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A nucleobase–inorganic hybrid polymer consisting of copper bis(phosphopentamolybdate) and cytosine

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A nucleobase–inorganic hybrid polymer built from $P_2Mo_5O_{23}$ and Cu(II)–cytosine subunits has been prepared; X-ray crystal structure analysis reveals the cytosine molecules weakly coordinate to copper(II) and connect the $P_2Mo_5O_{23}$ subunit through hydrogen bonds to form extended 2D networks with complicated hydrogen bonding modes; a bathochromic shift, compared to free cytosine, can be observed in the fluorescence spectra of the hybrid polymer.

The introduction of an organic component into inorganic material can alter the microstructure,[1,2] which affords a powerful method for the preparation of novel solid-state materials. Such organic–inorganic hybrid materials exploit the unique characteristics, or even new properties, in the complementary design of solid-state structures with different composites. Although many organic molecules have been used in this area, the assembly built from non-covalent interactions between bioactive nucleobases and inorganic materials is less considered. Polyoxomolybdate-phosphorus is a well-known material applied in chemical synthesis because of its capability of allowing a variety of chemical reactions to take place in the intracrystalline region.[3–7] Accordingly, assembly of bioactive nucleobasic and polyoxomolybdate-phosphorus building blocks may yield novel complexes with interesting structures. Herein we report on a novel two-dimensional Mo–P–Cu polymer, $[CuP_2Mo_5O_{23}(H_2O)_2(Hcyt)_4]_n$ (**1**) (cyt = cytosine), which is constructed by copper bis(phosphopentamolybdate) and cytosine, a bioactive basic group, through hydrogen bonding. To our knowledge, complex **1** is the first example of a copper bis(phosphopentamolybdate) complex containing a bio-basic group.

Reaction of cytosine, Na_2MoO_4 and $Cu(NO_3)_2\cdot 6H_2O$ in water, followed by slow addition of a 1 : 1 H_3PO_4 aqueous solution to adjust the pH value to 3.2, gave rise to pale blue crystals suitable for X-ray structure determination.† Single-crystal X-ray crystallographic analysis‡ reveals that the structure of **1** is constructed of $P_2Mo_5O_{23}$ and $[Cu(H_2O)_2(Cyt)_2]$ subunits and two cytosine molecules hydrogen bonding with $P_2Mo_5O_{23}$, as shown in Fig. 1. The core structure of the $P_2Mo_5O_{23}$ anion is a five-membered ring formed by five distorted MoO_6 octahedra, in which two oxygen atoms come from tetrahedral PO_4 through sharing of the oxygen vertex, quite similar to that reported by Lu *et al.*[8b] The EPR spectrum of **1** shows hyperfine structure in the $g_\parallel$ region: the EPR parameters are $g_\parallel = 2.40$; $g_\perp = 2.08$ and $A_\parallel = 121$ G. The value of the $g_\parallel/A_\parallel$ quotient of 177 cm for the compound suggests a distorted tetragonal octahedral geometry around Cu(II).[9] The crystallographic analysis showed that each Cu(II) ion is coordinated by four oxygen atoms, two from coordinated water molecules and two from different PO_4 tetrahedra in a square plane geometry. There is a weak interaction, with a Cu–O distance of 2.77 Å, between Cu(II) and the oxygen atom from cytosine, thus Cu(II) may also be regarded as a distorted octahedron with high axial elongation. Each PO_4 tetrahedron acts as μ_6-bridge linking five molybdenum and one copper atoms, hence each Cu(II) can be viewed as a linker connecting two $P_2Mo_5O_{23}$ units, forming a one-dimensional chain structure along the *c* axis. Fig. 2(a) is a representation of the polymeric chain structure viewed down the *b* axis with a period length between adjacent $P_2Mo_5O_{23}$ subunits of 9.77 Å. Coordinated water molecules are embedded between the two subunits.

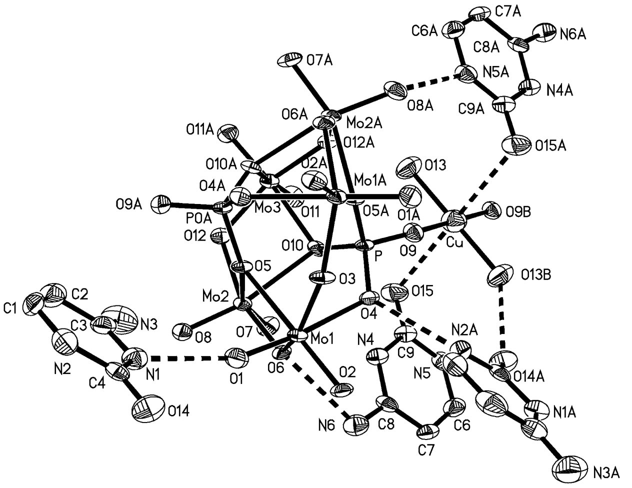

Fig. 1 A subunit of **1** in the crystal, hydrogen atoms are omitted. The weak coordination between Cu(II) and the carbonyl oxygen atom of cytosine and hydrogen bonding interactions are represented by dashed lines.

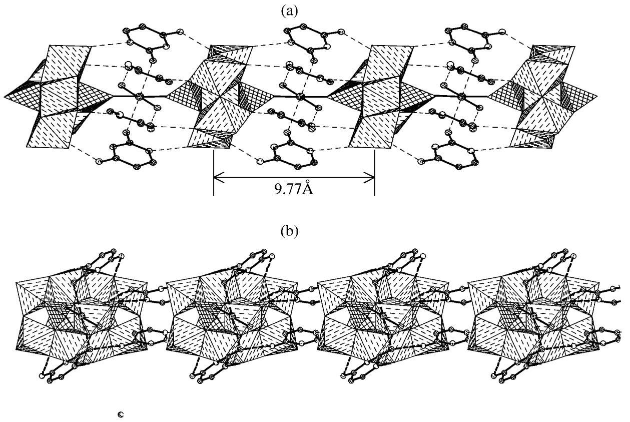

Fig. 2 A polyhedral and ball-stick packing view of the $[CuMo_5O_{22}(H_2O)_2(Hcyt)_4]_n$ chain of **1** viewed down the *b* axis (a) and *c* axis (b). Octahedra and tetrahedra represent Mo and P atoms respectively.

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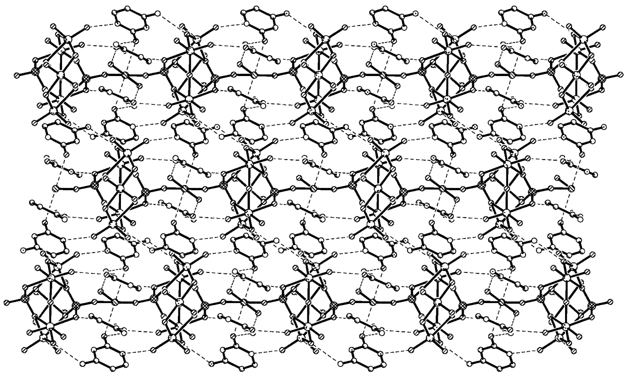

Fig. 3 Packing diagram of **1** viewed down the *c* axis.

As shown in Fig. 1, 2 and 3, along the *c* axis of the Cu–P–Mo chain, the cytosine molecules are weakly coordinated with Cu(II), and the two nitrogen atoms N(5) and N(6), which hydrogen bond with O(8) and O(6) from adjacent $P_2Mo_5O_{23}$ subunits, bridge the two subunits. Along the *b* axis, the cytosine molecules use the carbonyl oxygen atoms to hydrogen bond with the coordinated water molecules and two nitrogen atoms, N(1) and N(2), with O(1) and O(2) of the MoO_6 octahedra in the adjacent Cu–P–Mo chain, which joins the adjacent Cu–P–Mo chains to form an extended two-dimensional network parallel to the *bc* plane.

Although experiments carried out with different pHs for the reaction system, only in the system with pH = 3.2 were crystals obtained, which indicates that the pH of the reaction system plays a key role in the assembly process. The successful isolation of **1** provides a novel example of assembling phosphomolybdate subunits *via* a cytosine template. This may open up a new method for the design of organic–inorganic hybrid materials which are usually obtained by hydrothermal techniques.[8]

The free cytosine molecule has an emission at $\lambda = 420$ nm in the solid-state when irradiated with UV light at $\lambda = 330$ nm. In contrast, complex **1** displays a more intense fluorescence emission ($\lambda = 435$ nm), as shown in Fig. 4. This fluorescence emission may originate from an intraligand $\pi \longrightarrow \pi^*$ transition which gives the electronic absorption of 255 nm for free ligand and 235 nm for the moiety of **1**. As compared to free cytosine, it is observed that the fluorescence intensity of **1** is *ca.* two times larger and bathochromically shifted and that the IR absorption band assigned to $\nu_{C=O}$ is shifted to lower frequencies and the bands related to ν_{ring} and ν_{C-N} centered at about 1466, 1366, 1279 and 1283 cm^{-1} exhibit appreciatable intensity changes and shifts in their frequency, which may be ascribed to the rigidity enhancement in **1** owing to the hydrogen bonding of cytosine with the $[P_2Mo_5O_{23}]$ subunit,[10] though detailed studies may still be needed.

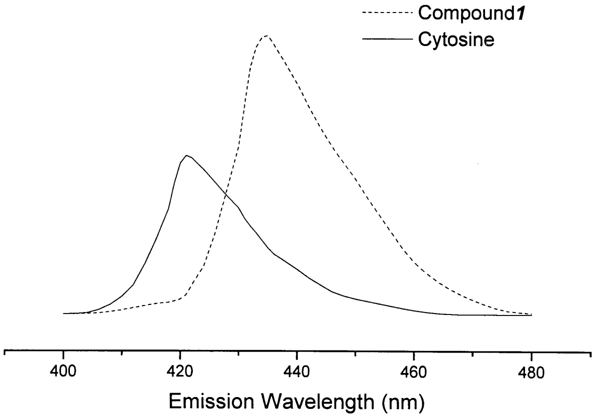

Fig. 4 The fluorescence spectra of cytosine and compound **1**. The excitation wavelength is 330 nm.

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Notes and references

† Preparation: $Na_2MoO_4{\cdot}2H_2O$ (2.0 mmol, 484 mg) was added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1.0 mmol, 242 mg) and cytosine, $C_4H_5N_3O$, (1.0 mmol, 110 mg) in distilled water (25 ml). The mixture was stirred for 30 min and then the 1 : 1 (v/v) H_3PO_4 aqueous solution was slowly added into the reaction system until the pH reached 3.2. The final reaction solution was filtered. The pale blue single crystals suitable for X-ray analysis were obtained after evaporating the filtrate at room temperature for several days. The yield based on Na_2MoO_4 was 42%. IR (solid state): 3375(s), 3192(s, br), 2926(m), 2710(m), 1701(s), 1660(s), 1585(m), 1543(w), 1410(w), 1238(s), 1150(m), 1115(s), 1045(s), 991(m), 918(s), 901(s), 787(m), 762(m), 704(m), 671(s, br), 580(m), 525(m), 440(m), 415(w) cm^{-1}.

‡ Reflection data were collected on a Bruker Smart CCD system with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods using the SHELXTL program.[11] Non-hydrogen atoms of the complex were refined with anisotropy thermal parameters. Refinement was performed by full-matrix least squares on F^2. Crystal data: $CuP_2Mo_5O_{23}(H_2O)_2(C_4H_6N_3O)_4$, crystal size 0.35 × 0.30 × 0.30 mm, $M = 1202.91$, monoclinic, space group *C*2/*c*, $a = 19.3411(4)$ Å, $b = 11.4945(2)$, $c = 19.4712(1)$ Å, $\beta = 117.6170(10)°$, $V = 3835.57(11)$ Å^3, $Z = 4$, $D_c = 1.262$ Mg m^{-3}, $\mu = 1.167$ mm^{-1}, $2.13 < \theta < 25.04°$, $R(R_w) = 0.0617(0.1653)$ for 3374 independent reflections with $I > 2\sigma(I)$ and 296 parameters, and $R(R_w) = 0.0825(0.1802)$ for all the data. The goodness-of-fit on F^2 was 1.072, and the residual electron density (min./max.) was 1.965/−2.772 e Å^{-3}. CCDC reference number 169347. See http://www.rsc.org/suppdata/dt/b1/b111457n/ for crystallographic data in CIF or other electronic format.

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