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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

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First published on: 22 September 2010

To cite this Article Bartyzel, Agata , Kula, Alina , Rzączyńska, Zofia , Pikus, Stanisław and Sawka-Dobrowolska, Wanda(2008) 'X-ray studies of lanthanide(III) complexes with 4-hydroxy-3-methoxybenzoate anion', Journal of Coordination Chemistry, 61: 6, 836 – 846, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970701420438

URL: <http://dx.doi.org/10.1080/00958970701420438>

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X-ray studies of lanthanide(III) complexes with 4-hydroxy-3-methoxybenzoate anion

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(Received 7 July 2006; in final form 22 January 2007)

Polycrystalline complexes of lanthanide(III) with 4-hydroxy-3-methoxybenzoic acid were obtained as hydrated compounds of general formula $\text{Ln}(\text{C}_8\text{H}_7\text{O}_4)_3 \cdot n\text{H}_2\text{O}$. After slow recrystallization we obtained single crystals of complexes and determined their structures. Praseodymium(III) and neodymium(III) form isostructural dihydrated complexes $[\text{Ln}(\text{C}_8\text{H}_7\text{O}_4)_3(\text{H}_2\text{O})_2]$, which crystallize in the triclinic system, space group *Pt*. Sm(III), Eu(III), Gd(III), Ho(III) and Tb(III) compounds are hexahydrates and also crystallize in the triclinic system, space group *Pt*. Dihydrated compounds form polymeric chains with metal centres linked by oxygen atoms of bridging carboxylates. Each metal ion is coordinated by chelating carboxylic group and two water molecules. Complexes of the second isostructural group form dinuclear units $[\text{Ln}_2(\text{C}_8\text{H}_7\text{O}_4)_6(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$. Lanthanide(III) ions are linked by oxygen atoms of two chelating-bridging carboxylate groups. In the dimeric structure each metal ion coordinates additionally two chelating carboxylic groups and two water molecules.

Keywords: 4-Hydroxy-3-methoxybenzoate; Lanthanide complexes; X-ray analysis; Crystal structure

1. Introduction

Attention has focused on metal carboxylates for their interesting coordination chemistry, unusual structural features, remarkable physical and chemical properties, and extensive practical application [1]. Lanthanide complexes with aromatic carboxylic acids have higher thermal and luminescent stability than other systems because they form dimeric or infinite polymeric structures readily [2]. This work is a continuation of our studies of the spectral, thermal and structural properties of metal complexes with benzoic acid derivatives containing methoxy and hydroxy functional groups. The aim of our research was synthesis and characterization of metal ions with 4-hydroxy-3-methoxybenzoic acid. 4-hydroxy-3-methoxybenzoic acid (vanillic acid) is a phenolic derivative, present in many plant materials and an integral part of human and

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animal diets. Vanillic acid is a major metabolic product of vanillin in humans and rats. 4-hydroxy-3-methoxybenzoic acid is also one of the main degradation products of wood constituent lignin [3–6]. Phenolic compounds exhibit antioxidative properties [3, 7–11]. 4-hydroxy benzoic acid shows activity in preservation of human low-density lipoprotein oxidation and protecting protein molecules from radical attacks, as determined by the oxygen radical absorbing capacity assay [3, 7, 9–12]. Vanillic acid possesses excellent UV-rays absorption ability and has been used as a sun care product [12].

In a previous paper [13] we described thermal and spectral properties of a series of lanthanide(III) complexes with 4-hydroxy-3-methoxybenzoic acid. The lanthanide(III) complexes with 4-hydroxy-3-methoxybenzoic acid were obtained as polycrystalline, hydrated products of general formula is $\text{Ln}(\text{C}_8\text{H}_7\text{O}_4)_3 \cdot n\text{H}_2\text{O}$, where $n=2$ for La(III), Pr(III), $n=3$ for Nd(III), $n=4$ for Sm(III), $n=5$ for Ce(III) and $n=6$ for Y(III), Eu(III)–Lu(III). All compounds are sparingly soluble in water at room temperature in the range 2×10^{-4} – 6×10^{-4} mol dm⁻³. The complexes are stable at room temperature. During heating in air hydrated complexes lose all their crystallization water in one step (except for Nd(III) complex). The trihydrated complex of neodymium(III) loses water in two steps. Next, the anhydrous compounds heated in air decomposed to oxides of respective metals with intermediate formation (except for cerium(III)). The anhydrous complexes of Ce(III) decomposed directly to CeO₂ [13]. In this paper we describe crystal structure of some complexes. During slow recrystallization of the polycrystalline compounds single crystals of praseodymium(III), neodymium(III), samarium(III), europium(III), terbium(III) and holmium(III) ions with 4-hydroxy-3-methoxybenzoate ligand were obtained.

2. Experimental

4-Hydroxy-3-methoxybenzoates of lanthanide(III) were obtained by dissolving the freshly precipitated lanthanide(III) carbonates in a solution of 4-hydroxy-3-methoxybenzoic acid (0.06 M). The precipitates were removed by filtration, washed with water and dried at 300 K. The polycrystalline complexes were dissolved in water; suitable crystals were obtained by slow evaporation after a few weeks.

Crystals were mounted on glass fibre and then flash-frozen to 100 K (Oxford Cryosystem-Cryostream Cooler). Preliminary examination and intensity data collections were carried out on a Kuma KM4CCD κ -axis diffractometer with graphite-monochromated Mo-K α radiation. The crystallographic data and the refinement procedure details are given in table 1. All data were corrected for Lorentz, polarization and absorption effects [14]. The structures were solved by direct methods (program SHELXS97 [15, 16]) and refined by full-matrix least-squares on all F^2 data using the SHELXL97 [17] programs. Hydrogen atoms were found by Fourier syntheses or included in calculated positions with the isotropic thermal parameters proportional to those of the connected carbon atoms.

Powder diffraction data were collected on a PHILIPS XPERT PRO (Holland) automated X-ray diffractometer. The experimental conditions were: Cu target X-ray tube operated at 45 kV and 30 mA, 6° take-off angle, 1° divergence slit, 0.15 mm receiving slit, curved graphite diffracted beam monochromator and scintillation counter

Table 1. Summary of the crystallographic data.

Crystal	1	2	3	4	5	6
Empirical formula	$C_{24}H_{25}O_{14}Pr$	$C_{24}H_{25}O_{14}Nd$	$C_{48}H_{66}O_{36}Sm_2$	$C_{48}H_{66}O_{36}Eu_2$	$C_{48}H_{66}O_{36}Tb_2$	$C_{48}H_{66}O_{36}Ho_2$
Formula weight	678.35	681.68	1519.71	1522.93	1536.85	1548.87
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)						
<i>a</i>	9.500(1)	9.477(1)	10.841(1)	10.797(2)	10.821(1)	10.865(2)
<i>b</i>	10.972(1)	10.970(1)	11.381(1)	11.379(2)	11.376(1)	11.323(2)
<i>c</i>	12.537(1)	12.535(1)	13.224(2)	13.276(2)	13.175(2)	13.098(2)
α	107.24(1)	107.18(1)	114.75(1)	114.80(1)	114.58(1)	114.17(1)
β	95.40(1)	95.66(5)	97.45(1)	97.57(1)	97.65(1)	97.81(1)
γ	90.58(1)	90.74(1)	97.69(1)	97.69(1)	97.88(1)	98.15(1)
Volume (Å ³)	1241.5(2)	1237.7(2)	1436.8(2)	1435.0(4)	1428.1(2)	1421.3(4)
<i>Z</i>	2	2	1	1	1	1
Calculated density (Mg m ⁻³)	1.815	1.829	1.756	1.762	1.787	1.810
Absorption coefficient (mm ⁻¹)	2.037	2.173	2.127	2.269	2.560	2.868
Absorption correction	Analytical	Analytical	Analytical	Analytical	Analytical	Analytical
<i>F</i> (000)	680	682	766	768	772	776
Crystal size (mm ³)	0.12 × 0.15 × 0.10	0.14 × 0.10 × 0.10	0.35 × 0.30 × 0.15	0.12 × 0.08 × 0.06	0.25 × 0.15 × 0.10	0.16 × 0.12 × 0.10
θ range for data collection (°)	3.42 to 27.50	3.49 to 27.50	3.07 to 30.00	3.46 to 27.50	3.48 to 28.45	3.61 to 27.50
Index ranges	-10 ≤ <i>h</i> ≤ 12, -14 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 16	2 ≤ <i>h</i> ≤ 9, -14 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 16	-14 ≤ <i>h</i> ≤ 15, -16 ≤ <i>k</i> ≤ 13, -18 ≤ <i>l</i> ≤ 18	-14 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 15	-14 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 15, -17 ≤ <i>l</i> ≤ 17	-11 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 16
Number of collected reflections	8533	10433	21682	14590	9839	11685
Number of unique reflections (<i>R</i> _{int})	5348 (0.0399)	5445 (0.0577)	8106 (0.0273)	6473 (0.0581)	6272 (0.0307)	6258 (0.0294)
Max. and min. transmission	0.863 and 0.755	0.841 and 0.711	0.767 and 0.433	0.865 and 0.675	0.589 and 0.490	0.702 and 0.490
Goodness-of-fit on <i>F</i> ²	1.007	1.027	1.075	1.050	1.073	1.043
Final <i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2σ(<i>I</i>)]	0.0308, 0.0637	0.0328, 0.0797	0.0200, 0.0485	0.0380, 0.0771	0.0201, 0.0499	0.0238, 0.0590
<i>R</i> ₁ , <i>wR</i> ₂ indices (all data)	0.0400, 0.0669	0.0375, 0.0821	0.0210, 0.0490	0.0491, 0.0823	0.0212, 0.0505	0.0259, 0.0601
Largest diff. peak and hole (e Å ⁻³)	1.062 and -0.880	0.852 and -1.230	1.020 and -0.553	0.986 and -0.979	0.930 and -0.725	0.862 and -0.931

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

with pulse height analyzer. The powder diffraction pattern was collected by step scanning between 4° and 70° in 2θ with a step equal to 0.02° and a count time of 10 s/step. The diffractometer was calibrated by using a SRM 1976 standard. Throughout the measurement, temperature was maintained at $20 \pm 1^\circ\text{C}$. The XRAYAN program was used for determining peak intensities and positions. Pattern indexing was carried out with the PC-version of TREOR program [18]. For this sample, all the 2θ peak positions were used.

3. Results and discussion

The lanthanide(III) complexes with 4-hydroxy-3-methoxybenzoic acid were synthesized as polycrystalline compounds. During slow recrystallization from aqueous solution we obtained single crystals of praseodymium(III), neodymium(III), samarium(III), europium(III), terbium(III) and holmium(III). In the case of neodymium(III) and samarium(III) complexes the number of water molecules was changed. The X-ray diffraction studies show that the complexes form two isostructural series as dihydrated compounds of Pr(III), Nd(III) and the other complexes are hexahydrated.

Polycrystalline praseodymium(III) compound is dihydrated while neodymium 4-hydroxy-3-methoxybenzoate is trihydrate. These compounds were investigated by X-ray powder analysis. The obtained data indicate that the polycrystalline praseodymium(III) complex crystallizes in triclinic crystal system with the elemental cell parameters $a = 10.19 \text{ \AA}$, $b = 11.52 \text{ \AA}$, $c = 12.21 \text{ \AA}$, and $\alpha = 97.66^\circ$, $\beta = 110.08^\circ$, $\gamma = 91.72^\circ$, $V = 1329.7 \text{ \AA}^3$. The figure of merit F_N [19] of the present data set is $F_{30} = 7.6(0.0206, 191)$. The structure refinement was performed with 40 reflections. The polycrystalline neodymium(III) complex crystallizes in triclinic crystal system. The unit-cell parameters, refined from all 96 reflections by the least-squares method, are $a = 10.84 \text{ \AA}$, $b = 10.97 \text{ \AA}$, $c = 12.46 \text{ \AA}$, $\alpha = 93.7^\circ$, $\beta = 103.5^\circ$, $\gamma = 101.3^\circ$ and $V = 1413.5 \text{ \AA}^3$. The figure of merit F_N [19] for the powder data is $F_{30} = 7.1(0.0379, 112)$.

Single crystals of $[\text{PrL}_3(\text{H}_2\text{O})_2]$ (**1**) and $[\text{NdL}_3(\text{H}_2\text{O})_2]$ (**2**), where L = 4-hydroxy-3-methoxybenzoate, are isostructural. The structures consist of infinite chains that run along the a -axis, figure 1(a). Neighbouring chains are connected to each other via hydrogen interactions, figure 1(b). In chains each metal ion is connected to two neighbouring ones through μ -carboxylato- O, O' groups (figure 2). Pr(III) and Nd(III) ions are coordinated by six oxygen atoms from five 4-hydroxy-3-methoxybenzoate ligands and two aqua ligands giving coordination number 8. The Ln–O_{carboxylate} distances falls in the range 2.342(2)–2.548(3) Å for praseodymium and 2.327(2)–2.531(2) Å for neodymium (table 2). The Ln–O_{aqua} bond lengths are 2.498(2) Å, 2.588(3) Å for Pr(III) and 2.487(2) Å, 2.571(3) Å for Nd(III). The carboxylate groups O11–C1–O12 and O31–C3–O32, which bind two lanthanide ions adopt syn-anti bidentate bridging modes [torsion angle: Pr–O(11)–C(1)–C(11) $160.6(2)^\circ$; Prⁱ–O(12)–C(1)–C(11) $-93.0(2)^\circ$, Pr–O(31)–C(3)–C(31) $146.5(2)^\circ$; Prⁱⁱ–O(32)–C(3)–C(31) $-33.2(1)^\circ$ for **1** and Nd–O(11)–C(1)–C(11) $161.3(2)^\circ$; Ndⁱ–O(12)–C(1)–C(11) $-92.8(2)^\circ$; Nd–O(31)–C(3)–C(31) $145.9(2)^\circ$; Ndⁱⁱ–O(32)–C(3)–C(31) $-36.3(1)^\circ$ for **2**]. The syn-anti bridging mode is very common in polymeric structures of metal carboxylate complexes [20–22]. The carboxylate group O(21)–C(2)–O(22) is bidentate chelating coordination mode. The modes of carboxylate coordination do not influence

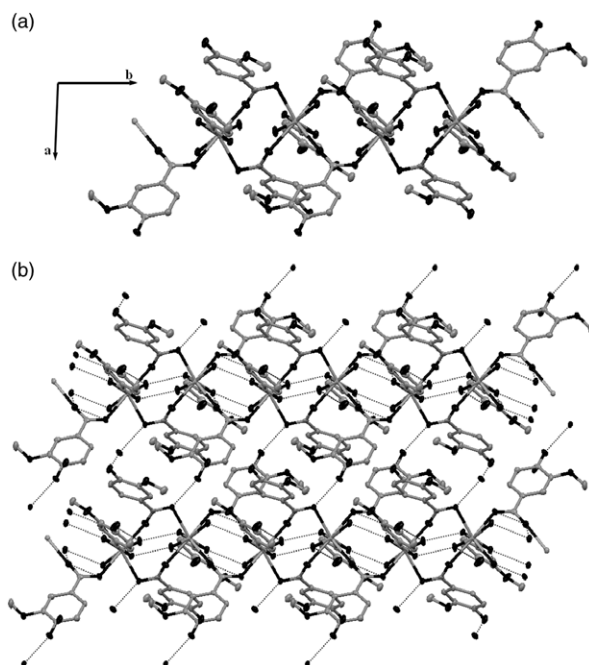


Figure 1. (a) View along the *c* axis of single chain in **1** and **2**; (b) Hydrogen-bonding interactions between chains (hydrogen bonds are indicated by dotted lines). Hydrogen atoms have been omitted for clarity.

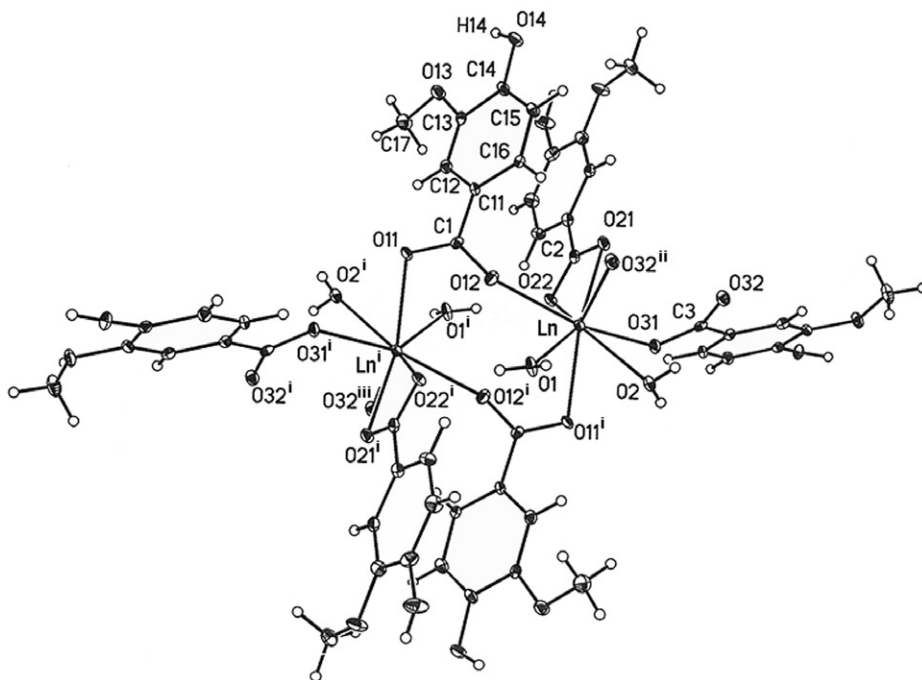


Figure 2. Coordination environment of Ln(III) ions in $[\text{Ln}(\text{C}_8\text{H}_7\text{O}_4)_3(\text{H}_2\text{O})_2]$, where Ln=Pr and Nd. Symmetry transformations used to generate equivalent atoms: (i) $-x+1, -y+1, -z+1$ (ii) $-x, -y+1, -z+1$, (iii) $x+1, y, z$.

Table 2. Selected bond distances (Å) and bond angles (°).

	1	2		3	4	5	6
Ln–O(12) ⁱ	2.342(2)	2.327(2)	Ln–O(21)	2.398(1)	2.386(3)	2.357(2)	2.329(2)
Ln–O(11)	2.414(2)	2.412(2)	Ln–O(2W)	2.412(1)	2.400(3)	2.358(2)	2.336(2)
Ln–O(32) ⁱⁱ	2.463(2)	2.446(2)	Ln–O(31) ⁱⁱⁱ	2.416(1)	2.401(3)	2.372(2)	2.343(2)
Ln–O(31)	2.475(2)	2.449(2)	Ln–O(32)	2.421(1)	2.406(3)	2.381(2)	2.344(2)
Ln–O(2W)	2.498(2)	2.487(2)	Ln–O(1W)	2.428(1)	2.402(3)	2.380(2)	2.355(2)
Ln–O(21)	2.519(2)	2.501(2)	Ln–O(11)	2.440(1)	2.435(3)	2.409(2)	2.379(2)
Ln–O(22)	2.548(2)	2.531(2)	Ln–O(12)	2.493(1)	2.466(3)	2.451(2)	2.438(2)
Ln–O(1W)	2.588(3)	2.571(3)	Ln–O(22)	2.659(1)	2.644(3)	2.644(2)	2.645(2)
O(11)–C(1)	1.262(4)	1.258(4)	Ln–O(31)	2.704(1)	2.695(3)	2.702(2)	2.700(2)
O(12)–C(1)	1.280(4)	1.261(4)	O(11)–C(1)	1.260(2)	1.249(5)	1.256(3)	1.263(3)
O(13)–C(13)	1.379(4)	1.383(4)	O(12)–C(1)	1.294(2)	1.296(5)	1.289(3)	1.288(3)
O(13)–C(17)	1.429(4)	1.435(4)	O(13)–C(13)	1.366(2)	1.368(5)	1.365(3)	1.360(3)
O(14)–C(14)	1.372(4)	1.367(4)	O(13)–C(17)	1.430(2)	1.429(5)	1.427(3)	1.432(3)
O(21)–C(2)	1.270(4)	1.269(4)	O(14)–C(14)	1.361(2)	1.363(5)	1.360(3)	1.361(3)
O(22)–C(2)	1.274(4)	1.265(4)	O(21)–C(2)	1.274(2)	1.265(5)	1.274(3)	1.282(3)
O(23)–C(23)	1.374(4)	1.366(4)	O(22)–C(2)	1.275(2)	1.279(5)	1.272(3)	1.271(3)
O(23)–C(27)	1.428(4)	1.416(4)	O(23)–C(23)	1.368(2)	1.368(5)	1.366(3)	1.365(3)
O(24)–C(24)	1.360(4)	1.370(4)	O(23)–C(27)	1.436(2)	1.435(5)	1.436(3)	1.443(3)
O(31)–C(3)	1.277(4)	1.277(4)	O(24)–C(24)	1.367(2)	1.370(4)	1.360(3)	1.367(3)
O(32)–C(3)	1.270(4)	1.269(4)	O(31)–C(3)	1.283(2)	1.288(5)	1.282(3)	1.279(3)
O(33)–C(33)	1.371(4)	1.366(4)	O(32)–C(3)	1.272(2)	1.275(4)	1.266(3)	1.270(3)
O(33)–C(37)	1.425(4)	1.416(4)	O(33)–C(33)	1.369(2)	1.375(4)	1.363(3)	1.366(3)
O(34)–C(34)	1.364(4)	1.365(4)	O(33)–C(37)	1.440(2)	1.438(5)	1.442(3)	1.445(3)
O(11)–C(1)–O(12)	123.8(3)	124.1(3)	O(34)–C(34)	1.372(3)	1.380(5)	1.372(3)	1.360(3)
O(22)–C(2)–O(21)	120.7(3)	120.1(3)	O(11)–C(1)–O(12)	119.7(1)	119.3(3)	119.7(2)	118.9(2)
O(32)–C(3)–O(31)	120.5(3)	120.9(3)	O(22)–C(2)–O(21)	119.4(2)	119.9(3)	119.5(2)	119.1(2)
			O(32)–C(3)–O(31)	119.2(1)	117.9(4)	119.2(2)	119.3(2)

Symmetry transformations used to generate equivalent atoms: (i) $-x+1, -y+1, -z+1$ (ii) $-x, -y+1, -z+1$, for **1** and **2** and (iii) $-x, -y, -z$ for **3, 4, 5** and **6**.

significantly the O–C–O angles and bond distances. The angles are 123.8(3)°, 120.5(3)° for **1** and 124.1(3)°, 120.9(3)° for **2** in bridging group and 120.7(3)° for **1** and 120.1(3)° for **2** in chelating groups. The phenyl rings are nearly planar. The carboxylate groups in the structure are rotated from the phenyl ring by 14.25(5)°, 4.96(2)° and 36.05(2)° for **1** and 14.46(5)°, 4.96(2)° and 35.76(2)° for **2**, the smallest value is for chelating carboxylate.

The structures of praseodymium(III) and neodymium(III) 4-hydroxy-3-methoxybenzoates are stabilized by the system of interchain and intrachain hydrogen bonds. Chains are connected via hydrogen bonds where O(14) is the proton acceptor and donor, O(1)–H(2)⋯O(14) and O(14)–H(14)⋯O(31), respectively. O(14) is also engaged in intrachain hydrogen bonds as the proton acceptor. The water molecules take part in hydrogen bonds only as proton donors. The proton acceptors in this structure are oxygen atoms of carboxylates and hydroxyl groups. Hydrogen bond geometry is given in table 3.

Polycrystalline complexes of terbium(III) and holmium(III) are also hexahydrates while polycrystalline samarium(III) compound is tetrahydrate. Tetrahydrate samarium(III) compound crystallizes in monoclinic crystal system $a=9.78$ Å, $b=16.54$ Å, $c=8.26$ Å and $\beta=91.4^\circ$, elemental cell volume is 1335.8 Å³. The figure of merit F_N [19] for the powder data is $F_{30}=12.0(0.0301, 859)$. The structure refinement was performed with 30 reflections. We also characterized

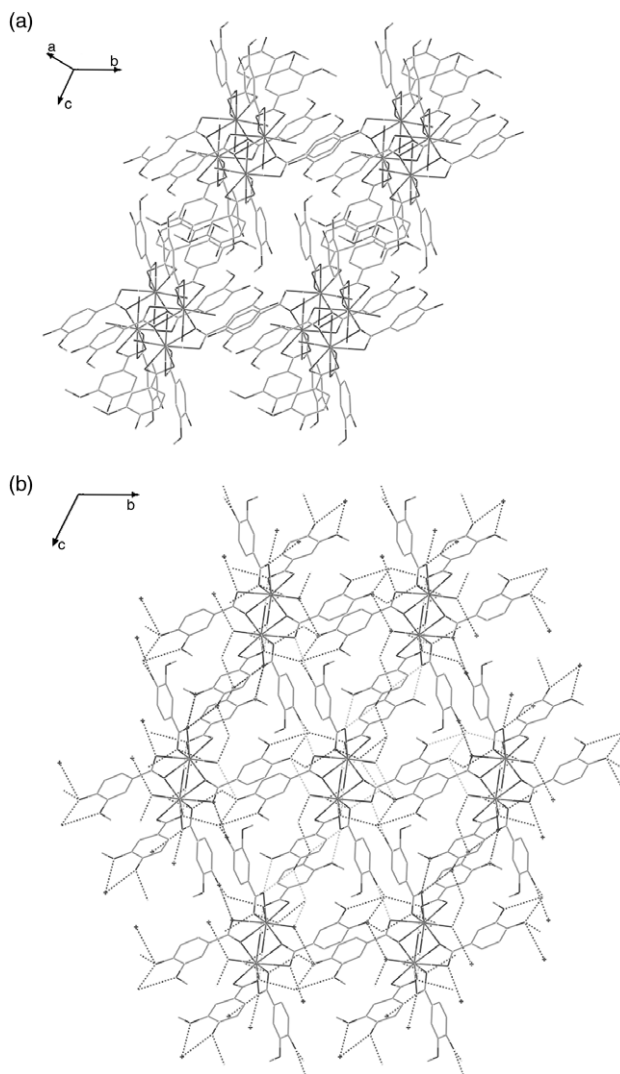


Figure 4. (a) Crystal packing of $[\text{Ln}_2(\text{C}_8\text{H}_7\text{O}_4)_6(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ complexes along the a axis; (b) Hydrogen-bonding interactions between dimeric units (hydrogen bonds are indicated by dotted lines). Uncoordinated water and all hydrogen atoms are omitted for clarity.

refined from all 29 reflections by least-squares, are $a = 11.16 \text{ \AA}$, $b = 11.65 \text{ \AA}$, $c = 12.57 \text{ \AA}$ and $\alpha = 104.7^\circ$, $\beta = 101.9^\circ$, $\gamma = 108.0^\circ$, $V = 1489.2 \text{ \AA}^3$. The figure of merit F_N [19] for the powder data is $F_{29} = 3.3(0.0152, 584)$. The other studied compound, holmium(III) 4-hydroxy-3-methoxybenzoate, also crystallizes in the triclinic crystal system. The holmium(III) 4-hydroxy-3-methoxybenzoate cell parameters are: $a = 11.34 \text{ \AA}$, $b = 11.59 \text{ \AA}$, $c = 12.02 \text{ \AA}$ and $\alpha = 95.8^\circ$, $\beta = 90.7^\circ$, $\gamma = 112.9^\circ$ and elemental cell volume is 1446.3 \AA^3 . The figure of merit F_N [19] for the powder data is $F_{30} = 8.1(0.0223, 166)$. The structure refinement was performed with 71 reflections.

We obtained single crystals of samarium(III) (3), europium(III) (4), terbium(III) (5) and holmium(III) (6) compounds, which form a second isostructural group.

Table 4. Hydrogen bond lengths (Å) and angles (°) for $[\text{Ln}(\text{C}_8\text{H}_7\text{O}_4)_6(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$, where Ln = Sm, Tb, Eu and Ho.

D-H...A	3			4			5			6		
	D-H	H...A	$\angle\text{DH}\dots\text{A}$	D-H	H...A	$\angle\text{DH}\dots\text{A}$	D-H	H...A	$\angle\text{DH}\dots\text{A}$	D-H	H...A	$\angle\text{DH}\dots\text{A}$
O(1W)-H(1W)...	0.82(3)	1.87(3)	2.690(2)	0.92(5)	1.77(5)	2.677(4)	0.75(4)	1.93(5)	2.680(3)	0.75(5)	1.94(5)	2.676(3)
O(1W)-H(2W)...	0.77(3)	2.27(3)	3.015(2)	0.77(5)	2.29(6)	3.033(4)	0.79(4)	2.27(4)	3.028(3)	0.81(5)	2.26(5)	3.037(3)
O(2W)-H(3W)...	0.81(3)	1.86(3)	2.674(2)	0.82(6)	1.88(7)	2.674(5)	0.76(4)	1.92(4)	2.680(3)	0.82(4)	1.87(5)	2.682(3)
O(2W)-H(4W)...	0.78(3)	1.94(3)	2.711(2)	0.76(5)	1.99(5)	2.714(4)	0.73(4)	1.99(4)	2.707(2)	0.83(4)	1.89(4)	2.707(3)
O(14)-H(14)...	0.77(3)	2.00(3)	2.715(2)	0.70(5)	2.10(5)	2.737(4)	0.77(3)	2.00(3)	2.727(2)	0.72(4)	2.06(5)	2.717(3)
O(14)-H(14)...	0.77(3)	2.24(3)	2.665(2)	0.70(5)	2.25(5)	2.652(4)	0.77(3)	2.27(3)	2.666(2)	0.72(4)	2.24(4)	2.677(3)
O(24)-H(24)...	0.82(3)	2.05(3)	2.742(2)	0.73(5)	2.09(5)	2.748(4)	0.74(4)	2.12(4)	2.753(2)	0.77(4)	2.11(4)	2.767(3)
O(24)-H(24)...	0.82(3)	2.25(3)	2.681(2)	0.73(5)	2.35(5)	2.684(4)	0.74(4)	2.30(4)	2.683(2)	0.77(4)	2.30(4)	2.689(3)
O(34)-H(34)...	0.77(3)	1.93(3)	2.659(2)	0.89(6)	1.82(6)	2.652(4)	0.84(4)	1.85(4)	2.651(3)	0.85(4)	1.82(4)	2.644(3)
O(34)-H(34)...	0.77(3)	2.33(3)	2.726(2)	0.89(6)	2.31(6)	2.717(4)	0.84(4)	2.31(3)	2.721(2)	0.85(4)	2.35(3)	2.721(3)
O(3W)-H(5W)...	0.77(3)	2.15(3)	2.884(2)	0.75(6)	2.16(6)	2.878(5)	0.84(1)	2.09(1)	2.878(3)	0.82(5)	2.09(5)	2.883(3)
O(3W)-H(6W)...	0.85(4)	2.31(4)	2.989(2)	0.89(6)	2.31(6)	3.060(6)	0.84(1)	2.37(2)	3.035(3)	0.84(5)	2.34(5)	3.028(4)
O(4W)-H(7W)...	0.80(3)	2.08(3)	2.846(2)	0.78(5)	2.09(5)	2.843(4)	0.78(4)	2.10(4)	2.842(2)	0.78(4)	2.12(4)	2.848(3)
O(4W)-H(8W)...	0.75(3)	2.10(3)	2.842(2)	0.75(5)	2.10(5)	2.842(4)	0.75(4)	2.09(4)	2.839(2)	0.78(4)	2.06(4)	2.834(3)
O(5W)-H(9W)...	0.94(4)	1.90(4)	2.815(2)	0.91(7)	1.92(7)	2.813(4)	0.86(5)	2.04(5)	2.827(3)	0.88(4)	1.99(4)	2.835(3)
O(5W)-H(10W)...	0.85(3)	1.92(3)	2.722(2)	0.90(8)	1.82(8)	2.721(5)	0.84(4)	1.88(4)	2.724(3)	0.93(5)	1.81(5)	2.720(3)
O(6W)-H(11W)...	0.98(4)	1.84(4)	2.798(2)	0.81(6)	1.99(6)	2.800(4)	0.80(4)	2.00(5)	2.800(2)	0.88(4)	1.93(4)	2.788(3)
O(6W)-H(12W)...	1.01(4)	1.94(4)	2.883(2)	0.84(6)	2.07(6)	2.870(4)	0.81(5)	2.11(5)	2.880(3)	0.83(5)	2.12(5)	2.884(3)

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y, -z$; (ii) $-x, -y, -z + 1$; (iii) $x, y, -1, z$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x - 1, y, z + 1$; (vi) $x - 1, y, z - 1$; (vii) $-x, -y + 1, -z$; (viii) $-x + 1, -y + 1, -z$.

Single crystals indicate that during recrystallization crystal units changed and are isostructural. The crystal structures of hexahydrated complexes consist of $[\text{Ln}_2(\text{C}_8\text{H}_7\text{O}_4)_6(\text{H}_2\text{O})_4]$ molecules (figure 3) and solvate water molecules. The metal centres are linked by two carboxylate groups of 4-hydroxy-3-methoxybenzoate ligands. The coordination environment of Ln ions are the same; coordinated with nine oxygen atoms in which seven oxygen atoms come from the carboxylate ligands and the other two from coordinated water. The Ln–O_{carboxylate} distances fall in the range: 2.398(1)–2.704(1) Å for samarium, 2.386(3)–2.644(3) Å for erbium, 2.357(2)–2.702(2) Å for terbium and 2.329(2)–2.700(2) Å for holmium (table 2). The La–O_{aqua} bond lengths are 2.412(1) Å, 2.428(1) Å for **3**; 2.400(3) Å, 2.402(3) Å for **4**; 2.358(2) Å, 2.380(2) Å for **5** and 2.336(2), 2.355(2) for **6**. The carboxylate groups which bind two lanthanide ions are tridentate bridging–chelating. In this structure there are also bidentate chelating ligands. The coordination modes of carboxylate in these compounds do not influence the O–C–O angle, 119.7(1)°, 119.4(2)°, 119.2(1)° for **3**; 119.3(3)°, 119.9(3)°, 117.9(4)° for **4**; 119.7(2)°, 119.5(2)°, 119.2(2)° for **5** and 118.9(2)°, 119.2(2)°, 119.3(2)° for **6**. The carboxylate groups are rotated from the aromatic ring by 7.5(3)°, 6.0(2)°, 16.1(3)° for **3**, 7.5(3)°, 6.0(1)°, 16.2(2)° for **4**; 7.5(4)°, 6.5(2)°, 15.2(3)° for **5** and 6.9(4)°, 6.8(4)°, 15.9(3)° for **6**, the highest values are for dihedral angles of bridging–chelating carboxylate groups.

Dinuclear units are linked by hydrogen bonds to form a three dimensional structure, figure 4. The water molecules and the hydroxy group of 4-hydroxy-3-methoxybenzoate ligands are proton donors while oxygen atoms of carboxyl groups as well as lattice water molecules are proton acceptors. Each coordinated water molecule O1w and O2w is involved in two hydrogen bonds, whereas lattice water molecules form three (O3W, O4W and O6W) and four (O5W) hydrogen bonds. Hydrogen bond geometry is listed in table 4.

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition numbers 607152, 607153, 610416, 610417, 610418 and 630680 (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

References

- [1] C.N.R. Rao, S. Natarajan, R. Vaidyanathan. *Angew. Chem. Int. Ed.*, **43**, 1466 (2004).
- [2] Y. Song, B. Yan, Z. Chen. *J. Coord. Chem.*, **57**, 1413 (2004).
- [3] M. Andjelković, J. Van Camp, B. De Meulenaer, G. Depaemelaere, C. Socaciu, M. Verloo, R. Verhe. *Food Chem.*, **98**, 23 (2006).
- [4] Z. Zhou, K. Robards, S. Helliwell, C. Blanchard. *Food Chem.*, **87**, 401 (2004).
- [5] K. Lirdprapamongkol, H. Sakurai, N. Kawasaki, M.-K. Choo, Y. Saitoh, Y. Aozuka, P. Singhirunnusorn, S. Ruchirawat, J. Svasti, I. Saiki. *Eur. J. Pharm. Sci.*, **25**, 57 (2005).
- [6] D. Vulpius, G. Geipel, L. Baraniak, G. Bernhard. *Spectrochim. Acta A*, **63**, 603 (2006).
- [7] K. Zhou, J.-J. Yin, L. Yu. *Food Chem.*, **95**, 446 (2006).
- [8] K. Robards, P.D. Prenzler, G. Tucker, P. Swatsitang, W. Glover. *Food Chem.*, **66**, 401 (1999).
- [9] S. McDonald, P.D. Prenzler, M. Antolovich, K. Robards. *Food Chem.*, **73**, 73 (2001).

- [10] F. Natella, M. Nardini, M. Di Felice, C. Scaccini. *J. Agric. Food Chem.*, **47**, 1453 (1999).
- [11] C.-T. Yeh, G.-C. Yen. *J. Agric. Food Chem.*, **51**, 1474 (2003).
- [12] A.M. El-Toni, S. Yin, T. Sato. *Mater. Chem. Phys.*, **89**, 154 (2005).
- [13] A. Kula. *J. Therm. Anal. Cal.*, **81**, 381 (2005).
- [14] Kuma Diffraction. KM-4 CCD Software: version 1.171. KUMA Diffraction Instruments GmbH, Poland (1995–1999).
- [15] G.M. Sheldrick. *Acta Cryst.*, **A46**, 467 (1990).
- [16] G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).
- [17] G.M. Sheldrick. *SHELXL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
- [18] P.E. Werner. *TREOR, Trial and Error Program for Indexing of Unknown Powder Patterns*, University of Stockholm, Stockholm, Sweden (1984).
- [19] G.S. Smith, R.I. Snyder. *J. Appl. Cryst.*, **12**, 60 (1979).
- [20] R.C. Mehrota, R. Bohra. *Metal Carboxylates*, Academic Press, London (1983).
- [21] J.G. Mao, H.J. Zhang, J.Z. Ni, S.B. Wang, T.C.W. Mak. *Polyhedron*, **18**, 1519 (1999).
- [22] P.R. Wei, Q. Li, W.P. Leung, T.C.W. Mak. *Polyhedron*, **16**, 897 (1997).