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Journal Name

COMMUNICATION

Synthesis and characterization of the $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{8-}$: A new redox active heteropoly blue cluster with layered shape containing phosphite template that self-assembly under controlled microwave irradiation
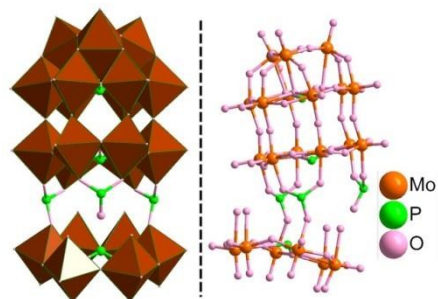
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The microwave-driven synthesis of a heteropoly blue cluster synthesis yields a redox active cluster, $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{8-}$, templated by six phosphite anions whereby two phosphites template a tri-lucunary {Mo$_{15}$} Dawson structure, and one templates a {Mo$_6$} ring with two of the three remaining phosphites acting as bridging ligands conencting the ring to the {Mo$_{15}$}.

In recent years, Polyoxometalates (POMs) have received extensive attention for their various structures, remarkable properties and wide investigations in many fields, such as host–guest chemistry, molecular devices and catalysis and medicine.[1] Of the class of POMs, heteropoly Blues (HB), are important subclasses which are deep blue mixed-valence molybdates or tungstates and are obtained by the one or more-electron reduction of the fully oxidised parent polyoxoanions containing M^{VI} (M = Mo or W) centers.[2] They have been intensely studied with respect to inter- and intramolecular electron transfer, mixed metal oxide conductivity, various types, mechanisms and pathways for mixed valence electron delocalization, electron spin coupling and paramagnetic spin-coupled systems, therefore various new applications are emerging based on this family of nano-clusters.[3] Generally speaking, the reduction of molybdate will give rise to metal oxide fragments that increase in nuclearity as the pH of the solution decreases. This means that the vast majority HB clusters are synthesised and isolated from complex "one-pot" reactions, and the synthesis a single given cluster is an ongoing challenge. The generation of the cluster fragments are diversified by tuning the synthetic variables such as concentration/type of metal oxide anion, pH and type of acid, type and concentration of electrolyte, heteroatom concentration, reducing agent, and other basic parameters

such as temperature and solvent.[1d]
Therefore the design of clusters is rather haphazard although there are some general strategies that can help in the isolation of new archetypes. For instance Cronin has pioneered the synthesis of HB clusters using a range of organo-cations, which effectively associate with the cluster superstructure helping direct the self-assembly process.[4] Consequently, the exploration of new technology such as microwave-assisted reactions may provide a new way to explore the chemistry. Microwave-assisted synthesis is fairly common in organic compound and inorganic materials synthesis including molecular sieves, nanoparticles and complexes, but surprisingly reactions of POM assembly have received little attention.[5] This is perhaps surprising since the synthesis of HBs normally uses solvent with high polarizability and clusters are highly charged and can be polar. Also, the superheating effect of using microwave heating may lead to novel products by permitting access to alternative kinetic pathways.[6] To our best knowledge, there are only very few examples of POM derivatives be synthesised under microwave irradiation, and all are coordination reactions between preformed lacunary cluster and active metal ions.[7] Herein we report the first HB cluster $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{8-}$ **(1a)** assembled from molybdates and phosphites under controlled microwave

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Fig. 1. Representation of the structure of the anion $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{8-}$ **(1a)**. Left: front-view in polyhedron mode. right: side-view in ball and stick mode. Mo = orange; P = green; O = pink. The H atoms are omitted for clarity.

irradiation which can be isolated and characterized as a DMA salt $(C_2H_8N)_8[(HPO_3)_6Mo_{21}O_{64}H_8]\cdot16H_2O$ **(1)** with two electrons reduced.

The cluster **1a** was synthesized in a microwave reactor after which dark blue crystals formed over a two-day period. It is worth noting that when the equivalent synthetic procedure is also carried out using traditional heating instead of microwave, did not result in the isolation of **1a**, but instead resulting in yielding the reduced Keggin Cluster $[PMo_{12}O_{40}]^{4-}$ **(2a)** as major product (see supporting information). The phosphite was oxidized to phosphate even in the presence of excess hydrazine, whilst part of Mo^{VI} is reduced to Mo^{V} in solution. Consequently, phenomenologically speaking, the use of microwave heating appears to facilitate the assembly of compound **1**. Furthermore, although the role is uncertain, the use of organic cations, organic solvent and reduce agents are essential for embedded phosphite in this molybdate oxide framework and stabilizing the cluster, as shown in scheme 1. T In the absence of the reducing agent, the formation of the well-known isopolyoxomolybdate framework $[Mo_8O_{26}]^{4-}$ is observed.[8] While the self-assembly behaviour of H^+-MoO_4^{2-}-$(HP)O_3^{2-}$ in acidic aqueous solution without organic cations has been documented and no cluster **1a** has been detected.[9a] although Cronin *et. al.* have recently published a paper describing the isolation of a phosphite embedded into a Dawson-like cluster.[9b]

Single-crystal structural analysis of **1** revealed that the cluster is a layered type cluster templated with a phosphite moiety. As shown in Fig. 1, the top part of the cluster is a $\{(HPO_3)_2Mo_{15}O_{42}\}$ which can be regarded as a tri-vacant Dawson-type heteropolyanion, with three $\{MoO_6\}$ units removed at the capping positions with HPO_3^{2-} central templates. This unit can also be considered as a layered building block containing a $\{HPMo_9O_{33}\}$ tri-vacant Keggin fragment and a $\{(HPO_3)Mo_6O_{18}\}$ unit. Both the P-H bond of the central $\{PO_3\}$ triangular pyramid templates are arranged so that they point towards the open-end of the building block with average P-O bond length of 1.52(1)Å. At the bottom part of the cluster there is another $\{(HPO_3)Mo_6O_{18}\}$ unit with a water ligand that is involved in a O…H-P interaction with the $\{HPO_3\}$ template located at the center of the cluster. The two parts are linked together by two oxo ligands shared from the phosphite moiety. The terminal oxo ligands that form a plane at the bottom of the Dawson-like part cluster with cuts the plane defined by the terminal oxyo ligands of the bottom $\{(HPO_3)Mo_6O_{18}\}$ part at an angle of ca. 19.46(2)°. to top unit and form the three layer cluster in a "L"
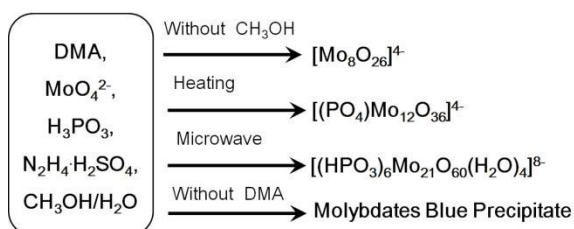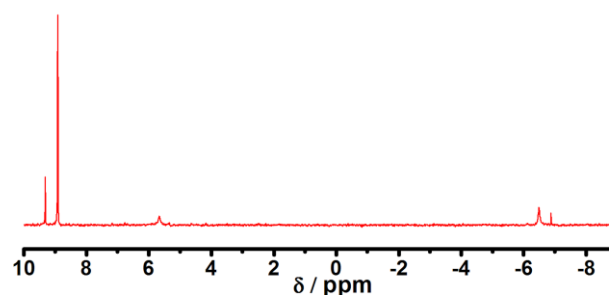
shape instead of the rod cluster as found in tungstotellurite.[10] Two of the HPO_3^- ligands act as linkers and the third one connects the top part by P-O-Mo bond and form a P=O with bond length of 1.48(1) Å. Electrochemical investigations show that **1a** is two an electron reduced HB, which is consistent with the BVS calculation.

Spectroscopic investigations of compound 1 shows an infrared P-O band at 1130 cm^{-1} and 1144 cm^{-1} belong to P^{III}-O stretching meanwhile the band at 1072 cm^{-1} and 1079 cm^{-1} belong to P-H bending (see fig. S8). Also, the thermogravimetric analysis of compound **1** confirms the water content within the crystal form (see fig. S10) The UV- visible spectrum shows a typical HB absorption at about 650 nm attributed to the intervalence charge-transfer optical absorption of HBs (see fig. S7).[2a]

The ^{31}P-NMR and ESI-MS are powerful ways to determine whether the cluster framework is maintained in solution and to probe the nature of the compounds in solution.[11, 12] The cluster can be detected in freshly prepared CH_3CN solution and three main peaks are observed at m/z 600.48, 907.07 and 1832.61 which can be assigned as $(C_2H_8N)_4H[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{3-}$, $(C_2H_8N)_2H_2$ $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{4-}$, and $(C_2H_8N)_2$ $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_3]^{6-}$ respectively (see fig. S3, S4). Due to the loss of the water ligands on the cluster, the main peaks are broadened and small fragments seen from the cluster are also detected. The proton-decoupled ^{31}P-NMR in CD_3CN exhibits five resonances at -6.88ppm, -6.49ppm, 5.66ppm, 8.91ppm, 9.31ppm respectively, which are consistent with the fact there are five different type of phosphite in **1a**. The signals at -6.88ppm, -6.49ppm may be attributed to two types of phosphite linker due to their low symmetric coordination modes, and the other three peaks are from the phosphite templates, and no free phosphite signal was detected. Additionally, when compound **1** is dissolved in D_2O it gives a blue solution, and the peaks associated cluster in ESI-MS are no longer seen. The proton-coupled ^{31}P-NMR spectrum of compound **1** exhibits two doublets as a result of phosphorus in two varieties which indicates the degradation of the cluster. The signal at δ10.4 ppm with $^1J_{PH}$ = 682.7Hz indicates the form of $\{HPMo_6O_{21}(H_2O)_6\}$ building block and the free $H(HPO_3)^-$ signal is observed at δ2.5 ppm with $^1J_{PH}$ = 627.5Hz, which is consist with previously report on the cluster containing similar building block.[13] (see fig. S2)

Scheme 1. Illustration of synthetic varies effect the formation of **1a** HB clusters. (DMA: Dimethylamine).

Fig. 2. Proton-decoupled ^{31}P-NMR spectra of compound **1** dissolved in CD_3CN. Number data are given in the text.

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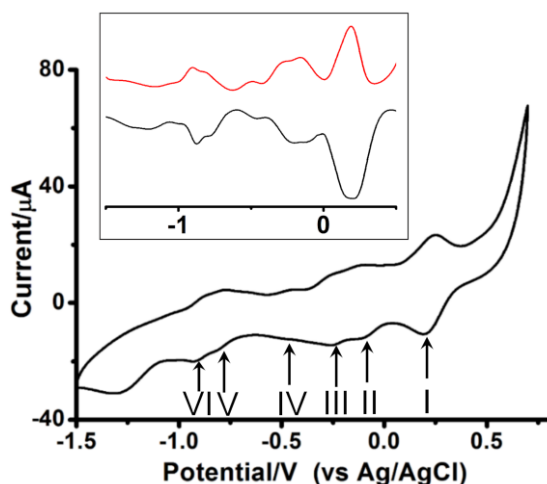
Fig. 3. Cyclic voltammograms and Differential pulse voltammetry (embedded) of 2.5×10^{-5} M solution of **1** in CH_3CN. The scan rate were $100 mV \cdot s^{-1}$. The working electrode was glassy carbon, the counter electrode was Pt wire, and the reference electrode was Ag/AgCl.

Further, the redox natures of this cluster are examined by cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) showing on its mix valences of compound **1**, six redox couples including an oxidation waves and five reduction waves were observed, as shown in Fig.3 and S5. The cluster can go through revisable two single electron oxidation processes with merged $E_{1/2}$ at 0.225V and further electrochemical oxidation may decomposed the cluster. Also, due to existence of the lacunary Dowson-like fragments, two single electron revisable reduction process most likely also observed in the potential range from 0V to -0.50V like the electrochemical behavior of the $[Mo_{18}O_{54}(SO_3)_2]^{4-}$ and other Dawson clusters.[14] The $E_{1/2}$ is -0.13V and -0.25V with $\triangle E_p \approx$ 60 mV and 56mV separately at 100mV/s scan rate. Because of the presence of protons and water ligands on **1a**, which can be involved in the redox process, when compound **1** is further reduced at more negative potential. Here, three more quasi-revisable redox processes are perceived with $E_{1/2}$ = -0.48V, -0.78V and -0.89V respectively and followed by an irreversible reduction.

Conclusions

In conclusion, a microwave-assistant method is utilized for HB synthesis for the first time and a new cluster $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{8-}$ was isolated and characterized. The synthetic study shows that microwave heating can be used to tune the assembly process of the molybdate, and the redox course of the precursor, which has demonstrated a new way to generate new redox active POMs. The stability and electrochemical study show that the cluster is a good candidate for specific reducing agent and electron storage, as well as a layered building precursor in target-designed synthesis of POMs, and related experiments are underway.

Notes and references

Elemental analysis (%) calc. for $C_{16}H_{110}N_8P_6Mo_{21}O_{98}$: C, 4.59; H, 2.65; N, 2.68; found: C, 4.60; H, 2.75; N, 2.61. IR (KBr, cm^{-1}): IR (KBr,cm^{-1}): 1620(m), 1462 (m),1130 (m), 1072 (m), 945 (s), 677 (m), 505(w).

Crystal data for $C_{16}H_{110}Mo_{21}N_8O_{98}P_6$ (1): M = 4183.68, triclinic, P-1, a = 13.5799(6) Å, b = 20.0897(9) Å, c = 23.0045(10) Å, α = 99.020(3), β = 90.469(3), γ = 107.358(2), V = 5906.0(5) Å^3, Z = 2, T = 296(2) K, D_c = 2.353 g/cm^3. 84891 reflections were measured on a Bruker Apex diffractometer, of which 22826 were unique (R_{int} = 0.0825) and 10990 were observed with I>$2\delta(I)$. Empirical absorption corrections were applied using the SADABS. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the Wingx software package. Final R-factors were: R_1 = 0.0733 for 22826 observed reflections, wR_2 = 0.2034 and GooF = 0.966 for all reflections with 1161 refined parameters. CCDC 1436128

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