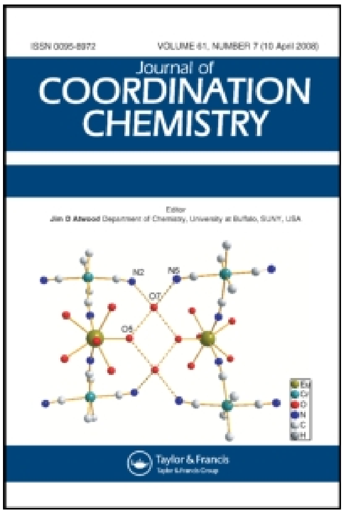

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Two- and three-dimensional coordination polymers of lanthanide tartrate: synthesis, crystal structures and luminescence

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Two- and three-dimensional coordination polymers of lanthanide tartrate: synthesis, crystal structures and luminescence

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Several new coordination polymers of lanthanide tartrate with three types of topological structures, namely $[Ln_2(DL\text{-}tart)_3(H_2O)_3]\cdot 1.5H_2O$ [Ln = La (**1**), Nd (**2**), and Sm (**3**)], $[Ln_2(D\text{-}tart)_3(H_2O)_2]\cdot 3H_2O$ [Ln = Eu (**4**), Tb (**5**), and Dy (**6**)], and $[Lu(C_4H_4O_6)(C_4H_5O_6)]\cdot 2.5H_2O$ (**7**), have been synthesized by hydrothermal synthesis. X-ray crystallographic analysis reveals that **1** is a unique 3-D network, whereas **5** with a 3-D network and **7** with a 2-D network are isomorphous with their analogs. All lanthanide ions are nine-coordinate through oxygen donors. Four different coordination modes of tartrate occur in these complexes. Luminescence spectra reveal that **4**, **5**, and **6** emit characteristic luminescence of corresponding lanthanide ions.

Keywords: Synthesis; Structure; Lanthanide tartrate; Luminescence

1. Introduction

The design and synthesis of lanthanide compounds attract interest because of their structures and potential applications in magnetism [1], catalysis [2], and luminescence [3–23]. As a simple and important organic acid, tartaric acid has been employed in synthesis of lanthanide tartrate. There are several lanthanide tartrates known, $[Er_2(D\text{-}tart)_3(H_2O)_2]\cdot 3H_2O$ [24], $[Gd_2(D\text{-}tart)_3(H_2O)_2]\cdot 3H_2O$ [25], $[Sm(C_4H_4O_6)(C_4H_5O_6)]\cdot 3H_2O$ [26], $[Y(C_4H_4O_6)(C_4H_5O_6)]\cdot 2.5H_2O$ [27], $[Er(C_4H_4O_6)(C_4H_5O_6)(H_2O)_3]$ [28], and $[Eu^{II}(C_4H_4O_6)(H_2O)_2]\cdot 2H_2O$ [29]. However, to our knowledge, almost all of the reports were focused on the synthesis and crystal structures. Magnetic properties of only $[Gd_2(D\text{-}tart)_3(H_2O)_2]\cdot 3H_2O$ [25] were discussed and information on physicochemical properties of other lanthanide tartrate complexes was unknown. Tartaric acid is a simple and inexpensive chiral source. Kim and co-workers reported that a metal coordination polymer containing tartrate exhibited chiral catalytic properties [30]. In this article, reactions of tartaric acid and corresponding lanthanide nitrate under hydrothermal conditions afford several coordination polymers. X-ray

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crystallographic analysis reveals that **1**, **5**, and **7** belong to *$P2_1/n$*, *P1*, and *$P4_12_12$* space groups, respectively. Compound **1** displays a unique 3-D network structure, while **5** and **7** show 3-D and 2-D frameworks in accord with their analogs. Compounds **4**, **5**, and **6** exhibit the characteristic luminescence of Eu(III), Tb(III), and Dy(III) ions, respectively.

2. Experimental

2.1. *General*

$Ln(NO_3)_3 \cdot 6H_2O$ were prepared by reactions of Ln_2O_3 and nitric acid. Other materials are commercially available and used as supplied. Elemental analyses were performed on a Perkin–Elmer 2400 analyzer. IR spectra were obtained on a Perkin–Elmer 60000 spectrophotometer using KBr disks in the range 4000–370 cm^{-1}. UV–Vis spectra were recorded on a Shimadzu UV2240 spectrophotometer. Fluorescence spectra were taken on a Perkin–Elmer LS-55 fluorescence photometer. Thermal analyses were conducted on a DTA-1700 with a heating rate of 10°C min^{-1} in a temperature range of 30–830°C in N_2 atmosphere.

2.2. *Crystallographic data collection and refinement*

Crystal data for **1**, **5**, and **7** were collected on a Rigaku Raxis-Rapid X-ray diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The intensity data sets were collected with the ω-scan technique. Empirical absorption corrections based on equivalent reflections were applied. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were performed with the SHELXS-97 package. Pertinent crystal data and structure refinement results for **1**, **5**, and **7** are listed in table 1.

2.3. *Synthesis of [La_2(DL-tart)$_3$(H_2O)$_3$] • 1.5H_2O (1)*

An aqueous solution (30 mL) of DL-tartaric acid (0.2250 g, 1.5 mmol) and $La(NO_3)_3 \cdot 6H_2O$ (0.4329 g, 1.0 mmol) was transferred to a Teflon lined steel vessel (50 mL) and the hydrothermal reaction was carried out maintaining the temperature at 140°C in an oven for 48 h. After cooling the reaction vessel to room temperature, the resultant mixture was transferred to a beaker. Partial evaporation of the solution affords colorless crystals of [La_2(DL-tart)$_3$(H_2O)$_3$] · 1.5H_2O (**1**). Yield: 70% (0.2807 g). Elemental analysis (%): Calcd for $C_{24}H_{40}La_4O_{45}$ (1604.17): C, 17.97; H, 2.51. Found: C, 17.99; H, 2.52. IR (KBr, cm^{-1}): 3419 (s, v, br), 2902 (vw), 2649 (s), 1594 (vs), 1459 (vw), 1384(s), 1313 (w), 1278 (w), 1135 (w), 1056 (w), 1019 (w), 940 (w), 906 (w), 820 (w), 686 (w), and 543 (w). TG-DTA: 55–200°C (weight loss 10.1%, –4.5H_2O); 280–600°C (weight loss 55.4%, –3H_4tart).

2.4. *Synthesis of [Nd_2(D-tart)$_3$(H_2O)$_3$] • 1.5H_2O (2)*

An aqueous solution (30 mL) of D-tartaric acid (0.2250 g, 1.5 mmol) and $Nd(NO_3)_3 \cdot 6H_2O$ (0.4360 g, 1.0 mmol) was treated similarly as above to afford light

Table 1. Crystal data for **1**, **5**, and **7**.

Crystal parameters	**1**	**5**	**7**
Empirical formula	$C_{12}H_{20}La_2O_{22.5}$	$C_{12}H_{18}O_{23}Tb_2$	$C_8H_{14}LuO_{14.5}$
Formula weight	802.1	848.10	516.7
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Tetragonal
Space group	$P2_1/n$	$P1$ (no.1)	$P4_12_12$ (no. 92)
Unit cell dimensions (Å, °)			
a	12.546(3)	5.990(4)	5.9747(8)
b	12.872(3)	7.435(3)	5.9747(8)
c	13.314(3)	13.323(3)	36.366(7)
α	90	102.89(3)	90
β	100.22(3)	101.55(3)	90
γ	90	90.85(3)	90
Volume (Å^3)	2116.0(9)	565.5(5)	1298.16(4)
Z	4	1	2
Calculated density (mg m^{-3})	2.518	2.490	2.643
Absorption coefficient (mm^{-1})	4.099	6.312	4.099
$F(000)$	1544	404	994
Crystal size (mm^3)	$0.16 \times 0.14 \times 0.14$	$0.22 \times 0.20 \times 0.19$	$0.11 \times 0.12 \times 0.24$
θ range (°)	3.08–27.43	3.27–27.48	3.46–27.48
Limiting indices	$-16 \le h \le 15$ $-16 \le k \le 16$ $-17 \le l \le 15$	$-7 \le h \le 6$ $-8 \le k \le 8$ $-15 \le l \le 15$	$-7 \le h \le 7$ $-7 \le k \le 7$ $-47 \le l \le 47$
Reflections collected	16935	4467	11978
Completeness to theta = 27.48°	95.8%	99.7%	99.8%
Max. and min. transmission	0.6016 and 0.5673	0.7015 and 0.4915	0.4038 and 0.3064
Data/restraints/parameters	4657/24/385	2280/0/146	1488/7/115
Goodness-of-fit on F^2	1.100	1.223	1.105
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0267$ $wR_2 = 0.0463$	$R_1 = 0.0243$ $wR_2 = 0.0736$	$R_1 = 0.0210$ $wR_2 = 0.0417$
R indices (all data)	$R_1 = 0.0347$ $wR_2 = 0.0481$	$R_1 = 0.0255$ $wR_2 = 0.0815$	$R_1 = 0.0221$ $wR_2 = 0.0420$

pink crystals of $[Nd_2(D\text{-tart})_3(H_2O)_3]\cdot 1.5H_2O$ (**2**). Yield: 72% (0.2924 g). Elemental analysis (%): Calcd for $C_{24}H_{40}Nd_4O_{45}$ (1625.51): C, 17.73; H, 2.48. Found: C, 17.70; H, 2.42. IR (KBr, cm^{-1}): 3500–3022 (s, v, br), 2821 (w), 2687 (w), 2537 (w), 1614 (vs), 1556 (vs), 1411 (vs), 1314 (w), 1133 (w), 1071 (w), 936 (w), 881 (w), 844 (w), 711 (w), and 604 (w).

2.5. *Synthesis of $[Sm_2(D\text{-tart})_3(H_2O)_3]\cdot 1.5H_2O$ (3)*

An aqueous solution (30 mL) of D-tartaric acid (0.2250 g, 1.5 mmol) and $Sm(NO_3)_3 \cdot 6H_2O$ (0.4460 g, 1.0 mmol) was treated similar to **1** to afford light yellow crystals of $[Sm_2(D\text{-tart})_3(H_2O)_3] \cdot 3H_2O$ (**3**). Yield: 74% (0.3051 g). Elemental analysis (%): Calcd for $C_{24}H_{40}O_{45}Sm_4$ (1649.99): C, 17.47; H, 2.44. Found: C, 17.42; H, 2.39. IR (KBr, cm^{-1}): 3500–3052 (s, v, br), 2805 (w), 2686 (w), 2529 (w), 1608 (vs), 1563 (vs), 1410 (vs), 1313 (w), 1132 (w), 1069 (w), 935 (w), 880 (w), 844 (w), 710 (w), and 604 (w).

2.6. *Synthesis of [Eu_2(D-tart)$_3$(H_2O)$_2$]•3H_2O (4)*

An aqueous solution (30 mL) of D-tartaric acid (0.2250 g, 1.5 mmol) and $Eu(NO_3)_3 \cdot 6H_2O$ (0.4470 g, 1.0 mmol) was treated similarly as above to afford colorless crystals of [Eu_2(D-tart)$_3$(H_2O)$_2$] · 3H_2O (**4**). Yield: 68% (0.2815 g). Elemental analysis (%): Calcd for $C_{12}H_{18}O_{23}Eu_2$ (834.2): C, 17.28; H, 2.17. Found: C, 17.32; H, 2.21. IR (KBr, cm^{-1}): 3500–3029 (s, v, br), 2798 (w), 2701 (w), 2537 (w), 1621 (vs), 1559 (vs), 1411 (vs), 1313 (w), 1133 (w), 1071 (w), 936 (w), 882 (w), 845 (w), 711 (w), and 603 (w).

2.7. *Synthesis of [Tb_2(D-tart)$_3$(H_2O)$_2$]•3H_2O (5)*

An aqueous solution (30 mL) of D-tartaric acid (0.2250 g, 1.5 mmol) and $Tb(NO_3)_3 \cdot 6H_2O$ (0.4530 g, 1.0 mmol) was treated similar to **1** to afford colorless crystals of [Tb_2(D-tart)$_3$(H_2O)$_2$] · 3H_2O (**5**). Yield: 65% (0.2769 g). Elemental analysis (%): Calcd for $C_{12}H_{18}O_{23}Tb_2$ (848.11): C, 16.99; H, 2.14. Found: C, 16.90; H, 2.20. IR (KBr, cm^{-1}): 3500–3037 (s, v, br), 2805 (w), 2708 (w), 2537 (w), 1621 (vs), 1567 (vs), 1410 (vs), 1317 (w), 1133 (w), 1082 (w), 940 (w), 883 (w), 843 (w), 712 (w), and 608 (w). TG-DTA: 90–200°C (weight loss 10.6%, –5H_2O); 300–640°C (weight loss 52.1%, –3H_4tart).

2.8. *Synthesis of [Dy_2(D-tart)$_3$(H_2O)$_2$]•3H_2O (6)*

An aqueous solution (30 mL) of D-tartaric acid (0.2250 g, 1.5 mmol) and $Dy(NO_3)_3 \cdot 6H_2O$ (0.4580 g, 1.0 mmol) was treated similarly as above to afford light yellow crystals of [Dy_2(D-tart)$_3$(H_2O)$_2$] · 3H_2O (**6**). Yield: 62% (0.2663 g). Elemental analysis (%): Calcd for $C_{12}H_{22}Dy_2O_{23}$ (859.29): C, 16.77; H, 2.58. Found: C, 16.72; H, 2.54. IR (KBr, cm^{-1}): 3500–3029 (s, v, br), 2817 (w), 2692 (w), 2537 (w), 1615 (vs), 1559 (vs), 1412 (vs), 1314 (w), 1133 (w), 1071 (w), 938 (w), 883 (w), 845 (w), 711 (w), and 597 (w).

2.9. *Synthesis of [Lu($C_4H_4O_6$)($C_4H_5O_6$)]•2.5H_2O (7)*

An aqueous solution (30 mL) of D-tartaric acid (0.1500 g, 1.0 mmol) and $Lu(NO_3)_3 \cdot 6H_2O$ (0.2345 g, 0.5 mmol) was treated similarly as above to afford colorless crystals of [Lu($C_4H_4O_6$)($C_4H_5O_6$)] · 2.5H_2O (**7**). Yield: 53% (0.1369 g). Elemental analysis (%): Calcd for $C_{16}H_{28}Lu_2O_{29}$ (1034.31): C, 18.58; H, 2.73. Found: C, 18.54; H, 2.68. IR (KBr, cm^{-1}): 3432 (s, v), 3261 (vw), 2671 (vw), 1719 (m, vw), 1611 (vs), 1559 (vs), 1411 (vs), 1304 (w), 1138 (w), 1066 (w), 943 (w), 839 (w), 843 (w), 712 (w), and 603 (w). TG-DTA: 95–180°C (weight loss 8.7%, –2.5H_2O); 280–600°C (weight loss 57.5%, –H_4tart and H_5tart).

3. Results and discussion

3.1. *Description of the structures*

3.1.1. [La_2(DL-tart)$_3$(H_2O)$_3$]•1.5H_2O (1). Compound **1**, crystallizing in a monoclinic system with a *P2₁/n* space group, has a 3-D network built by connecting the La(III) ions with their neighboring tartrate ligand (figure 1). This has a 3-D open framework with a low-level ancillary aquation. The structure has hydrophilic channels of ca. 5 × 9 Å. Obviously, two La(III) ions are pseudo-inversion related. Although both La(III) ions are nine-coordinate by nine oxygens, their chemical environments are different. La1 has two oxygens from two waters and seven oxygens from four tartrates in a distorted monocapped square-antiprism (figure 2a). The distorted square-antiprism consists of O(1), O(3), O(19), O(9), O(7), O(18), O(12), and O(20). The O(17) atom is at the top of the cap. However, La2 ion has one oxygen from water and eight oxygens from five tartrates, adopting a distorted tricapped trigonal prism (figure 2b). The distorted trigonal prism is composed of O(2), O(15), O(21), O(13), O(11), and O(4) atoms. The O(6), O(10), and O(14) atoms are at the vertices of each square pyramid. In **1**, the bond distances of La1–O and La2–O are in the range of 2.427(3)–2.679(3) and 2.451(2)–2.705 (3) Å, respectively. Although the three tartrate ligands are each crystallographically independent, they are chemically consistent and can be classed as μ_3, κ^5 (figure 3a), namely, they bind to three La(III) ions using five oxygen atoms of the tartrate. Half of the tartrate has "1,2-chelation" involving a carboxylate oxygen and the ortho-hydroxy. The other half has chelation involving carboxylate oxygen and the ortho-hydroxy. A bonding mode, to our knowledge, was not previously reported. This ligand combines with La(III) to form a condensed 2-D slab of [La_2(DL-tart)$_2$] in the *ab*-plane.

3.1.2. [Tb_2(D-tart)$_3$(H_2O)$_2$]·$3H_2O$ (5). Compound **5**, crystallizing in the triclinic system in the *P1* space group, has a 3-D network by connecting the Tb(III) ions with neighboring tartrates (figure 4). It is similar to **1** having a 3-D open framework with a higher level of ancillary aquation than **1**. The structure has hydrophilic channels of ca. 4 × 7 Å. Although two Tb(III) ions are pseudo-inversion related, their chemical environments are similar with coordination by nine oxygens, one oxygen from water and eight oxygens from five tartrates (figure 5a). Tb1 adopts a distorted monocapped square-antiprism coordination geometry (figure 5b), whereas Tb2 is a distorted tricapped trigonal prism (figure 5c). Although the three tartrate ligands are

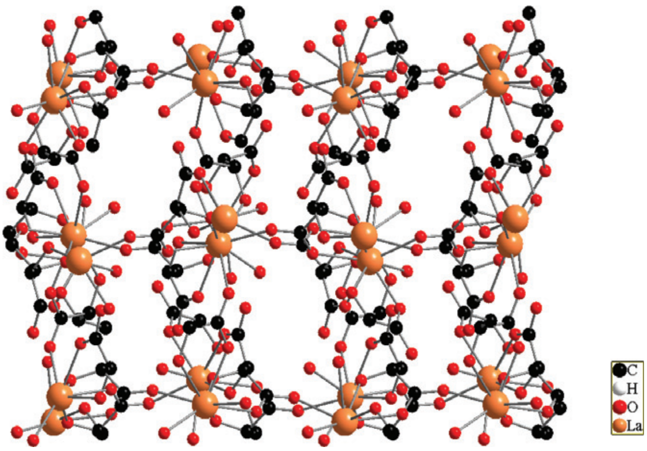

Figure 1. Molecular structure of **1** viewing along *c* axis (hydrogen atoms and interstitial water molecules were omitted for clarity).

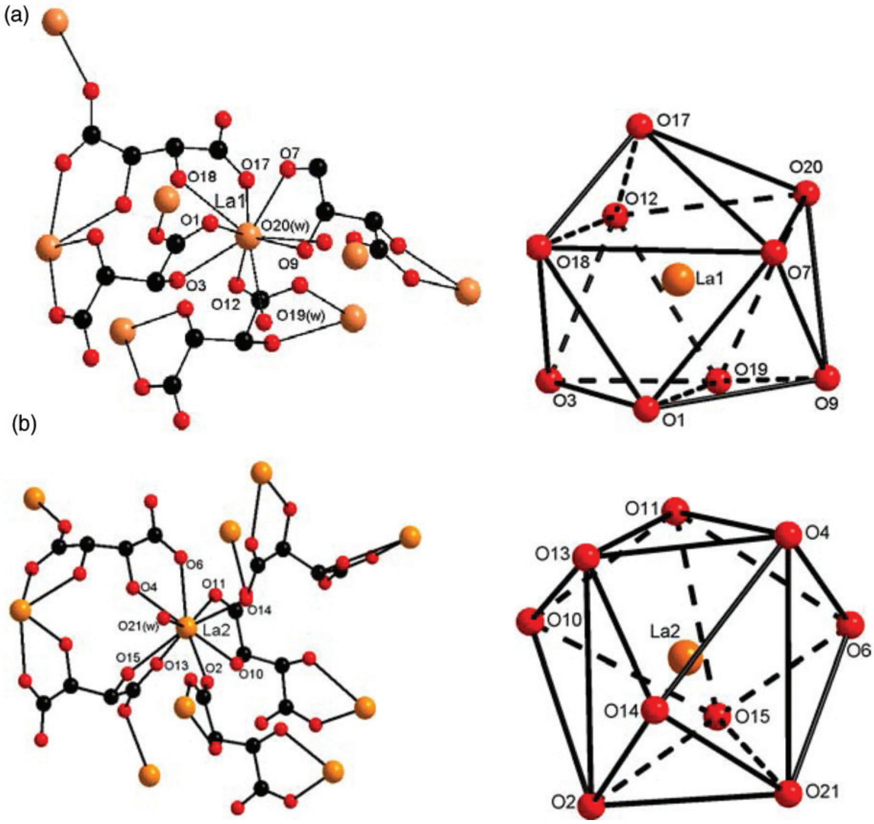

Figure 2. Coordination environments of (a) distorted monocapped square-antiprism for La1 ion and (b) distorted tricapped trigonal prism for La2 ion in **1**. Selected bond lengths (Å) and angles (°) for **1**: La(1)–O(17) 2.427(3), La(1)–O(7) 2.444(3), La(1)–O(20) 2.478(3), La(1)–O(1) 2.495(2), La(1)–O(12) 2.509(3), La(1)–O(3) 2.511(3), La(1)–O(19) 2.542(3), La(1)–O(18) 2.662(3), La(1)–O(9) 2.679(3); O(7)–La(1)–O(9) 60.04(9), O(19)–La(1)–O(9) 65.47(9), O(2)–La(2)–O(21) 70.57(9), O(7)–La(1)–O(1) 76.02(9), O(7)–La(1)–O(20) 76.21(9), O(1)–La(1)–O(19) 92.51(1), O(7)–La(1)–O(19) 124.95(1), O(20)–La(1)–O(1) 140.56(9), O(20)–La(1)–O(3) 144.56(9); La(2)–O(11) 2.451(2), La(2)–O(6) 2.470(3), La(2)–O(2) 2.473(2), La(2)–O(21) 2.473(3), La(2)–O(13) 2.507(3), La(2)–O(10) 2.548(3), La(2)–O(14) 2.592(3), La(2)–O(4) 2.625(3), La(2)–O(15) 2.705(3); O(13)–La(2)–O(15) 58.86(8), O(6)–La(2)–O(21) 70.05(1), O(21)–La(2)–O(15) 70.06(1), O(2)–La(2)–O(21) 70.57(9), O(2)–La(2)–O(15) 73.11(9), O(2)–La(2)–O(13) 100.95(9), O(21)–La(2)–O(13) 128.12(1), O(6)–La(2)–O(2) 130.72(8), O(21)–La(2)–O(10) 140.23(9).

crystallographically independent, two are chemically consistent and can be classed as μ_4, κ^6 mode (figure 3b), namely, they bind to three Tb(III) ions using all six oxygen atoms of the tartrate. Each half of the tartrate has "1,2-chelation" involving a carboxylate oxygen and the ortho-hydroxy. Two tartrates combine with metal ions to form a condensed 2-D slab of $[Tb_2(\mu_4,\kappa^6\text{-D-TAR})_2]$ in the *ab*-plane. The third tartrate is quite different and bridges only two Tb(III) ions via two bidentate carboxylates and may be described as μ_2, κ^4 mode (figure 3c). In **5**, the bond distances of Tb1–O and Tb2–O are in the range of 2.351(8)–2.691(9) and 2.366(8)–2.614(8) Å, respectively (figure 5). The crystal structure and the coordination mode of tatrate ligands are isomorphous with those of previously reported complexes $[Er_2(\text{D-tart})_3(H_2O)_2]\cdot 3H_2O$ [24] and $[Gd_2(\text{D-tart})_3(H_2O)_2]\cdot 3H_2O$ [25].

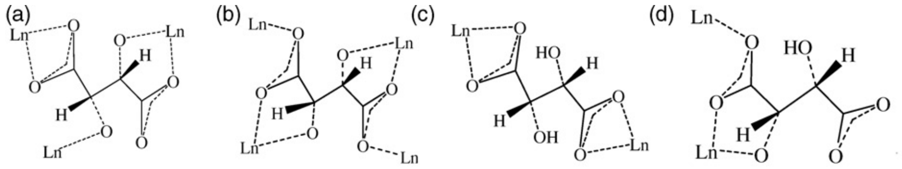

Figure 3. Binding modes of tartrate: (a) μ_3, κ^5 in **1**; (b) μ_4, κ^6 and (c) μ_2, κ^4 in **5**; (d) $\mu_{2,}$ κ^3 in **7**.

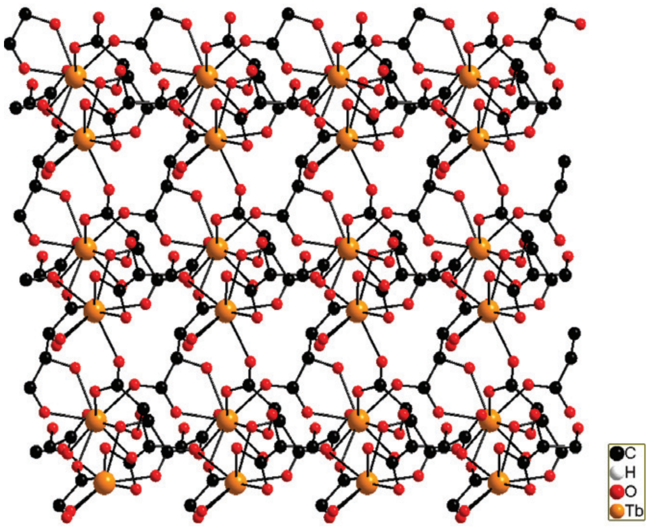

Figure 4. Perspective view of **5** along *c* axis (hydrogen atoms and interstitial water molecules were omitted for clarity).

3.1.3. [Lu($C_4H_4O_6$)($C_4H_5O_6$)] · 2.5H_2O (7). Compound **7**, crystallizing in the tetragonal system in the $P4_12_12$ space group, is a 2-D chiral sheet built by connecting Lu(III) ions with bridging tartrates (figure 6a). Each Lu(III) ion is nine-coordinate from three oxygens from three waters and six oxygens from four tartates in a tricapped trigonal prism coordination geometry (figure 6b). The dihedral angle between the two triangular faces is ca. 3.23°. The O3, O8, and O3′ are on the tops of the three square pyramids. Each tartrate bridges two Lu(III) ions through "1,2-chelation" involving a carboxylate oxygen and the ortho-hydroxy in μ_2, κ^3 mode (figure 3d). Interestingly, it is just half of the coordination mode of μ_4, κ^6 for tartrate in **5**. The bond lengths of Lu–O are in the range of 2.275(3)–2.629(6) Å. The molecular structure has two-fold symmetry with Lu and O8 on the symmetry axis. The Lu–O(8) bond distance of 2.629(6) Å is the longest, implying disorder in the structure such that the non-coordinated carboxylate is protonated 50% of the time. The crystal structure and the coordination of tatrate ligands of **7** are isomorphous with those of previously reported complexes [Sm($C_4H_4O_6$)($C_4H_5O_6$)] · 3H_2O [26], [Y($C_4H_4O_6$)($C_4H_5O_6$)] · 2.5H_2O [27], and [Er($C_4H_4O_6$)($C_4H_5O_6$)] · 3H_2O [28].

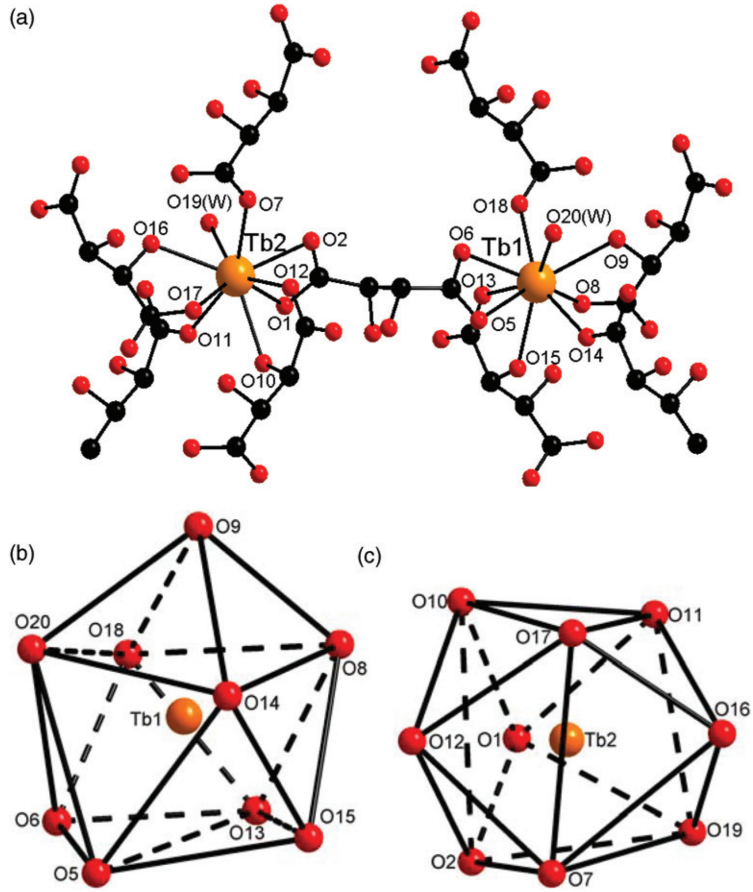

Figure 5. (a) Perspective view of Tb ion in **5**. Coordination environments of (b) distorted monocapped square-antiprism for Tb1 ion and (c) distorted tricapped trigonal prism for Tb2 ion. Selected bond lengths (Å) and angles (°) for **5**: Tb(1)–O(14) 2.351(8), Tb(1)–O(8) 2.363(8), Tb(1) – (O13) 2.380(9), Tb(1)–O(18) 2.387(8), Tb(1)–O(20) 2.411(8), Tb(1)–O(6) 2.417(9), Tb(1)–O(15) 2.463(9), Tb(1)–O(9) 2.607(8), Tb(1)–O(5) 2.691(9); O(14)–Tb(1)–O(8) 83.1(3), O(14)–Tb(1)–O(13) 131.6(3), O(8)–Tb(1)–O(13) 74.6(3), O(14)–Tb(1)–O(18) 152.0(3), O(8)–Tb(1)–O(18) 89.9(3), O(13)–Tb(1)–O(18) 71.3(3), O(14)–Tb(1)–O(20) 80.8(3), O(8)–Tb(1)–O(20) 131.9(3), O(13)–Tb(1)–O(20) 144.4(3); Tb(2)–O(11) 2.366(9), Tb(2)–O(17) 2.366(8), Tb(2)–O(12) 2.383(8), Tb(2)–O(19) 2.411(8), Tb(2)–O(7) 2.410(8), Tb(2)–O(1) 2.500(8), Tb(2)–O(2) 2.502(8), Tb(2)–O(10) 2.519(8), Tb(2)–O(16) 2.614(8); O(11)–Tb(2)–O(17) 79.3(3), O(11)–Tb(2)–O(12) 130.3(3), O(12)–Tb(2)–O(19) 146.4(3), O(12)–Tb(2)–O(1) 97.9(3), O(19)–Tb(2)–O(1) 79.0(3), O(7)–Tb(2)–O(1) 124.6(3), O(1)–Tb(2)–O(2) 52.1(3), O(2)–Tb(2)–O(16) 137.4(2), O(7)–Tb(2)–O(16) 76.3(3).

3.2. *Thermogravimetric analysis*

Thermogravimetric analysis shows that curves for **1**–**7** are similar. A representative TG-DTA curve of **1** is displayed in figure 7. The first step corresponds to loss of non-coordinated water from 50 to 150°C. The second step is correlated to the loss of coordinated water from 180 to 200°C, suggesting that these molecules are also involved in hydrogen bonding. After losing all water, molecules remain stable in the temperature range of 200–300°C and then start to decompose. The final residue is Ln_2O_3.

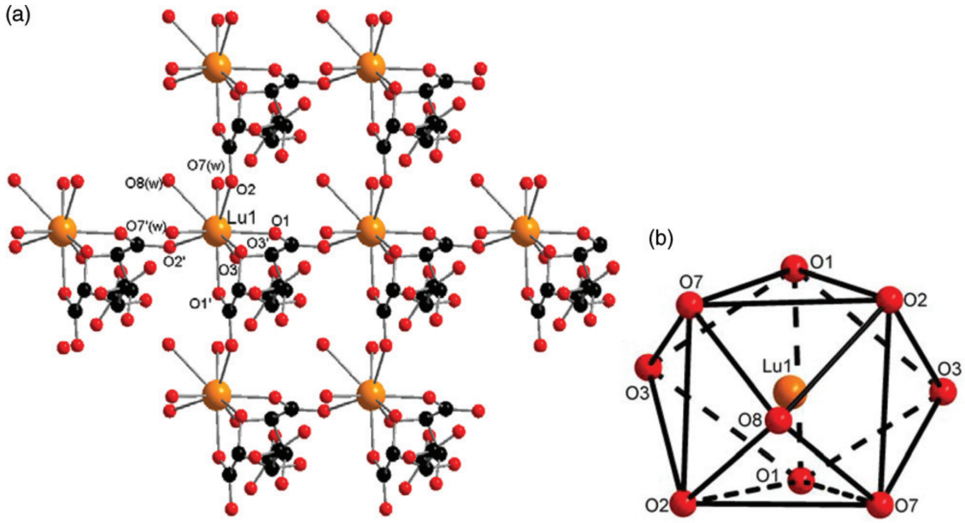

Figure 6. (a) Perspective view of **7** along *c* axis; hydrogen atoms and interstitial water molecules were omitted for clarity. (b) Coordination environment of distorted tricapped trigonal prism for Lu1 ion. Selected bond lengths (Å) and angles (°) for **7**: Lu(1)–O(1) 2.275(3), Lu(1)–O(1′) 2.275(3), Lu(1)–O(2) 2.297(3), Lu(1)–O(2′) 2.297(3), Lu(1)–O(3) 2.458(3), Lu(1)–O(3′) 2.458(3), Lu(1)–O(7) 2.329(4), Lu(1)–O(7′) 2.329(4), Lu(1)–O(8) 2.629(6); O(1)–Lu(1)–O(2) 80.99(1), O(1)–Lu(1)–O(2′) 80.99(1), O(1)–Lu(1)–O(7) 86.28(1), O(1′)–Lu(1)–O(7′) 86.28(1), O(1)–Lu(1)–O(3) 65.17(1), O(1′)–Lu(1)–O(3′) 65.17(10), O(1)–Lu(1)–O(8) 136.91(8), O(1′)–Lu(1)–O(8) 136.91(8).

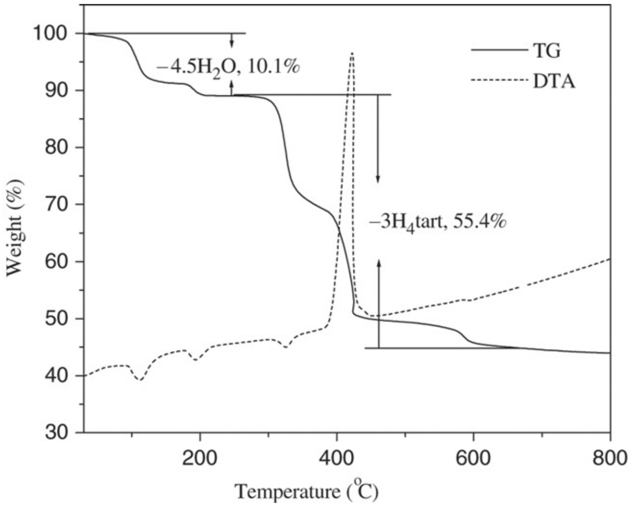

Figure 7. TG-DTA curve of **1**.

3.3. *Luminescent properties*

The luminescent properties of **4**, **5**, and **6** were investigated in solid state. The emission spectra of the three complexes exhibit the characteristic emissions of Eu(III), Tb(III), and Dy(III), respectively (figure 8). For **4**, five emission bands at 558, 590, 616, 650, and

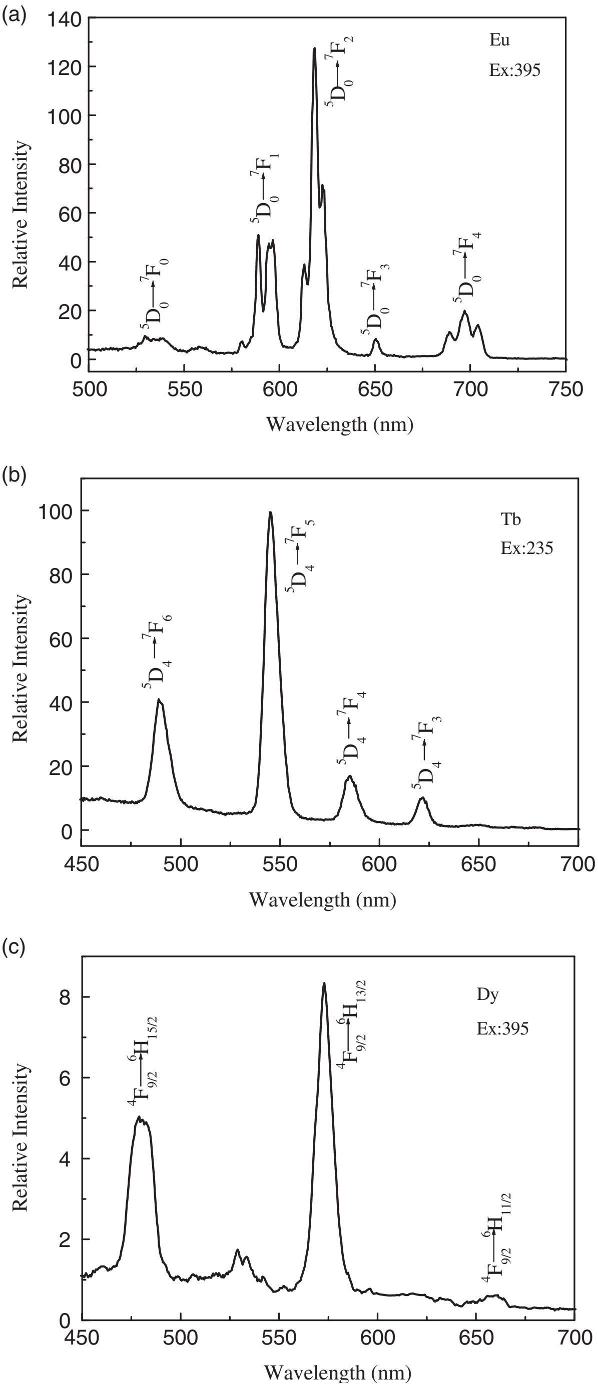

Figure 8. Luminescence spectra for (a) **4**, (b) **5**, and (c) **6**.

700 nm are observed upon excitation at 395 nm, assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. The bands at 590, 616, and 700 nm were obviously split into doublet, triplet, and triplet, respectively, and can be attributed to sublevel splitting from the $^7F_1$, $^7F_2$, and $^7F_4$ energy levels by the ligand field. The band at 616 nm is the strongest so that **4** emits red luminescence. It is similar to the characteristic emission of Eu(III) in several known complexes, e.g. $\{[Eu_2(HL)_3(H_2O)_3] \cdot 3H_2O\}_n$ (H_3L = 3,5-pyrazoledicarboxylic acid) [3], $[Eu_2(XA)_6(DMSO)_2]$ (HXA = xanthene-9-carboxylic acid; DMSO = dimethylsulfoxide) [4], $[Eu_5L_4(OH)_2(NO_3)_4(H_2O)_2] \cdot NO_3 \cdot 3H_2O$, ($H_2L$ = *N*, *N′*-*bis*(5-bromo-3-methoxysalicylidene)phenylene-1, 2-diamine) [5], $[EuCd(C_8H_7O_3)_5(phen)(H_2O)]$ ($C_8H_7O_3$ = 4-methoxybenzoato; phen = 1,10-phenanthroline) [6], $[L_3Eu_2]$ [(L = chiral tartaric acid derived *bis*(β-diketonate)] [7], $[Eu(tta)_3(Fc_2phen)]$ (tta = 2-thenoyltrifluoroacetonate, Fc_2phen = *bis*(ferrocenyl-ethynyl)-1,10-phenanthroline), $[Eu(fta)_3(phen)]$ (fta = ferrocenoyltrifluoroacetone; phen = 1,10-phenanthroline) [8] and $[Eu(H_2salen)_{1.5}(NO_3)_3]$ [H_2salen = *N*, *N′*-ethylene*bis*(salicylideneimine)] [9]. Although the emission spectra for these complexes were slightly different, their main emitting bands were very similar at ca. 616 nm. For **5**, four emission bands at 491, 545, 585, and 621 nm are observed upon excitation at 235 nm. These are assigned to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$ transitions, respectively. The main emitting band at 545 nm corresponds to green emission, in agreement to the characteristic emission of Tb(III) ion in $[Tb_3(BDC)_{4.5}(DMF)_2(H_2O)_3 \cdot (DMF)(H_2O)]$ (BDC = 1,4-benzenedicarboxylic acid, DMF = *N*, *N′*-dimethylformamide) [10], $\{[Tb_2(HL)_3(H_2O)_3 \cdot 3H_2O]\}_n$ [3], $[Tb_2(XA)_6(DMSO)_2]$ [4], $[TbCd(C_8H_7O_3)_5(phen)(H_2O)]$, $[Tb(H_2L)(NO_3)_3]$ [H_2L = *N*, *N′*-ethylene-bis(3-methoxysalicylideneimine)] [11] and $[(H_2L)Tb(NO_3)_3]$ [H_2L = *N*, *N′*-*bis*(2-hydroxy-3-methoxybenzylidene)-*N*-ethylic-1,2-dimine] [12]. For **6**, three emission bands at 480, 573, and 660 nm are observed upon excitation at 395 nm, assigned to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions, respectively. The main emission band is at 573 nm so that **6** has emission, consistent to the characteristic emission of Dy(III) in $\{[Dy(HL)(H_2L)(H_2O)_2]\}_n$ [3], $[Dy(H_2L^1)_2)]$ [13], $[Dy_2(PDOA)_3(phen)_2(H_2O)_2] \cdot 2H_2O$ (H_2PDOA = 1, 2-phenylenedioxydiacetic acid) [14], $[Dy(pytpy)(NO_3)_2(\mu\text{-}OCH_3)]_2$ (pytpy = 4′-(3-pyridyl)-2,2′ : 6′,2″-terpyridine) [15], $[Dy(pmida)(NO_3)(H_2O)]_n$ [$pmida^{2-}$ = *N*-(2-pyridylmethyl)iminodiacetate] [16] and $[Dy(isophth)(Hisophth)(H_2O)_4 \cdot 4H_2O]_n$ [17] ($H_2isophth$ = isophthalic acid). The characteristic luminescence of Sm(III) in **3** was not observed, probably attributed to poor efficiency of the intramolecular energy transfer between the triplet state of tartrate and the emitting state of Sm(III).

4. Conclusions

Isolation and characterization of **1**, **5**, and **7** suggests that diverse tartrate lanthanide assemblies are possible, depending on the preparing route and the reaction conditions. The assemblies depend not only on the metal choice, but also on the coordination modes of the tartrate, further demonstrated by **1**, in which a new coordination mode of tartrate is found. Luminescence analysis indicates that energy levels between triplet state of tartrate and emitting states of Eu(III), Tb(III) and Dy(III) favor energy transfer, but not for the Sm(III) complex. Current initiatives at our laboratory are directed to applications of these chiral lanthanide tartrates on catalysis of asymmetric organic reactions.

Supplementary material

CCDC Nos. 634818 (**1**), 666421 (**5**), 666422 (**7**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

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References

[1] (a) S. Tanase, J. Reedijk. *Coord. Chem. Rev.*, **250**, 2501 (2006); (b) G.-M. Li, T. Akitsu, O. Sato, Y. Einaga. *J. Am. Chem. Soc.*, **125**, 12396 (2003); (c) M. Sakamoto, K. Manseki, H. Okawa. *Coord. Chem. Rev.*, **219–221**, 379 (2001); (d) Y.F. Huang, H.H. Wei, M. Ktada. *J. Coord. Chem.*, **61**, 2683 (2008).

[2] (a) S. Handa, K. Nagawa, Y. Sohtome, S. Matsunaga, M. Shibasaki. *Angew. Chem. Int. Ed.*, **47**, 3230 (2008); (b) T. Nitabaru, N. Kumagai, M. Shibasaki. *Tetrahedron Lett.*, **49**, 272 (2008); (c) S. Handa, V. Gnanadesikan, S. Matsunaga, M. Shibasaki. *J. Am. Chem. Soc.*, **129**, 4900 (2007); (d) K. Ohno, Y. Kataoka, K. Mashima. *Org. Lett.*, **6**, 4695 (2004); (e) K. Mikami, M. Terada, H. Matsuzawa. *Angew. Chem. Int. Ed.*, **41**, 3554 (2002); (f) J. Inanaga, H. Furuno, T. Hayano. *Chem. Rev.*, **102**, 2211 (2002).

[3] J. Xia, B. Zhao, H.-S. Wang, W. Shi, Y. Ma, H.-B. Song, P. Cheng, D.-Z. Liao, S.-P. Yan. *Inorg. Chem.*, **46**, 3450 (2007).

[4] R. Shyni, S. Biju, M.L.P. Reddy, A.H. Cowley, M. Findlater. *Inorg. Chem.*, **46**, 11025 (2007).

[5] X.P. Yang, R.A. Jones, W.K. Wong. *Dalton Trans.*, 1676 (2008).

[6] Y.-X. Chi, S.-Y. Niu, Z.-L. Wang, J. Jin. *Eur. J. Inorg. Chem.*, 2336 (2008).

[7] M. Albrecht, S. Schmid, S. Dehn, C. Wickleder, S. Zhang, A.P. Bassett, Z. Pikramenouc, R. Fröhlich. *New J. Chem.*, **31**, 1755 (2007).

[8] Y.-F. Yuan, T. Cardinaels, K. Lunstroot, K. Van Hecke, L. Van Meervelt, C. Gorller-Walrand, K. Binnemans, P. Nockemann. *Inorg. Chem.*, **46**, 5302 (2007).

[9] T. Gao, P.-F. Yan, G.-M. Li, G.-F. Hou, J.-S. Gao. *Polyhedron*, **26**, 5382 (2007).

[10] X.-D. Guo, G.-S. Zhu, F.-X. Sun, Z.-Y. Li, X.-J. Zhao, X.-T. Li, H.-C. Wang, S.-L. Qiu. *Inorg. Chem.*, **45**, 2581 (2006).

[11] T. Gao, P.-F. Yan, G.-M. Li, G.-F. Hou, J.-S. Gao. *Inorg. Chim. Acta*, **361**, 2051 (2008).

[12] W. Dou, J.-N. Yao, W.-S. Liu, Y.-W. Wang, J.-R. Zheng, D.-Q. Wang. *Inorg. Chem. Commun.*, **10**, 105 (2007).

[13] S. Petoud, S.M. Cohen, J.-C.G. Bünzli, K.N. Raymond. *J. Am. Chem. Soc.*, **125**, 13324 (2003).

[14] X. Li, Y.-Q. Li, X.-J. Zheng, H.-L. Sun. *Inorg. Chem. Commun.*, **11**, 779 (2008).

[15] L. Gou, Q.-R. Wu, H.-M. Hu, T. Qin, G.-L. Xue, M.-L. Yang, Z.-X. Tang. *Inorg. Chim. Acta*, **361**, 1922 (2008).

[16] Y. Li, F.-P. Liang, C.-F. Jiang, X.-L. Li, Z.-L. Chen. *Inorg. Chim. Acta*, **361**, 219 (2008).

[17] B. Yan, Y. Bai, Z. Chen. *J. Mol. Struct.*, **741**, 141 (2005).

[18] S. Sivakumar, F.C.J.M. Van Veggel, M. Raudsepp. *J. Am. Chem. Soc.*, **127**, 12464 (2005).

[19] G. Zucchi, A.-C. Ferrand, R. Scopelliti, J.-C.G. Bünzli. *Inorg. Chem.*, **41**, 2459 (2002).

[20] J.-C.G. Bünzli, C. Piguet. *Chem. Rev.*, **102**, 1897 (2002).

[21] D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, J.A.K. Howard. *Chem. Rev.*, **102**, 1977 (2002).

[22] S. Petoud, G. Muller, E.G. Moore, J. Xu, J. Sokolnicki, J.P. Riehl, U.N. Le, S.M. Cohen, K.N. Raymond. *J. Am. Chem. Soc.*, **129**, 77 (2007).

[23] P.F. Yan, W.B. Sun, G.M. Li, C.H. Nie, T. Gao, Z.Y. Yue. *J. Coord. Chem.*, **60**, 1973 (2007).

[24] S. Thushari, J.A.K. Cha, H.H.Y. Sung, S.S.-Y. Chui, A.L.F. Leung, Y.-F. Yen, I.D. Williams. *Chem. Commun.*, 5515 (2005).

[25] S.C. Manna, E. Zangrando, J. Ribas, N.R. Chaudhuri. *Polyhedron*, **25**, 1779 (2006).

[26] C.-D. Wu, X.-P. Zhan, C.-Z. Lu, H.-H. Zhuang, J.-S. Huang. *Acta Cryst.*, **E58**, m228 (2002).

[27] M.J. Almond, M.G.B. Drew, S. Morris, D.A. Rice. *Polyhedron*, **15**, 3377 (1996).

[28] F.C. Hawthorne, I. Borys, R.B. Ferguson. *Acta Cryst.*, **C39**, 540 (1983).

[29] P. Starynowicz, G. Meyer. *Z. Anorg. Allg. Chem.*, **626**, 2441 (2000).

[30] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim. *Nature*, **404**, 982 (2000).