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Graphical Abstract

With the help of *in situ* generation of sulfate anion, three Ln(III)-K(I) sulfate and oxalate coordination polymers have been synthesized. These compounds display thermal and chemical stability, as well as good temperature and pH sensing ability.

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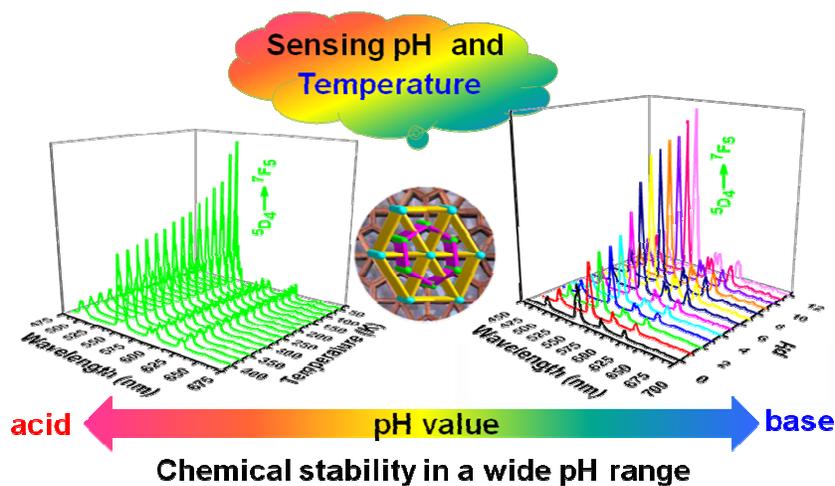
ARTICLE

Chemical stability and tunable luminescence of Ln(III)-K(I) coordination polymers featuring a tracery-like architecture

Qipeng Li,[a,c] Zeli Yuan,[b] Jinjie Qian,[a,c] and Shaowu Du*[a]

With the help of *in situ* generation of sulfate anion, three heterometallic Ln(III)-K(I) sulfate and oxalate coordination polymers, formulated as [KLn(ox)(SO$_4$)(H$_2$O)] (ox = oxalate, Ln = Eu **1**, Tb **2** and Dy **3**) have been successfully synthesized and structurally characterized. They are isomorphic and each displays a tracery-like structure inlaid with two different kinds of hexagons. In addition, compound **2** is thermally stable up to 350°C and exhibits unusual chemical stability in a wide pH range of 0–12, as confirmed by the variable temperature XRD and pH dependent XRD. Tunable luminescence of **2** is achieved by changing the temperature and pH, which indicates that it can be potentially used as probe for sensing temperature and pH.

Introduction

In recent years, the design and synthesis of coordination polymers (Cps) has spurred great interest, not only because of their aesthetically pleasing structures but also because of their potential applications in areas such as catalysis, gas storage, adsorption separation, ion exchange and non-linear optics.[1] In the design and synthesis of Cps, suitable choices of metals and ligands based on their coordination habits and geometric preferences often produce novel structures with interesting and specific properties. For example, the high and variable coordination numbers and flexible coordination environments of lanthanide ions usually lead to complicated architectures as well as fascinating network topologies, and the fluorescence efficiency of lanthanides can be tuned by variation of organic bridging ligands (antenna connector).[2] Thus, by combination of lanthanide ions and various organic ligands, many lanthanide-based Cps, which show promising potential for applications in luminescence sensors, light-emitting devices (LEDs, OLEDs), etc., can be constructed.[3–6] However, in comparison with transition metal ions, lanthanide-based Cps have shown limited success in the design, synthesis and property study. In particular, lanthanide Cps with both thermal and chemical stability are extremely rare, which might hinder their practical applications.[7]

Very recently, lanthanide Cps have shown great potential to be excellent candidates for luminescent thermometers and pH-sensors as luminescence is one of the most sensitive and easy-

observable detection signals. A great advantage of these materials in terms of temperature and pH sensors is that they can be non-destructive, accurate, rapid and highly sensitive, and work in biological environments. To date, several mixed lanthanide Cps have been reported to exhibit linear temperature responses in a certain temperature range based on the emissions of Tb(III) at 545 nm and Eu(III) at 613 nm.[8–10] By comparison, chemical stable lanthanide Cps are far more difficult to achieve. As a result, so far there are only two examples of lanthanide Cps which can exhibit pH sensing ability on a scale that ranges from 5 to 7.5 and 1 to 12, respectively.[7, 11]

In our present work, we have successfully synthesized three Ln(III)-K(I) sulfate and oxalate coordination polymers under hydro(solvo)thermal conditions *via* the *in situ* generation of sulfate anion and simultaneous introduction of oxalate anion, namely, [KLn(ox)(SO$_4$)(H$_2$O)] (ox = oxalate, Ln = Eu **1**, Tb **2** and Dy **3**). They are isomorphic and their structures feature a 3D tracery-like framework, inlaid with two different types of hexagons. Furthermore, **2** exhibits good thermal stability and unusual chemical stability. Tunable luminescence of **2** was observed by changing the temperature and pH and the results showed that the luminescent intensity of **2** exhibited near-linear temperature and pH responses in a broad ranges of temperature (50–400 K) and pH (0–12).

Result and discussion

Synthesis and characterization

A general strategy to construct inorganic sulfate materials is to use sulphuric acid or sulfates under hydro(solvo)thermal conditions in the presence of organic amines as structure-directing templates. For example, several organically templated open frameworks of lanthanide sulfates as well as a layered iron sulfate with a distorted Kagome lattice have been prepared by this way.[12] However, the products obtained by this method are usually one- or two-dimensional complexes and the formation of three-dimensionally extended sulfate frameworks is relatively difficult presumably due to the low reactivity of sulfate anions. Previously, we have successfully obtained a family of new 3D Ln(III)-K(I) heterometallic sulfate open frameworks, $[KLn(SO_4)_2(H_2O)]$ by the *in situ* generation of sulfate anions through the decomposition of dimethyl sulfoxide (DMSO) under hydro(solvo)thermal conditions.[13] The resulting sulfate frameworks exhibit exceptional thermal stability but poor chemical resistance to strong acids and bases. In order to synthesize lanthanide sulfate frameworks with both thermal and chemical stability, we introduce oxalate anion as an auxiliary ligand to the framework because this small and simplest dicarboxylic acid can give a wide variety of connectivity to lanthanide ions, thus enhance the stability of the framework.

Compounds **1**–**3** were synthesized by treating corresponding lanthanide nitrates with two equiv. oxalic acid in a mixed solvent of water and DMSO (v/v = 1:1) at 120°C for 3 days. During the reactions, *in situ* generation of sulfate anions occurs through the decomposition of DMSO at hydro(solvo)thermal conditions and both sulfate and oxalate anions are coordinated to lanthanide ions to afford 3D heterometallic Ln(III)/K(I) Cps. The powder X-ray diffractions (XRD) were recorded at room temperature to test the purity of these compounds. The experimental results match well with the simulated XRD patterns, indicating phase purity of the as-synthesized samples (Fig. S3). Thermogravimetric analysis (TGA) measurements were conducted in the temperature range of 30–800°C under a flow of nitrogen with the heating rate of 10°C min^{-1}. TG analyses indicate that **1**–**3** exhibit similar thermal behaviour (Fig. S4). The TGA curve of **2** indicates that the first step from 30 to 130°C with a weight loss of 4.7% is due to the loss of one coordinated water molecule (calcd 4.5%), which is followed by a steady plateau up to 350ºC. The framework starts to collapse from 350 to 800ºC with the loss of oxalate anions.

Structure description

Compounds **1**–**3** are isomorphic and both crystallize in the monoclinic system with space group $P2_1$/c, therefore only the structure of **1** is discussed in detail. The asymmetric unit of **1** contains one Eu(III) ion, one K(I) ion, one SO_4^{2-} anion, one oxalate anion and one μ-H_2O molecule. The Eu(III) ion is eight-coordinated by one water molecule, four oxygen atoms from two different oxalate anions and three oxygen atoms from three different sulfate anions with the Eu–O bond lengths being in the normal range of 2.339(5)–2.461(4) Å. The K(I) ion is nine-coordinated by one μ-H_2O molecule, six oxygen atoms from four different oxalate anions and two oxygen atoms from two

different sulfate anions with the K–O bond lengths varying from 2.752(5) to 3.102(5) Å (Fig. S1).
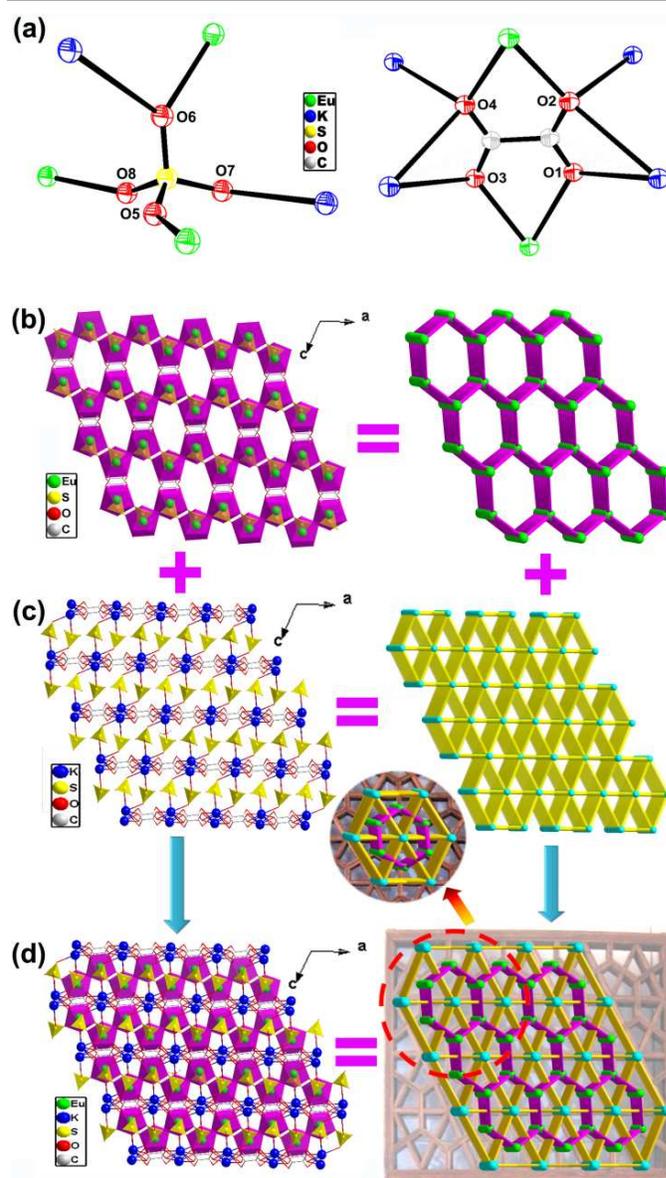
Fig. 1 (a) The coordination modes of sulfate and oxalate anions in **1**. (b) The 3D hexagonal Eu(III) framework in **1**. (c) The 3D hexagonal K(I) framework with the dinuclear K(I) units being simplified as nodes. (d) The 3D tracery-like Eu(III) and K(I) framework inlaid with two different kinds of hexagons.

The sulfate anion in the structure of **1** links Eu(III) and K(I) ions with the coordination mode of $(k_1$-k_2-k_1-$k_1)$-μ_5 (O5, O6, O7 and O8), while the oxalate anion connects the Eu(III) and K(I) ions with the $(\mu_2$-μ_3-μ_2-$\mu_3)$-μ_6 (O1, O2, O3 and O4) coordination mode (Fig. 1a). In addition, the coordinated water molecule bridges the Eu(III) and K(I) ions. The adjacent Eu(III) ions are bridged by sulfate anions into a zigzag chain, then such chains are further chelated *via* oxalate anions to afford a 3D Eu(III) hexagonal framework (Fig. 1b). Each oxalate anion links four K(I) ions with a $(k_1$-μ_2-k_1-$\mu_2)$-μ_4 coordination mode, generating a K(I) oxalate chain. The K(I) oxalate chains are connected by

sulfate anions into a 3D K(I) hexagonal framework with the dinuclear potassium units being simplified as nodes (Fig. 1c). Owing to the coexistence of 3D Eu(III) and K(I) hexagonal frameworks, the overall framework of **1** can be regarded as a complicated 3D tracery-like structure inlaid with two different kinds of hexagons (Fig. 1d and Fig. S2).

Thermal and chemical stability of 2
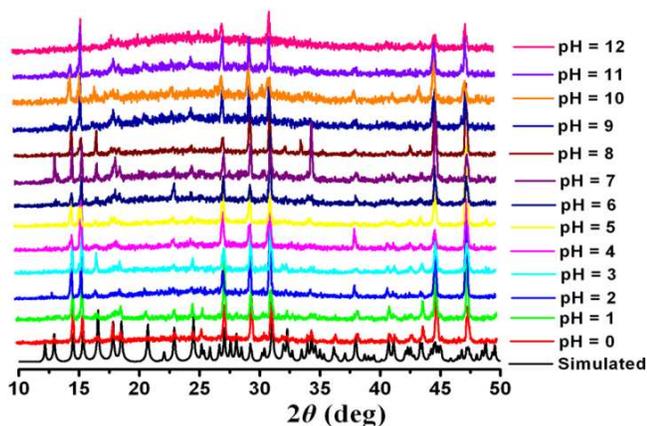
Fig. 2 PXRD profiles for **2** soaked aqueous solutions with pH values of 0–12 for 24 h.

Stability is one of the primary concerns in development of new luminescent materials.[14] Temperature dependent XRD experiments were conducted for **2** after calcination at elevated temperatures to study its thermostability. With the increase of temperature from 100 to 350°C, the XRD patterns essentially match well with the as-synthesized sample except that some peaks disappear (Fig. S5). Such phenomenon is frequently observed for metal-organic frameworks, which probably arises from the loss of solvent molecules. These results suggest that the whole framework remains steady before 350°C and then the long range order of the structure lose and the anamorphous phase generate.[2e] The pH dependent XRD patterns were also performed to demonstrate the chemical stability of **2**. The XRD patterns of **2** are almost unaltered in aqueous solutions with pH values ranging from 0 to 12, indicating that **2** can retain crystallinity and is stable in a wide pH range (Fig. 2). While many lanthanide Cps can exhibit good thermal stability,[8d] the exceptional chemical stability of **2** is uncommon.[7]

Photoluminescence properties

The solid-state excitation and emission spectra of **1** and **2** were explored at room temperature, which emitted the intense red and green fluorescence under UV light, respectively. The excitation spectrum of **1** exhibits typical transition lines from the $^7F_0$ ground state to various excited states of the Eu(III) ions. Upon excitation at 393 nm, the characteristic emissions of Eu(III) ions are observed in the range of 570–720 nm. The typical emission peaks are associated with the 4f → 4f transitions of the $^5D_0$ excited state to the low-lying ^7F_J (J = 0–4) levels, and the $^5D_0 \to ^7F_2$ transition of Eu(III) centers at 614 nm dominates the whole emission spectrum (Fig. 3a).[13] When

excited at 370 nm, the emission spectrum of **2** displays green luminescence with typical emission peaks at 488, 543, 582 and 621 nm, which are assigned to $^5D_4 \to ^7F_J$ (J = 6–3) transitions.[13] The strong emission band at 488 nm arises from the $^5D_4 \to ^7F_6$ transition, and the stronger band at 543 nm is attributed to the $^5D_4 \to ^7F_5$ transition. The band at 582 nm corresponds to the $^5D_4 \to ^7F_4$ transition and the band at 621 nm is attributed to the $^5D_4 \to ^7F_3$ transition (Fig.3b). The quantum yields (Φ) and luminescence lifetime were measured for **1** and **2** at room temperature under the excitation wave lengths (393 and 370 nm, respectively). The Φ values are 29.15% for **1** and 14.69% for **2**, and the corresponding lifetimes are *ca*. 0.6217 ms for **1** and *ca*. 1.291 ms for **2**, respectively.
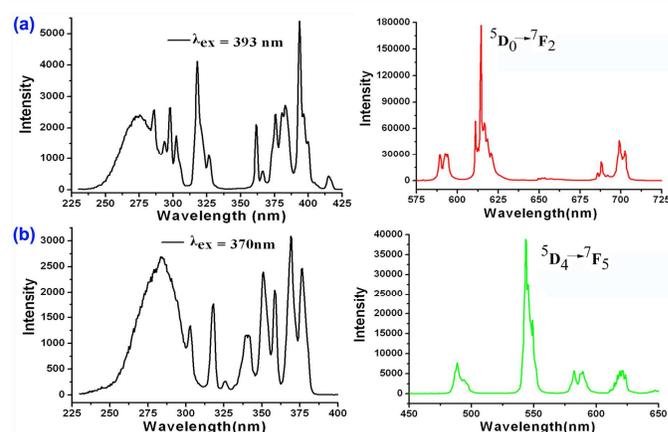
Fig. 3 Solid-state excitation and emission spectra of **1** (a) and **2** (b) at room temperature

Tunable luminescence of 2

The temperature-dependent luminescent properties of **2** were investigated in terms of intensity to establish its potential as a temperature sensor. The temperature dependent emission spectra of **2** with the intensities of the $^5D_4 \to ^7F_5$ (λ_{em} = 543 nm) from 50 to 400 K are illustrated in Fig. 4a. The emission intensities of $^5D_4 \to ^7F_5$ decrease gradually with an increase in temperature and the normalized intensities show a nearly linear relationship from 100 to 400 K (Fig. 4b), which is normally due to the reduction of molecular thermal vibration with decreasing temperature.[10]
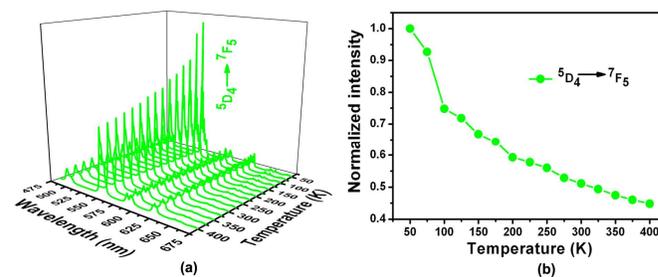
Fig.4 (a) Temperature dependence of the emission spectra of **2** recorded between 50 and 400 K (excited at 370 nm). (b) The normalized intensity at different temperatures (50–400 K).

Since compound **2** is stable over a wide pH range, the pH-dependent fluorescence of **2** is explored at room temperature. Crystal samples of **2** (50 mg) have been immersed in aqueous solutions (5 mL) of different pH values and then the mixtures were agitated ultrasonically for 30 min to form emulsions. Their fluorescent spectra are shown in Fig. 5a. The fluorescence intensities of **2** rise along with the increase of pH in the range of 0-12. The most acidic solution gives the weakest fluorescence, whereas the highest emission intensity is obtained at pH = 12. Their normalized intensities display a nearly linear relationship in a pH range of 4–7 (Fig. 5b). Our preliminary results indicate that **2** may have potential applications as fluorescent probes for temperature and pH. In comparison with the temperature or pH sensors based on mixed lanthanide Cps, the ratio between temperature and luminescence intensity of **2** can cover a wider temperature range from cryogenic (100–298 K) to physiological temperature (298–320 K) and even to high temperature (320–400 K). Besides, compound **2** has near-linear response to pH over the whole pH range. To our knowledge, so far there has been only one mixed lanthanide Cp that is able to function as both a pH-sensor and a luminescent thermometer.[7]
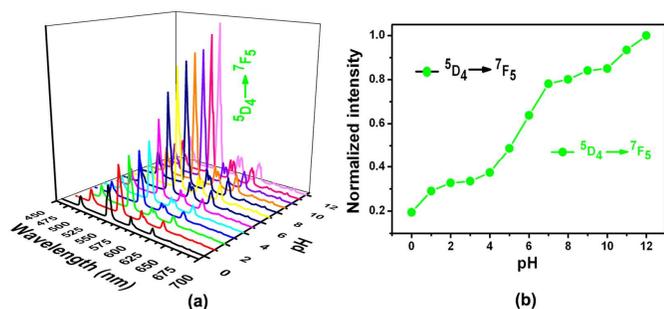
Fig.5 (a) The pH dependent fluorescence of compound **2** with different pH measured under excitation of 370 nm. (b) The normalized intensity of different pH (0–12).

Conclusions

In summary, three novel heterometallic 3D Ln(III)-K(I) sulfate and oxalate coordination polymers were hydro(solvo)thermally synthesized *via* the *in situ* generation of sulfate anions. They are isomorphic and feature a tracery-like structure inlaid with two different types of hexagons. In addition, **2** exhibits both thermal stability and unusual chemical stability in a wide pH range of 0–12. Tunable luminescence of **2** is observed by changing the temperature and pH and the results indicated that it may have potential applications as temperature and pH sensors. Furthermore, the strategy employed in this work may be useful for the preparation of more sulfate and oxalate multifunctional materials with exceptional stability in the future.

Experimental Section

Materials and Instruments

All chemicals were purchased commercially and were used as received. Thermogravimetric analysis was conducted using a TGA/ NETZSCH STA449C instrument heated from 30 to 800 ºC (heating rate of 10 ºC min^{-1}, nitrogen stream). The powder X-ray diffraction (PXRD) patterns were recorded on crushed single crystals in the 2θ range of 5–50º using Cu-Kα radiation. Elemental analyses were measured with an elemental Vairo EL III analyzer. Inductively coupled plasma element analysis for metal ions was performed with an Ultima2 X-ray inductively coupled plasma optical emission spectrometer. Fluorescence spectra for the solid samples were recorded on an Edinburgh Analytical instrument FLS920.

Synthesis of [KLn(ox)(SO$_4$)(H$_2$O)] (Ln = Eu 1, Tb 2 and Dy)

A mixture of Eu(NO$_3$)$_3$·6H$_2$O (0.25 mmol) and K$_2$C$_2$O$_4$·H$_2$O (0.50 mmol) were placed in a 20 mL of Teflon-lined stainless steel vessel with 6 mL of mixed solvent of DMSO and H$_2$O (V/V = 1:1). The mixture was heated to 120 ºC in 4 h and kept to this temperature for 3 days. The reaction system was cooled slowly to room temperature during another 2 days. Colourless crystals of **1** were collected and washed with DMSO, and dried in air (yield: 31%, based on K$_2$C$_2$O$_4$·H$_2$O). Elemental anal. calcd. for **1** C$_2$H$_2$EuKO$_9$S (339.62) (%): Eu, 38.65; K, 9.94; S, 8.15; C, 6.11; H, 0.51. Found (%): Eu, 38.80; K, 9.91; S, 8.35; C, 6.07; H, 0.55.

Colorless prismatic crystals of **2** and **3** were obtained in yields ranged from 28–40% by a procedure similar to that described for **1** using the corresponding Ln(NO$_3$)$_3$·6H$_2$O instead of Eu(NO$_3$)$_3$·6H$_2$O. Elemental anal. calcd. for **2** C$_2$H$_2$TbKO$_9$S (400.14) (%): Tb, 39.72; K, 9.77; S, 8.01; C, 6.00; H, 0.50. Found (%): Tb, 39.73; K, 9.97; S, 7.45; C, 6.27; H, 0.65. Elemental anal. calcd. for **3** C$_2$H$_2$EuKO$_9$S (403.71) (%): Dy, 40.25; K, 9.69; S, 7.94; C, 5.95; H, 0.50. Found (%): Dy, 40.32; K, 9.78; S, 8.00; C, 6.01; H, 0.50.

Acid-base stability experiments

Aqueous solutions of pH = 0-12 were prepared. Then 50 mg of the sample was soaked in each solution for 24 h. After that, all the samples are centrifuged, washed several times and dried in the air before measuring powder XRD for pH stability.

Crystallographic data collection and refinement

Single-crystal X-ray diffraction data were collected on a Rigaku diffractometer with a Mercury CCD area detector (Mo Kα; λ = 0.71073Å) at room temperature. Empirical absorption corrections were applied to the data using the Crystal Clear program.[15] The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using SHELXTL-97 program.[16] Metal atoms in each compound were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal parameters on F^2. All non-hydrogen atoms were refined anisotropically. Atoms of water molecules were located using difference Fourier method and refined freely. Hydrogen atoms were positioned geometrically. Crystallographic data and other pertinent information for **1**–**3** are summarized in Table 1. Selected bond lengths and angles

are listed in Table S1. The CCDC numbers for **1–3** are 1008577–1008579, respectively.

Table 1 Crystal Data and Structure Refinement Results for **1–3**

Compounds	**1**	**2**	**3**
CCDC	1008577	1008578	1008579
Formula	$C_2H_2EuKO_9S$	$C_2H_2TbKO_9S$	$C_2H_2DyKO_9S$
Mr	393.18	400.14	403.71
Cryst syst	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	6.603(3)	6.574(9)	6.551(2)
b (Å)	8.575(3)	8.561(12)	8.512(3)
c (Å)	14.794(5)	14.775(19)	14.719(4)
α (deg)	90	90	90
β (deg)	112.346(2)	112.60(5)	112.515(1)
γ (deg)	90	90	90
V (Å^3)	774.7(5)	767.7(18)	758.2(4)
Z	4	4	4
D_c (g cm^{-3})	3.371	3.462	3.537
M (mm^{-1})	8.932	10.055	10.709
$F(000)$	736.0	744.0	748.0
GOF	1.160	1.242	1.105
$R_1{}^a$	0.0279	0.0362	0.0188
$wR_2{}^a$	0.0727	0.1101	0.0490

$^a R = \sum (||F_o| - |F_c||)/\sum |F_o|, wR = \{ \sum w[(F_o{}^2 - F_c{}^2)^2]/ \sum w[(F_o{}^2)^2]\}^{1/2}$

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Notes and references

^{a} State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: swdu@fjirsm.ac.cn; Fax: (+86) 591 83709470

^{b} School of Pharmacy, Zunyi Medical University, Zunyi, Guizhou, 563003, P. R. China.

^{c} University of Chinese Academy of Sciences, Beijing 100039, P. R. China.
†Electronic Supplementary Information (ESI) available: table of bond lengths and angles, additional figures, XRD patterns and TGA curves of the compounds. CCDC numbers: 1008577–1008579 for compounds **1–3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

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