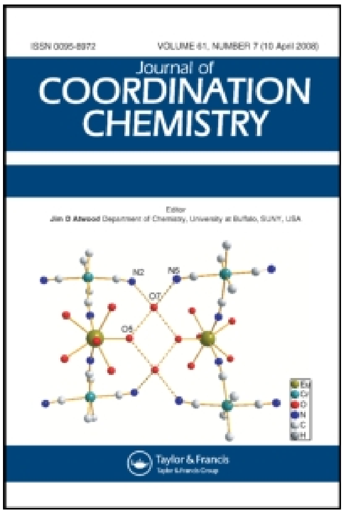

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Synthesis and characterization of a new transition-metal complex of the Lindqvist polyanion $Na[Cu(1,3\text{-pda})_2]_3[HNb_6O_{19}] \cdot 3H_2O$

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A new transition-metal (TM) complex of the Lindqvist polyanion $Na[Cu(1,3\text{-pda})_2]_3[HNb_6O_{19}] \cdot 3H_2O$ (1,3-pda = 1,3-diaminopropane) has been prepared using pre-prepared $TBA_4[H_4Nb_6O_{19}] \cdot 7H_2O$ as a precursor and characterized by single crystal X-ray diffraction, elemental analyses, IR spectra, and thermogravimetric analysis. Crystal data for the compound: rhombohedral, space group *R-3c*, $a = 14.927(4)$ Å, $b = 14.927(4)$ Å, $c = 36.940(18)$ Å, $\gamma = 120°$, $V = 7128(4)$ Å^3, $Z = 6$. The structural unit of the title compound consists of a polyanion $[HNb_6O_{19}]^{7-}$, a Na^+, three $[Cu(1,3\text{-pda})_2]^{2+}$, and three crystal water molecules. The occupancy of all Cu atoms and water molecules is 0.5. X-ray diffraction indicated that the cations and the polyanion were linked through electrostatic interactions and intermolecular forces.

Keywords: Polyoxoniobate; Lindqvist ion; Hexaniobate

1. Introduction

Polyoxometalates attract interest due to their remarkable structures and potential applications in catalysis, biochemical analysis, medicinal chemistry, and material science [1–5].

Most of the work so far is reported on polyanions of W, Mo, and V, since they can be formed simply by acidification of their oxoanion solutions at ambient conditions [1]. The chemistry of Nb(V) is less evolved because of the lack of soluble monomeric precursors [1, 6]. Polyoxoniobates are stable in basic solutions and hydrolyzed in acidic solutions, whereas most other POMs are stable only under acidic conditions [7]. Niobate clusters have much larger negative charges per cluster than the tungstate and molybdate clusters [8].

Polyoxoniobate chemistry was limited to the Lindqvist ion $[Nb_6O_{19}]^{8-}$ (also known as hexaniobate) because it is dominant at pH > 7 in niobium oxide solutions [1, 9]. Due to the basicity and the great surface-charge densities of $[Nb_6O_{19}]^{8-}$, it could be expected that this anion can be used as coordinating "ligands" to bind additional metal centers.

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In fact, hexaniobate cluster has been used as a precursor for synthesis of other polyoxoniobate geometries [10].

Flynn synthesized the dimeric structures $[Mn(Nb_6O_{19})_2]^{12-}$ and $[Ni(Nb_6O_{19})_2]^{12-}$ [11]. Yamase *et al.* [12] reported a large composite polyoxoanion containing hexaniobate subunits, $[\{Eu_3O(OH)_3(OH_2)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$. Besserguenev *et al.* [13] synthesized the tricarbonyl metal derivatives of hexaniobate anions $[Nb_6O_{19}\{M(CO)_3\}_n]^{(8-n)-}$ (M = Re, Mn), which contain two $M(CO)_3$ groups attached to the surface bridging oxygen atoms, and these exhibited promising stability in aqueous solution. Moreover, Bontchev *et al.* [14] obtained five complexes based on the linkage of $[Nb_6O_{19}]$ clusters and $[CuL_x]$ (L = ethylenediamine (en), $NH_3 \cdot H_2O$). Our research group synthesized a new neutral polyoxoniobate decorated with four copper complex moieties $\{Nb_6O_{19}[Cu(2,2'\text{-bipy})]_2[Cu(2,2'\text{-bipy})_2]_2\} \cdot 19H_2O$ [15].

In the present article, complex formation of $[Nb_6O_{19}]^{8-}$ with $[Cu(1,3\text{-pda})_2]^{2+}$ is described with 1,3-diaminopropane as organic chelator to copper. We isolated ionic cluster-type phases, $Na[Cu(1,3\text{-pda})_2]_3[HNb_6O_{19}] \cdot 3H_2O$, which can be described as isolated $[HNb_6O_{19}]^{7-}$ clusters symmetrically diluted by $[Cu(1,3\text{-pda})_2]^{2+}$ and H_2O.

2. Experimental

2.1. *Materials and physical measurements*

C, H, and N elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. Infrared absorption spectra were recorded on a Nicolet 170SXFT-IR spectrometer using KBr pellets in the range 400–4000 cm^{-1}. TG-DTA measurements were carried out on a Perkin–Elmer7 thermal analyzer in flowing N_2 between 25 and 1000°C at a heating rate of 10°C min^{-1}.

The $H_3PW_{12}O_{40} \cdot nH_2O$ and $TBA_4[H_4Nb_6O_{19}] \cdot 7H_2O$ complexes were prepared as described in the literature [16, 17]. All other reagents were purchased from commercial sources and used as received.

2.2. *Synthesis of $Na[Cu(1,3\text{-pda})_2]_3[HNb_6O_{19}] \cdot 3H_2O$*

$CuCl_2 \cdot 2H_2O$ (0.341 g, 2.0 mmol) and $H_3PW_{12}O_{40} \cdot nH_2O$ (3.84 g, *ca* 1.33 mmol) were dissolved in water (10 mL) and the resulting solution was heated at 70°C with continuous stirring until the solution was nearly dry. The obtained solid was redissolved in 10 mL water. $TBA_4[H_4Nb_6O_{19}] \cdot 14H_2O$ and 1,3-diaminopropane (0.35 mL, 4.0 mmol) were dissolved in 20 mL of distilled water, then the first solution was added quickly with vigorous stirring and large quantities of white precipitate formed rapidly. The precipitate was removed by filtration and the pH of the solution was adjusted to 10 with a dilute NaOH solution (1 M); the aqueous solution was heated at 60°C with gently stirring for 1 h, filtered again, and the filtrate was allowed to evaporate at room temperature. The blue block crystals suitable for X-ray diffraction were obtained from the mother liquor within 2 weeks. Anal. Calcd Found: C, 13.3(13.7); H, 4.17(4.26); N, 10.3(10.7)%.

2.3. *X-ray structure determination and refinement*

Intensity data were collected on a Bruker APEX-II CCD detector at 296(2) K using Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range $1.92 < \theta < 25.00°$ with $-14 \le h \le 17$, $-16 \le k \le 17$, $-43 \le l \le 39$. A total of 11,004 (1396 independent reflections, $R_{\text{int}} = 0.0492$) reflections were measured. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program. The intensities were corrected by Lorentz-polarization factors and empirical absorption. All non-hydrogen atoms were refined anisotropically. Crystallographic data and structure refinement of the title compound are listed in table 1. Selected bond distances and angles are given in table 2.

Table 1. Crystallographic data and structure refinement parameters of the title compound.

Empirical formula	$C_{18}H_{67}Cu_3N_{12}NaNb_6O_{22}$
Formula weight	1573.90
Crystal system	Rhombohedral
Space group	R-3c
T (K)	296(2)
Units of cell dimensions (Å, °)	
λ	0.71073
a	14.927(4)
b	14.927(4)
c	36.940(18)
γ	120.00
Volume (Å^3)	7128(4)
Z	6
Crystal size (mm^3)	$0.18 \times 0.13 \times 0.10$
D_{Cal} (g cm^{-3})	2.200
Absorption coefficient (mm^{-1})	2.798
Reflections collected	11,004
Independent reflections	1396 [$R_{(\text{int})} = 0.0492$]
Data/restraints/parameters	1396/3/107
Goodness-of-fit on F^2	1.109
$F(000)$	4668
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0626$, $wR_2 = 0.1790$
R indices (all data)	$R_1 = 0.0722$, $wR_2 = 0.1855$
Index range	$-14 \le h \le 17$, $-16 \le k \le 17$, $-43 \le l \le 39$

$R = \Sigma||F_o| - F_c||/\Sigma|F_c|$; $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) of the title compound.

Nb1–O1	1.740(8)	O1–Nb1–O4i	101.5(3)
Nb1–O4i	1.944(8)	O1–Nb1–O2ii	103.3(3)
Nb1–O2ii	1.958(8)	O4i–Nb1–O2ii	155.1(3)
Nb1–O4	1.958(8)	O1–Nb1–O4	103.4(4)
Nb1–O2	1.968(7)	O4i–Nb1–O4	89.0(4)
Nb1–O3	2.3346(8)	O1–Nb1–O2	101.9(3)
Cu1–N1	2.013(11)	O4i–Nb1–O2	86.1(3)
Cu1–N2	2.015(11)	O2ii–Nb1–O2	86.53(9)
N2v–Cu1–N2	90.3(6)	O4–Nb1–O2	154.8(3)
N1v–Cu1–N1	91.2(7)	O1–Nb1–O3	178.7(3)
N1v–Cu1–N2v	90.5(4)	O4i–Nb1–O3	78.1(2)
N1–Cu1–N2v	167.8(4)	O2ii–Nb1–O3	77.1(2)
N1v–Cu1–N2	167.8(4)	O4–Nb1–O3	77.9(2)
N1–Cu1–N2	90.5(4)	O2–Nb1–O3	76.9(2)

3. Results and discussion

3.1. *Preparation of the title compound*

$TBA_4[H_4Nb_6O_{19}] \cdot 7H_2O$, with tetrabutylammonium as the charge-balancing cations, was used as precursor rather than alkali salts of $[Nb_6O_{19}]^{8-}$. The literature on niobium oxide aqueous chemistry gives much evidence that alkali salts of $[Nb_6O_{19}]^{8-}$ are easily precipitated below 100°C, because alkali cations have high-charge density [10]. It is more difficult to precipitate with large cations such as organic cations or metal-ligand cations.

In the syntheses of the title compound, 1,3-diaminopropane was chosen as the ligand because it can interact with Cu^{2+}, is stable in the system of hexaniobate, and can be used to control the pH of the solution.

During the synthetic processes, $PW_{12}O_{40}^{3-}$ played a crucial role in formation by combining with tetrabutylammonium and resulting in a white precipitate, $TBA_3PW_{12}O_{40}$, leaving $[HNb_6O_{19}]^{7-}$ and $[Cu(1,3\text{-pda})_2]^{2+}$ in the reacting system.

Basicity of solution is the key to successful single crystal synthesis. The Lindqvist anion $[Nb_6O_{19}]^{8-}$ is stable in alkaline solutions of pH ~ 8–14 [10], and alkaline conditions during the reaction were ensured by addition of a small quantity of NaOH, resulting in pH ~10.

3.2. *Structure description*

Single-crystal X-ray diffraction analysis revealed that the title compound consists of four subunits, $[HNb_6O_{19}]^{7-}$ polyanion, one Na^+ cation, three $[Cu(1,3\text{-pda})_2]^{2+}$ cations, and three waters of crystallization. The occupancy of all Cu's and waters is 0.5. As shown in figure 1(a), the polyanion of the title compound, $[HNb_6O_{19}]^{7-}$, adopts the well-known, superoctahedral Lindqvist structure [18] formed by six NbO_6 octahedra connected with each other through edge-sharing oxygens and exhibits approximate

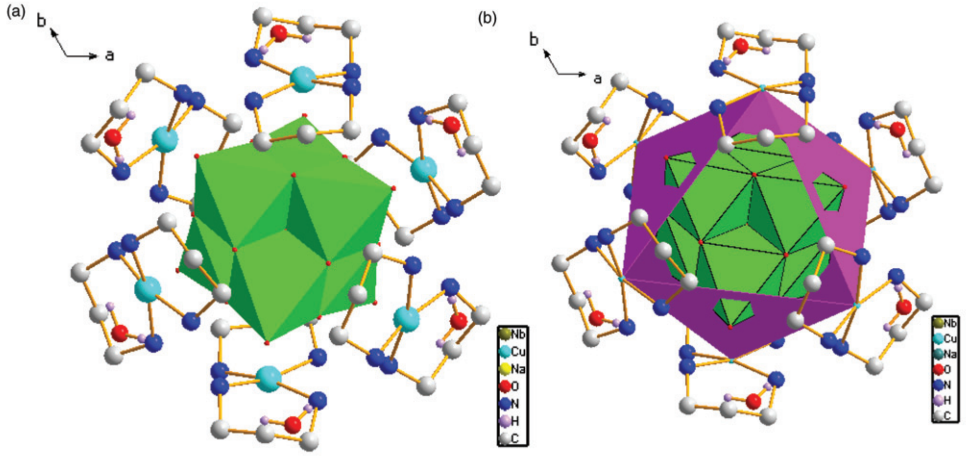

Figure 1. Ball-and-stick/polyhedral representation of the title compound. Some H atoms and Na^+ are omitted for clarity. Color code: NbO_6, green; Cu_6, pink.

Oh symmetry. In the Lindqvist cluster, the NbO_6 octahedra have a long central Nb–Oc bond of 2.3347(8) Å *trans* to a short terminal Nb–Ot bond of 1.7405(7) Å. The distances of Nb atoms to the oxygen atoms which bridge two niobium atoms range from 1.9448(1) to 1.9677(8) Å (average 1.958 Å). The angles of Nb–Oc–Nb are from 89.399(26) to 90.601(25)°. The geometric parameters are in agreement with those reported previously for related $[Nb_6O_{19}]^{8-}$ structures [11, 12, 18, 19].

Each Cu is four-coordinate, defined by four N atoms from two 1,3-diaminopropane molecules with Cu–N distances of 2.0131(120)–2.0154(112) Å. $[HNb_6O_{19}]^{7-}$ is surrounded by six $[Cu(1,3\text{-pda})_2]^{2+}$ cations interlinked to construct a big octahedron, with six external waters connected to form one octahedron. The Na^+ fills the gaps [figure 1(b)].

The central anions and cations join together through electrostatic interactions to form a 3-D architecture (figure 2). The 3-D supramolecular packing is also constructed through hydrogen bonding N–H···O, Ow–H···O, and N–H···Ow [N1–H1C···O1W: 2.421 Å; N1–H1D···O2: 2.071 Å; N2–H2C···O2: 2.134 Å; N2–H2D···O1: 2.256 Å; O1W–H1AW···O1: 2.353 Å]. The distances between the nitrogens of 1,3-diaminopropane ligands and the oxygen atoms of $[HNb_6O_{19}]^{7-}$ or aqua ligands are in the range 2.965–3.199 Å, and the distances between aqua ligands and the oxygens of $[HNb_6O_{19}]^{7-}$ are 2.353 Å. Each coordinated cation forms seven hydrogen bonds with its four 1,3-diaminopropane molecules linking two polyoxoanions and two water molecules; each anion is involved in sixteen hydrogen bonds. Obviously, such classical hydrogen bonds are responsible for stabilizing the supramolecular fabrication of the title compound. Therefore, the whole crystal is stabilized by double forces, electrostatic attraction, and hydrogen-bonding interactions (figure 3 and table 3).

3.3. *IR spectra*

The infrared spectrum of the title compound exhibits a series of characteristic vibrations of 1,3-diaminopropane ligands at 1000–1470 and 2850–3500 cm^{-1}. In addition, the title compound anion has characteristic peaks at 872, 758, 711, 669,

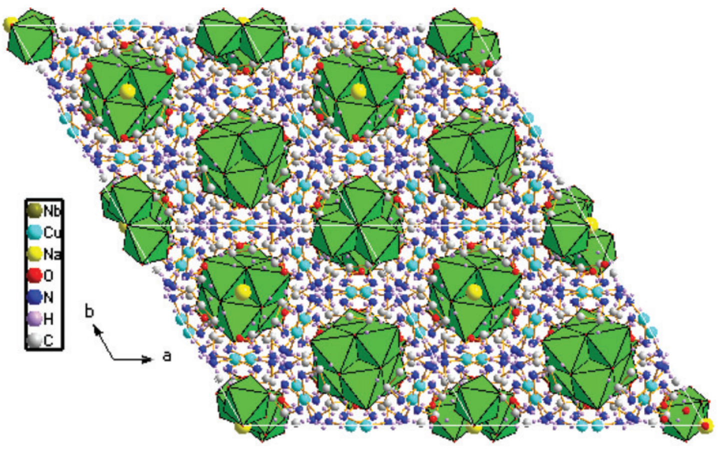

Figure 2. Molecular packing arrangement viewed down the *c*-axis.

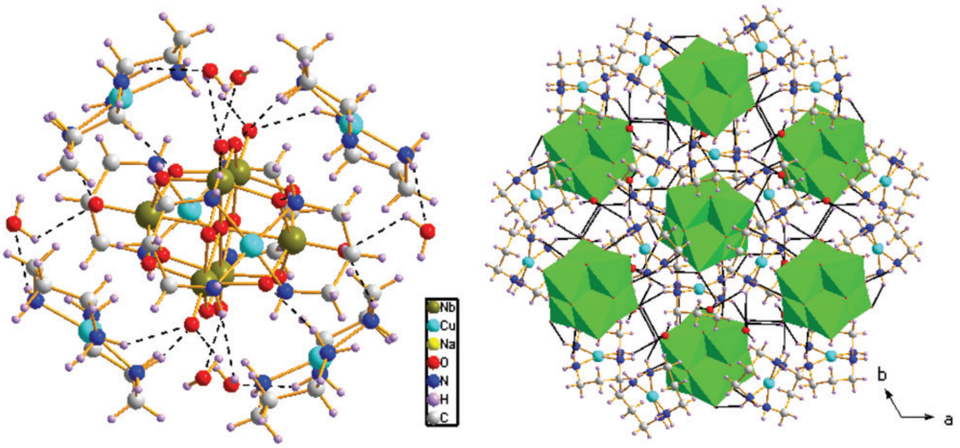

Figure 3. View of hydrogen bond in the title compound. Na^+ is omitted for clarity.

Table 3. Hydrogen bond lengths (Å) and angles (°) of the title compound.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N1–H1C···O1W	0.900	2.421	3.199	144.82
N1–H1D···O2	0.900	2.071	2.965	172.27
N2–H2C···O2	0.900	2.134	3.005	172.27
N2–H2D···O1	0.900	2.256	3.033	144.42
O1W–H1AW···O1	0.830	2.353	2.779	112.62

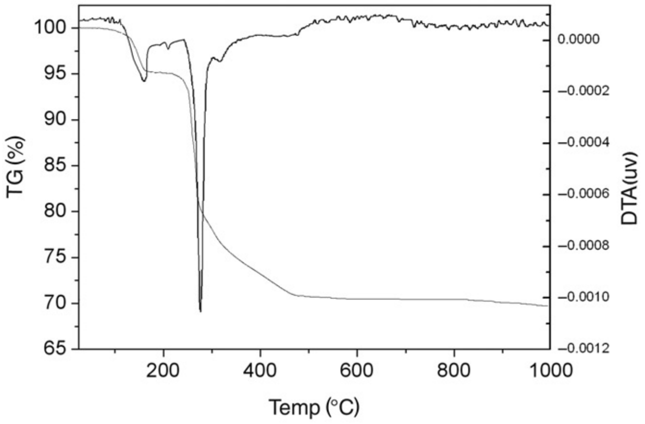

Figure 4. TG-DTA curves of the title compound.

557, 505, 427, 415 cm^{-1} attributed to $\nu_{(Nb\text{-}Ot)}$, $\nu_{(Nb\text{-}Ob)}$, and $\nu_{(Nb\text{-}Oc)}$, respectively. Comparing the IR spectra of the precursor $TBA_4[H_4Nb_6O_{19}] \cdot 7H_2O$ [17], the vibrations show slight red shifts, indicating that the $[Nb_6O_{19}]^{8-}$ is weakly effected by the counter cations.

3.4. *Thermal behavior analysis*

The thermal gravimetric (TG) curve of the title complex have two weight losses in the temperature range 25–1000°C, giving a total loss of 25.03% (Anal. Calcd 25.22%) (figure 4). The first weight loss of 3.43% in the temperature range 133–182°C corresponds to release of three water molecules, and one endothermal peak at 178°C is observed in the DTA. The second stage, which occurs from 233 to 471°C, is attributed to loss of six organic molecules; the observed weight loss (28.32%) is in agreement with the calculated value (28.21%) and there is a strong endothermal peak at 283°C in the corresponding DTA curve.

4. Conclusions

We have synthesized a polyoxoniobate by using pre-prepared $TBA_4[H_4Nb_6O_{19}] \cdot 7H_2O$ as precursor. The compound forms a supramolecular framework with hydrogen bonds and electrostatic interactions. The complex demonstrates that choice of starting materials affect the crystal growth and the structure of products.

Supplementary material

Crystallographic data for the structural analysis reported in this article have been deposited with the Cambridge Crystallographic Data Centre with the deposited CCDC number 696897. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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