

Organic–inorganic hybrids assembled by bis(undecatungstophosphate) lanthanates and dinuclear copper(II)–oxalate complexes†‡

Jianfang Cao, Shuxia Liu,* Ruige Cao, Linhua Xie, Yuanhang Ren, Chaoying Gao and Lin Xu*

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A series of organic–inorganic hybrid compounds, $K_2H_7[\{Ln(PW_{11}O_{39})_2\}\{Cu_2(bpy)_2(\mu-ox)\}] \cdot xH_2O$ ($Ln = La, x \approx 18$ (**1**); $Ln = Pr, x \approx 18$ (**2**); $Ln = Eu, x \approx 16$ (**3**); $Ln = Gd, x \approx 22$ (**4**); $Ln = Yb, x \approx 19$ (**5**); $bpy = 2,2'$ -bipyridine and $ox = oxalate$), have been isolated by the conventional solution method. Single-crystal X-ray diffraction studies reveal that compounds **1–5** are isomorphous and consist of one-dimensional chains, which are constructed by alternating bis(undecatungstophosphate) lanthanates $[Ln(PW_{11}O_{39})_2]^{11-}$ and dinuclear copper(II)–oxalate complexes $[Cu_2(bpy)_2(\mu-ox)]^{2+}$. π – π interactions of the bpy ligands from adjacent chains lead to their three-dimensional structures. An analogue of potassium $K_2H_9[\{K(PW_{11}O_{39})_2\}\{Cu_2(bpy)_2(\mu-ox)\}] \cdot \sim 20.5H_2O$ (**6**) has also been obtained. The syntheses and structures of these compounds are reported here. Magnetic properties of **1**, **2** and **3** are discussed as well. Attempts to crystallize similar compounds containing Co(II) and Ni(II) were unsuccessful.

Introduction

Polyoxometalates (POMs) are discrete anionic metal–oxygen clusters with many potential applications due to their electronic versatility and structural diversity.¹ A current interest in this area is to modulate the properties of interesting POM building blocks by secondary metal coordination complexes to obtain functionalized organic–inorganic hybrid materials.² So far, the inorganic building blocks of this type of hybrid compound are mainly well-defined Keggin,^{3–4} Wells–Dawson,⁵ Anderson⁶ and Lindquist⁷ types of POMs, or new POM units, such as spherical vanadium oxides,⁸ and capped clusters.⁹ Recently, our group have also reported several organic–inorganic hybrid compounds of this type based on $[MnV_{13}O_{38}]^{7-10}$, $[V^{IV}_7V^V_9O_{38}Cl]^{4-11}$ and $[M(OH)_7Mo_6O_{17}]^{2-}$ ($M = Al, Cr$)¹² polyanions. However, we note that reported hybrid compounds containing lanthanopolyoxometalates (LnPOMs) are comparatively rare.^{5b,c,13} One type of LnPOM is the 1 : 2 compounds bis(undecatungstophosphate) lanthanates $[Ln(PW_{11}O_{39})_2]^{11-}$ ($Ln(PW_{11})_2$), which were first reported by Peacock and Weakley.¹⁴ Although several compounds related to this type of polyanion have been reported,¹⁵ the synthetic system of $Ln(PW_{11})_2$ and the transition metal coordination complexes have not been investigated to date. The oxalato-bridged dinuclear copper complex has proven to be a versatile building block with a unique magnetic property when combined with various polyanions. Consequently, we investigated the reactions of $Ln(PW_{11})_2$ polyanions and the oxalato-bridged dinuclear copper

complex $[Cu_2(bpy)_2(\mu-ox)]^{2+}$. A series of organic–inorganic hybrid compounds, $K_2H_7[\{Ln(PW_{11}O_{39})_2\}\{Cu_2(bpy)_2(\mu-ox)\}] \cdot xH_2O$ ($Ln = La, x \approx 17$ (**1**); $Ln = Pr, x \approx 18$ (**2**); $Ln = Eu, x \approx 16$ (**3**); $Ln = Gd, x \approx 22$ (**4**); $Ln = Yb, x \approx 19$ (**5**); $bpy = 2,2'$ -bipyridine and $ox = oxalate$), which consist of one-dimensional chains constructed by alternating bis(undecatungstophosphate) lanthanates $[Ln(PW_{11}O_{39})_2]^{11-}$ and dinuclear copper(II)–oxalate complexes $[Cu_2(bpy)_2(\mu-ox)]^{2+}$, have been isolated. An analogue of potassium $K_2H_9[\{K(PW_{11}O_{39})_2\}\{Cu_2(bpy)_2(\mu-ox)\}] \cdot \sim 20.5H_2O$ (**6**) has also been obtained. Attempts to crystallize similar compounds containing Co(II) and Ni(II) were unsuccessful. The syntheses and structures of these compounds are reported here. Magnetic studies of **1**, **2** and **3** have also been carried out and discussed.

Experimental

Materials and methods

The $H_3PW_{12}O_{40} \cdot xH_2O$ precursor was synthesized according to the procedure described in the literature¹⁶ and characterized by IR spectrum. The $Pr(ClO_4)_3 \cdot xH_2O$ ($x \approx 6–8$) was prepared by the reaction of Pr_4O_6 and $HClO_4$. All other chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer, W, K and Ln were determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT/IR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 $^\circ C min^{-1}$. Powder X-ray diffraction measurements were performed on a Rigaku D/MAX-3 instrument with $Cu-K\alpha$ radiation in the angular range $2\theta = 3–50^\circ$ at 293 K. The magnetic susceptibilities were measured over 300–2 K at the magnetic field of 1000 Oe for **1**, **2** and **3** on a Quantum Design MPMS-5 SQUID magnetometer.

A Key Laboratory of Polyoxometalates Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun City, JiLin, P. R. China 130024. E-mail: liusx@nenu.edu.cn, linxu@nenu.edu.cn; Fax: +86-431-85099328

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‡ Electronic supplementary information (ESI) available: Additional structural views of **1** and the structural information on compounds **1–6**. IR spectra of **1–6**, TG curve of **1** and XRPD patterns of **1–3**. See DOI: 10.1039/b713275a

Synthesis of $K_2H_7\{[La(PW_{11}O_{39})_2]\{Cu_2(bpy)_2(\mu-ox)\}}\cdot 18H_2O$ (1). The cationic complex $[Cu_2(bpy)_2(\mu-ox)]^{2+}$ (**A**) and the anion $[La(PW_{11}O_{39})_2]^{11-}$ (**B**) were prepared *in situ*.^{3d,e,12} For **A**, a 10 mL ethanol solution of 2,2'-bipyridine (41 mg, 0.27 mmol) and 10 mL aqueous solution of oxalic acid dihydrate (17 mg, 0.14 mmol) were added to a 20 mL aqueous solution of $CuCl_2\cdot 2H_2O$ (46.5 mg, 0.27 mmol). For **B**, $H_3PW_{12}O_{40}\cdot xH_2O$ (400 mg, 0.14 mmol) and $LaCl_3\cdot 7H_2O$ (16.8 mg, 0.069 mmol) were dissolved in hot water (20 mL), and potassium acetate (400 mg, 4.08 mmol) in hot water (1 mL), and added dropwise under stirring. Solution **A** was added dropwise to solution **B**, and a blue precipitate appeared. The mixture was stirred for 30 min, and then filtered; the filtrate was allowed to stand at room temperature for crystallization. Blue block crystals of compound **1** were obtained after 6 days. Yield: 51% (based on **W**). Anal. Calcd for $C_{22}H_{59}N_4Cu_2K_2LaP_2W_{22}O_{100}$: C, 4.11; H, 0.92; N, 0.87; W, 62.90; K, 1.22; La, 2.17 (%). Found: C, 4.03; H, 0.93; N, 0.90; W, 62.83; K, 1.16; La, 2.12 (%).

Synthesis of $K_2H_7\{[Pr(PW_{11}O_{39})_2]\{Cu_2(bpy)_2(\mu-ox)\}}\cdot 18H_2O$ (2). Compound **2** was prepared following the procedure described for compound **1**, but $Pr(ClO_4)_3\cdot xH_2O$ was used instead of $LaCl_3\cdot 7H_2O$. Glaucous block crystals were obtained after 4 days. Yield: 53% (based on **W**). Anal. Calcd for $C_{22}H_{59}N_4Cu_2K_2PrP_2W_{22}O_{100}$: C, 4.11; H, 0.92; N, 0.87; W, 62.88; K, 1.22; Pr, 2.19 (%). Found: C, 4.01; H, 0.94; N, 0.79; W, 62.80; K, 1.17; Pr, 2.11 (%).

Synthesis of $K_2H_7\{[Eu(PW_{11}O_{39})_2]\{Cu_2(bpy)_2(\mu-ox)\}}\cdot 16H_2O$ (3). Compound **3** was prepared following the procedure described for compound **1**, but $Eu(ClO_4)_3\cdot xH_2O$ was used instead of $LaCl_3\cdot 7H_2O$. Blue block crystals were obtained after 6 days. Yield: 47% (based on **W**). Anal. Calcd for $C_{22}H_{59}N_4Cu_2K_2EuP_2W_{22}O_{98}$: C, 4.12; H, 0.87; N, 0.87; W, 63.12; K, 1.22; Eu, 2.37 (%). Found: C, 4.05; H, 0.85; N, 0.82; W, 63.05; K, 1.13; Eu, 2.29 (%).

Synthesis of $K_2H_7\{[Gd(PW_{11}O_{39})_2]\{Cu_2(bpy)_2(\mu-ox)\}}\cdot 22H_2O$ (4). Compound **4** was prepared following the procedure described for compound **1**, but $GdCl_3\cdot 6H_2O$ was used instead of $LaCl_3\cdot 7H_2O$. Blue block crystals were obtained after 5 days. Yield: 52% (based on **W**). Anal. Calcd for $C_{22}H_{67}N_4Cu_2K_2GdP_2W_{22}O_{104}$: C, 4.05; H, 1.04; N, 0.86; W, 62.03; K, 1.20; Gd, 2.41 (%). Found: C, 3.91; H, 0.99; N, 0.87; W, 62.12; K, 1.13; Gd, 2.29 (%).

Synthesis of $K_2H_7\{[Yb(PW_{11}O_{39})_2]\{Cu_2(bpy)_2(\mu-ox)\}}\cdot 19H_2O$ (5). Compound **5** was prepared following the procedure described for compound **1**, but $YbCl_3\cdot 6H_2O$ was used instead of $LaCl_3\cdot 7H_2O$. Blue block crystals were obtained after 6 days. Yield: 49% (based on **W**). Anal. Calcd for $C_{22}H_{61}N_4Cu_2K_2YbP_2W_{22}O_{101}$: C, 4.08; H, 0.95; N, 0.86; W, 62.39; K, 1.21; Yb, 2.67 (%). Found: C, 3.96; H, 0.99; N, 0.81; W, 62.31; K, 1.13; Yb, 2.61 (%).

Synthesis of $K_2H_9\{[K(PW_{11}O_{39})_2]\{Cu_2(bpy)_2(\mu-ox)\}}\cdot 20.5H_2O$ (6). The cationic complex $[Cu_2(bpy)_2(\mu-ox)]^{2+}$ (**A**) and the anion $[K(PW_{11}O_{39})_2]^{13-}$ (**C**) were prepared *in situ*. For **A**, it was prepared following the procedure described above. For **C**, $H_3PW_{12}O_{40}\cdot xH_2O$ (400 mg, 0.27 mmol) was dissolved in 40 mL 1.0 mol L⁻¹ potassium acetate aqueous solution and heated for 30 min. Solution **A** was added dropwise to solution **C**, and a blue precipitate appeared. The mixture was stirred for 30 min, and then filtered; the filtrate was allowed to stand at room temperature for crystallization. Light-blue block crystals were obtained after two weeks. Yield: 37%

(based on **W**). Anal. Calcd for $C_{22}H_{66}N_4Cu_2K_3P_2W_{22}O_{102.5}$: C, 4.14; H, 1.04; N, 0.88; W, 63.42; K, 1.84 (%). Found: C, 4.05; H, 1.12; N, 0.92; W, 63.34; K, 1.75 (%).

X-Ray crystallography

Data for compounds **1** and **3–6** were collected on a Siemens Smart CCD diffractometer (a Rigaku R-AXIS RAPID IP diffractometer for **2**) with Mo-K α monochromated radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Empirical absorption corrections were applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms except for O36, C4 of compound **4** and O9, C1, C11 of compound **6**. The hydrogen atoms for bpy were fixed in ideal positions. Inside the frameworks of all the compounds, there are a large number of disordered lattice waters, which show many peaks of low electronic density in the difference Fourier maps. So the SQUEEZE subroutine of PLATON software¹⁷ was applied to create new reflection data where contributions from the disordered lattice waters were removed from the original data but were included in the structure factor calculations. The crystal data and structure refinements of compounds **1–6** based on the new reflection data are summarized in Table 1. The number of lattice waters for **1–6** were determined by elemental analyses, TG and calculations of electron count inside the frameworks with SQUEEZE.¹⁸ The experimental and simulated X-ray powder diffraction patterns (XRPD) of compounds **1–3** are shown in Fig. S6.† The diffraction peaks on both experimental and simulated patterns match well in position, indicating their phase purity. Additionally, the XRPD of **1**, **2** and **3** are similar, which is in agreement with their isomorphous structures determined by single-crystal X-ray diffraction.

CCDC reference numbers 651554–651559 for **1–6**.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713275a

Results and discussion

Synthesis

Compounds **1–5** were obtained from the reaction of $[Cu_2(bpy)_2(\mu-ox)]^{2+}$ and inorganic building blocks $[Ln(PW_{11}O_{39})_2]^{11-}$ at room temperature. An analogue of potassium $K_2H_9\{[K(PW_{11}O_{39})_2]\{Cu_2(bpy)_2(\mu-ox)\}}\cdot 20.5H_2O$ (**6**) was also isolated in the absence of Ln^{3+} . The successful introduction of K^+ into the 1D chains may be for similar ionic radii (radii: $K^+ = 133 \text{ pm}$; $Ln^{3+} = 106–98.5 \text{ pm}$), oxophilicity and coordination requirements of the two types of cations. Our previous work also demonstrated a similar result, both K^+ and Ln^{3+} coordinated with 1 : 13 heteropolyanion $[MnV_{13}O_{38}]^{7-}$ leading to 2D frameworks.^{10,19}

On the other hand, the isolation of these compounds depends on the choice of the transition metal coordination complexes. If the Cu(II) was replaced by the Co(II) or Ni(II) under the same conditions, we could not obtain the expected compounds but only an amorphous precipitate. It may be that for the peculiar

Table 1 Crystal data and structure refinements for 1–6

	1	2	3	4	5	6
Formula	C ₂₂ H ₅₉ N ₄ Cu ₂ K ₂ La P ₂ W ₂₂ O ₁₀₀	C ₂₂ H ₅₉ N ₄ Cu ₂ K ₂ Pr P ₂ W ₂₂ O ₁₀₀	C ₂₂ H ₅₅ N ₄ Cu ₂ K ₂ Eu P ₂ W ₂₂ O ₉₈	C ₂₂ H ₆₇ N ₄ Cu ₂ K ₂ Gd P ₂ W ₂₂ O ₁₀₄	C ₂₂ H ₈₁ N ₄ Cu ₂ K ₂ Yb P ₂ W ₂₂ O ₁₀₉	C ₂₂ H ₆₆ N ₄ Cu ₂ K ₃ P ₂ W ₂₂ O _{102.5}
Fw	6430.55	6432.56	6407.58	6520.97	6482.71	6377.81
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c
a/Å	14.8120(8)	14.697(3)	14.764(2)	14.747(5)	14.6697(5)	15.1688(11)
b/Å	20.5146(8)	20.431(4)	20.448(2)	20.484(5)	20.4327(7)	20.2868(11)
c/Å	38.791(2)	38.639(8)	38.477(4)	38.466(1)	38.3365(12)	38.630(2)
β/°	99.2840(1)	99.53(3)	99.961(3)	99.707(7)	100.197(1)	99.987(2)
V/Å ³	11632.6(1)	11442(4)	11440(2)	11453(5)	11309.5(7)	11707.3(13)
Z	4	4	4	4	4	4
D _c /mg m ⁻³	3.662	3.734	3.720	3.782	3.807	3.618
Abs. coeff./mm ⁻¹	22.573	23.002	23.126	23.139	23.670	22.114
Reflns collected	30558	54304	34707	28876	35009	29356
Independent reflns	10889	13075	13711	10692	13294	10351
θ range/°	1.89–25.60	3.17–27.48	1.72–28.22	1.72–25.60	1.73–28.28	1.69–25.10
GOF on F ²	0.920	0.963	0.966	0.951	0.916	0.955
R _{int}	0.0567	0.0935	0.0828	0.1058	0.0584	0.1090
R ₁ [I > 2σ(I)] ^a	0.0341	0.0458	0.0448	0.0458	0.0387	0.0540
wR ₂ (all data) ^b	0.0674	0.1010	0.1001	0.1274	0.0650	0.1184

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

coordination geometries of Cu²⁺ cations the Jahn–Teller effect may play an important role in the formation of the compounds.

Crystal structures

Compounds 1–6 are isomorphic only with slight differences in bond length, bond angle and the number of lattice waters; 1 is described as an example below. Compound 1 consists of 1D chains

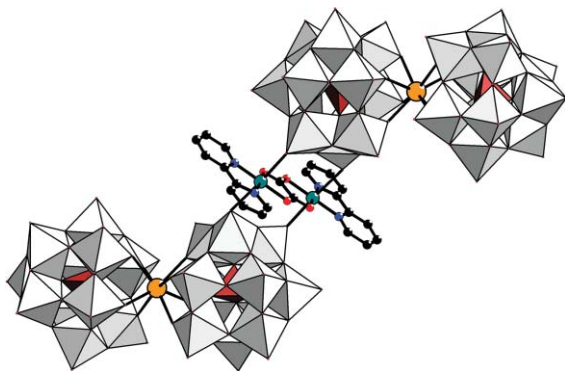


Fig. 1 Perspective view of the building blocks of 1 with the polyanions represented by polyhedra. Color codes: La, orange; W, gray; P, dark red; Cu, teal; O, red; N, blue; C, black.

built up of [Cu₂(bpy)₂(μ-ox)]²⁺ and [La(PW₁₁O₃₉)₂]¹¹⁻, potassium cations and water molecules located inside the frameworks between adjacent chains. The centrosymmetric [Cu₂(bpy)₂(μ-ox)]²⁺ is made up of two copper atoms bridged by an oxalate in the usual bis-bidentate fashion with a Cu···Cu distance of 5.15(7) Å (Fig. 1). Each copper atom in the dinuclear copper unit is coordinated in the equatorial plane with two nitrogen atoms from a bpy ligand, two oxygen atoms from an oxalate ligand with Cu–N and Cu–O bond lengths ranging from 1.93(9)–1.97(1) and 1.99(1)–1.99(7) Å, and two terminal oxygen atoms from two [La(PW₁₁O₃₉)₂]¹¹⁻ polyanions in polar positions with Cu–O bond lengths of 2.37(9) and 2.54(8) Å, adopting a distorted octahedral coordination environment. The La atom in the [La(PW₁₁O₃₉)₂]¹¹⁻ unit is coordinated with eight unsaturated O atoms from two α-[PW₁₁O₃₉]⁷⁻ units in a distorted square antiprismatic geometry with La–O bond lengths ranging from 2.46(7) to 2.51(3) Å (ESI, Fig. S2†). The bond lengths and angles in the α-[PW₁₁O₃₉]⁷⁻ units are within the usual range.²⁰ With such coordination geometries, each [Cu₂(bpy)₂(μ-ox)]²⁺ unit in 1 connects with two [La(PW₁₁O₃₉)₂]¹¹⁻ polyanions and each [La(PW₁₁O₃₉)₂]¹¹⁻ polyanion bridges to two [Cu₂(bpy)₂(μ-ox)]²⁺ units, resulting in an infinite chain running along the *c*-axis (Fig. 2). π–π interactions of the bpy ligands from adjacent chains (Fig. 3) lead further to the three-dimensional structure of 1. (ESI, Fig. S3†). Distances

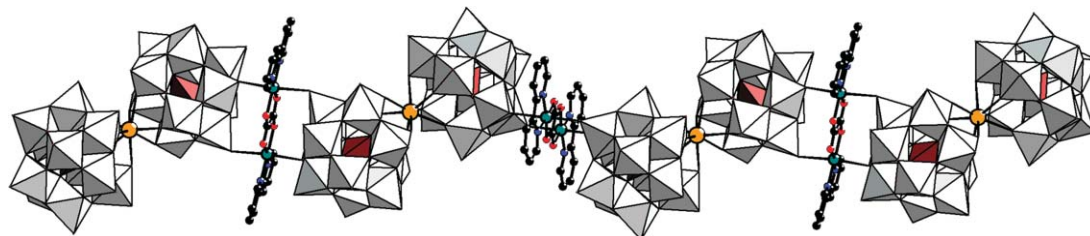


Fig. 2 View of the 1D chain of 1 along the *c*-axis. All potassium cations, lattice water molecules and hydrogen atoms are omitted for clarity. Color codes: La, orange; W, gray; P, dark red; Cu, teal; O, red; N, blue; C, black.

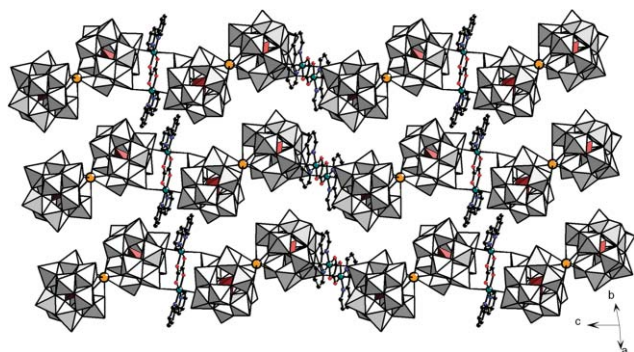


Fig. 3 π - π interactions of the bpy ligands from adjacent chains. All potassium cations, lattice water molecules and hydrogen atoms are omitted for clarity. Color codes: La, orange; W, gray; P, dark red; Cu, teal; O, red; N, blue; C, black.

between the least-square planes²¹ of the bpy ligands are about 3.40(7) Å.

The bond-valence calculations²² indicate that in **1** that all W atoms are in the +6 oxidation state, all Cu atoms are in the +2 oxidation state, and the La atom is in the +3 oxidation state. The bond valence sums of all the O atoms in **1** are in their usual range from 1.63 to 2.10. Thus the overall charge of all atoms in the formula obtained from the single-crystal structure determination is -7 . The difference Fourier maps reveal that no other K ions are present inside the frameworks. Consequently, the negative charges ought to be compensated by the protonation of the disordered lattice water molecules and the formula of **1** should be $\text{K}_2\text{H}_7[\{\text{La}(\text{PW}_{11}\text{O}_{39})_2\}\{\text{Cu}_2(\text{bpy})_2(\mu\text{-ox})\}] \cdot 18\text{H}_2\text{O}$, which is also confirmed by elemental analyses. Similar results have also been obtained for compounds **2–6**. It is noteworthy that in compounds **1–5** the lengths of Ln–O (La³⁺, Pr³⁺, Eu³⁺, Gd³⁺, Yb³⁺) bonds decrease with increasing atomic number and decreasing ionic radii of the Ln³⁺ ions, (Table 2) which is in accordance with the effect of the lanthanide contraction.²³ In **6**, the $[\text{K}(\text{PW}_{11}\text{O}_{39})_2]^{13-}$ polyanion is similar to the reported $[\text{K}(\text{SiW}_{11}\text{O}_{39})_2]^{15-}$ polyanion.²⁴

IR spectroscopy

The infrared spectra of compounds **1–6** exhibit characteristic peaks of the Keggin anions in the low-wavenumber region (ESI, Fig. S3†). Bands ranging from 700–900 cm^{-1} belong to the W–O_{b/c}–W stretching modes and bands between 916 and 951 cm^{-1} are attributed to the W–O_i stretching vibration. The bands at around 1090 and 1046 cm^{-1} can be assigned to the P–O stretching vibration²⁵ (Table 3). Compared with that of the parent Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$, the band for the P–O stretching vibration of the $[\text{M}(\text{PW}_{11}\text{O}_{39})_2]^{n-}$ anion splits into two bands because of their lower symmetry than that of the parent $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (T_d) by removing

Table 2 Comparison of bond lengths (Å) of Ln–O in compounds **1–5**

Compound	Ln–O
1 (La ³⁺)	2.467(7)–2.513(6)
2 (Pr ³⁺)	2.430(9)–2.477(9)
3 (Eu ³⁺)	2.390(7)–2.436(9)
4 (Gd ³⁺)	2.382(1)–2.420(1)
5 (Yb ³⁺)	2.326(7)–2.351(7)

Table 3 Selected assignable infrared frequencies for polyanions of **1–6** and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$

Polyanion	Stretching frequency assignment/ cm^{-1}		
	P–O	W–O _i	W–O _{b/c} –W
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$	1079	981	890, 799
$[\text{La}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$	1091, 1046	951	890, 831, 773, 727
$[\text{Pr}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$	1093, 1044	950	885, 832, 765, 727
$[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$	1098, 1046	951	886, 830, 766, 727
$[\text{Gd}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$	1101, 1048	952	887, 833, 767, 724
$[\text{Yb}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$	1108, 1049	951	886, 832, 767, 727
$[\text{K}(\text{PW}_{11}\text{O}_{39})_2]^{13-}$	1051, 1007	917	877, 824, 759

an {W–O} unit. The weaker bands from 1120 to 1600 cm^{-1} are associated with the 2,2'-bipyridine ligands. In addition, the peaks at around 1645 cm^{-1} [$\nu_{\text{as}}(\text{CO})$]; 1350, 1315 cm^{-1} [$\nu_{\text{s}}(\text{CO})$] and 770 cm^{-1} [$\nu(\text{OCO})$] are assigned to the oxalate ligands.²⁶

TG analyses

The thermal gravimetric (TG) analysis was performed with a N₂ atmosphere for compound **1** (ESI, Fig. S3†). It shows a total weight loss of 11.29% in the range of 20–780 °C, which agrees with the calculated value of 11.38%. The weight loss of 5.21% at 20–230 °C corresponds to the loss of all lattice and coordinated water molecules (calcd 5.15%). The weight loss of 6.08% at 230–780 °C arises from the decomposition of 2,2'-bipyridine and oxalate ligands (calcd 6.23%).

Magnetic properties

The thermal evolution of the magnetic molar susceptibility and the $\chi_m T$ product of **1**, **2** and **3** in the temperature range 300–2 K are shown in Fig. 4. For **1**, χ_m value increases continuously with decreasing temperature and no maximum is observed, the magnetic susceptibility does not conform to the Curie–Weiss behavior even at high temperatures. The value of $\chi_m T$ is 0.410 $\text{cm}^3 \text{K mol}^{-1}$ at 300 K, is lower than the calculated value ($\chi_m T = \mu_{\text{eff}}^2/8$, 0.750 $\text{cm}^3 \text{K mol}^{-1}$, considering $g = 2$) for two uncoupled Cu²⁺ centres. Upon cooling, $\chi_m T$ decreases from 300 K to 63 K, and remains approximately constant around 0.0191 $\text{cm}^3 \text{K mol}^{-1}$ when $T < 63 \text{ K}$ which may be attributed to the paramagnetic impurities. The decrease of $\chi_m T$ can be associated with an antiferromagnetic coupling in the Cu^{II}–oxalate dimers while the plateau corresponds to the Curie law expected for the paramagnetic impurities with no detectable interaction between them. The experimental data closely follow the Bleaney–Bowers equation for isotropic exchange in the copper(II) dimer.²⁷

$$\chi_m = A \left[\frac{(1-\rho)Ng^2\beta^2}{kT[3 + \exp(-J/kT)]} + \frac{\rho Ng^2\beta^2}{4kT} \right] \quad (1)$$

This equation has been modified to take into account the admixture of paramagnetic impurities, where N , β and k have their usual meanings, ρ is the fraction of noncoupled impurities, g is the g factor of the dinuclear copper complex. The singlet–triplet energy gap (J) is defined by the Hamiltonian $H = -JS_A S_B$ ($S_A = S_B = 1/2$). The A factor is the number of Cu²⁺, with $A = 2$ for **1**.

Least-squares fitting of the experimental data is performed by minimizing eqn (2),

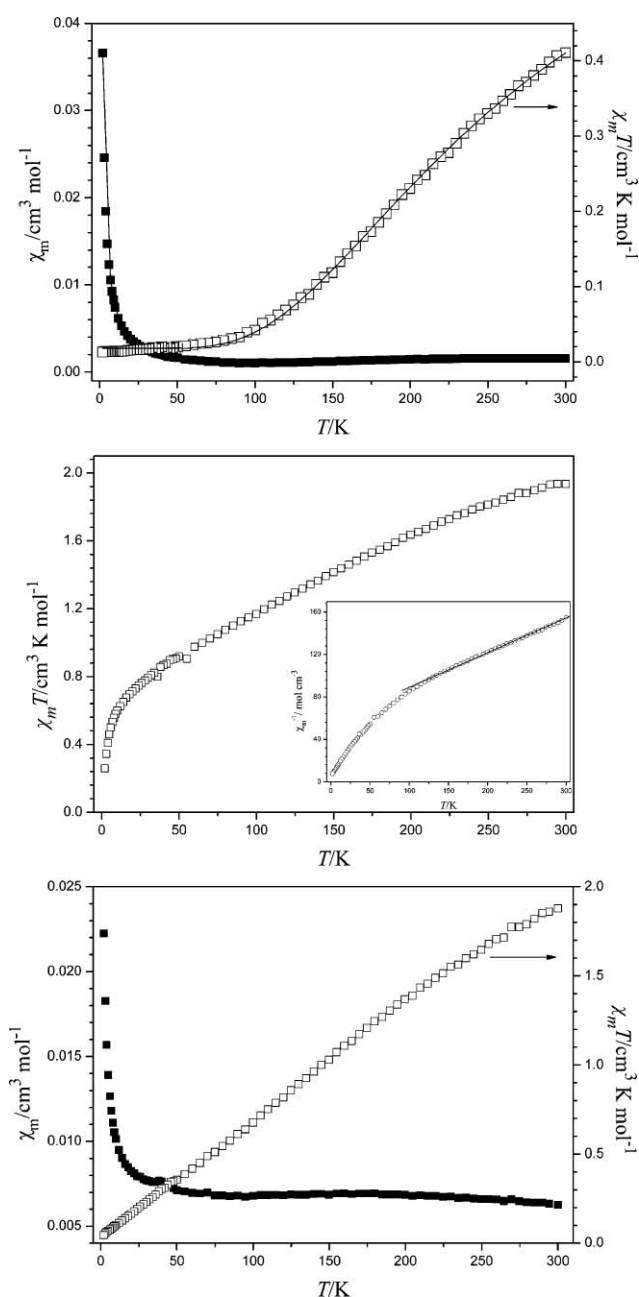


Fig. 4 The magnetic curves of compounds **1** (top), **2** (middle) and **3** (bottom). The solid lines present the theoretical values based on the equations of compound **1**.

$$R = \left\{ \sum_{i=1}^{NP} [\chi_m(\text{exp})_i - \chi_m(\text{cal})_i]^2 / (NP - NV) \right\}^{1/2} \quad (2)$$

where NP is the number of data points and NV is the number of variable parameters,^{3d,e,28} which lead to the following set of parameters: $g = 2.10$, $J = -347 \text{ cm}^{-1}$, $\rho = 2.16\%$ and $R = 1.0 \times 10^{-5}$. The value of J indicates that the strong antiferromagnetic interactions occur when the bridging oxalate ion is coplanar with the copper $d_{x^2-y^2}$ magnetic orbitals.²⁹ These results are in agreement with the structure of compound **1**, in which the bridging oxalate ion is coplanar with the copper.

For compound **2**, the relationship of $1/\chi_m$ versus T in 100–300 K can be fitted to the Curie–Weiss law, giving $C = 3.064 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -172.927 \text{ K}$. The $\chi_m T$ value at room temperature is $1.936 \text{ cm}^3 \text{ K mol}^{-1}$, smaller than $2.350 \text{ cm}^3 \text{ K mol}^{-1}$ for one free Pr^{3+} in the $^3\text{H}_4$ ground state ($g = 4/5$) and two insulated Cu^{2+} (considering $g = 2$). The $\chi_m T$ value decreases continuously with decreasing temperature, indicating the antiferromagnetic coupling in the oxalate bridging copper(II) dimers. A decrease of the $\chi_m T$ at the temperature below 10 K, may be attributed to crystal field effects due to the intrinsic nature of the lanthanide series.³⁰

The magnetic property of **3** is different from that of **1** because of the presence of paramagnetic Eu^{3+} ion. From 300 to 2 K, the χ_m value increases gradually with decreasing temperature, and neither the maximum of χ_m nor Curie–Weiss behavior is observed. The $\chi_m T$ value at room temperature is equal to $1.878 \text{ cm}^3 \text{ K mol}^{-1}$, lower than the expected value of $2.250 \text{ cm}^3 \text{ K mol}^{-1}$ for two uncoupled Cu^{2+} centres and one Eu^{3+} ion. The $\chi_m T$ value of a Eu^{3+} ion is $1.5 \text{ cm}^3 \text{ K mol}^{-1}$ calculated by van Vleck allowing for population of the excited state with higher values of J at 293 K. Upon cooling the sample, $\chi_m T$ value decreases continually, which should be attributed to the depopulation of the Stark levels for a single $\text{Eu}(\text{III})$ ion and antiferromagnetic interaction between the oxalato-bridging $\text{Cu}(\text{II})$ dimers. At 2 K, the value of $\chi_m T$ is close to zero, indicating a $J = 0$ ground state of the $\text{Eu}(\text{III})$ ion ($^7\text{F}_0$)³¹ and a singlet ground state of the dinuclear $\text{Cu}(\text{II})$ complex.

Conclusions

In summary, the bis(undecatungstophosphate) lanthanates or potassium polyanions have been introduced into the organic–inorganic hybrid system forming a series of new compounds with a 1D chain-like structure consisting of alternating inorganic polyanions and transition metal coordination complexes. These compounds are the first example of organic–inorganic hybrid based on 1 : 2 polyanions as inorganic building blocks. The magnetic studies of compounds **1**, **2** and **3** showed that there were strong antiferromagnetic coupling in the oxalato-bridging $\text{Cu}(\text{II})$ dimers, and the lanthanide cations slightly influence the magnetic properties of **2** and **3**, which are in agreement with the structural feature of these compounds.

In our studies¹² and the work of Gutiérrez-Zorrilla's group^{3d,e} based on the oxalato-bridging $\text{Cu}(\text{II})$ dimers, we found that the hybrid compounds were all low dimensional structures in which the polyanions were supported by one or two oxalato-bridging $\text{Cu}(\text{II})$ dimers. It may be due to the steric hindrance among the dimeric copper complexes containing large bpy ligands. We are attempting to use smaller ligand or a linear connector with an extensive coordination capability in the transition metal coordination complexes to form new compounds with higher dimensions.

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