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Two novel *R*- and *S*-malato-bridged coordination polymers by reacting lanthanide chloride and maleic anhydride, 1,10-phenanthroline at hydrothermal condition

Li-Ping Zhang ^{a,b}, Liang Huang ^a, Ling-bo Qu ^{a,b}, Hua Peng ^a, Yu-Fen Zhao ^{b,c,*}

^a Department of Chemistry, Anyang Teachers College, Anyang 455002, China

^b Key Laboratory of Chem-biology and Organic of Henan Province, Zhengzhou University, 450052, China ^c Key Laboratory of Bioorganic Phosphorus Chemistry of the Education Ministry, Department of Chemistry,

School of Life Sciences and Engineering, Tsinghua University, Beijing 100084, China

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Abstract

Two less common lanthanide coordination polymers, $[Ln_2(fum)(malate)_2(phen)_2]_n \cdot n1.25H_2O$ (Ln = Eu, 1; Pr, 2. fum = fumarate, phen = 1,10phenanthroline) were synthesized and characterized by IR spectra and X-ray crystallography. Single crystal X-ray diffraction analysis shows that complex 1 is isostructural with complex 2. In the two complexes, we found a pair of enantiomers (*R*-malate and *S*-malate) which are obtained by addition reaction between maleate and water and fumarate which result from configurational tranformation of maleate. The two structures consist of coordination polymer chains along the *c*-axis which are held together solely through hydrogen bonding and π - π stacking. Three-dimension supramolecular structures are formed through the two types of weak interaction. The IR data are also described and compared with those of other similar complexes.

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Keywords: Lanthanide; Maleic; Complex; Hydrothermal; Crystal structure

1. Introduction

Coordination polymers are of great interest due to their physical properties and potential application in functional materials [1–3]. Though the use of various saturated aliphatic α,ω -dicarboxylic acid to form bridges between metal centers has been extensively studied [4], the use of unsaturated aliphatic α,ω -dicarboxylic acid is scanty in the literature [5]. Fumaric and maleic acid are the simplest unsaturated aliphatic diacid. In our previous work, we reported three lanthanide fumarate complexes containing 1,10-phenanthroline [6]. We found that fumarate ligand is very stable at hydrothermal condition. It is well known that maleic acid is at thermodynamical unstable constitution. In some case, the double bond of maleic has a tendency to react with electrophilic reagents as Lewis base and the molecular *syn*-configuration may be changes into *anti*-configuration. So we selected maleic anhydride, 1,10-phenanthroline as ligands coordinating to lanthanide ions. We expected that maleic may react with H₂O at the position of C=C or change its configuration into fumaric under 150 °C hydrothermal condition. In this paper, two novel 3D supramolecular complexes $[Eu_2(fum) (malate)_2$ $(phen)_2]_n \cdot n1.25H_2O$ 1 and $[Pr_2(fum)(malate)_2(phen)_2]_n \oplus$ $n1.25H_2O$ 2 were obtained. The two structures are very interesting just because maleate does not exist in but fumarate, *R*- and *S*-malates. To our knowledge, there is no similar structure in the literature so far. Herein, we report the synthesis and crystal structures of the two complexes which have 3D supramolecular architecture assembled from 1D chains via hydrogen bonding and π - π stacking.

2. Experimental

2.1. Materials and apparatus

 $LnCl_3 \cdot 6H_2O$ (Ln=Eu or Pr) were prepared by dissolving lanthanide oxide in dilute hydrochloric acid and then dried. All other materials were purchased and used as received without further purification. Infrared spectra were recorded with a

^{*} Corresponding author. Address: Department of Chemistry, Anyang Teachers College, Anyang 455002, China. Tel.: +86 037 2290 3668; fax: +86 037 2290 2048.

E-mail address: lpzhang@aytc.edu.cn (L.-P. Zhang).

Table 1 Crystallographic data for complexes 1 and 2

	1	2
Formula	Eu ₂ C ₃₆ H _{28.50} N ₄ O _{15.25}	Pr ₂ C ₃₆ H _{28.50} N ₄ O _{15.25}
Formula weight	1065.05	1042.95
Crystal size (mm)	$0.20 \times 0.20 \times 0.15$	$0.15 \times 0.08 \times 0.04$
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions		
a (Å)	11.762(4)	11.825(4)
<i>b</i> (Å)	12.687(4)	12.742(4)
<i>c</i> (Å)	13.226(4)	13.367(4)
α (°)	75.635(6)	75.684(6)
β (°)	88.918(6)	88.803(6)
γ (°)	71.647(5)	71.601(6)
$V(\text{\AA}^3)$	1810.9(10)	1848.1(11)
Ζ	2	2
$D_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.953	1.874
F(000)	1041	1025
$\mu (\text{mm}^{-1})$	3.513	2.685
Limiting indices	$-13 \le h \le 12$	$-14 \le h \le 14$
	$-15 \le k \le 14$	$-13 \leq k \leq 15$
	$-15 \le l \le 10$	$-16 \le l \le 13$
Completeness to, theta $= 25.01$	98.9(%)	97.97(%)
Maximum and minimum trans- mission	1.00 and 0.82	1.00 and 0.61
Data/restraints/par- ameters	6298/24/532	7406/0/548
Goodness-of-fit on F^2	0.925	0.953
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	R1 = 0.0494,	R1 = 0.0500
	wR2 = 0.0751	wR2 = 0.0797
R indices (all data)	R1 = 0.1136	R1 = 0.1082
	wR2 = 0.0919	wR2 = 0.0938
Largest diff. peak and hole (e $Å^{-3}$)	1.089 and -0.781	1.377 and -0.799

Nicolet Avatar 360 FT-IR spectrometer. Elemental analyses were obtained on a PE 2400 II CHNS/O elemental analyzer.

2.2. Synthesis of complexes 1 and 2

A mixture of $EuCl_3 \cdot 6H_2O$ (0.109 g), phenanthroline (0.059 g), maleic anhydride (0.0294 g) and H₂O (10 ml) was placed in a Teflon-lined stainless steel autoclave (25 ml). The pH value was adjusted to about five with sodium hydroxide aqueous solution. After stirred, the mixture was sealed in the bomb and heated at 150 °C for four days, then the bomb was cooled slowly to room temperature. After filtration, the product was washed with ethanol and then dried at room temperature. Colorless needle-like crystals suitable to X-ray diffraction analysis were obtained (45% yield). Elemental analysis indicates that the formula of complex 1 is $[Eu_2(fum)]$ $(malate)_2(phen)_2]_n \cdot n1.25H_2O$ (Calcd (%): C, 40.60; H, 2.70; N, 5.26. Found (%): C, 40.13; H, 2.79; N, 5.09). Similar procedures were used to obtain green needles of [Pr₂(fum) $(malate)_2(phen)_2]_n \cdot n1.25H_2O 2$ (yield: 30 %, Calcd (%): C, 41.46; H, 2.75; N, 5.37. Found (%): C, 41.24; H, 2.39; N, 5.60).

IR (KBr pellet, cm⁻¹) for complex 1: 3442.12(m), 3065.89(w), 2922.67(w), 1598.69(vs), 1426.60(s), 1389.60(s), 1282.48(s), 1081.83(s), 990.93(w), 967.95(m), 839.94(s), 725.00(s), 662.61(s), 597.84(m), 491.73(m). IR (KBr pellet, cm⁻¹) for complex 2: 3448.53(m), 3065.20(w), 2925.98(w), 1594.64(vs), 1426.79(s), 1389.02(s), 1382.60(m), 1101.40(m), 1083.17(m), 840.48(s), 726.02(s), 661.51(s), 634.12(w), 596.67(w).

2.3. Single-crystal X-ray diffraction

Single-crystal X-ray diffraction data were collected on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromatized Mo K α radiation (λ =0.71073 Å). Semiempirical absorption corrections were applied using the SADABS program. All calculations were carried out with use of SHELXS-97 and SHELXL-97 programs [7]. The structures were solved by the direct methods. All structures were refined on F^2 by full-matrix least-squares methods. The crystallographic data of the complexes are summarized in Table 1 and the selected bond lengths in Table 2.

3. Results and discussion

3.1. Structural description of $[Ln_2(fum) (malate)_2(phen)_2]_n \cdot n1.25H_2O$

Single crystal X-ray diffraction studies reveal that complexes 1 and 2 are isostructural and complex 1 will be described in detail. There are two units of formula $[Eu_2(fum) (malate)_2(phen)_2] \cdot 1.25H_2O$ per cell in complex 1. The asymmetric unit comprises of two independent Europium atoms, one fumarate ligand, a pair of enantiomers (*R*-malate and *S*-malate), two 1,10-phenanthroline ligands and three kinds of lattice water molecules noted as O (15) (occupancy 0.5), O (16) (occupancy 0.5) and O (17) (occupancy 0.25). As depicted in Fig. 1, Eu (1) is nine-coordinated by two carboxylate oxygen

Table 2 Selected bond distances (Å) for complexes 1 and 2

Eu(1)–O(11)	2.336(8)	Eu(2)-O(2A)	2.353(6)	
Eu(1)–O(6)	2.367(6)	Eu(2)–O(12)	2.354(7)	
Eu(1)–O(1)	2.393(6)	Eu(2)-O(7B)	2.357(7)	
Eu(1)–O(3)	2.458(7)	Eu(2)–O(9)	2.515(6)	
Eu(1)–O(8)	2.47(6)	Eu(2)–O(4)	2.526(7)	
Eu(1)–O(4)	2.541(6)	Eu(2)–O(5)	2.528(7)	
Eu(1)-O(9)	2.558(7)	Eu(2)–O(10)	2.539(6)	
Eu(1)-N(2)	2.64 (9)	Eu(2)–N(3)	2.567(8)	
Eu(1)-N(1)	2.649(9)	Eu(2)–N(4)	2.605(9)	
Pr(1)–O(14A)	2.396(5)	Pr(2)-O(1)	2.392(6)	
Pr(1)-O(9B)	2.399(5)	Pr(2)–O(13)	2.435(5)	
Pr(1)–O(2)	2.402(5)	Pr(2)–O(7)	2.449(5)	
Pr(1)–O(10)	2.569(5)	Pr(2)–O(8)	2.514(5)	
Pr(1)–O(5)	2.571(5)	Pr(2)–O(12)	2.518(5)	
Pr(1)–O(11)	2.572(5)	Pr(2)–O(6)	2.568(5)	
Pr(1)–O(6)	2.581(5)	Pr(2)–O(10)	2.578(5)	
Pr(1) - N(1)	2.630(6)	Pr(2) - N(4)	2.677(6)	
Pr(1)–N(2)	2.669(7)	Pr(2)–N(3)	2.703(7)	

Symmetry transformations used to generate equivalent atoms: 1: A -x+2, -y, -z+1; B -x+2, -y, -z+2. 2: A -x+1, -y+2, -z; B -x+1, -y+2, -z+1.



Fig. 1. Coordination environment of Eu(III) ions in complex 1 showing 50% thermal ellipsoids. All H atoms and C atoms from phen are omitted for clarity.

atoms [O (1) and O (4)] and one hydroxyl oxygen atom [O (3)] from *R*-malate (1), two carboxylate oxygen atoms [O (6) and O (9)] and one hydroxyl oxygen atom [O (8)] from *S*-malate (1), one carboxylate oxygen atom [O (11)] from fumarate and two nitrogen atoms [N (1) and N (2)] from phen. Eu (2) is also ninecoordinated but with different environment. Eu (2) is coordinated by two carboxylate oxygen atoms [O (4) and O (5)] from *R*-malate (1), two carboxylate oxygen atoms [O (9) and O (10)] from *S*-malate (1), two nitrogen atoms [N (3) and N (4)] from phen, one carboxylate oxygen atom [O (12)] from fumarate, one carboxylate oxygen atom [O (2A)] from S-malate (1A) which is generated through symmetry transformation (-x+2, -y, -z+1) from *R*-malate (1), and one carboxylate oxygen atom [O (7B)] from R-malate (1B) which is generated through symmetry transformation (-x+2, -y, -y)-z+2) from S-malate (1). Eu (III) ions are connected into 1D chains by R- and S-malate ligands (Fig. 2). One carboxylate group of fumarate ligand coordinates to Eu (III) ions in bridging bidentate mode, and the other protrude from the chain hydrogen bonding to hydroxyl groups from neighboring chain. Phen ligands coordinate to Eu (III) ions in chelating mode and protrude from the polymeric chain. Two types of π - π stacking interactions exist between two adjacent chains (Fig. 3). The average distances between two phen ligands from two neighboring chains are 3.2779 and 3.2771 Å, respectively. Besides, weak C-H-O hydrogen bonds are observed between phen and malate ligands from different chains, and between phen and lattice water molecules. Relevant hydrogen bond parameters are listed in Table 3. The coordinates of hydrogen atoms marked with an asterisk from lattice water could not be specified because of disordered state. So we can only guess the probably hydrogen bonding interactions between lattice water and uncoordinated carboxylate group from fumarate. The complicated hydrogen bonding and π - π stacking interactions between chains result in 3D supramolecular structure (Fig. 3).

3.2. IR spectra

In both spectra, C–H (from phen) stretching vibrations appear above 3000 cm^{-1} and characteristic C–H out-of-plane bending vibrations are seen at about 840 and 725 cm⁻¹, indicating the presence of phen ligands [8]. The O–H (from



Fig. 2. Projection of complex 1 down *b*-axis showing hydrogen bonding between carboxylate of fumarate and hydroxyl of malate from two adjacent chains (all C and H atoms from phen are omitted for clarity).



Fig. 3. Packing diagram of complex 1 viewed along c-axis. All H atoms are omitted for clarity.

Table 3						
Hydrogen	bonds	parameters	(Å,	°) for	complex	tes 1

D–H	d(D-H)	$d(\mathbf{H}\cdots\mathbf{A})$	∠DHA	$d(\mathbf{D}\cdots\mathbf{A})$	Position of A
O(3)-H(3A)	0.930	1.663	146.8	2.494	O(14)[x-1,y,z]
O(8)-H(8A)	0.930	1.723	141.3	2.517	O(13)[x-1,y,z]
C(8)–H(8)	0.930	2.482	144.4	3.284	O(1) [-x+2, -y+1, -z+1]
C(15)-H(15)	0.930	2.691	128.5	3.350	O(6) $[x,y-1,z]$
C(5)–H(5)	0.930	2.575	152.6	3.428	O(17)
C(18)–H(18)	0.930	2.599	128.8	3.263	O(16)
O(16)-H(16 [*])				2.651	O(13)[x,y-1,z]
O(16)-H(16 [*])				2.727	O(13)[-x+3,-y-1,-z+2]
O(17)-H(17 [*])				2.554	O(14) [x-1,y+1,z]
$O(17) - H(17^*)$				2.833	O(14)[-x+2,-y+1,-z+1]

* The hydrogen atoms marked with asterisks are disordered which coordinations could not be specified.

lattice water molecules or hydroxyl of malate ligands) stretching bands centered at 3442 cm^{-1} are broadened by hydrogen bonding [9]. Asymmetric and symmetric C–O stretching bands are very prominent between 1599 and 1389 cm⁻¹.

4. Supporting information available

The crystallographic data have been deposited at Cambridge Crystallographic Data Centre, CCDC Nos 227337 for 1, and 227338 for 2. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk; Fax: +44 1223 336033; http://www.ccdc.cam.ac.uk).

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