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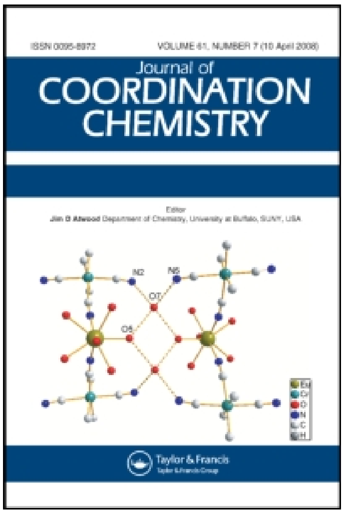

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3-D Hydrogen-bonded networks of metal complexes with chelidamic acid and 1,10-phenanthroline: syntheses, structures, and optical properties

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The title complexes, $(C_{12}H_8N_2)\cdot[La(C_7H_3NO_5)(C_7H_4NO_5)\cdot 3H_2O]\cdot 1.75H_2O$ (**1**), $(C_{12}H_8N_2)\cdot[Pr(C_7H_3NO_5)(C_7H_4NO_5)\cdot 3H_2O]\cdot 2H_2O$ (**2**), $(C_{12}H_8N_2)[Nd(C_7H_3NO_5)(C_7H_4NO_5)\cdot 3H_2O]\cdot 2.25H_2O$ (**3**), and $(C_{12}H_8N_2)\cdot[Fe(C_7H_3NO_5)(C_7H_4NO_5)]\cdot 2H_2O$ (**4**), were synthesized and characterized by single-crystal X-ray diffraction. The crystal structures of **1**–**3** reveal that they are isomorphous, among which the metal atoms are all nine-coordinate with distorted tricapped trigonal prismatic coordination geometries. The Fe is six-coordinate with a distorted octahedron by two chelidamic acid ligands in **4**. Complexes **1**–**4** are formed into 3-D networks by H-bonds and π–π stacking interactions. The fluorescence spectra of **1**–**3** were investigated and all exhibit strong luminescence.

Keywords: 1,10-Phenanthroline; Chelidamic acid; Crystal structure; Optical properties; Syntheses

1. Introduction

Chelidamic acid (2,6-dicarboxy-4-hydroxypyridine), a polydentate ligand, has been widely used in coordination chemistry, biochemistry, organic chemistry, and medicinal chemistry [1–5]. Many metal complexes containing chelidamic acid ligand have been reported, and they play a significant role in designing molecules for functional materials [6–14]. However, few reports have appeared on the use of bridging ligands, such as 1,10-phenanthroline, 4,4′-bipyridine, or 2,2′-bipyridine, combined with chelidamic acid for building metal complexes [6–16]. In addition, compared with investigations on transition metal complexes with chelidamic acid, lanthanide complexes are less researched [8, 11, 12, 17, 18]. Therefore, we selected 1,10-phenanthroline and chelidamic acid to react with rare earth or transition metal ions. Herein, we report the syntheses,

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structures, and luminescent properties of four metal complexes containing chelidamic acid and 1,10-phenanthroline, $(C_{12}H_8N_2) \cdot [La(C_7H_3NO_5)(C_7H_4NO_5) \cdot 3H_2O] \cdot 1.75H_2O$ (**1**), $(C_{12}H_8N_2) \cdot [Pr(C_7H_3NO_5)(C_7H_4NO_5) \cdot 3H_2O] \cdot 2H_2O$ (**2**), $(C_{12}H_8N_2)[Nd(C_7H_3NO_5)(C_7H_4NO_5) \cdot 3H_2O] \cdot 2.25H_2O$ (**3**), and $(C_{12}H_8N_2) \cdot [Fe(C_7H_3NO_5)(C_7H_4NO_5)] \cdot 2H_2O$ (**4**), and all feature 3-D supramolecular structures through hydrogen bonds and π–π stacking interactions.

2. Experimental

2.1. *Apparatus*

All reagents were commercially purchased and used without purification. Elemental analyses (C, H, and N) were carried out with a Perkin Elmer 2400 II elemental analyzer. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets from 4000 to 400 cm^{-1}. Thermogravimetry–differential thermal analyses (TG–DTA) were performed on a Perkin Elmer Diamond thermoanalyzer under N_2 atmosphere at 30–800°C with a heating rate of 5°C min^{-1}.

2.2. *Syntheses*

2.2.1. $(C_{12}H_8N_2) \cdot [La(C_7H_3NO_5)(C_7H_4NO_5) \cdot 3H_2O] \cdot 1.75H_2O$ (1). $LaCl_3 \cdot 7H_2O$ (0.05 mmol), 1,10-phenanthroline (0.05 mmol), and chelidamic acid (0.1 mmol) were dissolved in 10 mL of water and stirred for 6 h, after which the solution was filtered. The filtrate was left as such at room temperature and colorless prismatic crystals of **1** that are stable in air were obtained over a few days. Yield based on chelidamic acid: 47.2%. Elemental analysis calculated (%) for **1**: C, 40.67; H, 3.22; and N, 7.30. Found (%): C, 40.63; H, 3.19; and N, 7.29. IR (KBr, cm^{-1}): 3365(s), 3012(w), 1682(s), 1610(vs), 1585(vs), 1517(w), 1451(s), 1339(s), 1130(m), 1013(s), 898(w), 843(m), 810(m), 762(m), 735(m), 712(m), and 521(w).

2.2.2. $(C_{12}H_8N_2) \cdot [Pr(C_7H_3NO_5)(C_7H_4NO_5) \cdot 3H_2O] \cdot 2H_2O$ (2). The synthesis is the same as that for **1** except for amounts (for **2**: $PrCl_3 \cdot 7H_2O$ (0.05 mmol), 1,10-phenanthroline (0.03 mmol), and chelidamic acid (0.1 mmol)). Green prismatic crystals of **2** that are stable in air were obtained over a few days. Yield based on chelidamic acid: 46.8%. Elemental analysis calculated (%) for **2**: C, 40.33; H, 3.25; and N, 7.23. Found (%): C, 40.29; H, 3.23; and N, 7.23. IR (KBr, cm^{-1}): 3372(s), 3015(w), 1680(s), 1613(vs), 1592(vs), 1519(w), 1454(s), 1344(m), 1133(m), 1011(s), 891(w), 845(m), 812(m), 760(m), 737(m), 710(m), and 519(w).

2.2.3. $(C_{12}H_8N_2)[Nd(C_7H_3NO_5)(C_7H_4NO_5) \cdot 3H_2O] \cdot 2.25H_2O$ (3). The synthesis is the same as that for **1** except for amounts (for **3**: $NdCl_3 \cdot 6H_2O$ (0.05 mmol), 1,10-phenanthroline (0.07 mmol), and chelidamic acid (0.1 mmol)). Light pink block crystals of **3** were obtained over a few days. Yield based on chelidamic acid: 46.3%.

Elemental analysis calculated (%) for **3**: C, 40.33; H, 3.34; and N, 7.24. Found (%): C, 39.89; H, 3.32; and N, 7.16. IR (KBr, cm^{-1}): 3355(s), 3021(w), 1685(s), 1620(vs), 1583(vs), 1516(w), 1455(s), 1342(s), 1136(m), 1018(s), 894(w), 841(m), 816(m), 765(m), 738(m), 718(m), and 524(w).

2.2.4. $(C_{12}H_8N_2)\cdot[Fe(C_7H_3NO_5)(C_7H_4NO_5)]\cdot 2H_2O$ (4). The synthesis is the same as that for **1** except for amounts (for **4**: $FeCl_3 \cdot 6H_2O$ (0.07 mmol), 1,10-phenanthroline (0.04 mmol), and chelidamic acid (0.1 mmol)). Red prismatic crystals of **4** that are stable in air were obtained over a few days. Yield based on chelidamic acid: 28.7%. Elemental analysis calculated (%) for **4**: C, 50.54; H, 2.75; and N, 9.08. Found (%): C, 50.62; H, 2.60; and N, 9.07. IR (KBr, cm^{-1}): 3385(s), 3020(w), 1681(s), 1615(vs), 1586(vs), 1508(w), 1450(s), 1338(m), 1139(m), 1017(s), 896(w), 848(m), 817(m), 758(m), 745(m), 720(m), and 539(w).

2.3. *Single-crystal X-ray structure determination*

Single crystals of **1**–**4** suitable for X-ray analyses were mounted, respectively, at the apex of a glass fiber for X-ray diffraction data collection. Data sets of **1** and **3** were collected on Rigaku Mercury CCD and Rigaku AFC7R diffractometers, respectively, using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) from a rotating anode generator; those of **2** and **4** were collected on Siemens SMART CCD diffractometers using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) from a fine focus sealed tube at 293(2) K. The intensity data were collected with an ω scan technique and corrected for LP factors. The structures were solved by direct methods and difference Fourier synthesis, refined by full-matrix least-squares, and finally refined anisotropically for all non-hydrogen atoms.

In **1**–**4**, all hydrogens of coordinated and discrete water (except for O(4W), O(5W), and O(6W) in **1**; O(5W) and O(6W) in **2**; O(5W) and O(6W) in **3**; and O(2W) in **4**) and the oxygens from the hydroxyl group were placed in calculated positions, with O–H distances of 0.85 Å, and refined in riding mode with $U_{iso}(H)$ values of 1.5 $U_{eq}(O)$. Other hydrogens were allowed to ride on their respective parent atoms with C–H distances of 0.93 Å, and were included in the refinement with isotropic displacement parameters $U_{iso}(H) = 1.2\, U_{eq}(C)$. All calculations were performed with Siemens SHELXTL™ version 5.0 package of crystallographic software [19]. Further details of the X-ray structural analyses are given in table 1. Selected bond lengths are listed in table 2 and hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. *Crystal structures of 1–3*

Single-crystal X-ray diffraction analyses reveal that **1**–**3** are isomorphous, so we only choose **1** for detailed structure discussion. As shown in figure 1, compound **1** contains one metal, two chelidamic acid ligands, three coordinated waters, one non-coordinated 1,10-phenanthroline molecule, and one and three quarters of uncoordinated water.

Table 1. Crystallographic data and structure refinement of **1**–**4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{26}H_{24.5}N_4O_{14.75}La$	$C_{26}H_{25}N_4O_{15}Pr$	$C_{26}H_{25.5}N_4O_{15.25}Nd$	$C_{26}H_{17}N_4O_{11}Fe$
Formula weight ($g\,mol^{-1}$)	767.91	774.41	782.24	617.29
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2$
Unit cell dimensions (Å, °)				
a	10.826(3)	10.770(2)	10.7736(18)	27.411(10)
b	11.670(3)	11.629(2)	11.6439(18)	9.108(3)
c	12.333(3)	12.270(3)	12.287(2)	20.290(8)
α	101.451(2)	101.646(2)	101.439(13)	90
β	92.834(2)	92.901(2)	93.147(14)	98.996(4)
γ	104.331(4)	104.486(2)	104.497(12)	90
Volume (Å^3), Z	1471.6(7), 2	1449.0(5), 2	1453.7(4), 2	5003(3), 8
Calculated density ($g\,cm^{-3}$)	1.733	1.775	1.787	1.639
Absorption coefficient (mm^{-1})	1.532	1.764	1.870	0.677
$F(0\,0\,0)$	767	776	783	2520
Crystal size (mm^3)	0.25 × 0.20 × 0.20	0.347 × 0.218 × 0.144	0.13 × 0.10 × 0.083	0.12 × 0.10 × 0.08
θ range for data collection (°)	2.74–25.50	2.32–25.05	1.85–25.05	3.04–25.25
Reflections collected	10492	10544	5529	17710
Independent reflections	5448 [$R(\text{int}) = 0.0188$]	5066 [$R(\text{int}) = 0.0178$]	5140 [$R(\text{int}) = 0.0227$]	4477 [$R(\text{int}) = 0.0594$]
Goodness-of-fit on F^2	0.972	1.051	1.004	1.000
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0339$, $wR_2 = 0.0981$	$R_1 = 0.0450$, $wR_2 = 0.1307$	$R_1 = 0.0304$, $wR_2 = 0.0860$	$R_1 = 0.0523$, $wR_2 = 0.1236$
R indices (all data)	$R_1 = 0.0365$, $wR_2 = 0.1012$	$R_1 = 0.0490$, $wR_2 = 0.1377$	$R_1 = 0.0344$, $wR_2 = 0.0899$	$R_1 = 0.0677$, $wR_2 = 0.1343$

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

Table 2. Selected bond lengths (Å) of **1**–**4**.

Bond	Distance (Å)	Bond	Distance (Å)
1			
La(1)–O(8)	2.5027(19)	O(1)–C(16)	1.294(3)
La(1)–O(3)	2.522(2)	O(2)–C(16)	1.218(4)
La(1)–O(1w)	2.553(2)	O(3)–C(17)	1.260(3)
La(1)–O(1)	2.555(2)	O(4)–C(17)	1.233(3)
La(1)–O(6)	2.565(2)	O(5)–C(13)	1.345(3)
La(1)–O(3W)	2.571(2)	O(6)–C(26)	1.277(4)
La(1)–O(2W)	2.611(2)	O(7)–C(17)	1.233(3)
La(1)–N(2)	2.641(2)	O(7)–C(26)	1.227(4)
La(1)–N(1)	2.647(2)	O(8)–C(27)	1.268(3)
O(10)–C(23)	1.346(3)	O(9)–C(27)	1.239(3)
2			
Pr(1)–O(13)	2.466(2)	O(11)–C(16)	1.266(4)
Pr(1)–O(23)	2.478(2)	O(12)–C(16)	1.232(4)
Pr(1)–O(11)	2.508(2)	O(13)–C(17)	1.261(3)
Pr(1)–O(1W)	2.510(2)	O(14)–C(17)	1.229(4)
Pr(1)–O(21)	2.521(2)	O(15)–C(13)	1.349(4)
Pr(1)–O(3W)	2.524(2)	O(21)–C(26)	1.284(4)
Pr(1)–O(2W)	2.571(2)	O(22)–C(26)	1.222(4)
Pr(1)–N(1)	2.591(2)	O(23)–C(27)	1.256(4)
Pr(1)–N(2)	2.600(2)	O(24)–C(27)	1.233(4)
		O(25)–C(23)	1.331(4)
3			
Nd(1)–O(3)	2.461(2)	O(1)–C(6)	1.280(4)
Nd(1)–O(8)	2.478(2)	O(2)–C(6)	1.221(5)
Nd(1)–O(1W)	2.494(2)	O(3)–C(7)	1.266(4)
Nd(1)–O(1)	2.501(3)	O(4)–C(7)	1.235(4)
Nd(1)–O(3W)	2.510(2)	O(5)–C(3)	1.339(4)
Nd(1)–O(6)	2.516(2)	O(6)–C(13)	1.286(4)
Nd(1)–O(2W)	2.555(3)	O(7)–C(13)	1.222(4)
Nd(1)–N(1)	2.578(3)	O(8)–C(14)	1.260(4)
Nd(1)–N(2)	2.586(3)	O(9)–C(14)	1.245(4)
		O(10)–C(10)	1.340(4)
4			
Fe(1)–O(8)	1.998(2)	O(1)–C(16)	1.278(4)
Fe(1)–O(1)	2.014(2)	O(2)–C(16)	1.234(4)
Fe(1)–O(3)	2.067(2)	O(3)–C(17)	1.289(4)
Fe(1)–O(6)	2.071(2)	O(4)–C(17)	1.233(4)
Fe(1)–N(2)	2.033(3)	O(5)–C(13)	1.338(4)
Fe(1)–N(1)	2.041(3)	O(6)–C(26)	1.289(4)
O(9)–C(27)	1.220(4)	O(7)–C(26)	1.224(4)
O(10)–C(23)	1.322(4)	O(8)–C(27)	1.296(4)

The La is nine-coordinate in a distorted tricapped trigonal prismatic coordination polyhedron made up of two nitrogens and four oxygens from two tridentate chelating chelidamic acid ligands and three coordinated water molecules. The bond distances between La and O range from 2.5027(19) to 2.611(2) Å, in the normal range of those reported for lanthanum complexes [20–22]. La–N bond distances (La(1)–N(1) = 2.641(2) Å, La(1)–N(2) = 2.647(2) Å) are a bit shorter than those reported in lanthanum complexes [20–22].

In **1**, there are weak π–π stacking interactions between aromatic rings of coordinated chelidamic acid and discrete 1,10-phenanthrolines with distances of 3.797(1) Å and

Table 3. Hydrogen bonds of **1**–**4**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
1				
O(1W)–H(1WA)···O(5)$^{\mathrm{i}}$	0.82(3)	1.98(3)	2.779(3)	163(4)
O(1W)–H(1WB)···O(6)$^{\mathrm{ii}}$	0.84(3)	1.93(3)	2.774(3)	177(4)
O(2W)–H(2WB)···O(4W)$^{\mathrm{iii}}$	0.77(3)	2.22(3)	2.952(3)	160(4)
O(3W)–H(3WA)···O(9)$^{\mathrm{iv}}$	0.88(2)	1.82(2)	2.684(3)	164(4)
O(5)–H(5A)···O(4W)	0.82	1.79	2.581(3)	160.3
O(10)–H(10A)···O(1)$^{\mathrm{v}}$	0.82	1.76	2.567(3)	165.4
2				
O(1W)–H(1WA)···O(25)$^{\mathrm{i}}$	0.83(2)	1.99(3)	2.776(3)	157(3)
O(1W)–H(1WB)···O(11)$^{\mathrm{ii}}$	0.83(3)	1.97(3)	2.799(3)	173(4)
O(2W)–H(2WB)···O(4W)$^{\mathrm{iii}}$	0.81(3)	2.26(3)	2.942(4)	142(3)
O(3W)–H(3WA)···O(14)$^{\mathrm{iv}}$	0.83(2)	1.98(2)	2.689(3)	144(3)
O(3W)–H(3WB)···O(6W)	0.87(2)	2.00(3)	2.804(7)	154(4)
O(4W)–H(4WA)···O(24)$^{\mathrm{v}}$	0.88(2)	1.77(3)	2.643(3)	168(4)
O(4W)–H(4WB)···O(15)$^{\mathrm{vi}}$	0.88(2)	2.07(3)	2.827(3)	145(3)
O(15)–H(15A)···O(21)$^{\mathrm{vii}}$	0.82	1.76	2.563(3)	166.2
O(25)–H(25A)···O(4W)	0.82	1.79	2.571(3)	158.5
3				
O(1W)–H(1WA)···O(1)$^{\mathrm{i}}$	0.84(3)	1.99(3)	2.813(4)	165(4)
O(1W)–H(1WB)···O(10)$^{\mathrm{ii}}$	0.82(3)	1.99(3)	2.775(4)	159(4)
O(2W)–H(2WA)···O(4W)$^{\mathrm{iii}}$	0.77(2)	2.36(4)	2.931(4)	132(4)
O(2W)–H(2WA)···O(3W)	0.77(2)	2.58(4)	2.824(3)	101(4)
O(3W)–H(3WB)···O(4)$^{\mathrm{iv}}$	0.84(2)	1.89(2)	2.707(3)	167(4)
O(4W)–H(4WA)···O(5)$^{\mathrm{v}}$	0.85(2)	2.04(3)	2.834(3)	154(4)
O(4W)–H(4WB)···O(9)$^{\mathrm{vi}}$	0.83(2)	1.83(3)	2.655(4)	173(4)
O(5)–H(5A)···O(6)$^{\mathrm{vii}}$	0.82	1.76	2.565(3)	165.8
O(10)–H(10A)···O(4W)	0.82	1.80	2.577(4)	158.6
4				
O(1W)–H(1WA)···O(2W)$^{\mathrm{i}}$	0.94(3)	1.68(4)	2.607(7)	168(10)
O(5)–H(5A)···O(7)$^{\mathrm{ii}}$	0.82	1.85	2.669(3)	175.6
O(10)–H(10A)···O(4)$^{\mathrm{iii}}$	0.82	1.83	2.629(3)	165.3

Symmetry transformations used to generate equivalent atoms: For **1**: $^{\mathrm{i}}-x+1, -y+1, -z$; $^{\mathrm{ii}}-x+1, -y+1, -z+1$; $^{\mathrm{iii}}x, y, z+1$; $^{\mathrm{iv}}-x+2, -y+2, -z+1$; and $^{\mathrm{v}}-x+1, -y+2, -z+1$. For **2**: $^{\mathrm{i}}x+1, -y+1, -z$; $^{\mathrm{ii}}-x+1, -y+1, -z+1$; $^{\mathrm{iii}}x, y, z+1$; $^{\mathrm{iv}}-x+2, -y+2, -z+1$; $^{\mathrm{v}}-x+2, -y+1, -z$; $^{\mathrm{vi}}x, y-1, z-1$; and $^{\mathrm{vii}}-x+1, -y+2, -z+1$. For **3**: $^{\mathrm{i}}-x+1, -y+1, -z$; $^{\mathrm{ii}}-x+1, -y+1, -z+1$; $^{\mathrm{iii}}x, y, z-1$; $^{\mathrm{iv}}-x, -y, -z$; $^{\mathrm{v}}x, y+1, z+1$; $^{\mathrm{vi}}-x, -y+1, -z+1$; and $^{\mathrm{vii}}-x+1, -y, -z$. For **4**: $^{\mathrm{i}}x, y+1, z$; $^{\mathrm{ii}}x, -y, z-1/2$; and $^{\mathrm{iii}}-x+1/2, y+1/2, -z+1/2$.

a dihedral angle of 0.48° (3.782 Å and a dihedral angle of 1.13° for **2**; 3.810 Å and a dihedral angle of 2.13° for **3**, respectively) (figure 2).

As shown in figure 3, independent molecules of **1** are linked through hydrogen bonds between O(1W) and O(5), as well as O(1) and O(10) (O(1W)···O(5) = 2.779(3) Å and O(1)···O(10) = 2.567(3) Å) to form a 1-D chain along the *a* direction. Neighboring chains are connected into layers in the *bc* plane through hydrogen bonds between O1W and O6 (O(1W)···O(6) = 2.774(3) Å) (figure 3 and table 3). These layers are interlinked through *π*–*π* stacking interactions and a very complex hydrogen bonding network involving water and oxygen from chelidamic acid to form a 3-D network (figure S1).

There exist two chelidamic acid ligands with different ionized forms for charge neutralization in **1**. One exists as $(C_7H_3NO_5)^{2-}$ while the other as $(C_7H_4NO_5)^{-}$, but they are difficult to distinguish because the hydrogens cannot be located from the difference map. Nevertheless, the protonated atom can be confirmed by the structural analysis. The distance between O(8) and N(4)$^{\mathrm{i}}$ (O(8)–N(4)$^{\mathrm{i}}$ = 2.776 Å; i: x, y, $-1+z$) is

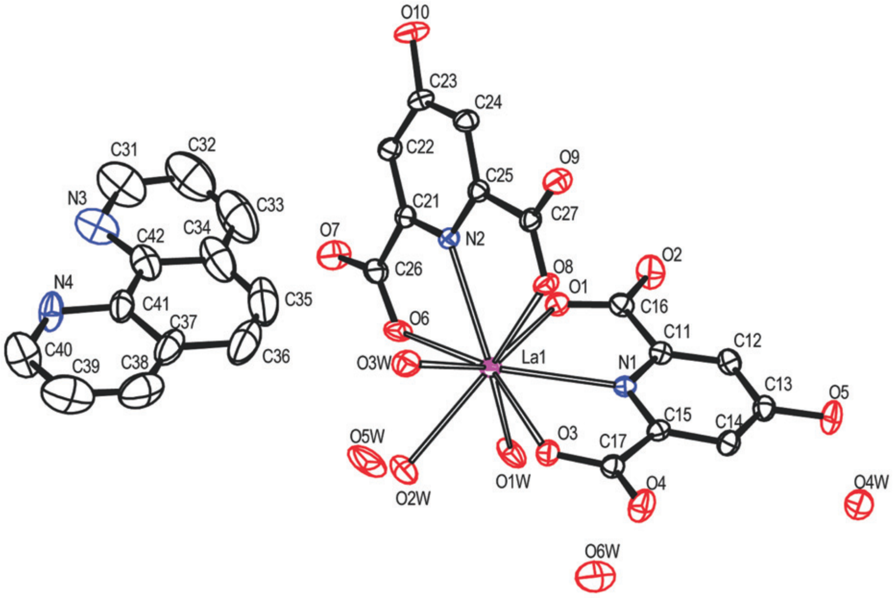

Figure 1. Molecular structure of **1** showing 30% displacement ellipsoids for non-H atoms. Hydrogens are omitted for clarity.

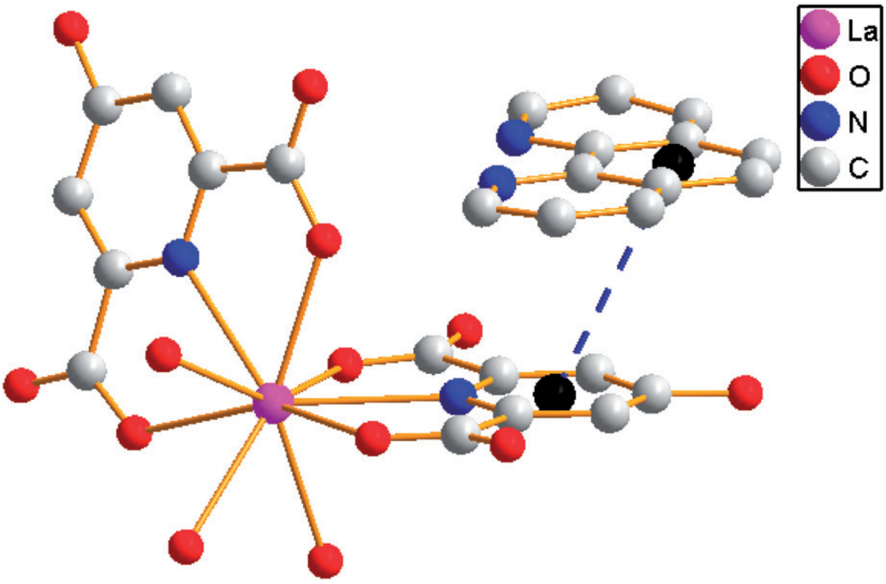

Figure 2. A view of the π–π stacking interactions between aromatic rings of 1,10-phenanthroline and chelidamic acid at 3.797 Å for **1**.

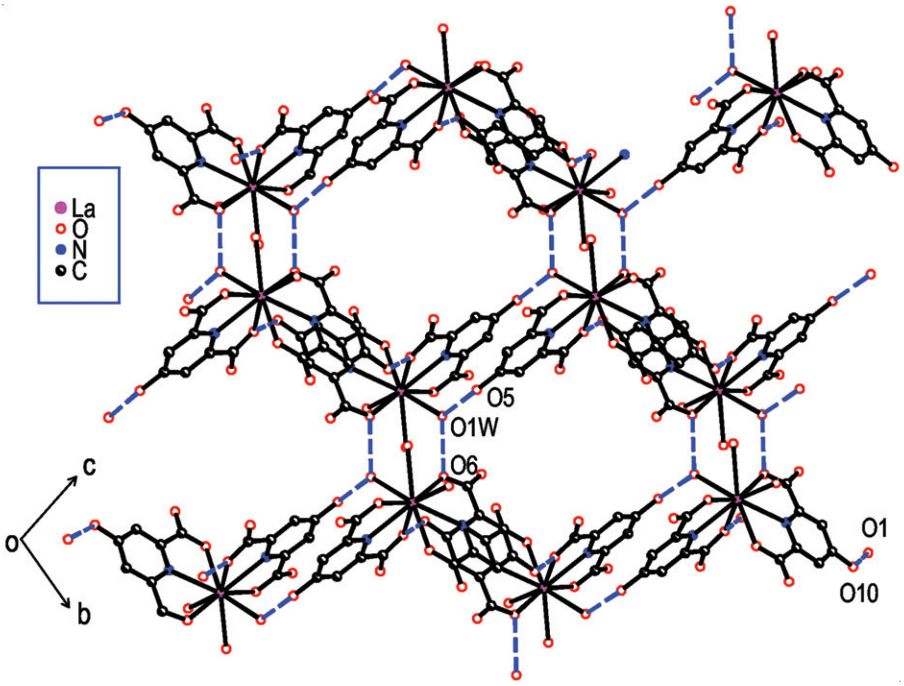

Figure 3. A view of the 2-D layer of **1** in the *bc* plane. Dashed lines represent hydrogen bonds. Hydrogens are omitted for clarity.

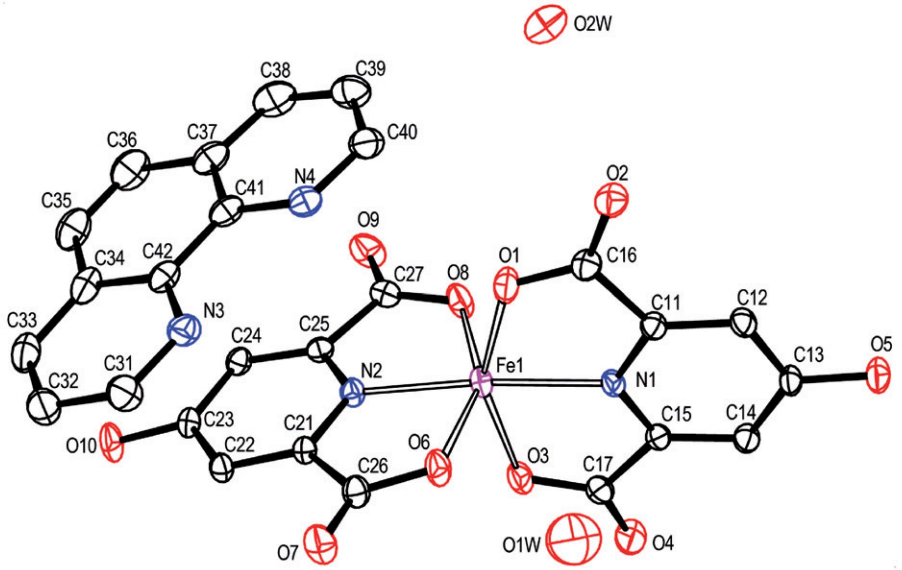

Figure 4. A view of the molecular structure of **4** showing 30% displacement ellipsoids for non-H atoms. Hydrogens are omitted for clarity.

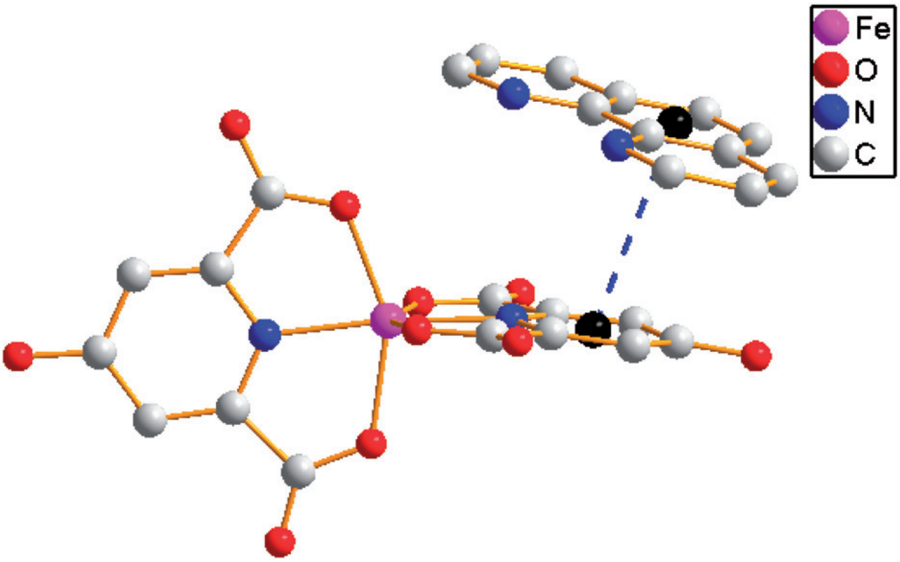

Figure 5. A view of the π–π stacking interactions between aromatic rings of 1,10-phenanthroline and chelidamic acid at 3.639 Å for **4**.

abnormally short. Thus, it can be concluded that O(8) should be protonated; the larger bond distance of C(27)–O(8) (1.268(3) Å) also supports this deduction. Similar to the analysis for **1**, we conclude that O(13) and O(3) are protonated in **2** and **3**, respectively.

3.2. *Crystal structure of 4*

As shown in figure 4, complex **4** consists of one Fe, two chelidamic acid ligands, two discrete waters, and one discrete 1,10-phenanthroline. The Fe is six-coordinate with two nitrogens and four oxygens from two tridentate chelating chelidamic acid ligands. The Fe–O bond distances range from 1.998(2) to 2.071(2) Å; except for Fe(1)–O(6), 2.071(2) Å, all are in the normal range for Fe complexes [23, 24]; Fe–N bond distances (Fe(1)–N(1) = 2.033(3) Å, Fe(1)–N(2) = 2.041(3) Å) are a little shorter than those in reported Fe complexes [23, 24].

In **4**, there are weak π–π stacking interactions between the aromatic rings of coordinated chelidamic acid and 1,10-phenanthroline with distances of 3.639(1) Å and a dihedral angle of 8.80° (figure 5).

As shown in figure 6, independent molecules are linked by hydrogen bonds between O(5) and O(7) (O(5)···O(7) = 2.669(3) Å) to form a 1-D infinite chain along the *c* direction. The neighboring chains are connected into a layer in the *bc* plane through hydrogen bonds between O(4) and O(10) (O(4)···O(10) = 2.629(3) Å), as shown in figure 6 and table 3. These layers are linked through π–π stacking interactions and a very complex hydrogen bonding network involving water and oxygen from chelidamic acid to form a 3-D network (figure S2). Complexes **1**–**4** are the first ones with chelidamic acid featuring 3-D supramolecular structures through hydrogen bonds and π–π stacking interactions.

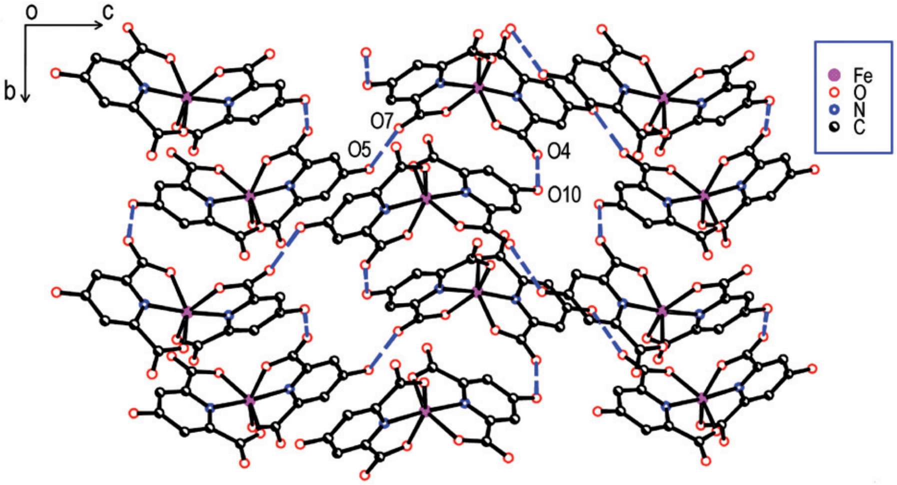

Figure 6. The 2-D layer of **4** in the *bc* plane. Dashed lines represent hydrogen bonds. Hydrogens are omitted for clarity.

Similar to the structure of **1**, there also exist two chelidamic acid ligands with different ionization for charge neutralization in **4**. One exists as $(C_7H_3NO_5)^{2-}$ while the other as $(C_7H_4NO_5)^{-}$, but they are difficult to distinguish. The protonated atom is O(2) based on the same structural analysis as with **1**.

Compared with other lanthanide complexes with pyridinedicarboxylates recently reported in the literature [25–27], the chelidamic acid in **1**–**4** has tridentate coordination, resulting in discrete structures. As for 2,2′-bipyridine-3,3-dicarboxylic acid and pyrazine-2,6-dicarboxylic acid reported in the lanthanide complexes [26], they act as bidentate or tridentate ligands resulting in discrete or 1-D structures, while pyridine-3,5-dicarboxylic acid as monodentate ligands are bridged by lanthanide ions to form 3-D structures [27]. Therefore, we conclude that coordination modes of ligands affect the structures of the lanthanide complexes.

3.3. *Luminescent properties*

Solid state electronic emission spectra of **1**–**3** show luminescent features (figure 7). Complex **1** possesses two emission peaks at 365 and 542 nm upon excitation at 335 nm, while **3** displays two maxima at 418 and 540 nm upon excitation at 352 nm. Complex **2** exhibits blue fluorescence with maximum emission at 438 nm with $\lambda_{ex} = 350$ nm. Compared to free chelidamic acid with maximum emission at 525 nm [28–30], **1** results in a blue shift of 160 nm and a small red shift of 17 nm, whereas **3** results in a blue shift of 107 nm and a small red shift of 15 nm. These indicate that the first emissions of **1** and **3** may be attributed to charge transition between the chelidamic acid ligands and the rare earth ions, while the second emissions of **1** and **3** both originated from intraligand π–π^* transitions of chelidamic acid [12, 28–30]. For **2**, compared to the free chelidamic acid, a blue shift of 87 nm can be found, which implies that the emission originates from charge transition between chelidamic acid ligand and Pr^{3+}. The good luminescence efficiency indicates that the complexes may be candidates for luminescent materials. Photoluminescence of **4** was not observed from the wavelength range 200–900 nm.

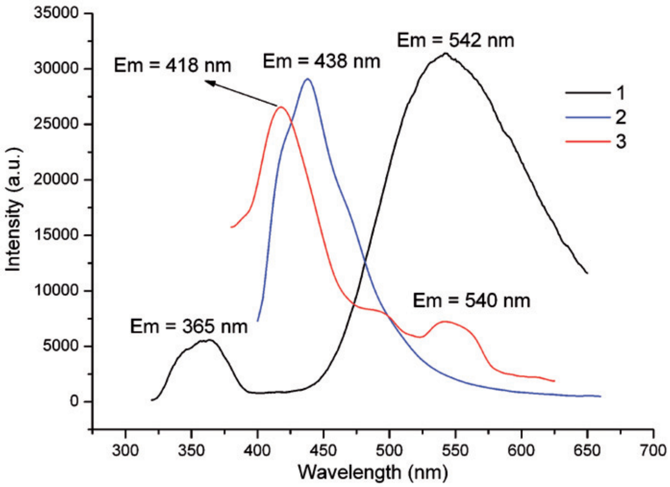

Figure 7. Solid state emission spectra of **1**–**3**.

3.4. *IR spectra*

IR spectra of **1**–**4** show broad peaks at 3600–3200 cm^{-1} due to hydrogen bonding between water molecules. Strong peaks at 1690–1680, 1620–1610, and 1460–1450 cm^{-1} indicate the existence of two different carboxylates (COOH and COO^-), which supports the existence of two chelidamic acid ligands with different ionized form in **1**–**4**. Characteristic peaks at 3050–3000 and 860–750 cm^{-1} in **1**–**4** are due to the existence of 1,10-phenanthroline.

3.5. *TGA analysis*

Since **1**–**3** are isomorphous, thermogravimetric analysis (TGA) was only carried out on **3**. The TG–DTA curve shows that **3** undergoes three-step decomposition between 30°C and 820°C, as shown in figure S3. The first weight loss of 10.96% (Calcd 9.78%) is completed at 100°C, corresponding to the loss of 4.25 waters (two and one quarter discrete water molecules and two coordinated water molecules) per formula unit. The second weight loss of 2.35% (Calcd 2.55%) from 100°C to 195°C indicates the loss of another coordinated water molecule. From 195°C to 370°C, the weight loss is 26.58% (Calcd 26.19%), corresponding to the loss of one 1,10-phenanthroline. These results are well consistent with the X-ray crystal structure.

4. Conclusions

Four complexes with chelidamic acid and 1,10-phenanthroline have been synthesized and structurally characterized by single-crystal X-ray diffraction. The structures of **1**–**3** are isomorphic, with nine-coordinate metal in distorted tricapped trigonal prismatic coordination geometries. In **1**–**4**, 1-D chains are formed by H-bonds, which are further linked through H-bonds and π–π stacking interactions to generate 3-D supramolecular networks. Complexes **1**–**3** exhibit good luminescence while **4** has no fluorescence.

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 772078, 772079, 772080, and 772081 for **1**–**4**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk). In addition, the figure of TG–DTA of **3** and 3-D structural figures of **1** and **4** are also available.

Acknowledgments

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