

Synthesis and Crystal Structure of a New 3D Copper B-Paradodecatungstate Compound: $[\text{Na}_2(\text{H}_2\text{O})_8][\text{Na}_8(\text{H}_2\text{O})_{20}][\text{Cu}(\text{en})_2][\text{W}_{12}\text{O}_{42}] \cdot 3 \text{H}_2\text{O}$

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A new polyoxotungstate complex $[\text{Na}_2(\text{H}_2\text{O})_8][\text{Na}_8(\text{H}_2\text{O})_{20}][\text{Cu}(\text{en})_2][\text{W}_{12}\text{O}_{42}] \cdot 3 \text{H}_2\text{O}$ (**1**) (en = ethylenediamine) has been synthesized in aqueous solution and characterized by elemental analysis, IR spectroscopy and TG analysis, together with a single crystal X-ray diffraction study. In compound **1**, the $\text{Cu}(\text{en})_2^{2+}$ complex cation links the $[\text{W}_{12}\text{O}_{42}]^{12-}$ anions to form a 1D chain, and the 1D chains are further interconnected with $\text{Na}_8(\text{H}_2\text{O})_{20}^{8+}$ and $\text{Na}_2(\text{H}_2\text{O})_8^{2+}$ cations to construct a new 3D framework.

Key words: Paradodecatungstate, 1D Chain, 3D Extended Framework, Crystal Structure, Metal Organic Complex

Introduction

Polyoxometalates (POMs), as one kind of significant nanosized metal oxide clusters with variable topologies, have attracted considerable interest in fields such as catalysis, electrochemistry, electrochromism, and magnetism [1–6]. There has been a growing interest in the synthesis of composite solids assembled from inorganic oxides and metal complexes in recent years. One of the challenging tasks in POM chemistry is to link up the discrete polyanion units into 1D, 2D and even 3D extended frameworks with desired properties [7–9].

To date, the commonly used POM building units among others are mainly limited to well-known Keggin-, Well-Dawson-, Anderson-, Silverton-, and Lindquist-type anions. Among these types of polyanions, the protonated paradodecatungstate anion $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ with its particular structural features, sufficient charge density and multiple coordination sites, provides numerous possibilities for intermolecular linkages according to the functional patterns of selected building blocks. Known examples utilizing this anion for the design and synthesis of POM complexes with extended structures include $\text{K}_6[\text{Co}(\text{H}_2\text{O})_4]_2-$

$[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 14 \text{H}_2\text{O}$ [10], $\text{Na}_3[\text{NaCo}_3\text{H}_2\text{W}_{12}\text{O}_{42}(\text{H}_2\text{O})_{16}] \cdot 22 \text{H}_2\text{O}$ [11], $\text{Na}_8[\{\text{Cd}(\text{H}_2\text{O})_2\}(\text{H}_2\text{W}_{12}\text{O}_{42})] \cdot 32 \text{H}_2\text{O}$ [12], $\text{Na}_6[\{\text{Co}(\text{H}_2\text{O})_3\}\{\text{Co}(\text{H}_2\text{O})_4\}(\text{H}_2\text{W}_{12}\text{O}_{42})] \cdot 29 \text{H}_2\text{O}$ [12], $(\text{NH}_4)_7[\text{Bi}(\text{H}_2\text{W}_{12}\text{O}_{42})] \cdot 20 \text{H}_2\text{O}$ [13], $[\text{Cu}(\text{H}_2\text{O})_6][\{\text{Cu}(\text{H}_2\text{O})_2\}_2\{\text{Cu}(\text{H}_2\text{O})_4\}(\text{H}_4\text{W}_{12}\text{O}_{42})] \cdot 12 \text{H}_2\text{O}$ [14], *etc.* [15–19]. In contrast, bridging this anion by metal organic complexes to generate inorganic-organic hybrid materials is still a largely unexplored concept [20–24].

In this context, we obtained a new 3D extended framework, $[\text{Na}_2(\text{H}_2\text{O})_8][\text{Na}_8(\text{H}_2\text{O})_{20}][\text{Cu}(\text{en})_2][\text{W}_{12}\text{O}_{42}] \cdot 3 \text{H}_2\text{O}$ (**1**), by an aqueous synthetic method.

Results and Discussion

Synthesis

Compound **1** was obtained from a mixture of $\text{Na}_2\text{WO}_4 \cdot 2 \text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, and en. It was an unexpected product during our attempt to synthesize compounds based on the $[\text{BiW}_9\text{O}_{33}]^{9-}$ POM anion. Surprisingly, there was no Bi^{3+} in compound **1** although $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ proved to be necessary for its synthesis.

In order to explain why Bi(III) is necessary, the following additional experiments were undertaken.

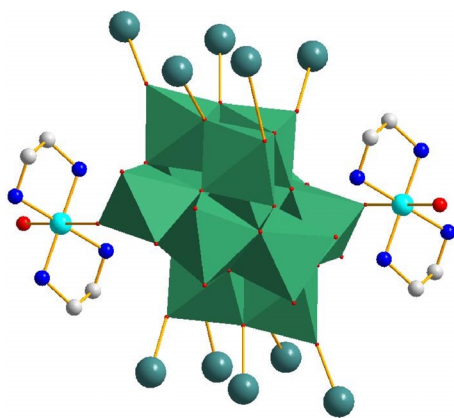


Fig. 1. View of the $[\text{W}_{12}\text{O}_{42}]^{12-}$ anion in the crystal.

(i) Synthesis of the target compound with a mixture of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and en only, in the absence of $\text{Bi}(\text{NO}_3)_3$. In this experiment only a deposit of blue $\text{Cu}(\text{OH})_2$ was obtained at $\text{pH} = 6.5$. (ii) In attempts to use $\text{Al}(\text{NO}_3)_3$ to replace $\text{Bi}(\text{NO}_3)_3$ we synthesized the target compound from a mixture of $\text{Al}(\text{NO}_3)_3$, CuCl_2 , Na_2WO_4 and en. Complex **1** was indeed obtained, but the quality of the single crystals obtained that way was not sufficient for an X-ray structure analysis. Therefore, we believe that $\text{Bi}(\text{III})$, though not being essential, is useful for the synthesis of our target compound.

The formation mechanism of compound **1** is not very clear as yet. It may be that upon addition of $\text{Bi}(\text{NO}_3)_3$ the anion $\{[(\text{Cu}(\text{H}_2\text{O}))_3][(\text{Na}(\text{H}_2\text{O}))_2]_3[(\alpha\text{-BiW}_9\text{O}_{33})_2]\}^{9-}$ initially forms [25], which prevents the Cu^{2+} cation from being deposited as $\text{Cu}(\text{OH})_2$ at $\text{pH} = 6.5$. Upon addition of en the anion $\{[\text{Cu}(\text{H}_2\text{O})_3]-[(\text{BiW}_9\text{O}_{33})_2]\}^{12-}$ then decomposes, and the anion $[\text{W}_{12}\text{O}_{42}]^{12-}$ forms. The $[\text{W}_{12}\text{O}_{42}]^{12-}$ anion has two cap-type W_3O_{10} groups and two belt-type W_3O_{11} groups. In the belt-type W_3O_{11} groups, two terminal O atoms coordinated to W atoms are prone to link metal organic complexes which should be beneficial for the synthesis of **1**.

Structure description

The compound **1** is constructed from a $[\text{W}_{12}\text{O}_{42}]^{12-}$ anion, the complex cation $\text{Cu}(\text{en})_2^{2+}$, and $\text{Na}_8(\text{H}_2\text{O})_{20}^{8+}$ and $\text{Na}_2(\text{H}_2\text{O})_8^{2+}$ cations. The $[\text{W}_{12}\text{O}_{42}]^{12-}$ anion shown in Fig. 1 is a centrosymmetric unit which consists of two cap-type W_3O_{10} groups and two belt-type W_3O_{11} groups, in which all the W atoms possess distorted octahedral coordination geometries.

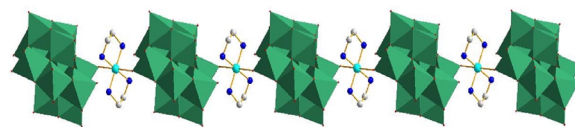


Fig. 2. Part of a 1D chain $[\text{W}_{12}\text{O}_{42}]^{12-}-[\text{Cu}(\text{en})_2]^{2+}-[\text{W}_{12}\text{O}_{42}]^{12-}$.

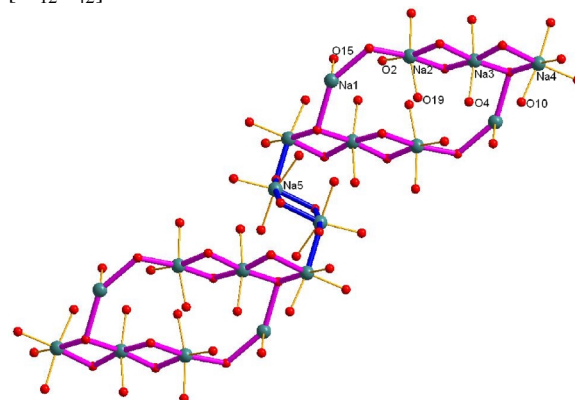


Fig. 3. View of the coordination geometries of the Na atoms.

Acting as a dodeca-dentate ligand, this polyanion connects two $\text{Cu}(\text{en})_2^{2+}$ complexes through the terminal O atoms of belt-type W_3O_{11} groups, and ten sodium ions through the terminal and bridging O atoms of the cap-type W_3O_{10} groups.

The Cu (II) center exhibits a distorted octahedral coordination geometry, which is defined by four N atoms from two en ligands and two terminal O atoms from two $[\text{W}_{12}\text{O}_{42}]^{12-}$ anions. The bond lengths are $1.997(1)-2.019(1)$ Å and $2.525(2)$ Å for Cu–N and Cu–O, respectively. A 1D chain is formed by the ion sequence $[\text{W}_{12}\text{O}_{42}]^{12-}-\text{Cu}(\text{en})_2^{2+}-[\text{W}_{12}\text{O}_{42}]^{12-}$ (Fig. 2).

In compound **1**, there are five crystallographically unique Na atoms (Fig. 3). Na(1) adopts a distorted trigonal-pyramidal geometry, which is coordinated by one bridging O atom of a $[\text{W}_{12}\text{O}_{42}]^{12-}$ anion and two water molecules. The Na(2) octahedron is formed by one terminal O atom and one bridging O atom of two different $[\text{W}_{12}\text{O}_{42}]^{12-}$ anions and four water molecules, and the octahedron around Na(3) is formed by one bridging O atom of a $[\text{W}_{12}\text{O}_{42}]^{12-}$ anion and five water molecules. The octahedral configuration of the Na(4) center is formed by one terminal O atom of a $[\text{W}_{12}\text{O}_{42}]^{12-}$ anion and five water molecules, whereas the Na(5) atom is coordinated with six water molecules to form an octahedral configuration. Na(1), Na(2), Na(3) and its symmetry-equivalent counterparts form a cyclic fourteen-membered $\{\text{Na}_6\text{O}_8\}$ ring, and

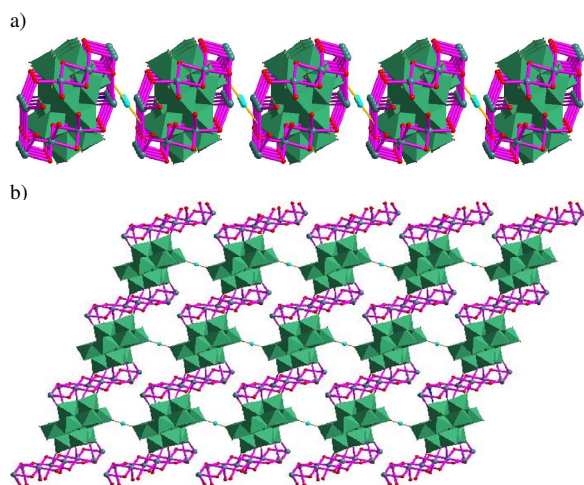


Fig. 4. Schematic illustration of the 2D layer of compound **1**: (a) the 2D layer structure viewed along the crystallographic *b* axis, (b) the 2D layer structure viewed along the *c* axis.

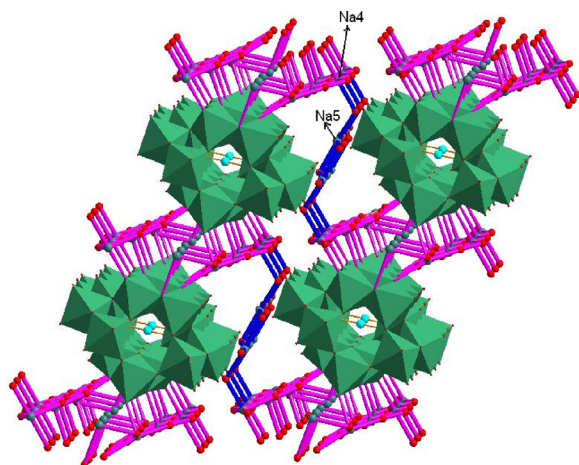


Fig. 5. View of the entire 3D framework of compound **1**.

this $\{\text{Na}_6\text{O}_8\}$ ring is linked to Na(4) and its symmetry counterpart to form a $[\text{Na}_8\text{O}_{20}]^{8+}$ unit. Then, the $[\text{Na}_8\text{O}_{20}]^{8+}$ units link the anions $[\text{W}_{12}\text{O}_{42}]^{12-}$ by Na–O bonds to form a 2D layer structure (Fig. 4). Finally, the binuclear units $\text{Na}_2(\text{H}_2\text{O})_8^{2+}$, formed by Na(5) and its symmetry counterpart, is linked to $[\text{Na}_8\text{O}_{20}]^{8+}$ units of different layers by Na–O bonds to construct a 3D extended framework (Fig. 5).

IR spectrum of compound **1**

The IR spectrum of compound **1** exhibits a strong band at 1040 cm^{-1} indicative of $\nu(\text{W}=\text{O})$. Characteristic bands at 935 and 872 cm^{-1} originate from $\nu(\text{W}-\text{O})$

and $\nu(\text{W}-\text{O}-\text{Cu})$, respectively. The bands at 2960 , 2880 , 1630 , and 1460 cm^{-1} are attributed to the en molecules, while the bands at 3420 and 1590 cm^{-1} are assigned to water molecules.

Thermal analysis

The TG curve of compound **1** can be divided into five stages. The first three steps in the range 44 – $235\text{ }^\circ\text{C}$ are ascribed to the loss of crystal and coordination water molecules. The observed weight loss (14.47%) is in good agreement with the calculated value (14.51%). The final two continuous steps occurring in the range 285 – $730\text{ }^\circ\text{C}$ are due to the loss of coordinated en molecules and the decomposition of $[\text{W}_{12}\text{O}_{42}]^{12-}$ (observed: 4.91%, calcd.: 5.20%).

In summary, a new 3D structure $[\text{Na}_2(\text{H}_2\text{O})_8][\text{Na}_8(\text{H}_2\text{O})_{20}][\text{Cu}(\text{en})_2][\text{W}_{12}\text{O}_{42}] \cdot 3\text{H}_2\text{O}$ (**1**) has been synthesized under non-hydrothermal conditions. The synthesis of compound **1** from well-defined discrete building blocks indicates the diversity of pathways available upon using metastable precursors to synthesize novel structures and species. It appears that the B-paradodecatungstate anion is a good candidate with sufficient charge density and multiple coordination sites for the synthesis of new complexes.

Experimental Section

General methods and materials

All reagents were purchased and used without further purification. Deionized water was used as solvent. The infrared spectrum was recorded on a Nicolet 170SX FT-IR spectrophotometer with a KBr pellet in the 4000 – 400 cm^{-1} region. TG analysis was performed on a Netzsch STA 449C microanalyzer in an atmosphere of nitrogen with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 25 to $800\text{ }^\circ\text{C}$.

Synthesis



In a typical preparation, 1.650 g (5 mmol) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 50 mL of deionized water, and the pH was adjusted to 7.0 by addition of 6 M HCl . This solution was heated to $80\text{ }^\circ\text{C}$, and a solution of 0.243 g (0.5 mmol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 1 mL of 6 M HCl was added dropwise. If a light turbidity occurred, addition was discontinued until the solution was clear again before the next drop was added. Then $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.171 g , 1 mmol) and en (0.05 mL , 0.75 mmol) were added in succession. The final pH of the mixture was adjusted to 6.5 by addition of 6 M HCl , and the resulting mixture was

Table 1. Details of data collection and structure refinement for compound **1**.

Formula	C ₄ H ₇₈ O ₇₃ N ₄ Na ₁₀ CuW ₁₂
<i>M_r</i>	3850.17
Cryst. size, mm ³	0.28 × 0.25 × 0.23
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.831
<i>b</i> , Å	12.965
<i>c</i> , Å	14.185
α , deg	63.318(10)
β , deg	82.904(10)
γ , deg	68.883(10)
<i>V</i> , Å ³	1811.0(3)
<i>Z</i>	1
<i>D</i> _{calcd} , g cm ⁻³	3.472
<i>F</i> (000), e	1679
<i>hkl</i> range	−14 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 13, −16 ≤ <i>l</i> ≤ 12
θ range, deg	1.61–25.00
Reflections collected / unique / <i>R</i> _{int}	9259 / 6311 / 0.0266
Absorption coefficient, mm ⁻¹	19.433
Data / refined parameters	6311 / 476
GoF (<i>F</i> ²)	1.006
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.037 / 0.079
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.051 / 0.086
Largest diff. peak / hole, e Å ⁻³	1.643 / −2.045

stirred and heated at 80 °C for half an hour. After it had cooled to r.t., the mixture was filtered to remove insoluble solids and the filtrate allowed to evaporate slowly. After two weeks, light-purple columnar single crystals crystallized out of the solution. Na₁₀CuW₁₂C₄N₄O₇₃H₇₈: calcd. Na 5.97, Cu 1.65, W 57.30, C 1.25, N 1.46, H 2.04; found Na 6.01, Cu 1.70, W 57.34, C 1.21, N 1.41, H 2.01.

Crystal structure determination

Single crystal X-ray diffraction data for compound **1** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 296 K. Absorption corrections were applied using multi-scan techniques. The structure was solved by Direct Methods using SHELXS-97 [26] and refined by full-matrix least-squares on *F*² with SHELXL-97 [27]. All the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms attached to nitrogen atoms and carbon atoms were fixed in ideal positions. Other hydrogen atoms could not be located because the scattering of the hydrogen atoms in the presence of the paradodecatungstate anions is not

Table 2. Selected bond lengths (Å) and angles (deg) for Na₂(H₂O)₈[Na₈(H₂O)₂₀][Cu(en)₂][W₁₂O₄₂] · 3 H₂O (**1**)^a.

Na(1)–O(15)	2.865(1)	Na(4)–O(10)	2.385(1)
Na(1)–O(36)	2.883(2)	Na(4)–O(24)	2.379(2)
Na(1)–O(38)	2.832(2)	Na(4)–O(31)	2.498(1)
Na(2)–O(2)	2.677(1)	Na(4)–O(33)	2.442(1)
Na(2)–O(19)	2.372(1)	Na(4)–O(36)	2.406(1)
Na(2)–O(32)	2.362(1)	Na(4)–O(37)	2.487(1)
Na(2)–O(34)	2.469(1)	Na(5)–O(22)	2.359(2)
Na(2)–O(35)	2.426(1)	Na(5)–O(24)	2.407(2)
Na(2)–O(38)	2.404(1)	Na(5)–O(25)	2.403(2)
Na(3)–O(4)	2.455(1)	Na(5)–O(25) ^{#1}	2.445(1)
Na(3)–O(23)	2.448(1)	Na(5)–O(26)	2.407(2)
Na(3)–O(34)	2.416(1)	Na(5)–O(27)	2.381(2)
Na(3)–O(35)	2.488(1)	Cu(1)–N(1)	2.019(1)
Na(3)–O(36)	2.388(1)	Cu(1)–O(5)	2.525(2)
Na(3)–O(37)	2.423(1)	Cu(1)–N(2)	1.997(1)
O(38)–Na(1)–O(36)	147.9(5)	O(15)–Na(1)–O(36)	97.7(4)
O(38)–Na(1)–O(15)	91.9(4)	O(2)–Na(2)–O(38)	79.3(3)
O(38)–Na(2)–O(35)	107.3(4)	O(35)–Na(2)–O(34)	89.1(3)
O(34)–Na(2)–O(2)	84.9(3)	O(19)–Na(2)–O(34)	78.3(3)
O(32)–Na(2)–O(34)	96.8(4)	O(37)–Na(3)–O(36)	88.5(3)
O(36)–Na(3)–O(34)	94.5(4)	O(34)–Na(3)–O(35)	88.8(3)
O(35)–Na(3)–O(37)	87.3(3)	O(4)–Na(3)–O(37)	94.8(3)
O(23)–Na(3)–O(37)	92.1(5)	O(31)–Na(4)–O(33)	84.7(4)
O(33)–Na(4)–O(36)	103.0(4)	O(36)–Na(4)–O(37)	86.7(4)
O(37)–Na(4)–O(31)	85.6(4)	O(10)–Na(4)–O(31)	90.2(4)
O(24)–Na(4)–O(31)	90.3(5)	O(22)–Na(5)–O(27)	87.9(6)
O(27)–Na(5)–O(25)	88.3(5)	O(25)–Na(5)–O(26)	78.8(5)
O(26)–Na(5)–O(22)	104.2(6)	O(24)–Na(5)–O(22)	99.6(6)
O(25)–Na(5)–O(22)	89.8(6)	O(5)–Cu(1)–N(2)	90.3(1)
N(1)–Cu(1)–N(2)	96.2(4)		

^a Symmetry operation: ^{#1} −*x*, −*y*, −*z*.

sufficient. Hydrogen bonds between the “free” water molecules Ow₁, Ow₂ and between the water molecules and O atoms O(14), O(17), O(22), O(23), O(32) and O(5), O(24), O(31), O(33) can be expected leading to the observed short O···O contacts.

Details of data collection and structure refinement are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC 695121 contains the supplementary crystallographic data for compound **1**. They can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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