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## Introduction

Polyoxometalates (POMs) are anionic metal-oxo clusters that are formed by group V and VI transition metal cations. Due to their outstanding performance in *e.g.* catalysis, medicine and electrochemistry, the design of novel POMs is an important topic in current research.<sup>1</sup> Compared to polyoxoniobates (PONbs) is less developed due to the synthetic limitations and chemical inertness of niobium oxo clusters.<sup>2,3</sup> Nevertheless, several novel cluster geometries were discovered in the past decade. In the field of hetero-PONbs, Si or Ge *e.g.* could be incorporated into Keggin anion containing compounds, *e.g.* in Na<sub>16</sub>[XNb<sub>12</sub>O<sub>40</sub>]·4H<sub>2</sub>O<sup>4</sup> (X = Si, Ge), or transition metal cations like Ni and V, *e.g.* in K<sub>14</sub>Na<sub>6</sub>[H<sub>4</sub>Ni<sub>10</sub>(H<sub>2</sub>O)<sub>8</sub>Nb<sub>32</sub>O<sub>102</sub>]·73H<sub>2</sub>O<sup>5</sup> or Na<sub>18</sub>[Nb<sub>48</sub>V<sub>8</sub>(OH)<sub>30</sub>O<sub>130</sub>]·33H<sub>2</sub>O<sup>6</sup> and also lanthanide ions, *e.g.* in (CN<sub>3</sub>H<sub>6</sub>)<sub>7</sub>K<sub>3</sub>H<sub>17</sub>{Eu<sub>3</sub>(H<sub>2</sub>O)<sub>9</sub>Nb<sub>48</sub>O<sub>138</sub>(H<sub>2</sub>O)<sub>6</sub>}·40H<sub>2</sub>O.<sup>7</sup>

# On the influence of the titanium source on the composition and structure of novel titanoniobates<sup>†</sup>

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Systematic variation of the titanium source and the reaction temperature applied during hydrothermal synthesis led to crystallization of four new titanoniobates:  $\{[Ni(cyclam)]_4[Ti_2Nb_8O_{28}]\}_n \sim 28nH_2O$  (I),  $K[Ni(cyclam)]_3[TiNb_9O_{28}] \cdot xH_2O$ ; x = 18 (II), x = 14 (III) and  $x \sim 10$  (IV). These are the first titanoniobates with Ni<sup>2+</sup>-centered amine complexes acting as counter cations and additionally, this is the first report of transition metal complexes expanded by monotitanoniobates. While I is obtained using Ti(O<sup>i</sup>Pr)<sub>4</sub>, II–IV are formed using K<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)·2H<sub>2</sub>O as the educt. The presence of oxalate anions seems to influence the coordination environments of the Ni<sup>2+</sup> cations that are octahedrally coordinated in I, and in a square-planar environment in II–IV. The titanium source also affects the degree of substitution of Nb<sup>V</sup> by Ti<sup>IV</sup>. Temperature-dependent syntheses demonstrate that the formation of I does not depend on the reaction temperature, while the formation of II–IV is clearly affected by this parameter. Regarding the arrangement of crystal water molecules, patterns of different dimensionalities ranging from OD to 3D are formed which can be classified as water clusters. Each compound exhibits a pronounced plateau in the thermogravimetric curves after the removal of crystal H<sub>2</sub>O molecules. Rehydration experiments after water removal proved that except for compound III, the re-integration of water was successful.

The first examples of Ti<sup>IV</sup> integration into the PONb structure were  $A_{12}$  [Ti<sub>2</sub>O<sub>2</sub>] [XNb<sub>12</sub>O<sub>40</sub>]·*n*H<sub>2</sub>O (A = Na, K; X = Si, Ge) featuring the Keggin-type  $[XNb_{12}O_{40}]^{16-}$  anions, which are linked into chains via [Ti<sub>2</sub>O<sub>2</sub>]<sup>4+</sup> cations with Ti<sup>IV</sup> in a strongly distorted octahedral environment.8,9 These new compounds also represent the first PONb Keggin-type ions. In 2003, Nyman et al. described the synthesis of a dititanoniobate  $[Ti_2Nb_8O_{28}]^{8-}$  anion containing compound for the first time.<sup>10</sup> A hydrothermal reaction of Nb<sub>2</sub>O<sub>5</sub>·xH<sub>2</sub>O, Ti(O<sup>i</sup>Pr)<sub>4</sub>, NaOH and TMAOH·5H<sub>2</sub>O yielded Na<sub>8</sub>[Ti<sub>2</sub>Nb<sub>8</sub>O<sub>28</sub>]·34H<sub>2</sub>O. Its cluster anion exhibits the decaniobate  $[Nb_{10}O_{28}]^{6-}$  geometry, where two interior Nb<sup>V</sup> positions are substituted by Ti<sup>IV</sup> ions. Molecular modeling of the possible isomers revealed that interior cluster positions are favored for substitution, suggesting that repulsion is minimized when the number of edges shared by TiO<sub>6</sub> octahedra is as large as possible. A few years later, the "missing link" between the [Ti2Nb8O28]8- anion and [Nb<sub>10</sub>O<sub>28</sub>]<sup>6-</sup> - the monotitanoniobate anion - was reported.<sup>11</sup> The new compound (TMA)<sub>7</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·22H<sub>2</sub>O offered the opportunity for more systematic studies on the influence of substitution on the stability of the decametalate anions.

Integration of Ti into PONb cores may also lead to cluster geometries different from decametalates or Keggin geometry. Attempting to crystallize the monotitanoniobate salt, the  $[Ti_{12}Nb_6O_{44}]^{10-}$  anion was discovered. This Lindqvist type

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<sup>†</sup>Electronic supplementary information (ESI) available: Crystal structure refinement results, geometric parameters, additional figures of the structures, XRD patterns, DTA-TG curves, and IR- and UV/Vis spectra. CCDC 1854782, 1854780 and 1854781. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt02835d

"superoctahedron" consists of edge sharing  $TiO_6$  octahedra with NbO<sub>5</sub> units capping each face.<sup>12</sup> In the aspiring research on polyoxotantalates, upon Ti substitution the same cluster geometries are observed. Using a similar preparation procedure to Ti-PONbs,  $[Ti_{12}Ta_6O_{44}]^{10-}$  and  $[Ti_2Ta_8O_{28}]^{8-}$  anions were obtained.<sup>13</sup> The latter is stable in aqueous solution in contrast to the unsubstituted  $[Ta_{10}O_{28}]^{6-}$  anion, which so far is accessible only in non-aqueous solutions<sup>14</sup> and, unlike in the PONb chemistry, could not even be detected with the aid of ESI-MS in titanometalate solutions.<sup>13</sup>

Until today, only a single report about a TM (TM = transition metal)-substituted titanoniobate is available, which was synthesized by reacting  $Cu^{2+}$  ions, ethylenediamine, titanium isopropoxide  $Ti(O^{i}Pr)_{4}$  and potassium hexaniobate  $K_7HNb_6O_{19}\cdot13H_2O$  hydrothermally.<sup>15</sup> The compound  $[Cu(en)_2]$   $[Cu(en)_2(H_2O)_2]_3[Ti_2Nb_8O_{28}]\cdot8H_2O$  (en = ethylenediamine) consists of isolated  $[Ti_2Nb_8O_{28}]^{8-}$  clusters charge balanced by  $[Cu(en)(H_2O)_2]^{2+}$  and  $[Cu(en)_2]^{2+}$  molecules. This was a promising result, although the employment of other amine molecules or other TM cations did not lead to crystalline products under these reaction conditions.

Through the substitution of Nb<sup>V</sup> ions for Ti<sup>IV</sup>, the pH stability of decaniobate derivatives can be strongly affected, a phenomenon which was also observed for the titanotantalates.<sup>13</sup> As mentioned above, only the interior Nb<sup>5+</sup> cations are substituted by Ti<sup>4+</sup>. This results in the reduction of the formal charge on the  $\mu_3$ -oxo sites, which are the key for the dissociation of  $[Nb_{10}O_{28}]^{6-}$  to  $[Nb_6O_{19}]^{8-}$  in basic media.<sup>16</sup> <sup>17</sup>O NMR experiments of aqueous solutions of dititanoniobate anions proved that the integration of Ti<sup>IV</sup> leads to a stabilization of the molecule and inhibits the base-enhanced dissociation at higher pH values.<sup>17</sup> With the discovery of monotitanoniobate where only a single Nb<sup>V</sup> is substituted,<sup>11</sup> a systematic study was possible and a similar effect was observed: the dissociation of the  $\left[\text{TiNb}_9\text{O}_{28}\right]^{7-}$  anion takes place at pH  $\geq$  12,  $^{18}$  while the  $[Nb_{10}O_{28}]^{6-}$  anion starts to form  $[Nb_6O_{19}]^{8-}$  already at pH  $\geq$ 7.5.<sup>19</sup> For each ion, the  $pK_a$  values were determined, which increase with a higher substitution degree.<sup>18</sup> The experimentally determined pH-dependencies of oxygen exchange rates could be understood later by a theoretical approach.<sup>20</sup>

The chemical properties of PONbs may also be influenced *via* integration of TM complexes, but this approach still remains a challenge and as mentioned above, the examples are rare. Through their enhanced pH stability, titanoniobate clusters may be good candidates to introduce TM complexes into PONb clusters.

Herein, we present three new compounds composed of titanoniobate units,  ${[Ni(cyclam)]_4[Ti_2Nb_8O_{28}]}_n$ ··~28 $nH_2O$  (I),  $K[Ni(cyclam)]_3[TiNb_9O_{28}]$ ·18 $H_2O$  (II) and  $K[Ni(cyclam)]_3$  $[TiNb_9O_{28}]$ ·14 $H_2O$  (III) (cyclam = 1,4,8,11-tetraazacyclotetradecane). In addition to interesting structural features, *e.g.* arrangement of water molecules with different dimensionalities, these compounds and their syntheses possess several intriguing features:

(1) this is the first time that macrocyclic amine molecules and  $Ni^{2+}$  ions are incorporated into a titanoniobate network;

(2) compounds II and III are the first examples of inorganic–organic hybrids with  $[TiNb_9O_{28}]^{7-}$  anions as central structural motifs;

(3) the choice of the titanium source influences

(a) the number of  $Ti^{4+}$  ions in the cluster;

(b) the geometry of the nickel complex present in the structure and the resulting color of the products; in compound **I**, *cis*- and *trans*-configured isomers coexist;

(4) the compounds are obtained within short reaction times and the reaction temperature influences the formation of compounds II and III.

## Experimental section

#### Syntheses

All chemicals except  $K_7HNb_6O_{19}\cdot13H_2O$  were purchased and used without further purification. (Nb<sub>2</sub>O<sub>5</sub>: abcr, 99.5% Nb; KOH: abcr, 85%; Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O: Merck, >99%; 1,4,8,11-tetraazacyclotetradecane: Alfa Aesar, >98%; Ti(O<sup>i</sup>Pr)<sub>4</sub>: Merck, 98%;  $K_2TiO(C_2O_4)\cdot2H_2O$ : Sigma-Aldrich, 90%,  $K_2C_2O_4\cdotH_2O$ : Merck, 99%, NaHCO<sub>3</sub>: Gruessing, 99%.)  $K_7HNb_6O_{19}\cdot13H_2O$  was synthesized following a literature method.<sup>21</sup> Solid reactants were dispersed in 3 mL of distilled water. The pH value was adjusted with 1 M KOH. All reactions were carried out under hydrothermal conditions in DURAN® glass tubes with an inner volume of 11 mL.

### Synthesis of {[Ni(cyclam)]<sub>4</sub>[Ti<sub>2</sub>Nb<sub>8</sub>O<sub>28</sub>]}<sub>n</sub>·~28nH<sub>2</sub>O (I)

0.2 mmol K<sub>7</sub>HNb<sub>6</sub>O<sub>19</sub>·13H<sub>2</sub>O, 0.4 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.4 mmol 1,4,8,11-tetraazacyclotetradecane (cyclam) were dispersed in 3 mL H<sub>2</sub>O. 0.034 mmol (0.1 mL) Ti(O<sup>i</sup>Pr)<sub>4</sub> was added and the slurry was thoroughly mixed. Afterwards, the pH was adjusted with 0.2 mL 1 M KOH to 12.2 (after reaction: ~10.7). The mixture was reacted at 130 °C for 24 h. Light violet crystals of I (Fig. S1a<sup>†</sup>) and colourless X-ray amorphous powder were obtained. Yield: ~40 mg (~83% based on Ti).  $C_{40}H_{140}N_{16}Ni_4Nb_8Ti_2O_{50}$ : calcd in %: C 17.00, H 5.42, N 7.93; found C 16.55, H 5.01, N 7.63. TG analysis gives a hint that approx. two water molecules may be emitted during sample preparation.

#### Synthesis of K[Ni(cyclam)]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·18H<sub>2</sub>O (II)

The same method was applied as that for the synthesis of compound I, except that  $Ti(O^{i}Pr)_{4}$  was replaced by 0.034 mmol  $K_2TiO(C_2O_4)\cdot 2H_2O$ . After adding 0.2 mL 1 M KOH to the reaction mixture, the pH value was 11.3 (after reaction: ~9.5). The product crystallized as yellow block-like crystals (Fig. S1b†). Yield: 60 mg (71% based on Ti).  $C_{30}H_{108}N_{16}Ni_3Nb_9TiO_{46}$ : calcd in %: C 14.57, H 4.40, N 6.80; found C 14.67, H 4.40, N 6.87.

#### Synthesis of K[Ni(cyclam)]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·14H<sub>2</sub>O (III)

A few single crystals of compound **III** were found in a batch of **II**. The product crystallized as yellow block-like crystals (Fig. S1c†). Yield: <1 mg (~1% based on Ti) under given reac-

tion conditions (see Results)  $C_{30}H_{100}N_{16}Ni_3Nb_9TiO_{42}$ : calcd in %: C 15.01, H 4.20, N 7.00; found C 15.10, H 4.30, N 7.17.

We note that all compounds are stable in air for several weeks.

#### Structure determination

Data collection was performed using a STOE Imaging Plate Diffraction System (IPDS-2) with MoK $\alpha$  ( $\lambda$  = 0.71073 Å) and for all compounds, a numerical absorption correction was performed. The structures were solved with the program SHELXS-97<sup>22</sup> and refined was performed against  $F^2$  using SHELXL-2014.<sup>23</sup> The details of data collection and of the structure refinements are summarized in Table S1.<sup>†</sup>

All non-hydrogen atoms were refined anisotropically. The C-H and N-H H atoms were positioned with idealized geometry and refined isotropically with  $U_{iso}(H) = 1.2U_{eq}(C,N)$  using a riding model. The O-H H atoms were not located but considered in the calculation of the molecular formula and the molecular weight. In compound I, there is additional electron density indicating for disordered water molecules, for which no reasonable structure model was found. Therefore, the data were corrected for the disordered solvent using the Squeeze option in Platon.<sup>24</sup> During the SQUEEZE procedure, 140 electrons were collected. The accessible free space was calculated to be 360.5  $\text{\AA}^3$  (7.6% of unit cell volume). One of the two cyclam ligands is disordered and was refined using a split model. In compound II, the Ti atom is located on the same position as Nb5 and both atoms were refined with an occupancy of 0.5. The position of the K<sup>+</sup> cation is only half occupied and the other half was assigned to disordered water. In this case the model agrees with elemental analysis and if the K<sup>+</sup> cation is refined with full occupancy much too large displacement parameters are obtained. The low reliability factors originate from a poor crystal quality and contributions of at least a second much smaller individual. This kind of twinning cannot be resolved. In compound III, Nb9/Ti9 and Nb10/Ti10 occupy the same crystallographic positions and were refined with occupancies of 0.75/0.25 as well as 0.25/0.75 using restraints (EXYZ and EADP). The K<sup>+</sup> cation is also disordered and was refined using a split model.

Several water O atoms were found in the structure of **III**; two positions are not fully occupied with s.o.f. = 0.4, two O atoms have an occupancy of 0.6 and two further O atoms 0.5. Ten positions of O atoms are fully occupied and one O atom (O47) is disordered with a ratio of 50:50, giving rise to about fourteen water molecules per formula unit.

CCDC 1854782 (I), CCDC 1854780 (II), and CCDC 1854781 (III) contain the supplementary crystallographic data for this paper.†

#### X-ray powder diffraction

Phase purity of the compounds was checked with X-ray powder diffraction patterns that were measured with Cu-K $\alpha_1$  radiation on a STOE Stadi-P diffractometer (Ge monochromator) with a Mythen 1 K detector (Fig. S2†).

#### Infrared spectroscopy

Infrared spectra were recorded on a Bruker Alpha-P IR spectrometer from 4000–400 cm<sup>-1</sup> at room temperature.

#### Ultraviolet-visible spectroscopy

A UV/Vis two-channel spectrometer Cary 5 from Varian Techtron Pty was used to collect the UV/Vis reflection data using  $BaSO_4$  as a white standard. The data were calculated with the Kubelka–Munk relation for diffuse reflectance data.<sup>25</sup>

#### **Elemental analysis**

Elemental analyses were performed on a EURO EA elemental analyzer (EURO VEKTOR).

#### Difference thermogravimetry (TG)

A Netzsch STA 409 CD was used to obtain the TG curves under  $N_2$  flow with a heating rate of 4 K min<sup>-1</sup>.

## Results and discussion

#### Synthetic aspects

Recently, we used cyclam as a tetradentate ligand for the synthesis of TM-substituted PONbs, resulting in two novel compounds with [Cu(cyclam)]<sup>2+</sup> complexes as charge balancing agents.<sup>26</sup> Both compounds could be obtained in a short reaction time. Since the targeted integration of heteroatoms in the Cu<sup>2+</sup>/cyclam/Nb<sup>5+</sup> system was not yet successful, we replaced Cu<sup>2+</sup> by Ni<sup>2+</sup> ions as the TM source. Under similar reaction conditions to Cu-PONbs, we were able to prepare four novel titanoniobates {[Ni(cyclam)]<sub>4</sub>[Ti<sub>2</sub>Nb<sub>8</sub>O<sub>28</sub>]}<sub>n</sub>·~28nH<sub>2</sub>O (I), K[Ni-(cyclam)]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·xH<sub>2</sub>O with x = 18 for II, x = 14 for III and  $x \approx 10$  for IV. The first experiments were carried out with Ti-(O<sup>i</sup>Pr)<sub>4</sub>, which undergoes a hydrolysis in aqueous solution, forming <sup>i</sup>PrOH and titanium-oxo/hydroxo species.<sup>27</sup> On heating the reaction mixture solvothermally at 130 °C for 24 h, I was obtained from the orange-brown colored mother liquor as violet block shaped crystals (Fig. S1a<sup>†</sup>). Employing K<sub>2</sub>TiO-(C<sub>2</sub>O<sub>4</sub>)·2H<sub>2</sub>O and leaving all other reaction parameters constant, compound II was isolated as block-shaped yellow crystals (Scheme 1, Fig. S1b<sup>†</sup>).

When the red-violet colored mother liquor was evaporated, crystals of *cis*-[Ni<sub>2</sub>(cyclam)<sub>2</sub>(ox)](NO<sub>3</sub>)<sub>2</sub><sup>28</sup> were obtained. In a batch of **II**, a very small amount of **III** was found as yellow platelet-like crystals (Fig. S1c†). In order to improve the yield for further characterization, temperature dependent syntheses from 80 to 180 °C were performed, and fortunately, the yield of



Scheme 1 Synthesis scheme for the preparation of the title compounds.



Scheme 2 Influence of the reaction temperature on the formation of compounds II–IV.

**III** could be increased to ~35 mg (~43%) at reaction temperatures of 110 °C and lower. During the temperature dependent investigations (Scheme 2), another type of yellow crystals (**IV**) was obtained as very thin yellow platelets (Fig. S1d†), which were not appropriate for single crystal structure analysis. All attempts to improve the crystal quality failed. The material was fully characterized and all analytical data indicate that **IV** is a pseudo-polymorph of the compounds **II** and **III** with the general formulae K[Ni(cyclam)]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·*x*H<sub>2</sub>O with  $x \approx 10$ for compound **IV**.<sup>‡</sup>

We want to note that compound I can also be isolated under stirring 'dynamic' conditions in comparable yields. Dynamic conditions also lead to formation of II, which crystallizes from the mother liquor, while IV can be recovered from the same reaction mixture directly by filtration. This demonstrates that dynamic conditions are beneficial not only for the efficient synthesis of iso- but also of heteropolyoxoniobates. Interestingly, the formation of III could not be observed on applying stirring conditions.

It is not yet clear why the formation of the dititanoniobate is favored when  $Ti(O^{i}Pr)_{4}$  is employed and the monotitanoniobate is dominating when  $K_{2}TiO(C_{2}O_{4})\cdot 2H_{2}O$  is applied. But it is not surprising that the formation depends on the change of a single reaction parameter, since in aqueous solutions of the  $[TiNb_{9}O_{28}]^{7-}$  anion the  $[Ti_{2}Nb_{8}O_{28}]^{8-}$  cluster is present as a byproduct.<sup>11</sup>

On reacting  $Ti(O^iPr)_4$  and  $K_2TiO(C_2O_4)\cdot 2H_2O$  simultaneously in equimolar proportion, solely the  $[TiNb_9O_{28}]^{7-}$  containing compounds **II** and **IV** were obtained. The formation of the *cis*-[Ni<sub>2</sub>(cyclam)<sub>2</sub>(ox)](NO<sub>3</sub>)<sub>2</sub> complex, which crystallizes as a by-product might influence different coordination environments of the Ni<sup>II</sup> ion in compound **I** compared to compounds **II–IV**.

Carrying out the experiments using  $Ti(O^iPr)_4$  as a source and NaHCO<sub>3</sub> as an additive (pH = 11.1), only compound **IV** crystallized.

To investigate whether the formation of the dititanoniobate (I) or the monotitanoniobate anions (II–IV) predominantly depend on the pH value, the syntheses were conducted at pH

values ranging from 9 to 13. Applying  $K_2 TiO(C_2O_4) \cdot 2H_2O$  as the titanium source, only X-ray amorphous powders were obtained for pH = 12–13, while between 9 and 11 only the compounds with the monotitanoniobate anion are obtained. Using  $Ti(O^iPr)_4$  as the reactant, at higher pH values the dititanoniobate compound I exclusively crystallized, whereas at lower pH values phase mixtures of the mono- and dititanoniobate compounds I and II are formed. From these results it is obvious that the formation of the mono- and dititanoniobate anions do not only depend on the actual pH value but also on the titanium source. Here we want to note that solvothermal reactions are complex and that changing one parameter inevitably leads to the alteration of all other parameters.

Since the presence of  $C_2O_4^{2-}$  seems to influence the number of Ti<sup>4+</sup> cations in the cluster, it is possible that these anions interact with niobate fragments. In the  $[VNb_{12}O_{40}\{NbO(CO_3)\}_2]^{13-}$  and  $[H_{10}Nb_{31}O_{33}(CO_3)]^{23-}$  anions, the carbonate ligands are coordinated to  $Nb^{5+}$  via two  $O^{2-}$  anions and the sevenfold coordination is completed by five  $O^{2-}$  anions of the PONb anion in the solid state.<sup>29</sup> Therefore, it is imaginable that such intermediates are present, leading to a preferred crystallization of one product with a distinct composition.

Further investigations on the influence of  $C_2O_4^{2-}$  and other additives onto the formation of titanoniobates are underway.

#### **Crystal structures**

Crystal structure of { $[Ni(cyclam)]_4[Ti_2Nb_8O_{28}]_h \sim 28nH_2O$  (I). The compound { $[Ni(cyclam)]_4[Ti_2Nb_8O_{28}]_h \sim 28nH_2O$  (I) crystallizes in the monoclinic space group C2/m with Z = 2. Ti1, O2, O8, Ni2, N11, N13, and four water O atoms lie on a crystallographic mirror plane. Two water O atoms (O7, O17) are located on the twofold rotational axis and the second crystallographically independent Ni<sup>2+</sup> (Ni2) ion on a center of inversion. The main structural motif consists of a titanoniobate cluster anion, which is decorated by Ni<sup>2+</sup> centered complexes (Fig. 1).



**Fig. 1** Representation of the main structural motif in the structure of I. Only selected atoms are labeled. H atoms are omitted for clarity. Only one orientation of the disordered cyclam ligand is shown.

 $<sup>\</sup>ddagger$  Analytical data; optical micrographs (Fig. S1†), XRD patterns (Fig. S2†), IR (Fig. S17†), UV/Vis (Fig. S21†) spectra and DTA-TG curves (Fig. S25†) can be found in the ESI.†

#### **Dalton Transactions**

The anionic unit displays the Nyman-type cluster geometry  $\left[Ti_2Nb_8O_{28}\right]^{8-}$  with  $Nb^{5+}$  and  $Ti^{4+}$  cations octahedrally coordinated by oxygen.<sup>10</sup> In analogy to the known decaniobate geometry,<sup>30–33</sup> three octahedra are connected *via* edge-sharing and these are attached to another trimer by sharing the edges, forming a  $2 \times 3$  rectangle. The rectangle is capped by two edgesharing octahedra at the top and the bottom, respectively. The results of bond valence sum (BVS) analysis are in line with oxidation states +5 for Nb, +4 for Ti, and +2 for Ni (Table S2<sup>†</sup>). The Nb= $O_t$  (t = terminal), Nb- $\mu_2$ -O, Nb- $\mu_3$ -O and Nb- $\mu_6$ -O bonds (Table S3<sup>†</sup>) are in the range of 1.752(2)-1.768(2) Å, 1.924 (2)-2.0213(19) Å, 2.0787(17)-2.0852(17) Å and 2.3829(3)-2.4305 (19) Å, respectively, a bond length distribution that is known for other decaniobate compounds.<sup>30–33</sup> As expected, the  $TiO_6$ octahedron has no terminal Ti=O bonds. Like in Ti-PONbs, Ti-POWs and Ti-POMos, terminal Ti=O bonds were not observed, and Ti<sup>4+</sup> always prefers bonds to bridging O<sup>2-</sup> anions, favouring positions with lower distortion.<sup>10</sup> This is in agreement with the structures of lavered Ti<sup>IV</sup>/Nb<sup>V</sup> perovskite materials where Ti<sup>4+</sup> octahedra are located in the interior slab sites.<sup>34–37</sup> The Ti- $\mu_2$ -O, Ti- $\mu_3$ -O and Ti- $\mu_6$ -O bond lengths are 1.812(2), 1.962(3)-1.983(3) and 2.1889(17) Å, respectively and show the general trend of increasing bond lengths with an increasing number of bridging oxygen atoms.<sup>10</sup> The O-Ti-O angles (Table S4<sup>†</sup>) demonstrate a severe deviation from ideal geometry (O-Ti-O: 80.93-167.86°). Compared to the two literature known [Ti<sub>2</sub>Nb<sub>8</sub>O<sub>28</sub>]<sup>8-</sup> containing compounds  $(Na_8[Ti_2Nb_8O_{28}]\cdot 34H_2O^{10})$ and  $[Cu(en)_2][Cu(en)_2(H_2O)_2]_3$ [Ti<sub>2</sub>Nb<sub>8</sub>O<sub>28</sub>]·8H<sub>2</sub>O<sup>15</sup>) there are some slight differences in certain bond lengths as displayed in Fig. S3<sup>†</sup> and summarized in Table S5.† These differences are most probably caused by the multiple coordinations of the [Ni(cyclam)]<sup>2+</sup> units. The M- $\mu_3$ -O (M = Ti/Nb) and the Nb- $\mu_6$ -O bond lengths are slightly shorter and the Ti- $\mu_6$ -O distances are longer than reported for the two other compounds.

The O–Nb–O angles are 75.75–178.15° for Nb1 and 74.87–171.08° for Nb2 (Table S4†), demonstrating a stronger distortion of the NbO<sub>6</sub> octahedra which share more edges with neighboring units. Charge compensation in compound I is achieved through four Ni<sup>2+</sup> centered amine complexes per formula unit. The octahedral coordination sphere of the two unique Ni<sup>2+</sup> ions is formed by the four N atoms of one cyclam molecule and two terminal O<sup>2–</sup> anions of the  $[Ti_2Nb_8O_{28}]^{8-}$  cluster.

Each  $[Ti_2Nb_8O_{28}]^{8-}$  unit is decorated by two  $[Ni(cyclam)]^{2+}$ molecules *via* two terminal cluster O atoms in the *cis*-position. The cyclam molecule is disordered over two positions in ratio 50:50 (Fig. 2a). The Ni–N and the Ni–O bond lengths are 2.058(7)–2.138(6) Å and 2.111(2) Å, respectively (Table S6†). The corresponding values for equatorial N–Ni–N/O angles are 83.7(2)–99.3(2)° and for the *trans* N–Ni–N/O angles are 168.8 (2)–174.8(2)°, reflecting a significant distortion of the octahedral geometry. Besides the Ni(2)–N(12/13) bond lengths which are shorter (2.058(7)–2.080(5) Å) than most of the reported values but not unprecedented in complexes,<sup>28,38–41</sup> all geometrical parameters are in good agreement with those in



**Fig. 2** Coordination spheres around the two crystallographically independent Ni<sup>2+</sup> ions in the structure of I. The disorder of the cyclam ligand coordinated to Ni2 is indicated by orange and green lines (left).

 
 Table 1
 Comparison of the geometrical parameters of the two crystallographically independent [Ni(cyclam)]<sup>2+</sup> complexes in the structure of I

Type of bond /angle	<i>trans</i> -[Ni(cyclam)] <sup>2+</sup>	cis-[Ni(cyclam)] <sup>2+</sup>
Ni−N/Å	2.062(3)-2.073(3)	2.058(7)-2.138(6)
Ni−O/Å	2.087(2) Å	2.111(2)
2q. N−Ni−N/O/°	85.81(12)-94.19(12)°	83.7(2)-99.3(2)°
<i>rans</i> N−Ni−N/O/°	180.00°	168.8(2)-174.8(2)°

similar complexes with *cis*-configured cyclam molecules, *e.g.*  $[Ni_2(C_2O_4)(cyclam)_2](ClO_4)_2$ .<sup>39</sup> The anionic cluster is further expanded by four *trans*- $[Ni(cyclam)]^{2+}$  cations, where the O atoms of two neighboring clusters occupy the vertices of Ni<sup>2+</sup> centered octahedra with cyclam N-donors in axial positions (Fig. 2b). The Ni–N and the Ni–O distances (Table 1) match well with the literature data.<sup>42–44</sup> The equatorial N–Ni–N/O angles scatter between 85.81(12)–94.19(12)° and the *trans* N–Ni–N/O angles are 180.00°, being closer to ideal octahedral geometry compared to the complex discussed above.

It is unusual that the disordered cyclam molecule coordinated to Ni2 adopts *cis*-configuration, while the cyclam molecule surrounding Ni1 exhibits a *trans*-configuration, which is the most common configuration for metal cation centered cyclam complexes.<sup>45</sup> The coexistence of *cis*- and *trans*isomers in the solid state is rare and was reported only for  $[Ni_2(cyclam)_2(\mu_3-C_2O_4)]\cdot(ClO_4)_2\cdot H_2O.^{40}$ 

Overall, each  $[Ti_2Nb_8O_{28}]^{8-}$  unit is connected to four *trans*- $[Ni(cyclam)]^{2+}$  and two *cis*- $[Ni(cyclam)]^{2+}$  cations and may be viewed as a hexadentate ligand for the complexes. The *trans*- $[Ni(cyclam)]^{2+}$  moieties connect the anionic clusters in the *ab* plane into layers (Fig. S4†). The layers are separated by the *cis*- $[Ni(cyclam)]^{2+}$  complexes, which are arranged in a wave-like manner (Fig. 3).

H-bonding interactions are observed, which may explain some structural peculiarities (Table S7†). The Nb(2)–O(9)–Ni(2) angle is 134.04(12)° and significantly differs from the ideal value of 180°. This can be explained with the presence of H-bonds between the N–H and C–H atoms of the cyclam molecule and Nb- $\mu_2$ -O bridging atoms (N–H···O = 2.953(5) Å; < (NHO) = 146.3°; C–H···O = 3.391(17) Å; <(CHO) = 163.8°) which lead to a tilting of the *cis*-[Ni(cyclam)]<sup>2+</sup> complex relative to the anion (Fig. S5a†). Furthermore, a crystal H<sub>2</sub>O molecule located near the amine molecule is also involved in H-bonding with



**Fig. 3** View of the layers in the structure of I along [100]. H and water O atoms are omitted for clarity. Only one orientation of the disordered cyclam ligand is shown. Green polyhedra: NbO<sub>6</sub>, violet polyhedra: TiO<sub>6</sub>.

the N–H H atoms, additionally stabilizing the folded geometry of the cyclam ligand (Fig. S5b†), (N–H···O = 3.114(7)–3.122(7)Å; <(NHO) = 161.3– $167.3^{\circ}$ ). The tilting in the second unique *trans*-[Ni(cyclam)]<sup>2+</sup> cation is less pronounced (Nb(1)–O(1)–Ni (1):  $166.26(13)^{\circ}$ ) and only C–H groups are involved in H-bonding (Fig. S5c†), (C–H···O = 3.160(4) Å–3.553(4) Å; <(CHO) = 112.5– $169.0^{\circ}$ ). One N–H H atom of the *trans*-configured cyclam molecule interacts with a crystal water molecule (N–H···O = 3.147(4) Å; <(NHO) =  $155.6^{\circ}$ ).

Single crystal structure analysis revealed that there are 22 water molecules per formula unit in the structure of I. The water H atoms could not be located, but the water O atoms (O···O-distances up to the sum of the van der Waals radii: 3.05 Å, Table S8<sup>†</sup>) show an unusual arrangement. Following the notation of Infantes *et al.*,<sup>46,47</sup> the  $H_2O$  molecules form a L4(2)4(4)28(14) wallpaper-like layer-type water cluster, *i.e.* there are four-membered rings which share water molecules with two adjacent rings, a second type of four-membered ring surrounded by four other rings and 28-membered rings enclosed with 14 rings (Fig. 4). Bucket-like 4-membered fragments decorate the 4(4) rings (Fig. S6<sup>†</sup>). In the 28-membered rings, the [Ti<sub>2</sub>Nb<sub>8</sub>O<sub>28</sub>]<sup>8-</sup> anions are located, whereas the *cis*-[Ni  $(cyclam)^{2+}$  molecules are located in the plane formed by the rings (Fig. S7a<sup>†</sup>), and the *trans*-[Ni(cyclam)]<sup>2+</sup> molecules are found below and above these planes (Fig. S7b<sup>†</sup>).

Crystal structures of K[Ni(cyclam)]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·18H<sub>2</sub>O (II) and K[Ni(cyclam)]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·14H<sub>2</sub>O (III). K[Ni(cyclam)]<sub>3</sub> [TiNb<sub>9</sub>O<sub>28</sub>]·18H<sub>2</sub>O (II) crystallizes in the monoclinic space group *C*2/*c* with four formula units in the unit cell. All atoms except the central Ti/Nb cations, the K<sup>+</sup> cation and a H<sub>2</sub>O molecule are located at general positions. In the decaniobate cluster one Nb<sup>5+</sup> cation is replaced by a Ti<sup>4+</sup> ion (Fig. 5).

Similar to compound I and other titanoniobates, the Ti<sup>4+</sup> cation is located on an interior position of the anion, and in II these positions are occupied with 50% Ti and 50% Nb. For Nb and Ni, BVS provides oxidation states of +5 and +2, respectively. To calculate the BVS for Ti and Nb on the sites with mixed occupancy, the  $R_0$  values were weighted according to the



**Fig. 4** Arrangement of the crystal water molecules building a L4(2)4(4) 28(14) type cluster in the structure of I (top, H-bonds dashed lines), and location of the anions (bottom). C, N and H atoms are not displayed for clarity. Green:  $NbO_{6}$ , violet:  $TiO_{6}$ .



Fig. 5 View of the anionic cluster in the structure of compound II.

occupation factor leading to 4.52 (Table S2<sup>†</sup>), in accordance with the average oxidation state for Ti<sup>IV</sup> and Nb<sup>V</sup> on the interior position. The Nb-O bond lengths in the  $[TiNb_9O_{28}]^{7-}$ anion are 1.741(6)-1.763(4) Å for Nb=Ot, 1.905(4)-2.068(4) Å for Nb-µ2-O, 2.098(4)-2.116(4) Å for Nb-µ3-O and 2.390(4)-2.496(4) Å for Nb- $\mu_6$ -O (Table S9<sup>†</sup>) and agree with the data for decaniobates.<sup>31</sup> The Ti-/Nb-O bonds with values of 1.815(4)-1.827(4) Å for  $\mu_2$ - and 1.992(4)–1.999(4) Å for  $\mu_3$ -O atoms differ only slightly from other  $[TiNb_9O_{28}]^{7-}$  cluster containing compounds (Table S10<sup>†</sup>)<sup>11</sup> with Ti/Nb- $\mu_6$ -O bonds with 2.191(4)-2.208(4) Å matching the reported data. The O-Nb-O angles are comparable to that observed for I. The negative charge of  $[TiNb_9O_{28}]^{7-}$  is compensated through three  $[Ni(cyclam)]^{2+}$ complexes and a K<sup>+</sup> cation. In contrast to compound I, the two crystallographically independent Ni2+ ions are in a squareplanar coordination of four N atoms of the cyclam molecule (Fig. S8<sup> $\dagger$ </sup>). The nearest possible axial ligands are cluster O<sup>2-</sup> anions at 3.534(4) and 3.669(4) Å, which are too far away for bonding interactions. The Ni-N bonds (1.923(6)-1.941(6) Å) are significantly shorter than those in I, but are in agreement with the data reported for low-spin Ni<sup>II</sup> amine complexes.<sup>38,41,48-51</sup> The angles around Ni<sup>2+</sup> (Table S11†) are typical of square-planar [Ni(cyclam)]<sup>2+</sup> moieties.<sup>38,41,48,50-52</sup>

Each  $[TiNb_9O_{28}]^{7-}$  anion is surrounded by six  $[Ni(cyclam)]^{2+}$  molecules (Fig. S9†), yielding a layer-like arrangement (Fig. 6).

The K<sup>+</sup> cation is surrounded by five H<sub>2</sub>O molecules and two terminal O atoms of the anion, leading to the coordination number (CN) 7 (Fig. S10a<sup>†</sup>). The K–O distances scatter from 2.734(12) to 3.054(8) Å (Table S12,<sup>†</sup> average: 2.874 Å), and are partially longer than expected (2.81–2.84 Å,<sup>53</sup> depending on CN) but they are not unusual.<sup>54</sup> The KO<sub>7</sub> polyhedra share no atoms with each other and are arranged in a wave-like fashion along [010] (Fig. 7, Fig. S11<sup>†</sup>).

The C–H and N–H H atoms of the cyclam ligands are involved in intermolecular H bonding interactions with cluster O atoms (Table S13, Fig. S12†). (N–H···O = 2.828(7) Å–3.238(8)Å; C–H···O = 3.194(9)–3.574(9) Å; <(NHO) = 143.1– $170.4^{\circ}$ ; < (CHO) = 131.2– $165.0^{\circ}$ ). Furthermore, H<sub>2</sub>O also exhibits hydro-



Fig. 6 Arrangement of the  $[TiNb_9O_{28}]^{7-}$  anions and  $[Ni(cyclam)]^{2+}$  cations in the structure of compound II. Green polyhedra: NbO<sub>6</sub>, violet polyhedra: TiO<sub>6</sub>.



**Fig. 7** Arrangement of the KO<sub>7</sub> polyhedra (blue) and  $[TiNb_9O_{28}]^{7-}$  anions in the structure of II. The [Ni(cyclam)]<sup>2+</sup> cations and water O atoms which are not involved in K–O interactions are omitted. Green: NbO<sub>6</sub>, violet: Ti/NbO<sub>6</sub>, blue: KO<sub>7</sub> polyhedra.

gen bonding interactions with ligand C–H H atoms (C–H···O = 3.23(1) Å–3.595(9) Å; <(CHO) =  $122.7-163.1^{\circ}$ ).

The water O atoms in the structure of **II** form a layered cluster and considering only fully occupied water O atom positions, a L5(4)L30(18) type cluster along [010] can be identified (Fig. S13a†). Eight fragments consisting of two O atoms decorate each 30-membered ring. The layers are connected along the *b* axis *via* two H<sub>2</sub>O molecules (Fig. 13b†), forming a 3-dimensional network (Fig. S14†).

Because II and III are pseudopolymorphs, mainly the structural differences of K[Ni(cyclam]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·18H<sub>2</sub>O (III) compared to II are discussed. Compound III crystallizes in the triclinic space group  $P\bar{1}$  with two formula units in the unit cell. All atoms except Ni3 and Ni4 are located at general positions. In analogy to **II**, the Ti<sup>4+</sup> and Nb<sup>5+</sup> ions in the interior position of the [TiNb<sub>9</sub>O<sub>28</sub>]<sup>7-</sup> anion are disordered over the same crystallographic position, but with a different site occupancy of 25% (Ti9/Nb10)/75%(Nb9/Ti10). The K<sup>+</sup> cation is disordered over two positions with a 60:40 occupancy. Each of the K<sup>+</sup> cations is in a different coordination environment of H2O and cluster- $\mu_2$ -O atoms. Using a cut-off at 3.2 Å for K–O interactions, K<sup>+</sup> (60% occupancy) is surrounded by six H<sub>2</sub>O molecules and two O<sup>2-</sup> anions and two symmetry related face-sharing KO<sub>8</sub> polyhedra are linked with two  $[TiNb_9O_{28}]^{7-}$  anions (Fig. 8, top). The second  $K^+$  cation (s.o.f. = 0.4) is coordinated by six H<sub>2</sub>O molecules, building distorted edge-sharing octahedra (Fig. 8, bottom). Geometric parameters for the  $KO_x$  (x = 8, 6), for the [Ni(cyclam)]<sup>2+</sup> cations and the hydrogen bonding interactions are listed in Tables S12 and S14.<sup>†</sup>

Considering only fully occupied water O atoms (O–O distances: 2.698–3.038 Å (Table S8,† average: 2.791 Å), hexameric isolated R6 water clusters are found. Taking into account cluster O atoms being involved in H bonds, an extended water motif is formed (Fig. 9). Two adjacent cluster anions are linked *via* two water molecules along the *c* axis, which interact with terminal cluster O atoms building a four-membered ring. A second arrangement of H<sub>2</sub>O molecules and cluster O atoms connect the anions along the *a* axis, which may be denoted as



**Fig. 8** Different coordination environments of the disordered  $K^+$  cation in the structure of **III**; s.o.f = 0.6 (top), 0.4 (bottom) and the arrangement of the resulting K–O polyhedra (blue).



**Fig. 9** View on the extended water motif along [010] in the structure of III. O–O distances below the sum of the van der Waals radii shown in dashed lines. For clarity, the  $[Ni(cyclam)]^{2+}$  and  $K^+$  cations are not shown. Grey polyhedra: Ti/NbO<sub>6</sub>.

R6(2), *i.e.* there are five hexameric rings which share two O atoms with adjacent rings (Fig. S15<sup>†</sup>) and are attached to the clusters *via* a  $H_2O$  molecule.

#### Spectroscopic investigations

In the IR spectrum of each compound (Fig. S16–19†), characteristic absorptions of the organic ligands are observed between 3250 and 1000 cm<sup>-1</sup> (Table S15†). The O–H stretching vibrations of the crystal water molecules appear as very broad bands in the characteristic region at 3600–3300 cm<sup>-1</sup>.<sup>55</sup> Below 1000 cm<sup>-1</sup>, a definite assignment of the signals is difficult because the N–H and macrocyclic deformation vibrations occur in the same region as that of the Nb–O vibrations. The Nb–O<sub>t</sub> absorptions are found at 965, 885 and 857 cm<sup>-1</sup> for I, 880 and 864 cm<sup>-1</sup> for II and 876 and 857 cm<sup>-1</sup> for III. The bands below 800 cm<sup>-1</sup> are most probably caused by bridging  $M-O_b-M$  (M = Ti, Nb) vibrations.

In the UV/Vis spectrum of compound I, the characteristic transitions of high-spin octahedral  $Ni^{2+}$  complexes are observed (Fig. S20†). The bands at 354, 554 and 889 nm can be

assigned to the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}({}^{3}P)$ ,  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}({}^{3}F)$  and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$  d-d transitions, respectively.<sup>28,56,57</sup> The signal at 308 nm is most probably the O  $\rightarrow$  Nb CT transition, which is typically observed between 200 and 300 nm.<sup>7,58-61</sup> But this band is missing in the absorption spectra of compounds II and III and in the UV/Vis spectrum of the copper ethylenediamine salt of the  $[Ti_2Nb_8O_{28}]^{8-}$  anion.<sup>15</sup> Therefore, we assume that the band arises from splitting of the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}({}^{3}P)$  d-d transition due to the different coordination geometries of the  $[Ni(cyclam)]^{2+}$  complexes.

In the UV/Vis spectra of **II–IV**, a single broad band around 455 nm is observed (Fig. S21–23<sup>†</sup>), which is in accordance with the yellow color of the compounds. This band is most probably caused by the d–d transition in the low-spin square-planar [Ni (cyclam)]<sup>2+</sup> complex.<sup>48</sup>

#### Thermoanalytical investigations and dehydration experiments

Compound I decomposes in at least two steps (Fig. S24<sup>†</sup>). The first mass loss of ~17% is accompanied by an endothermic signal at a peak temperature  $(T_p)$  of 76 °C and can be assigned to the emission of crystal water molecules (calcd 17.8%). A plateau is observed ranging from ~110 to 180 °C, followed by successive decomposition steps. From ~200 to 630 °C, the mass loss of ~30% may be explained by the emission of the cyclam molecules (calcd 28.4%). In the DTA curve, two exothermic signals are observed at  $T_{\rm p}$  ~ 250 °C and ~460 °C (Fig. S24a<sup>+</sup>). Beyond 650 °C, no significant mass loss occurs and the yellow residue recovered after heating the sample to 1000 °C was identified as a mixture of NiTiNb2O8 and Ni<sub>0.5</sub>Ti<sub>0.5</sub>NbO<sub>4</sub>. The occurrence of exothermic signals during the decomposition of the sample under an inert atmosphere was unexpected. For TG measurements, the sample chamber is flushed with dry N<sub>2</sub>. To avoid the desorption of crystal H<sub>2</sub>O molecules, the chamber was not evacuated prior to the measurement. The residual moisture or air impurities may lead to chemical reactions when decomposing sensitive samples. We repeated the experiment thoroughly evacuating the chamber and in the resulting DTA curve, only a single endothermic event at  $T_p$  = 381 °C is present (Fig. S24b<sup>†</sup>). The decomposition steps are not well resolved. The first mass loss until 200 °C of ~6.2% may be assigned to the residual crystal H<sub>2</sub>O molecules. The following steps from 200 to 900 °C are accompanied by a mass loss of  $\sim$ 33%, but the decomposition is not finished at 1000 °C. In the XRDP (X-ray diffraction pattern) of the black powder that was recovered after heating of I to 1000 °C, most reflections are assignable to Ni and Ni0.5Ti0.5NbO4.

In the DTA-TG curves of **II** the first thermal event is finished at about 200 °C (Fig. S25†) and the mass loss of 13.1% is in excellent agreement with the removal of crystal water molecules (calcd 13.1%). The DTG and DTA (two endothermic events,  $T_p$  = 89, 126 °C) curves show that the dehydration process occurs in two not well resolved steps. A distinct plateau is observed after the removal of the H<sub>2</sub>O molecules followed by the next thermal reaction starting at about 270 °C which is accompanied by an endothermic signal in the DTA curve at  $T_{\rm p}$  = 393 °C. Upon further heating, the compound decomposes in at least two steps and the thermal reaction is not finished at 1000 °C. From 270 to 900 °C the mass loss of 24.0% may be explained by the emission of the cyclam molecules (calcd 24.3%), and the dark-green residue contains NiTiNb<sub>2</sub>O<sub>8</sub>, (NiNb<sub>2</sub>O<sub>6</sub>)<sub>0.6667</sub> and NiO but we note that not all reflections could be assigned.

The TG curve of III is similar to that of II (Fig. S26<sup>†</sup>) with two not well resolved thermal events between 50 °C and ~200 °C, where the mass loss of 10.5% is most likely caused by removal of the crystal  $H_2O$  molecules (calcd for  $14H_2O$  = 10.5%). The mass loss is accompanied by a peak at  $T_p = 96$  °C and a second signal with low intensity at  $T_p = 134$  °C. The following endothermic decomposition step ( $T_p = 400$  °C) starts at ~300 °C and ends at ~550 °C ( $\Delta m = -10.5\%$ ). A further mass decrease is observed between 600 and 900 °C (16.3%), but the thermal decomposition is not finished at the highest temperature of 1000 °C. The overall mass loss of 26.8% between 300 and 900 °C is in good agreement with the removal of the cyclam molecules (calcd 25.0%). In the XRDP of the dark green residue obtained after heating to 1000 °C, most reflections could be assigned to NiTiNb2O8, Ni0.5Ti0.5NbO4 and  $Nb_2O_5$ .

The TG curve of compound **IV** exhibits a mass loss of 8.2% caused by the removal of about  $11H_2O$  molecules (calcd 8.4%) (Fig. S27†). The thermal reaction is accompanied by an endothermal signal at  $T_p = 138$  °C. The second endothermic event ( $T_p = 394$  °C) and the third decomposition step from 600 °C to ~900 °C lead to an overall mass loss of 27.5%, indicating the removal of the cyclam molecules (calcd 25.6%). In analogy to **II** and **III**, the decomposition is not finished at 1000 °C. The XRDP of the residue contains reflections of Ti<sub>0.67</sub>Nb<sub>1.33</sub>O<sub>4</sub>, TiO<sub>2</sub> and NiO.

In the TG curves of the title compounds, distinct plateaus occur after dehydration. This encouraged us to stop the decomposition after water removal and investigate whether the crystal structure is affected and if rehydration recovers the starting material.

For I the decomposition was stopped at 160 °C and the color turned from violet to brownish. The XRDP of the dehydrated material differs significantly from that of the as-synthesized samples and demonstrates that the water free compound exhibits a reasonable good crystallinity after  $H_2O$  removal (Fig. S28†). Immersing the sample in  $H_2O$  leads to a brownish material exhibiting a similar powder pattern to I before dehydration, but with broader and low intensity reflections typical of a reduced crystallinity.

In the XRDP of the dark yellow colored material obtained after heating compound **II** to 250 °C, only three very broad reflections are observed (Fig. S29†). After stirring the sample in H<sub>2</sub>O, the XRDP matches well with that of the as-synthesized material demonstrating the reversibility of the water removal. Compound **III** was heated to 250 °C that led to partial decomposition of the sample, which is indicated by XRDP measurements, that shows only two not well resolved broad reflections between 6 and 8° 2 $\theta$ , respectively, as well as two reflections of weaker intensity at ~10°  $2\theta$  (Fig. S30†). In the XRDP of the recovered material after H<sub>2</sub>O treatment, a few reflections of low intensity are present between 6 and 10°  $2\theta$ , which do not match with reflections of the starting material, *i.e.* the dehydration seems to be not reversible. The XRDP of dehydrated compound **IV** is dominated by three broad and intense reflections. Interestingly, the XRD pattern of a dehydrated sample of compound **IV** shows some similarity to that of compound **II** (Fig. S31†). After recovering the sample treated in water, the XRDP shows a good crystallinity, but the reflections can be clearly assigned to compound **II**.

On storing the samples at room-temperature, no removal of water could be observed, which might be explained by the pronounced hydrogen bonding network between the crystal H<sub>2</sub>O molecules forming water clusters, several H-bonding interactions between cyclam molecules and water or cluster  $O^{2-}$  anions and close K-O<sub>cluster</sub> distances.

#### pH value stability investigations

To estimate the pH stabilities of the compounds, samples of **I** and **II** were immersed for 24 h in an aqueous solution of HCl or KOH at defined pH values. The powder XRD patterns of the samples (Fig. S32 and S33†) indicate that compound **I** is stable between pH 2 and 13. At pH = 14, the compound starts to decompose, clearly visible by the appearance of additional reflections. For compound **II**, a pH stability window from 2 to 13 was determined, while at pH = 14 the reflections start to diminish indicating decomposition. For pH < 2 both compounds decompose to form X-ray amorphous materials. Summarizing, the compounds exhibit good pH stability from pH = 2 to pH = 13.

## Conclusion

Employing [Ni(cyclam)]<sup>2+</sup> cations for charge compensation, we synthesized four novel titanoniobates with Ni<sup>II</sup> in two different spin states and different degrees of substitution of Nb<sup>V</sup> for Ti<sup>IV</sup>. These are the first titanoniobates with Ni<sup>2+</sup>-centered amine complexes and the first transition metal expanded monotitanoniobates. The anions are derivatives of the  $[Nb_{10}O_{28}]^{6-}$  decaniobate anion, where one or both interior Nb<sup>V</sup> positions are substituted with Ti<sup>IV</sup>, yielding the dititanoniobate  $[Ti_2Nb_8O_{28}]^{8-}$  or monotitanoniobate  $[TiNb_9O_{28}]^{7-}$  anion. In compound I, the  $Ni^{2+}$  cation of the  $[Ni(cyclam)O_2]^{2-}$  complex is in a high-spin state. The O<sup>2-</sup> anions occupy both the transand the cis-positions in the two crystallographically independent complexes, which is very rare. In compounds II-IV, a lowspin square-planar coordinated [Ni(cyclam)]<sup>2+</sup> cation is present. The different spin states of the Ni<sup>2+</sup> centers lead to different electronic transitions in the UV/Vis spectra and result in the different colors of the compounds. In the structure of the title compounds the crystal water molecules are joined by H-bonds yielding patterns of different dimensionalities.

Beyond the interesting structural characteristics, the product formation can be controlled to a certain extent.

Employing Ti(O<sup>i</sup>Pr)<sub>4</sub> as a titanium source, {[Ni(cyclam)]<sub>4</sub> [Ti<sub>2</sub>Nb<sub>8</sub>O<sub>28</sub>]}<sub>n</sub>~~28nH<sub>2</sub>O (I) with octahedrally coordinated Ni<sup>2+</sup> and a disubstituted anion is obtained, while the usage of K<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)·2H<sub>2</sub>O leads to K[Ni(cyclam)]<sub>3</sub>[TiNb<sub>9</sub>O<sub>28</sub>]·xH<sub>2</sub>O (II-IV) with a square planar environment around Ni<sup>2+</sup> and the monosubstituted anion. Further experiments demonstrated that the oxalate anion plays a crucial role in the preferential crystallization of one distinct compound.

The substitution of Nb<sup>V</sup> for Ti<sup>IV</sup> leads to an enhanced stability of the PONb anions in a wider range of the pH scale, extending the working pH range for future applications. The good pH stability of the compounds presented here was demonstrated with XRD experiments.

Therefore, the study presented here contributes to the systematic evaluation of the parameters that influence the formation of such compounds, which is the key for the efficient design of novel multifunctional materials.

# Conflicts of interest

There are no conflicts to declare.

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