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A novel compound with an interpenetrating 2D network structure constructed by $[Mo_5P_2O_{23}]$ and Ni–4,4′-bipyridine components: its synthesis, characterization and magnetic behaviour

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A novel compound $(Hbpy)_2\{[(H_2O)_3Ni(bpy)_{0.5}Ni(bpy)(H_2O)_4]_2[Mo_5P_2O_{23}][Ni((bpy)_{0.5})_2(H_2O)_2][Mo_5P_2O_{23}]\}\cdot 8H_2O$ 1 (bpy = 4,4′-bipyridine) with an interpenetrating 2D network structure was synthesized hydrothermally and characterized by elemental analyses, IR, X-ray single crystal structure analysis and temperature-dependent magnetic susceptibility.

Since the mid-1990s, organic–inorganic hybrid compounds have become a significant area of research for chemists on account of their pronounced structural diversity and controllability of their chemical and physical properties.[1,2] In addition, the potential applications of this type of compound in catalysis,[3,4] new functional materials[5] and biochemistry[6] *etc.* have attracted much attention from materials scientists and biological chemists. Recently, it is shown by Zubieta and coworkers that transition metal complexes with aromatic amines may act as 'bridging ligands' linking polyoxomolybdenum anion clusters into one- and two-dimensional networks.[7,8] As is clear from the extensive significance of this class of compounds, great efforts have also been made by us to investigate the assembly of polyoxomolybdenum–phosphates with secondary metal–aromatic amine ligand complexes. By using the hydrothermal method under suitable reaction conditions, a novel compound $(Hbpy)_2\{[(H_2O)_3Ni(bpy)_{0.5}Ni(bpy)(H_2O)_4]_2[Mo_5P_2O_{23}][Ni((bpy)_{0.5})_2(H_2O)_2][Mo_5P_2O_{23}]\}\cdot 8H_2O$ **1** (bpy = 4,4′-bipyridine) with a unique two-dimensional network has been obtained. As far as we know, this is the first example of 2D network in an anion–cation interpenetrative pattern constructed by polyoxomolybdophosphate anions and three nickel aromatic amine components *via* covalent bonds.

Compound **1** was prepared by hydrothermal reaction of $Na_2MoO_4\cdot 2H_2O$, 4,4′-bipyridine, $NiCl_2$, H_3PO_4 and H_2O in the mol ratio 3 : 1.7 : 1 : 4 : 3265 at 140 °C. Blue crystals of **1** were obtained from the solid product in a yield of 23% with respect to $NiCl_2\cdot 6H_2O$.† Crystals of **1** are air-stable and characterization was carried out by IR and X-ray single crystal structure analysis.[9] The IR spectrum of **1** exhibited intense bands at 891 and 904 cm^{-1}, attributed to ν(Mo=O), and bands at 1614, 1489, 1088, 1055 and 1001 cm^{-1} characteristic of 4,4′-bipyridine. In addition, the temperature-dependent magnetic susceptibility was also measured.

The structure of compound **1** consists of a two-dimensional extended network constructed by Mo–Ni building-blocks $\{[(H_2O)_3Ni(bpy)_{0.5}Ni(bpy)(H_2O)_4]_2[Mo_5P_2O_{23}][Ni((bpy)_{0.5})_2(H_2O)_2][Mo_5P_2O_{23}]\}^{2-}$, protonated bipyridine cations (4,4′-Hbpy) and crystal water molecules. As shown in Fig. 1, the structure of the Mo–Ni building-block is crystallographically centrosymmetric with nickel atom Ni(1) located at the inversion center. The $[Mo_5P_2O_{23}]^{6-}$ cluster anion can be described as a puckered ring of five edge-sharing distorted $[MoO_6]$ octahedra with two capping $[PO_4]$ tetrahedra on each side. In the building-block, each $[Mo_5P_2O_{23}]^{6-}$ cluster anion is linked to three nickel atoms (Ni(1), Ni(2) and Ni(3)) with different coordination spheres through two $[MoO_6]$ octahedra and one $[PO_4]$ tetrahedron to form Ni–O–Mo and Ni–O–P covalent interactions with bond lengths Ni(1)–O(MoO_6) 2.114(4) Å, Ni(2)–O(MoO_6) 2.107(5) Å and Ni(3)–O(PO_4) 2.045(4) Å. The coordinated geometry for all nickel atoms can be regarded as distorted octahedral. The Ni(1) atom is bound to two nitrogen atoms of two bipyridine ligands, two oxygen atoms from two $[MoO_6]$ octahedra belonging to two $[Mo_5P_2O_{23}]^{6-}$ cluster anions, as well as two oxygen atoms from two crystal H_2O molecules. Ni(2) is coordinated with two nitrogen atoms from two bipyridine ligands, one oxygen atom from the $[MoO_6]$ unit and three oxygen donors from three H_2O molecules. The Ni(3) atom, on the other hand, is linked to only one nitrogen atom from a bipyridine molecule, one oxygen atom from the $[PO_4]$ tetrahedron and four H_2O molecules. The different coordination environments of the nickel atoms play a critical role in the formation of the two-dimensional packing structure of compound **1**. It is interesting that Ni(2) and Ni(3) are connected to each other by sharing a bipyridine ligand in the building-block, and also there is a bridging 4,4′-bpy between Ni(1) and Ni(2), thus forming a linear five-Ni^{II} segment in the packing structure. The whole packing structure is shown in Fig. 2, in which the Mo–Ni building-blocks are connected alternately in cross-directions by Ni(1) with Ni(2) atoms of the adjacent block to

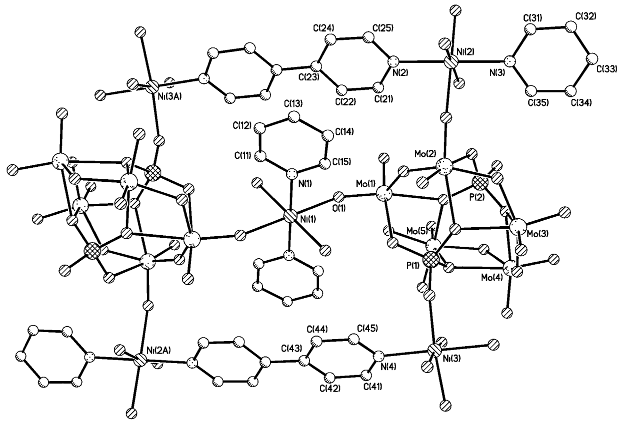

Fig. 1 The structure of the Mo–Ni building-block of compound **1**.

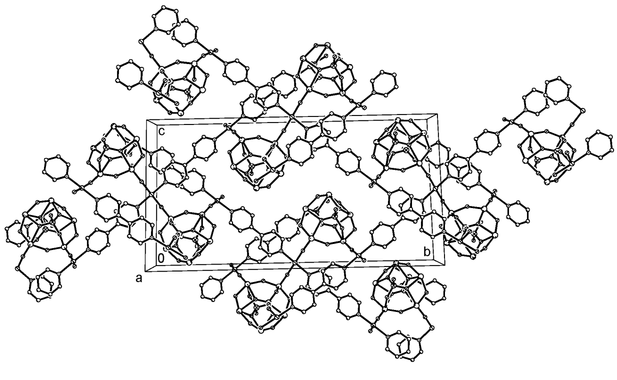

Fig. 2 A view of the packing structure in the *bc* plane. The terminal oxygen atoms, coordinated water, protonated Hbpy and crystal water are omitted for clarity.

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form two intersecting chains. In other words, each five-Ni^{II} segment is linked to two other such two segments on both sides by two $[Mo_5P_2O_{23}]^{6-}$ to form eventually a step-like one-dimensional infinite chain. Every building-block takes part in this formation of the two step-like chains, of which one passes through the Ni(2) atoms and the other the Ni(1) atoms. The angle between the two chains is about 79.3°. Crystal H_2O molecules and the protonated Hbpy cations occupy the vacancies of the network and are connected to the building-blocks by N–H(Hbpy)···O(coordinated water); O–H(crystal water)···O(coordinated water); O–H(crystal water)···O-[(MoO_6) or (PO_4)] hydrogen bonds with distances of 2.674–2.829 Å.

The temperature-dependence of the molar magnetic susceptibility χ_M and the magnetic moment μ_{eff} are depicted in Fig. 3. The susceptibility increases continuously down to the lowest measured temperature of 5.0 K. Fitting the measured data with the Curie–Weiss equation gives the Curie–Weiss parameters $C = 6.457$ and $\theta = -2.34$ K.

At 299.2 K, the measured μ_{eff} is 7.07 μ_B per Ni_5, which is close to the theoretical spin-only value (6.32 μ_B) for five Ni^{II} atoms that are coordinated octahedrally in high spin ($S = 1$) when no magnetic coupling is operative in the molecule. A slightly higher measured μ_{eff} relative to the theoretical value is ascribable to an appreciable orbital contribution. The μ_{eff} remains basically unchanged down to 13 K then decreases rapidly to 5.89 μ_B at 5 K.

The magnetic data was analyzed in terms of a model of single-ion zero-field splitting taking into account the exchange interaction in a molecular field approach. A least-squares fitting of the experimental data was carried out to give a set of the best fitting parameters with $g = 2.23$, $D = 6.56\ \mathrm{cm}^{-1}$ and $\theta' = -0.76$ K with the deviation factor defined by $R = \Sigma(\mu_{eff}^{obs} - \mu_{eff}^{calc})^2/\Sigma(\mu_{eff}^{obs})$ being 8×10^{-6}, where D and θ' are the parameters for the zero-field splitting and the magnetic coupling, respectively. As anticipated, the calculation indicates that the magnetic contribution from single anisotropy is much more predominant relative to the exchange interaction through the bridging 4,4′-bipyridine.

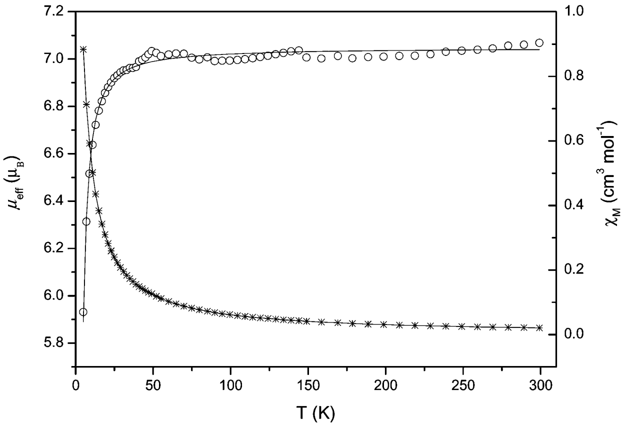

Fig. 3 . μ_{eff} and χ_M *vs.* T plots for **1**. The solid lines are the theoretical simulations; ○ indicates the observed μ_{eff}, and *, the observed χ_M.

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Notes and references

† *Experimental section*: a mixture of $Na_2MoO_4 \cdot 2H_2O$ (125 mg, 0.5 mmol), 4,4′-bipyridine (55 mg, 0.28 mmol), $NiCl_2 \cdot 6H_2O$ (40 mg, 0.17 mmol), 85% H_3PO_4 (*ca.* 60 mg, 0.62 mmol) and H_2O (10 mL, 555 mmol) was heated in a 25-mL stainless steel reactor with a Teflon-liner at 140 °C for 24 h. After cooling, the crude solid was isolated by filtration. This crude solid contains three phases, *i.e.*, a pale blue powder, pale blue crystals and colorless crystals. The pale blue powder was washed out with copious amounts of water. The pale blue crystals of **1** (27 mg, 23% yield) were separated by hand under a microscope. The colorless crystals were $(H_2bpy)_3(Mo_5P_2O_{23}) \cdot 3.5H_2O$. Elemental analysis: calc. for $C_{60}H_{98}Mo_{10}N_{12}Ni_5O_{70}P_4$ **1**: C, 20.68; H, 2.83; N, 4.82; found: C, 20.58; H, 2.96; N 4.82%. IR (KBr) ν/cm^{-1}: 3325vs, 3109m, 1614vs, 1541s, 1489s, 1421s, 1221m, 1088s, 1055s, 1039s, 1001s, 904vs, 891vs, 810s, 675vs, 642s, 569s. The temperature-dependent magnetic susceptibility was determined on a Quantum Design SQUID magnetometer on the MPMS-7 system under an external 10000 Oe magnetic field and recorded at intervals of 2–10 K in the range 5–300 K. The stability of the magnetic measurements across the temperature range suggests that there are no major structural changes. All samples were single crystals selected carefully under a microscope.

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9 *Crystal data* for **1**: crystal size = 0.30 × 0.10 × 0.10 mm, $C_{60}H_{98}Mo_{10}N_{12}Ni_5O_{70}P_4$, $M = 3484.33$, monoclinic, space group $P2_1/n$, $a = 10.7192(2)$, $b = 31.0886(6)$, $c = 16.4690(3)$ Å, $\beta = 104.331(1)°$, $V = 5317.4(2)$ Å^3, $Z = 2$, R ($wR2$) = 0.047 (0.099) for 6752 reflections with $I = 2.0\sigma(I)$. The diffraction data were collected on a Siemens SMART CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range $1.83 < \theta < 25.02°$ at 293 K. A total of 22337 reflections were obtained, of which 9299 unique reflections were used. The structure was solved by direct methods with the SHELXTL-97 program. Full-matrix least-squares refinement was based on F^2. The hydrogen atoms on the bipyridine ligands were idealized but those of the water molecules were not located in the refinement. The number of refined parameters was 707. CCDC 161607. See http://www.rsc.org/suppdata/cc/b2/b205486h/ for crystallographic data in CIF or other electronic format.