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Two-Dimensional Lanthanide Heteropolyvanadates of Manganese(IV) and Nickel(IV) Containing Two Types of Heteropoly Anions with 1:13 and 1:12 Stoichiometry

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Reactions of 1:13 heteropoly anions $[MV_{13}O_{38}]^{7-}$ (M = Mn, Ni) and lanthanide cations Ln^{3+} (Ln = La, Ce, or Pr) produce five isomorphic compounds, which are crystallized in the triclinic crystal system, space group $P\bar{1}$, and formulated as $[Ln_6(H_2O)_{25}(MV_{12}O_{38})(HMV_{13}O_{38})]\cdot nH_2O$ ((**1**) Ln = La, M = Mn, and $n \approx 31$; (**2**) Ln = Ce, M = Mn, and $n \approx 29$; (**3**) Ln = Pr, M = Mn, and $n \approx 31$; (**4**) Ln = La, M = Ni, and $n \approx 28$; (**5**) Ln = Pr, M = Ni, and $n \approx 33$). These compounds are two-dimensional polymeric structures constructed by hydrated lanthanide cations and two types of heteropoly anions, $[MV_{13}O_{38}]^{7-}$ and $[MV_{12}O_{38}]^{12-}$. In contrast to the previous reported 1:13 heteropoly anions, all with disordered structures, $[MV_{13}O_{38}]^{7-}$ clusters in **1**–**5** are non-disordered with a distinct mode. The second kind of anionic cluster $[MV_{12}O_{38}]^{12-}$ with O_h symmetry, which consists of 13 entire edge-sharing MO_6 (M = V, Mn or Ni) octahedra, has not been reported hitherto. The emergence of the new cluster may be correlated to the six capping lanthanide cations surrounding it with a stabilization effect. In this paper, the syntheses and structures of the five polymeric lanthanide heteropolyvanadates of manganese(IV) and nickel(IV) have been presented.

Introduction

Polyoxometalates (POMs), metal−oxygen clusters of the early transition elements (mostly vanadium, molybdenum, and tungsten) have been investigated extensively for many years because of their potential in many areas, especially for catalysis, medicine, and materials science.[1] However, there is still a major challenge with regard to the mechanism for the formation of POMs and especially the rational directed synthesis of specific structures.[2] Pope and Müller have put forward that there are three parent structures and many other POMs can be regarded as being their derivatives.[3] For the three parent structures, each retains the symmetry of its central oxygen polyhedron (tetrahedron, octahedron, and icosahedron). (Figure 1) The first and third parent structures with T_d and I_h symmetry have been separated early and named as Keggin and Silverton type structures,[4,5] whereas the second parent structure with O_h symmetry has not yet been observed for a discrete polyoxometalate,[3] although several of its derivatives have been reported, such as mineral sherwoodite $[AlV^{IV}_2V^{V}_{12}O_{40}]^{9-}$, $[AsV^{IV}_2V^{V}_{12}O_{40}]^{7-}$, and $[V^{IV}_5V^{V}_{12}O_{42}]^{4-}$.[6−8] The reasons for that still are not clear at the present time.

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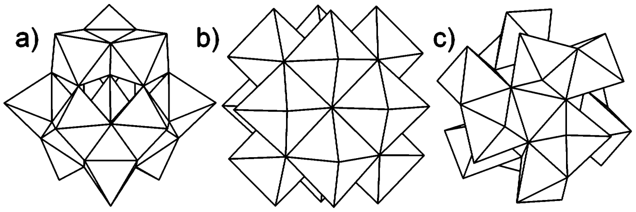

Figure 1. Three parent structures with (a) T_d, (b) O_h, and (c) I_h symmetry.

On the other hand, compared to the extensive works on heteropolymolybdates and heteropolytungstates, less research has been conducted in the field of heteropolyvanadates.[9−11] Commonly, for the different oxidation state and stereochemical preferences of vanadium compared with those of molybdenum and tungsten, the structures of vanadates have some differences from those of molybdates and tungstates. A typical example is the anion $[PV_{14}O_{42}]$,$^{9-}$ which has two additional capping VO^{3+} units, in contrast to the Keggin structure of Mo and W. Another example is the class of 1:13 heteropoly anions $[MV_{13}O_{38}]^{7-}$ (M = Mn, Ni), which were first isolated by Pope and co-workers[9a] and later crystallographically characterized by Sasaki's group.[12] Up to now, no stoichiometric analogues of this kind of anions have been observed in molybdates and tungstates. The inhibition of tumors and bacteria and the catalytic ability of this kind of anions have also been reported.[13−15] Recently, our group reported an inorganic−organic hybrid compound $K_3(HABOB)_4[MnV_{13}O_{38}]\cdot 9H_2O$ (ABOB = N-amidino-4-morpholincarboxamidine) from the $[MnV_{13}O_{38}]^{7-}$ anion.[16] While investigating the reaction of $[MV_{13}O_{38}]^{7-}$ anions and Ln^{3+} cations (Ln = La, Ce, or Pr), we obtained a series of isomorphic compounds formulized as $[La_6(H_2O)_{25}(MnV_{12}O_{38})(HMnV_{13}O_{38})]\cdot{\sim}31H_2O$ **1**, $[Ce_6(H_2O)_{25}(MnV_{12}O_{38})(HMnV_{13}O_{38})]\cdot{\sim}29H_2O$ **2**, $[Pr_6(H_2O)_{25}(MnV_{12}O_{38})(HMnV_{13}O_{38})]\cdot{\sim}31H_2O$ **3**, $[La_6(H_2O)_{25}(NiV_{12}O_{38})(HNiV_{13}O_{38})]\cdot{\sim}28H_2O$ **4**, and $[Pr_6(H_2O)_{25}(NiV_{12}O_{38})(H\ NiV_{13}O_{38})]\cdot{\sim}33H_2O$ **5**. They are two-dimensional (2D) polymeric structures based on $[MV_{13}O_{38}]^{7-}$ (M = Mn, Ni) (MV_{13}) clusters and unprecedented $[MnV_{12}O_{38}]^{12-}$ (M = Mn, Ni) (MV_{12}) clusters linked by hydrated lanthanide cations. In contrast to the previous reported 1:13 heteropoly anions crystallographically characterized, all with disorder,[12,16] the MV_{13} clusters in **1**−**5** are non-disordered with distinct structures. The MV_{12} clusters, just the second parent structure type with O_h symmetry, consist of 13 entire edge-sharing MO_6 (M = V, Mn or Ni) octahedra, which are stabilized by six $[Ln(H_2O)_5]^{3+}$ capping groups. To the best of our knowledge, the MV_{12} clusters have not been observed in heteropolyvanadates hitherto. Here, we report the syntheses and structures of these compounds.

Experimental Section

Materials. $K_7MnV_{13}O_{38}\cdot 18H_2O$ and $K_7NiV_{13}O_{38}\cdot 16H_2O$ were prepared according to the literature[9a] method. The $Pr(ClO_4)_3\cdot xH_2O$ ($x \approx 6-8$) was prepared by the reaction of Pr_4O_6 and $HClO_4$. All other chemicals were obtained from commercial sources and used without further purification.

Physical Measurements. Elemental analyses were performed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400−4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. TG analysis was performed on a Perkin−Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C/min. Powder X-ray diffraction measurements were performed on a Rigaku D/MAX-3 instrument with Cu−Kα radiation in the angular range $2\theta = 3-90°$ at 293 K. The sorption isotherm for N_2 was measured with an automatic volumetric adsorption apparatus (Micromertics ASAP 2010) at 77 K.

Preparations. $[La_6(H_2O)_{25}(MnV_{12}O_{38})(HMnV_{13}O_{38})]\cdot{\sim}31H_2O$ (1). The aqueous mixture of $K_7MnV_{13}O_{38}\cdot 18H_2O$ (0.38 g, 0.2 mmol) and $La(NO_3)_3\cdot 6H_2O$ (0.65 g, 1.5 mmol) adjusted with dilute hydrochloric acid to pH 3−5 was warmed at 80 °C and stirred for 7 h. The mixture was then filtered, and the filtrate was allowed to stand at room temperature for crystallization. After two weeks, orange parallelepiped crystals of **1** were collected. Yield: 0.346 g (78% based on Mn). Elemental anal. Calcd for **1**: La, 18.76; Mn, 2.47; V, 28.67. Found: La, 18.29; Mn, 2.46; V, 28.21. IR (KBr pellet, cm^{-1}): 444(m), 507(m), 611(m), 813(m), 916(s), 973(m), 1456(w), 1623(m), 3415(m).

$[Ce_6(H_2O)_{25}(MnV_{12}O_{38})(HMnV_{13}O_{38})]\cdot{\sim}29H_2O$ (2). Compound **2** was prepared following the procedure described for compound **1**, but $Ce(NO_3)_3\cdot 6H_2O$ was used instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 72% (based on Mn). Elemental anal. Calcd for **2**: Ce, 19.05; Mn, 2.49; V, 28.85. Found: Ce, 18.97; Mn, 2.33; V, 28.34. IR (KBr pellet, cm^{-1}): 432(m), 463(m), 497(m), 610(m), 803(m), 910(s), 981(m), 1455(w), 1630(m), 3414(m).

$[Pr_6(H_2O)_{25}(MnV_{12}O_{38})(HMnV_{13}O_{38})]\cdot{\sim}31H_2O$ (3). Compound **3** was prepared following the procedure described for compound **1**, except that $Pr(ClO_4)_3\cdot xH_2O$ was used instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 61% (based on Mn). Elemental anal. Calcd for **3**: Pr, 18.98; Mn, 2.39; V, 28.59. Found: Pr, 18.70; Mn, 2.41; V, 28.74. IR (KBr pellet, cm^{-1}): 448(m), 473(m), 507(m), 537(m), 626(s), 783(m), 910(s), 1451(w), 1618(m), 3410(m).

$[La_6(H_2O)_{25}(NiV_{12}O_{38})(HNiV_{13}O_{38})]\cdot{\sim}28H_2O$ (4) Compound **4** was prepared following a procedure similar to that for compound **1**, except that at the beginning, $K_7NiV_{13}O_{38}\cdot 16H_2O$ was used instead of $K_7MnV_{13}O_{38}\cdot 18H_2O$ and at the end, wine parallelepiped crystals of **4** were obtained. Yield: 69% (based on Ni) Elemental anal. Calcd for **4**: La, 18.96; Ni, 2.67; V, 28.97. Found: La, 18.70; Ni, 2.59; V, 28.89. IR (KBr pellet, cm^{-1}): 435(m), 493(m), 611(m), 734(w), 815(m), 920(s), 983(m), 1396(s), 1630(m), 3411(m).

$[Pr_6(H_2O)_{25}(NiV_{12}O_{38})(HNiV_{13}O_{38})]\cdot{\sim}33H_2O$ (5) Compound **5** was prepared following the procedure for **4** but $Pr(ClO_4)_3\cdot xH_2O$ was used instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 73% (based on Ni). Elemental anal. Calcd for **5**: Pr, 18.80; Ni, 2.61; V, 28.31. Found: Pr, 18.67; Ni, 2.66; V, 28.10. IR (KBr pellet, cm^{-1}): 440(m), 475(m), 509(m), 533(m), 628(s), 761(m), 932(s), 1450(w), 1620(m), 3412(m).

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Table 1. Crystal Data and Structure Refinements for **1**−**5**

	1	**2**	**3**	**4**	**5**
empirical formula	$H_{113}La_6Mn_2O_{132}V_{25}$	$H_{109}Ce_6Mn_2O_{130}V_{25}$	$H_{113}Pr_6Mn_2O_{132}V_{25}$	$H_{107}La_6Ni_2O_{129}V_{25}$	$H_{117}Pr_6Ni_2O_{134}V_{25}$
mol wt	4442.74	4413.97	4454.74	4396.24	4498.32
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.269(3)	13.228(3)	13.286(3)	13.264(3)	13.2461
b (Å)	15.855(3)	15.811(3)	15.775(3)	15.846(3)	16.0084(6)
c (Å)	29.942(6)	29.844(6)	29.883(6)	29.850(6)	27.8371(11)
α (deg)	85.65(3)	85.49(3)	85.04(3)	85.64(3)	88.6390(10)
β (deg)	78.29(3)	78.37(3)	77.99(3)	78.45(3)	80.3420(10)
γ (deg)	89.66(3)	89.55(3)	89.41(3)	89.59(3)	89.7060(10)
V (Å^3)	6150(2)	6095(2)	6103(2)	6129(2)	5817.5(4)
Z	2	2	2	2	2
P_{calcd} (mg m^{-3})	2.399	2.405	2.424	2.382	2.568
μ (mm^{-1})	4.156	4.329	4.483	4.269	4.812
no. of reflns collected	48056	47597	46690	46460	31992
no. of independent reflns	21 019	22 512	20 924	21 162	22 339
θ range (deg)	2.99−25.00	3.00−26.00	2.99−25.00	2.99−25.00	1.46−26.00
GOF	0.947	1.033	1.147	0.974	1.024
R_1 [$I > 2\sigma(I)$]^a	0.0641	0.0454	0.0872	0.0531	0.0303
wR_2 (all data)^b	0.1288	0.1016	0.2708	0.1097	0.0761

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

X-ray Crystallography. Diffraction intensities for compounds **1**−**4** were collected on a Rigaku R-AXIS RAPID IP diffractometer (a Siemens Smart CCD diffractometer for **5**) with Mo Kα monochromated radiation ($\lambda = 0.71073$ Å) at 293 K. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Empirical absorption corrections were applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. All the hydrogen atoms for water molecules and protonation were not located but were included in the structure factor calculations. For all the compounds, the voids of the 2D frameworks are occupied by a large number of disordered lattice waters, which show many peaks of low electronic density in the difference Fourier maps. So the SQUEEZE subroutine of PLATON software[17] was applied to create new reflection data in which contributions from the disordered lattice waters were removed from the original data. The crystal data and structure refinement of compounds **1**−**5** on the basis of the new reflection data are summarized in Table 1. The number of lattice waters for **1**−**5** is determined by elemental analyses and calculations of electron count in the voids with SQUEEZE.

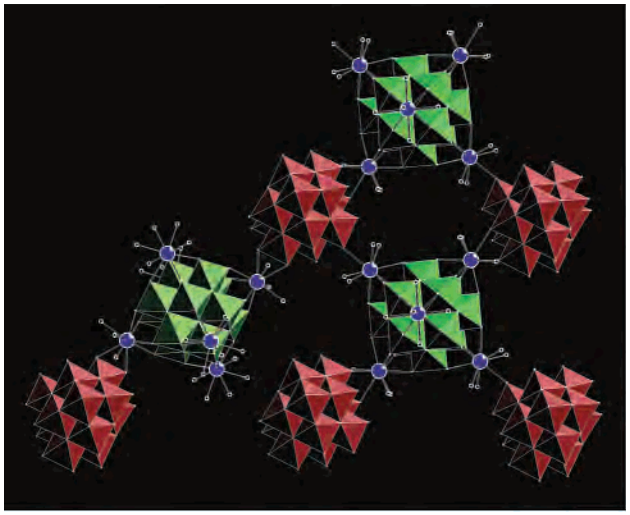

Figure 2. Perspective view of a segment of the 2D framework of **1** to illustrate the connection mode for the MnV_{13} cluster (dark red polyhedra) and the two types of MnV_{12} clusters (green polyhedra). Indigo and gray represent La and O atoms, respectively.

Results

For compounds **1**−**5** that are isomorphic with only slight differences in bond lengths and angles and the number of lattice waters, **1** is described as an example below. The asymmetric unit of **1** consists of one MnV_{13}, one-half of each of two MnV_{12} clusters, and six hydrated La^{3+}. (see the Supporting Information, Figure S1) The two Mn atoms in the two MnV_{12} clusters (Mn2, Mn3) are located on the inversion center position. Further studies reveal that **1** is a 2D polymeric structure, in which each MnV_{13} cluster in **1** is connected with three MnV_{12} clusters by three bridging hydrated La^{3+} cations. For MnV_{12} clusters, there are two types of coordination environments. One type of MnV_{12} cluster is connected with four MnV_{13} clusters by four bridging hydrated La^{3+} cations and capped by two additional terminal hydrated La^{3+} cations. The other type is connected with two MnV_{13} clusters by two bridging hydrated La^{3+} cations and capped by four additional terminal hydrated La^{3+} cations. (Figure 2) All the La^{3+} cations in **1** are coordinated by nine O atoms in distorted monocapped square-antiprism geometry. Four of the nine are terminal O atoms of one side of a MnV_{12} cluster and the others are either water molecules or the terminal O atoms of the MnV_{13} clusters. The La−O bond lengths range from 2.507(9) to 2.773(7) Å (see the Supporting Information, Table S1) and those for Mn−O and V−O bonds range from 1.833(8) to 1.913(7) Å and 1.582(7) to 2.422(7) Å, respectively (see the Supporting Information, Table S2). The connection of alternate MnV_{13} and

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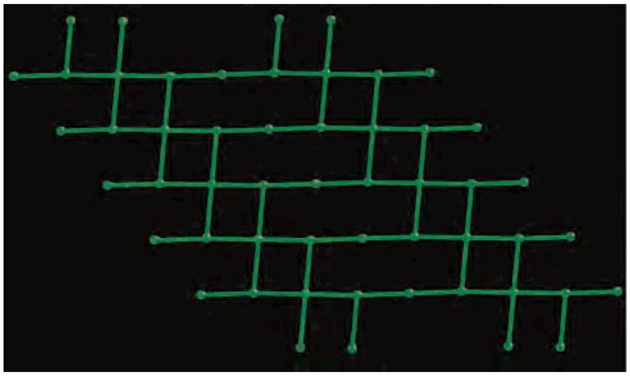

Figure 3. Schematic illustration of the 2D framework of **1** approximately along the [100] direction.

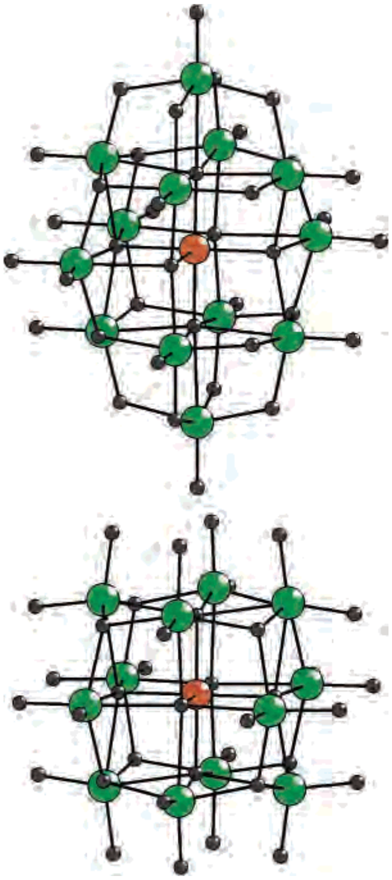

Figure 4. Ball and stick representation of the structures of cluster MV_{13} (up) and MV_{12} (down). Green, orange, and gray represent V, Mn (or Ni), and O atoms, respectively.

MnV_{12} clusters with hydrated La^{3+} cations forms a unique 2D framework. For perspicuous representation, each MnV_{13} cluster is represented as a 3-connected node, and the two types of MnV_{12} clusters are represented as 4-connected and 2-connected nodes, respectively. The 2D framework can be simplified as a brick-wall-like motif. (Figure 3) Parallel stacking of these 2D layers along the crystallographic [100] direction forms the three-dimensional structure. And along the [100] direction, there are two types of channels that are occupied by numerous lattice water molecules. The van der Waals free space of the channels per unit cell (after all the lattice water molecules have been hypothetically removed) is approximately 2417.1 Å^3, corresponding to 39.3% of the volume of the unit cell.[17]

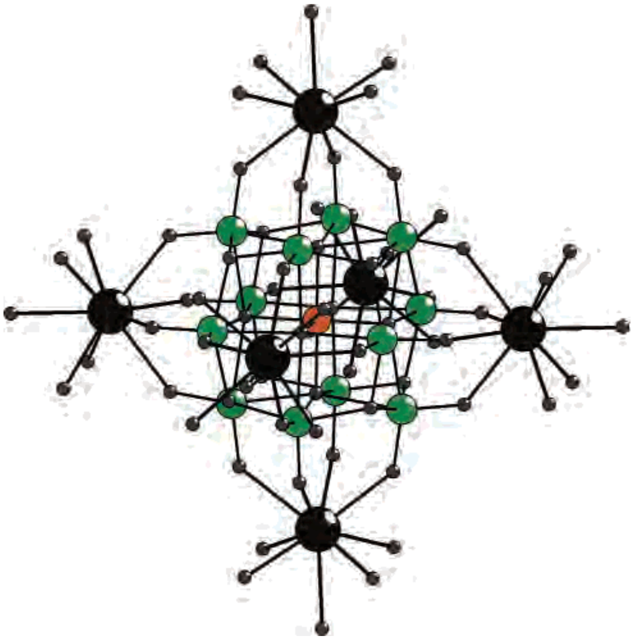

Figure 5. Ball and stick representation of MV_{12} cluster capped by six Ln^{3+} centers. Black, green, orange, and gray represent Ln, V, Mn (or Ni), and O atoms, respectively.

The bond-valence calculations[18] suggest that in **1**, all Mn atoms are in the +4 oxidation state and all V atoms are in the +5 oxidation state. The overall charge of all Mn, V, La, and O atoms in the formula obtained form the single-crystal structure determination is thus −1. The difference Fourier map reveals that there is no K ion present, which was further confirmed by elemental analyses. For the acidic synthetic condition for **1**, we presume that there are protonated O atoms. On the basis of the bond-valence calculations for all the O atoms in **1**, it is likely that two terminal O atoms of the MnV_{13} cluster (O13 and O15) are partly protonated. The bond-valence sums of the two O atoms (1.549 and 1.644) are less than that of other O atoms (1.736 to 2.132). Consequently, the formula of **1** was regarded as being $[La_6(H_2O)_{25}(MnV_{12}O_{38})(HMnV_{13}O_{38})]\cdot{\sim}31H_2O$. Similar results have also been obtained for compounds **2**−**5**.

Discussion

It is remarkable that in the compounds, the MV_{13} clusters are non-disordered, and a new type of cluster MV_{12} has been produced. Previous reported MV_{13} structures are disordered for random orientation of the anions.[12,16] The three VO_6 octahedra on the equatorial plan are statistically disordered at four sites around the apparent 4-fold axis. Here, the fact that the MV_{13} clusters are non-disordered in **1**−**5** may be attributed to the 2D polymeric structures formed by rigid Ln−O coordination bonds, which prevent the anions from orienting with randomness. Furthermore, from the solid-state structures, the reaction of MV_{13} anions and Ln^{3+} cations produces a new type of cluster, MV_{12}. To the best of our

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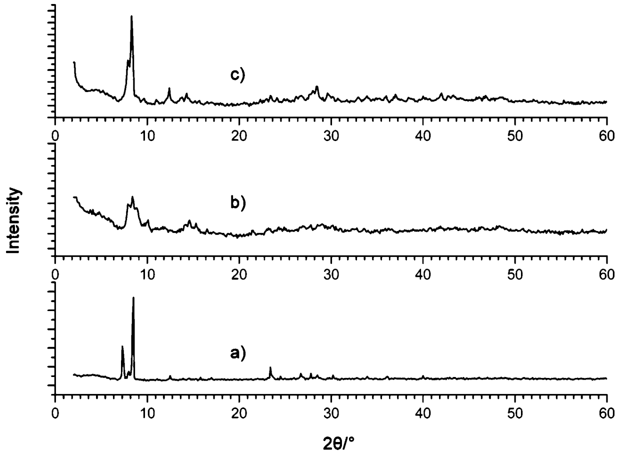

Figure 6. XRPD patterns for the (a) as-synthesized, (b) lattice-water-molecule evacuated, and (c) water re-adsorbed samples of **1**.

knowledge, there are no such clusters reported hitherto. The MV_{12} clusters are formed by 12 VO_6 octahedra entirely surrounding a central MO_6 (M = Mn, Ni) octahedron by edge-shared contacts. Comparing with the MV_{13} clusters, they lack two VO_6 octahedra at the two poles but have one more VO_6 octahedron at the equatorial plan. (Figure 4) Consequently, the C_{2v} symmetry for the MV_{13} turns to be O_h symmetry for MV_{12} clusters. The formation mechanism of the new clusters is not clear. However, the solid-state structures indicate that the emergence of the new type of cluster may be correlated to the six capping lanthanide cations surrounding it (Figure 5) with a stabilization effect, and it is more likely that cations $[\{Ln(H_2O)_5\}_6(MV_{12}O_{38})]^{6+}$ are the species in solution instead of naked anions $[MV_{12}O_{38}]^{12-}$. But the possibility that the MV_{12} anions are metastable species that are gradually formed in the process of crystallization cannot be excluded. Difficulties were encountered when we attempted to examine the ^{51}V NMR spectrum of the compounds for their low solubility. Further investigations for addressing the question ought to be conducted in future.

Stability Studies

To examine the stability of the 2D frameworks, we carried out thermal gravimetric (TG) analyses and N_2 sorption experiment for compound **1**. The TG curve shows that all the lattice water molecules (12.6%) can be removed up to 100 °C. However, the N_2 sorption experiment reveals that **1** exhibits low surface adsorption, with a Langmuir surface area 1.8396 $m^2\ g^{-1}$ after the sample was treated at 60 °C under a high vacuum condition. The result indicates that the compound loses its long-range order with the lattice waters removed. However, it is interesting that when the evacuated sample of **1** was exposed to atmospheric humidity at room-temperature overnight, its X-ray powder diffraction pattern (**XRPD**) demonstrated that the sample adsorbs water molecules and recovers the original structure with only some loss of crystallinity. (Figure 6)

Conclusion

In conclusion, we have synthesized five unusual 2D lanthanide heteropolyvanadates of manganese(IV) and nickel-(IV) that consist of MV_{13} and MV_{12} clusters and hydrated Ln^{3+} cations. The MV_{13} clusters here are non-disordered and they provide a more distinct mode for future investigations on this type of polyanion. The solid-state structures of these compounds also provide indirect evidence that the unique 1:12 heteropoly anions can be transformed from the 1:13 heteroploy anions at relevant conditions, which may be a promising way to synthesize the special structure type POMs. It is hoped that the MV_{12} clusters will be separated soon for further investigation.

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Supporting Information Available: Crystallographic data of **1**−**5** in cif format; TG curve, XRPD patterns, additional figures and tables related to compound **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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