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Preliminary communication

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A hexaniobate expanded by six $[Hg(cyclam)]^{2+}$ complexes via Hg–O bonds yields a positively charged polyoxoniobate cluster

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Abstract: The room temperature reaction of $Hg(NO_3)_2 \cdot H_2O$, cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) and $K_8\{Nb_6O_{19}\} \cdot 16\ H_2O$ in a mixture of H_2O and DMSO led to crystallization of the novel compound $\{[Hg(cyclam)]_6Nb_6O_{19}\}(NO_3)_4 \cdot 14\ H_2O$, which is the first mercury containing polyoxoniobate. The structure consists of a $\{Nb_6O_{19}\}^{8-}$ cluster core which is expanded by six $[Hg(cyclam)]^{2+}$ complexes via Hg–μ_2-O–Nb bond formation. The title compound contains a positively charged polyoxoniobate cluster. The crystal water molecules form small aggregates by O–H···O hydrogen bonding which are joined into larger aggregates by N–O···H–O hydrogen bonding integrating the nitrate anions.

Keywords: crystal structure; cyclam ligands; mercury; polyoxoniobates (PONbs); room temperature synthesis.

Dedicated to: Professor Dr. h.c. mult. Arndt Simon on the occasion of his 80th birthday.

1 Introduction

Polyoxometalates (POMs) of group 5 and group 6 cations are intensively investigated due to their pronounced structural variety, partially unusual properties and potential applications in several scientific and technological areas [1–11]. Polyoxoniobates (PONbs) are a sub-class of POMs featuring mainly the Lindqvist $\{Nb_6O_{19}\}$ [12–15] or Keggin clusters $\{XNb_{12}O_{40}\}$ (X = Si, Ge) [16–19]. Using $K_8\{Nb_6O_{19}\} \cdot 16\ H_2O$ and $K_7\{HNb_6O_{19}\} \cdot 13\ H_2O$ [12, 20] as precursors large PONb clusters were prepared, like, e.g. $\{Nb_{12}O_{40}\}$ [21, 22], $\{Nb_{16}O_{56}\}$ [23], $\{Nb_{18}O_{54}\}$ [19, 24], $\{Nb_{24}O_{72}\}$ [25, 26], $\{Nb_{27}O_{76}\}$ [27], $\{Nb_{31}O_{93}(CO_3)\}$ [27], $\{Nb_{32}O_{96}\}$ [26], $\{Nb_{52}O_{150}\}$ [28], $\{Nb_{114}O_{316}\}$ [28] and $\{Nb_{288}O_{768}(OH)_{48}(CO_3)_{12}\}$ [29]. In addition, the PONbs could be chemically modified as observed in $[Cu(en)_2]_2\{[Cu(bipy)][Cu(bipy)(H_2O)]Nb_6O_{19}\} \cdot 9\ H_2O$ [30] (bipy = 2,2′-bipyridine), $K_{10}[(Nb_6O_{19})Cr(H_2O)_2]_2 \cdot 28\ H_2O$ [31], $K_5[H_2AgNb_6O_{19}] \cdot 11\ H_2O$ [32], $K_5[Cu(H_2O)_2(cyclam)]_{1.5}\{[Cu\text{-}(cyclam)][Cu(H_2O)(cyclam)]_2HSiNb_{18}O_{54}\}(NO_3) \cdot 30\ H_2O$ [33], $\{[Ni(cyclam)]_4[Ti_2Nb_9O_{28}]\}_n \cdot \sim 28n\ H_2O$ [34] or $[Cu(cyclam)(H_2O)]\{[Cu(cyclam)]_2[HTiNb_9O_{28}]\} \cdot 26\ H_2O$ [35].

To further chemically modify PONb clusters, transition metal complexes offering free binding sites are attractive components offering functionalities for bond formation to oxygen atoms of the cluster anion. Hence, we hypothesized that complexes with the cyclam ligand are suitable candidates because the axial positions are either unoccupied or often contain labile ligands, that can easily be replaced by other ligands. In a preliminary study we selected $[Hg(cyclam)]^{2+}$ considering its large stability constant (log $\beta = 23.0$) [36]. Reacting $Hg(NO_3)_2 \cdot H_2O$, cyclam and $K_8\{Nb_6O_{19}\} \cdot 16\ H_2O$ in a H_2O-DMSO mixed solvent afforded crystallization of $\{[Hg(cyclam)]_6Nb_6O_{19}\}(NO_3)_4 \cdot 14\ H_2O$ which consists of a rarely encountered positively charged PONb cluster. Here we report the synthesis and crystal structure of this compound.

2 Results and discussion

The compound $\{[Hg(cyclam)]_6Nb_6O_{19}\}(NO_3)_4 \cdot 14\ H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with all atoms except one O atom located on a general position. The unique Nb^{5+} cations are surrounded by six O^{2-} anions to form NbO_6 octahedra, which share common edges yielding the well-known Lindqvist cluster anion (Fig. 1). Three

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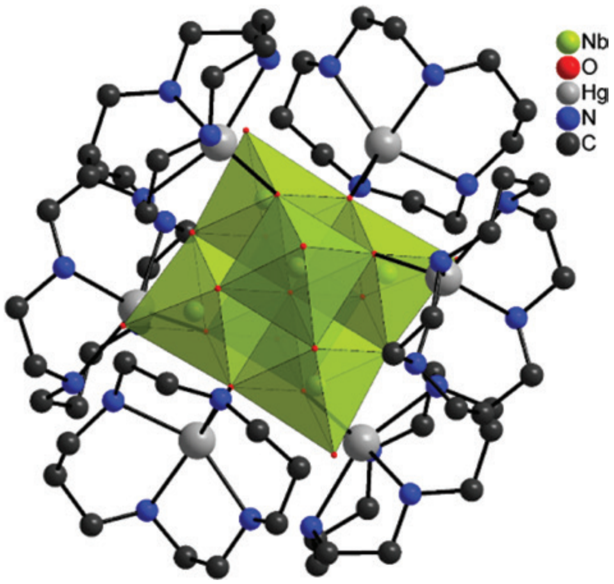


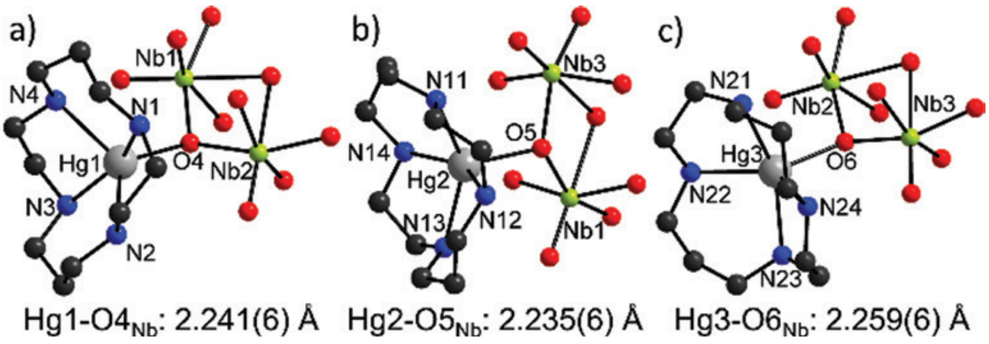
Fig. 1: View of the crystal structure of the cluster $\{[Hg(cyclam)]_6Nb_6O_{19}\}^{4+}$. H atoms are not shown for clarity.

types of Nb–O bonds can be distinguished: terminal Nb = O_t bonds between 1.755(6) and 1.779(7) Å, Nb–μ_2-O bridging bonds from 1.953(6) to 2.039(6) Å and Nb–μ_6-O bridging bonds ranging from 2.3686(8) to 2.3835(7) Å (Table S1; Supporting information available online). The bond valence sum analysis confirms an oxidation state 5+ with values between 5.01 and 5.09 (average: 5.06) for the niobium atom (Table S2). The three crystallographically independent Hg^{2+} cations are pentacoordinated by four N atoms of the cyclam ligand and one μ_2-O atom of the heptaniobate anion (Fig. 2). The resulting polyhedra are severely distorted rectangular pyramids with the Hg^{2+} cations residing above the plane formed by the four N atoms of the cyclam ligand. This distortion is not unexpected, since the optimal ionic radius to coordinate a cation in a square-planar fashion for this ligand lies between 0.65 and 0.7 Å, which is exceeded by Hg^{2+} ($r_{Hg^{2+}}$ for CN = 4: 1.10 Å) [37, 38].

The Hg–N bonds range from 2.294(8) to 2.391(9) Å with corresponding N–Hg–N *cis*-angles between 77.2(3) and 95.3(3)° and N–Hg–N *trans*-angles ranging from 126.8(3) to 155.5(3)° (Table S3) matching the values for other $[Hg(cyclam)]^{2+}$ complexes [38, 39]. The Hg–O bond lengths are between 2.235(6) and 2.259(6) Å (Table S3). The corresponding N–Hg–O angles are between 98.6(3) and 131.4(3)° (Table S3).

Using the minimal bonding ellipsoid approach [40] the calculated volumes of the polyhedra are 52.07 Å^3 (Hg1), 50.56 Å^3 (Hg2), and 50.61 Å^3 (Hg3). The shape parameter S indicating deviations from a sphere are 0.006 (Hg1), 0.078 (Hg2), and 0.027 (Hg3). According to these values all polyhedra are axially stretched, which is most pronounced for the polyhedron containing Hg2. The $\{Nb_6O_{19}\}^{8-}$ anion is expanded by the six Hg^{2+} centred complexes yielding a $\{[Hg(cyclam)]_6Nb_6O_{19}\}^{4+}$ moiety (Figs. 1 and 2). The positive charge is compensated by NO_3^- anions. The $\{[Hg(cyclam)]_6Nb_6O_{19}\}^{4+}$ molecules are arranged in a layer like fashion with the stacking sequence ··· ABAB ··· (Fig. 3, top).

The clusters are linked to the water molecules by intermolecular N–H ··· O hydrogen bonds between the amino hydrogen atoms of the cyclam ligands and the water oxygen atoms that act as acceptors (Fig. 3: bottom and Table S4). These H_2O molecules are further connected via additional water molecules to the NO_3^- anions by intermolecular N–O ··· H–O hydrogen bonding (Fig. 3: bottom). The O–H ··· O angles are close to linearity indicative for strong interactions (Table S4). For some of the water molecules not all hydrogen atoms could be located but if O ··· O distances below 3.04 Å are considered (Table S5), water clusters can be identified that



$Hg1\text{-}O4_{Nb}$: 2.241(6) Å $Hg2\text{-}O5_{Nb}$: 2.235(6) Å $Hg3\text{-}O6_{Nb}$: 2.259(6) Å

Fig. 2: Coordination environments of the niobium and mercury atoms; the Hg–O bond lengths of the peripheral complex units are given; hydrogen atoms are omitted for clarity and only selected atoms are labelled.

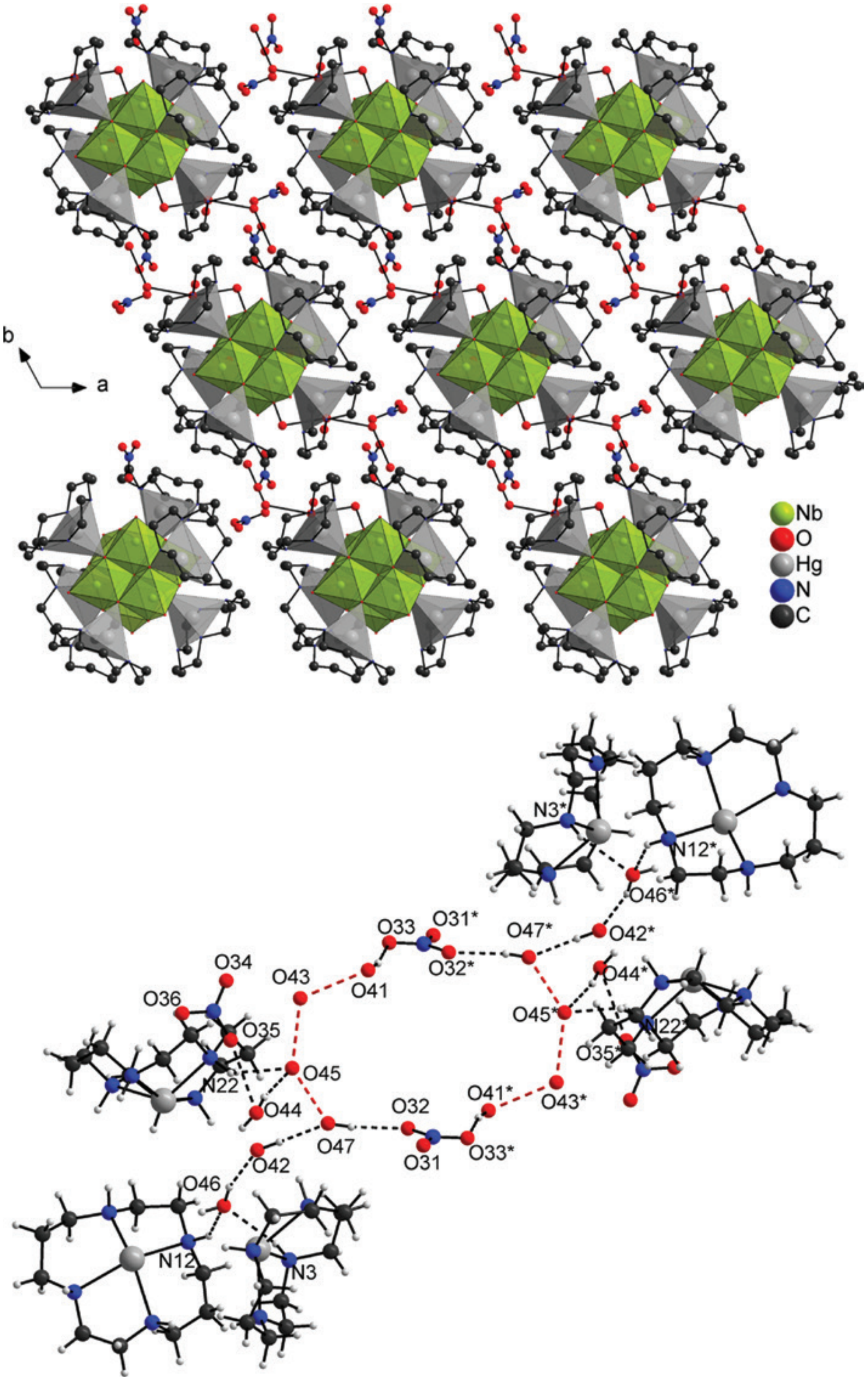


Fig. 3: Top: Crystal structure of the title compound as viewed along the crystallographic *c* axis. Bottom: Hydrogen bonding network with labelling of selected atoms. Intermolecular N–H···O and O–H···O hydrogen bonding shown as black and intermolecular O···O distances as red dashed lines. Please note that not all O–H hydrogen atoms were located. Symmetry code for the generation of equivalent atoms: * –*x*, –*y*+1, –*z*+1.

can be described as D6 according to the nomenclature given in Refs. [41–43]. There are additional intermolecular C–H···O interactions between C–H hydrogen atoms and water molecules but also intramolecular C–H···O and C–H···N hydrogen bonds within the clusters that might stabilize the structure (Table S4).

3 Experimental section

3.1 Single crystal structure determination

Data collection was performed using an IPDS-2 diffractometer from STOE & Cie using Mo*Kα* radiation. The data was corrected for absorption. The structure was solved with SHELXT [44] and refinement was carried out with SHELXL-2018 [45]. All non-hydrogen atoms were refined anisotropically. The carbon-bound H atoms were positioned with idealized geometry and were refined isotropically with $U_{iso}(H) = 1.2\ U_{eq}(C)$ using a riding model. Some of the oxygen-bound H atoms were located in difference maps, their bond lengths set to ideal values and finally refined isotropically with $U_{iso}(H) = 1.5\ U_{eq}(O)$ using a riding model. The oxygen-bound H atoms that could not be located were considered in the calculation of the formula and the molecular weight. Selected crystal data and details of the structure refinement can be found in Table S6.

CCDC 1960903 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.2 Synthesis

For the syntheses all chemicals were used as purchased without further purification ($Nb_2O_5 \cdot x\ H_2O$: H. C. Starck; $Hg(NO_3)_2 \cdot H_2O$: Fluka, >97%; cyclam: Acros organics, 98%; KOH: Grüssing, 85%; dimethylsulfoxide (DMSO): Grüssing, 99%). The precursor $K_8\{Nb_6O_{19}\} \cdot 16\ H_2O$ was synthesized by adding 13.3 g Nb_2O_5 slowly to a melt of 26 g KOH in a nickel crucible. After heating for 30 min the mixture was dissolved in 100 mL of water, filtered off and the volume of the filtrate was reduced to 50 mL. This solution was stored at 4°C and within 1 day colourless crystals of $K_8\{Nb_6O_{19}\} \cdot 16\ H_2O$ were obtained. For the preparation of the title compound, 6.1 mg cyclam and 10.3 mg $Hg(NO_3)_2 \cdot H_2O$ (0.03 mmol) were dissolved in a mixture of 0.1 mL DMSO and 1.9 mL H_2O in a 5 mL snap-cap vial. 13.7 mg $K_8\{Nb_6O_{19}\} \cdot 16\ H_2O$ (0.009 mmol) were dissolved in 1 mL H_2O and added to the first solution. After shaking the mixture the pH value was 11.1. The cap was perforated allowing slow evaporation of the solvents. After a few weeks colourless crystals were obtained in a low yield of about 6% based on Nb. The crystals were filtered, washed with EtOH and dried.

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