Inorg. Chem. **2007**, *46*, 8469–8471

Inorganic Chemistry
Communication

Direct Evidence on the Existence of [Mo_{132}] Keplerate-Type Species in Aqueous Solution[†]

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Received June 1, 2007

We demonstrate the existence of discrete single molecular [Mo_{132}] Keplerate-type clusters in aqueous solution. Starting from a discrete spherical [Mo_{132}] cluster, the formation of an open-basket-type [Mo_{116}] defect structure is shown for the first time in solution using analytical ultracentrifugation sedimentation velocity experiments.

Giant polyoxomolybdates, especially the spherical [Mo_{132}] Keplerate[1]-type anionic clusters, have gained significant interest as cation carriers[2−4] and nanosponges[5,6] and for various other material science applications in the solid state.[7] Recently, it has been shown, also in the solid state, that it is possible to "open" such a [Mo_{132}]-type cluster to form a basket-like [Mo_{116}]-type defect cluster.[8] Although a significant volume of literature is available on these clusters in the solid state, their chemistry in solution has only been studied qualitatively.[9] Hence, questions arise: (1) Is it possible to demonstrate experimentally the existence of discrete single molecular [Mo_{132}] clusters in aqueous solution? (2) Can the opening of such a molecular [Mo_{132}] cluster to generate an open-"basket"-like [Mo_{116}] cluster be demonstrated in situ in aqueous solution? In this Communication, we address these questions for the first time.

To answer these questions, analytical ultracentrifugation sedimentation velocity (AUC SV) experiments were conducted on two model [Mo_{132}] clusters, **1** and **2**.

$$(NH_4)_{72}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(H_2O)_{72}(SO_4)_{30}]\cdot\text{ca. }280H_2O\ (\mathbf{1})^{10}$$

$$(NH_4)_{42}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(H_2O)_{72}(CH_3COO)_{30}]\cdot\text{ca. }300H_2O\cdot 10CH_3COONH_4\ (\mathbf{2})^{11}$$

Cluster **1** is less stable than **2** because **1** is more prone to oxidation. However, upon controlled oxidation, **2** is known to form a basket-like defect structure [Mo_{116}] with one missing [Mo_{16}] unit as compared to [Mo_{132}]. Therefore, we employed **1** and **2** as model systems for our experiments. More explicitly, we had the expectation that **1** will allow us to show the existence of discrete single molecular [Mo_{132}] clusters whereas **2** may show the coexistence of discrete [Mo_{132}] clusters and basket-like [Mo_{116}] structures (**3**) in solution. To date, the latter is isolated as crystals only.

$$(NH_4)_{46}[Mo^{VI}{}_{66}Mo^{V}{}_{50}O_{331}(CH_3COO)_{30}]\cdot\text{ca. }300H_2O\ (\mathbf{3})^{8}$$

All of these clusters are colored and hence can be monitored quantitatively by using AUC equipped with absorbance optics. Each cluster type has a distinct attenuance spectrum, and because the optical density at the wavelengths used here is linear with concentration, the absolute amounts can be determined from the attenuance. AUC has been used extensively for, among others, the analysis of protein−protein and protein−DNA/RNA interactions,[12,13] polymers,[14] oxo-

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10.1021/ic701076s CCC: $37.00

molybdates,[15] and even polyoxometalate-based dendrimers in solution.[16] The earliest AUC experiments on polyoxometalates[17] that we are aware of date back to 1950, where the sedimentation and diffusion coefficients of silicotungstate were determined in aqueous solution to critically and accurately test the AUC technique. In this test, the determined hydrodynamic radii agree well with crystallographic radii of the silicotungstates.[17]

For the AUC SV experiments, ca. 2.5 mM aqueous solutions were obtained by dissolving freshly prepared dried crystals of **1** and **2** in water (for experimental details, see the Supporting Information). To achieve a maximum signal-to-noise ratio, the absorbance maxima of **1** and **2**, with an attenuance between 0.6 and 0.9 OD, were matched with local emission maxima of the Xe flash lamp. The absorbance bands in the electronic absorption spectra of clusters **1** and **2** are in the region of 460−480 nm. The red-brown color of these clusters stems from a transition within the $[\mathrm{Mo^{V}}_2\mathrm{O}_4]^{2+}$ groups containing localized metal−metal bonds.[10,11] Clusters **1** and **2** share the same architecture with the icosahedral disposition of the 12 pentagonal $[(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}}_5\mathrm{O}_{21}(\mathrm{H_2O})_6]$ units linked by 30 $[\mathrm{Mo^{V}}_2\mathrm{O}_4(\mathrm{L})]$ linkers where L = $\mathrm{SO_4}^{2-}$ and $\mathrm{CH_3COO^-}$ for **1** and **2**, respectively. For our experiments, the absorbance at $\lambda = 459$ and 484 nm for **1** and **2** was monitored. An enhanced van Holde−Weischet analysis, as implemented in *UltraScan*,[18] was performed on the SV data to obtain the integral and the envelope of the differential sedimentation coefficient distributions.

The envelope of the differential sedimentation coefficient distribution for **1** shows the dominant abundance (ca. 96%) of a monodisperse species with a sedimentation coefficient of 8.7 S (Figure 1). We now ascertain the nature of this species using

$$s = \frac{M(1 - \bar{\nu}\rho)}{6\pi\eta r N} \qquad \text{(i)}$$

From the above equation using the crystallographic molecular weight M (accounting for the loss of 50 water molecules) of **1** as 28 237.2 g/mol,[10] the density of the solvent at 20 °C as 0.998 21 g/mL,[19] the partial specific volume $\bar{\nu}$ as 0.47 mL/g,[10] the viscosity of water η as 1.002 mPa s,[19] and the radius of the cluster r as 1.5 nm, the sedimentation coefficient is calculated to be 8.8 S. This s value corresponds to the rate at which the clusters would sediment in an aqueous solution at infinite dilution, provided that they exist as discrete molecular entities without any interparticle interaction (i.e., no electrostatic, hydrodynamic, and excluded volume effects) and that the single molecular composition as in the crystals is retained. The calculated and experimental values match. It demonstrates that in aqueous solution discrete single molecular clusters of **1** exist and their abundance is highly monodisperse.

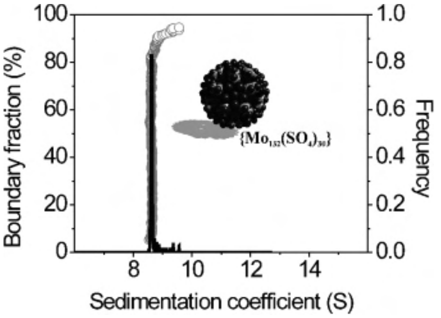

Figure 1. Sedimentation coefficient distributions for **1**. The envelope of the differential sedimentation coefficient distribution is shown with a continuous line (right *y* axis), while the integral is shown with open circles (left *y* axis). A space-filling representation (generated with DIAMOND 2.1 from Dr. K. Brandenburg, Crystal Impact GbR, 2001, and POV-Ray 3.5 freeware from C. J. Cason; same holds for Figure 2) of **1**[10] is further shown.

Having shown the monodisperse existence of discrete single molecular $[\mathrm{Mo_{132}}]$ clusters in aqueous solution, we now address our second question. Can we show the coexistence of the discrete $[\mathrm{Mo_{132}}]$ cluster (**2**) with its oxidized "open"-basket-like $[\mathrm{Mo_{116}}]$ (**3**)?

Assuming that both clusters **2** and **3** are spherical, the sedimentation coefficients for **2** and **3** are, according to eq i, 8.4 S ($M = 26\,456.2$, $\bar{\nu} = 0.457$, and $r = 1.5$ nm) and 7.5 S ($M = 23\,494.3$, $\bar{\nu} = 0.457$, and $r = 1.5$ nm), respectively. The friction coefficient f is not significantly increased upon removal of a cap from cluster **2** because it is likely that in aqueous solution the clusters are hydrated, resulting in a nearly overall spherical geometry. The sedimentation profiles of **2** revealed an interesting pattern. In contrast to **1**, the envelope of the differential sedimentation coefficient distribution is a broad Gaussian peak and reveals ca. 85% abundance of a species with a sedimentation coefficient of 8.1 S but without any peak at 8.4 or 7.5 S as calculated above (Figure 1). The broad distribution implies an abundance of a heterogeneous species in solution. This observed broad distribution, with a peak centered at 8.1 S, should be interpreted as an overall picture for two coexisting species in the solution. The two cluster types **2** and **3** are not resolved during the sedimentation velocity run and sediment but apparently as one fairly polydisperse species because the sedimentation coefficients are similar and both species have large diffusion coefficients. The fact that two species with similar particle densities have sedimentation coefficients of 7.5 and 8.4 S are not resolved can already be demonstrated by a finite element SV simulation for single non-interacting species. In line with our explanation and interpreting the broad peak in Figure 2 as a weight-average s value, the solution is comprised of ca. 67% of **2**, which sediments individually at 8.4 S, and ca. 33% of the defect open-basket-

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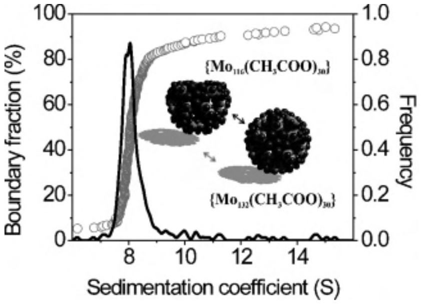

Figure 2. Sedimentation coefficient distributions for **2**. The envelope of the differential sedimentation coefficient distribution is shown with a continuous line (right *y* axis), while the integral is shown with open circles (left *y* axis). A space-filling representation of **2**[11] and a defect cluster **3**,[8] which may coexist in the solution, is further shown. Refer to the text for further details.

type structure **3**, which sediments individually at 7.5 S. [Mo_{132}] and [Mo_{116}] structures apparently coexist in solution almost in a ratio of 2:1, which is demonstrated for the first time in situ in solution. In fact, what we observe from our envelope of the differential sedimentation coefficient distribution for **2** is the following: the opening of a complete [Mo_{132}] cluster (**2**) to form, by the loss of a [Mo_{16}] cap, an open-basket-like [Mo_{116}] (**3**) during the course of oxidation. This observation is interesting in the sense that it offers the option to "open" a structure under mild conditions (i.e., aerial oxidation or in this case oxidation by dissolved oxygen during the run) and then to "close" it again by reducing agents. It would, in principle, be possible to study such a dynamic opening and closing of a structure in solution with options of ion transport.

Additionally, we also observe the presence of larger aggregates (ca. 12%) constituted of type **2** clusters, with a weight-average sedimentation coefficient of 11.7 S. These species might allude to aggregates or small superstructures that have been reported recently,[20,21] a detailed discussion of which is beyond the scope of the present Communication.

It is worth comparing and contrasting the behavior of the clusters **1** and **2** in aqueous solution. (1) Both of the clusters are essentially monodisperse. (2) The distribution of **1** is narrower than that of **2** because of the oxidation of **2**. (3) In the case of **1**, the clusters exist *only* as discrete [Mo_{132}], whereas in the case of **2**, the complete [Mo_{132}] cluster slowly gets oxidized under experimental conditions to form a more open-basket-like [Mo_{116}] structure. Structures **2** and **3** coexist in a ratio of approximately 2:1. (4) In contrast to **1**, the aqueous solution of **2** further points to the presence of larger aggregates (almost 12%). This suggests that cluster **2** spontaneously forms superstructures. However, the issue of superstructure formation requires further experimentation.

We have shown in this Communication that in aqueous solution of a [Mo_{132}]-type cluster discrete single molecular clusters exist. In the case of the cluster compound with acetate, in addition to discrete molecular clusters, we suggest that oxidation results in the opening of clusters to form an "open"-basket-type [Mo_{116}], which then coexists with a closed [Mo_{132}]-type cluster. Such a coexistence is shown for the first time in aqueous solution experimentally. Results of this study further imply that it is, in principle, possible to open and close these clusters by simple variation of the reducing conditions. It could also be possible to open and close these clusters, fill these clusters with cations, and monitor the entire phenomena in a fashion similar to that described here. These studies we believe can be further extended to understand the "uptake" and "release" of various cations involving these clusters and demonstrate the potential of AUC in studying intricate phenomena involving large inorganic clusters in situ as described here.

Acknowledgment. NWO/CW is thanked for financial support.

Supporting Information Available: Experimental details with instrument specification. This material is available free of charge via the Internet at http://pubs.acs.org.

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