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Supramolecular Structures of Polyoxomolybdate-Based Giant Molecules in Aqueous Solution

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Since the early explorations made by C. W. Scheele and J. J. Berzelius over two centuries ago, the nature of molybdenum blue solutions has remained a fascinating enigma for inorganic chemists.[1] While it is well-known that these solutions are prepared by partially reducing Mo^{VI} in acidic aqueous solutions, major breakthroughs in this field have only come in the past decade, when a series of giant polyoxomolybdate (POM) molecules were separated from various molybdenum blue solutions, beginning with the pioneering work of Müller and co-workers at University of Bielefeld. Various POMs, including some wheel-shaped and hollow, spherical "Keplerate" molecules, were synthesized by partially reducing Mo^{VI} to Mo^{V} via simple inorganic synthesis approaches.[2] The spherical "Keplerate" POM $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot ca.300H_20\cdot ca.10CH_3COONH_4$ ($\{Mo_{132}\}$) has a very similar structure to that of C_{60}. Moreover, the 60 Mo^{V} can be replaced by 30 Fe^{III} ions, leading to the formation of giant molecules ($Mo^{VI}_{72}Fe^{III}_{30}O_{252}L_{102}\cdot ca\cdot 180H_2O$ with L = $H_2O/CH_3COO^-/Mo_2O_{8/9}{}^{n-}$, $\{Mo_{72}Fe_{30}\}$) with novel magnetic properties (Figure 1).[2,3]

Despite this progress, the second part of the "molybdenum blue solution puzzle" remains unsolved. It was realized a long time ago that these water-soluble POMs usually did not exist as single ions in water or in other polar solvents. Instead, they tended to further aggregate into large spherical clusters with a relatively narrow size distribution, as shown by dynamic light-scattering (DLS) and scanning electron microscope (SEM) studies.[3] Depending on the nature of the solvent and the POM's chemical composition, the size of these aggregates ranged from tens to hundreds of nanometers. However, the structures of these aggregates remained unclear, preventing a further understanding of the fascinating solution behavior of the POMs. Although lacking direct evidence, Müller's et al. suggested that the aggregates might be hollow, on the basis of an SEM observation of a considerable amount of solvent inside the aggregates formed by a wheel-shape POM and on the fact that aggregates broke in a high-vacuum environment.[3]

In this communication, a detailed laser light-scattering (LLS) study on such aggregates in aqueous solution is reported, providing the first clear picture of the structure of these aggregates. Detailed study is focused on $\{Mo_{72}Fe_{30}\}$, because of its large size (2.5 nm) and light color, as well as the fact it shows the same aggregation behavior as that of the other POMs. The sample was prepared following the descriptions in the literature.[4] LLS technique has been widely applied in studying macromolecular and colloidal systems in solutions. However, it is difficult to use LLS to study single inorganic molecules because they are usually too small to be detected. This is even true for C_{60} molecules (0.71 nm in size). Here the first successful detection of single inorganic molecules by LLS is reported, along with their unique association behavior.

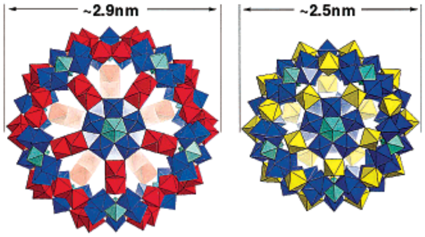

Figure 1. Structures of$\{Mo_{132}\}$ and $\{Mo_{72}Fe_{30}\}$ "Keplerate" giant molecules. Reprinted from ref 2, page 198, Figure 5, copyright 2001, with permission from Elsevier Science.

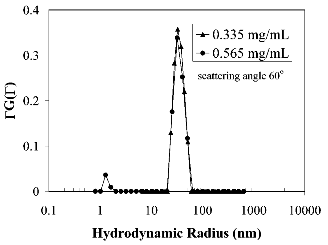

Figure 2. CONTIN analysis of DLS study on $\{Mo_{72}Fe_{30}\}$ aqueous solutions.

A commercial Brookhaven Instrument laser light-scattering spectrometer was used for the LLS experiments. It is capable of making measurements of both the angular dependence of absolute integrated scattered intensity (static light scattering, SLS), and the photon correlation (DLS, with a BI-9000 AT digital correlator). SLS experiments were performed at scattering angles between 10 and 150°, at 2° intervals. The CONTIN method[5] was used to analyze the first-order field correlation function $g^{(1)}(\tau)$ as determined by DLS. Then, the hydrodynamic radius (R_h) of the particles can be calculated from the characteristic line width Γ. DLS measurements also provide information on the particle-size distribution in solution from a plot of ΓG(Γ) versus R_h.

A typical CONTIN analysis from DLS study of $\{Mo_{72}Fe_{30}\}$ is shown in Figure 2, where two modes can be identified. The small peak has an average R_h of about 1.3 nm, corresponding to single $\{Mo_{72}Fe_{30}\}$ spheres. The small peak cannot be detected at low concentrations. The second peak also has a very narrow size distribution, with an apparent R_h of 32 nm, suggesting the formation of uniform aggregates in solution. Extrapolating the R_h value of the aggregates to zero concentration and zero scattering angle one obtains $R_{h,0} = 34.5 \pm 1.0$ nm. The size distribution of the aggregates is narrow, consistent with earlier studies. In addition, the weak angular dependence of the value of R_h suggests that the aggregates are mostly spherical, consistent with SEM results in early literature.[3]

The basis of the SLS data analysis is the Rayleigh−Gans−Debye equation: $H\cdot c/R_\theta = 1/M_w(1 + q^2\langle R_g^2\rangle/3)(1 + 2A_2c)$ with $H = 4\pi^2n^2(dn/dc)^2/N_A\lambda_0^4$ and $q = (4\pi n/\lambda_0)/\sin(\theta/2)$ where the Rayleigh ratio

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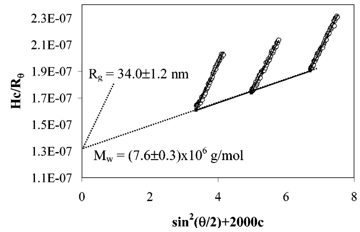

Figure 3. Zimm plot based on SLS measurements.

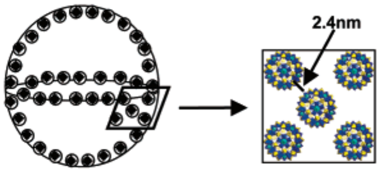

Figure 4. Schematic figure of the vesicle structure formed in $\{Mo_{72}Fe_{30}\}$ aqueous solution.

R_θ depends on the scattered intensity at different scattering angles θ, c, q, $\langle R_g\rangle^2$, A_2, n, N_A and λ_0 being the solute concentration, the magnitude of the scattering wave vector, the mean square radius of gyration of the particles, the second virial coefficient, the refractive index of the solvent, the Avogadro constant, and the wavelength of incident light in a vacuum, respectively. The refractive index increment (dn/dc) of $\{Mo_{72}Fe_{30}\}$ in H_2O was determined as 1.42 ± 0.01 mL/g. POMs are colorful, indicating possible absorption of the incident laser beam. Therefore, the adsorption coefficients of the solutions were measured by using an UV/visible spectrophotometer at 532 nm.

The SLS data was analyzed by using the well-known Zimm Plot, in which the experimental data was extrapolated to zero concentration, zero scattering angle (Figure 3). From the plot, it is determined that for the aggregates, $M_w = (7.6 \pm 0.3) \times 10^6$g/mol, and $R_g = 34.0 \pm 1.2$ nm. It is noteworthy that the R_g and $R_{h,0}$ values of the spherical aggregates are roughly the same. In contrast, for a solid spherical particle, $R_g = 0.77\ R_{h,0}$, i.e., ~26 nm for $\{Mo_{72}Fe_{30}\}$ aggregates. The ratio of R_g/R_h will rise if more mass in a sphere distributes closer to the surface. If the spherical aggregates have all their mass on their surfaces, $R_g/R_h = 1$. This is a typical model for a vesicle structure, as shown schematically in Figure 4.

Further evidence for this comes from the M_w of the aggregates. Considering that the $\{Mo_{72}Fe_{30}\}$ exists as anionic ions in aqueous solution, its "effective" molecular weight is ~12 700 Dalton. Thus, each aggregate has on average ~600 ± 25 $\{Mo_{72}Fe_{30}\}$ spheres. The small, soluble cationic counterions, water, and the CH_3COO^- ligands will not contribute to the total scattered intensity. It is a fact that ~600 $\{Mo_{72}Fe_{30}\}$ spheres are not enough to form 34-nm solid aggregates. In $\{Mo_{72}Fe_{30}\}$ crystal, there are 12 $\{Mo_{72}Fe_{30}\}$ spheres in each unit cell of 158.4 nm^3. Therefore, if the aggregates were $\{Mo_{72}Fe_{30}\}$ nanocrystals, each aggregate would contain ~12 500 spheres. This large discrepancy strongly suggests that the aggregates cannot be solid. Furthermore, 600 spheres are not even enough to form a 2-dimensional closed packing layer on the aggregates' surface (2530 spheres are needed for this). Assuming that the 600 $\{Mo_{72}Fe_{30}\}$ spheres are homogeneously distributed on the surface of the aggregates, the calculated closest distance between two adjacent spheres is ~2.4 nm, larger than the distance in single crystal (0.67 nm). Therefore, together with the evidence that $R_g = R_h$, we believe that the $\{Mo_{72}Fe_{30}\}$ aggregates in aqueous solution are vesicles formed by roughly one layer of $\{Mo_{72}Fe_{30}\}$ single spheres. The $\{Mo_{72}Fe_{30}\}$ spheres keep a certain distance with each other due to the electrostatic interactions. This conclusion can also explain why Müller et al. observed considerable amount of solvent existing inside the aggregates.

Vesicle structures are common for amphiphilic surfactants in a selective solvent. It is the free energy-favored structure when the solvent-phobic part of the surfactant is dominant, e.g., in the bilayer membranes. However, this is the first time that such a vesicle structure has been found in giant inorganic molecular systems. Also, the formation mechanism here will be different from that of surfactants because the $\{Mo_{72}Fe_{30}\}$ molecules do not have any hydrophobic parts. Thus, the driving force for the supramolecular structure formation may be due to electric interactions. The $\{Mo_{72}Fe_{30}\}$ spheres are negatively charged in water, and the charge−charge interaction among the spheres in colloidal size tends to aggregate, similar to the behavior of polyelectrolytes. However, the $\{Mo_{72}Fe_{30}\}$ spheres also contain a lot of H_2O ligands on their surfaces, which prefer a hydrophilic environment. A vesicle structure could ensure the maximum percentage of $\{Mo_{72}Fe_{30}\}$'s hydrophilic surface is still exposed to water. And this hydrophilic interaction is strong enough to compensate the solute−solute interaction so that the $\{Mo_{72}Fe_{30}\}$ spheres do not further aggregate and precipitate.

Studies on other spherical POM systems, including a very large one just discovered,[6] showed very similar results. It is possible that the vesicle structure should be considered a general self-assembly structure for POM-based giant molecules in polar solvents. The large size of POMs compared to solvent molecules and the moderate amount of charges on them should be important factors for the vesicle formation. For large, heavily charged colloidal particles, they tend to aggregate into large aggregates and precipitate due to strong solute−solute interactions. Therefore, the POM's vesicle structure could represent a unique stable supramolecular structure in polar solvents when solutes have certain sizes and charges.

Since these aggregates are not nanocrystals, they cannot be used as "seeds" for the single-crystal growth from solution. It is reasonable to postulate that crystal growth should start with single molecules that coexist with vesicles. And there should be equilibrium between them.

In summary, a combination of SLS and DLS is used to clarify the nature of large aggregates formed by $\{Mo_{72}Fe_{30}\}$ in aqueous solution. The results indicate that the aggregates are vesicles, formed by a loose packing of a single layer of $\{Mo_{72}Fe_{30}\}$ spheres. These vesicles coexist with single $\{Mo_{72}Fe_{30}\}$ molecules. These conclusions present a clearer picture to the long-time unsolved enigma of molybdenum blue solution. More detailed study is under way.

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