DALTON
COMMUNICATION

A novel polyoxometalate chain formed from heteropolyanion building blocks and rare earth metal ion linkers: $[La(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ †

Vaddypally Shivaiah,[a] Puram V. Narasimha Reddy,[a] Leroy Cronin *‡[b] and Samar K. Das *[a]

[a] *School of Chemistry, University of Hyderabad, Hyderabad, 500 046, India.*
E-mail: skdsc@uohyd.ernet.in
[b] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ.*
E-mail: L.Cronin@chem.gla.ac.uk

Received 22nd July 2002, Accepted 3rd September 2002

The structure of the complex $[La(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ is the first example of a 1D extended chain in which an Anderson type heteropolyanion is linked by rare earth metal ions in zig-zag chains that arrange "head to tail" in the structure; furthermore the chains are themselves linked into an extensive three-dimensional hydrogen bonded network.

Polyoxometalates, in addition to their importance in catalysis, biochemical separation and medicinal chemistry,[1] play an important role for the design of new designer materials with novel electronic, magnetic and topological properties.[2] Linking polyanion clusters in one-, two- and three-dimensions results in the construction of extended metal-oxide based materials from molecular building blocks. These clusters, which act as building blocks, have well-defined structures and include Anderson,[3] Keggin,[4] paradodecatungstate[5] anions, heteropolyanion of the type[6] $[UMo_{12}O_{42}]^{8-}$ and isopolyanions of the types[7,8] $[Mo_8O_{27}]^{6-}$, and $[Mo_{36}O_{108}(NO)_4(H_2O)_6]^{12-}$. However, such polyoxoanion clusters[4–8] (except Anderson type anions) show chain-like 1D structures sharing transition metal cation linkers which, in most cases, are mainly rare earth ions, whereby the polyanions act as ligands to form cation–anion complexes of increasing nuclearities. For instance, Anderson type anions are known to construct three- and two-dimensional framework structures[3a,b] sharing sodium and cobalt/sodium cation linkers respectively but never before the one-dimensional chain-like structure. In addressing this anomoly we have been trying to synthesise Anderson type anions that are linked in a more diverse manner. In this respect we report here the synthesis and structure of the first characterized compound containing an 1D chain of Anderson polyoxoanions: $[La(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ **1**. The novelty of this material lies in the fact that we have demonstrated, for the first time, an example in which an extended Anderson anion polymer is formed by the use of rare earth (transition) metal cation linkers. Therefore the use of such linkers offers the possibility for the design of polymeric ionic materials, based on molecular building blocks, to yield a solid-state material of a given composition and properties.

Compound **1** was synthesized by dissolving $La(NO_3)_3 \cdot 6H_2O$ (1.0 g, 2.31 mmol) in water (100 mL) followed by the addition of CH_3CO_2H (15 mL, 100%), $Na_2MoO_4 \cdot 2H_2O$ (3.5 g, 14.46 mmol) and $AlCl_3 \cdot 6H_2O$ (1.5 g, 6.21 mmol). The pH of the resulting solution was adjusted to 2.60 with nitric acid and the filtered solution kept in an open flask at room temperature for five days, after which time the solution afforded white block-shaped crystals of **1** (yield 0.8 g, 25% based on Mo). The crystals of **1** were characterized with energy dispersive spectroscopy microanalysis (EDS), thermogravimetric analysis, IR spectra § and single crystal X-ray diffraction. ¶

The structure of **1** is formed by Anderson type anions $[Al(OH)_6Mo_6O_{18}]^{3-}$ linked by La^{3+} ions to yield a polymer chain running parallel to the crystallographic *b* axis (Fig. 1).

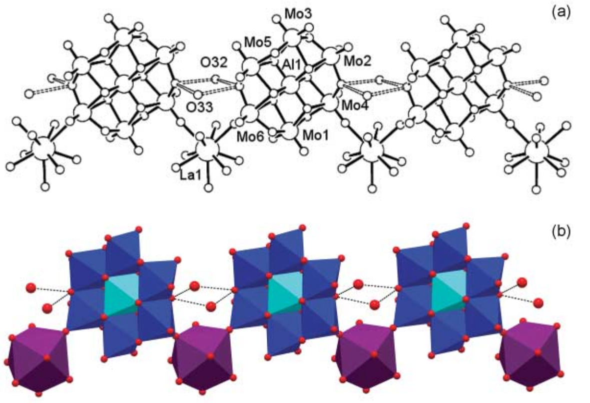

Fig. 1 (a) An ORTEP[12] representation showing the linked Anderson anions to lanthanum cations in a "head to tail" fashion. The Anderson anions are additionally linked through hydrogen bonding *via* O(32) and O(33) waters along the chain. (b) Polyhedral representation of the 1D "zig-zag" chain running parallel to the crystallographic *b* axis (colour code: La, purple; Mo, blue; Al, cyan; O, red).

The structure of the Anderson anion $[Al(OH)_6Mo_6O_{18}]^{3-}$ in **1** is similar to the structures reported for other Anderson type anions.[9] This consists of seven edge-shared-octahedra, six of which are Mo-octahedra arranged hexagonally around the central octahedron containing hetero metal ion, which is Al^{3+} in the present case (Fig. 1b). In the crystal strucure of **1**, molybdenum–oxygen distances as expected are divided into four groups: molybdenum–terminal oxygen, 1.68–1.73 Å; molybdenum–oxygen linked to lanthanum, 1.72 Å; molybdenum–bridging oxygen, 1.88–1.99 Å; molybdenum–internal oxygen common to two molybdenum atoms and an aluminium atom, 2.26–2.33 Å. In the polymer chain the Anderson anion acts as a bidentate ligand coordinating two lanthanum(III) ions through the terminal oxygen atoms (Fig. 1) of two non-adjacent MoO_6 octahedra.

In the chain, lanthanum(III) has a coordination number of nine and is in the centre of a tricapped-trigonal prism (Fig. 1b) formed by two terminal oxygen atoms from two $[Al(OH)_6Mo_6O_{18}]^{3-}$ units (average La–O 2.604 Å) and by seven water molecules (average La–OH_2 2.546 Å). The average bond length between the lanthanum cation and oxygen atom in **1** (2.56 Å) is

---

† Electronic supplementary information (ESI) available: representations of the structure of **1** with the atom numbering scheme and hydrogen bonding interactions shown and a list of relevant hydrogen bonding distances. See http://www.rsc.org/suppdata/dt/b2/b207149e/

‡ Previous address: School of Chemical Sciences, University of Birmingham, Birmingham, UK B15 2TT.

DOI: 10.1039/b207149e

comparable to the sum of the ionic radii for nine-coordinate La^{3+} and two-coordinate O^{2-} ions (2.566 Å).[10] Along the chain the lanthanum ions are well separated, with lanthanum–lanthanum distances longer than 11 Å (Fig. 1b).

Interestingly, these polymeric chains $[La(H_2O)_7Al(OH)_6Mo_6O_{18}]_n$, which are arranged parallel to the crystallographic *b* axis, are linked by an extensive hydrogen bonded network between the "zig-zag" polymer chains (Fig. 1) to a 2D network and then to a 3D network by hydrogen bonded interactions between the zig-zag layers (Fig. 2). This extensive hydrogen bonded network is constructed by the interaction of the water molecules coordinated to the lanthanum ion, the coordinated hydroxide ions of the central $Al(OH)_6$ moiety, and four solvent water molecules which all interact with the peripheral terminal and bridging oxygen atoms of the heteropolyanion.

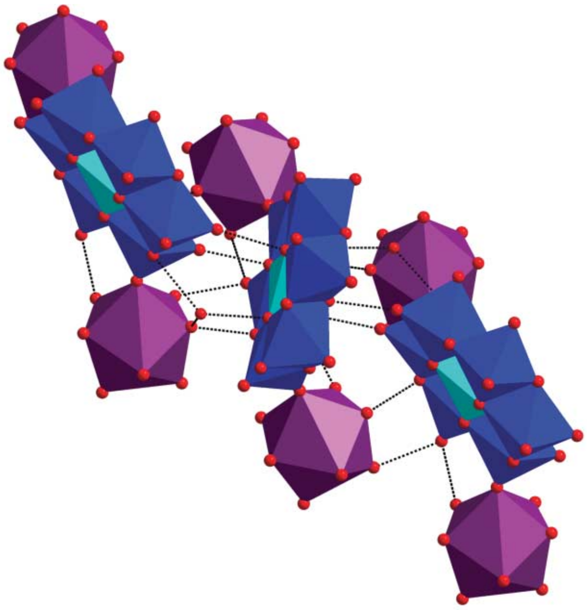

Fig. 2 Polyhedral representation of **1** showing a supramolecular 3D network, where lanthanum–Anderson anion chains are interlinked *via* hydrogen bonding (colour code: La, purple; Mo, blue; Al, cyan; O, red). Solvent waters are omitted for clarity.

Two of the crystal waters [O(32) and O(33)] connect two adjacent polyanions within the polymeric chain formed by the polyanions and the bridging lanthanum ion in a type of crab pincer like arrangement—see Fig. 1. In addition there are two further crystal waters [O(34) and O(35)], which are involved in hydrogen bonding, these are surrounded by four coordination polymer chains and assist in linking these chains together *via* hydrogen bonds into a three-dimensional network.

More specifically, the three coordinated hydroxides on each face of the heteropolyanion (O1 to O6) are involved in hydrogen bonded interactions (O···O distances range between 2.71–2.86 Å) both above and below the face of the anion which extend into a chain linking to the edges of two adjacent anions (and the faces of these anions connect to further edges and so on). These interactions are in addition to hydrogen bonded interactions between the lanthanide ions and polyanions above and below the same plane (O···O distances range 2.74–3.01 Å).

Intricate hydrogen bonded interactions between the base of the heteropolyanion (in one zig-zag chain) and the La^{3+} ion in the zig-zag chain directly below extend the network into a third dimension (distances range 2.74–3.01 Å). Examination of Fig. 2. demonstrates the head to tail configuration for the zig-zag chains.

This hydrogen bonding scheme suggests that the heteropolyanion chains, formed by La^{3+} linkers, running parallel to the crystallographic *b* axis are intersected by planes [containing O(34) and O(35) waters and associated hydrogen bonds] parallel to the crystallographic *ac* plane. These result in a three-dimensional supramolecular network. (No hydrogen atoms were located in the crystal structure. The hydrogen bonding discussion is based on O···O distances.) The results from the TGA analysis are in agreement with the number of water molecules/hydroxide ions present.

In summary, we have reported here for the first time a chain-like extended structure based on an Anderson type polyanion and a lanthanide cation linker. The construction of this material **1** from well-defined discrete building blocks provides the opportunity to synthesise a new class of 1D inorganic solids simply by replacing La^{3+} (in **1**) with other rare earth metal ions, Sm^{3+}, Eu^{3+}, Gd^{3+} *etc.*

We thank the University of Birmingham for access to the diffractometer and Bozid Menna for the TGA analysis.

Notes and references

§ The number of Al and La sites revealed by X-ray analysis is consistent with the result of EDS analysis, which gave an average value of Mo : Al of ≈6.0 and Mo : La of ≈6.0. Infrared data (cm^{-1}): 445(w), 661(vs), 840(m), 908(vs), 947(s), 1622(s), 3331(vs).

¶ Crystal data for **1**: $H_{28}AlLaMo_6O_{35}$, $M = 1329.75$ g mol^{-1}, orthorhombic, space group $Pca2_1$, $a = 11.844(2)$, $b = 11.010(2)$, $c = 22.643(5)$ Å, $V = 2952.7(10)$ Å^3, $Z = 4$, $D_c = 2.991$ g cm^{-3}, μ(Cu-Kα) = 32.618 mm^{-1}, $F(000) = 2520$, crystal size = 0.2 × 0.2 × 0.2 mm^3. A total of 5272 reflections ($3.90 < \theta < 70.60°$) were collected of which 5272 unique reflections ($R_{int} = 0.0502$) were used. Data were measured at 296(2) K on a Bruker SMART CCD 6000 diffractometer [λ(Cu-Kα) = 1.5418 Å], graphite monochromator, 3600 frames were recorded with an ω scan width of 0.3°, each for 10 s, crystal–detector distance 40 mm, collimator 0.5 mm. Data reduction by SAINTPLUS,[11a] structure solution using SHELXS-97[11b] and refined using SHELXL-97[11c] to $R = 0.0329$ for 5069 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. CCDC reference number 184859. See http://www.rsc.org/suppdata/dt/b2/b207149e/ for crystallographic data in CIF or other electronic format.

1 (*a*) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983; (*b*) M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; (*c*) Y. Izumi, K. Urabe and M. Onaka, *Zeolites, Clay, and Heteropoly Acid in Organic Reactions*, Kodanshal, Tokyo, 1992; (*d*) C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407; (*e*) T. Okumara, N. Mizuno and M. Misono, *Adv. Catal.*, 1996, **41**, 113; (*f*) C. L. Hill (ed.), *Chem. Rev.*, 1998, **98**, 1–389, special edition on polyoxometalates.

2 A. Müller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239.

3 (*a*) A. Perloff, *Inorg. Chem.*, 1970, **9**, 2228; (*b*) C. Rosu and M. H. Dickman, *Acta Crystallogr., Sect. C*, 1999, **55**, 11.

4 (*a*) M. Sadakane, M. H. Dickman and M. T. Pope, *Angew. Chem., Int. Ed.*, 2000, **39**, 2914; (*b*) J. M. Galan-Mascaros, C. Gimenez-Saiz, S. Triki, C. J. Gomez-Garcia, E. Coronado and L. Ouahab, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1460; (*c*) A. Müller, M. Koop, P. Schiffels and H. Bögge, *Chem. Commun.*, 1997, 1715.

5 C. Gimenez-Saiz, J. M. Galan-Mascaros, S. Triki, E. Coronado and L. Ouahab, *Inorg. Chem.*, 1995, **34**, 524.

6 V. N. Molchanov, I. V. Tatjanina, E. A. Torchenkova and L. P. Kazansky, *J. Chem. Soc., Chem. Commun.*, 1981, 93.

7 T. Yamase and H. Naruke, *J. Chem. Soc., Dalton Trans.*, 1991, 285.

8 (*a*) S.-W. Zhang, Y.-G. Wei, Q. Yu, M.-C. Shao and Y.-Q. Tang, *J. Am. Chem. Soc.*, 1997, **119**, 6440; (*b*) G. Liu, Y.-G. Wei, Q. Yu, Q. Liu and S.-W. Zhang, *Inorg. Chem. Commun.*, 1999, **2**, 434.

9 (*a*) H. Kondo, A. Kobayashi and Y. Sasaki, *Acta Crystallogr., Sect. B*, 1980, **36**, 661; (*b*) F. Ito, T. Ozeki, H. Ichida, H. Miyamae and Y. Sasaki, *Acta Crystallogr., Sect. C*, 1989, **45**, 946; (*c*) H. Y. Lee, K. M. Park, U. Lee and H. Ichida, *Acta Crystallogr., Sect. C*, 1991, **47**, 1959.

10 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

11 (*a*) SAINTPLUS, Software for the CCD Detector System, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998; (*b*) G. M. Sheldrick, SHELXS-97, Program for structure solution, University of Göttingen, Germany, 1997; (*c*) G. M. Sheldrick, SHELXL-97, Program for crystal structure analysis, University of Göttingen, Germany, 1997.

12 M. N. Burnett and C. K. Johnson, ORTEP, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.