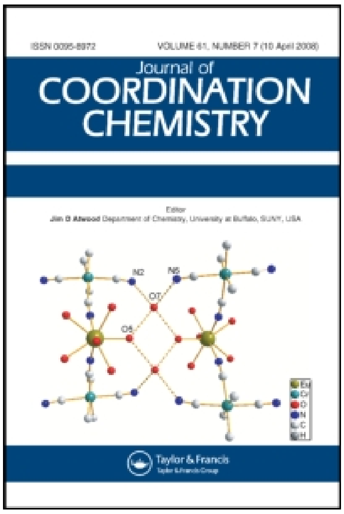

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CRYSTAL STRUCTURE OF THE ISOMORPHOUS COMPLEXES TETRAAQUABIS(2,6-DIHYDROXY-BENZOATO-O)(2,6-DIHYDROXY-BENZOATO-O,O)TERBIUM(III) AND HOLMIUM(III) DIHYDRATE

T. Glowiak[a]; W. Brzyska[b]; A. Kula[b]; Z. Rzaczynska[a]
[a] Faculty of Chemistry, University of Wroclaw, Wroclaw, Poland [b] Department of General Chemistry, Marie Curie Sklodowska University, Lublin, Poland

To cite this Article Glowiak, T. , Brzyska, W. , Kula, A. and Rzaczynska, Z.(1999) 'CRYSTAL STRUCTURE OF THE ISOMORPHOUS COMPLEXES TETRAAQUABIS(2,6-DIHYDROXY-BENZOATO-O)(2,6-DIHYDROXY-BENZOATO-O,O)TERBIUM(III) AND HOLMIUM(III) DIHYDRATE', Journal of Coordination Chemistry, 48: 4, 477 — 486

To link to this Article: DOI: 10.1080/00958979908023587

URL: http://dx.doi.org/10.1080/00958979908023587

J. Coord. Chem., 1999, Vol. 48, pp. 477–486
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

CRYSTAL STRUCTURE OF THE ISOMORPHOUS COMPLEXES TETRAAQUABIS(2,6-DIHYDROXY-BENZOATO-*O*)(2,6-DIHYDROXY-BENZOATO-*O,O*)TERBIUM(III) AND HOLMIUM(III) DIHYDRATE

T. GŁOWIAK[a], W. BRZYSKA[b], A. KULA[b] and
Z. RZĄCZYŃSKA[b,*]

[a]*Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland;*
[b]*Department of General Chemistry, Marie Curie Skłodowska University,*
20-031 Lublin, Poland

(Received 12 October 1998)

The structures of isomorphic Tb(III) and Ho(III) complexes with 2,6-dihydroxybenzoic acid of formula $[Tb(C_7H_5O_4)_3 \cdot 4H_2O] \cdot 2H_2O$ and $[Ho(C_7H_5O_4)_3 \cdot 4H_2O] \cdot 2H_2O$ has been determined by X-ray diffraction and refined to a residual $R = 0.030$ for 5376 observed reflections and $R = 0.0284$ for 5660 observed reflections, for Tb(III) and Ho(III) complexes, respectively. Crystals are triclinic, space group $P\bar{1}$ with $a = 10.748(2)$, $b = 11.309(2)$, $c = 12.452(2)$ Å, $\alpha = 82.28(3)$, $\beta = 73.05(5)$, $\gamma = 68.27(3)°$ for Tb(III) and $a = 10.731(2)$, $b = 11.269(2)$, $c = 12.436(2)$ Å, $\alpha = 82.25(3)$, $\beta = 72.92(3)$, $\gamma = 68.46(3)°$ for Ho(III).

In the structure of these monomeric complexes the metal ions are coordinated by oxygen atoms of one bidentate chelating and two monodentate carboxylate groups and four molecules of water. Tb–O distances are in the range 2.323(3)–2.506(3) Å and Ho–O 2.297(3)–2.486(3) Å. The crystal structure, consisting of discrete units of neutral complexes with two molecules of water of crystallization is stabilized by intra- and intermolecular hydrogen bonds.

Keywords: Terbium(III); holmium(III); 2,6-dihydrobenzoate; crystal structure

---

[*] Corresponding author.

INTRODUCTION

Interaction of hydroxybenzoic acid with common metal ions is of particular interest for a basic understanding of metal complexation in the environment. Soil organic matter consists of polymeric molecules, referred to as humic and fulvic acids, whose cores contain aromatic nuclei bearing carboxylic and phenolic groups. Hydroxybenzoic acids are useful simple models to investigate the ligand behaviour of the soil organic matter.[1,2] 2,6-Dihydroxybenzoic acid, with a great diversity of hydrogen bond formation,[3] binds metal ions very efficiently. Complexes of Mn(II), Fe(III), Co(II), Ni(II), Zn(II) and Cu(II) were obtained.[2,4] Structure of 2,6-dihydroxybenzoates of Cu(II), Zn(II),[2] Ag(I),[5,6] Pb(II),[7] UO_2(II)[8] have been determinated. The simultaneous presence three donors in the ligand which may participate in metal ion binding leads to a great diversity of coordination models and in most cases polynuclear species. In spite of the fact that lanthanides do not occur in natural biomolecules, many investigations in solution as well as in the solid state on their interaction with organic acids and simple peptides have been carried out. Lanthanide(III) ions possess unique properties which make them valuable for investigation of more complicated biological systems, especially in the determination of the nature of calcium-containing proteins. Complexes of La(III), Pr(III), Nd(III), Sm(III) and Gd(III) with 2,6-dihydroxybenzoic acid were prepared in the solid state as $Ln(C_7H_5O_4)_3 \cdot nH_2O$ and their properties studied.[9] Here we report the structures of the isomorphous Tb(III) and Ho(III) complexes.

EXPERIMENTAL

Synthesis

The complexes of Tb(III) and Ho(III) were prepared by adding a solution of ammonium 2,6-dihydroxybenzoate (pH 4.4–5.0) to hot solutions of separate lanthanide chlorides and crystallization at room temperature by the method described in a previous paper.[10] The complexes gave satisfactory analyses.

X-ray Structure Determination

Preliminary Weisenberg photographs gave the crystal system and approximate unit cell dimensions. Crystallographic data and refinement procedures are given in Table I. The data were corrected for Lorentz and polarization effects. The structures were solved by the heavy atom method using SHELXS-86[11] and refined by full-matrix least-squares methods using SHELXL-93.[12] H-Atoms of water molecules were located from a difference Fourier map. The other hydrogen atoms were placed in geometrically calculated positions with isotropic temperature factors taken as being 1.2 U_{eq} of the neighbouring heavier atoms. Afterwards, positional parameters were calculated in riding mode with U_{iso} fixed. Several cycles of refinement of coordinates and anisotropic thermal parameters for non-hydrogen atoms reduced the R value to 0.030 for the Tb(III) and 0.028 for the Ho(III) complex. Scattering factors were those incorporated in SHELXL-93. Final

TABLE I Crystal data and summary of intensity data collection and structure refinement

Formula	$C_{21}H_{27}O_{18}Tb$	$C_{21}H_{27}O_{18}Ho$
M_r	726.35	732.36
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Temp. °C	23	22
Cell constants	50 reflections, $15.7 < \theta < 22.0$	50 reflections, $15.0 < \theta < 22.0$
a, Å	10.748(2)	10.731(2)
b, Å	11.309(2)	11.269(2)
c, Å	12.452(2)	12.436(2)
α, °	82.28(3)	82.25(3)
β, °	73.05(3)	72.92(3)
γ, °	68.27(3)	68.46(3)
Cell volume, Å^3	1344.3(4)	1336.5(4)
Z	2	2
$F(000)$	724	728
Radiation, λ (Å)	Mo Kα, 0.71069	Mo Kα, 0.71069
D_c, g · cm^{-3}	1.794	1.820
D_m (flotation $CCl_4/C_2H_4Br_2$) g cm^{-3}	1.80	1.82
μ_{calc}, cm^{-1}	27.14	30.44
Crystal size, mm	$0.12 \times 0.15 \times 0.15$	$0.15 \times 0.15 \times 0.15$
Scan width	$1.2 + 0.35 \tan\theta$	$1.2 + 0.35 \tan\theta$
No. of standard reflections	3 (100 ref.)	3 (100 ref.)
Decay of standards	< 3%	< 3%
Reflection measured	6198	6152
2θ range, deg	4.2–55.2	4.2–55.2
Range of h, k, l	$0 \rightarrow 13$, $-13 \rightarrow 14$, $-15 \rightarrow 16$	$0 \rightarrow 13$, $-13 \rightarrow 14$, $-15 \rightarrow 16$
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of observed reflections	5376	5660
Weights* (a, b, f)	0.0456, 1.8904, 1/3	0.0546, 1.2083, 1/3
GOF	1.064	1.089
$R_1 = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum(\lvert F_o\rvert)$	0.0302	0.0284
$wR_2 = [\sum w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2/\sum w\lvert F_o^2\rvert^2]^{1/2}$	0.0793	0.0805
Function minimized	$\sum w(\Delta F^2)^2$	$\sum w(\Delta F^2)^2$
Largest diff. peak and hole (e Å^{-3})	1.351, −0.923	1.516, −1.570

*$w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$ where $P = [f \cdot \text{Max. of } (0 \text{ or } F_o^2) + (1 - f) \cdot F_c^2]$.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for the Tb complex

	x/a	y/b	z/c	U_{eq}
Tb	0.20161(1)	0.25099(1)	0.16629(1)	0.02623(6)
O(11)	0.2970(4)	0.1432(3)	−0.0121(2)	0.0427(7)
O(12)	0.2172(3)	0.3506(3)	−0.0273(2)	0.0429(7)
O(13)	0.4128(5)	0.0083(3)	−0.1854(3)	0.0618(10)
O(14)	0.2636(4)	0.4616(3)	−0.2200(3)	0.0663(11)
O(21)	0.1031(3)	0.4684(2)	0.1963(2)	0.0382(6)
O(22)	−0.0057(4)	0.4959(3)	0.3775(2)	0.0527(8)
O(23)	0.0981(4)	0.6605(3)	0.0630(2)	0.0459(7)
O(24)	−0.1144(4)	0.7142(3)	0.4590(2)	0.0477(8)
O(31)	0.2451(3)	0.0351(2)	0.2096(2)	0.0368(6)
O(32)	0.1504(4)	0.0129(3)	0.3926(2)	0.0515(8)
O(33)	0.3699(4)	−0.1603(3)	0.0871(3)	0.0517(8)
O(34)	0.1794(4)	−0.2035(3)	0.4844(3)	0.0572(9)
O(1)	0.4274(3)	0.2650(3)	0.0999(2)	0.0454(7)
O(2)	0.2921(3)	0.2438(3)	0.3236(2)	0.0435(7)
O(3)	0.0249(3)	0.2606(3)	0.3332(2)	0.0383(6)
O(4)	−0.0029(3)	0.2588(3)	0.1239(2)	0.0438(7)
O(5)	0.4355(3)	−0.2127(3)	−0.2653(3)	0.0542(8)
O(6)	0.2541(4)	0.7020(3)	−0.3067(3)	0.0535(8)
C(11)	0.3370(4)	0.2349(4)	−0.1957(3)	0.0349(8)
C(12)	0.4038(5)	0.1175(4)	−0.2472(4)	0.0433(9)
C(13)	0.4633(6)	0.1088(5)	−0.3619(4)	0.0547(12)
C(14)	0.4566(6)	0.2164(6)	−0.4250(4)	0.0607(14)
C(15)	0.3908(6)	0.3360(6)	−0.3791(4)	0.0586(13)
C(16)	0.3290(5)	0.3454(4)	−0.2639(3)	0.0430(9)
C(17)	0.2796(4)	0.2448(4)	−0.0734(3)	0.0339(8)
C(21)	−0.0054(4)	0.6794(3)	0.2622(3)	0.0321(7)
C(22)	0.0269(4)	0.7352(4)	0.1564(3)	0.0327(8)
C(23)	−0.0056(5)	0.8649(4)	0.1404(4)	0.0483(10)
C(24)	−0.0747(6)	0.9418(4)	0.2312(5)	0.0537(12)
C(25)	−0.1128(5)	0.8920(4)	0.3372(4)	0.0490(11)
C(26)	−0.0787(4)	0.7618(4)	0.3540(3)	0.0350(8)
C(27)	0.0317(4)	0.5395(4)	0.2818(3)	0.0354(8)
C(31)	0.2709(4)	−0.1734(4)	0.2859(3)	0.0337(8)
C(32)	0.3407(4)	−0.2308(4)	0.1823(4)	0.0377(8)
C(33)	0.3848(6)	−0.3611(4)	0.1737(5)	0.0537(12)
C(34)	0.3570(6)	−0.4357(4)	0.2680(5)	0.0602(14)
C(35)	0.2881(6)	−0.3831(4)	0.3726(5)	0.0543(12)
C(36)	0.2457(5)	−0.2523(4)	0.3813(4)	0.0415(9)
C(37)	0.2183(4)	−0.0331(3)	0.2984(3)	0.0327(8)

positional parameters for the non-hydrogen atoms and estimated standard deviations are listed in Tables II and III.

RESULTS AND DISCUSSION

The compounds represent the isomorphic group of lanthanide complexes from Gd(III) to Lu(III).[10] The structure of the monomeric terbium(III)

TABLE III Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for the Ho complex

	x/a	y/b	z/c	U_{eq}^*
Ho	0.20019(1)	0.25106(1)	0.16707(1)	0.0263(6)
O(11)	0.2944(3)	0.1434(3)	−0.0096(2)	0.0417(6)
O(12)	0.2152(3)	0.3515(3)	−0.0248(2)	0.0433(6)
O(13)	0.4077(4)	0.0095(3)	−0.1839(3)	0.0623(9)
O(14)	0.2621(4)	0.4634(3)	−0.2183(3)	0.0677(10)
O(21)	0.1028(3)	0.4670(2)	0.1968(2)	0.0374(6)
O(22)	−0.0059(4)	0.4951(3)	0.3776(2)	0.0534(8)
O(23)	0.0989(3)	0.6580(3)	0.0616(2)	0.0463(7)
O(24)	−0.1123(3)	0.7139(3)	0.4586(2)	0.0494(7)
O(31)	0.2448(3)	0.0372(2)	0.2100(2)	0.0373(6)
O(32)	0.1507(4)	0.0130(3)	0.3923(2)	0.0516(8)
O(33)	0.3713(4)	−0.1567(3)	0.0863(2)	0.0521(8)
O(34)	0.1818(4)	−0.2055(3)	0.4835(3)	0.0590(9)
O(1)	0.4247(3)	0.2628(3)	0.1010(2)	0.0462(7)
O(2)	0.2902(3)	0.2446(3)	0.3222(2)	0.0443(7)
O(3)	0.0261(3)	0.2594(3)	0.3330(2)	0.0377(5)
O(4)	−0.0021(3)	0.2597(3)	0.1252(2)	0.0442(6)
O(5)	0.4380(3)	−0.2133(3)	−0.2654(3)	0.0578(8)
O(6)	0.2545(4)	0.7025(3)	−0.3066(3)	0.0545(8)
C(11)	0.3347(4)	0.2360(4)	−0.1943(3)	0.0354(7)
C(12)	0.4002(5)	0.1177(4)	−0.2448(3)	0.0447(9)
C(13)	0.4599(6)	0.1107(6)	−0.3603(4)	0.0589(12)
C(14)	0.4531(6)	0.2184(6)	−0.4237(4)	0.0634(14)
C(15)	0.3879(5)	0.3368(6)	−0.3776(4)	0.0598(13)
C(16)	0.3276(4)	0.3462(4)	−0.2631(3)	0.0442(9)
C(17)	0.2778(4)	0.2442(3)	−0.0715(3)	0.0342(7)
C(21)	−0.0042(4)	0.6783(3)	0.2611(3)	0.0314(7)
C(22)	0.0293(4)	0.7334(3)	0.1546(3)	0.0340(7)
C(23)	−0.0037(5)	0.8635(4)	0.1375(4)	0.0498(10)
C(24)	−0.0736(5)	0.9400(4)	0.2290(4)	0.0540(11)
C(25)	−0.1101(5)	0.8907(4)	0.3368(4)	0.0470(9)
C(26)	−0.0767(4)	0.7607(4)	0.3530(3)	0.0372(7)
C(27)	0.0328(4)	0.5389(3)	0.2809(3)	0.0338(7)
C(31)	0.2717(4)	−0.1728(3)	0.2850(3)	0.0333(7)
C(32)	0.3422(4)	−0.2289(4)	0.1810(4)	0.0392(8)
C(33)	0.3879(5)	−0.3607(4)	0.1706(5)	0.0547(11)
C(34)	0.3595(5)	−0.4347(4)	0.2647(5)	0.0600(13)
C(35)	0.2904(5)	−0.3825(4)	0.3693(5)	0.0558(12)
C(36)	0.2479(4)	−0.2537(4)	0.3804(3)	0.0415(8)
C(37)	0.2187(4)	−0.0328(3)	0.2982(3)	0.0335(7)

*$U_{eq} = \frac{1}{3}\sum_{ij} U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

complex is shown in Figure 1. Selected bond lengths and angles for both complexes are presented in Table IV.

The metal ion coordinates three 2,6-dihydroxybenzoate ligands (making the complex neutral) as well as four water molecules. The remaining two water molecules are in the external coordination sphere. Each metal ion is surrounded by eight oxygen atoms. One of organic ligands is bidentate and

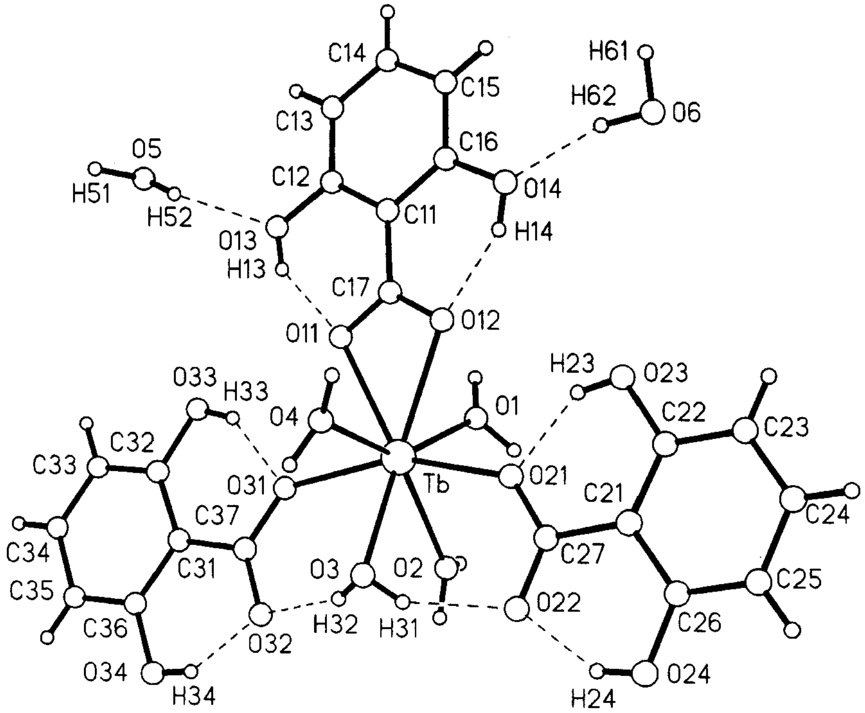

FIGURE 1 The molecular structure of $[Tb(C_7H_5O_4)_3 \cdot 4H_2O] \cdot 2H_2O$.

coordinates terbium by two oxygen atoms of the carboxylate group; the other 2,6-dihydroxybenzoate ligands are monodentate (carboxylate group). The remaining oxygen atoms of the carboxylate groups form hydrogen bonds with the O3 atom of one molecule of coordination water. The mode of coordination of the carboxylate group does not significantly influence the values of O–C–O angles. O–C–O angles in the carboxylate groups are 119.0(3) and 118.6(3)° in bidentate-chelating groups and from 119.8(3) to 123.2(3)° in monodentate carboxylate groups, in comparison to 117.8(2) and 117.3(4)° in the free acid and its monohydrate.[3] In monodentate carboxylate groups of known benzoate complexes are observed even larger O–C–O angles[13] of 126°. The oxygen atoms of hydroxylic groups do not take part in metal ion coordination.

The eight oxygen atoms around Tb(III) and Ho(III) atoms form the coordination polyhedron, which may be best represented by a dodecahedron for which the value of Δ_{dod} is 0.0443 Å^2 for terbium and 0.0399 Å^2 for the holmium complex, where $\Delta = d_i^2/8$ and d_i values are the distances between

TABLE IV Selected bond lengths (Å) and angles (°) with esd's in parentheses for the Tb(III) and Ho(III) complexes

	Ln = Tb	Ln = Ho
Ln–O(11)	2.438(3)	2.416(3)
Ln–O(12)	2.506(3)	2.486(3)
Ln–O(21)	2.323(3)	2.302(3)
Ln–O(31)	2.328(3)	2.297(3)
Ln–O(1)	2.383(3)	2.354(3)
Ln–O(2)	2.408(3)	2.380(3)
Ln–O(3)	2.354(3)	2.328(3)
Ln–O(4)	2.374(3)	2.343(3)
C(17)–O(11)	1.276(5)	1.269(4)
C(17)–O(12)	1.256(5)	1.271(4)
C(27)–O(21)	1.291(4)	1.278(4)
C(27)–O(22)	1.239(5)	1.249(4)
C(37)–O(31)	1.284(4)	1.286(4)
C(37)–O(32)	1.250(5)	1.247(4)
C(12)–O(13)	1.350(5)	1.335(5)
C(16)–O(14)	1.344(6)	1.355(6)
C(22)–O(23)	1.386(5)	1.382(4)
C(26)–O(24)	1.348(5)	1.347(5)
C(32)–O(33)	1.362(5)	1.363(5)
C(36)–O(34)	1.352(6)	1.347(5)
C(17)–C(11)	1.469(5)	1.470(5)
C(27)–C(21)	1.487(5)	1.477(5)
C(37)–C(31)	1.488(5)	1.481(5)
O(11)–C(17)–O(12)	119.0(3)	118.6(3)
O(21)–C(27)–O(22)	119.8(3)	122.2(3)
O(31)–C(37)–O(32)	123.2(3)	122.4(3)

the real position of the *i*-th atom and the corresponding vertex in the ideal, least-squares-fitted polyhedron. The oxygen atoms O11, O12 and O2, O3 as well as O1, O4 and O21, O31 form tetrahedral peaks. Coordination of the metal ion does not cause changes in the geometry of anions. The phenyl rings form a planar system and the carboxylic groups are rotated from the ring plane by only 4.8(7), 2.9(1) and 3.0(1)° in the terbium(III) complex and 4.7(7), 3.0(1), and 2.8(1)° in the holmium(III) one. In known lanthanide carboxylates the carboxylates groups are rotated from the phenyl ring plane much more in polymeric[14] than in monomeric lanthanide benzoates.[15,16] The small value of phenyl ring carboxylate group rotation results from intramolecular hydrogen bond formation with participation of OH groups in 2,6 positions (Table V). In the Tb(III) and Ho(III) 2,6-dihydroxybenzoates the lanthanide ions do not lie exactly in the carboxylate group plane. Distances of the central ion from the carboxylate group plane of the bidentate ligand are 0.276(6) Å in terbium and 0.273(6) Å in the holmium complex but only 0.081(7)–0.016(7) Å for monodentate ligands in both

TABLE V Hydrogen bond lengths (Å) and bond angles (°)

D–H···A		Tb				Ho			
		D–H	H···A	D···A	∠D–H···A	D–H	H···A	D···A	∠D–H···A
O(13)–H(13)···O(11)		0.82	1.81	2.539(4)	148	0.82	1.81	2.538(4)	148
O(14)–H(14)···O(12)		0.82	1.82	2.558(4)	148	0.82	1.83	2.563(4)	149
O(23)–H(23)···O(21)		0.82	1.81	2.544(4)	147	0.82	1.81	2.542(4)	147
O(24)–H(24)···O(22)		0.82	1.78	2.516(4)	149	0.82	1.78	2.515(4)	148
O(33)–H(33)···O(31)		0.82	1.83	2.555(4)	147	0.82	1.82	2.546(4)	148
O(34)–H(34)···O(32)		0.82	1.78	2.508(4)	148	0.82	1.78	2.515(4)	148
O(1)–H(11)···O(5)	$(1-x, -y, -z)$	0.92	2.08	2.749(5)	128	0.97	2.05	2.742(5)	127
O(1)–H(12)···O(33)	$(1-x, -y, -z)$	0.91	1.83	2.729(4)	169	0.92	1.84	2.735(4)	165
O(2)–H(21)···O(24)	$(-x, 1-y, 1-z)$	0.90	1.92	2.804(4)	166	0.87	1.96	2.815(4)	166
O(3)–H(31)···O(22)		0.82	1.92	2.671(4)	151	0.87	1.86	2.664(4)	153
O(3)–H(32)···O(32)		0.72	2.06	2.728(4)	155	0.88	1.85	2.709(4)	166
O(4)–H(41)···O(6)	$(-x, 1-y, -z)$	0.94	1.99	2.909(5)	174	0.84	2.07	2.903(5)	172
O(4)–H(42)···O(23)	$(-x, 1-y, -z)$	1.00	1.82	2.725(4)	150	0.97	1.78	2.731(4)	165
O(5)–H(51)···O(6)	$(x, -1+y, z)$	1.02	1.66	2.666(4)	168	1.03	1.65	2.670(4)	169
O(5)–H(52)···O(13)		0.83	1.98	2.716(4)	148	0.93	1.94	2.708(5)	133
O(6)–H(61)···O(34)	$(x, 1+y, -1+z)$	1.00	1.93	2.897(5)	163	0.93	2.01	2.894(4)	158
O(6)–H(61)···O(3)	$(-x, 1-y, -z)$	1.00	2.58	2.980(4)	104	0.93	2.46	2.993(4)	117
O(6)–H(62)···O(14)		0.91	1.89	2.763(5)	160	0.90	1.97	2.751(5)	144

structures. That distance in other lanthanide benzoates is much larger, above 1 Å in a dysprosium complex.[17]

The coordination arrangement in the investigated complexes is similar to that of a neodymium(III) complex with 3,4-diaminobenzoic acid,[14] but its geometry is much more regular. In the terbium complex, Tb–O distances to the O11 and O12 oxygen atoms of chelating carboxylate group are 2.438(3) and 2.506(3) Å, respectively, and they are the longest Tb–O distances. The shortest Tb–O distances are to the O21 and O31 oxygens (2.323(3); 2.328(3) Å) belonging to monodentate carboxylate groups. Tb–O distances to the oxygens of four water molecules O(1), O(2), O(3) and O(4) are in the range 2.354(3)–2.408(3) Å. In the isomorphous holmium(III) complex Ho–O distances are smaller by 0.02–0.03 Å due to the smaller ionic radius of the holmium(III) ion.

Hydrogen atoms of all water molecules are linked in intra- and intermolecular hydrogen bonds forming a stable network (Table V). Coordinated water O2 participates only in one hydrogen bond O24 at $-x, 1-y, 1-z$, but water molecule O1, O3, O4 atoms form two hydrogen bonds each as proton donors and O3 additionally acts as proton acceptor. In the crystal structure of the investigated complexes there are two molecules of crystallization water O(5), O(6) hydrogen bonded with a hydroxyl group of the chelating ligand. Additionally, water molecule O5 is hydrogen bonded with O6 at $x, -1+y, z$ and O6 with O3 at $-x, 1-y, -z$ and with O34 at $x, 1+y, -1+z$. The oxygen atoms of three carboxylate groups form hydrogen bonds with hydroxylic groups forming six-membered rings but uncoordinated O22 and O32 oxygen atoms additionally bind the same molecule of coordinated water, O3.

Supplementary Material

List of H atom positions, thermal parameters and observed and calculated structure factors are available from the authors upon request.

References

[1] T. Głowiak, H. Kozłowski, L. Strinna Erre, B. Gulinati, G. Micera, A. Pozzi and S. Bruni, *J. Coord. Chem.*, **25**, 75 (1992).
[2] F. Cariati, L. Erre, G. Micera, A. Panzanelli, G. Ciani and A. Sironi, *Inorg. Chim. Acta*, **80**, 57 (1983).
[3] M. Gdaniec, M. Gilski and G.S. Denisov, *Acta Crystallogr.*, **C50**, 1622 (1994).
[4] G. Micera, P. Pin, L. Strinna Erre and F. Cariati, *Thermochim. Acta*, **84**, 175 (1985).
[5] G. Smith, C.H.L. Kennard and T.C.W. Mak, *Z. Kristallogr.*, **184**, 275 (1988).
[6] T.C.W. Mak, G. Smith and C.H.L. Kennard, *Z. Kristallogr.*, **207**, 33 (1993).

[7] T. Głowiak, H. Kozłowski, E.L. Strinna Erre, G. Micera and B. Gulinati, *Inorg. Chim. Acta*, **202**, 43 (1992).

[8] G. Micera, L. Strinna Erre, F. Cariati, D.A. Clemente, A. Marzotto and G. Ciani, *Inorg. Chim. Acta*, **109**, 135 (1985).

[9] A.S. Frazal Mahidi and V.R. Rao, *J. Inorg. Nucl. Chem.*, **37**, 1041 (1975).

[10] W. Brzyska, A. Kula, Z. Rzączyńska and J. Jaroniec, *Polish J. Chem.*, **72**, 2524 (1998).

[11] G.M. Sheldrick, *SHELXL86. Program for Crystal Structure Solution*, University of Gottingen, Germany (1986).

[12] G.M. Sheldrick, *SHELXL96. Program for Refinement of Crystal Structures*, University of Gottingen, Germany (1994).

[13] Z. Rzączyńska, W. Brzyska, R. Mrozek, W. Ożga and T. Głowiak, *J. Coord. Chem.*, **43**, 321 (1998).

[14] Z. Rzączyńska, A.N. Sobolev and V.K. Belsky, *Polish J. Chem.*, **68**, 1179 (1994).

[15] Z. Rzączyńska and V.K. Belsky, *Polish J. Chem.*, **68**, 369 (1994).

[16] Z. Rzączyńska, V.K. Belsky and V.E. Zavodnik, *Polish J. Chem.*, **68**, 1639 (1994).

[17] M.S. Khiyalov, I.R. Amiraslanov, K.S. Mamedov and E.M. Movsumov, *Koord. Khim.*, **7**, 445 (1981).