

A two-dimensional framework of novel vanadium clusters bridged by $[\text{Ni}(\text{en})_2]^{2+}$: $\text{K}\{\text{V}_{12}^{\text{IV}}\text{V}_6^{\text{V}}\text{O}_{42}\text{Cl}[\text{Ni}(\text{en})_2]_3\} \cdot 8\text{H}_2\text{O}$

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Received 20th November 2002, Accepted 8th January 2003

First published as an Advance Article on the web 16th January 2003

The hydrothermal reaction of V_2O_5 , $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, en, KOH and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ gives a new two-dimensional open-framework solid; the extended structure consists of a two-dimensional network formed by the interconnection of each $[\text{V}_{18}\text{O}_{42}\text{Cl}]$ cage to four other neighboring units *via* six $[\text{Ni}(\text{en})_2]^{2+}$ bridging groups.

Polyoxovanadates constitute an important subclass of metal oxide cluster with an exceptional capacity to form mixed-valence compounds that exhibit rich electronic and magnetic properties and have relevance to catalysis, medicine, and materials science.¹ Polyoxovanadates have been extensively studied with many structurally characterized examples now known, such as $[\text{V}_5\text{O}_{14}]^{3-}$, $[\text{V}_6\text{O}_{19}]^{8-}$, $[\text{V}_{10}\text{O}_{28}]^{6-}$, $[\text{V}_{12}\text{O}_{32}]^{4-}$, $[\text{V}_{13}\text{O}_{34}]^{3-}$, $[\text{V}_{15}\text{O}_{36}]^{5-}$, $[\text{V}_{15}\text{O}_{42}]^{9-}$, $[\text{V}_{17}\text{O}_{42}]^{4-}$, $[\text{V}_{18}\text{O}_{42}]^{12-}$, $[\text{V}_{19}\text{O}_{49}]^{9-}$ and $[\text{V}_{34}\text{O}_{82}]^{10-}$.² Although polyoxovanadate clusters emerging as discrete ions are common, synthetically prepared examples of extended structures with polyanions are relatively rare. Some new mixed-valence vanadium oxide layers have also been observed in $[\text{Ni}(\text{en})_2][\text{V}_6\text{O}_{14}]$,³ $[\text{Zn}(\text{en})_2][\text{V}_6\text{O}_{14}]$, $[\text{Cu}(\text{en})_2][\text{V}_6\text{O}_{14}]$, $[\text{Cu}(\text{en})_2][\text{V}_{10}\text{O}_{25}]$,⁴ and $[\text{Cd}(\text{enMe})_2][\text{V}_8\text{O}_{20}]$.⁵ Khan *et al.* have reported several three-dimensional frameworks which consist of spherical $[\text{V}_{18}\text{O}_{42}(\text{XO}_4)]$ cages linked by bridging $[\text{M}(\text{H}_2\text{O})_4]$ groups ($\text{X} = \text{V}, \text{S}$; $\text{M} = \text{Fe}, \text{Co}, \text{Mn}, \text{Zn}$).⁶ We are currently undertaking a systematic investigation of polyoxovanadates of Group V transition elements in order to find the best strategies to design and synthesize metal oxide clusters with new and interesting structures. Herein, we report on an entirely new type of mixed-valence ion, $[\text{V}_{18}\text{O}_{42}\text{Cl}]^{7-}$, as a building block which is bridged by $[\text{Ni}(\text{en})_2]^{2+}$ leading to a two-dimensional network, $\text{K}\{\text{V}_{12}^{\text{IV}}\text{V}_6^{\text{V}}\text{O}_{42}\text{Cl}[\text{Ni}(\text{en})_2]_3\} \cdot 8\text{H}_2\text{O}$ **1** which is different to most known materials with extended structures composed of well-characterized metal oxo cluster types. †

The single crystal X-ray structure analysis ‡ revealed that the extended structure of **1** (Fig. 1) consists of a two-dimensional

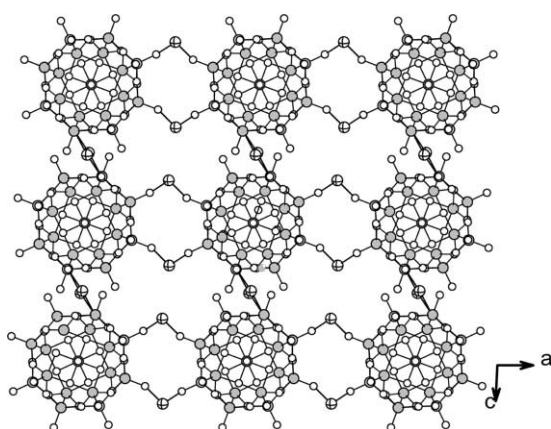


Fig. 1 View of the extended structure of $\text{K}\{\text{V}_{12}^{\text{IV}}\text{V}_6^{\text{V}}\text{O}_{42}\text{Cl}[\text{Ni}(\text{en})_2]_3\} \cdot 8\text{H}_2\text{O}$ showing the framework of $[\text{V}_{18}\text{O}_{42}\text{Cl}]$ clusters interconnected through $[\text{Ni}(\text{en})_2]^{2+}$ bridging groups like an undulating plane. For clarity H_2O , en and K^+ have been omitted.

network of $[\text{V}_{18}\text{O}_{42}\text{Cl}]$ cages, with each cage connected to four other neighboring units *via* $[\text{Ni}(\text{en})_2]^{2+}$ bridging groups. This generates a two-dimensional network of $[-\{\text{V}_{18}\text{O}_{42}\}-\{\text{Ni}(\text{en})_2\}-\{\text{V}_{18}\text{O}_{42}\}-]_n$. It is of interest to observe carefully the two-dimensional structure. Along the crystallographic *a* axis, the neighboring clusters are bridged by double $[\text{Ni}(\text{en})_2]^{2+}$ forming straight chains, while the neighboring structure units are bridged by one $[\text{Ni}(\text{en})_2]^{2+}$ along the *c* axis, constituting zigzag chains. To our knowledge, it is rare to observe such an extended structure.

The $[\text{V}_{18}\text{O}_{42}\text{Cl}]^{7-}$ unit is a novel type of polyoxovanadium ion, as shown in Fig. 2. The new vanadium cluster exhibits only

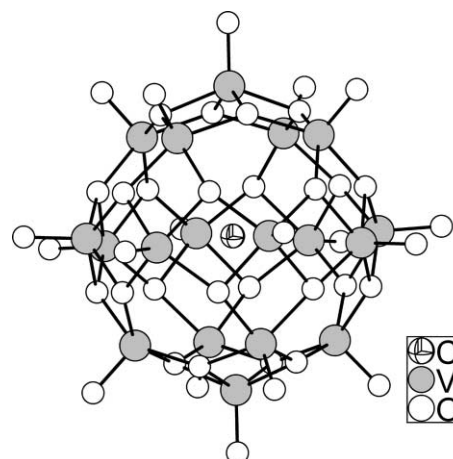


Fig. 2 Structure of the $[\text{V}_{18}\text{O}_{42}\text{Cl}]^{7-}$ anion showing the novel cluster. Selected distances (Å): V–O, 1.601(9)–1.613(5); V– μ -O (–Ni), 1.630(5)–1.641(5); V– μ_3 -O, 1.893(5)–1.958(5); Ni–O, 2.098(5)–2.17(10); Ni–N, 2.01(7)–2.18(7).

one type of coordination: tetragonal pyramidal V. The host shell constituted of $18\{\text{VO}_3\}$ square pyramids sharing edges through 24 μ_3 -oxygen atoms. All average bond lengths in this cluster are within normal ranges. The six-coordinated Ni is completed by four N of en and two O from two cluster units. What is more, each surface of the cluster supports six $[\text{Ni}(\text{en})_2]^{2+}$. Curiously, the $[\text{Ni}(\text{en})_2]^{2+}$, by corner-sharing with two cluster units through μ -oxo groups, leads to a two-dimensional network. The building block in the structure of **1** may be viewed as a 'basketball'-like $[\text{V}_{18}\text{O}_{42}]$ shell encapsulating a central Cl ion. Indeed, an unusual property of reduced polyoxovanadates is their tendency to form cages encapsulating a guest atom. Compound **1** represents a most unusual member of this class of clusters with the encapsulated Cl ion. In comparison with other $[\text{V}_{18}\text{O}_{42}]$ cages,⁶ all cages are found to have the center of XO_4 ($\text{X} = \text{V}, \text{S}$). To the best of our knowledge, the $[\text{V}_{18}\text{O}_{42}\text{Cl}]^{7-}$ cluster in **1** represents the first observation of an octadecavanadium structure with Cl^- at the center as a guest in polyoxovanadate chemistry.

The assignment of oxidation state for the vanadium are consistent with their coordination geometries and are confirmed by

valence sum calculations.⁷ Besides, the room temperature EPR spectrum of a crystalline sample of the compound exhibits a signal of $g = 2.15$, indicating the presence of V^{IV} . According to the results of EPR, bond valence sum calculations, charge balance and elemental analyses, compound **1** is formulated as $K\{V_{12}^{IV}V_6^VO_4Cl[Ni(en)]_3\} \cdot 8H_2O$.

Magneto-structural data of complex **1** and the $Ni(en)_2$ bridge allow us to foresee magnetic exchange coupling. The variable temperature magnetic susceptibility of **1** was measured between 5 and 300 K. While μ_{eff} for **1** increases with temperature, consistent with $\theta < 0$, showing weak antiferromagnetic exchange coupling, no suitable theoretical model is available in the literature⁸ for such a complex system, and further studies on magnetic properties and similar systems are therefore ongoing in our laboratory.

Hydrothermal techniques exploit the principle of "self-assembly" of a metastable solid phase from soluble precursors. Complex **1** is synthesized from V_2O_5 by exploiting the reducing ability of $H_2C_2O_4 \cdot 2H_2O$ and en . The presence of $H_2C_2O_4$ and en are absolutely essential to product formation. Under more reducing conditions the fully reduced V^{IV} clusters are isolated. V^{IV} and V^{IV}/V^V clusters tend to form spherical structures. This feature is evident in the class of reduced and mixed-valence polyoxovanadium as described by Zubieta *et al.*⁹ However, high dimensional results may originate from the natures of the transition metal ions employed. The nickel ion favors a six-coordinated octahedral geometry. It is noted that the pH values of the starting mixture have a big influence on the resulting products. The crystals of **1** can only be prepared in a system with pH values from 6.5 to 7.5. The $Ni-O-V$ linkages play a critical role in constructing the chain structure. One approach to resolving this question may be to employ preformed clusters at different pH values or to have some control of the organometallic components. Although the architecture of the two-dimensional network could not be predicted, its synthesis was reproducible.

This work was supported by the National Natural Science Foundation of China (20271021).

Notes and references

† Raw materials used in the synthesis were V_2O_5 , $H_2C_2O_4 \cdot 2H_2O$, KOH, $NiCl_2 \cdot 6H_2O$, en , and distilled water. In a typical synthesis of compound **1**, 0.68 g of V_2O_5 , 0.5 g of KOH and 1.24 g of $H_2C_2O_4 \cdot 2H_2O$ was first added to 12 mL of distilled water, to which 0.95 g of $NiCl_2 \cdot 6H_2O$ and 0.8 mL of en , were added with stirring. The reaction mixture (pH ~ 7.0) was sealed in a 20 mL Teflon-lined autoclave and heated under autogenous pressure at 160 °C for 4 days. The resulting crystalline product was filtered, washed with distilled water, and dried at ambient temperature to give 0.32 g of compound **1**. IR/cm⁻¹: 1591(s), 1452(w),

1398(m), 1277(w), 1121(w), 1098(w), 1013(m), 964(s), 688(m), 624(m), 518(w). Calc. for $C_{12}H_{64}N_{12}ClKNi_3O_{50}V_{18}$: C, 6.15; H, 2.73; N, 7.17; K, 1.64; Ni, 7.51; V, 39.08. Found: C, 6.23; H, 3.04; N, 7.28; K, 1.31; Ni, 7.63; V, 39.19%. Thermal analysis: the TGA of **1** showed that water was removed first, and the en molecule was removed at 250–469 °C and the weight gain at 469–589 °C was consistent with the oxidation from V^{IV} to V^V .

‡ Crystal data for $C_{12}H_{64}N_{12}ClKNi_3O_{50}V_{18}$ (**1**): $0.38 \times 0.18 \times 0.07$ mm, monoclinic, space group $C2/c$, $a = 12.799(3)$, $b = 27.717(6)$, $c = 21.096(4)$ Å, $\beta = 92.68(3)^\circ$, $V = 7475(3)$ Å³, $Z = 4$, $D_c = 2.083$ Mg m⁻³, $\mu(Mo-K\alpha) = 3.054$ mm⁻¹. The data were collected at 293 K using a Rigaku R-Axis RAPID diffractometer (graphite monochromated Mo-K α radiation; $\lambda = 0.71073$ Å, $1.47 \leq \theta \leq 27.48^\circ$) unique reflections were used to solve the structure by direct methods (SHELXTL-97) and refine it on F^2 by full-matrix least-squares techniques. At convergence, $R = 0.0490$ [$I > 2\sigma(I)$] and the goodness-of-fit on F^2 was 0.986 for 474 parameters and 16370 reflections, 8563 unique [$R(int) = 0.0319$]. The V(9), V(10), O(1) and O(2) have only an occupancy of 0.5 because of its special position, and Ni(2) has only an occupancy of 0.5 because of its splitting. All non-hydrogen atoms were refined anisotropically. CCDC reference number 187586. See <http://www.rsc.org/suppdata/dt/b211530c/> for crystallographic data in CIF or other electronic format.

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