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Assembly of a polyoxometalate into an anisotropic gel

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The self-assembly of the polyoxomolybdate $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2]^{3-}$ and $[PdCl_2(PhCN)_2]$ yields a transparent and birefringent gel.

Polyoxometalates (POMs) are of current interest for their photochemical, electrochemical and catalytic properties.[1] The preparation of POM based materials is therefore an active field of research, and in particular the combination of POMs with organic molecules has given rise to a variety of organic–inorganic hybrid materials.[2,3] Different strategies are explored. In one approach, organic polymers contain covalently bonded POMs in their backbone or as pendant groups.[4,5] Such compounds form gels under suitable conditions.[6] In another approach, coordination compounds (mainly organodiimine coordination polymers of transition metals) have been combined with polyoxomolybdates to yield new oxide materials with a designed scaffolding.[7] The organic component plays a role as template for the oxide structure. Our approach consists of the combination of these two strategies, *i.e.* scaffolding POMs by metal coordination to organic ligands that are covalently bound to the POMs.[8] We have therefore prepared POMs with pendant ligands that have free binding sites for metal ions and studied their coordination chemistry. We present here our results of the coordination of Pd^{II} to pyridine ligands grafted onto an Anderson type polyoxomolybdate.

The complex $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2]^{3-}$ **1** was obtained by the treatment of $(N(C_4H_9)_4)_4[\alpha-Mo_8O_{26}]$ with $Mn(CH_3COO)_3$ and $(HOCH_2)_3CNHCO(4-C_5H_4N)$ in refluxing acetonitrile, following our published procedure.[9] Single crystals of the compound were grown by slow ether diffusion. The molecular structure of **1** was determined by X-ray diffraction (Fig. 1).† It consists of the planar, hexagonal Anderson polyanion with a tris-alkoxo ligand on each side. The structure corresponds to the δ isomer, where the alkoxo ligands cap the central heteroatom. Bond distances and angles within the polyoxomolybdate are similar to those observed in previously reported compounds.[9] The pyridine rings of the two tris-alkoxo ligands are not involved in metal binding. It follows from the symmetry and the rigidity of the structure of **1**, that it can be compared to 4,4′-bipyridine with

a large spacer between the pyridine rings. The pyridine nitrogens are almost 2 nm apart from each other.

As 4,4′-bipyridine has proven to be a valuable ligand in supramolecular coordination chemistry (in solution and in the solid state), an exciting coordination chemistry can be expected for **1**.

The substitution of benzonitrile coordinated to Pd^{II} by pyridine is known to proceed smoothly.[10] Thus, on addition of $[PdCl_2(C_6H_5CN)_2]$ **2**[11] to a solution of **1** in acetonitrile at millimolar concentrations, the compound $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2(PdCl_2)]_n^{3n-}$ **3** was formed.‡ We followed the stepwise addition of **2** to **1** by ^{1}H-NMR (Fig. 2), although the signals were broadened by the presence of the paramagnetic Mn^{III} ion, and the protons in the 3,5-position of pyridine (H$_b$) were masked by benzonitrile. With increasing amount of **2**, a new signal at 8.81 ppm for the protons in positions 2 and 6 on the pyridine rings (H$_a$) increased, while the signal at 8.65 ppm decreased. This new signal can be attributed to pyridine coordinated to Pd^{II}. From the integration of the two signals, the mole fraction of complexed pyridine can be estimated. It is found to be about 85% of the amount of **2** added. This indicates an equilibrium of complexed and uncomplexed pyridine rings of **1** strongly in favour of the complex. As the geometric constraints of the Anderson structure prevent the binding of both pyridine rings of one molecule of **1** to the same Pd centre, compound **3** should present a cyclic or linear oligomeric or polymeric structure.
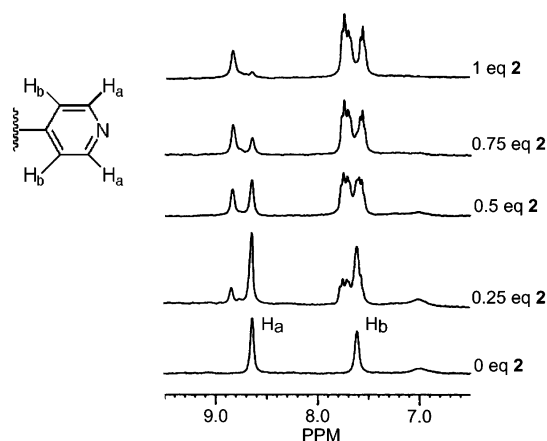
Fig. 2 Part of the ^{1}H NMR spectra of the titration of $[PdCl_2(C_6H_5CN)_2]$ **2** to a solution of $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2]^{3-}$ **1**.

Addition of methanol to the acetonitrile solution of **3** yielded after 1–2 days a transparent gel with the consistency of gummi candy, although it is not as flexible. It can be cut in slices, and it breaks into pieces on stress. The orange colour of the gel is identical to the initial solution. Ageing at room temperature over a week produced syneresis, and this process resulted in the shrinkage of the gel. Whereas the original gel appeared dark under crossed polarized light, observation after ageing through crossed polarizers showed a homogeneous, birefringent gel
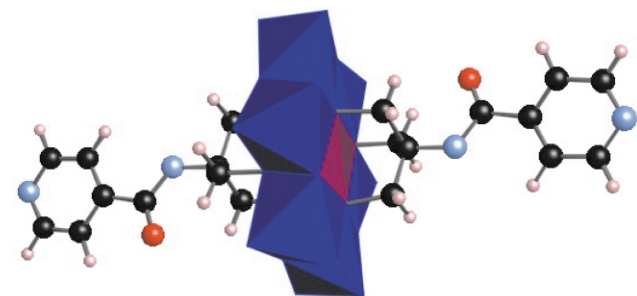
Fig. 1 Structure of $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2]^{3-}$ **1**. The oxometalate core is represented by coordination polyhedra (blue Mo, purple Mn), the organic ligands as ball-and-stick models (black C, red O, light blue N, pink H).

(Fig. 3). This birefringence clearly indicates an anisotropic order in the material.

The gel appeared to be thermally stable. On heating up to the boiling point of the solvents, no melting of the gel was observed. This excludes a physical gel.
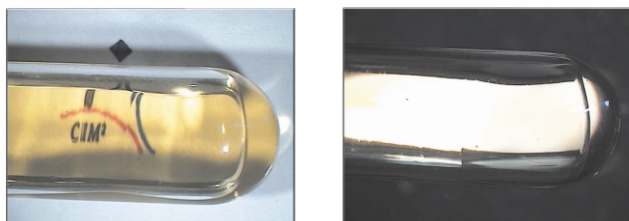
Fig. 3 Two photographs of the gel in a test tube of 1 cm in diameter. Left: taken under ambient light to show the transparency of the gel; Right: taken through crossed polarizers to show the birefringence of the gel.

After total evaporation of the solvents, a transparent orange film was obtained which was still birefringent. IR spectroscopic analysis of this xerogel showed the intact Anderson structure of **1** and the absence of benzonitrile, in agreement with the formulation $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2(PdCl_2)]_n^{3n-}$ for **3**. The compound did not swell or redissolve in acetonitrile or any other solvent.

It should be noted that no gel was formed from a solution of **1** in the absence of **2**. Furthermore, no reaction was observed between the ligand $(HOCH_2)_3CNHCO(4-C_5H_4N)$ and **2** in acetonitrile because of the insolubility of the former compound. Thus, the functionalized POM **1** and the assembling metal **2** are required to obtain the gel.

We investigated the influence of co-solvents and concentration of **1** and **2** on the gel forming process. Acetonitrile solutions of an equimolar amount of **1** and **2** at concentrations between $5 \cdot 10^{-4}$ M and 10^{-2} M were prepared and mixed with the same volume of methanol, hexane or ether. All mixtures formed birefringent gels, but with hexane or ether some precipitation occurred. The time of gelification and of syneresis depended largely on the concentration. A visual change in the viscosity of the solution was observed after hours in the most concentrated mixture, and after almost three weeks in the most dilute. Rheological measurements are currently being undertaken to determine precisely the gelation time and the viscoelastic properties of the gel. Birefringence also depended on the concentration. The more concentrated the solution, the brighter the gel looks under crossed polarizers.

Gelification occurs when a macromolecular or colloidal solid is dispersed in a liquid. We are currently investigating the structure of these gels. Our working hypothesis is that the coordination of **2** to **1** forms polymeric strands. The strands could then be reticulated by supramolecular interactions with neighboring strands[12] and/or solvent molecules.[10] During the syneresis, these intermolecular interactions increase, causing an alignment of the polymer strands. This would explain the observed birefringence. According to this hypothesis, our system is comparable to polymer gels, and differs from colloidal organization observed in other POM containing systems.[13–15]

We have shown here the possibility of preparing gels incorporating functionalized POMs by metal coordination. This approach is complementary to the covalent polymers of POMs reported in the literature. A particularly interesting feature of these gels is their birefringence, which proves an anisotropic arrangement in the material.

Generally speaking, this work extends the known organic–inorganic hybrid materials. We are now evaluating ways to modify the chemical and physical properties of the gel by using different POMs and other assembling metal ions.

Notes and references

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