In the past decades, transition-metal decorated POMs have attracted intensive research interest. However, due to the greater inertness of niobium, potassium hexaniobate (Nb$_6$), which is usually used as the precursor of the reaction, is dissolved in water, and its self-buffering pH range is alkaline, which is usually above 10.5. At this pH value, most metal ions precipitate as hydroxides. The current solutions are mainly as follows: (1) Nb$_6$ reacts with excess hydrogen peroxide to form peroxo-Nb$_6$ which can exist in the acidic system, thus providing the possibility for further reactions with transition-metal ions; (2) the transition-metal ions coordinate with the protecting ligand firstly and then react with Nb$_6$. The protection ligands commonly used are N-containing bidentate chelating ligands, for example, 1,3-diaminopropane (1,3-dap), 1,2-diaminopropane (1,2-dap), and 1.10-phenanthroline (phen). In the past decades, transition-metal decorated POMs have attracted intensive research interest. However, due to the greater inertness of niobium, potassium hexaniobate (Nb$_6$), which is usually used as the precursor of the reaction, is dissolved in water, and its self-buffering pH range is alkaline, which is usually above 10.5. At this pH value, most metal ions precipitate as hydroxides. The current solutions are mainly as follows: (1) Nb$_6$ reacts with excess hydrogen peroxide to form peroxo-Nb$_6$ which can exist in the acidic system, thus providing the possibility for further reactions with transition-metal ions; (2) the transition-metal ions coordinate with the protecting ligand firstly and then react with Nb$_6$. The protection ligands commonly used are N-containing bidentate chelating ligands, for example, 1,3-diaminopropane (1,3-dap), 1,2-diaminopropane (1,2-dap), and 1.10-phenanthroline (phen). In the past decades, transition-metal decorated POMs have attracted intensive research interest. However, due to the greater inertness of niobium, potassium hexaniobate (Nb$_6$), which is usually used as the precursor of the reaction, is dissolved in water, and its self-buffering pH range is alkaline, which is usually above 10.5. At this pH value, most metal ions precipitate as hydroxides. The current solutions are mainly as follows: (1) Nb$_6$ reacts with excess hydrogen peroxide to form peroxo-Nb$_6$ which can exist in the acidic system, thus providing the possibility for further reactions with transition-metal ions; (2) the transition-metal ions coordinate with the protecting ligand firstly and then react with Nb$_6$. The protection ligands commonly used are N-containing bidentate chelating ligands, for example, 1,3-diaminopropane (1,3-dap), 1,2-diaminopropane (1,2-dap), and 1.10-phenanthroline (phen). According to whether they contains heteroatoms or not, PONbs can be divided into iso- and hetero-PONbs. In recent years, with a series of high-nuclearity PONd species being reported one after another, such as [Nb$_{23}$O$_{45}$O], [Nb$_{81}$O$_{225}$], [Nb$_{114}$O$_{116}$] and [Nb$_{28}$O$_{758}$]$_{18}$([CO$_{3}$])$_{12}$], great progress has been made in iso-PONbs. In comparison, the development of...
hetero-PONbs is slower. At present, the research on hetero-PONbs was mainly focused on classical heteroanions, for example, [PO₄]⁻², [SiO₄]⁻² and [GeO₄]⁻². In the last three years, our group tried to introduce [TeO₃]²⁻ ions into the synthesis of PONbs. Compared to those four-coordinated heteroatoms, the embedding of anionic templates containing lone electron pairs can inhibit the formation of saturated Keggin-type clusters, thus significantly varying the self-assembly process in solution and providing greater possibilities for the isolation of novel clusters. Based on the above theory, through unremitting efforts, we have successfully synthesized two unique telluroniobates containing the {TeNb₉} subunit, {H₂Te₄Nb₂₉O₄₃} and {Te₂Nb₁₅.₅Cu₅.₅O₅₇}. In addition, when [TeO₃]²⁻ and [SiO₄]²⁻ ions were added to the reaction system at the same time, a novel hetero-PONb directed by a mixed-heteroanion, {H₆SiTe₂Nb₁₅O₆₄}, was obtained. The synthesis of the above compounds shows again that the [TeO₃]²⁻ ion containing lone electron pairs is a good structure-directing agent (Table 1).

Both V and Nb belong to the VB group and have similar electronegativities and ionic radii. They can hydrolyze or condense under alkaline conditions. Many vanadium-containing PONbs have been reported so far, for example, {VNB₁₂}, {XNB₁₂V₂} (X = P, V, Si, and Ge), {XNB₁₂V₄} (X = P and As), {XNB₁₂V₆} (X = P and V), {AsNb₁₂V₇}, {AsNb₈V₈}, {V₉Nb₂₄}, {H₂Te₂Nb₂₄O₇₂} and {Te₅Nb¹⁵.₅Cu⁰.₅O₅₇}. In addition, when [VON₄]⁻³ ions were added to the reaction system, followed by protecting the transition metal ions Cu²⁺ with nitrogen-containing organic ligands, and ultimately synthesized three novel oxo NbTeV clusters under alkaline conditions (Fig. S1†). The molecular formulas of such compounds are: H₄K(CN₃H₆)₂{Cu₄(2,2'-bidy)(H₂O)}₃{TeNb₉V₉O₃₉}·10H₂O (1), H₅K₃Na₆₂{[Cu(en)H₂O]₃[TeNb₂V₂O₃₉]}·11H₂O (2), and K₆Na₃{[Cu(1,3-dap)H₂O]₃[TeNb₂V₂O₃₉]}·11H₂O (3).

It is worth noting that compound 1 can be prepared by a one-pot reaction but compounds 2 and 3 can only be obtained by combining the conventional aqueous solution and diffusion methods. Compounds 1–3 all contain a trivacant B-type α-Keggin ion [TeNb₉O₃₉], which is also observed in other telluroniobates. In 1, each of the two [VO₄] units is attached to two coplanar NbO₆ octahedra on the {TeNb₉} cluster of the {TeNb₉O₃₉} unit. However, the three [VO₄] units in 2 and 3 are linked to two edge-sharing NbO₆ octahedra, respectively. Compounds 1–3 are the first oxo NbTeV clusters and also the first vanadoniobates based on the trivacant Keggin PONb unit. Furthermore, we studied the behavior of compounds 1–3 in aqueous solutions by negative-mode electrospray ionization mass spectrometry (ESI-MS) and solution-phase ⁵¹V NMR spectroscopy. The magnetic properties show that compounds 1–3 display mainly antiferromagnetic coupling.

### Experimental section

#### Materials and instruments

K₂H[Nb₁₉O₄₉]·13H₂O (Nb₉) was synthesized according to the literature methods. The others were purchased through commercial channels. The IR spectra were obtained by using a Bruker Vertex 70 IR spectrometer using KBr pellets. Thermogravimetric analyses (TGA) of these compounds were performed using a Mettler-Toledo TGA/SDTA 851e instrument under an N₂ atmosphere. Inductively coupled plasma (ICP) analyses were performed using a PerkinElmer Optima 2000 ICP-OES spectrometer. The C, H and N elemental analyses were performed using a Perkin-Elmer 2400-II CHNS/O analyzer. The PXRD measurements were performed using a Bruker AXS D8 Advance diffractometer instrument with Cu Kα radiation at 293 K. The magnetic properties were analysed using a Quantum Design SQUID magnetometer (MPMS-VSM). The XPS spectra were recorded using a PHI5000 VersaProbe photoelectron spectroscope using monochromatic Al Kα radiation. The electrospray-ionization mass spectrometry (ESI-MS)

#### Table 1 The crystal data of compounds 1–3

<table>
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<th>Empirical formula</th>
<th>C₆₆H₅₀N₄O₄₉K₃Cu₄Nb₅Te</th>
<th>C₆₆H₅₀N₄O₄₉Na₂₃K₇V₃Cu₇Nb₅Te</th>
<th>C₆₆H₅₆N₄O₄₉Na₃K₇V₇Cu₇Nb₅Te</th>
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<td>12.8502(5)</td>
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<tr>
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<td>92.939(2)</td>
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<tr>
<td>β°</td>
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<td>3487.6(3)</td>
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<td>0.0457, 0.1068</td>
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<tr>
<td>R₁, wR₁ [All data]</td>
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<td>0.0561, 0.1136</td>
<td>0.0592, 0.0928</td>
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measurements were performed using an AB SCIEX Triple TOF 4600 spectrometer working in the negative ion mode and the data were analyzed using the Peakview 2.0 software. The solution $^{51}$V NMR spectra were collected using the Bruker AVANCE NEO 500 MHz (11.74 T) liquid instrument with a BBO 500 S2 probe, and the pulse program is onepulse. The chemical shift uses Na$_3$VO$_4$ as a reference at $-535.7$ ppm.

### Synthetic procedures

**Synthesis of compound 1.** For A, a blue solution was obtained by adding Cu(Ac)$_2$·H$_2$O (0.40 g, 2.00 mmol) and 2,2'-bipy (0.31 g, 1.98 mmol) into 2mL of CH$_3$CN + 5 mL of H$_2$O in turn. K$_2$HNB$_6$O$_6$·13H$_2$O (2.72 g, 1.99 mmol) was dissolved in 120 mL of H$_2$O, and TeO$_2$ (0.31 g, 1.94 mmol) and NH$_4$VO$_3$ (0.69 g, 5.90 mmol) were added (B). A was dropped into B to get a sky blue turbid solution. Then 1 mL of 2 M CN$_3$H$_5$·HCl was added. After stirring for 20 minutes, the obtained solution was adjusted to pH = 11.30 with 2 M NaOH and heated at 90 °C for 4 h. After cooling, the mixture was filtered and slowly evaporated in a beaker. Three weeks later, blue bulk crystals were obtained. Yield: ca. 50% (based on the Nb$_6$ precursor). IR (KBr disks): 1470, 1443, 1404, 1279, 1254, 1104, 1050, 887, 787, 697, 645, 526 cm$^{-1}$. Anal. (Calcd.) for 1: C 17.90 (17.78), H 3.31 (3.41), N 5.85 (5.80), Nb 32.17 (32.30), Te 4.84 (4.75), V 5.79 (5.83).

**Synthesis of compound 2.** The same procedures as for 1 but change ligand 2,2'-bipy to en (0.1 mL). The filtrate was transferred to a glass tube instead of a beaker. The mixed solution of CH$_3$CH$_2$OH and H$_2$O with a volume ratio of 1 : 2 was carefully layered onto the blue filtrate and then CH$_3$CH$_2$OH was layered onto the mixed solvent carefully. Three weeks later, crystals of compound 2 were obtained by three-phase diffusion. Yield: ca. 30% (based on the Nb$_6$ precursor). IR (KBr disks): 1466, 1281, 1104, 1050, 887, 787, 697, 645, 526 cm$^{-1}$. Anal. (Calcd.) for 2: C 2.77 (2.80), H 1.96 (1.80), N 3.23 (3.15), Nb 32.17 (32.30), Te 3.80 (3.69), V 3.04 (3.15), Cu 7.58 (7.52).

**Synthesis of compound 3.** The same procedures as for 2 but change ligand en to 1,3-dap (0.1 mL). The filtrate was added with Cu(Ac)$_2$·H$_2$O and NH$_4$VO$_3$ to obtain a light yellow clear liquid, then the mixture of Cu(Ac)$_2$·H$_2$O and 2,2'-bipy was added to get a blue liquid, followed by adding CN$_3$H$_5$·HCl. The solution’s pH value was adjusted to 11.30 by 2 M NaOH. The solution was heated and filtered, and the filtrate was slowly evaporated in a beaker. After two weeks, blue block-like crystals of 3 were isolated from the solution. The synthetic methods of 2 and 3 are similar to 1 except that aromatic amine ligands 2,2'-bipy were replaced with aliphatic ligands en or 1,3-dap.

It is worth noting that the methods of crystal isolation are different: compound 1 can be obtained directly by volatilizing the solvent in air, while compounds 2 and 3 can only be isolated via diffusion of solution and alcohol; when the filtrates of compounds 2 and 3 were volatilized in the air, only a large amount of precipitate is obtained. In addition, compound 1 can be obtained by diffusion.

The choice of N-donor ligands is very important for the synthesis of PONb clusters. Due to the steric hindrance effects of the ligands, the configuration of the generated compounds may be affected to some extent. When using the aromatic ligand, 2,2'-bipy, a [TeNb$_9$V$_2$O$_{37}$] cluster was isolated. When the aliphatic ligands en and 1,3-dap with a relatively small steric hindrance effect were used, a trivacant α-Keggin ion [TeNb$_5$O$_{13}$]$_3$ surrounded by three {VO$_4$} tetrahedral units was formed. We also attempted to introduce other nitrogen-containing ligands, such as Phen, 4,4'-bipy into the reaction system in order to get other configurations of PONb clusters, but we failed. We speculate that the N-donor ligands cannot only protect transition-metal ions but also play the role of structural orientation to lead the formation of PONbs.

In addition, the selection of transition-metal ions is also very important for the isolation of PONbs. When Cu$^{2+}$ ions were replaced with Co$^{2+}$, Fe$^{3+}$ or Zn$^{2+}$ ions, there is no crystal formation and only a large amount of precipitate was obtained. Furthermore, the addition of CN$_3$H$_5$·HCl to the reactions is crucial to their preparations. When we use other counter cations, for example, (CH$_3$)$_3$N$^+$, Cs$^+$ and Na$^+$, the target product cannot be synthesized. It is speculated that the crystallization of POMs may be affected by the symmetry, size, charge and solubility of the counter cations. In addition, the solubility of compounds 1–3 in aqueous solutions was explored. The experimental results show that compounds 1–3 are soluble in water, but the solubility of compound 1 is far less than that of the other two compounds. We speculate that the reasons are as follows: (1) Compared with the polyoxoanion [TeNb$_9$V$_2$O$_{37}$]$^{15-}$, the charge of polyoxoanion [TeNb$_9$V$_2$O$_{37}$]$^{15-}$ is relatively high. (2) The counterions of compound 1 are 4 [Cu(2,2'-bipy)]$^{2+}$, 2 (CN$_3$H$_5$) and 1 K$^+$, those of compound 2 are 3 [Cu(en)]$^{2+}$, 5 K$^+$, and 2.5 Na$^+$ and those of compound 3 are 3 [Cu(1,3-dap)]$^{2+}$, 3 K$^+$, and 5 Na$^+$. Compared to compounds 2 and 3, compound 1 undergoes a stronger cation association which also controls its behavior.

### Structural analysis

Single crystal X-ray structural analysis shows that 1 is composed of one {[Cu$_2$(2,2'-bipy)$_2$(H$_2$O)$_2$][TeNb$_9$V$_2$O$_{37}$]}$^{7-}$ polyoxoanion (1a), 1 K$^+$, 2 (CN$_3$H$_5$), 4 H$^+$ for charge balance and 29 water molecules. The [TeNb$_9$V$_2$O$_{37}$]$^{15-}$ cluster of 1a can be regarded as a trivacant B-type α-Keggin ion [TeNb$_5$O$_{13}$]$^{17-}$ bound with two {VO$_4$} tetrahedra (Fig. 1 and Fig. S4a†). The trivacant B-type α-Keggin cluster is formed by removing a triad of coplanar NbO$_6$ octahedra from the plenary α-Keggin cluster. Then, every decorating {VO$_4$} tetrahedron is connected to two...
coplanar NbO₆ octahedra on the \{Nb₃O₁₅\} cluster by three \(\mu_2\)-O atoms. One \([\text{Cu}(2,2\text{-bipy})(\text{H}_2\text{O})]^{2+}\) group (Cu2) is grafted on the equivalent position occupied by two \([\text{VO}_2]^-\) tetrahedra of a \([\text{TeNb}_9\text{O}_{33}]^{17-}\) ion through two \(\mu_2\)-O atoms. In addition, two \([\text{VO}_2]\) moieties bridge to two \([\text{Cu}(2,2\text{-bipy})(\text{H}_2\text{O})]^{2+}\) complexes (Cu1 and Cu3) through one \(\mu_1\)-O and \(\mu_2\)-O bridge, respectively. Another \([\text{Cu}(2,2\text{-bipy})]^{2+}\) fragment is connected to the \([\text{TeNb}_9\text{O}_{33}]^{17-}\) ion through four \(\mu_1\)-O atoms. Furthermore, the adjacent \([\text{Cu}(2,2\text{-bipy})_2(\text{H}_2\text{O})][\text{TeNb}_9\text{V}_2\text{O}_{37}]^{-}\) cluster forms a dimer by two Cu–O–(Cu) bonds (Fig. 1a).

According to the different coordination configurations of the four supporting Cu⁺ ions, they are classified into two groups. Cu1, Cu2 and Cu3 are all tetragonal pyramid configurations, which are five-coordinated to two O atoms bridged to the \([\text{TeNb}_9\text{O}_{33}]^{17-}\) cluster, one O atom from the water molecule and two N atoms of the chelating 2,2'-bipy ligand (Fig. S7†). The Cu–O bond lengths of Cu1–Cu3 are 1.949(8)–2.040(8), 1.945(8)–2.030(8), and 1.938(9)–2.384(8) Å and the Cu–N bond lengths are 1.976(14)–2.008(11), 1.978(10)–1.982(11), and 1.985(14)–2.016(14) Å, respectively, which are similar to those of the other Cu complexes with a 2,2'-bipy ligand (Table S7†). The corresponding values for cis N/O–Cu–N/O angles are 80.6(6)–102.5(3), 81.9(4)–97.9(3), and 83.0(3)–101.5(4) and the trans N/O–Cu–N/O angles are 166.4(4)–172.4(5), 169.1(4)–171.2(4), and 162.4(4)–173.9(5)°, reflecting a significant distortion of the tetragonal pyramid geometry. Differently, Cu4 bonds with four O atoms from the \([\text{TeNb}_9\text{O}_{33}]^{17-}\) cluster and two N atoms from the 2,2'-bipy ligand. The Cu–N and the Cu–O bond lengths are 1.987(11)–1.989(11) and 1.992(8)–2.450(6) Å, respectively. The cis N/O–Cu–N/O angles are 73.4(7)–109.5(8) and the trans N/O–Cu–N/O angles are 136.1(0)–173.9(4)°, demonstrating a stronger distortion of the \([\text{Cu}_4\text{N}_6\text{O}_8]\) octahedra compared to other hexacoordinated Cu atoms (Table S7†).

Structural analysis reveals that compound 2 is composed of a \([\text{Cu}(\text{en})\text{H}_2\text{O}][\text{TeNb}_9\text{V}_2\text{O}_{39}]^{-}\)° cluster (2a) with 10 lattice water molecules and charge-balanced by 5 K⁺, 2.5 Na⁺ and 0.5 H⁺ (Fig. 2). Compound 3 possesses the cluster of \([\text{Cu}(1.3\text{-dap})\text{H}_2\text{O}][\text{TeNb}_9\text{V}_2\text{O}_{39}]^{-}\)† (3a) along with 3 K⁺, 5 Na⁺ and 11 lattice water molecules. Anions 2a and 3a have similar cluster geometries, although they differ in the chelating ligands (Fig. S6†). So, in this article, we chose to describe compound 2 in detail as an example. The \([\text{TeNb}_9\text{V}_2\text{O}_{39}]^{14-}\) cluster of 2a can be regarded as three \([\text{VO}_2]^-\) units captured by the trivacant building block \([\text{TeNb}_9\text{O}_{33}]^{17-}\). The modified positions of the \([\text{VO}_2]^-\) units are different from that of compound 1. The three \([\text{VO}_2]^-\) units are successively decorated above the two edge-sharing NbO₆ octahedra of the \([\text{TeNb}_9\text{O}_{33}]^{17-}\) ions rather than the coplanar NbO₆ octahedra. The three \([\text{Cu}(\text{en})\text{H}_2\text{O}]^{2+}\) fragments are modified on the \([\text{TeNb}_9\text{V}_2\text{O}_{39}]^{14-}\) cluster, and each of them is connected to two coplanar NbO₆ octahedra through three Cu–O–(Nb) bridges. In addition, polyanion 2a can be perceived as follows: three \([\text{VO}_2]^-\) units and three \([\text{Cu}(\text{en})\text{H}_2\text{O}]^{2+}\) fragments are connected in sequence through six \(\mu_3\)-O atoms to form a closed ring. This closed annular structure is then capped on a \([\text{TeNb}_9\text{O}_{33}]^{17-}\) ion forming 2a. The vanadium and copper atoms are connected in a hexagon configuration, if not considering oxygen atoms (Fig. 2d). All of the Cu⁺ ions in compound 2 adopt a hexacoordinated octahedral configuration and coordinate with three O atoms of the \([\text{TeNb}_9\text{V}_2\text{O}_{39}]^{14-}\) cluster, two N atoms of the en ligand and one water molecule (Fig. S8†). The trans N/O–Cu–N/O angles of Cu1–Cu3 are in the range of 167.7(2)–170.3(0), 166.6(2)–174.3(2), and 166.3(3)–168.0(2)° and those of the cis ones are in the range of 76.63(17)–96.7(9), 78.07(17)–102.7(2), and 77.35(18)–101.6(5)°; both are significantly deviated from the ideal angles 180 and 90°. By comparison, we find that all the geometrical parameters of Cu1–Cu3 are in good agreement with those of the compounds whose ligands are en (Table S8†). The Cu–N bond lengths of Cu1–Cu3 are 1.979 (7)–2.022(6), 1.983(7)–1.999(6) and 1.983(8)–2.017(6) Å, respect-
Oxides: The Cu–O bond lengths are 1.988(4)–2.574(8), 1.971(5)–2.732(7) and 1.995(5)–2.701(8) Å, which are similar to the data reported for Cu complexes with the en ligand (Table S8†). In compound 3, the copper atoms also adopt a hexacoordinated octahedral configuration and their bond lengths and bond angles are shown in Table S9.† The analysis shows that their geometric parameters are similar to those of Cu complexes having a 1,3-dap ligand.14

Infrared spectroscopy

The IR spectra of 1-3 were recorded from 4000 to 450 cm⁻¹, in order to investigate their characteristic band vibrations (Fig. S13†). For 1, the vibration of terminal M=O (M = Nb and V) occurs at 918 and 868 cm⁻¹, while the peaks at 774, 712, 662 and 547 cm⁻¹ can be assigned to the bridging M–O–M vibrations.10c The peaks around 1660–1013 cm⁻¹ can be assigned to the absorption bands of the 2,2’-bipy ligands.12 The IR spectra of 1 and 2 are very similar. For 2, the characteristic peaks at 787, 697, 645 and 526 cm⁻¹ are consistent with the bridging M–O–M vibrations. The peak at 887 cm⁻¹ is attributed to M=O vibration. The bands of the N-donor organic groups (en/1,3-dap) in compound 2 or 3 appear at 1646–1033 cm⁻¹.13,14

Magnetic properties

Under an external field of 1000 Oe, the magnetic susceptibilities of 1–3 between 300 and 1.8 K were studied. For 1, when the temperature drops from 300 K to 18 K, the value of χm rises slowly from 0.0087 emu K mol⁻¹ to 0.070 emu K mol⁻¹ (Fig. 3). With the continuous decrease of temperature, the χm value continuously decreases and the lowest value is 0.88 emu K mol⁻¹ at 1.8 K (Fig. 3). In the range of 300 to 20 K, the curve fitting for 1/χm versus T plots follows the Curie–Weiss law, with C = 2.85 cm³ K mol⁻¹ and θ = −35.53 K (Fig. S17†). This behavior represents the dominant antiferromagnetic coupling in 1. For 2, the χmT value gradually decreases with the temperature decrease and reaches a minimum of 0.80 emu K mol⁻¹ at 1.8 K (Fig. S18†), and the curve fitting for 1/χm versus T plots with the Curie–Weiss law in the range of 40–210 K results in C = 1.62 emu K mol⁻¹ and θ = −24.92 K (Fig. S19†), which indicates the presence of antiferromagnetic exchange interactions. The χmT value at room temperature (300 K) is 1.68 emu K mol⁻¹ with an expected value of χmT = 1.24 emu K mol⁻¹ for three uncoupled Cu²⁺ centers (S = 1/2).16 For 3, the χmT value shows a slightly faster decreasing trend between 1.8 and 300 K, indicating that the Cu²⁺ ions in 3 also show an antiferromagnetic interaction (Fig. S20†). The χmT value at room temperature is 1.50 emu K mol⁻¹, which is slightly higher than that of three uncoupled Cu²⁺ centers. The 1/χm versus T curve between 300 K and 85 K conforms to the Curie–Weiss law with C = 1.78 emu K mol⁻¹ and θ = −66.70 K (Fig. S21†).

Mass spectrometry

Electrospray ionization mass spectrometry (ESI-MS) with an excellent detection limit can detect both cationic and anionic species in aqueous solvents semi-quantitatively, thus clarifying the solution phase equilibrium upon ionization, which is widely used in polyoxometalate chemistry.17 To examine the aqueous solution behaviors of compounds 1–3, their crystals were directly dissolved in water (concentration of compound 1: 200 ppm) and the products were measured by ESI-MS, respectively. For 1, the self-buffering pH value of the aqueous solution is about 9.7 and the ESI-MS spectrum showed three envelopes that correspond to the [TeNb9V3O39] clusters (Fig. 4a). These can be found at the charge of 4− and 3− at 456.28 [HnK(CN3H6)3(TeNb9V2O37)], 461.39 [HnK(CN3H6)4(TeNb9V2O37)], 508.88 [HnK2(CN3H6)4(Cu2,2’-bipy)][TeNb9V2O37][H2O]], 620.69 [HnK(CN3H6)5(TeNb9V2O37)](H2O)], 641.75 [HnK[Cu(2,2’-bipy)][TeNb9V2O37]], and 693.20 [HnK(CN3H6)5(Cu2,2’-bipy)][TeNb9V2O37][H2O]], respectively (Table S10 and Fig. S22, S25†). The above analysis indicated that the [TeNb9V2O37] clusters could stably exist in the aqueous solution. The ESI-MS spectrum of compound 2 (concentration of compound 2: 400 ppm) shows two envelopes corresponding to the [TeNb9V2O39] cluster (Fig. 4b). These can be found at the charge value of 3− at m/z 630.39 [HnNaCu(en)][TeNb9V2O39](H2O)], 643.90 [HnNaCu(en)][TeNb9V2O39](H2O)2, and 744.83 [H2NaK2Cu(en)2][TeNb9V2O39] (H2O)2 etc. (Table S11 and Fig. S23, S26†). The above analysis shows that the [TeNb9V2O39] cluster can stably exist in aqueous solutions, but the supported [Cu(en)]²⁺ ions tend to fall off from the [TeNb9V2O39] cluster in aqueous solutions; thus, polyamions that support different numbers of [Cu(en)]²⁺ ions are obtained. For 3 (the concentration of compound 3: 350 ppm), which shares similar solutions to 2, the ESI-MS spectrum also showed two 3− charged ion envelopes that match with the calculated peak positions for the [TeNb9V2O39] adducts of potassium cations, protons, sodium cations, [Cu(en)]²⁺ ions and water molecules (Table S12 and Fig. 4c, S24, S27†).

Due to the relatively good solubility of compounds 2 and 3 in water, the influences of the pH values on the structure were...
studied (Fig. 5 and 6). When a sample of compound 2 was dissolved in water (the concentration of compound 2: 400 ppm), the self-buffering pH value of the solution was about 9.5. The addition of HAc or NaOH to the solution will lead to the decomposition of the clusters, which obviously shows that the abundance of peaks assigned to the clusters decreases and some impurity peaks that are difficult to distribute appear. When the pH value was adjusted in the range of 7.39–11.02, the polyoxoanion \{TeNb₉V₃O₃₉\} remains intact, although the intensity ratio of the peaks belonging to the \{TeNb₉V₃O₃₉\} cluster changed to some extent. Upon increasing the pH value at 11.98, most of the \{TeNb₉V₃O₃₉\} clusters were decomposed.

Fig. 4  Negative-mode ESI-MS of compounds 1–3 in aqueous solution.

Fig. 5  ESI-MS of compound 2 upon varying pH using HAc/NaOH.

Fig. 6  ESI-MS of compound 3 upon varying pH using HAc/NaOH.
When the pH value of the solution continues to increase, the peaks belonging to the \( \{\text{TeNb}_9\text{V}_2\text{O}_{39}\} \) adducts disappear completely, and only a large number of fragment peaks that are difficult to assign appear, indicating that the cluster is completely decomposed. Upon decreasing the pH value below 7.39 using HAc, the peaks of the intact polyanion \( \{\text{TeNb}_9\text{V}_2\text{O}_{39}\} \) also disappear, which indicates that compound 2 has completely decomposed at this pH value. The pH-dependent ESI-MS spectrum of compound 3 was also measured. For 3, the self-buffering pH value is 8.8 (the concentration of compound 3: 350 pmm) and the stable pH range is 7.64–11.06, which is similar to the stability of 2. The detailed assignments can be observed in Fig. 6.

\( ^{51}\text{V} \) nuclear magnetic resonance

Since the 1970s, nuclear magnetic resonance (NMR) spectroscopy has been applied to polyoxometalates containing NMR-active nuclei, i.e. \( ^{31}\text{P}, \ ^{51}\text{V}, \ ^{29}\text{Si}, \ ^{95}\text{Mo} \) and \( ^{183}\text{W} \), in order to study their solution structures and dynamics.\(^{18}\) Until now, the maximum measurement amount of polyoxometalates is at \( ^{51}\text{V} \), a core nucleus with relatively high sensitivity, which provides spectra with line widths ranging from 10 to 800 Hz in diamagnetic polyoxocations.\(^{19}\) For example, the \( ^{51}\text{V} \) NMR spectra of \( [\text{VV}_{12}\text{O}_{40}(\text{VO})_{2}]^{9-} \) show a sharp peak at \(-507 \) ppm and a wide peak at \(-531 \) ppm, corresponding to a central VO\(_4\) and other \( \{\text{VO}_5\} \) units in the cluster.\(^{20}\) The assignment of a \( \{\text{VO}_4\} \) unit in the \( [\text{VV}_{12}\text{O}_{40}(\text{VO})_{2}]^{9-} \) cluster agrees well with \( [\gamma-1,2\cdot\text{H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-} \), which shows a signal at \(-530 \) ppm.\(^{21}\) Furthermore, for \( [\text{PV}_{12}\text{O}_{40}(\text{VO})_{2}]^{2-} \), the \(-523 \) ppm peak was assigned to the VO\(_3\) caps and the \(-575 \) ppm peak to the VO\(_6\) addenda.\(^{22}\)

Introducing NMR-active nuclei \( ^{51}\text{V} \) into polyoxoniobates not only enriches the structural types of polyoxoniobates but also provides another strategy that can promote the understanding of the solution behavior of this class of clusters. However, there are few studies on the \( ^{51}\text{V} \) NMR of vanadoniobates and only a few capped Keggin-type vanadoniobates were studied.\(^{6m,10e,l}\) For instance, the \( ^{51}\text{V} \) NMR spectrum of \( [\text{TMA}]_9[\text{V}_2\text{Nb}_{12}\text{O}_{42}]\cdot18\text{H}_2\text{O} \) shows a sharp peak at \(-520.0 \) ppm and a broad peak at \(-528.1 \) ppm with an intensity ratio of 1:2, corresponding to the central \( \{\text{VO}_4\} \) unit and the two capping \( \{\text{VO}_5\} \) units in the cluster.\(^{10l}\) The \( ^{51}\text{V} \) NMR peak position of the capping \( \{\text{VO}_5\} \) units of \( [\text{TMA}]_9[\text{V}_2\text{Nb}_{12}\text{O}_{42}]\cdot19\text{H}_2\text{O} \) is located at \(-542 \) ppm.\(^{6m}\) The positions of the signal peaks of capped Keggin-type vanadoniobates are similar to those of V-capped POMs, but have a big difference between V-POMs and other structural types.\(^{23}\)

Based on the previous work of other chemists, the behavior of compounds 1–3 in solution was investigated by \( ^{51}\text{V} \) NMR (131.5 MHz, \( \text{D}_2\text{O} \)) (Fig. 7). The NMR spectrum of 1 (concentration of compound 1: 200 pmm, self-buffering pH 9.7) exhibits one resonance located at \(-536.43 \) ppm which is similar to the signal from the capping \( \{\text{VO}_5\} \) unit in V-capped POMs.\(^{6m,20,21}\) Two VO\(_4\) units capped on the \( \{\text{TeNb}_9\text{O}_{39}\} \) cluster of compound 1 are obviously different in crystallography due to the different order of the \( \{\text{CN}_3\text{H}_6\}^+ \) counter cations and \( [\text{Cu}(2,2’\cdot\text{bipy})]^2+ \) fragments around them. However, it is clear that the two symmetric VO\(_4\) units are equivalent in the cluster \( \{\text{TeNb}_9\text{V}_2\text{O}_{37}\} \), which is consistent with the fact that only one signal peak in the solution \( ^{51}\text{V} \) NMR spectra of compound 1 was represented. The solution \( ^{51}\text{V} \) NMR spectra of 2 and 3 all exhibited a broad peak at \(-534.04 \) and \(-534.22 \) ppm, corresponding to the three capping VO\(_4\) units in the cluster (Fig. 5b and c). Similar to compound 1, the peaks of the three crystallographically unique vanadium ions would be coalesced by rapid tumbling into a single signal for solution NMR spectra. In addition, the peaks of symmetric VO\(_4\) units in compounds 1–3 are widened to some extent, which is due to the influence of the surrounding copper ions.

To study the pH-dependent stability of 2 and 3, the pH-varied \( ^{51}\text{V} \) NMR spectra were measured in aqueous solutions at different pH values (Fig. 8 and 9). For compound 2 (concentration: 3000 pmm; self-buffering pH 10.02), the signal at \(-534.04 \) ppm was essentially unchanged between pH 8.10 and
11.04, which shows that it was stable in this pH range. When the pH value is higher than 11.04, the signal at −534.12 ppm disappears, and at the same time, a peak appears at −539.07 ppm. This phenomenon indicates the decomposition of the cluster and the formation of another kind of unidentifiable cluster. At pH 7.18, the peaks at −545.78, −567.47 and −574.91 ppm appear as the peak of the \{TeNb\_9V\_3O\_39\} cluster disappears, suggesting that the peaks originate from vanadate ions formed by the decomposition of \{TeNb\_9V\_3O\_39\}. The solutions after the concentration: 3500 ppm; self-buffering pH 10.02, the signal at −534.22 ppm is maintained for the pH values 8.05–11.09 which shows that compound 3 is stable in this pH region.

Conclusions

In summary, three novel polyoxoniobates were prepared for the first time and structurally characterized by TG analysis, IR spectra, single crystal X-ray diffraction, PXRD, magnetism and solution behavior. Compounds 1–3 are the first oxo NbTeV clusters and also the first vanadoniobates based on the triva-
cant Keggin PONb unit. Furthermore, applying the appropriate crystal growth methods turns out to be crucial in the synthesis of these novel polyoxoniobates. In the future, we will continue to explore novel oxo NbTeV clusters by the assembly of \{Nb\_6O\_19\} units with transition-metal ions, with the mission of greatly enriching the versatility of polyoxoniobates.

Conflicts of interest

There are no conflicts to declare.

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