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A Polyoxometalate–Cyanometalate Multilayered Coordination Network

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Supporting Information

ABSTRACT: The reaction of the ε-Keggin polyoxometalate (POM) $[PMo_{12}O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5+}$ with $Fe^{II}(CN)_6{}^{4-}$ under typical bench conditions at room temperature and ambient pressure has afforded the novel $[\varepsilon\text{-}PMo_{12}O_{37}(OH)_3\{La(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]$ network, which exhibits a three-dimensional multilayered structure. The compound has been fully characterized by synchrotron-radiation X-ray crystallography, IR spectroscopy, elemental analysis, and thermogravimetric analysis. This coordination network constitutes the first example of a cyanometalate bonded to a POM unit.

Polyoxometalates (POMs) are molecular metal–oxygen clusters that have received much attention because of their numerous applications in domains ranging from catalysis to molecular magnetism.[1] Although most of the POMs identified to date still consist of discrete molecules, the number of POM-containing multidimensional infinite species is growing steadily, from organometallic networks where POM units act as noncoordinating templates[2] to systems directly incorporating covalently bonded POMs. Among the systems with direct POM coordination, a large variety of architectures have been described over the years, most of them synthesized under hydrothermal conditions. Although condensation of clusters of polyoxomolybdates or polyoxovanadates via intermolecular oxo bridges has been reported,[3] the linkages are more often provided by transition-metal[4] or lanthanide complexes;[5] because of their potential to combine magnetic and luminescent properties, lanthanide-containing POMs look especially attractive. Recently, metal–organic frameworks built from POM clusters and polycarboxylates have been characterized as well,[6] with some of them being electrocatalytically active.[6a] At the same time, since the discovery of magnetic ordering with a high Curie temperature in Prussian blue analogues,[7] hexacyanometalate- and octacyanometalate-based multidimensional complexes have been extensively studied. They exhibit fascinating behaviors such as photomagnetism,[8] light-, electric-field-, or temperature-induced phase transition,[9] or chemically sensitive magnetism.[10]

However, to the best of our knowledge, an assembly combining a cyanometalate complex with a POM entity had yet to be reported. One reason may be that cyanometalates are not particularly stable under hydrothermal conditions. In the present study, we synthesized a multilayered coordination network, $[\varepsilon\text{-}PMo^V{}_8Mo^{VI}{}_4O_{37}(OH)_3\{La(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]\cdot 12H_2O$ (**1**), built from the mixed-valent ε-Keggin POM $[\varepsilon\text{-}PMo^V{}_8Mo^{VI}{}_4O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5+}$ (written as $\{PMo_{12}La_4\}$) and hexacyanoferrate(II). This compound has been characterized by single-crystal X-ray crystallography using a synchrotron beam, Fourier transform infrared spectroscopy (FTIR), diffuse-reflectance UV–vis spectroscopy, elemental analysis, and thermogravimetric analysis (TGA).

To prepare a cyanometalate–POM hybrid at room temperature, selection of a suitable POM precursor is highly important. Indeed, multidimensional POM networks synthesized under ambient conditions have previously been reported, but only with strongly binding ligands such as oxalate,[11] where charge repulsion between both the negatively charged ligand and the POM is not much of an issue. In contrast, coordination of the weakly binding hexacyanoferrate has proven a greater challenge. Hence, to negate charge repulsion, we had to choose one of the few positively charged POMs reported so far, the $\{PMo_{12}La_4\}$ cluster, which was first identified by Sécheresse et al. nearly 10 years ago[12] and has recently been proven as an efficient Lewis acid catalyst.[12b]

Compound **1** is quickly and easily obtained at room temperature by reaction in water of $\{PMo_{12}La_4\}$ with a sodium hexacyanoferrate(II) solution [see the Supporting Information (SI) for details]. It precipitates as a red-brown powder of low crystallinity, with a good yield (above 80%). This powder proved to be completely insoluble in all common solvents. Slow diffusion of the same POM and hexacyanoferrate solutions in an H-shaped tube carefully filled with water affords small deep-red platelike single crystals, which are air-stable and suitable for X-ray diffraction, after about 1 week. The FTIR spectrum of **1** features, as expected, two distinct C≡N stretching vibration bands at ν = 2056 and 2026 cm^{-1}, which are likely to correspond to bridging and terminal cyanide ligands, respectively. In the 1200–700 cm^{-1} region, the P–O and Mo–O vibrational bands characteristic of the $\{PMo_{12}La_4\}$ core are retained (Figure S1 in the SI).[12] When taken out of the reaction medium, the crystals are stable to air for at least several weeks. Because of the small size of the single crystals of **1**, X-ray diffraction using a synchrotron beam (λ = 0.6889 Å) of the High Energy Accelerator Research Organization (KEK) was needed to determine the structure (see the SI). The unmodified $\{PMo_{12}La_4\}$ blocks are assembled in two-dimensional zigzag layers via the hexacyanoferrate complexes after a water molecule from each La^{III} center has been substituted by a

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N atom of a cyanide bridge (Figure 1). Similar to what had previously been observed for several $\{PMo_{12}La_4\}$/polycarboxylate species,[6c] the coordination number of those centers has changed from 7 in the isolated POM to 9 in the multidimensional network.

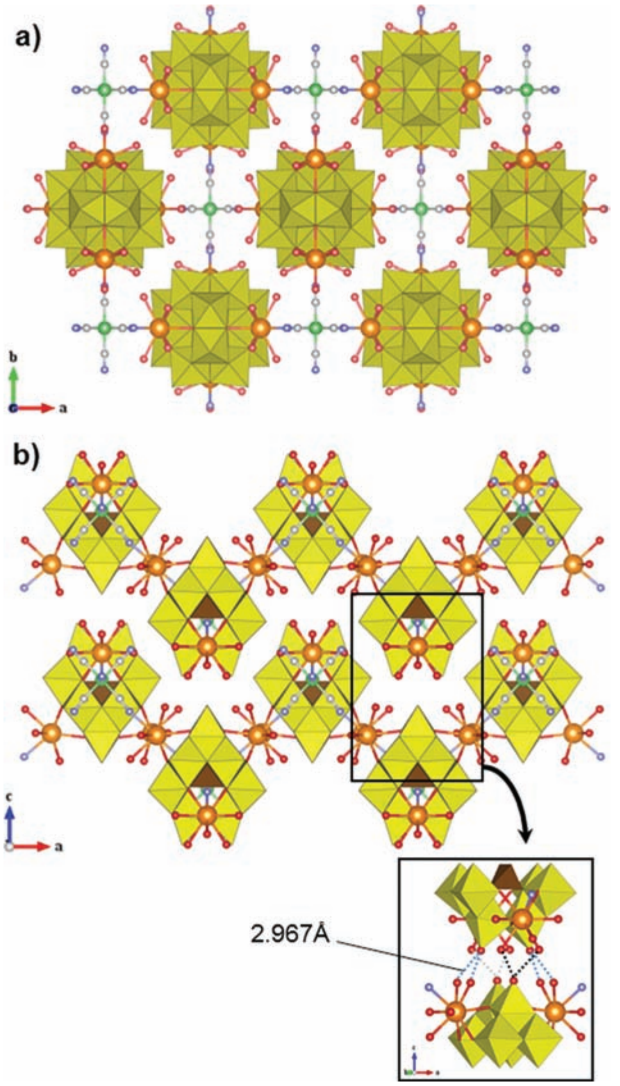

Figure 1. (a) View of **1** along the *c* axis, showing a single $\{PMo_{12}La_4Fe(CN)_6\}_n$ layer. (b) View along the *b* axis showing the three-dimensional packing of the successive $\{PMo_{12}La_4Fe(CN)_6\}_n$ layers. Inset: pathways of interlayer hydrogen bonds (dotted lines). Color code: yellow octahedra, MoO_6; brown tetrahedra, PO_4; gray spheres, C; green spheres, Fe; large orange spheres, La; blue spheres, N; small red spheres, O. Noncoordinating water molecules are omitted for clarity.

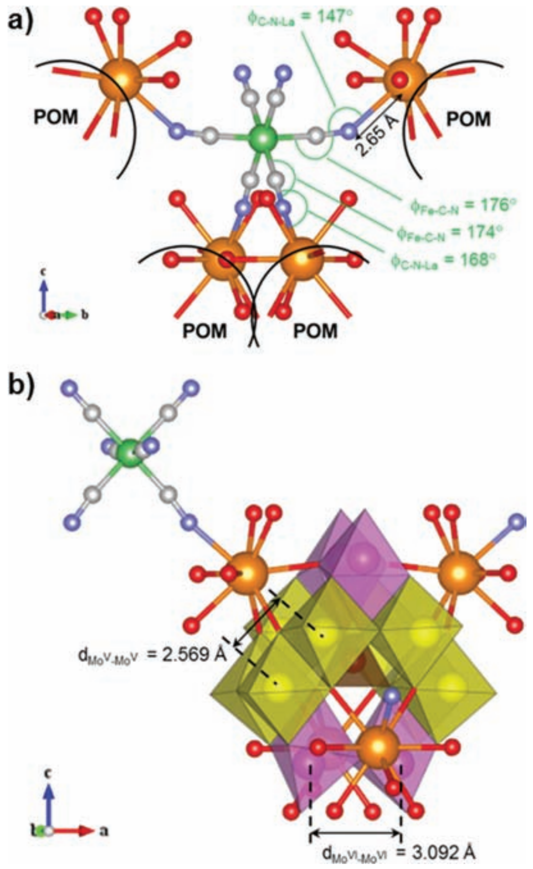

Figure 2. (a) Local arrangement around the Fe^{II} centers. (b) Mixed polyhedral/ball-and-stick representation of the asymmetric unit in **1**, with localized Mo^V (yellow) and Mo^{VI} (pink) centers.

Two different sites can be distinguished for the La^{III} centers. On the two La centers aligned along the crystallographic *a* axis, the "axial" water molecule directly opposite to the POM has been substituted and the La, N, C, and Fe atoms are roughly aligned (ϕ_{Fe-C-N} = 174° and ϕ_{C-N-La} = 168°; Figure 2a), while on the two La centers aligned along the *b* axis, one of the five "equatorial" water molecules has been substituted and the C−N−La angle is much more pronounced (ϕ_{Fe-C-N} = 176° and ϕ_{C-N-La} = 147°). In both cases, the La−N distance has been found to be equal to 2.65 Å, which is slightly longer than the La−OH_2 distances (2.53−2.63 Å). In turn, each hexacyanoferrate is connected to four different $\{PMo_{12}La_4\}$, leaving two nonbridging cyanides in the syn position, obviously because the bulky POMs prevent any further coordination. The stoichiometry of the final product is thus of one POM for one Fe^{II} center and seems independent of the initial reagent proportions, but working with an excess of hexacyanoferrate, nonetheless, improves the yield. Even though the H atoms could not be located precisely, the $\{PMo_{12}La_4Fe(CN)_6\}_n$ layers are obviously packed together via hydrogen bonds, as indicated by the O···O distance of 2.967 ± 0.01 Å measured between two of the water molecules coordinated to the La centers and the terminal O atom of the Mo^{VI} centers from the neighboring layer (Figures 1b (inset) and S2 in the SI).

Because of the lower symmetry of **1** compared to the $\{PMo_{12}La_4\}$ precursor, the oxidation state of each of the 12 Mo centers can be determined through Mo−Mo bond lengths and bond-valence-sum (BVS) calculations (Figure S3 and Table S1 in the SI).[13] Eight of them were found to be in the V+ oxidation state (d_{Mo-Mo} = 2.569 Å; BVS = 5.26 ± 0.02) and four in the VI+ state (d_{Mo-Mo} = 3.092 ± 0.014 Å; BVS = 6.00 ± 0.04). This proportion is the same as that in the original $\{PMo_{12}La_4\}$, demonstrating that no redox reaction occurred between the mixed-valent POM and the Fe^{II} complex (Figure 2b). A total of 12 crystallization water molecules have been located unambiguously on the Fourier difference maps, a number later confirmed by TGA (Figure S4 in the SI); the absence of any other strong residue corresponding to hypothetical counterions suggests a neutral network, which accounts for the insolubility. This also implies three additional

H atoms must be delocalized on the bridging O atom of the polyoxomolybdate, a hypothesis confirmed by BVS calculations: eight of the μ_2-O atom show BVS values of 1.97, corresponding to nonprotonated oxo bridges, while the four others exhibit BVS values of 1.31 (×2) and 1.44 (×2), which are consistent with disordered protonation. The 12 μ_3-O linking the La centers to the $\{Mo_{12}\}$ core all show BVS values between 2.07 and 2.12, again indicating an absence of protonation. Eventually, a measured distance of 2.663 Å between the N atom from the nonbonding cyanide and one of the protonated bridging O atoms suggests that O−H···N hydrogen bonds may further enhance cohesion of the network.

In conclusion, we were able to isolate the first three-dimensional multilayered structure obtained by condensation of a POM with a cyanometalate by an easy synthesis under the usual bench conditions. In our efforts to realize a new class of POM−cyanometalate hybrid materials that have the potential to exhibit various properties like magnetism and luminescence, we are currently working on expanding this family by isolating the neodymium-, samarium-, and europium-containing species as well.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, detailed synthesis and characterizations (elemental analysis, FTIR, TGA, and magnetic data), selected bond distances, and BVS calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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