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Synthesis of a cluster containing Eu(III) α_2-P$_2$W$_{17}$O$_{61}$$^{10-}$ and preliminary luminescence experiments

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This paper is dedicated to Francis Sécheresse, on the occasion of his sixtieth birthday, and in honor of his contributions in polyoxometalate chemistry

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Abstract

We have prepared an unique cluster, $[Eu(H_2O)_3(\alpha_2$-P$_2$W$_{17}$O$_{61}$)(Eu$_2$(H$_2$O)$_7$)]$_4$$^{4-}$, **1**, in high yield and the preparation and crystallization is highly reproducible. This compound is based on the 1:1 $[Eu (\alpha_2$-P$_2$W$_{17}$O$_{61}$)]$_2$$^{14-}$ cluster where Eu2 is bound in the defect of the cap region of the α_2-P$_2$W$_{17}$O$_{61}$. Two other Eu(III) ions, Eu1 and Eu3 are each bound to two terminal oxygen atoms in that defect cap region. These two Eu(III) ions are bound through a bridging oxygen to other $[Eu (\alpha_2$-P$_2$W$_{17}$O$_{61}$)]$_2$$^{14-}$ clusters to form a network of $[Eu (\alpha_2$-P$_2$W$_{17}$O$_{61}$)]$_2$$^{14-}$ dimers, each connected by two aquated Eu(III) ions. Preliminary luminescence studies of a crystalline sample of **1**, suspended in methanol and reacted with organic ligands, show that the organic ligands indeed are capable of sensitizing the luminescence of the Eu(III). For comparison in solution, the organic soluble TBA$_3$H[EuPW$_{11}$O$_{39}$], **3**, was prepared and characterized. As shown from luminescence titrations and ^{31}P and ^{1}H NMR spectroscopy, this species reacts with phenanthroline and bipyridine, in acetonitrile, to form the 2:1 organic ligand: [Eu (PW$_{11}$O$_{39}$)] adduct. *To cite this article: C. Zhang et al., C. R. Chimie 8 (2005).*
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Résumé

Nous avons préparé un cluster original $[Eu(H_2O)_3(\alpha_2$-P$_2$W$_{17}$O$_{61}$)(Eu$_2$(H$_2$O)$_7$)]$_4$$^{4-}$, **1**, avec un bon rendement, sa synthèse et sa cristallisation étant parfaitement reproductibles. Ce composé est basé sur le cluster 1:1 $[Eu(\alpha_2$-P$_2$W$_{17}$O$_{61}$)]$_2$$^{14-}$, où Eu2 est lié à la vacance de la couronne à trois de α_2-P$_2$W$_{17}$O$_{61}$. Deux autres ions Eu(III), Eu1 et Eu3, sont chacun liés à deux atomes d'oxygène terminaux de cette vacance. Ces deux ions Eu(III) sont liés par un atome d'oxygène pontant à d'autres clusters $[Eu(\alpha_2$-P$_2$W$_{17}$O$_{61}$)]$_2$$^{14-}$ et génèrent un réseau de dimères $[Eu(\alpha_2$-P$_2$W$_{17}$O$_{61}$)]$_2$$^{14-}$, chaque dimère étant connecté par deux ions Eu(III) solvatés. Des études préliminaires en luminescence d'un échantillon cristallin de **1**, en suspension dans le méthanol, après réaction avec des ligands organiques, montrent que les ligands organiques agissent comme des sensibilisateurs pour la luminescence de l'Eu(III). Pour des études comparatives en solution, le composé soluble en solvant organique,

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TBA$_3$H[EuPW$_{11}$O$_{39}$], **3**, a été préparé et caractérisé. Comme le montrent des titrages en luminescence et des études par spectroscopie de RMN ^{31}P et ^{1}H, ce composé réagit avec la phénantroline et la bipyridine, dans l'acétonitrile, pour former le produit d'addition 2:1 ligand organique:[Eu (PW$_{11}$O$_{39}$)]. ***Pour citer cet article : C. Zhang et al., C. R. Chimie 8 (2005).***

Keywords: Polyoxometalates; Europium; Luminescence; Sensitizers

Mots clés : Polyoxométallates ; Europium ; Luminescence ; Sensibilisateurs

1. Introduction

Polyoxometalates (POMs) are metal oxide clusters that are chemically robust and can be easily modified with respect to incorporation of transition metal ions, charge, size, potential, and can be rendered soluble in water or organic solution. Due to these features, POMs have been developed as catalysts for oxidation and acid-dependent reactions. However there are many potential applications that can exploit their unique properties. The combination of lanthanide (Ln) ions with polyoxometalates can offer unique functionality. We and others have focused on examination of the solution and solid state chemistry of lanthanide (Ln) polyoxometalates for a variety of reasons. One important opportunity for polyoxometalates is in the realm of materials chemistry and nanotechnology. For example, the use of lanthanide ions to 'link' POMs into solid-state oligomers [1,2] and large wheel structures [3–6] has been observed in solid-state X-ray crystal structures. Solution studies demonstrate that lanthanide ions can also serve as connectors and transfer agents for different monolacunary POMs. [7] We envision that incorporation of lanthanide ions into POMs offer additional useful functionality, for example, in the creation of luminescent [8,9] , magnetic, Lewis acid catalytic centers [10].

The title complex, **1**, [Eu(H$_2$O)$_3$(α_2-P$_2$W$_{17}$O$_{61}$)-(Eu$_2$(H$_2$O)$_7$)]$_4^{4-}$, isolated in this study is a cluster of Eu(III) ions tied together by the [Eu(α_2-P$_2$W$_{17}$O$_{61}$)]$^{7-}$ polyoxometalate, that is formed in a high yield, highly reproducible reaction. We thought that this material would be an excellent crystalline framework to study the effect of the reaction with organic ligands to form ternary complexes that may sensitize the lanthanide luminescence.

Photosensitization of lanthanides is a strategy to produce new sensor materials. Indeed, EuCl$_3$ and TbCl$_3$ have been tested in viscous solution, imbedded in organic ligands, supported on materials or in polymers as sensors for detecting nerve agents [11], dipicolinic acid (the chemical marker for bacterial spores) [12] and other biological and chemical entities. [13] Polyoxometalates and metal oxides, in general, may offer useful matrices or support materials for lanthanides.

Lanthanide emission bands are very sharp (often a few cm^{-1} in width), yielding pure colors, and are largely independent of coordination environment due to the shielding of the f electrons. The absorption coefficients of lanthanides are very low due to the Laporte-forbidden and often spin-forbidden f–f transitions and therefore, lanthanides require direct excitation or photosensitization to observe high luminescence. [14–16]

One way to obtain relatively high luminescence yields is through photoexcitation of the metal oxygen framework of the polyoxometalates with UV light. Using this technique, Yamase has studied the intramolecular energy transfer processes in polyoxometalloeuropate complexes. Photoexcitation of the O→M (M=Nb,Mo,W) ligand to metal charge transfer (LMCT) bands of the polyoxometalates leads to Eu^{III} emission with single exponential decay. [17] The quantum yield for [Eu(W$_5$O$_{19}$)$_2$]$^{9-}$ is the highest found for Eu(III) polyoxometalates. [18]

We propose the use of photosensitizing organic ligands to sensitize the lanthanide luminescence in lanthanide polyoxometalates. In this case, the chromophore absorbs UV light efficiently (large ϵ) and is excited to the singlet state; intersystem crossing to the triplet state occurs and energy transfer to the lanthanide occurs by a Dexter mechanism [19], resulting in emission from the Ln ion, Scheme 1.

The position of the organic ligand triplet state energy at 2000 cm^{-1} above the receiving lanthanide 4f state ensures a fast and irreversible energy transfer. [20] This restricts the range of chromophores to those with high
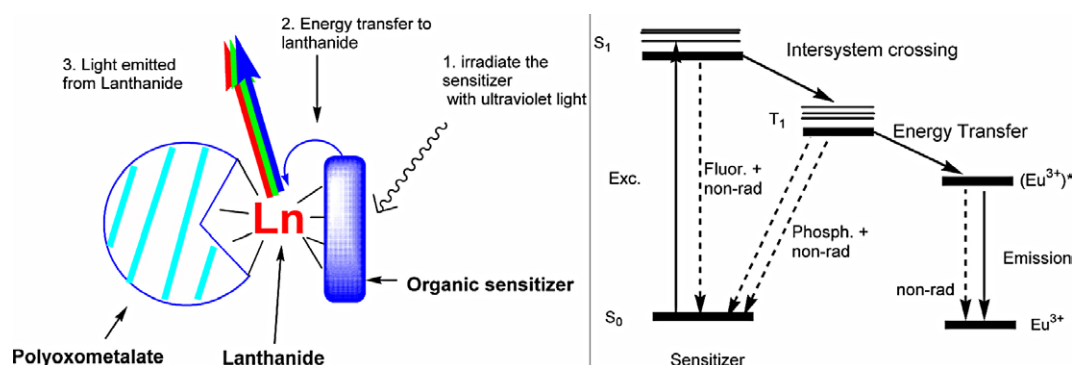
Scheme 1. Left: concept of ternary complex for sensitization of lanthanide luminescence. Right: energy level diagram of sensitizer-Eu^{3+} energy-transfer process.

triplet energy and a small S-T energy gap if excitation is to be achieved in the 315 – 430 nm range. The quantum yield depends on the efficiency of the individual steps: the intersystem crossing efficiency, the energy transfer efficiency and the Ln(III) luminescence quantum yield (Scheme 1).

High-frequency oscillators, like the O–H, N–H vibrations of the solvent and ligands, play an important role in removing energy nonradiatively from the lanthanide excited state, thus quenching the luminescence. Deactivation of the luminescence from excited Ln^{3+} ions in solution occurs by a vibrational energy-transfer process, involving high-energy vibrations of water molecules – both bound and closely diffusing – or of ligand (N–H) oscillators. To prevent this nonradiative quenching, Ln ions should be shielded by the ligand from their environment.

Polyoxometalates and metal oxides, in general, may offer excellent matrices or support materials to shield the lanthanide ion/ions from non-radiative removal of energy from the solvent. Much longer lifetimes for excited Er^{3+} ($^4I_{13/2}$), Nd^{3+} ($^4F_{3/2}$) and Yb^{3+} ($^2F_{5/2}$) species have been found in inorganic matrices. We and others have seen that the 1:2 Eu: POM (in our work, the α-1 and α-2 $P_2W_{17}O_{61}^{10-}$) complexes effectively shield the Eu^{3+} from the water solvent and exhibit lifetimes in the millisecond range.

The objective of this work is to incorporate sensitizing organic molecules into lanthanide polyoxometalate complexes to test if the luminescence is enhanced. To achieve this objective we attempted to prepare stable systems wherein the H_2O molecules bound to the lanthanide ion(s) will be replaced by organic sensitizing molecules. Thus, the lanthanide ions will be bound to the sensitizing molecule as well as to the polyoxometalate, in a 'ternary' system. We are taking two approaches: 1) to employ the crystal, **1**, as a solid, where the POM anchors the Eu(III) ions in three binding modes, for reaction with organic ligands and 2) to render a simple 1:1 Eu: POM soluble in organic solution and react that with sensitizing ligands. We report here the synthesis and crystal structure of the cluster, **1**, and preliminary solid-state luminescence data of **1** and the 1:1 $[Eu(\alpha_2-P_2W_{17}O_{61})]^{7-}$ species, **2**, [21] after reaction with organic ligands and the synthesis, characterization of organic soluble $TBA_3H[EuPW_{11}O_{39}]$, **3**, and preliminary luminescence data for its titration with the sensitizing ligands, phenanthroline and 2,2′-bipyridine.

2. Experimental section

2.1. General

All reagents were commercially available and used without further purification. Elemental analyses were carried out by Inductive Coupled Plasma Atomic Emission Spectrometry (ICP-AES, SPECTROFLAME M120E) using a method described previously. [22] Steady-state emission and excitation spectra were acquired using a Fluorolog ISA JOBIN YVON SPEX Spectrofluorimeter. NMR data were collected as described previously. [22]

2.2. Preparation and crystallization of $Al(H_3O)_2$-$[Eu(H_2O)_3(\alpha_2-P_2W_{17}O_{61})(Eu_2(H_2O)_7)]_4Cl\cdot20\ H_2O$ (1)

The lacunary $K_{10}[\alpha_2-P_2W_{17}O_{61}]$ (3.14 g, 0.639 mmol) was dissolved in 30 ml of 0.5 M sodium acetate buffer at

pH = 5.5 at 70 °C to form a clear solution. $EuCl_3$ (0.82 g, 2.24 mmol) was dissolved in a minimum amount of water and added dropwise to the stirring $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ solution. $AlCl_3$ (3.08 g, 12.77 mmol) was added to the reaction mixture, and the clear solution was allowed to slowly evaporate at room temperature, after one night, colorless small diamond-like crystals were formed. X-ray quality crystals were selected from the bulk crystals. Yield: 2.32 g, 65%. Anal. Calcd for $Al(H_3O)_2[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})(Eu_2(H_2O)_7)]_4Cl\cdot20\ H_2O$; W, 59.82; Eu, 8.16; P, 1.19; Al, 0.52. Found: W, 61.29; Eu, 8.22; P, 1.20; Al, 0.56. ^{31}P NMR Spectroscopy: H_2O/D_2O: δ, ppm: 8.4391 and 8.3475 and –12.2054.

2.3. Sample preparation for solid-state luminescence

1) Cluster, **1**, and 1:1 Eu^{3+}: $\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$, **2**, prepared by reacting 0.055 g (0.15 mmol) of $EuCl_3$ and 0.74 g (0.15 mmol) of $\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$ in water [21] and precipitating out with ether and methanol, were employed in these studies. Solid samples (0.15 mmol) were suspended in methanol for reaction with organic sensitizing ligands. To wash away any excess Eu^{3+} that may be occluded in the crystals, the solid samples of **1** and **2** were suspended in 1ml of methanol and vortexed; the supernatant was decanted; this procedure was repeated. 2) Solutions of organic sensitizing ligands (phenanthroline, bipyridine, phthalic acid, 0.01 M) were made by dissolving the ligands in methanol. Dipicolinic acid was also used and that was a suspension in methanol. Samples of phthalic acid and dipicolinic acid were used as is and also were deprotonated by the addition of a stoichiometric amount of sodium methoxide. The sodium dipicolinate was also a suspension. 3) Suspensions of **1** and **2** were placed into small plastic tubes; the suspensions were centrifuged (5.5 ×1000 rpm) for 1 min, followed by decanting the supernatant. Organic ligands (0.02ml) were added to the solid, followed by 0.1ml of methanol; the suspension was vortexed for 15 s and centrifuged. The supernatant was decanted. Two drops of methanol were added to the remaining pellet, resulting in a slurry; the slurry was micropipetted on a microscope slide in a thin layer and allowed to dry. For the control reactions, $EuCl_3$ was suspended in methanol and mixed with a suspension of the organic ligand. The mixture was vortexed for 15 s, centrifuged; the supernatant was decanted and the slurry was spread on

a microscope slide, as described above. Excitation and emission spectra were recorded of the microscope slides containing dried suspensions of the Eu polyoxometalates, Eu POMs with organic ligands and control Eu(III) with organic ligands.

2.4. Preparation of organic soluble 1:1 Eu(III):POM, 1:1 Eu(III):(PW$_{11}$O$_{39}$), TBA$_3$H[EuPW$_{11}$O$_{39}$], 3

2.4.1. Method A

$EuCl_3\cdot6\ H_2O$ (0.75 g, 2.047 mmol) was dissolved in 10 ml of distilled H_2O. To this solution, $K_7PW_{11}O_{39}$ (6.09 g, 2.047 mmol), dissolved in 25 ml of distilled H_2O at 40 °C, was added dropwise. The resulting solution was stirred vigorously for 1 min followed by the simultaneous addition of 4.62 g of saturated TBABr and 0.2 M HCl to control the pH at 3.6. The mixture was stirred for 1–2 min; the white precipitate was separated by filtration, and dried under air suction.

2.4.2. Method B

A solution of $K_7PW_{11}O_{39}$ (6.09 g, 2.047 mmol),dissolved in 25 ml of distilled H_2O at 40 °C, was added dropwise to a solution of $EuCl_3\cdot6\ H_2O$ (0.75 g, 2.047 mmol, 10 ml H_2O). The resulting solution was stirred vigorously for a few minutes, followed by the addition of LiCl (0.87 g, 20.47 mmol) and 105 ml of EtOH . A white precipitate formed quickly and was collected by filtration, and dried under suction, ^{31}P NMR shows the formation of only 1:1 $[EuPW_{11}O_{39}]^{4-}$ complex. This white solid was dissolved in 15 ml of H_2O; 4.62 g of saturated TBABr and 0.2 M HCl were simulataneously added dropwise to control the pH at 3.6. The mixture was stirred for 1–2 min; the white precipitate was separated by filtration, and dried under air suction.

The protonation states were calculated as described in the literature. [23] Elemental anal. Calcd for $TBA_3H[Eu(H_2O)_4PW_{11}O_{39}]$: Eu, 4.18; W, 55.72; P, 0.85. Found: Eu, 4.36; W, 57.96; P, 0.89. The ^{31}P NMR spectra vary slightly with solution content: ^{31}P NMR: δ, 5.6 ppm (CD_3CN, H_2O), 9.6 ppm, (CD_3CN). This compound is identical to the species isolated from the reaction of Eu(III) and $A\text{–}PW_9O_{34}{}^{9-}$ in H_2O, in both 1:1 or 2:1 Eu: $A\text{–}PW_9O_{34}{}^{9-}$ stoichiometry, with the addition of TBA^+ or TEA^+. [24]

Table 1
Crystal data and structure refinement for the complex **1**

	1
Empirical formula	$AlClEu_{12}O_{376}P_8W_{68}$
Fw	5257.70
Cryst. syst.	monoclinic
Space group	$P2(1)/n$
temp, K	100 (2)
Wavelength, Å	0.71073
a, Å	17.378(4)
b, Å	23.650(5)
c, Å	19.124(4)
α, deg	90
β, deg	101.41(3)
γ, deg	90
Vol, Å^3	7705(3)
Z	4
Calcd density, g/cm^3	4.491
Abs coeff, mm^{-1}	27.889
F (000)	9036
θ range, deg	2.10 to 20.82
limiting indices	$-17 \leq h \leq 17$
	$-23 \leq k \leq 23$
	$-19 \leq l \leq 19$
Reflns collected/unique	30967 / 8051 [R(int) = 0.0675]
Refinement method	full-matrix least- squares on F^2
Data/ restraints/ parameters	8051 / 0 / 583
GOF on F^2	1.067
Final R indices [I > 2σ(I)]	$R1 = 0.0657$, $wR2 = 0.1727$
R indices (all data)	$R1 = 0.0737$, $wR2 = 0.1818$
Largest diff.peak and hole (e Å^{-3})	4.652 and −8.644

2.5. Single-crystal x-ray structure determination

Crystals of **1** was examined under a thin layer of mineral oil using a polarizing microscope. Selected crystals were mounted on a glass fiber and quickly placed in a stream cold nitrogen on a Bruker SMART CCD diffractometer equipped with a sealed tube Mo anode (K$_\alpha$ radiation, $\lambda = 0.71073$ Å) and graphite monochromator or Nonius Kappa CCD diffractome-

ter. The data were collected at around 100 K. The SHELX package of software was used to solve and refine the structure. [25] The heaviest atoms were located by direct methods, and the remaining atoms were found in subsequent Fourier difference syntheses. For the ammonium salt **1**, the data did not support discrimination between oxygen and nitrogen atoms. All refinements were full-squares on F^2. Crystal data and structure refinement parameters for **1** are listed in Table 1. Selected bond distances for **1** are given in Table 2. The final thermal parameters for oxygen atoms in the encapsulated phosphate are very small (< 0.0001) and thus beyond the lower limit of the defined thermal parameter. As a result there is a remaining shift of 0.25 for Uij in the final structure.

2.6. Luminescence spectroscopy

2.6.1. Solid state

The excitation spectra for each sample were measured by scanning over the range 250 to 500 nm while monitoring the emission at 614 nm. The Eu(III) emission spectra were measured by exciting at 280 nm and using a longpass filter (OG – 570 nm, size 50.80 × 50.80, thickness 2.00 mm) to avoid interference from harmonic doubling.

2.6.2. Solution

Titration of $TBA_3H[EuPW_{11}O_{39}]$ with 1,10-phenanthroline and 2,2′- bipyridine. The following example is typical of the experimental procedure: 358 µl of 0.01589 M TBA$_3$H [Eu (PW$_{11}$O$_{39}$)] stock solution (concentration was determined by ICP measurements of Eu, P, W) and 2142 µl of CH$_3$CN were placed in a clean 0.5 ml of luminescence cuvette. Using a volumetric pipette, a total of 22.77 mmol of 1,10-phenanthroline solution was added in 15-µl (1–8), 20-µl

Table 2
Selected bond lengths (Å) for Eu–O bonds in complex **1**

Eu1		**Eu2**		**Eu3**	
Eu(1)–O(67)	2.35(6)	Eu(2)–O(23)	2.33(2)	Eu(3)–O(51)	2.36(2)
Eu(1)–O(28)	2.41(2)	Eu(2)–O(22)	2.36(2)	Eu(3)–O(75)	2.38(9)
Eu(1)–O(63)	2.47(5)	Eu(2)–O(48)	2.37(2)	Eu(3)–O(73)	2.43(8)
Eu(1)–O(68)	2.49(10)	Eu(2)–O(50)	2.39(2)	Eu(3)–O(64)#1	2.75(6)
Eu(1)–O(65)	2.49(4)	Eu(2)–O(71)	2.45(2)	Eu(3)–O(72)	2.77(15)
Eu(1)–O(62)	2.50(4)	Eu(2)–O(55)#2	2.45(2)	Eu(3)–O(74)	3.2(2)
Eu(1)–O(64)	2.52(6)	Eu(2)–O(70)	2.46(3)		
		Eu(2)–O(69)	2.46(3)		

(9–14) and 40-μl (15–18) increments of 0.05693 M 1,10-phenanthroline stock solution. The excitation (monitored at 614 nm) and emission (excited at 319 nm) spectra were collected at each data point. The relative luminescence intensity was plotted as a function of added ligand.

3. Results and discussion

3.1. Solid-state chemistry

3.1.1. Description of crystal structure

The formulation of $Al(H_3O)_2[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})(Eu_2(H_2O)_7)]_4Cl \cdot 20\,H_2O$ was determined by a combination of elemental analysis and X-ray crystallography. One Al(III) ion and one Cl$^-$ anion were found in the crystal structure. Under the acidic conditions of the preparation, it is very likely that hydronium ions are present in the formulation. The polyoxometalate unit in the crystal structure of **1** has the formulation $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})(Eu_2(H_2O)_7)]_4{}^{4-}$ and can be viewed as the 1:1 $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ species where the Eu^{3+} (Eu2) ions are each substituted for a $[WO]^{4+}$ unit in the 'cap' region of the tungsten–oxygen framework of the parent Wells-Dawson ion. In the solid state, the Eu(III) ions are bound to four oxygen atoms of the POM and to three water molecules. To complete eight coordination, the Eu(III) ions are also bound to terminal W=O of the 'belt' region of the adjacent $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]^{7-}$ unit, thus forming the dimeric unit. The bond lengths of the Eu2-O$_{bridging}$ and Eu2-O$_{H_2O}$ in the vacancy average 2.360 Å and 2.456 Å, respectively. These bond lengths as well as the Eu2–O$_{H2O}$ bond length of 2.451 Å are similar to other $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ species [21,24].

The dimeric structure of **1** is similar to the crystal structure of the 1:1 $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ prepared by reacting $(\alpha_2\text{-}P_2W_{17}O_{61})^{10-}$ with a slight excess of Eu(III) [21] and also similar to the 1:1 $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ prepared by reaction of A-α-PW$_9$O$_{34}{}^{9-}$ with Eu(III) and Al(III) under acidic conditions. [24] The structure of **1** is distinguished from those $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ crystalline complexes due to the surface bound Eu(III) ions, Eu1 and Eu3, that are themselves, bound to at least six and four water molecules respectively.

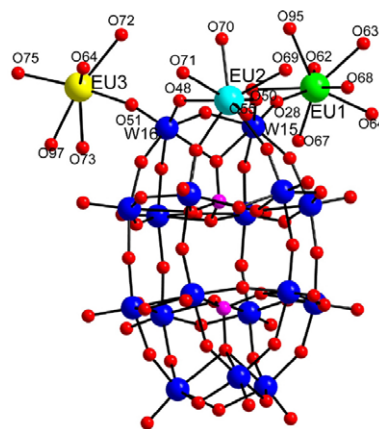Eu1 and Eu3 are bound to the terminal W=O oxygen atoms in the same 'cap' region that is substituted

Fig. 1. Representation of the monomeric unit of **1**, $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})(Eu_2(H_2O)_7)]^-$, as 50% ellipsoids, showing the types of Eu(III) atoms in the structure. One Eu(III) is bound in the $(\alpha_2\text{-}P_2W_{17}O_{61})$ defect. The other two Eu(III) are bound to terminal W=O atoms from the 'cap' region. Legend: W: blue; O: red; Eu (cyan: Eu2 incorporated into defect, green: Eu1 that is 8-coordinate, yellow: Eu3 that is 6-coordinate); P: purple.

with Eu2. The monomeric unit, showing the three non-equivalent Eu^{3+} ions is presented in Fig. 1. The dimeric unit, including the surface bound Eu(III) ions and the Al(III) bound to a terminal W=O in a cap that is remote from the substitution site is shown in Fig. 2 (**A**). A Cl$^-$ anion (not shown) is found in the void close to the region of the polyoxometalate containing the bound Eu2 and the surface bound Eu1 and Eu 3.

The two surface bound aquated Eu(III) ions (Eu1 and Eu3) further connect the $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ units. This is shown in Fig. 2, B and C, where, the dimeric unit is viewed along the *a* and *c* crystal axes, respectively. The aquated Eu1 of one dimer connects to Eu3 of another dimer via an oxo bridge to form a network of dimeric $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ units. This network, viewed along the crystallographic *a* axis, is shown in Fig. 3; some of the dimeric units are shown in boxes.

3.1.2. ^{31}P NMR

There is slight difference on the ^{31}P NMR spectroscopy compared with that of 1:1 $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ isolated as a K$^+$ salt [21]. The downfield peak found at 8.23 ppm in the K$^+$ salt of the dimer is split into doublet at 8.4391 and 8.3475 ppm in this new compound, **1** indicating the slight difference of the environment of P atom which is close to Eu^{3+} binding site in the molecule.
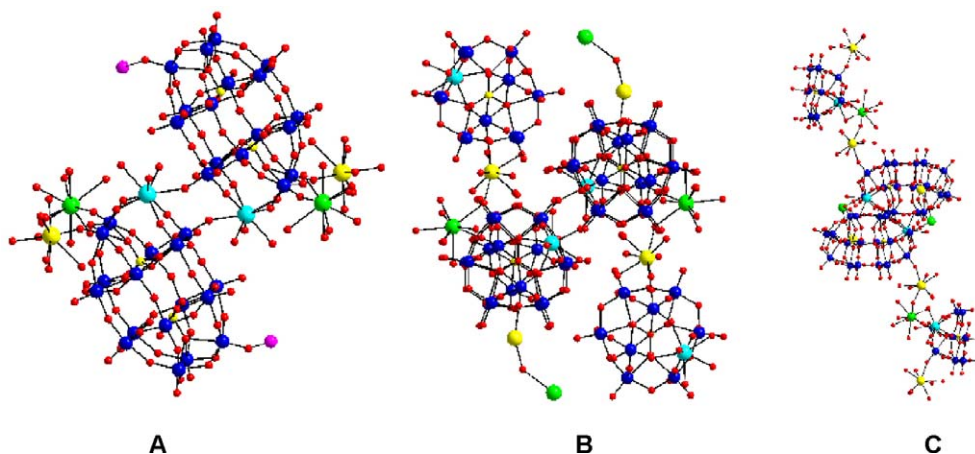
Fig. 2. Representation of the polyoxometalate unit of **1**, $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})(Eu_2(H_2O)_7)]_4^{4-}$, as 50% ellipsoids, showing the $[Eu(\alpha_2\text{-}P_2W_{17}O_{61})]_2^{14-}$ cluster and connectivity of the two surface-bound Eu(III) ions. **A**. The dimeric unit including the surface-bound Eu(III) ions. Eu2 is colored green and Eu3 is colored yellow. An Al(III) ion is bound to a terminal W=O in the remote cap. A Cl⁻ anion (not shown) is found in the void close to the region of the polyoxometalate containing the bound Eu2 and the surface-bound Eu1 and Eu 3. **B**. The dimer viewed along the a crystal axis showing the connectivity of the surface-bound Eu2. C. the dimer viewed along the *c* axis showing the connectivity of the surface-bound Eu3.
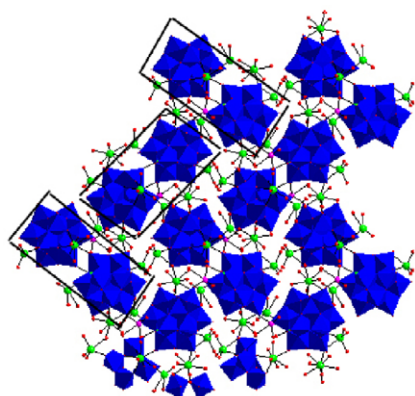

Fig. 3. Representation of the polyoxometalate unit of **1**, $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})(Eu_2(H_2O)_7)]_4^{4-}$, viewed along the crystallographic *a* axis, showing the extended structure. Boxes surround some of the dimeric units.

3.1.3. Solid-state luminescence

All of the organic ligands that were reacted with the cluster, **1** and the 1:1 $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})]_2^{14-}$, **2**, behaved in a similar fashion, sensitizing the Eu(III) in **1** and **2**. Fig. 4 shows a typical example of the solid-state emission spectrum of a suspension of the cluster, **1**, contacted with a suspension of sodium dipicolinate. Upon excitation at 280 nm, the emission spectra all showed a peak at 614 nm, assigned to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition that results in the typical red emission of Eu(III). Also observed are broad peaks in the region of 590 nm; these are typically assigned to non-degenerate $^5D_0 \rightarrow {}^7F_1$ transition. The electric dipole allowed $^5D_0 \rightarrow {}^7F_4$ transition is found at 690 nm.

The excitation spectrum for this sample, Fig. 5, clearly shows a strong, broad band at 280 nm, that is assigned to the organic sensitizing ligand and a sharp band at 394 nm; the latter band arises from the Eu POM framework and has been observed in solid state excitation spectra of $Eu(P_2W_{17}O_{61})_2{}^{17-}$. Eu(III) complexes of $PW_{11}O_{39}{}^{7-}$ also show this feature. Also, the typical oxygen to metal charge transfer bands usually found in polyoxometalate Eu(III) complexes in the 250–360 nm range are absent for $Eu(P_2W_{17}O_{61})_2$ [17–27] and $Eu(PW_{11}O_{39})_2$ [13–28]; each show only a feature at 394 nm with some broader features to higher energy. The observation of these bands at ca. 394 suggests that
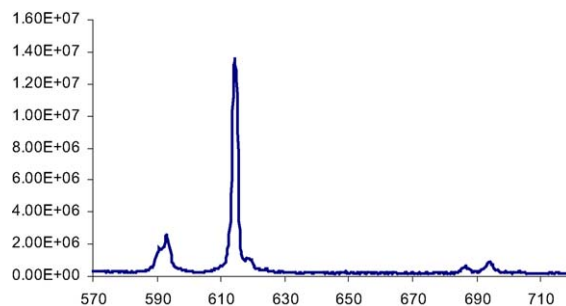

Fig. 4. Emission spectrum of cluster **1** reacted with sodium dipicolinate in methanol. Excitation wavelength: 280 nm.
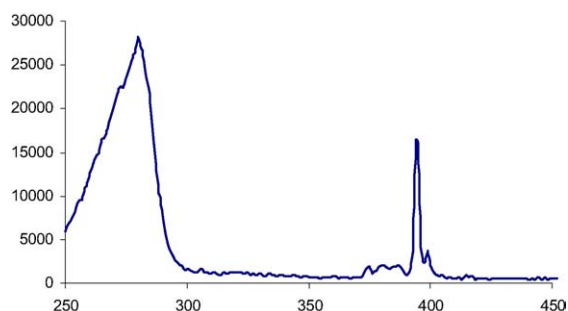
Fig. 5. Excitation spectrum of cluster **1** reacted with sodium dipicolinate in methanol. Emission monitored at 614 nm; filter (OG-570 nm filter, size 50.80 × 50.80, thickness 2.00 mm) was used to avoid interference from harmonic doubling.

the Eu(III) polyoxometalate part is contributing to the luminescence along with the excitation into the organic sensitizing moiety.

Fig. 6 shows a visualization of the slides on which the emission and excitation spectra were collected. In this Figure, the cluster, **1**, was reacted, as a suspension, with a palette of organic ligands. Excitation was achieved using a simple short wavelength (254–344nm) UV lamp. There is no luminescence from the cluster alone (Fig. 6A), as expected. All other samples display luminescence and the phthalic acid and dipicolinic acid, both deprotonated and untreated, appear to luminesce brightly. The phthalic acid and dipicolinic acid form stronger bonds to the Eu(III) center through the carboxylate moieties than the soft heterocyclic nitrogen atoms of the phenanthroline and bipyridine. The strong bonding likely contributes to the luminescence intensity. Efforts are underway to quantitate the luminescence of these complexes.

The controls, 1:1 $[Eu(H_2O)_3(\alpha_2-P_2W_{17}O_{61})]_2^{14-}$, **2**, and $EuCl_3$, that are both components of the cluster, show similar excitation and emission spectra, compared to **1**, when reacted with organic ligands. Both of the controls, show similar luminescence when excited with short wavelength light

3.2. Solution chemistry

To investigate the formation of soluble ternary organic Eu(III) POM species and their luminescent properties, the 1:1 $TBA_3H[EuPW_{11}O_{39}]$ was reacted with organic ligands in acetonitrile. Preliminary titration data for the 1:1 $TBA_3H[EuPW_{11}O_{39}]$ in CH_3CN also suggest that the 1:1 species is maintained in organic solution. [29] Experiments wherein phenanthroline (phen) or bipyridine (bipy) are titrated into the TBA salts of 1:1 Eu: $PW_{11}O_{39}^{4-}$ in CH_3CN with λ_{exc}=350 nm, show an increase in emission ($\lambda_{emission}$= 614 nm) of the Eu(III) that levels off at 2 equivalents of organic ligand per equivalent of $[EuPW_{11}O_{39}]$, consistent with 2:1 ligand: EuPOM formulation and energy transfer from the organic sensitizing ligand to the Eu(III) center (Fig. 7). This is expected because two bidentate organic ligands bind to the $[EuPW_{11}O_{39}]$ unit to complete the eight coordination of Eu(III). Excitation spectra taken at each titration point confirm the energy transfer process from the organic moiety to the Eu(III). Quantum yields are 0.12 for the bipy:Eu: $PW_{11}O_{39}$ compared to < 0.01 for $Eu(\alpha_2-P_2W_{17}O_{61})_2^{17-}$ and other 1:2 Ln: POM complexes, measured against a rhodamine dye standard. [30,31] The control, $Eu(ClO_4)_3$ shows a peak at 4–5 equivalents of organic ligand added, consistent with all of the 8–9 coordination sites taken up by the bidentate ligand. Similar luminescence titrations have been performed for crown ether lanthanide complexes with
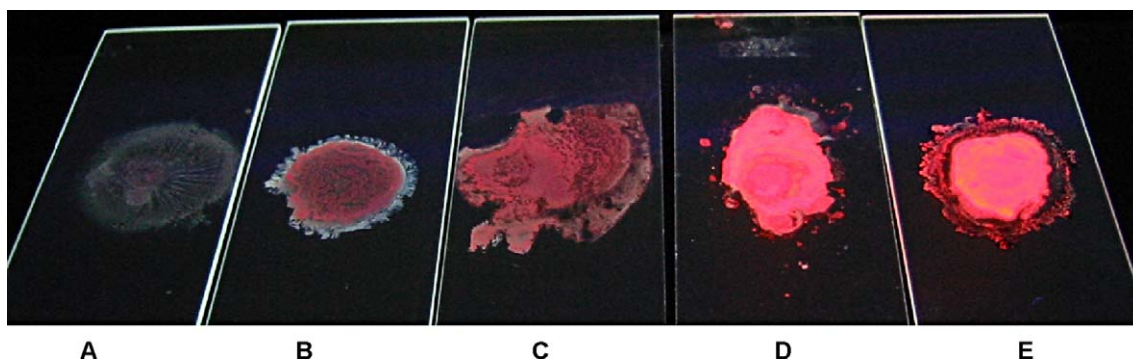

Fig. 6. Images of cluster **1** with different organic ligands under UV light (short wavelength, 254–344nm). **A**. cluster **1**without any organic ligand, **B**. phenanthroline, **C**. bipyridine, **D**. deprotonated phthalic acid, **E**. deprotonated dipicolinic acid.
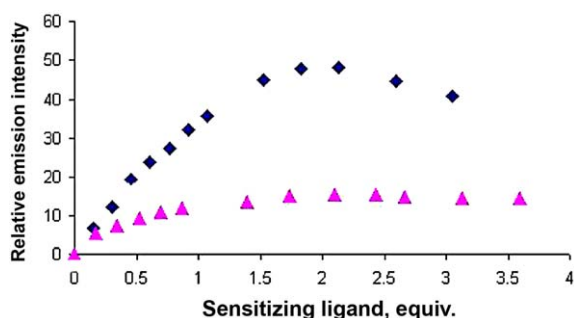
Fig. 7. Relative emission intensity of $[Eu(PW_{11}O_{39})]^{4-}$ upon addition of ▲ 2,2′-bipyridine ♦ Phenanthroline in CH_3CN, $[TBA_3HEu(PW_{11}O_{39})] = 7.02 \times 10^{-4}$ M, $\lambda_{exc} = 319$ nm.

sensitizing organic ligands to indicate ternary Ln (crown ether) (sensitizer ligand) complexes. [32]

^{31}P NMR spectra monitoring the titration of phenanthroline into $EuPW_{11}O_{39}{}^{4-}$ in acetonitrile (D_2O added to prevent multiple peaks due to protonation) confirm that the EuPOM remains intact during and after reaction (EuPOM plus phen: ^{31}P, δ +14.50 ppm; free $EuPW_{11}O_{39}{}^{4-}$: ^{31}P, δ +5.5 ppm). Proton (^{1}H) NMR spectra taken, in CD_3CN, as $TBA_3H[EuPW_{11}O_{39}]$ is added to phenanthroline, Fig. 8, or the reverse addition, shows that the resonances of the phenanthroline shift upon complexation to the paramagnetic Eu(III). However, a dynamic process is also occurring that results in a broadening of the resonances representing the free and bound phenanthroline. Upon addition of
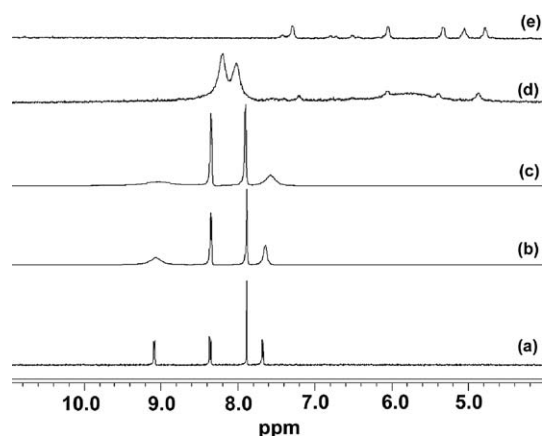

Fig. 8. ^{1}H NMR spectra of titration of phenanthroline with $[EuPW_{11}O_{39}]^{4-}$ in acetonitrile, showing resonances assigned to phenanthroline. TBA resonances are found between 0 and 3.4 ppm and are not seen on these spectra. Phenanthroline: $[EuPW_{11}O_{39}]^{4-}$; **a**, phenanthroline only; **b**, 20: 1; **c**, 1:1; **d**, 1:2; **e**, 1:4.

the $EuPW_{11}O_{39}{}^{4-}$ to phenanthroline, the four phenanthroline resonances broaden and coalesce into two peaks at ca 8.2 ppm, an average of the four original resonances. As the EuPOM content increases, a broad peak around 5.9 ppm is observed along with small peaks in the range of 4.8 to 7.2 ppm; these are likely due to phen bound to EuPOM. The broad peak at ca 5.9 ppm is due to exchange of these phen ligands bound to the Eu POM with themselves and with the unbound phen. When the Eu POM: phen stoichiometry is 4:1 (Fig. 8e) there are no broad peaks, only five relatively sharp peaks at 4.77, 5.04, 5.32, 6.04, and 7.28, ppm and three broader peaks at 6.50, 6.77, and 7.41, each integrating for about 1, suggesting that two phen ligands are bound to the Eu center. Exchange of bound bipy or phen with free ligand is expected and found, even under rigorous anhydrous conditions, due to the relatively low log K of phenanthroline bound to lanthanide(III) ions. [33]

4. Conclusion

We have prepared an unique cluster, $[Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})(Eu_2(H_2O)_7)]_4{}^{-}$, **1**, in high yield and the preparation and crystallization is highly reproducible. The crystal structure shows three types of Eu(III) ions, Eu2 is bound in the defect of the cap region of the $\alpha_2\text{-}P_2W_{17}O_{61}$. The other two Eu(III) ions, Eu1 and Eu3 are each bound to two terminal oxygen atoms in that defect cap region. These two Eu(III) ions are bound through a bridging oxygen to other $[Eu(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ clusters (Eu1 of one dimer is bound to Eu3 of another dimer) to form a network of $[Eu(\alpha_2\text{-}P_2W_{17}O_{61})]_2{}^{14-}$ dimers connected by aquated Eu(III) ions.

Preliminary luminescence studies of a crystalline sample of **1**, suspended in methanol and reacted with organic ligands, show that the organic ligands indeed are capable of sensitizing the luminescence of the Eu(III). For comparison in solution, the organic soluble $TBA_3H[EuPW_{11}O_{39}]$, **3**, was prepared and characterized. As shown from luminescence titrations and ^{31}P and ^{1}H NMR spectroscopy, this species reacts with phenanthroline and bipyridine, in acetonitrile, to form the 2:1 organic ligand: $[Eu(PW_{11}O_{39})]$ adduct.

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