



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

SPECTROSCOPIC AND CRYSTAL STRUCTURE INVESTIGATION OF A NEW BISMUTH (III) CONTAINING POLYOXOMETALATE CLUSTER

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A new polyoxometalate cluster containing bismuth (III) was synthesized as a neutral salt. The cluster, which corresponds to the formula $\text{Na}_{11}\text{H}[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x] \cdot 46\text{H}_2\text{O}$ ($x = 1.4$), comprises two Bi^{III} heteroatoms with an unshared electron pair and W^{VI} atoms as metal centres. Structural investigation of the new substance was performed by FT-IR, Raman, electronic spectroscopy and by X-ray diffraction, as well. According to the single-crystal X-ray diffraction analysis, the $[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]^{12-}$ ($x=1.4$) polyoxometalate molecule consists of two $\beta\beta$ - $[\text{BiW}_9\text{O}_{33}]$ pseudo-Keggin type units, which are connected by two WO_2 and by two *facial* $\text{WO}_2(\text{OH})$ groups. The determined molecular formula, which can be abbreviated as $\text{Bi}_2\text{W}_{21.4}$, shows that the new polyoxometalate is a mixture of the complete parent cluster Bi_2W_{22} and of its dilacunary derivative Bi_2W_{20} , in a proportion of 70% : 30%.

INTRODUCTION

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. Polyoxometalate clusters 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. 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.¹⁻³

Heteropolyoxometalates in which the X heteroatom has an unshared electron pair exhibit particular 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 or 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)⁴. Beside the $[\text{X}^{\text{III}}\text{W}_9\text{O}_{33}]^{3-}$ -type anion, which was erroneously considered a kind of trilacunary Keggin structure,

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two new series were synthesized and investigated over the past two decades.

The first series of heteropolyoxometalates of this type, with 18 addenda metal centres, has the $[H_nX^{III}W_{18}O_{60}]^{(9-n)-}$ ($X = As^{III}, Sb^{III}$ or Bi^{III}) general formula and the $X^{III}W_{18}$ short formula, which notes only the heteroatoms and addenda. Its structure contains a primary XO_3 group only in the centre of one trilacunary *pseudo*-Keggin unit, while the centre of the other unit is lacunary⁴⁻⁶. The new structure was termed by Krebs as *non*-Dawson⁴, while we preferred to call it as *pseudo*-Dawson⁷. Research demonstrated that one or two addenda can be substituted with other metal atoms.

The most interesting is, however, the series with 22 addenda metal, with the $X^{III}_2W_{22}$ short formula and a theoretical general formula $[X^{III}_2W_{22}O_{74}(OH)_2]^{12-}$ ($X = Sb^{III}$ or Bi^{III})^{8, 9}. The parent structure is made up of two trilacunary $X^{III}W_9O_{33}$ *pseudo*-Keggin units, linked by two WO_2 units to form the hypothetical dilacunary $X^{III}_2W_{20}$ anion, and further by two *facial* $WO_2(OH)$ units to generate the complete anion. Several works reported transition metal substituted derivatives, in which the two *facial* $WO_2(OH)$ units are replaced by $M(H_2O)_3$ groups to form $[X^{III}_2W_{20}M^n_2O_{70}(H_2O)_3]^{(14-2n)-}$ ($M^n = Fe^{III}, Co^{II}, Zn^{II}, Mn^{II}$ etc.) clusters.⁸⁻¹³ These $X^{III}_2W_{20}M^n_2$ derivatives can be considered complexes of the hypothetical $X^{III}_2W_{20}$ dilacunary structure.

Two formulae have been reported for the parent Bi_2W_{22} oxotungstate, *i.e.*, $[Bi^{III}_2W_{22}O_{74}(OH)_2]^{12-}$ and $[Bi^{III}_2W_{22}O_{70}(OH)_6]^{8-}$, respectively.^{8, 9} The first structure, with one protonated terminal oxygen of the *facial* WO_3 units⁸, was also determined on crystals that we have synthesized¹⁴. For the second structure, all three terminal oxygen atoms of the *facial* WO_3 units are protonated.⁹ No direct evidence was found until yet for the existence of the dilacunary Bi_2W_{20} structure.

Here we report the synthesis and investigation of a new Bi (III) containing polyoxotungstate, which was prepared as sodium salt, *i.e.*, $Na_{11}H[H_{(2-x)}Bi_2W_{20}O_{70}(HWO_3)_x] \cdot 46H_2O$ ($x = 1.4$), abbreviated as $Na_{11}H[Bi_2W_{21.4}]$. The new cluster was investigated by vibrational (FT-IR, Raman) and electronic (UV-Vis-NIR) spectroscopy and by X-ray diffraction, as well.

RESULTS AND DISCUSSION

Chemical analysis

Results (wt %): found (calculated for $Na_{11}H[H_2Bi_2W_{21.4}O_{74.2}] \cdot 46H_2O$ ($M = 6623.91$) Na

3.74 (3.82), Bi 6.18 (6.31), W 59.50 (59.39), H_2O 12.53 (12.51).

Vibrational spectra

FT-IR spectrum. The vibration bands of the FT-IR spectrum (in cm^{-1}) and their assignment are the following: 1625 (m) $\delta H-O-H$, 970 (m) $\nu_{as}W=O$, 892 (s) $\nu_{as}Bi-O$, 840 (m), 796 (s) and 765 (s) $\nu_{as}W-O-W$, 636 (vs) $\delta O-Bi-O$, 540 (m) $\delta W-O-W$.

The four antisymmetric stretching vibrations $\nu_{as}W=O$ and $\nu_{as}W-O-W$, which are characteristic to the W-O bonds, are recorded in the 700-1000 cm^{-1} range.¹⁵ They demonstrate the polyoxotungstate nature of the investigated cluster. The main vibration due to the heteroatom, *i.e.*, $\nu_{as}Bi-O$, is recorded at 892 cm^{-1} and shows the presence of Bi as a heteroatom in the polyoxometalate framework.

Raman spectrum. The vibration bands of the Raman spectrum (in cm^{-1}) are: 955 (s), 881 (vs), 472 (w), 381 (s), 308 (m), 224 (m).

The three characteristic strong and very strong bands, recorded at 955, 881 and 381 cm^{-1} , are assigned to the $\nu_sW=O$, $\nu_{as}W=O$ and ν_sW-O vibrations.¹⁵

Electronic spectra

UV spectrum. The absorption bands (in nm/cm^{-1}), their assignment and the molar absorptivity [in $L mol^{-1} cm^{-1}$] are: 208/48,077 [202,800] (CT) $W=O_{terminal}$, 268/37,313 sh (CT) $W-O-W$.

UV spectra of polyoxometalate clusters generally exhibit two charge-transfer (CT) bands, characteristic to the polyoxoanionic framework, which are ascribed to oxygen-to-metal-transitions.¹⁶ In the UV spectrum of the $Bi_2W_{21.4}$ cluster, the broad ν_1 CT band, due to $d\pi-p\pi-d\pi$ transitions from the tricentric W-O-W bonds, is reduced to a shoulder recorded at 255 nm (39,215 cm^{-1}). The sharper ν_2 CT band, due to $d\pi-p\pi$ transitions of the $W=O_{terminal}$ bonds, has the maximum detected at 208 nm (48,100 cm^{-1}). Its high intensity ($\epsilon = 2.03 \cdot 10^5 L mol^{-1} cm^{-1}$) is probably the result of the distortion of WO_6 octahedra.

Vis-NIR spectrum. The investigated cluster with only W^{6+} addenda (electronic structure d^0) has no d-d absorption bands in the visible and in the near IR domain. However, the broad ν_1 CT band is prolonged from the UV into the visible.

X-Ray diffraction

Crystallographic data of the $Na_{11}H[H_{(2-x)}Bi_2W_{20}O_{70}(HWO_3)_x] \cdot 46H_2O$ ($x = 1.4$) substance are summarized in Table 1.

Table 1

Crystal data and structure refinement for $\text{Na}_{11}\text{H}[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]\cdot 46\text{H}_2\text{O}$ ($x = 1.4$)

Empirical formula	$\text{H}_{95}\text{Bi}_2\text{Na}_{11}\text{O}_{120.20}\text{W}_{21.40}$	
Formula weight	6623.91	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 36.1622(12)$ Å	$\beta = 90.826(1)^\circ$
	$b = 25.8237(9)$ Å	
	$c = 13.0491(5)$ Å	
Volume	$11502.0(7)$ Å ³	
Z	4	
Density (calculated)	3.838×10^3 kg m ⁻³	
Absorption coefficient	24.517 mm ⁻¹	
F(000)	11749	
Crystal size	0.40 x 0.04 x 0.04 mm ³	
Theta range for data collection	0.99 to 27.01°	
Index ranges	$-43 \leq h \leq 34, -32 \leq k \leq 32, -16 \leq l \leq 16$	
Reflections collected	33153	
Independent reflections	12339 (R(int) = 0.0325)	
Observed reflections ($I > 2\sigma(I)$)	9918	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12305 / 0 / 615	
Goodness-of-fit on F^2	1.029	
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0286, wR2 = 0.0625	
R indices (all data)	R1 = 0.0447, wR2 = 0.0811	
Largest diff. peak and hole	2.276 and -1.358 e Å ⁻³	

Single-crystal X-ray diffraction analysis shows that the $\text{Na}_{11}\text{H}[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]\cdot 46\text{H}_2\text{O}$ ($x = 1.4$) substance crystallizes in the space group C2/c, with four units per unit cell. The unit cell is monoclinic, with the following parameters: $a = 36.1622(12)$ Å, $b = 25.8237(9)$ Å, $c = 13.0491(5)$ Å, $\beta = 90.826(1)^\circ$, $V = 11502.0(7)$ Å³.

The $[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]^{12-}$ ($x=1.4$) polyoxometalate molecule consists of two identical trilacunary $B\beta$ -[BiW₉O₃₃] pseudo-Keggin type units, in which one W₃O₁₃ group is turned by 60° relative to the $B\alpha$ -[BiW₉O₃₃] unit. Each Bi^{III} heteroatom is tricoordinated, building a trigonal BiO₃ pyramid inside the [BiW₉O₃₃] unit. The two units are connected by two WO₂ and also by two *facial* WO₂(OH) groups. The polyhedral representation of the $[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]^{12-}$ ($x=1.4$) molecule is given in Fig. 1 and reveals that all addenda metal centres are octahedrally surrounded. Practically, the polyoxometalate anion is composed of two Bi^{III}W₁₁ units, if only heteroatoms and addenda are mentioned, which are related by a crystallographic centre of symmetry. The ball-and-stick representation, with the numbering of the atoms, is displayed in Fig. 2.

The three Bi-O bonds have almost the same length, namely Bi(1)-O(19) = Bi(1)-O(28) = 2.137(6)

and Bi(1)-O(6) = 2.143(6) Å. The valence bond sum for the two Bi(III) heteroatoms is of only 2.628, suggesting that they may be slightly reduced.

The three W(11)-O_{terminal} bonds of the *facial* WO₃ groups are: W(11)-O(36) = 2.029(6), W(11)-O(37) = 1.774(6) and W(11)-O(38) = 1.747(6) Å. The two shorter values correspond to W = O double bonds, while the longer W(11)-O(36) bond corresponds to a protonated W-OH group. According to the six bonds, the valence sum of the two W(11) atoms is of 5.412, showing that they are partially reduced. On the other hand, the occupancy factor of the W(11) positions is of only 0.70. Therefore, we formulated the two *facial* groups as (HWO₃)_x = [WO₂(OH)]_x, where $x = 1.4$. There are some slight evidence for the existence of a third proton, which is highly delocalized inside the molecule. We designated it as H_(2-x) in the molecular formula, in order to account for the charge 12- of the anion, which was determined by potentiometric titration. All bonds shown in the ball-and-stick representation are covalent, namely the bonds between addenda/metal centres and oxygen atoms, as well as those between the heteroatom and oxygen atoms, *i.e.*, W-O and Bi-O. As can be noticed, the addenda/metal centres are linked between each other and with the heteroatom exclusively *via* W-O-W and Bi-O-W oxygen

bridged covalent bonds. The addenda, which are located in the centre of a distorted WO_6 octahedron occupy an off-centre position towards the external edges, due probably to certain $\pi \text{W} \rightarrow \text{O}$ ($d\pi\text{-}p\pi$)

bonds, which reinforce the coordinative covalent $\text{W} \leftarrow \text{O}$ bonds.

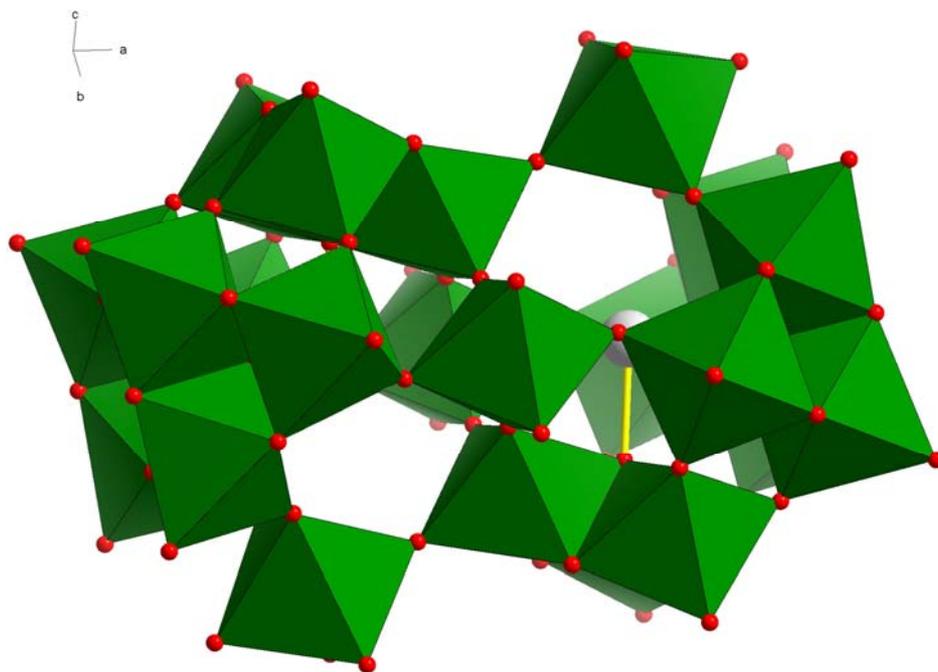


Fig. 1 – Polyhedral representation of the $[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]^{12-}$ ($x=1.4$) polyoxometalate anion (Colour code: Bi large grey circle; WO_6 green octahedra; O small red circles).

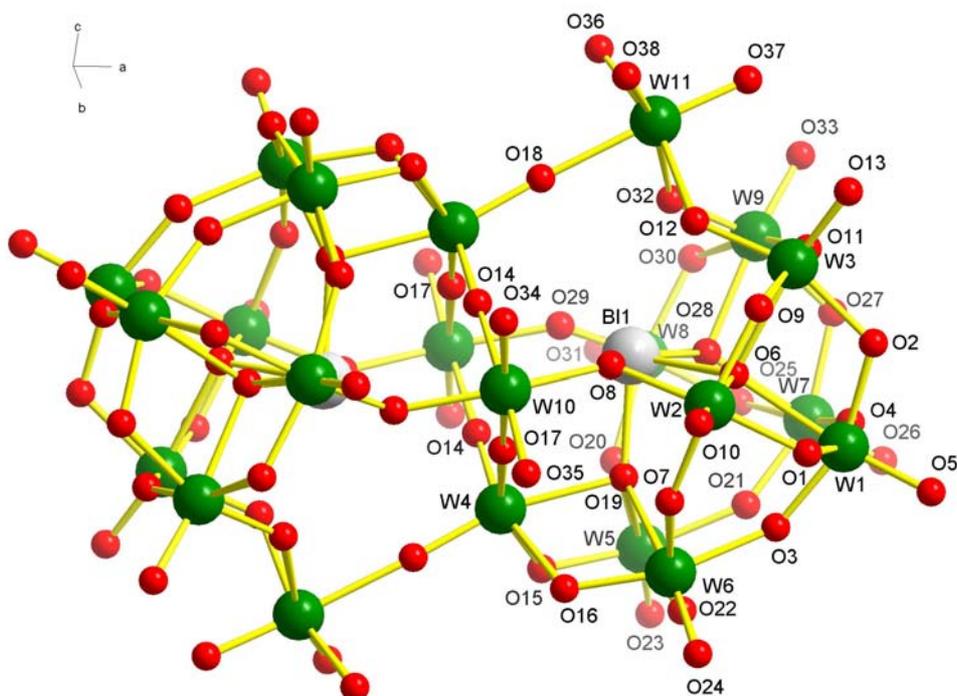


Fig. 2 – Ball-and-stick representation of the $[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]^{12-}$ ($x=1.4$) polyoxometalate anion (Colour code: Bi grey; W green; O red).

There are seven sodium positions in each half-unit (the unit includes the molecular anion, the external cations and the crystal water). Four positions of each half-unit are occupied, while the other three have an occupancy factor of only 0.50. This results in 5.50 Na⁺ ions per half-unit and 11 Na⁺ ions per unit, which is in good accordance with the chemical analysis. We completed the formula of the substance with one external proton, which is necessary for electroneutrality. The Na⁺ ions have an octahedral environment, which consists of six oxygens belonging either to the polyoxometalate anion or to crystal water molecules.

The molecular formula of the polyoxometalate cluster, determined by single-crystal X-ray diffraction is $[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]^{12-}$ ($x = 1.4$), which corresponds to $[\text{H}_2\text{Bi}_2\text{W}_{21.4}\text{O}_{74.2}]^{12-}$, abbreviated as $\text{Bi}_2\text{W}_{21.4}$. The formula demonstrates that the crystal of the investigated substance is in fact a mixture of the complete parent polyoxometalate cluster Bi_2W_{22} and of the dilacunary cluster Bi_2W_{20} , in a proportion of 70% : 30%.

In the dilacunary Bi_2W_{20} structure, the two W(11) positions are missing. Our research is the first evidence for the existence of the dilacunary Bi_2W_{20} polyoxometalate, which was until now hypothetical only. Mention should be made that in the case of our substance, which was prepared according to a slightly different procedure, the monoclinic cell is larger and contains four units, as compared to the smaller cell with only two units, found in the previous X-ray diffraction analyses performed on the "pure" Bi_2W_{22} cluster.^{8,9}

EXPERIMENTAL

Synthesis

An amount of 25.0 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (75.792 mmol) was dissolved in 100 mL hot water (80-90 °C). Then, to the hot solution another solution containing 3.4 g (7.009 mmol) $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ dissolved in 4 mL HCl ($d=1.18$) and 25 mL $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ (pH 4) buffer solution was added dropwise, under stirring. The obtained mixture was heated again for 1 h at 90 °C, after which 5 g (52.637 mmol) of finely ground NaNO_3 were added. Next, the solution was purified by filtration and stored at room temperature for several hours, until pale yellow needle-shaped crystals separated. The crystals were filtered off, washed with distilled water and dried in air. Eventually, they were recrystallized twice from water acidulated at pH 4. Yield: 21.1 g (3.185 mmol ; 89.8 % based on W).

Analysis

Elemental analysis of Bi and W was performed by OES-ICP with a BIRD 2070 spectrophotometer. Na was determined by FEP with an Eppendorf flame photometer. Water content

was determined by weight loss at 350 °C, with a Niztsch SPA 409A simultaneous thermoanalyser.

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 ($\lambda_e = 1064$ 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-K α radiation, graphite monochromator). The structure was solved with the SHELXS-97 software and refined using the SHELXL-93 software.

CONCLUSIONS

The paper reports the synthesis and structural investigation of a new $\text{Na}_{11}\text{H}[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x] \cdot 46\text{H}_2\text{O}$ ($x = 1.4$) nano-sized polyoxometalate cluster. The substance is the neutral salt of a heteropolyoxometalate, which contains two heteroatoms Bi^{III} with an unshared electron pair and W^{VI} atoms as addenda/metal centres.

The main vibration of the FTIR spectrum, $\nu_{\text{as}}\text{Bi-O}$, registered at 892 cm^{-1} , shows the presence of Bi as a heteroatom. The vibration bands of the Raman spectrum are characteristic to the polyoxometalate framework.

The UV spectrum shows two charge-transfer (CT) bands, recorded at 208 and 268 nm, which are characteristic to the polyoxometalate building. There are no absorption bands in the Vis-NIR spectrum.

The crystal structure analysis demonstrates that the investigated substance crystallizes in a C2/c space group and a monoclinic crystal system. It also shows that the $[\text{H}_{(2-x)}\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{HWO}_3)_x]^{12-}$ ($x=1.4$) polyoxometalate molecule is made up of two $B\beta$ - $[\text{BiW}_9\text{O}_{33}]$ pseudo-Keggin type units, which are connected by two WO_2 and also by two *facial* $\text{WO}_2(\text{OH})$ groups. The Bi^{III} heteroatom builds an unusual trigonal BiO_3 pyramid, which acts as a primary heterogroup.

The molecular formula of the polyoxotungstate cluster corresponds to $[\text{H}_2\text{Bi}_2\text{W}_{21.4}\text{O}_{74.2}]^{12-}$, abbreviated as $\text{Bi}_2\text{W}_{21.4}$. This formula demonstrates that the investigated substance is a mixture of the complete parent polyoxometalate cluster Bi_2W_{22} and of the dilacunary cluster Bi_2W_{20} , in a proportion of 70% : 30%. The reported research also represents the first evidence for the existence of the dilacunary Bi_2W_{20} polyoxometalate cluster.

Supplementary Material

The complete crystallographic data for structural analysis have been entered in the FIZ Karlsruhe – ICSD Inorganic Crystal Structure Database under the registration No. 421640. Copies of this 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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