

Microstructure of new metal-organic gels obtained by low-molecular gelators

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We have studied self-assembly properties of recently synthesized L-Valine and pyridine containing low-molecular compounds, in the presence of some metal ions. It turned out that availability of CuCl₂ in ethanol solution of these compounds leads to metal-organic framework (MOF) gel formation. Hydrogels including Na⁺ and K⁺ ions are also concerned. Here we present some topological features of such gels including Na⁺, K⁺ and Cu²⁺ ions in their structures.

Key words: Metal-organic polymers, xerogel, porous structure, pH responsive gels.

INTRODUCTION

Investigations of gels based on low-molecular organic molecules have received increased attention in the recent years [1–7]. Physical and chemical properties of such gels are useful for the development of functional materials that have potential applications in fields including tissue engineering, catalysts, photonic materials, pharmaceutical diagnosis, *etc.* [8–11]. Gels structure consists of nano- and micro-shaped objects. That is why their study is also of great interest for application as templates for preparation of nanotubular materials [12–15]. A few cases of low-molecular gelators containing pyridine units have been reported until now [16–20]. The presence of a pyridine moiety in this type of molecules provides the basis for the formation of pH-responsive gels and for the incorporation of catalytic metals onto the fibres. Here we report on the formation of physical gels of two pyridine and L-Valine containing compounds (Fig. 1) in the presence of some metal ions. In some cases of metal-organic compounds, the metal ions are able to serve as centres linked into one-, two- or three-dimensional structures by directional bonding with small organic molecules. This type of hybrid materials is known in literature as metal-organic frameworks (MOFs). Although MOF research is still in its very beginning, this concept has been developed extremely rapidly in the recent years [21–23]. Like other gels, these ones obtained by MOF, consist of nano- and micro-sized particles and after removing (evaporating) the solvent they convert into

porous materials with unique properties that found applications as catalytic, absorbents, sensors and other responsive materials [24–26], endowed with complex behaviours by the presence of metal centres. On the other hand, their porous structure was found very useful, moreover they can be used as templates for other porous materials [27], as microporous materials have properties with exploitable industrial applications (e.g. as molecular sieves or supports), as well as every day use, e.g. laundry detergent [28]. Perhaps the most fundamental and important aspect of the syntheses of microporous materials is the control over pore topology (i.e. pore dimensions and shape). The experimental data obtained reveal topology of two types of metal-organic gels. The first one is obtained in water solutions by adjusting pH in the presence of Na⁺ or K⁺ ions. The second type – where a simple mix between two clear solutions of the organic compound and the cupro salt in a short time led to coloured gel formation, although in the absence of this salt, the used organic compounds (substances) never made gels in methanol, ethanol or propanol.

EXPERIMENTAL

Organic compounds used for the experiments (Fig. 1) were synthesized by applying previously reported procedures [19–20].

As it was mentioned above, two main types of metal containing gels were prepared. The first one was hydrogel containing alkali metals Na or K. The second one was organogel obtained in ethanol by reacting of organic molecule (**1** or **2**) with CuCl₂. Preparation was done following next recipes:

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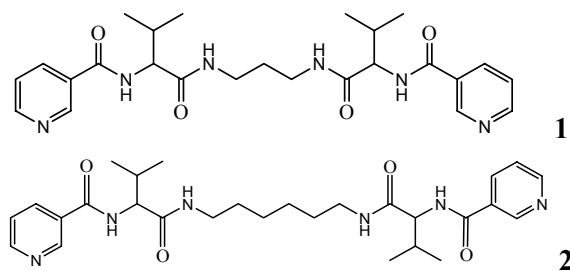


Fig. 1. Organic compounds used in the described experiments with codes **1** and **2**.

I. 5 mg of the organic compound (**1** or **2**) were dissolved in 500 μl of 0.1 M HCl. Adequate amount of water solution of NaOH, NaHCO_3 or K_2CO_3 , prepared in the range from 0.2 to 1 M, was added to the above described acidic solution. The obtained mixture turned into gel. The time for gelation depended on the concentration of the substance and varied from seconds, for the most concentrated, to days for the most diluted. At these conditions, compound **2** gave opaque to white gels, while compound **1** gelled in opaque to transparent formations in dependence on the concentration.

II. 5 mg of the organic compound (**1** or **2**) were dissolved in 500 μl hot ethanol. Solutions of 20 mM CuCl_2 in ethanol in equivalent amount were added to the hot solution of organic compound and the mixture obtained immediately turned into gel coloured in blue and green nuances.

Scanning electron micrographs were taken in a JEOL JSM 6390, as well as LEO 440I microscopes equipped with digital cameras. The accelerating voltage was 10 keV in all cases. Before electron microscope observations the xerogel samples were

covered by thin (nano-size) layer of amorphous carbon or Au/Pd for their better conductivity.

RESULTS AND DISCUSSION

Bearing in mind that the molecules of the studied compounds possess two pyridine rings and the calculated and measured for both compounds protonation constants K_{a1} and K_{a2} are between 3 and 4 [10], it is obvious that they are soluble in water at $\text{pH} < 3$ as both pyridine groups are protonated. After dissolving of any of the compounds in acidic water (HCl, higher than 0.1 M), gels were easily obtained (immediately or in a few minutes to hours) after addition of solutions of NaOH, NaHCO_3 or K_2CO_3 in relevant concentrations and amount. The stability of the obtained gels increased with increasing the ionic strength of the solution (NaCl, 0.1 M).

The second type of gel was obtained as a result of the reaction between organic compound and CuCl_2 in hot ethanol and most probably, the resulting coloured gels are coordination polymers, the so-called MOFs. The fast gelation of the metal and ligand suggests that there is a rapid cross-linking polymerisation between Cu^{2+} and organic molecule (**1** and **2**), leading to the growth of coordination polymer particles, which themselves subsequently cross-link to leave macroscopic solvent-filled cavities. In fact, compounds **1** and **2** are able to make gels in some organic solvents (e.g. toluene, dioxane) but having high solubility in lower alcohols, they never made any kind of gels in methanol, ethanol or propanol.

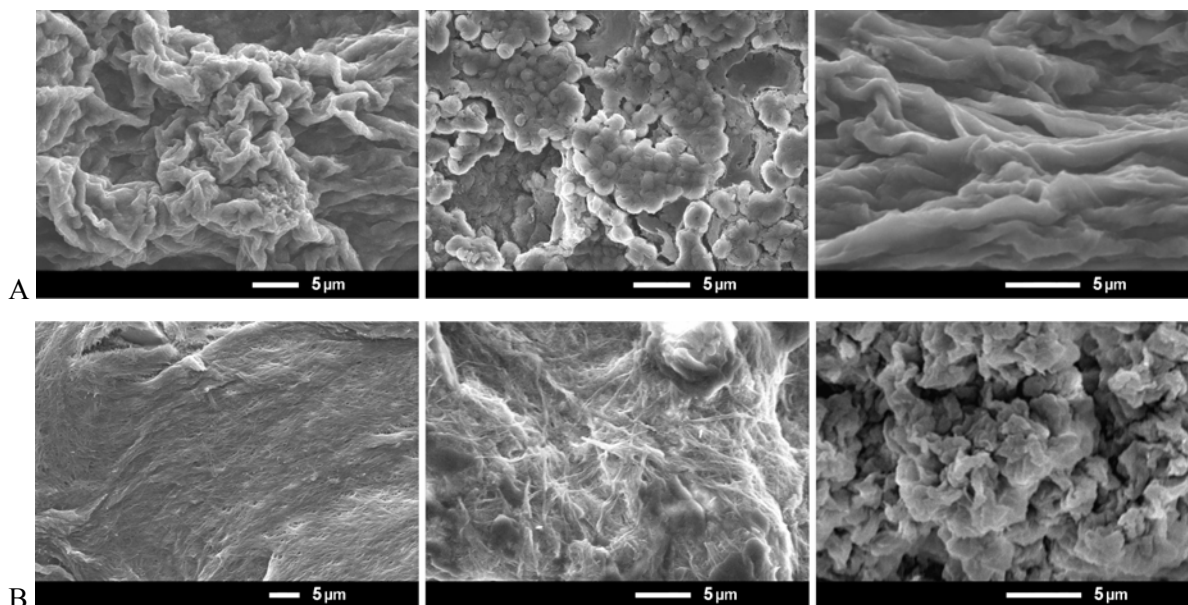


Fig. 2. A. SEM microphotographs of xerogels obtained from compound **1**: a) only organic compound in CH_2Cl_2 ; b) from hydrogel containing NaCl; c) **1**: CuCl_2 = 1:1 in ethanol; B. SEM microphotographs of xerogels obtained from compound **2**: a) only organic compound in dioxane; b) from hydrogel containing KCl; c) **2**: CuCl_2 = 1:1 in ethanol.

SEM study of the microstructures of dried gels (xerogels) obtained only by organic compound, hydrogels containing Na⁺ or K⁺ ions and these obtained as organogels in the presence of CuCl₂ show pronounced differences in the topology of materials, some of them are shown in Fig. 2. The observations of gels obtained reveal that both organic compounds can make gels with different microstructure: fibril (Fig. 2Ba) and laminar (Fig. 2Aa). Most probably, the gel structure depends also on the solvent used, as previously published data show that gels of compound **1** in some solvents are constructed by very thin fibres [19]. That is why we do not exclude that this laminar structure, presented in Figure. 2Aa, consists of fibers, which diameter is in the range of several nm (below the resolution of the used microscope technique). Nevertheless, from the photo (Fig. 2Aa) it is obvious that the gel obtained from compound **1** has very large pores due to undulation of the lamellas, while this formed by compound **2** (Fig. 2Ba) could be regarded as mesoporous.

Comparison of hydrogels, containing alkali metals (Na, K) presented in Figs 2Ab and 2Bb, displays that both gels have fibril structures with 10 to 30 nm diameter of a fibre and in case of 2Ab, fibrils are additionally organized in spheres, which diameter is lower than 2 μm. Again the material obtained from compound **1** possesses higher pores than **2** (Fig. 2Bb) because of the space included among the micro-spheres (Fig. 2Ab).

Figures 2Ac and 2Bc present xerogels, obtained after reaction between organic compounds and CuCl₂ and most probably they belong to MOFs. Fibrillar structure was not observed in gels obtained and obviously, these materials are macroporous, as their pores are in the range of microns.

CONCLUSIONS

In summary, we report the formation of novel metal-organic hydro- and organogels with different porous structures. Further studies into their porosity, magnetic property and other characteristics of these materials as well as the molecular structure defining are in progress.

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МИКРОСТРУКТУРА НА НОВИ МЕТАЛО-ОРГАНИЧНИ ГЕЛОВЕ
ПОЛУЧЕНИ ОТ ГЕЛООБРАЗОВАТЕЛИ С НИСКА МОЛЕКУЛНА МАСА

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(Резюме)

Изследвано е свойството самоорганизация на наскоро синтезирани нискомолекулни съединения съдържащи L-валин и пиридинови компоненти в молекулите си в присъствието на някои метални йони. Установено бе, че в етанолов разтвор те реагират с CuCl_2 до образуване на метало-органични полимери с гелова структура. Разгледани са също хидрогелове на същите органични съединения, включващи Na^+ и K^+ йони. Тук са представени някои топологични характеристики на такива продукти, включващи Na^+ , K^+ и Cu^{2+} йони в структурата си.