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Porous Crystal Formation from Polyoxometalate Building Blocks: Single-Crystal Structure of $[AlO_4Al_{12}(OH)_{12}(H_2O)_{24}][Al(OH)_6Mo_6O_{18}]_2((OH)\cdot 29.5H_2O$

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Low-temperature building block approaches to design and synthesize porous 3D crystals have been exploited employing a variety of building blocks mostly in the form of organic or organometallic molecules that can bind to metal ions[1] or form hydrogen bonds to other molecules.[2] Intuitively, clusters can be good candidates for this approach because of their discrete structures and solubility in solutions.[3] Indeed, there are some examples of porous 3D compounds in which clusters are coordinatively bonded to metal ions[4] and giant clusters are packed leaving some void spaces.[5] Toward this end, we have explored the reactions between polyoxometalate cluster ions and synthesized a nanocomposite gel composed of $[V_{10}O_{28}]^{6-}$ (V_{10}) and $[AlO_4Al_{12}(OH)_{12}(H_2O)_{24}]^{7+}$ (Al_{13}) clusters.[6] The clusters in this gel are compactly packed and show only a short range ordering. The reaction between the two clusters was too instantaneous to produce any crystalline materials. To grow sizable single crystals of insoluble compounds, a special method such as gel crystallization technique is used to control the reaction rate. The same effect can be achieved when one of the reagent clusters is formed during the reaction. Anderson-type $[Al(OH)_6Mo_6O_{18}]^{3-}$ ($AlMo_6$) clusters are reported to form when $[Mo_7O_{24}]^{6-}$ (Mo_7) is reacted with either $Al(OH)_3$ or Al_2O_3 at room temperature,[7] which property may be useful in growing single crystals of a $AlMo_6$-containing compound. We, therefore, have studied the reactions between Al_{13} and Mo_7 clusters. While in most of the reactions nanocomposites of Al_{13} and Mo_7 were formed,[8] we were able to obtain single crystals of a nanocomposite compound between Al_{13} and $AlMo_6$ clusters, $[AlO_4Al_{12}(OH)_{12}(H_2O)_{24}]$ $[Al(OH)_6Mo_6O_{18}]_2(OH)\cdot 29.5H_2O$, **1**, whose crystal structure and sorption properties are reported here. The novelty of this compound is manifold: It is the first nanocomposite between cluster ions that is well characterized including its single-crystal structure. It demonstrates that ionic interactions between clusters or particles can be utilized in designing new solid-state materials. The crystal structure gives some insight into the nature of ionic interactions between particles.

Single crystals of **1** were obtained by reacting Al_{13} and Mo_7 in an aqueous solution at room temperature. An Al_{13} solution ([Al] = 0.25M; pH 4.25) was prepared starting from $AlCl_3\cdot 6H_2O$ or $Al(NO_3)_3$ according to the literature,[9] and $(NH_4)_6[Mo_7O_{24}]$ was dissolved in distilled water to make a Mo_7 solution ([Mo] = 0.15M; pH 5.3). The Mo_7 solution was slowly added into that of Al_{13} with stirring. Immediate white precipitate of Al_{13}−Mo_7 nanocomposite was formed.[8] The solution pH instantly dropped to 2.9, slowly rose back to 3.6 in 15−20 min, and remained at this value. Colorless long rhombus crystals of **1** were grown from the solution by standing overnight with the precipitate in the solution.[10] The [Al]/[Mo] ratio in the solution was varied from 1/2 to 2, and only the reaction with [Al]/[Mo] = 1.25 yielded a large amount of compound **1**.

The crystal structure of **1**, determined by X-ray single crystallography, is shown in Figure 1.[11] The two building block clusters, Al_{13} and $AlMo_6$, can be identified in this figure. There are two types of crystallographically different but chemically identical $AlMo_6$ clusters; these will be called $AlMo_6$-I and $AlMo_6$-II. The structure can be described with layers formed by Al_{13} and $AlMo_6$-I clusters parallel to the *bc*-plane of the monoclinic unit cell and $AlMo_6$-II pillars between the layers. There is an empty space between the pillars to make intersecting 2D channels running parallel to the *bc*-plane. The channel dimension was estimated to be 3.1 × 5.9 Å^2 (A in Figure 1a) for the smallest and 6.2 × 3.9 Å^2 (B) for the widest cross-sectional areas,[12] comparable to those of zeolites.

The way the cluster ions are disposed with respect to the others conforms to the ionic bonding rules. For example, the cluster ions within the layer (Figure 1a) are packed to maximize the contacts between the oppositely charged ions. The faces of the platelike $AlMo_6$-I ions are almost parallel to those of the neighboring pseudotetrahedral Al_{13} ions.[13] At the same time, the close-packed oxygen layers on the faces of $AlMo_6$-I and Al_{13} are displaced from each other to minimize their mutual repulsion. Their relative arrangement is reminiscent of the packing of two close-packed layers.

The charges of the clusters found in the crystal structure do not balance and require an additional negatively charged species, which is determined to be OH^-.[14] The OH^- was located by inspecting the environments of the oxygen atoms of lattice water

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[1] (a) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651. (b)Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474 and references therein.

[2] Selected references: (a) Aakeroy, C. B.; Beatty, A. M.; Leinen, D. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1815. (b) Palmore, G. T. R.; Luo, T.-J. M.; McBride-Wieser, M. T.; Picciotto, E. A.; Reynoso-Paz, M. *Chem. Mater.* **1999**, *11*, 3315. (c) Papoutsakis, D.; Kirby, J. P.; Jackson, J. S.; Nocera, D. G. *Chem. Eur. J.* **1999**, *5*, 1474. (d) Ranganathan, A.; Pedireddi, V. R.; Chatterjee, S.; Rao, C. N. R. *J. Mater. Chem.* **1999**, *9*, 2407. (e) Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1999**, 1. (f) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.

[3] Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

[4] (a) Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775. (b) Beauvais, L. G.; Shores, M. P.; Long, J. R. *Chem. Mater.* **1998**, *10*, 3783. (c) Bowes, C. L.; Huynh, W. U.; Kirby, S. J.; Malek, A.; Ozin, G. A.; Petrov, S.; Twardowski, M.; Young, D.; Bedard, R. L.; Broach, R. *Chem. Mater.* **1996**, *8*, 2147. (d) Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807.

[5] (a) Mûller, A.; Serain, C. *Acc. Chem. Res.* **2000**, *33*, 2. (b) Müller, A.; Kögerler, P.; Kuhlmann, C. *Chem. Commun.* **1999**, 1347.

[6] Choi, H.; Kwon, Y.-U.; Han, O.-H. *Chem. Mater.* **1999**, *11*, 1641.

[7] (a) Carrier, X.; Lambert, J. F.; Che, M. *J. Am. Chem. Soc.* **1997**, *119*, 10137. (b) Ohman, L.-O. *Inorg. Chem.* **1989**, *28*, 3629.

[8] Son, J.-H.; Choi, H.; Kwon, Y.-U.; Han, O. H. To be submitted for publication.

[9] Johansson, G. *Ark. Kemi*. **1962**, *20*, 305.

[10] ICP elemental analysis. Calcd for $[AlO_4Al_{12}(OH)_{12}(H_2O)_{24}][Al(OH)_6Mo_6O_{18}]_2(OH)\cdot 29.5H_2O$ (in wt %): Al, 11.33; Mo, 32.24. Found: Al, 11.93; Mo, 34.55.

[11] Colorless elongated rhombic crystals of $[AlO_4Al_{12}(OH)_{12}(H_2O)_{24}]$ $[Al(OH)_6Mo_6O_{18}]_2(OH)\cdot 29.5H_2O$, **1**, were analyzed at 188(2) K: monoclinic, space group *C*2/*c* with $a = 28.2492(9)$ Å, $b = 15.7094(4)$ Å, $c = 24.4240(5)$ Å, $\beta = 102.337(1)°$, $V = 10588.5(5)$ Å^3, $Z = 4$, $d_{calc} = 2.169$ g·cm^{-3}, and μ_a (Mo $K\alpha$) = 1.636 mm^{-1}. Data were collected on a Siemens SMART CCD diffractometer utilizing graphite-monchromated Mo $K\alpha$ radiation. The positional parameters of the metal atoms and most of the cluster oxygen atoms were determined by the direct method (SHELXS-86). Several cycles of refinement and difference Fourier synthesis (SHELXL-93) revealed the other atoms including the lattice water and OH^- ion. Numerical absorption correction (DIFABS) was applied. The final least-squares refinement on 7810 reflections (F_o^2) with 745 variables and no restraints gave wR_2/R_1=0.1818/0.0703 ($I > 2\sigma$) and 0.1960/0.0824 (all data). All the atoms were refined anisotropically.

[12] The pore dimensions were calculated from the distances between the cluster oxygen atoms across the pore minus two of the van der Waals radii of oxygen (2 × 1.4 Å).

[13] The angle between the least-squares planes of the surface oxygen atoms of the Al_{13} and $AlMo_6$-I clusters was calculated to be 2.7(1)°.

[14] Looking into the procedure we have used, this anion could be Cl^-, NO_3^-, or OH^-. The first two possibilities could be ruled out based on several observations: The same crystals were obtained from reactions using either chloride or nitrate of aluminum, and the elemental analysis data on compound **1** showed no signal for Cl or N atoms.

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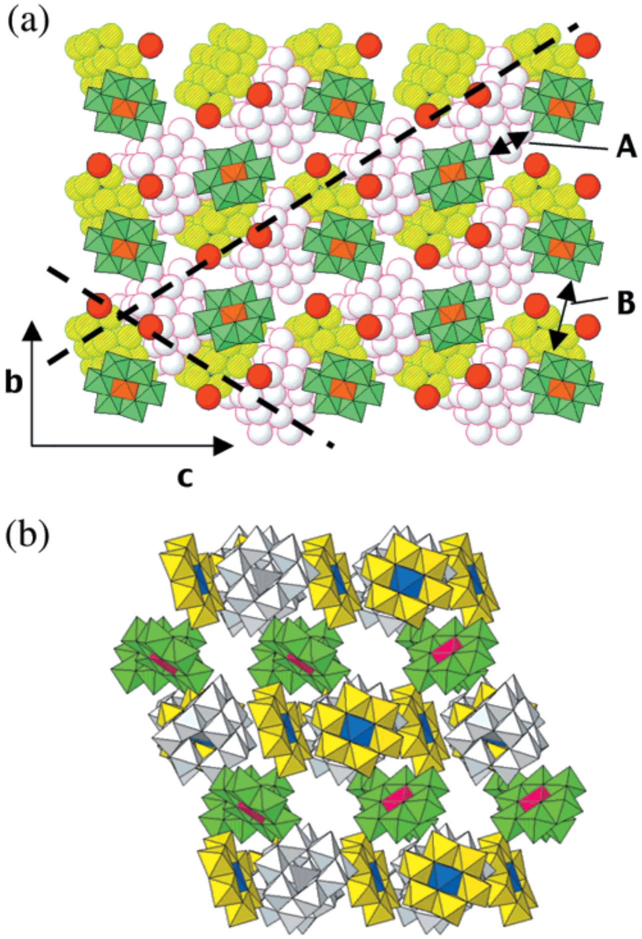

Figure 1. Crystal structure of compound **1**. (a) The layer composed of Al_{13} (white spheres) and $AlMo_6$-I (yellow spheres) clusters, shown by their surface oxygen atoms (radius of 1.4 Å), and the pillar $AlMo_6$-II (green polyhedra) and OH^- ions (red balls) on top of the layer. The two broken lines show the channel directions, and the two arrows indicate the smallest (A) and widest (B) openings. (b) A view along the channel direction. The Al_{13}, $AlMo_6$-I, and $AlMo_6$-II clusters are shown as white, yellow (blue for the central Al), and green (red for the central Al) polyhedra, respectively. The pores shown in this figure correspond to the smaller ones (A) of part a.

molecules found from the difference Fourier syntheses.[15] While the other oxygen atoms are in the vicinity of either type of cluster ions with distances of hydrogen bonds to the cluster oxygen atoms, this one does not have any direct cluster neighbors and is surrounded by the other water molecules (Figure 1a). The refined occupancy factor of 0.60(4) for this oxygen in a general position agrees well with the theoretical 0.5 to balance the charges of the clusters.

Thermogravimetric analysis (TG) on compound **1** under a flow of air (Figure 2) shows three major weight loss steps. The first step below 150 °C by 13.5% is due to the loss of lattice water. The second steps between 150 and 500 °C (15.5% loss in total) are due to the losses of H_2O and OH groups of Al_{13} and $AlMo_6$. The third step above 800 °C corresponds to the vaporization of MoO_3.[16] Powder X-ray diffraction (XRD) on a sample heated at 550 °C showed a pattern of $Al_2Mo_3O_{12}$,[17] with the remaining Al probably in the form of amorphous Al_2O_3 because of the low temperature. A sample from a 1400 °C heat treatment showed a XRD pattern of Al_2O_3, in agreement with the assignments for the weight loss steps.

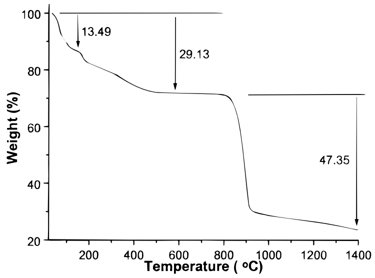

Figure 2. Thermogravimetric analysis data of compound **1**.

Our preliminary data indicate that compound **1** can undergo a few desorption and adsorption cycles. A vacuum-dried sample of **1** at room temperature showed only a residual 2% weight loss below 150 °C, indicating that most of the lattice water was lost under vacuum. When this dried sample was exposed to atmospheric humidity at room temperature overnight, water was readsorbed, as shown by the recovery of the 14% weight loss below 150 °C upon a second thermal treatment. Although vacuum-drying collapses the lattice and renders it amorphous, the original crystal structure is essentially recovered on rehydration (with some loss of crystallinity) as found by XRD experiments. The reason for these observations is not clear. It appears that the lattice water is necessary to hold the clusters in place and maintain the crystal structure.

There seem to be some requirements that need to be met to form porous nanocomposites from polyoxometalate clusters. The compact precipitates of $Al_{13}-V_{10}$ and $Al_{13}-Mo_7$ nanocomposites may be due to the charges of the clusters being close to each other. The crystal structure of compound **1** suggests that the clusters should have distinguished structures so that their packing can leave some void spaces between them. Most importantly, the in situ generation of $AlMo_6$ clusters appears to be the key for the synthesis and crystal growth of this compound. The crystals of **1** could not be obtained when the first precipitate was removed from the solution.

In conclusion, we have synthesized $[AlO_4Al_{12}(OH)_{12}(H_2O)_{24}][Al(OH)_6Mo_6O_{18}]_2(OH)\cdot 29.5H_2O$ and determined its crystal structure. This compound has some novel features including its nanocomposite nature, ionic bondings between clusters, porous structure, and sorption property. Because there are many cluster ions reported in the literature, other compounds of this type of architecture are highly possible that may find applications such as sorption materials and catalysts.

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Supporting Information Available: Crystallographic data for $[AlO_4Al_{12}(OH)_{12}(H_2O)_{24}][Al(OH)_6Mo_6O_{18}]_2(OH)\cdot 29.5H_2O$, including crystal structure analysis report, positional parameters, thermal parameters, and interatomic distances and angles and powder XRD patterns of pristine, vacuum-dried, and re-adsorbed samples of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The oxygen atoms of the lattice water molecules and the OH^- ion were located from the difference Fourier syntheses of the diffraction data. The water molecules are disordered within the channels with partial occupancy factors. The amount of the lattice water was calculated from their refined occupancy factors, and this value of 29.5 per formula unit agrees well with the ICP and the TG data.

(16) Calculated weight losses based on the crystal structure: 14.9%, $T < 150$ °C; 15.4%, 150 °C $< T <$ 450 °C, 48.4%, 800 °C $< T$.

(17) Harrison, W. T. A.; Cheetham, A. K.; Faber, J., Jr. *J. Solid State Chem.* **1988**, *76*, 328.