A Three-Dimensional Framework of Novel Vanadium Clusters Bridged by $[Ni(en)_2]^{2+}$: $Ni(en)_3\{V^{IV}_{11}V^{V}_{5}O_{38}$ Cl [Ni (en)$_2]_3\}\cdot 8.5H_2O$

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The hydrothermal reaction of V_2O_5, $H_2C_2O_4\cdot 2H_2O$, KOH, en and $NiCl_2\cdot 6H_2O$ yields a new three-dimensional open-framework solid. The extended structure consists of a three-dimensional network of $[V_{16}O_{38}Cl]^{8-}$ cages, with each cage connected to six other neighboring units through $[Ni(en)_2]^{2+}$ bridging groups.

The systematic construction of specific architectures from molecular building blocks has been an area of active research over the past few years.[1] Examples range from coordination polymers [2] to larger cluster-based building blocks.[3] The mechanism of the formation of polyoxometalates (POMs) is still not yet fully understood and is often described as self-assembly. What appears to be evident in exploiting suitable molecular building blocks is to employ polyoxoanions linked through some kinds of tethers to form extended structures. While a synthetic method leading to rational design remains a challenging topic, there seems to be an increasing use of a combination of hydrothermal synthesis and structure-directing templates. Small changes in the synthetic technique, such as solvent, pH value or counterion, can lead to different products.[4] However, once structure principles are recognized, the synthesis of targeted species can be designed, as has been demonstrated by the work of Müller and co-works with the large polymolybdates. Zubieta and co-workers have reported one- and two-dimensional polymeric oxometalates in several organic-inorganic hybrid materials.[3a] On-going research has demonstrated that transition metal (e.g. Fe, Co, Ni, Cu, Zn, and Mn) coordination complexes may serve as inorganic bridging ligands linking polyanion clusters into one-, two- and three-dimensional networks.[5]

POMs are 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 in materials science.[6] Polyoxovanadates have been extensively studied, with many structurally characterized examples now known, such as $[V_4O_{12}]^{4-}$, $[V_5O_{14}]^{3-}$, $[V_6O_{19}]^{8-}$, $[V_{10}O_{28}]^{6-}$, $[V_{12}O_{32}]^{4-}$, $[V_{13}O_{34}]^{3-}$, $[V_{15}O_{36}]^{5-}$, $[V_{15}O_{42}]^{9-}$, $[V_{17}O_{42}]^{4-}$ and $[V_{18}O_{42}]^{12-}$, $[V_{19}O_{49}]^{9-}$ and $[V_{34}O_{82}]^{10-}$.[7] Although polyoxovanadate clusters emerging as discrete ions are common, synthetically prepared examples of extended structures with polyoxoanions are relatively rare. Some new mixed-valance vanadium oxide layers have also been observed in $[Ni(en)_2][V_6O_{14}]$,[8] $[Zn(en)_2][V_6O_{14}]$, $[Cu(en)_2][V_6O_{14}]$, $[Cu(en)_2][V_{10}O_{25}]$[9] and $[Cd(enMe)_2][V_8O_{20}]$.[10] Khan et al. have reported several three-dimensional frameworks which consist of spherical $[V_{18}O_{42}(XO_4)]$ clusters linked by bridging $[M(H_2O)_4]$ groups (X: V, S; M: Fe, Co, Mn, Zn).[5a] At present, we are making a systematic investigation of POMs of group V transition elements for finding the best strategies to design and synthesize metal oxide clusters with new structures. Here, we report an entirely new type of mixed-valence ion $[V_{16}O_{38}Cl]^{8-}$ as a building block, which is bridged by $[Ni(en)_2]^{2+}$ leading to the three-dimensional network $Ni(en)_3\{V^{IV}_{11}V^{V}_{5}O_{38}Cl[Ni(en)_2]_3\}\cdot 8.5H_2O$ (**1**). As far as we are aware, compound **1** is composed of a new type of mixed-valance vanadium-oxygen cluster $[V_{16}O_{38}Cl]^{8-}$ as structural motif, unlike most of the known materials with extended structures, which are composed of well-characterized metal-oxygen cluster types.

The X-ray structure analysis reveals that the extended structure of **1** (Figure 1), consists of a three-dimensional network of $[V_{16}O_{38}Cl]^{8-}$ cages, with each cage connected to six other neighboring units through $[Ni(en)_2]^{2+}$ bridging groups. This generates a network of $\{-[V_{16}O_{38}Cl]-[Ni(en)_2]-[V_{16}O_{38}Cl]-\}_n$ arrays running along two mutually non-perpendicular directions, so the overall topology of the six-connected network is simple cubic. The building block in the structure of **1** may be viewed as a "rugby ball"-like $[V_{16}O_{38}Cl]$ shell encapsulating a Cl^- ion at its center, as has been reported by Müller in the polyoxovanadate $[V_{15}O_{36}Cl]^{6-}$.[7g] Indeed, an unusual property of reduced polyoxovanadates is their tendency to form cages encapsulating a guest atom. To the best of our knowledge, there

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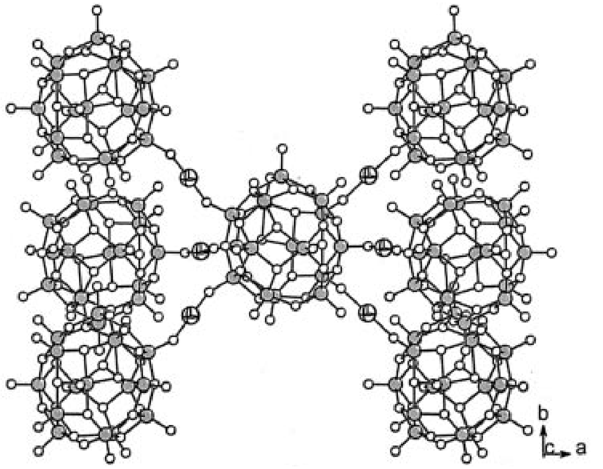

Figure 1. View of the extended structure of $Ni(en)_3\{V_{16}O_{38}Cl[Ni(en)_2]_3\}\cdot 8.5H_2O$, showing nets of $[V_{16}O_{38}Cl]$ clusters interconnected through $[Ni(en)_2]^{2+}$ bridging groups like reticular framework; H_2O, Cl^-, en and $[Ni(en)_3]^{2+}$ groups have been omitted for clarity

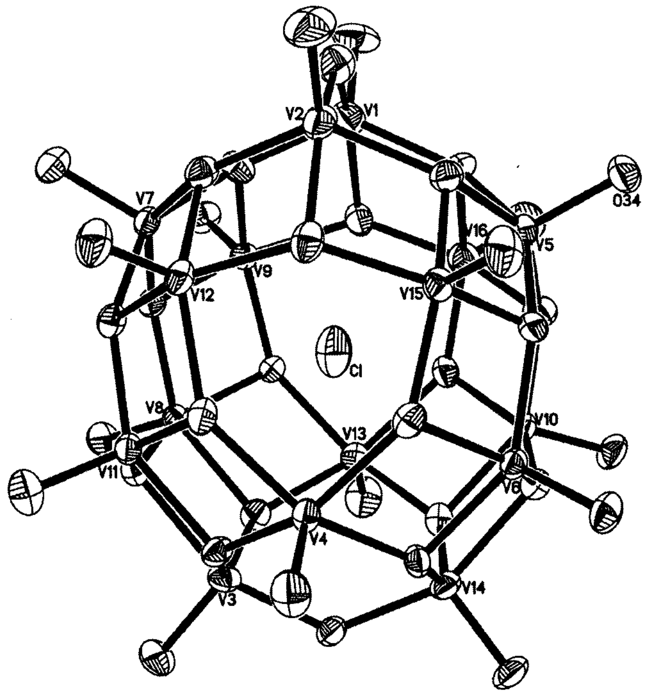

Figure 2. Structure of the $[V_{16}O_{38}Cl]^{8-}$ anion showing a novel cage; selected distances (Å) are as follows: $V-O_t$ 1.584(6)−1.619(6), $V-\mu_2-O(-Ni)$ 1.620(5)−1.641(6), $V-\mu_2-O(-V)$ 1.760(6)−1.898(7), $V-\mu_3-O$ 1.846(5)−2.242(5), Ni−O 2.062(6)−2.131(6)

are no examples where a $[V_{16}O_{38}Cl]$ cage forms a three-dimensional network by $[Ni(en)_2]^{2+}$ bridging.

The $[V_{16}O_{38}Cl]^{8-}$ unit is a novel type of polyoxovanadate cage, as shown in Figure 2. The new vanadium exhibits only one type of coordination i.e. pyramidal. The host shell is made up of 16 VO_5 square pyramids sharing edges through 20 μ_3-oxygen atoms, 8 μ_2-oxygen atoms, and 10 μ_1-oxygen atoms. All the average bond lengths in the cluster are within normal ranges.[7] Fivefold-coordinated VO_5 units are interconnected to form polyoxovanadate $[V_{16}O_{38}]$ units, and the environment around V1 is defined by three μ_3-oxygen groups, a μ_2-O, and an apical O1 moiety. Interestingly, O34 is also bonded to the Ni center of one of the six $Ni(en)_2$ bridges that interlink the other $[V_{16}O_{38}Cl]^{8-}$ clusters; the six-coordination of Ni^{2+} is completed by four N and two O atoms. Furthermore, each surface of the cluster supports six $[Ni(en)_2]^{2+}$ groups which connect different cages by μ_2-oxygen, leading to a three-dimensional network. To the best of our knowledge, the $[V_{16}O_{38}Cl]^{8-}$ cluster in **1** is the first observation of a hexadecavanadium structure containing an included Cl^- anion.

The assignment of the oxidation state of the vanadium is consistent with the coordination geometry and was confirmed by bond valence sum calculations (BVS).[11] The room temperature EPR spectrum of a crystalline sample of compound consists of one signal ($g = 2.002$), indicating the presence of V^{IV}. According to bond valence sum calculations and charge balance, compound **1** is formulated as $Ni(en)_3\{V^{IV}_{11}V^{V}_{5}O_{38}Cl[Ni(en)_2]_3\}\cdot 8.5H_2O$.

Each terminal oxygen of the six VO_5 pyramids (V5−V10) in compound **1** is linearly bonded to the nickel(II) center, in contrast to the $[M(en)_2][V_6O_{14}]$ (M = Cu, Zn)[9] structures where the V=O oxygen atoms of the VO_4 tetrahedron are bonded to the metal cations. The octahedral geometry around each nickel is completed by two en groups. The bridging Ni^{2+} ions exhibit strong covalent attachments to the two adjacent clusters with an average Ni−O distance of 2.087 Å, which is much shorter than that in $[M(en)_2][V_6O_{14}]$ (Cu−O: 2.53 Å; Zn−O: 2.54 Å).

The structure of highly reduced polyoxovanadate bridged by $[Ni(en)_2]^{2+}$ in the compound allows us to predict the existence of magnetic exchange coupling. The variable temperature magnetic susceptibility of **1** was measured between 5 and 300 K. The effective magnetic moment of **1** at room temperature (300 K), determined by the equation $\mu_{eff} = 2.83(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility per formula unit, is 8.72 μ_B, and is therefore smaller than the value expected for the total spin-only value of 11 uncoupled $S = 1/2$ spins of V^{4+} atoms and four uncoupled $S = 1$ spins of Ni^{2+} atoms. Figure 3 shows that the effective magnetic moment of **1** increases as the temperature decreases from 300 to 14 K, which is in agreement with a Weiss constant of $\theta > 0$, indicating the presence of a weak ferromagnetic exchange interaction in compound **1**. In the range 14−5 K, the effective magnetic moment decreases with the temperature decreasing, showing there is antiferromagnetic coupled interaction in **1** in this temperature range. Because no suitable theoretical model is available in the literature[12] for such a complex system, further studies on the magnetic properties of similar systems are ongoing in our lab.

Hydrothermal techniques exploit the principle of "self-assembly" of a metastable solid phase from soluble precur-

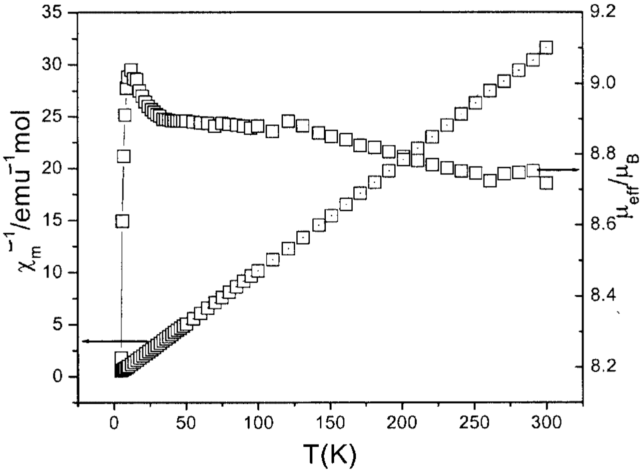

Figure 3. A plot of the effective magnetic moment μ_{eff} and inverse molar susceptibility vs. temperature for compound **1**

sors.[5b] 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 for product formation. Under more reducing conditions the fully reduced V^{IV} clusters are isolated. V^{IV} and V^{IV}/V^{V} clusters are cryptands and tend to form spherical structures. This feature is evident in the class of reduced and mixed-valence polyoxovanadates described by Zubieta et al.[13] However, this result may originate from the nature of the transition metal ions employed. The nickel ion favors a six-coordinate octahedral geometry. It should be noted that the pH value of the starting mixture has a big influence on the resulting products. Crystals of **1** can only be prepared in a system with pH values in the range from 8.5 to 9.5. The Ni−O−V linkages play a critical role in constructing the chain structure. Although the architecture of a one-, two- and three-dimensional network could not be predicted, we managed to synthesize the compound and obtain high productivity.

Experimental Section

Synthesis of 1: The raw materials used in the synthesis are 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**, 0.82 g of V_2O_5, 0.5 g of KOH and 1.24 g of $H_2C_2O_4{\cdot}2H_2O$ were first added to 12 mL of distilled water, and then 0.95 g of $NiCl_2{\cdot}6H_2O$ and 0.8 mL of en were added whilst stirring. The reaction mixture, with a pH value about 9.0, was sealed in a 20 mL Teflon-lined autoclave and heated under autogenous pressure at 160 °C for four days. The crystalline product was filtered, washed with distilled water, and dried at ambient temperature to give 0.46 g of **1**. IR: 1582(s) cm^{-1}, 1458(m), 1394(w), 1369(w), 1327(w), 1277(w), 1142(w), 1103(w), 1022(s), 967(s), 650(s), 512(s). $C_{18}H_{89}ClN_{18}Ni_4O_{46.5}V_{16}$ (2387.4): C 9.05, H 3.73, N 10.56; found C 7.36, H 2.08, N 12.94. The TGA of **1** showed that water is lost first, followed by the en molecules in the range 250−469 °C, and a weight gain at 469−583 °C, consistent with the oxidation from V^{IV} to V^{V}.

X-ray Crystallography: Crystal data for $C_{18}H_{89}ClN_{18}Ni_4O_{46.5}V_{16}$, dimensions 0.52 × 0.46 × 0.42 mm, monoclinic, space group $P2_1/n$, a = 21.953(4), b = 15.896(3), c = 25.086(5) Å, β = 109.39(3)°, V = 8258(3) $Å^3$, Z = 4, Dc = 1.920 g/cm^3, $\mu(Mo\text{-}K_\alpha)$ = 2.726 mm^{-1}, T = 293(2) K, $R[I < 2\sigma(I)]$ = 0.0754] and the goodness-of-fit on F^2 is 1.007.
CCDC-183112 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2000**, *39*, 3052−3054. [1b] M. J. Zaworotko, *J. Chem. Soc. Rev.* **1994**, 283−288.

[2] [2a] O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **1995**, *117*, 10401−10402. [2b] O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **1996**, *118*, 295−296. [2c] L. Carlucci, C. Gianfranco, D. M. Prosperio, A. Sironi, *J. Am. Chem. Soc.* **1995**, *117*, 12861−12862. [2d] L. R. MacGillivray, S. Subramanian, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1994**, 1325−1326.

[3] [3a] P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2638−2684 and references therein. [3b] D. E. Hagram, J. Zubieta, *J. Solid State Chem.* **2000**, *152*, 141−151. [3c] A. Müller, E. Krickemeyer, H. Bogge, M. Schmidtmann, F. Peters, C. Menke, J. Meyer, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 484−486. [3d] A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, P. Kogerler, B. Hauptfleisch, A. X. Trautwein, V. Schunemann, *Angew. Chem. Int. Ed.* **1999**, *38*, 3238−3241. [3e] B. T. Holland, P. K. Isbester, C. F. Blanford, E. J. Munson, A. Stein, *J. Am. Chem. Soc.* **1997**, *119*, 6798−6803.

[4] [4a] S. Subramanian, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2127−2129. [4b] B. J. S. Johnson, R. C. Schroden, C. Zhu, A. Stein, *Inorg. Chem.* **2001**, *40*, 5972−5978. [4c] R. W. Gable, B. F. Hoskins, R. Robson, *J. Chem. Soc., Chem. Commun.* **1990**, 1677−1678.

[5] [5a] M. I. Khan, *J. Solid State Chem.* **2000**, *152*, 105−112. [5b] J. Lu, Y. Xu, N. K. Goh, L. S. Chia, *Chem. Commun.* **1998**, 2733. [5c] W. M. Bu, G. Y. Yang, L. Ye, J. Q. Xu, Y. G. Fan, *Chem. Lett.* **2000**, 462−463. [5d] C. M Liu, D. Q. Zhang, M. Xiong, D. B. Zhu, *Chem. Commun.* **2002**, 1416−1417.

[6] [6a] M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34−48. [6b] A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239−271. [6c] A. Müller, *Nature* **1991**, *352*, 115−116.

[7] [7a] J. Fuchs, S. Mahjour, J. Pickardt, *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 374−375. [7b] V. W. Way, W. G. Klemperer, O. M. Yaghi, *J. Am. Chem. Soc.* **1989**, *111*, 4518−4519. [7c] H. K. Chae, W. G. Klemperer, V. W. Day, *Inorg. Chem.* **1989**, *28*, 1423−1424. [7d] V. W. Day, W. G. Klemperer, D. J. Maltbie, *J. Am. Chem. Soc.* **1987**, *109*, 2991−2992. [7e] V. W. Day, W. G. Klemperer, O. M. Yaghi, *J. Am. Chem. Soc.* **1989**, *111*, 5959−5960. [7f] D. Hou, K. S. Hagen, C. L. Hill, *J. Am. Chem. Soc.* **1992**, *114*, 5864−5865. [7g] A. Müller, E. Krickemeyer, M.

Penk, H. J. Walberg, H. Bögge, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1045−1046. [7h] D. Hou, K. S. Hagen, C. L. Hill, *J. Chem. Soc., Chem. Commun.* **1993**, 426−427. [7i] Y. Hayashi, K. Fukuyama, T. Takatera, A. Uehara, *Chem. Lett.* **2000**, 770−771. [7j] G. K. Johnson, E. O. Schlemper, *J. Am. Chem. Soc.* **1978**, 3645−3646. [7k] A. Müller, M. Penk, E. Krickemeyer, H. Bögge, H. J. Wallberg, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1719−1720. [7l] A. Müller, R. Rohlfing, J. Döring, M. Penk, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 588−590.

[8] B. Z. Lin, S. X. Liu, *J. Chem. Soc., Dalton Trans.* **2002**, 865−869.

[9] Y. Zhang, J. R. D. DeBord, C. J. O'Connor, R. C. Haushalter, J. Zubieta, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 989−991.

[10] L. Zhang, Z. Shi, G. Yang, X. Chen, S. Feng, *J. Chem. Soc., Dalton Trans.* **2000**, 275−278.

[11] I. D. Brown, *Structure and Bonding in Crystals*, Vol. 2 (Eds.: M. O'Keeffe and A. Navrotsky), Academic press, New York, **1981**.

[12] O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.

[13] M. I. Kahn, Q. Chen, J. Zubieta, *Inorg. Chim. Acta* **1993**, *212*, 199−206.

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