synthesized by intermolecular condensation of certain oxoanions, which generates polyoxoanionic buildings. In a simplified classification, polyoxometalates are divided into isopolyoxometalates and heteropolyoxometalates, according to whether oxoanions from one or several atomic species are involved in the condensation process. Rigorously speaking, for isopolyoxometalates one or more atomic species act as addenda, while in the case of heteropolyoxometalates, beside the addenda, there are also one or several atomic species playing the role of heteroatom(s). The positions of addenda and heteroatom(s) are well defined in each structure [7-9].

Heteropolyoxometalates in which the X heteroatom has an unshared electron pair are of particular importance, owing to their structural features and specific properties. Due to the stereochemical activity of the lone pair, the XO_n primary group cannot adopt the usual tetrahedral (XO_4) symmetry and, much less, an octahedral (XO_6), cubical (XO_8) or icosahedral (XO_{12}) symmetry. Several studies have revealed that in such clusters, the primary group exhibits an unusual XO_3 trigonal pyramid shape. The role of the X heteroatom with an unshared electron pair is usually played by subvalent group 15 elements, namely As (III), Sb (III) or Bi (III) [10-12].

The first heteropolyoxometalate of this type, with 18 addenda metal centres and corresponding to the $[H_2AsW_{18}O_{60}]^{7-}$ formula, was obtained by Jeannin şi Martin-Frère [10]. Later, the analogous clusters with As (III) and Sb (III) were obtained, *i.e.*, $[H_3BiW_{18}O_{60}]^{6-}$ [11] and $[H_2SbW_{18}O_{60}]^{7-}$ [12]. These new anionic molecules can be related to the usual Dawson structure, $[X_2M_{18}O_{62}]^{6-}$ (X = P(V), As(V); M = Mo(VI), W(VI)), which contains in each of its halves a trilacunary Kegin unit with a tetrahedral XO_4 primary group. Unlike this, the new clusters, with the $[H_nX^{III}W_{18}O_{60}]^{(9-n)-}$ general formula,

contain a primary XO_3 group only in the centre of one trilacunary Kegin unit, while the centre of the other unit is lacunary. This is why the new structure was termed by Krebs as *non*-Dawson [12].

In this paper we describe the synthesis of a new heteropolyoxometalate cluster of this series with mixed addenda, which corresponds to the $[H_3Sb^{III}V^{IV}W_{17}O_{60}]^{8-}$ formula and is abbreviated as $[Sb^{III}V^{IV}W_{17}]$ or $[SbVW_{17}]$. The new cluster was investigated by vibrational (FT-IR, Raman) and electronic (UV-Vis-NIR) spectroscopy, magnetic susceptibility measurements and by X-ray diffraction, as well.

2. Experimental section

2.1. Synthesis

The hexaammonium and dinatrium salt of the novel polyoxometalate was prepared in two steps, as follows:

Synthesis of $Na_7[H_2SbW_{18}O_{60}] \cdot 15H_2O$

The substance was prepared according to the procedure for the tetramethylammonium salt, $[(CH_3)_4N]_7[H_2SbW_{18}O_{60}]\cdot 3H_2O$, described only very sketchily in the literature [12]. 25 g (75.801 mmol) $Na_2WO_4\cdot 2H_2O$ was dissolved in 100 mL of hot water (70-80 °C). Then, to the first hot solution a second solution consisting of 1.6 g (7.014 mmol) $SbCl_3$ dissolved in 10 mL HCl 0.1 mol L^{-1} was added dropwise, under stirring. Next, pH was adjusted to 3 with NaOH 0.1 mol L^{-1} and the solution was heated again for 15-20 min, at 70-80°C, after which 5 g of finely ground $NaNO_3$ were added. The yellow-orange solution was purified by filtration and stored at room temperature for several hours, until white-yellow needle-shaped crystals separed. The crystals were filtered off, washed with distilled water and dried. Eventually, they were recrystallized twice from water acidulated at pH 3-4. Yield: 14.30 g (2.964 mmol; 70.4 % based on W).

Synthesis of $Na_2(NH_4)_6[H_3SbVW_{17}O_{60}] \cdot 14H_2O$

An amount of 5 g (1.037 mmol) $Na_7[H_2SbW_{18}O_{60}]\cdot 15H_2O$ was dissolved in 40 mL hot water (70-80 °C). Then, to the hot solution another solution containing 0.5 g (1.976 mmol) $VOSO_4\cdot 5H_2O$ dissolved in 10 mL water was added dropwise, under stirring. After the pH of the mixture was adjusted to 3-3.5 with NaOH 0.1 mol L^{-1}, the solution was heated again to 70-80 °C, for 30 min. Then, 8 g of solid NH_4Cl were added. After 48 hours, small black crystals were obtained. The crystals were filtered off, washed with distilled water and dried. Eventually, they were recrystallized twice from acidulated water (pH 3). Yield: 4.30 g (0.914 mmol; 88.1 % based on W).

2.2. Analysis

The synthesized substance was initially characterized by elemental and thermogravimetric analysis, as follows:

Na was determined by FEP with an Eppendorf flame photometre.

N was determined with a Leco CHN-932 elementaranalyser.

Sb was determined gravimetrically. The substance was degraded by boiling for 30 min with NaOH 11 mol dm^{-3}. $Na[Sb(OH)_6]$ precipitated out from the solution, which was eventually weighed.

W and V were determined by OES-ICP with a Bird 2070 spectrophotometer.

Water content was measured by weight loss at 350°C, with a Nietzsch SPA 409A simultaneous thermoanalyser.

Results (wt %): found (calculated for $Na_2(NH_4)_6[H_3SbVW_{17}O_{60}]\cdot 14H_2O$; M=4667.62) Na 1.05 (0.98); N 1.75 (1.80); Sb 2,65 (2.61); V 1.03 (1.09); W 67.80 (66.97); H_2O 5.46 (5.40).

2.3. Investigation

FTIR spectra were recorded in the 4000-350 cm^{-1} range on a Jasco FT/IR 615 spectrophotometer, using KBr pellets.

Raman spectra were registered on a Bruker FTIR IFS 66 with a Raman FRA 106 unit spectrophotometer (λ_e = 1064 nm), using KBr pellets.

Electronic spectra in aqueous solution were obtained in the 190-1300 nm range on a Shimadzu 3101 UV-VIS-NIR spectrophotometer.

For single crystal X-ray structure analysis, crystals were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS Smart diffractometer (three circle goniometres with 1 K CCD detector, Mo-Kα radiation, graphite monochromator). The structure was solved with the SHELXS-97 software and refined using the SHELXL-93 software.

Magnetic susceptibility data were performed at external fields from 0.1 to 5.0 Tesla, in a temperature range from 2 to 290 K, employing a Quantum Design MPMS 5 SQUID magnetometer.

3. Results and discussion

3.1. Vibrational spectra

FT-IR spectrum.

The vibration bands of the FT-IR spectrum (in cm^{-1}) and their assignment are the following: 1624 (m) δH-O-H, 1401 (m) $\delta_{as}NH_4^+$, 970 (m) and 930 (m) υ_{as}M=O, 875 (s) υ_{as}Sb-O, 802 (m) and 731 (s) υ_{as} M-O-M, 642 (m) δO-Sb-O, 571 (s) and 515 (m) δM-O-M, where M = W, V (Fig. 1).

The four antisymmetric stretching vibrations υ_{as}M=O and υ_{as}M-O-M, characteristic to the M-O bonds, are recorded in the 700-1000 cm^{-1} range [13]. They evince the polyoxotungstate nature of the $SbVW_{17}$ cluster. The main

vibration due to the heteroatom, υ_{as}Sb-O, is recorded at 875 cm^{-1} and indicates the presence of Sb as a heteroatom in the polyoxometalate framework.

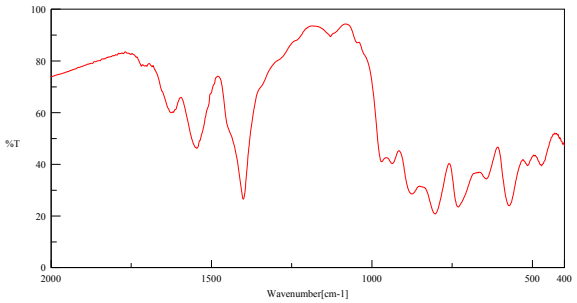

Fig. 1. FT-IR spectrum of $Na_2(NH_4)_6[H_3SbVW_{17}O_{60}]\cdot 14H_2O$.

Raman spectrum.

The vibration bands of the Raman spectrum (in cm^{-1}) are: 959 (s), 882 (vs), 478 (w), 378 (s), 312 (m), 220 (m), 129 (w).

The three characteristic strong and very strong bands, registered at 959, 882 and 378 cm^{-1}, are assigned to the ν_sM=O, ν_{as}M=O and ν_sM-O vibrations, respectively [14].

3.2. Electronic spectra

UV spectrum.

The absorption bands (in nm/cm^{-1}), their assignment and the molar absorptivity [in L mol^{-1} cm^{-1}] are: 198/50,500 [268,000] (CT) M=O$_{terminal}$, 255/39,215 sh [99,000] (CT) M-O-M, where M = W, V.

UV spectra of POM clusters generally exhibit two charge-transfer (CT) bands, characteristic to the polyoxoanionic framework and ascribed to oxygen-to-metal-transitions [15, 16]. In the UV spectrum of the $SbVW_{17}$ cluster, the broad ν_1 CT band, due to dπ-pπ-dπ transitions from the tricentric M-O-M bonds, is reduced to a shoulder, recorded at 255 nm (39,215 cm^{-1}). The sharper ν_2 CT band, due to dπ-pπ transitions of the M=O$_{terminal}$ bonds, has the maximum positioned at 198 nm (50,500 cm^{-1}). Its intensity, which for Keggin-derived structures is proportional to the number of addenda atoms, is in this case almost twice greater as compared to the corresponding Dawson structure ($\varepsilon = 2.68 \cdot 10^5$ L mol^{-1} cm^{-1}). This increase is probably the result of a larger distortion of the MO_6 octahedra.

Vis-NIR spectrum.

The absorption bands (in nm/cm^{-1}), their assignment and the molar absorptivity [in L mol^{-1} cm^{-1}] are: 524/19,085 [1,650] (IVCT) V^{IV}-W^{VI}, 645/15,500 sh [1,030] (IVCT) V^{IV}-W^{VI}, 817/12,240 sh [410] (IVCT) V^{IV}-W^{VI} (Fig. 2).

In polyoxometalates with one or several reduced addenda, new intervalence charge-transfer (IVCT) bands arise in the visible and NIR. In most cases, three IVCT bands are observed, marked by A, B and C. Their intensities are proportional to the number of electrons involved in the transfer, with a molar absorptivity up to $1.2–2 \cdot 10^3$ per electron [17]. For the $SbV^{IV}W_{17}$ cluster, the reduced addendum is the V^{IV} metal centre, which yields to the presence of heteronuclear IVCT V^{IV}-W^{VI} (more precisely, V^{IV}-O-W^{VI}) bands. Practically, the recorded spectrum shows a strong absorption over the entire visible range, which extends in NIR and accounts for the black color of the substance, in both solid state and solution.

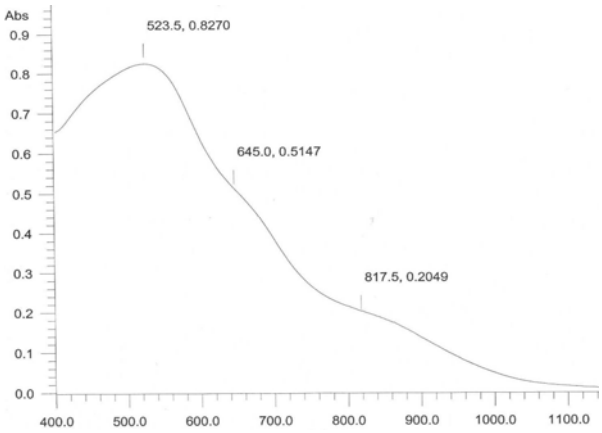

Fig. 2. Vis-NIR absorption electronic spectrum of $Na_2(NH_4)_6[H_3SbVW_{17}O_{60}]\cdot 14H_2O$ in aqueous solution ($c = 5 \cdot 10^{-4}$ mol L^{-1}).

The A IVCT band, located in NIR at 817 nm (12,240 cm^{-1}), as well as the B IVCT band, recorded at 645 nm (15,500 cm^{-1}), are each reduced to a shoulder. On the other hand, the broad C IVCT band exhibit an obvious maximum at 524 nm (19,085 cm^{-1}). Its intensity ($\varepsilon = 1.65 \cdot 10^3$ L mol^{-1} cm^{-1}) corresponds to the one-electron transfer. The intense C IVCT band covers the d-d electron-transfer (ET) band, characteristic to the V^{4+} ion (of d^1 electron configuration), in octahedral field. This ET band, specific to the $^2E_g \leftarrow {}^2T_{2g}$ transition, would have been expected at approximately 550 nm (17,860 cm^{-1}).

3.3. Magnetic investigation

The magnetic susceptibility data were corrected for diamagnetic and temperature-independent paramagnetic (TIP) contributions, calculated both from tabulated values and results from diamagnetic polyoxotungstates ($\chi_{dia/TIP} = 5.95 \times 10^{-3}$ emu mol^{-1}).

The temperature dependence of the low-field (0.1 Tesla) magnetic susceptibility of the investigated polyoxometalate is consistent with the presence of a single

paramagnetic V^{4+} centre (more precisely a VO^{2+} vanadyl group), *i.e.*, a spin-1/2 group, per molecule (g_{iso} = 1.94), with virtually no intermolecular (nearest neighbor dipole-dipole) coupling. While χT remains virtually constant over the entire temperature range (Fig. 3), χ^{-1} follows a Curie-Weiss expression with a Weiss temperature of θ = 0.08 ± 0.5 K (Fig. 4).

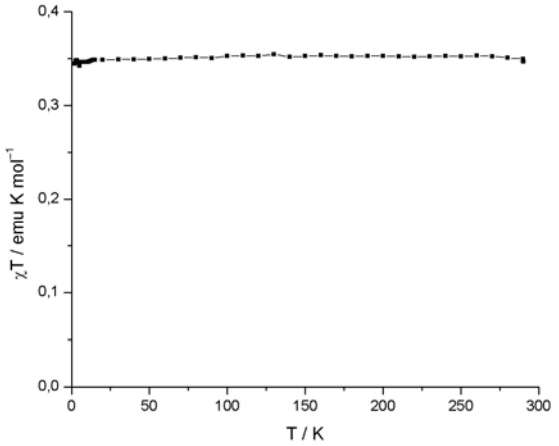

Fig. 3. Temperature dependence of χT (for 0.1 Tesla).

Further, a magnetization curve at 2.0 K for B = 0.1 to 5 Tesla produces a corresponding B (s = 1/2) Brillouin curve.

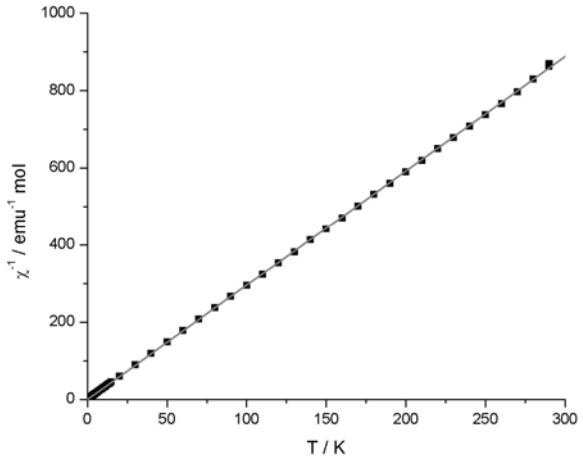

Fig. 4. Temperature dependence of χ^{-1} (for 0.1 Tesla)

3.4. Crystal structure analysis

Crystallographic data of the $Na_2(NH_4)_6[H_3SbVW_{17}O_{60}]\cdot 14H_2O$ substance are summarized in Table 1.

Table 1. Crystal data and structure refinement for $Na_2(NH_4)_6[H_3SbVW_{17}O_{60}]\cdot 14H_2O$.

Empirical formula	$H_{55}\ N_6\ O_{74}\ Na_2\ Sb\ V\ W_{17}$
Formula weight	4667.62
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a = 24.5582(11) Å b = 21.3363(10) Å β= 90.826(1)° c = 12.8835(6) Å
Volume	6750.0(5) $Å^{-3}$
Z	4
Density (calculated)	4.593 10^3 kg m^{-3}
Absorption coefficient	29.50 mm^{-1}
F(000)	8172
Crystal size	0.20 x 0.16 x 0.06 mm^3
Theta range for data collection	1.91 to 26.97°
Index ranges	-27<=h<=31, -26<=k<=26, -13<=l<=16
Reflections collected	19506
Independent reflections	7226 (R(int) = 0.0533)
Observed reflections (I>2σ(I))	5930
Absorption correction	
Semi-empirical from equivalents	
Max. and min. transmission	0.0637 and 0.0205
Refinement method	
Full-matrix least-squares on F^2	
Data / restraints / parameters	7225 / 0 / 414
Goodness-of-fit on F^2	1.047
Final R indices (I>2σ(I))	R1 = 0.0426, wR2 = 0.1062
R indices (all data)	R1 = 0.0555, wR2 = 0.1115
Largest diff. peak and hole	2.839 and -2.482 e $Å^{-3}$

Single-crystal X-ray diffraction analysis shows that the $[H_3Sb^{III}V^{IV}W_{17}O_{60}]^{8-}$ POM molecule is made up of two halves, each of trilacunary Keggin-type, *i.e.*, *Bα*-$[SbM_9O_{33}]$ and *Bα*-$[H_3M_9O_{33}]$, linked by corners and edges and sharing 6 oxygen atoms. The Sb^{III} heteroatom is statistically distributed between the two halves. The Sb^{III} heteroatom is tricoordinated, building a trigonal SbO_3 pyramid in the $[SbM_9O_{33}]$ unit. The polyhedral representation of the $[H_3SbVW_{17}O_{60}]^{8-}$ POM molecule is displayed in Fig. 5, while the ball-and-stick representation is shown in Fig. 6.

The three Sb-O bonds are almost of the same length, namely 2,022(9), 2,012(9) şi 2,014(9)Å. The unshared pair of electrons of Sb^{III}, which has a nonbonding character, is pointed towards the other half-anion, which accounts for the lack of another Sb^{III} atom in the respective half. If two Sb^{III} heteroatoms were present, with their lone pair electrons oriented towards each other, a strong repulsion would occur.

The V^{IV} atom is disordered over all 18 addenda positions, noted with M (M=W, V). Practically, all 18 addenda/metal centres, *i.e.*, the 17 W atoms and the V^{IV} atom, are disordered and cannot be differentiated.

All bonds shown in the ball-and-stick representation are covalent, namely the bonds between addenda/metal

centres and oxygen atoms and those between the heteroatom and oxygen atoms, *i.e.*, M-O and X-O. As can be noticed, the addenda/metal centres are linked between each other and with the heteroatom exclusively by M-O-M and Sb-O-M oxygen bridged covalent bonds.

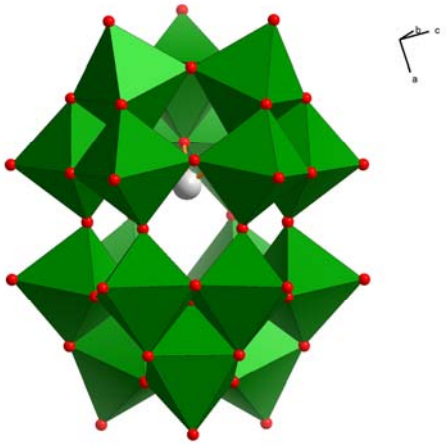

Fig. 5. Polyhedral representation of the $[H_3SbVW_{17}O_{60}]^{8-}$ POM molecule. (Colour code: Sb large grey circle; MO_6 = WO_6, VO_6 green octahedra; O small red circles).

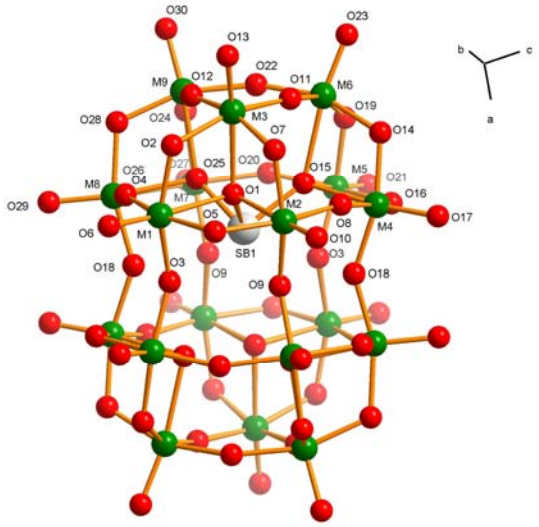

Fig. 6. Ball-and-stick representation of the $[H_3SbVW_{17}O_{60}]^{8-}$ POM molecule. (Colour code: Sb grey; M = W, V green; O red).

It should also be mentioned that every M addendum/metal centre is located in a distorted MO_6 octahedron. The addenda occupy an off-centre position towards the external edges, due to certain π M→O (dπ-pπ) bonds, which reinforce the coordinative covalent M←O bonds.

As its structure originates from trilacunary *Bα*-Keggin units, the investigated $[H_3SbVW_{17}O_{60}]^{8-}$ POM could also contain MO_6 octahedra with no or 3 terminal oxygens beyond the usual case with one or two terminal oxygens.The crystallographic results, also displayed in the ball-and-stick representation shows, however, that each of the 18 M addenda has only one terminal oxygen.

Chemical analysis of the neutral substance under study indicates that it needs three protons for electroneutrality. Investigations on POM clusters corresponding to the general formula $[H_nXM_{18}O_{60}]^{p-}$ have revealed that the H atoms are non-ionizable and belong to the anionic building. Evidently, the small H atoms cannot be identified by single-crystal X-ray diffraction. Given that Keggin-type and Keggin-derived structures with central lacunae (in the place reserved for the heteroatom) are not known, it was considered that the non-ionizable H atoms are to be found inside the O_3 cavity [10, 12]. The nature of bonds in the unusual H_3O_3 group is not known, but it probably is a weak multicentre covalent bonds.

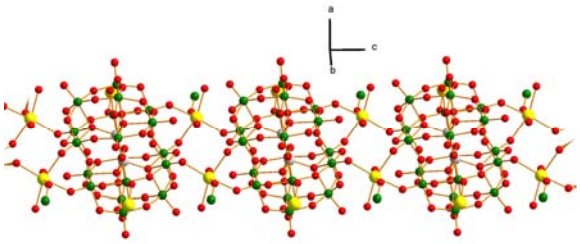

Fig. 7. Infinite chains formed by $[H_3SbVW_{17}O_{60}]^{8-}$ discrete molecules linked by $Na(H_2O)_2^+$ units. (Colour code: Sb grey; M=W, V green; O red; Na yellow).

The $[H_3SbVW_{17}O_{60}]^{8-}$ POM molecule has one C_3 axis, as well as an orthogonal and three mirror planes intersecting at that axis. The structure of POM clusters with the $[H_nXM_{18}O_{60}]^{p-}$ general formula show similarities, but also differences to the well-known Dawson structure of POMs with the formula $[X_2M_{18}O_{62}]^{q-}$. The latter structure contains an X heteroatom in each half, located in the centre of a tetrahedral XO_4 unit. Therefore, Krebs and Klein proposed the unfortunate term *non*-Dawson for the structure of these POM clusters [12]. As we have serious concerns on the use of the *non*- prefix in denominations, we prefer to call this structure as *pseudo*-Dawson.

The $[H_3SbVW_{17}O_{60}]^{8-}$ POM molecules are non-covalently bonded by two $Na(H_2O)_2^+$ centres for each molecule to form infinite chains, which are parallel to the c crystallographic axis (Fig. 7). Furthermore, chains are also connected non-covalently by $Na(H_2O)_2^+$ units, perpendicular to the c axis, thus forming infinite layers (Fig. 8).

The distance between two molecular units linked to chains corresponds to c (c = 12.883 Å), while the distance between two neighbouring chains linked to layers corresponds to b/2 (b = 21.336 Å).

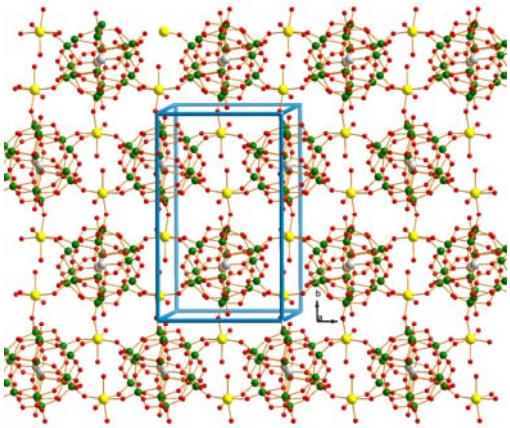

Fig. 8. Layer structure of the $Na_2(NH_4)_6[H_3SbVW_{17}O_{60}]\cdot 14H_2O$ lattice. An elementary cell is also figurated. (Colour code: Sb grey; M=W, V green; O red; Na yellow).

4. Conclusion

The paper reports the synthesis and structural investigation of the new $Na_2(NH_4)_6[H_3Sb^{III}V^{IV}W_{17}O_{60}]\cdot 14H_2O$ nano-sized inorganic cluster. The substance is the neutral salt of a novel heteropolyoxometalate, which contains a heteroatom Sb^{III} with an unshared electron pair and mixed addenda, namely W and V^{IV}.

The main vibration of the FTIR spectrum, υ_{as}Sb-O, registered at 875 cm^{-1}, reveals the presence of Sb as a heteroatom. The vibration bands of the Raman spectrum are characteristic to the polyoxometalate framework.

The UV spectrum shows two chage-transfer (CT) bands, recorded at 198 and 255 nm, specific to the polyoxometalate edifice. The Vis-NIR spectrum exhibits three heteronuclear intervalence charge-transfer (IVCT) bands, owing to the presence of the V^{IV} metal centre, as a reduced addendum. The V^{IV}-W^{VI} IVCT bands are recorded at 524, 645 and 817 nm.

Magnetic susceptibility measurements also demonstrate the existence of a single paramagnetic V^{4+} metal centre, with no intermolecular coupling. The results indicate a Curie-Weiss behaviour, with a Weiss temperature of $\theta = 0.08 \pm 0.5$ K.

Crystal structure analysis of the investigated substance points toward a C2/c space group and a monoclinic crystal system. It also shows that the $[H_3Sb^{III}V^{IV}W_{17}O_{60}]^{8-}$ polyoxometalate molecule is made up of two trilacunary Keggin fragments, *i.e.*, *Bα*-$[SbM_9O_{33}]$ and *Bα*-$[H_3M_9O_{33}]$, which are linked via corners and edges. The Sb^{III} heteroatom is statistically distributed between the two halves. It builds an unusual trigonal SbO_3 pyramid, which acts as a primary heterogroup. All 18 addenda/metal centres, namely the 17 W atoms and the V^{IV} atom, are disordered and cannot be differentiated. The $[H_3SbVW_{17}O_{60}]^{8-}$ POM molecules are non-covalently bonded by two $Na(H_2O)_2^+$ centres, thus generating infinite chains. Chains are connected non-covalently by $Na(H_2O)_2^+$ units and form infinite layers.

We propose to rename the corresponding polyoxometalate structure as *pseudo*-Dawson.

Supplementary Material

The complete crystallographic data for structural analysis have been entered in the FIZ Karslruhe – ISCD Inorganic Crystal Strucuture Database under the registration No. 418244. Copies of information may be obtained free of charge by sending request to e-mail CrysDATA@FIZ-Karlsruhe.DE or from http://www.fiz-karlsruhe.de/icsd.html .

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