Rare-Earth–Transition-Metal Organic–Inorganic Hybrids Based on Keggintype Polyoxometalates and Pyrazine-2,3-dicarboxylate

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Abstract: Five rare-earth-transitionmetal (RE-TM) heterometal organicinorganic hybrids based on Keggintype silicotungstates and mixed ligands H2pzda (pzda=pyrazine-2,3-dicarboxvlate) and en (en=ethylenediamine) $(enH2)[Cu(en)2(H2O)]2\{[Cu(en)2]$ $[Cu(en)2(H2O)][(\alpha-SiW11)]$ O39)RE-(H2O)(pzda)] $2 \cdot n H2O$ $(n \approx 4; RE =$ YIII (1), DyIII (2), YbIII (3), and LuIII (4)) [Cu(en)2and (H2O)]2{[Cu(en)2]2[Cu(pzda)2][(α-H2SiW11O39)Ce(H2O)]2]·nH2O (5; n \approx 8) have been hydrothermally synthesized and structurally characterized. Compounds 1–5 all contain the dimeric mono-RE substituted Keggin [RE(α -SiW11O39)]210– subunits linked by H2pzda ligands. Interestingly, **1–4** exhibit discrete structures, in which the H2pzda ligand acts as a tetradentate ligand to bind the RE and Cu cations,

Keywords: luminescence • organicinorganic hybrid composites • polyoxometalates • rare-earth metals • silicotungstates whereas 5 displays a 1D double-chain architecture, in which the H2pzda ligand adopts a new pentadentate mode to connect the Ce and Cu cations. To our knowledge, **1–5** represent the first monovacant Keggin-type silicotungstates containing both RE–TM heterometals and mixed ligands. The luminescence of **2** is derived from the combination of the DyIII cations and H2pzda ligands, whereas the luminescence properties of **1** and **3–5** are attributable to the H2pzda ligands.

Introduction

Polyoxometalates (POMs) of the early transition metals (Mo, W, V, Nb, and Ta) are a large and expanding subset of polynuclear metal-oxygen anionic clusters that can act as multidentate inorganic ligands to bind most transition metal (TM) and/or rare-earth (RE) cations, thereby resulting in a huge range of compounds with potential applications in various areas, such as materials chemistry, photochemistry, catalysis, electrochemistry, and magnetism.^[1-2] On the other hand, RE-TM heterometallic coordination polymers are of considerable interest because their meaningful structural architectures and fascinating properties recommend them as candidates for luminescent sensors, adsorption materials, and magnetic materials.^[3] However, to date, there have been few reports regarding heterometallic RE-TM POMs.^[4a] Kögerler and co-workers recently reported two $\mathrm{Ce}^{\mathrm{IV}}\text{-}\mathrm{Mn}^{\mathrm{IV}}$ clusters that were based on lacunary Dawson fragments.^[4b,c] Wang and co-workers have also synthesized a series of RE-TM POMs: a trimeric {Fe^{III}(μ_3 -O)₃Ce^{III}}-substituted arseno-

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tungstate $[K \subset \{FeCe(AsW_{10}O_{38})(H_2O)_2\}_3]^{14}$, [4d] two $\{P_2W_{12}\}_{10}$ [{GdMn(H₂O)₁₀}{HMnGd₂(Tart)O₂ based aggregates $(H_2O)_{15}$ { $P_6W_{42}O_{151}(H_2O)_7$ }]¹⁴⁻ (Tart = < tartrate)and $[{GdCo(H_2O)_{11}}_2 {P_6W_{41}O_{148}(H_2O)_7}]^{16-,[4e]}$ and one triplecompound $\{[Ce_3Mn_2O_6(OAc)_6]$ Dawson-type $(H_2O)_9]_2[Mn_2P_2W_{16}O_{60}]_3]^{20-.[4f]}$ In addition, $Dy^{III}-V^{IV}$ -sandwiched POM $[((VO)_2Dy(H_2O)_4(B-\alpha-AsW_9O_{33})_2]^{11-}, [4 g]$ Ce-Mn heterometallic germanotungstate $[{Ce(H_2O)_2}_2Mn_2(B-\alpha-$ GeW₉O₃₄)₂]^{8-,[4 h]} an inorganic Ce-Ag porous framework $[{Ag_3(H_2O)_2}]{Ce_2(H_2O)_{12}}{H_2W_{11}Ce(H_2O)_4O_{39}}_2]^{5-,[4i]}$ and a family of 1D chains constructed from $[RE(PW_{11}O_{39})_2]^{11-}$ and $[Cu(en)_2]^{2-}$ groups have also been reported.^[4j,k] In recent years, we have invested a great amount of effort into RE-TM heterometallic POMs and we have isolated several types of RE-TM POM derivatives: {[Cu(en)₂]₂[Dy₂(H₂O)₂ $(GeW_{11}O_{39})_3]^{14-,[5a]}$ $[As_2W_{18}Fe_2[Y(OH_2)_2]_2O_{68}]^{6-,[5b]}$ {[Cu- $(dap)_{2]_{4.5}} [Dy(\alpha - PW_{11}O_{39})_2]^{2^{-1}} (dap = 1,2 - diaminopropane),^{[5c]}$ $\{[Cu(en)_2]_{1.5}[Cu(en)(2,2'-bipy)(H_2O)_n]RE[(\alpha-PW_{11}O_{39})_2]\}^{6-1}$ $(\mathbf{RE} = \mathbf{Ce}^{\mathrm{III}}, \mathbf{Pr}^{\mathrm{III}}, \mathbf{Nd}^{\mathrm{III}}, \mathbf{Gd}^{\mathrm{III}}, \mathbf{Tb}^{\mathrm{III}}, \mathbf{Er}^{\mathrm{III}}).^{[5d]}$

There have been fewer reports on RE–TM heterometallic silicotungstates,^[6] including three unprecedented cubane-{RECu₃(OH)₃O} (RE=La^{III}, Gd^{III}, Eu^{III})-substituted [α -SiW₁₁O₃₉]^{8–} POMs,^[6a] a 1D double-chain derivative [(γ -SiW₁₀O₃₆)₂(Cr(OH)(H₂O))₃(La(H₂O)₇)₂]^{4–,[6b]} two [RE(μ_3 -O)₃Fe] (RE=Dy^{III}, Tb^{III}) cluster-based [α -SiW₁₀O₃₈]^{12–} fragments,^[6c] two inorganic sandwich-type assemblies [{Ce-(H₂O)₇}₂Mn₄Si₂W₁₈O₆₈(H₂O)₂]^{6–,[6d]} and {Nd₂(H₂O)₁₂Cu₄ (H₂O)₂(SiW₉O₃₄)₂]^{6–,[6e]} Nevertheless, silicotungstates that contained RE–TM heterometals and organic polycarboxy-late ligands have not been reported, although a series of 1D

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$$\begin{split} &RE-Cu \ phosphotungstates \ containing \ oxalate \ and \ 2,2'-bipyr-idine \ organic \ ligands \ [{RE(PW_{11}O_{39})_2}{Cu_2(bpy)_2(ox)}]^{9-} \\ &(RE=La^{III}, \ Pr^{III}, \ Eu^{III}, \ Gd^{III}, \ Yb^{III}) \ have \ been \ prepared \ by \ Liu \ and \ co-workers.^{[7]} \end{split}$$

We expect to discover new organic polycarboxylatebridged RE-Cu heterometallic silicotungstates from the reaction of K₄[α -SiW₁₂O₄₀]·17H₂O, RE^{III} cations, Cu^{II} cations, and mixed ligands (H₂pzda and en) based on the following considerations: 1) The saturated Keggin-type [α -SiW₁₂O₄₀]⁴⁻ polyoxoanions (POAs) readily degrade and isomerize to a form variety of silicotungstate derivatives,^[2c,d,8] such as [β -SiW₁₂O₄₀]⁴⁻, [α -SiW₁₁O₃₉]⁸⁻, [γ -SiW₁₀O₃₆]⁸⁻, [α -SiW₉O₃₄]¹⁰⁻, [β -SiW₈O₃₁]¹⁰⁻, and [γ -SiW₈O₃₁]¹⁰⁻, etc. 2) Compared with other TM cations, Cu^{II} ions exhibit more flexible, varied coordination modes (square, trigonal bipyramid, square pyramid, and octahedron); moreover, the presence of the Jahn– Teller effect of the octahedron and the pseudo-Jahn–Teller effect of the square pyramid for Cu^{II} cations can give different linkage modes to overcome steric hindrance, thereby



Scheme 1. Possible coordination sites of the H₂pzda ligand.

leading to new structures.^[5d] Hence, Cu^{II} cations can be thought of as TM-cation sources. 3) The H₂pzda ligand is chosen as a polyfunctional bridging ligand (Scheme 1), not only because the carboxylate groups can be completely or partially deprotonated to generate Hpzda⁻ and pzda²⁻,

thereby allowing various acidity-dependent coordination modes (Table 1),^[9] but also because the H₂pzda is a rigid ligand with O and N atoms that can act as hydrogen-bond donors and/or acceptors, which favor the construction of supramolecular structures.^[9b] 4) Most of the reported compounds are purely inorganic or contained only one type of organic ligand; only two phosphotungstates containing mixed ligands have been reported,^[5d,7] but no RE–TM heter-

Abstract in Chinese:

在水热条件下,以Keggin 类型的硅钨酸盐K4[a-SiW12O40] ·17H2O,稀土氯化物,CuCl2·2H2O,2,3-吡嗪二羧酸(H2 pzda)和乙二胺(en)为原料得到了五个新颖的有机-无机杂 化的超分子化合物。化合物进一步通过了元素分析,X-射线粉末衍射,红外光谱,热分析和X-射线单晶衍射表 征。化合物1-5的共同特征是都包含了由H2pzda 配体桥 连的二聚的单稀土取代的硅钨酸盐,有趣地是,1-4都显 示了孤立结构且H2pzda 配体作为四齿配体与RE和Cu 配 位,而5展示了一维双链结构,并且H2pzda 配体显示了 一种新的五齿配位模式与Ce和Cu 配位。五个化合物通 过氢键作用都可以形成三维超分子结构。据我们所知, 1-5代表了第一例同时包含稀土-过渡金属和混合配体 H2pzda 与 en 的硅钨酸盐。同时,化合物1-5的固体荧光 性质结果表明2的荧光信号来源于稀土 Dy和H2pzda 配 体的共同作用而其它的四个化合物来源于H2pzda 配体。 ometallic silicotungstates with mixed ligands have been reported to date. On the basis of these aforementioned points, we have separated a family of organic-inorganic hybrid silicotungstate derivatives with RE-TM heterometals and mixed ligands, which are formulated as: (enH₂)[Cu(en)₂ $(H_2O)]_2[[Cu(en)_2][Cu(en)_2(H_2O)]](\alpha-SiW_{11}O_{39})RE(H_2O) (pzda)]_{2} \cdot n H_{2}O$ ($n \approx 4$; RE = Y^{III} (1), Dy^{III} (2), Yb^{III} (3), and Lu^{III} (4)) and $[Cu(en)_2(H_2O)]_2[[Cu(en)_2]_2[Cu(pzda)_2]](\alpha$ - $H_2SiW_{11}O_{39})Ce(H_2O)]_2$ ·*n* H_2O (5; *n* \approx 8). Compounds 1–5 all contain the dimeric mono-RE-substituted Keggin [RE(a- $SiW_{11}O_{39}$]¹⁰⁻ POAs connected by H₂pzda ligands. The H₂pzda ligands in compounds 1-5 present two different coordination modes: compounds 1-4 exhibit discrete structures, in which the H₂pzda ligand acts as a tetradentate ligand to bind the RE and Cu cations, whereas compound 5 displays a 1D double-chain architecture, in which the H₂pzda ligand adopts a new pentadentate mode to connect the Ce and Cu cations. To the best of our knowledge, compounds 1-5 represent the first monovacant Keggin-type silicotungstates that contain both RE-TM heterometals and mixed ligands (H₂pzda and en). Furthermore, the room-temperature solid-state photoluminescence of compounds 1-5

Results and Discussion

has been examined.

Synthesis

In recent years, a number of heterometallic RE-TM structures have been reported that were constructed from metalligand building blocks with appropriate organic multidentate ligands.^[3b,9] However, the preparation of RE-TM heterometallic POMs has been a great challenge owing to the competition reactions between RE and TM cations with POMs and organic ligands, and this has usually led to immediate precipitation rather than crystallization.^[5d,6] Nevertheless, we found that the conventional aqueous-solution methods were not suitable for preparing organic-inorganic hybrid RE-TM POMs in the presence of an aliphatic diamine (en) and a rigid organic polycarboxylic ligand (H₂pzda). Thus, we chose hydrothermal methods to explore this system because the solubilities of the starting materials can be increased and a variety of inorganic and organic components can be employed under hydrothermal conditions.[5d]

Recently, by using this approach, we isolated several types of organic–inorganic hybrid RE–TM POMs.^[5] In a continuation of this work, five heterometallic RE–TM silicotungstates (1–5) with H₂pzda and en ligands have been successfully synthesized. Initially, compound 1 was synthesized by the reaction of $K_4[\alpha$ -SiW₁₂O₄₀], YCl₃, and CuCl₂ in the presence of H₂pzda and en by hydrothermal methods. The replacement of the Y^{III} cation with Dy^{III}, Yb^{III}, or Lu^{III} cations led to compounds 2–4. When CeCl₃ replaced YCl₃, compound 5 was obtained, which exhibited 1D double-chain architecture. However, the use of other RE^{III} salts as the RE source failed under the same conditions. These results suggested that the nature of RE cations may affect the

Table 1. Various coordination modes for the H₂pzda ligand.



structural diversity in the products, a phenomena that has been reported previously.^[5d,6a] To investigate the influence of different TM cations on structural diversity, we replaced the Cu^{II} cation with Cr^{III}, Mn^{II}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}, and Cd^{II} cations under the same conditions; unfortunately, only some amorphous precipitates appeared. We also replaced $CuCl_2$ with $Cu(NO_3)_2$, $CuSO_4$, $Cu(CH_3COO)_2$, and $Cu(OH)_2CO_3$ in the preparation of compounds 1–5, but no crystalline samples were formed. In addition, experimental results showed that increasing or decreasing the amount of CuCl₂ was unfavorable for the formation of the products. Furthermore, we replaced H₂pzda/en with H₂pzda/1,2-dap, H₂pzda/1,3-dap, 1,3,5-benzene- tricarboxylic acid/en, pyromellitic acid/en, and 4,5-imidazole dicarboxylic acid/en (dap=diaminopropane) under the same conditions, but no isostructural compounds were obtained. Therefore, the TM cation used, the nature of Cu^{II} salt, the amount of CuCl₂, and the use of H₂pzda and en organic ligands all played important roles in the formation of compounds 1-5. Another problem was that although $[\alpha-\text{SiW}_{12}\text{O}_{40}]^{4-}$ was employed as a starting material to prepare compound **1–5**, all of the products contained the $[\alpha-\text{SiW}_{11}\text{O}_{39}]^{8-}$ POAs. When $[\alpha-\text{SiW}_{11}\text{O}_{39}]^{8-}$ replaced $[\alpha-\text{SiW}_{12}\text{O}_{40}]^{4-}$ as the precursor under the same conditions, the reaction failed, which may be related to the distinct nature of the Keggin-type POM precursors and indicated that the transformation from $[\alpha-\text{SiW}_{12} \text{ O}_{40}]^{4-}$ to $[\alpha-\text{SiW}_{11}\text{O}_{39}]^{8-}$ was crucial for the preparation of compounds **1–5**.^[5d]

Structural Description

The experimental XRPD patterns for compounds 1–5 were in good agreement with the simulated XRPD patterns obtained by single-crystal X-ray diffraction, thus suggesting good phase purity for compounds 1–5 (see the Supporting Information, Figure S1). The differences in intensity between the experimental and simulated XRPD patterns might be due to the variation in the preferred orientation of the powder sample during collection of the experimental XRPD. The bond-valence sum calculations indicated that all of the W, Cu, and RE atoms in compounds 1–5 were in the +6, +2, and +3 oxidation states, respectively.^[10] Considering the charge balance of compound **5**, some protons needed to be added. To locate the positions of these protons, bond-valence sum calculations of all the oxygen atoms on the POM fragments were carried out, and the results showed that four protons could be considered as the average bond-valence sums of these O atoms (see the Supporting Information, Figure S2 and Table S1). The RE–O bond lengths (see the Supporting Information, Table S2) decreased as the ionic radius of the RE^{III} cations decreased, which was consistent with the effect of the lanthanide contraction.^[5d,7]

Compounds 1-4 were isostructural and crystallized in the triclinic space group $P\bar{1}$; therefore, only $(enH_2)[Cu(en)_2]$ $(H_2O)_2[Cu(en)_2][Cu(en)_2(H_2O)][(\alpha-SiW_{11}O_{39})Y(H_2O) (pzda)]_{2} \cdot n4H_{2}O$ (1; $n \approx 4$) is discussed in detail herein. The skeleton of compound 1 was made up of two $\{[Cu(en)_2]\}$ $[Cu(en)_2(H_2O)][(\alpha-SiW_{11}O_{39})Y(H_2O)(pzda)]]^{3-}$ POAs (Figure 1 a), one protonated $[enH_2]^{2+}$ ion, two free $[Cu(en)_2]$ (H₂O)]²⁺ ions and four lattice-water molecules. Three independent copper ions exhibited two types of coordination geometries. The Cu1 ion displayed a six-coordinate octahedral geometry that was constituted of four N atoms from two en ligands (Cu-N: 1.995(18)-2.022(17) Å), one O atom from the pzda²⁻ ligand (Cu-O: 2.374(13) Å), and one water ligand (Cu–O: 2.945(8) Å). The decorated $[Cu2(en)_2]^{2+}$ ion adopted a square-pyramid geometry with four N atoms from two en ligands (Cu-N: 1.963(20)-2.059(21) Å) and one terminal O atom from the $[Y(\alpha$ -Si $W_{11}O_{39})]^{5-}$ POA (Cu-O: 2.704(17) Å). The free $[Cu3(en)_2(H_2O)]^{2+}$ ion displayed the same geometry as the $[Cu2(en)_2]^{2+}$ ion, which was defined by four N atoms from the chelating en ligands (Cu-N: 1.985(16)-2.017(17) Å) and one water ligand (Cu-O: 2.258(8) Å). The $[(\alpha-\text{SiW}_{11}\text{O}_{39})Y(\text{H}_2\text{O})(\text{pzda})]^{7-}$ POA formed by the incorporation of one Y1^{III} cation into the monovacant $[\alpha$ -SiW₁₁O₃₉]⁸⁻ POA, which was derived from the classical Keggin-type $[\alpha$ -SiW₁₂O₄₀]⁴⁻ POA by removal of a W=O_d group. The Y1^{III} cation adopted a highly distorted doubly capped trigonal-prism geometry, which was bound to four available O atoms of the lacunary site of the $[\alpha$ - $SiW_{11}O_{39}]^{8-}$ POA, two O atoms from two pzda^{2-} ligands, one N atom from one pzda²⁻ ligand, and one water ligand, with Y1^{III}-O distances of 2.257(11)-2.549(7) Å and a Y-N distance of 2.651(16) Å (Figure 1b). In the coordination configuration of the Y1^{III} cation, the O23, O25, and O40 atoms, and the O31, O33, and O43 atoms constituted the two bottom surfaces of the trigonal prism with a dihedral angle for the two bottom planes of 24.0°, and the distances of the Y1^{III} cation and the two bottom planes were 1.539 and 0.704 Å, respectively. The O25, O31, O40, and O43 atoms, the O23, O33, O40, and O43 atoms, and the O23, O25, O31, and O33 atoms formed the three side-planes of the trigonal prism and their standard deviations from their least-squares were 0.101, 0.652, and 0.021 Å, respectively. The distances between the Y1^{III} cation and the three side-

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Figure 1. a) Polyhedra/ball-and-stick representation of the structural unit of compound **1**; b) coordination environment of the Y1^{III} cation; c) structure of the dinuclear cyclic unit; d) 3D supramolecular architecture, showing the ABAB mode, constructed by hydrogen-bonding interactions.

planes were 0.629, 1.195, and 1.108 Å, respectively. In addition, the O1W and N1 atoms occupied the two cap positions, covering the side-planes defined by the O25, O31, O40, and O43 atoms and the O23, O33, O40, and O43 atoms, respectively. The distances between the O1W atom and the two planes were 1.885 and 3.244 Å, whereas the distances between the N1 atom and the two planes were 1.639 and 0.045 Å, respectively. The above-mentioned data indicated that the doubly capped trigonal prism was severely distorted. Interestingly, each pzda^{2–} ligand was coordinated to two Y1^{III} cations and one Cu^{II} cation as a tetradentate ligand through the ring nitrogen atom and the carboxylate oxygen atoms (Table 1 w). Nevertheless, the presence of the RE centers in the [α -SiW₁₁O₃₉]^{8–} moieties generated the dimeric

subunits, with a distance between the two Y1^{III} cations of 7.564(4) Å. The pzda²⁻ ligands and Y1^{III} cations formed a square with dimensions of about 4.5×5.9 Å (Figure 1c). For each pzda²⁻ ligand, only one carboxy oxygen atom (O42) did not participate in coordination; instead, it formed O-H…O=C hydrogen bonds with both coordinated and uncoordinated water molecules. Moreover, the O atoms of both the coordinated water and crystal-water molecules were involved in intra- and intermolecular hydrogen bonding with the O atoms of the POMs, the carboxy group of the pzda²⁻ ligands, and the N atoms of the pzda2- and en ligands. All of these hydrogen-bonding interactions together afforded the 3D supramolecular network (Figure 1d). For details of the hydrogen bonding, see Table S3 in the Supporting Information. Analogous RE-substituted POMs containing organic polycarboxylate ligands have not been reported, although a series of 1D [{RE(PW₁₁O₃₉)₂}{Cu₂(bpy)₂(μ -ox)}]⁹⁻ (**A**) structures that contained oxalate ligands have been isolated by Liu and co-workers.^[7] Some obvious distinctions were observed in compound 1: 1) it was obtained under hydrothermal conditions rather than the conventional aqueous-solution methods; 2) adjacent $[Y(\alpha-SiW_{11}O_{39})]^{5-}$ POAs were interconnected through H2pzda organic ligands, whereas adjacent $[RE(\alpha-PW_{11}O_{39})_2]^{11-}$ POAs in $A^{[7]}$ were linked through $[Cu_2(bpy)_2(\mu-ox)]^{2+}$ bridges; 3) it was synthesized from the reaction of $[\alpha-SiW_{12} O_{40}]^{4-}$ with Y^{III} and Cu^{II} cations in the presence of H_2pzda and en, whilst $A^{[7]}$ was obtained from the reaction of $[RE(\alpha-PW_{11}O_{39})_2]^{11-}$ with $[Cu_2(bpy)_2(\mu$ ox)]²⁺; 4) most importantly, the organic polycarboxylate H_2 pzda ligand in compound 1 bound Y^{III} and Cu^{II} ions as a tetradentate ligand whereas the oxalate in $A^{[7]}$ connected two Cu^{II} ions to form the dinuclear copper-oxalate complexes.

Compound 5 crystallized in the triclinic space group $P\bar{1}$. The structural unit consisted of one $\{[Cu(en)_2]_2[Cu(pzda)_2]\}$ $[(\alpha-H_2SiW_{11}O_{39})Ce(H_2O)]_2]^{4-}$ POA (Figure 2a), two free $[Cu(en)_2(H_2O)]^{2+}$ ions, and eight lattice-water molecules. Three independent copper ions also displayed two types of coordination geometries. The Cu1 and Cu2 ions exhibited octahedral geometries whereas the free $[Cu3(en)_2(H_2O)]^{2+}$ ion showed a square-pyramidal geometry. The Ce1^{III} cation had the same coordination number (eight) and adopted the same highly distorted doubly capped trigonal-prism geometry as the Y1^{III} cation, but was defined by four available O atoms of the lacunary site of the $[\alpha$ -SiW₁₁O₃₉]⁸⁻ POA, three O atoms from two different pzda2- ligands, and one water ligand, with Ce1^{III}–O distances of 2.416(9)–2.599(9) Å (Figure 2b). Unlike the $pzda^{2-}$ ligand in compound 1, each pzda²⁻ ligand in compound 5 coordinated to two Ce1^{III} cations and one Cu^{II} cation as a pentadentate ligand through one N atom of the ring and four O atoms of the two carboxy groups (Figure 2c). Although the have been various possible coordination modes reported for the H2pzda ligand (Table 1 a-v), the coordination mode reported herein has not previously been reported. The two Ce1^{III} cations were doubly bridged by two carboxy groups of two different pzda²⁻ ligands, separated by a distance of two Ce1^{III} cations



Figure 2. a) Polyhedra/ball-and-stick representation of the structural unit of compound 5; b) coordination environment of the Ce^{III} cation; c) structure of the dinuclear cyclic unit; (d) The 1D double chain architecture of 5; (e) 3D supramolecular architecture constructed by hydrogen-bonding interactions.

(5.590(2) Å), which was shorter than the distance of the Y1^{III} cations. The pzda²⁻ ligands combined with two Ce1^{III} cations in a dimeric motif. This motif had previously been observed in RE-substituted POMs, including several dimers $[{(\alpha-PW_{11}O_{39})RE(H_2O)CH_3COO}]_2^{10-}$ $(RE = Sm^{III}, Eu^{III}, Eu^{III},$ Gd^{III}, Tb^{III}, Ho^{III}, and Er^{III}),^[11a] [{Yb(α -SiW₁₁O₃₉)(H₂O)₂]₂ $O)_2]^{12-,[11b]}$ (CH₃CO $[{La(\alpha_2 - P_2 W_{17} O_{61})(H_2 O)_2}]$ (CH₃COO)₂}]₂^{16-,[11c]} and one tetrameric Dawson unit [{Yb- $(P_2W_{17}O_{61})_4(C_2O_4)_3(H_2O_4)_4^{34-[11d]}$ Most of those reported dimers were connected through the acetate or oxalate ligands; the analogous organic aromatic polycarboxylatebridged RE-substituted POMs have not been reported. However, the connection motif in compound 5 differed distinctly from the dimeric unit in compound **1**, arising from the different coordination modes of the H₂pzda ligand between compounds **1** and **5**. The most-remarkable feature of compound **5** was that the adjacent {(pzda)Ce(H₂O)}₂²⁺ subunits were linked together through Cu1 ions, thereby generating 1D linear chains. The chains were connected by [α -SiW₁₁O₃₉]^{8–} POAs, thereby forming the 1D zigzag chain, whilst the adjacent [α -SiW₁₁O₃₉]^{8–} POAs were joined through [Cu2(en)₂]²⁺ ions, thus producing 1D double-chain architecture (Figure 2d). Similar to the case of compound **1**, the 3D supramolecular network of compound **5** was constructed from intra- and intermolecular hydrogen-bonding interactions (Figure 2e; for details of the hydrogen bonding, see the Supporting Information, Table S4).

IR Spectra

In the low-wavenumber region ($\nu < 1050 \text{ cm}^{-1}$), the IR spectra of compounds 1–5 all exhibited the characteristic v_{as} (Si– O_a), terminal ν_{as} (W– O_t), corner-sharing ν_{as} (W– O_b), and edge-sharing $v_{as}(W-O_c)$ asymmetric vibrations derived from the Keggin POA frameworks,^[12a] which were similar to those of the parent monovacant $[\alpha$ -SiW₁₁O₃₉]⁸⁻ POAs owing to the fact that the POAs displayed the same $C_{\rm s}$ symmetry, thus suggesting that the POM moiety of compounds 1-5 still retained the basic Keggin structure (see the Supporting Information, Figure S3 and Table S5). The Si-O mode, observed as a single signal at 925 cm^{-1} for the saturated Keggin $[\alpha$ -SiW₁₂O₄₀]⁴⁻ POA,^[12b] shifted to 991–983 cm⁻¹ in the spectra of mono-RE-substituted POM derivatives 1-5, mainly as a consequence of distortion of the SiO₄ groups encapsulated in Keggin POAs.^[5d] The W-O stretching vibration bands resulted from the Keggin-type structure, namely, $\nu_{as}(W-O_t)$, $\nu_{as}(W-O_b-W)$, and $\nu_{as}(W-O_c-W)$ appeared at 945-943, 882-822, and 794-700 cm⁻¹ for compounds 1-5, respectively. Compared to the monovacant POM $K_8[(\alpha$ - $SiW_{11}O_{39}$]-13H₂O, the ν_{as} (W–O_t) vibration peaks for compounds 1–5 had different red-shifts of between $14-16 \text{ cm}^{-1}$, the possible major reason for which may be that the RE^{III} cations had stronger interactions with the terminal oxygen atoms of the POAs, thereby impairing the W-O_t bonds, decreasing the W-Ot bond-force constant, and thus leading to a decrease in the W–O_t vibration frequency.^[5d] The ν_{as} (Si– O_a) and $v_{as}(W-O_c-W)$ vibration frequencies for compounds 1-5 had different blue-shifts of between 5-13 and 24-26 cm⁻¹, respectively, as a result of the lower symmetry of the $[\alpha-\text{SiW}_{11}\text{O}_{39}]^{8-}$ POAs than $K_8[(\alpha-\text{SiW}_{11}\text{O}_{39})]\cdot 13 \text{ H}_2\text{O}^{[5d]}$ There was no indication of the RE-O stretching vibration in the far-infrared region, perhaps because of the predominantly ionic characteristics of the interactions between the vacant POA and the RE^{III} cations.^[4k] For the coordination modes of the carboxylate group, the difference between the asymmetric (ν_{asym}) and symmetric (ν_{sym}) carboxylate stretches ($\Delta v = v_{asym} - v_{sym}$) is often used.^[9] Strong absorption bands in the regions 1754–1690 and 1397–1357 cm^{-1} can be regarded as the asymmetric and symmetric stretching vibrations of the carboxylate group of the free H2pzda ligand, respectively. These bands shifted to lower wavenumbers and were observed in the regions 1659–1577 and 1394–1360 cm⁻¹ for compounds **1–5**, thus indicating that the H₂pzda ligands were coordinated to the RE^{III} and Cu^{II} ions; the absence of strong peaks at around 1715 cm⁻¹ in compounds **1–5** suggested that all of the carboxylic groups were deprotonated. The Δv values indicated the presence of bridging coordination modes for the H₂pzda ligands.^[9] In addition, the NH₂ and CH₂ bending vibration bands were observed in the range 1630–1500 cm⁻¹ and 1458–1435 cm⁻¹ and the OH stretching vibration bands appeared in the range 3440–3422 cm⁻¹. The occurrence of these resonance signals demonstrated the presence of en ligands.^[4i] and were in good agreement with the results obtained from X-ray single-crystal analysis.

Photoluminescence Properties

It is well-known that the luminescence of lanthanide cations have low molar absorptivity and that the f-f transitions, which are usually generated through the "antenna effect", are spin- and parity-forbidden.^[13a,b] Moreover, it has been shown that the lanthanide-centered emission can be sensitized by molecules that contain π electrons and the bonding of N-containing ligands with lanthanide cations are more efficient at energy-transfer; thus, the success of the energytransfer is reflected in the suppression of the intraligand emission.^[13b] In this case, the H₂pzda ligands, which possess electron-conjugated systems that bind with the RE cations, may be good chromophores for the efficient luminescent sensitization of RE cations. Basing on these considerations, the photoluminescence spectra of solid samples of compounds 1-5 and the free H₂pzda ligand were examined at ambient temperature (Figure 3). Compounds 1 and 3-5 all exhibited obvious photoluminescence with an emission maxima at about 400 nm upon excitation at 220 nm (Figure 3b), whereas the free H₂pzda ligand displayed very strong emission with a maximum at about 385 nm at an excitation wavelength of 220 nm, which may be ascribed to $n \rightarrow$ π^* transitions of the H₂pzda ligands. However, when the free H₂pzda ligands coordinated to RE^{III} and Cu^{II} cations, the emission bands red-shifted about 15 nm relative to that of the free H₂pzda ligand, which could be tentatively assigned to the emission of ligand-to-metal-charge-transfer (LMCT) transitions.^[13c] Furthermore, the intensity of the four complexes based on the H2pzda ligands were much weaker than the H₂pzda ligands, thus suggesting the energytransfer from the H₂pzda ligands to the RE cations was efficient. These results clearly indicated that the emissions were due to the intraligand $n \rightarrow \pi^*$ transitions of the H₂pzda ligands, and LMCT transitions, which were observed in many lanthanide-carboxylate systems.^[5d, 13b,c] The excitation spectrum of compound 2, monitored at 578 nm, mainly consisted of three wide bands between 350 and 500 nm, with a maximum at 356 nm (see the Supporting Information, Figure S4a). Excitation of the as-synthesized solid of compound 2 at 356 nm revealed the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{J}$ (J=15/2, 13/2) emission



Figure 3. Solid-state emission spectra of 2 (a), and of free H₂pzda and compounds 1, 3, 4, and 5 (b) at RT.

peaks of the Dy^{III} ion,^[13c] which were attributed to ${}^4F_{9/2} \rightarrow$ ${}^{6}H_{15/2}$ (485 nm) and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (578 nm) transitions, respectively (Figure 3a). Moreover, the emission wavelength at 578 nm was the most-intense, in agreement with other previously reported Dy^{III}-containing compounds.^[13c] Moreover, the intensity of the blue emission, which corresponded to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transition, was stronger than the yellow emission of the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition, thus implying that the H₂pzda ligands may be suitable for the sensitization of the yellow luminescence for Dy^{III} cations.^[13c] In addition, the emission peak at about 400 nm was assigned to the intraligand $n \rightarrow \pi^*$ transitions of the H₂pzda ligands and LMCT transitions.^[5d, 13c] With respect to the photoluminescence spectra of the free H₂pzda ligand and the solid-state DyCl₃·6H₂O (λ_{ex} =356 nm; see the Supporting Information, Figure S4b), the emission bands of compound 2 may be derived from the combination of the $\mathbf{D}\mathbf{y}^{\text{III}}$ cations and the H₂pzda ligands. The high luminescence efficiency in the blue-light region suggests that compounds 1-5 are excellent candidates for blue fluorescent materials.

Conclusions

Two types of organic-inorganic hybrid monovacant Keggin silicotungstate derivatives with rare-earth-transition-metal heterometals and mixed ligands were successfully separated. Compounds 1-5 represent the first monovacant Keggin silicotungstates that contain both RE-TM heterometals and mixed ligands (H₂pzda and en), and the H₂pzda ligand in compound 5 adopts a pentadentate mode to link the Ce and Cu cations. A detailed study of the synthetic conditions revealed that the TM cations, the nature of Cu^{II} salt, the amount of CuCl₂·2H₂O, and the use of the H₂pzda and en organic ligands all played important roles in the preparation of RE-TM heterometallic POMs. Furthermore, the luminescence properties of compound 2 are assigned to the combination of Dy^{III} ions and H₂pzda ligands, whereas the luminescence properties of compounds 1 and 3-5 are assigned to the H₂pzda ligands. Further work in this area will focus on making other RE-TM heterometallic POMs with interesting structures and properties by the judicious choice of different POMs and/or organic ligands.

Experimental Section

General Methods and Materials

 $K_4[\alpha$ -SiW₁₂O₄₀]·17 H₂O was prepared according to a literature procedure^[12b] and confirmed by IR spectroscopy. Other chemical reagents were purchased without further purification. Elemental analysis (C, H, and N) was conducted on a Perkin–Elmer 2400-II CHNS/O analyzer. ICP analysis was performed on a Perkin–Elmer Optima 2000 ICP-AES spectrometer. IR spectra were obtained from solid samples palletized with KBr pellets on a Nicolet FT-IR 360 spectrometer in the range 4000–400 cm⁻¹. XRPD were performed on a Philips X'Pert-MPD instrument with Cu_k radiation (λ =1.54056 Å) in the range 2 θ =10–40° at 293 K. TG analysis was performed under a N₂ atmosphere on a Mettler-Toledo TGA/ SDTA851° instrument with a heating rate of 10°Cmin⁻¹ from 25–1000°C. Photoluminescence measurements were performed on an F-7000 fluorescence spectrophotometer.

$$\begin{split} &Synthesis \ of \ (enH_2)[Cu(en)_2(H_2O)]_2[[Cu(en)_2][Cu(en)_2(H_2O)]](a-SiW_{11}O_{39})Y(H_2O)(pzda)]]_2 \cdot n\,H_2O \ ({\bf I}; \ n\approx 4) \end{split}$$

 $K_4[\alpha-SiW_{12}O_{40}]$ · 17 H₂O (0.50 g, 0.15 mmol), YCl₃•6 H₂O (0.10 g. 0.33 mmol), CuCl₂·2H₂O (0.11 g, 0.65 mmol), H₂pzda (0.09 g, 0.54 mmol), and en (0.20 mL, 2.96 mmol) were successively dissolved in water (10 mL). After stirring for 45 min, the resulting mixture was transferred and sealed in a 30 mL Telfon-lined stainless steel autoclave, heated at 170°C for 117 h, and then slowly cooled to room temperature. Purple block crystals were collected by filtration, washed with distilled water, and dried in air. Yield: ca. 32% (based on K₄[α-SiW₁₂O₄₀]·17H₂O). IR (KBr): $\tilde{\nu} = 3426$ (w), 3302 (w), 3280(w), 3140 (sh), 2888 (w), 1650 (m), 1621 (m), 1589 (m), 1512 (w), 1456 (m), 1385 (m), 1361 (m), 1275 (w), 1103 (w), 1043 (s), 1010 (m), 983 (w), 944 (s), 882 (s), 824 (s), 791 (m), 775 (s), 744 (w), 700 cm⁻¹ (m); elemental analysis calcd. (%) for $C_{38}H_{130}Cu_6N_{30}O_{96}Si_2W_{22}Y_2$: C 6.34, H 1.82, N 5.83, Cu 5.29, Y 2.47, Si 0.78, W 56.15; found: C 6.16, H 1.68, N 5.65, Cu 5.17, Y 2.58, Si 0.92, W 56.03.

Synthesis of $(enH_2)[Cu(en)_2(H_2O)]_2[[Cu(en)_2][Cu(en)_2(H_2O)]](\alpha-SiW_{11}O_{39})Dy(H_2O)(pzda)]]_2 \cdot n H_2O$ (2; $n \approx 4$)

Compound **2** was synthesized according to a similar procedure to that of compound **1**, except that $DyCl_3-6H_2O$ (0.10 g, 0.27 mmol) replaced YCl_3-6H_2O. Yield: ca. 35 % (based on K₄[α -SiW₁₂O₄₀]-17H₂O). IR (KBr):

$$\begin{split} & \bar{\nu}\!=\!3429~(w),\,3301~(w),\,3140~(sh),\,2886~(w),\,1647~(m),\,1623~(m),\,1592~(m),\\ & 1508~(w),\,1456~(m),\,1394~(m),\,1360~(m),\,1275~(w),\,1103~(w),\,1043~(s),\\ & 1007~(m),\,988~(w),\,944~(s),\,881~(s),\,830~(s),\,791~(m),\,774~(s),\,742~(w),\\ & 702~cm^{-1}~(m);~elemental~analysis~calcd.~(\%)~for\\ & C_{38}H_{130}Cu_6N_{30}O_{96}Si_2W_{22}Dy_2;~C~6.21,~H~1.78,~N~5.72,~Cu~5.19,~Dy~4.42,\\ & Si~0.76,~W~55.02;~found:~C~6.35,~H~1.89,~N~5.85,~Cu~5.08,~Dy~4.29,~Si~0.88,\\ & W~54.89. \end{split}$$

$$\begin{split} &Synthesis \ of \ (enH_2)[Cu(en)_2(H_2O)]_2[[Cu(en)_2][Cu(en)_2(H_2O)]](a-SiW_{11}O_{39})Yb(H_2O)(pzda)]]_2 \cdot n\,H_2O \ (3;\ n\approx 4) \end{split}$$

Compound **3** was synthesized according to a similar procedure to that of compound **1**, except that YbCl₃·6 H₂O (0.10 g, 0.26 mmol) replaced YCl₃·6 H₂O. Yield: ca. 30 % (based on K₄[α -SiW₁₂O₄₀]·17 H₂O). IR (KBr): $\bar{\nu}$ = 3425 (w), 3302 (w), 3140 (sh), 2886 (w), 1648 (m), 1619 (m), 1590 (m), 1507 (w), 1458 (m), 1385 (m), 1361 (m), 1275 (w), 1101 (w), 1043 (s), 1012 (m), 983 (w), 943 (s), 882 (s), 823 (s), 791 (m), 770 (s), 744 (w), 700 cm⁻¹ (m); elemental analysis calcd. (%) for C₃₈H₁₃₀Cu₆N₃₀O₉₆Si₂W₂₂Yb₂: C 6.19, H 1.78, N 5.70, Cu 5.17, Yb 4.69, Si 0.76, W 54.87; found: C 6.07, H 1.91, N 5.82, Cu 5.05, Yb 4.54, Si 0.87, W 55.03.

Synthesis of $(enH_2)[Cu(en)_2(H_2O)]_2[[Cu(en)_2][Cu(en)_2(H_2O)]](a-SiW_{11}O_{39})Lu(H_2O)(pzda)]]_2 \cdot n H_2O$ (4; $n \approx 4$)

Compound 4 was synthesized according to a similar procedure to that of compound 1, except that LuCl₃·6H₂O (0.10 g, 0.26 mmol) replaced YCl₃·6H₂O. Yield: ca. 48% (based on $K_4[\alpha$ -SiW₁₂O₄₀]·17H₂O). IR (KBr): $\tilde{v} = 3422$ (w), 3300 (w), 3137 (sh), 2883 (w), 1649 (m), 1619 (m), 1589 (m), 1507 (w), 1458 (m), 1394 (m), 1361 (m), 1275 (w), 1101 (w), 1043 (s), 1013 (m), 991 (w), 944 (s), 881 (s), 822 (s), 794 (m), 775 (s), 742 (w), 700 cm^{-1} elemental (m); analysis calcd. (%) for C₃₈H₁₃₀Cu₆N₃₀O₉₆Si₂W₂₂Lu₂: C 6.19, H 1.78, N 5.70, Cu 5.17, Lu 4.74, Si 0.76, W 54.84; found: C 6.32, H 1.66, N 5.83, Cu 5.02, Lu 4.88, Si 0.89, W 54.67.

Synthesis of $[Cu(en)_2(H_2O)]_2[[Cu(en)_2]_2[Cu(pzda)_2]](a-H_2SiW_{11}O_{39})Ce(H_2O)]_2]\cdot nH_2O(5; n\approx 8)$

Compound **5** was synthesized according to a similar procedure to that of compound **1**, except that CeCl₃·6H₂O (0.10 g, 0.27 mmol) replaced YCl₃·6H₂O. Yield: ca. 25 % (based on K₄[α -SiW₁₂O₄₀]·17H₂O). IR (KBr): $\bar{\nu}$ = 3440 (w), 3314 (w), 3260(w), 2948 (w), 1659 (m), 1634 (m), 1577 (m), 1506 (w), 1455 (m), 1394 (m), 1275 (w), 1130 (m), 1039 (s), 988 (w), 945 (s), 878 (s), 830 (s), 786 (m), 762 (s), 702 cm⁻¹ (m); elemental analysis calcd. (%) for C₂₈H₉₆Cu₅N₂₀O₉₈Si₂W₂₂Ce₂: C 4.82, H 1.39, N 4.01, Cu 4.55, Ce 4.01, Si 0.80, W 57.95; found: C 4.97, H 1.53, N 3.88, Cu 4.38, Ce 4.17, Si 0.96, W 56.76.

X-ray Crystallography

Intensity data for compounds 1-5 were collected on a Bruker Apex-II CCD diffractometer with $Mo_{K\alpha}$ monochromated radiation ($\lambda =$ 0.71073 Å) at 296(2) K. Routine Lorentz polarization and empirical absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELXTL-97 program package.^[14] No hydrogen atoms associated with the water molecules were located from the difference Fourier map. Positions of the hydrogen atoms attached to the carbon and nitrogen atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode by using the default SHELXTL parameters. The restrains were used to resolve the ADP errors of some O, N, and C atoms by the ISOR and SIMU instructions in compounds 1--5. A summary of the crystallographic data and structural refinements for compounds 1-5 are shown in Table 2. CCDC 852930 (1), CCDC 852931 (2), CCDC 852932 (3), CCDC 852933 (4), CCDC 852934 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data and structural refinements for compounds 1–5.

	1	2	3	4	5
formula	C38H130Cu6N30O96Si2W22Y2	C38H130Cu6N30O96Si2W22Dy2	C38H130Cu6N30O96Si2W22Yb2	C38H130Cu6N30O96Si2W22Lu2	C ₂₈ H ₉₆ Cu ₅ N ₂₀ O ₉₈ Si ₂ W ₂₂ Ce
$Mr [gmol^{-1}]$	7203.64	7350.82	7387.92	7375.76	6980.04
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
crystal	triclinic	triclinic	triclinic	triclinic	triclinic
system					
a [Å]	12.922(4)	13.050(4)	12.823(4)	13.038(4)	12.097(4)
b [Å]	13.115(4)	13.243(4)	13.051(4)	13.209(4)	12.203(4)
c [Å]	21.868(6)	22.028(7)	21.758(7)	21.996(6)	22.757(8)
α [°]	79.111(5)	79.181(5)	79.162(6)	79.307(4)	84.973(6)
β [°]	84.603(5)	84.619(5)	84.489(5)	84.586(5)	84.005(6)
γ [°]	64.270(4)	64.181(4)	64.254(5)	64.358(4)	65.801(5)
$V[Å^3]$	3278.3(16)	3365.9(19)	3220.9(17)	3355.1(16)	3043.7(19)
Z	1	1	1	1	1
crystal size	$0.37 \times 0.26 \times 0.22$	$0.22 \times 0.18 \times 0.15$	$0.16 \times 0.12 \times 0.08$	$0.23 \times 0.19 \times 0.16$	$0.17 \times 0.15 \times 0.12$
[mm ³]					
ρ [gcm ⁻³]	3.648	3.625	3.809	3.649	3.806
$\mu [{\rm mm}^{-1}]$	21.161	20.854	22.086	21.279	22.403
R _{int}	0.0791	0.0338	0.0312	0.0828	0.0344
limiting indi-	$-15 \le h \le 8$	$-15 \le h \le 14$	$-15 \le h \le 15$	$-15 \le h \le 15$	$-11 \le h \le 14$
ces	$-15 \le k \le 15$	$-15 \le k \le 15$	-9 < k < 15	-15 < k < 14	-14 < k < 14
	-25 < l < 25	$-26 \le l \le 19$	-25 < l < 25	-26 < l < 12	-23 < l < 27
total reflns	16634	16922	16289	17019	15625
unique reflns	11 395	11664	11133	11601	10638
parameters	868	883	874	883	836
GOF on F^2	1.004	1.003	1.022	1.000	1.006
R_1, wR_2	0.0551 0.0998	0.0367 0.0836	0.0386 0.0962	0.0577 0.1476	0.0402 0.0947
$[I > 2\sigma(I)]$					
R_1, wR_2 [all data]	0.0873 0.1064	0.0476 0.0878	0.0462 0.0995	0.0659 0.1526	0.0563 0.1009

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