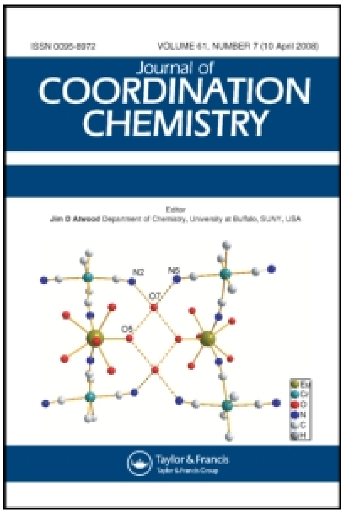

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# A two-dimensional zinc-molybdenum(V) phosphate organic-inorganic hybrid polymer with fluorescence

Hong-Xu Guo[a]; Jia-ming Liu[a]; Guo-hui Zhu[a]
[a] Department of Chemistry and Environmental Science, Zhangzhou Normal University, Zhangzhou 363000, P.R. China

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# A two-dimensional zinc-molybdenum(V) phosphate organic–inorganic hybrid polymer with fluorescence

HONG-XU GUO*, JIA-MING LIU and GUO-HUI ZHU

Department of Chemistry and Environmental Science, Zhangzhou Normal University, Zhangzhou 363000, P.R. China

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A novel zinc-molybdenum(V) phosphate hybrid polymer, $Zn[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]_2[Zn_6(H_2O)_8(phen)_4]\cdot 6H_2O$ (phen = 1,10-phenanthroline), was prepared under hydrothermal conditions and characterized by single-crystal X-ray diffraction, FT-IR, TGA and EPR spectra. The crystal structure analyses show that the compound is built from two anionic hexameric polyoxomolybdophosphate $[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]^{7-}$ moieties, bridged by a central octahedral $Zn^{2+}$ centre. The sandwich-type $Zn[Mo_6P_4]_2$ dimers are connected *via* additional $Zn^{2+}$ polyhedra, forming a two-dimensional network polymer. The luminescent properties of the title compound are also discussed.

*Keywords*: Zinc-molybdenum(V) phosphate; Organic–inorganic hybrid; Crystal structure; Layer-like structure; Luminescent property

## 1. Introduction

Hybrid organic–inorganic materials have attracted much attention in recent years because of the possibility of combining the different characteristics of the components to get unusual structures, properties and applications [1]. Polyoxometalates (POMs) are one of the most widely used inorganic components in a wide range of fields, such as catalysis, medicine and material science, owing to their extreme variability of composition, structure, electronic properties and applications [2]. Design of new composite materials incorporating POMs and transition-metal (TM)-complex moieties constitutes an emerging area of interest [3]. To date, several hybrid compounds based on vanadium [4], tungsten [5] and molybdenum [6] isopolyanions have been reported, but in contrast, examples of reduced molybdenum-phosphates constructed from $[Mo_6P_4]$ subunits containing an organic amine bound to an inorganic core of the structure are still limited [7].

Exploitation of hydrothermal techniques and the use of organic structure-directing agents have proved fruitful in the production of numerous organic–inorganic hybrid materials [8]. Currently, we are exploring the applicability of TM-reduced molybdenumphosphates POMs for preparation of novel hybrid compounds by auto-assembly

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*Corresponding author. Email: guohongxu919@yahoo.com.cn

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processes under mild temperature hydrothermal condition [9]. In this communication, we report the hydrothermal synthesis, crystal structure and luminescent properties of a novel 2-D zinc-molybdenum(V) phosphate organic–inorganic hybrid, $Zn[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]_2[Zn_6(H_2O)_8(phen)_4] \cdot 6H_2O$ (phen = 1,10-phenanthroline) (**1**).

## 2. Experimental

All chemicals were readily available from commercial sources and were used as received without further purification. The synthesis was carried out in PTFE-lined stainless-steel reaction vessels (ca 30 mL), under autogenous pressure and static conditions.

### 2.1. *Synthesis of $Zn[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]_2[Zn_6(H_2O)_8(phen)_4] \cdot 6H_2O$*

The title compound was synthesized from a reaction mixture containing 0.2202 g of zinc acetate (1.2 mmol), 0.4606 g of phosphoric acid (4.7 mmol), 0.1583 g of molybdenum trioxide (1.1 mmol) and 0.2577 g of 1,10-phenanthroline (1.3 mmol), in ca 20 mL of distilled water. The suspension was transferred to the reaction vessel and then placed inside a pre-heated oven at 190°C. The reaction proceeded for 5 days, after which the reaction vessel was allowed to cool slowly to ambient temperature before opening. The autoclave contents consisted of a large amount of red-brown block crystals. The resulting crystals were filtered off, washed with water, and dried at ambient temperature (yield 51% based on molybdenum). The title compound proved to be air- and light-stable, and insoluble in water and common organic solvents. Elemental analysis found: C, 14.95; H, 1.95; N, 2.84 (Calcd for $C_{48}H_{70}N_8O_{76}P_8Zn_7Mo_{12}$: C, 15.03; H, 1.83; N, 2.93).

### 2.2. *Instrumentation*

FT–IR spectra were collected using KBr pellets on a Perkin–Elmer Spectrum 2000 FTIR. Thermogravimetric analyses (TGA) were carried out using a NETZSCH TG 209 FI thermogravimetric analyzer, with a heating rate of $10^{\circ}C\,min^{-1}$, under a continuous nitrogen stream with a flow rate of $20\,cm^3\,min^{-1}$. Elemental analyses for C, H and N were performed with a CHNS-932 Elemental analyser. The EPR spectrum was recorded by a Bruker ESR-420 at room tempertature. Excitation and emission spectra were obtained on a Luminescence Spectrometer LS-55 in solid state at room temperature.

### 2.3. *Single-crystal X-ray diffraction*

A suitable single crystal of the title compound with dimensions of $0.38 \times 0.21 \times 0.16\,mm^3$ was fixed to the end of a glass capillary. Data were collected at 193(2) K on a Rigaku Mercury diffractometer with a CCD detector using graphite monochromated Mo-K$\alpha$ radiation. The structure of the single crystal was solved by direct method and

Table 1. Crystal data and structure refinement for compound **1**.

| Empirical formula | $C_{48}H_{70}Mo_{12}N_8O_{76}P_8Zn_7$ |
|---|---|
| Formula weight | 3831.75 |
| Temperature (K) | 193(2) |
| Wavelength (Å) | 0.71070 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 12.6040(16) |
| $b$ | 13.9039(17) |
| $c$ | 14.6239(16) |
| $\alpha$ | 78.345(6) |
| $\beta$ | 75.231(5) |
| $\gamma$ | 87.421(6) |
| Volume ($Å^{-3}$) | 2426.9(5) |
| $Z$, Calculated density ($mg\,m^{-3}$) | 1, 2.622 |
| Absorption coefficient ($mm^{-1}$) | 3.441 |
| $F(000)$ | 1856 |
| Crystal size ($mm^3$) | 0.38 × 0.21 × 0.16 |
| $\theta$ Range for data collection (°) | 3.02–25.35 |
| Limiting indices | $15 \le h \le 15$, $16 \le k \le 16$, $17 \le l \le 16$ |
| Reflections collected/unique | 23767/8819 ($R_{int} = 0.0239$) |
| Completeness to $\theta = 25.35$ (%) | 99.3 |
| Data/restraints/parameters | 8819/0/704 |
| Goodness of fit on $F^2$ | 1.037 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0373$, $wR_2 = 0.1463$ |
| $R$ indices (all data) | $R_1 = 0.0402$, $wR_2 = 0.1529$ |
| Largest diff. peak and hole ($e\,Å^{-3}$) | 1.994 and −1.277 |

refined by full-matrix least-squares calculations based on $F_o^2$ with empirical absorption corrections using Bruker SHELXTL programs [10]. A summary of the crystallographic data and structural determination for **1** is provided in table 1. Selected bond lengths and bond angles of **1** are listed in table 2. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters of **1** are available in supplementary crystallographic data. (CCDC reference number: 607405)

## 3. Results and discussion

The single crystal X-ray analysis reveals that compound **1** consists of anionic hexameric polyoxomolybdophosphate $[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]^{7-}$ moieties ($\equiv[Mo_6P_4]$), zinc cations, additional zinc coordination cations ($[Zn(H_2O)(phen)]^{2+}$, $[Zn(H_2O)_2(phen)]^{2+}$ and $[Zn(H_2O)]^{2+}$), and lattice water molecules.

In $[Mo_6P_4]$ of compound **1**, the six oxo-bridged molybdenum atoms [Mo–O: 1.667(4)–2.329(4) Å] are approximately in the same plane and constitute a hexameric molybdenum ring with alternating Mo–Mo single bonds (av. 2.59 Å) and non-bonding Mo–Mo contacts (av. 3.50 Å). Among four phosphate groups [P–O: 1.493(4)–1.565(4) Å], a central one bridges the hexamer internally and three peripheral ones each bridge the long Mo–Mo contact externally. Structurally, all molybdenum octahedra share an edge with each other [O–Mo–O: 74.5(1)–172.0(2)°] and all phosphate tetrahedra are corner sharing with the corresponding

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**.

| | | | | | |
|---|---|---|---|---|---|
| Mo(1)–O(6) | 1.667(4) | Mo(4)–O(12) | 2.039(4) | Zn(2)–O(20)#2 | 1.963(4) |
| Mo(1)–O(23) | 1.932(4) | Mo(4)–O(13) | 2.117(4) | Zn(2)–O(35) | 1.969(4) |
| Mo(1)–O(7) | 1.979(4) | Mo(4)–O(27) | 2.283(4) | Zn(3)–O(1) | 1.985(4) |
| Mo(1)–O(2) | 2.044(4) | Mo(5)–O(29) | 1.675(4) | Zn(3)–O(3)#3 | 1.997(4) |
| Mo(2)–O(30) | 1.680(4) | Mo(5)–O(28) | 1.963(4) | Zn(3)–O(32) | 2.068(4) |
| Mo(2)–O(28) | 1.959(4) | Mo(5)–O(26) | 1.991(4) | Zn(3)–N(1) | 2.121(5) |
| Mo(2)–O(26) | 1.980(4) | Mo(5)–O(11) | 2.039(4) | Zn(3)–N(2) | 2.141(5) |
| Mo(2)–O(10) | 2.034(4) | Mo(5)–O(27) | 2.287(4) | Zn(4)–O(33) | 2.016(4) |
| Mo(2)–O(21) | 2.091(4) | Mo(6)–O(16) | 1.684(4) | Zn(4)–O(28) | 2.025(4) |
| Mo(2)–O(22) | 2.289(4) | Mo(6)–O(19) | 1.932(4) | Zn(4)–N(3) | 2.061(5) |
| Mo(3)–O(23) | 1.928(4) | Mo(6)–O(24) | 2.095(4) | Zn(4)–O(34) | 2.083(4) |
| Mo(3)–O(7) | 1.983(4) | Mo(6)–O(25) | 2.273(4) | Zn(4)–N(4) | 2.114(5) |
| Mo(3)–O(9) | 2.030(4) | Zn(1)–O(7)#1 | 2.138(4) | P(1)–O(3) | 1.493(4) |
| Mo(3)–O(21) | 2.121(4) | Zn(1)–O(26)#1 | 2.147(4) | P(1)–O(9) | 1.541(4) |
| Mo(3)–O(22) | 2.288(4) | Zn(1)–O(15)#1 | 2.175(4) | P(2)–O(5) | 1.528(4) |
| Mo(4)–O(17) | 1.683(4) | Zn(2)–O(14) | 1.916(4) | P(3)–O(11) | 1.536(4) |
| Mo(4)–O(15) | 1.984(4) | Zn(2)–O(31) | 1.939(4) | P(4)–O(22) | 1.538(4) |
| O(6)–Mo(1)–O(23) | 105.21(18) | O(28)–Mo(5)–O(11) | 87.29(16) | O(31)–Zn(2)–O(20)#2 | 102.23(16) |
| O(6)–Mo(1)–O(7) | 101.17(18) | O(26)–Mo(5)–O(11) | 159.45(16) | O(14)–Zn(2)–O(35) | 107.29(18) |
| O(23)–Mo(1)–O(7) | 95.96(16) | O(29)–Mo(5)–O(13) | 97.39(17) | O(31)–Zn(2)–O(35) | 106.99(18) |
| O(6)–Mo(1)–O(2) | 97.59(18) | O(28)–Mo(5)–O(13) | 158.78(16) | O(1)–Zn(3)–N(1) | 118.73(18) |
| O(30)–Mo(2)–O(26) | 101.04(17) | O(16)–Mo(6)–O(24) | 96.62(17) | O(3)#3–Zn(3)–N(1) | 86.55(18) |
| O(28)–Mo(2)–O(26) | 96.06(15) | O(19)–Mo(6)–O(24) | 157.27(16) | O(32)–Zn(3)–N(1) | 137.45(19) |
| O(30)–Mo(2)–O(10) | 96.55(17) | O(15)–Mo(6)–O(24) | 86.12(15) | O(33)–Zn(4)–N(3) | 98.54(19) |
| O(10)–Mo(2)–O(21) | 81.52(15) | O(15)–Mo(6)–O(25) | 81.68(14) | O(28)–Zn(4)–N(3) | 107.10(17) |
| O(7)–Mo(3)–O(9) | 156.99(16) | O(24)–Mo(6)–O(25) | 74.20(14) | O(33)–Zn(4)–O(34) | 87.33(17) |
| O(8)–Mo(3)–O(21) | 94.19(18) | O(7)#1–Zn(1)–O(7) | 180.00(15) | O(28)–Zn(4)–O(34) | 109.82(16) |
| O(23)–Mo(3)–O(21) | 160.31(15) | O(7)#1–Zn(1)–O(26) | 84.69(14) | O(34)–Zn(4)–N(4) | 89.19(17) |
| O(7)–Mo(3)–O(21) | 84.46(15) | O(26)–Zn(1)–O(26)#1 | 180.00(17) | O(3)–P(1)–O(9) | 110.0(2) |
| O(19)–Mo(4)–O(15) | 95.20(16) | O(26)#1–Zn(1)–O(15) | 84.44(14) | O(1)–P(2)–O(5) | 110.6(2) |
| O(17)–Mo(4)–O(12) | 97.28(17) | O(7)#1–Zn(1)–O(15)#1 | 96.82(14) | O(11)–P(3)–O(12) | 110.1(2) |
| O(19)–Mo(4)–O(12) | 87.19(16) | O(7)–Zn(1)–O(15)#1 | 83.18(14) | O(31)–P(4)–O(25) | 111.1(2) |
| O(15)–Mo(4)–O(12) | 158.63(15) | O(26)–Zn(1)–O(15)#1 | 84.44(14) | O(27)–P(4)–O(25) | 109.0(2) |

Symmetry codes, #1: $-x$, $-y+1$, $-z+1$; #2: $-x$, $-y+1$, $-z$; #3: $x+1$, $y$, $z$.

molybdenum octahedron (O–P–O: 104.8(2)–113.2(2)°). As observed for some related compounds [11], this building unit [$Mo_6P_4$] has $C_3$ symmetry through a three-fold axis containing the geometrical centre of the moiety and perpendicular to the plane of the $Mo^{5+}$ centres.

The structure of **1** was constructed from molybdenum hexamers bonded together with octahedral $Zn^{2+}$ into a two-dimensional framework (see figure 3). There are four crystallographically independent Zn atoms in compound **1** (see figure 2a) which may be divided into four types: (i) Zn(**1**) bridges two {$Mo_6P_4$} units *via* three $\mu_3$-O atoms, which link the metal–metal-bonded molybdenum atoms together with Zn–O bonds at lengths of 2.138(4) Å × 2, 2.147(4) Å × 2, 2.175(4) Å × 2 to produce centrosymmetric [$Zn(Mo_6P_4)_2$] dimers; (ii) Zn(2) site is coordinated by four oxygen atoms to finish tetrahedral geometric configuration, in which two P–O groups from one [$Mo_6P_4$] unit ($d_{Zn(2)\text{–}O(14)} = 1.916(4)$ Å, $d_{Zn(2)\text{–}O(31)} = 1.939(4)$ Å), one from another [$Mo_6P_4$] unit ($d_{Zn(2)\text{–}O(20B)} = 1.963(4)$ Å, symmetry code B: $-x$, $-y+1$, $-z$) and the last one come from water ($d_{Zn(2)-O(35)} = 1.969(4)$ Å); (iii) Zn(3) links two P–O groups from two different {$Mo_6P_4$} units ($d_{Zn(3)\text{–}O(1)} = 1.985(4)$ Å, $d_{Zn(3)\text{–}O(3C)} = 1.997(4)$, symmetry code C: $x+1$, $y$, $z$), two nitrogen atoms from one 1,10-phenanthroline molecule ($d_{Zn(3)\text{–}N(1)} = 2.121(5)$ Å, $d_{Zn(3)\text{–}N(2)} = 2.141(5)$ Å) and one terminal coordinated water

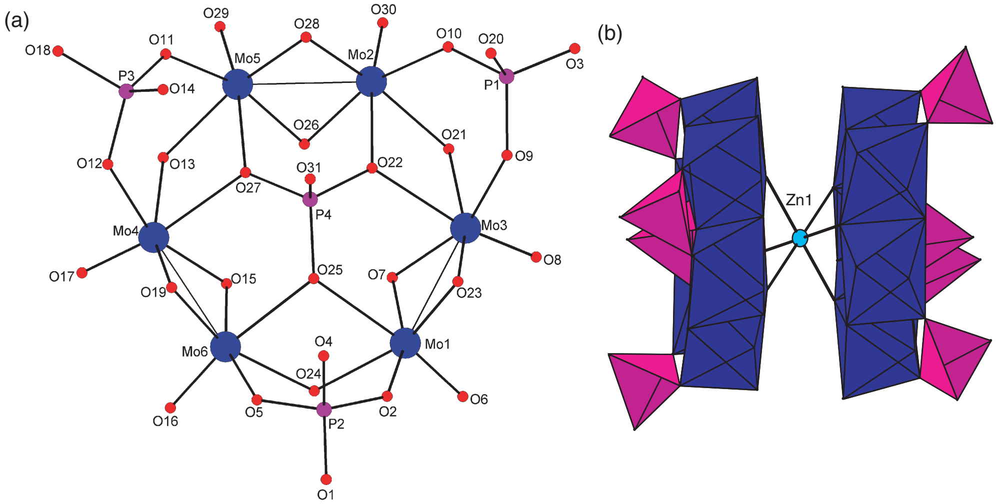

Figure 1. (a) Ball and stick representation of the anionic building unit $\{Mo_6P_4\}$ hexamer (left); (b) View of $\{Zn(Mo_6P_4)_2\}$ dimer (right).

molecule ($d_{Zn(3)\text{–}O(32)} = 2.068(4)\,Å$), to form the $\{Zn(phen)(H_2O)\}^{2+}$ fragment with bond angles O–Zn(3)–O and O–Zn(3)–N 88.9(2)–103.8(2)° and 86.6(2)–137.5(2)°, respectively. (iv) The coordinated environment of the Zn(4) is similar to that of Zn(3); Zn(4) is coordinated through two N atoms from one phen ligand ($d_{Zn(4)\text{–}N(3)} = 2.061(5)\,Å$, $d_{Zn(4)\text{–}N(4)} = 2.114(5)\,Å$), two water molecules ($d_{Zn(4)\text{–}O(33)} = 2.016(4)$, $d_{Zn(4)\text{–}O(34)} = 2.083(4)$), and one bridging oxygen linked by Mo(2) and Mo(5) from one $\{Mo_6P_4\}$ unit ($d_{Zn(4)\text{–}O(28)} = 2.025(4)\,Å$), to finish a distorted trigonal-bipyramidal coordination environment.

As shown in figure 3, the network structure of **1** may also be described in terms of one-dimensional chains along the *c* axis which consist of $\{Zn(Mo_6P_4)_2\}$ fragments linked by $\{Zn(2)(H_2O)\}$ and $\{Zn(2A)(H_2O)\}$ (symmetry code A: $-x$, $-y+1$, $-z+1$) subunits. Then each chain is connected to two other parallel chains by a $\{Zn(3)(H_2O)(phen)\}$ complex to yield a two-dimensional layer in the ac plane. The $\{Zn(4)(H_2O)_2(phen)\}$ complex makes no contribution to the 2-D network. The most unusual feature of **1** is that three types of tunnels are formed in the solid. The smaller tunnel is surrounded by two $\{Zn(2)(H_2O)\}^{2+}$ cations and two adjacent $\{Zn(Mo_6P_4)_2\}$ anions along the *c* axis while the largest tunnel in the aperture is surrounded by two $\{Zn(3)(H_2O)(phen)\}^{2+}$ cations and two adjacent $\{Zn(Mo_6P_4)_2\}$ anions along the *a* axis.

Based on Valence bond calculations (BVS) [12], the bond valence values for all the molybdenum and phosphorous atoms are in the ranges 5.14–5.30 and 4.82–4.88, respectively, indicating that all Mo and P have a +5 oxidation state. The EPR spectra at room temperature show that the $Mo^{5+}$ signal has $g = 1.9983$, in accord with the valence sum calculation. The values for O(4), O(13), O(18), O(21) and O(24) are in the range 1.07–1.17, indicating that they are $OH^-$ oxygens, while O(32), O(33), O(34) and O(35) have values in range of 0.37–0.49, indicating that they are coordinated water oxygens; all other oxygen atoms have values very close to 2.

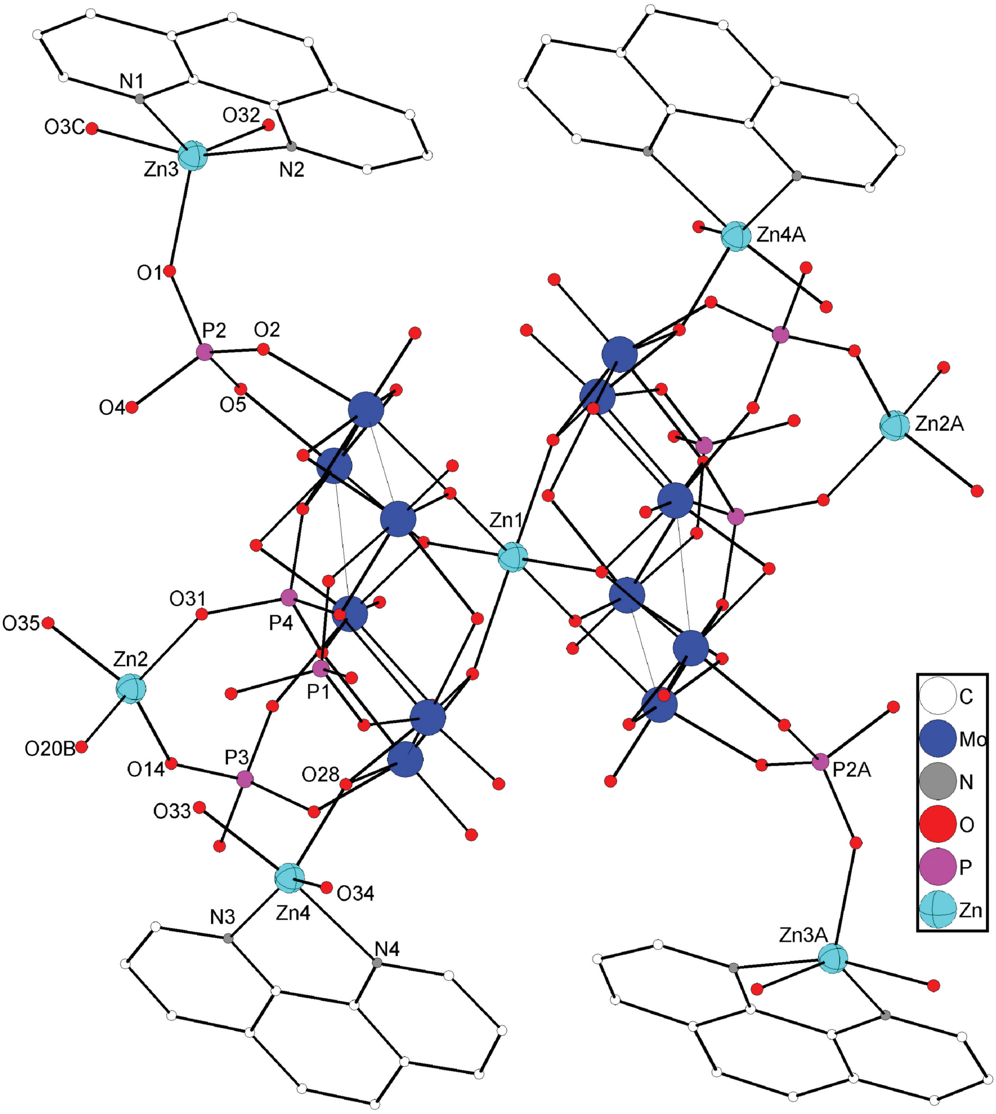

Figure 2. View of the structure of **1**.

In contrast with other reduced molybdenumphosphates with M[$Mo_6P_4$]$_2$ subunits [7, 9], the unusual characteristic of **1** is that there is not only coordination of the inorganic groups with transition metal cations, but also organic molecules incorporated into the 2-D framework of the reduced molybdenum phosphate.

### 3.1. *IR and TGA*

The IR spectrum and elemental analysis data are in accord with the chemical formula of compound **1**. The IR spectrum of **1** exhibits an intense band at 975 and 1043 cm$^{-1}$, characteristic of $\nu$(Mo–O) and features at 744, 725, 687 cm$^{-1}$ associated with $\nu$(P–O) or

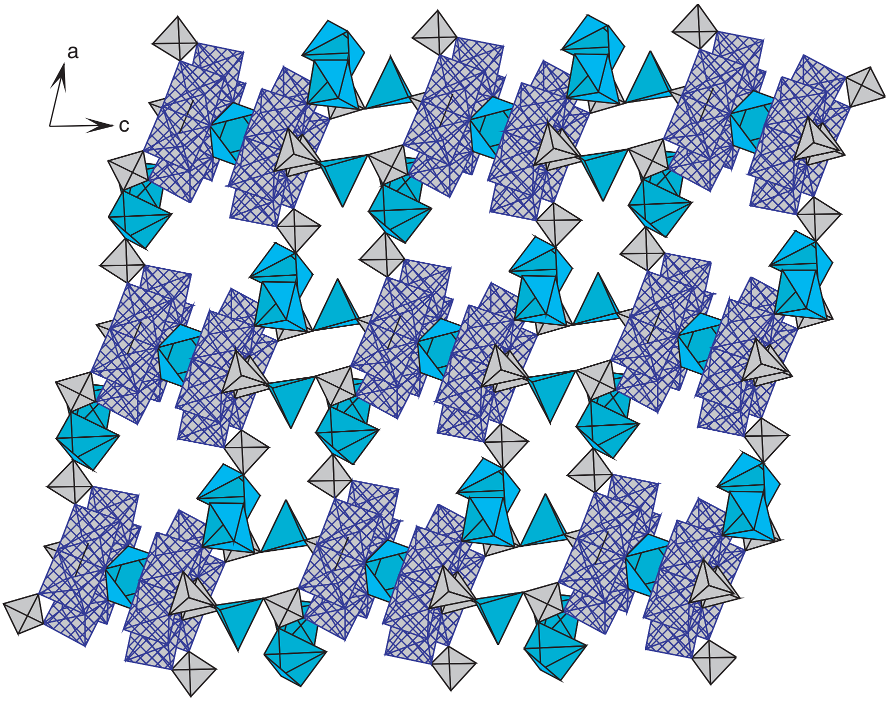

Figure 3. Polyhedral view of the two-dimensional network of **1** in the ac plane (All C, H, N and lattice water molecules are omitted for clarity).

$\nu$(P=O), respectively. The characteristic peak at 504 $\mathrm{cm}^{-1}$ is due to the $\nu$(Zn–O) vibration. The peaks at 1324, 1429, 1494 and 1521 $\mathrm{cm}^{-1}$ are characteristic of phen group, while the broad band at 3240 $\mathrm{cm}^{-1}$ is ascribed to water.

Thermogravimetric analysis (TGA) of compound **1**, carried out under $N_2$ with a heating rate of 10°C $\mathrm{min}^{-1}$, showed a first weight loss of 6.9% in the temperature range 80–290°C and a second weight loss of 19.9% in the temperature range 400–780°C. These two weight losses correspond to the release of crystal lattice (coordinated) water molecules (calculated value of 6.6%) and the 1,10-phenanthroline (calculated value of 20.7%), respectively. Compound **1** continued to lose weight gradually up to 940°C, the highest temperature measured.

### 3.2. *Luminescent properties*

At room temperature, **1** in the powdered solid state displays intense photoluminescence with an emission maximum that occurs at 703 nm upon excitation at 546.9 nm (see figure 4). It is likely that the origin of the emission involves an emissive state derived from an oxide-to-molybdenum charge transition. Luminescence properties have rarely been reported for reduced molybdenumphosphate hybrids. Since **1** is insoluble in water and common solvents such as ethanol, acetone, acetonitrile and benzene, it may be a good candidate for solvent-resistant fluorescent material.

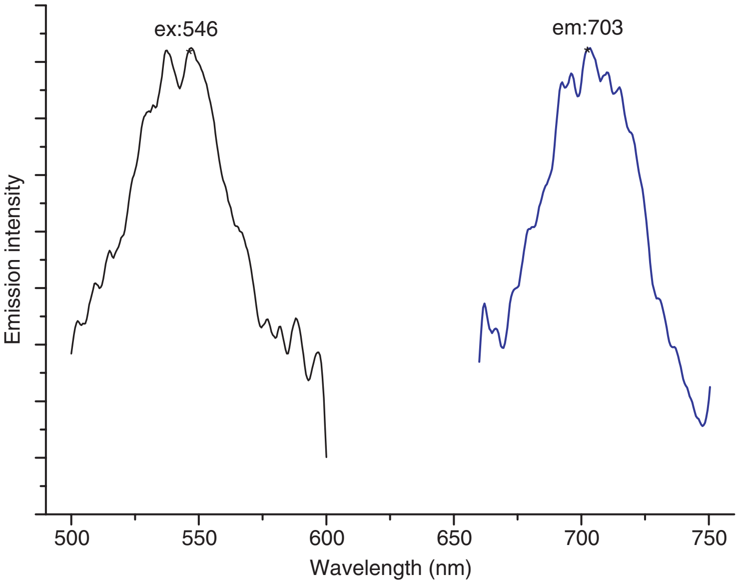

Figure 4. Luminesence excitation and emission spectra of compound **1** (solid) at room temperature.

In conclusion, a new two-dimensional layer-like compound with fluorescence, constructed from Zn[$Mo_6P_4$]$_2$ subunits linked by Zn-coordinated cations, has been synthesized under hydrothermal conditions. It represents the first example of reduced molybdenumphosphate hybrids constructed from [$Mo_6P_4$] with luminescene.

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