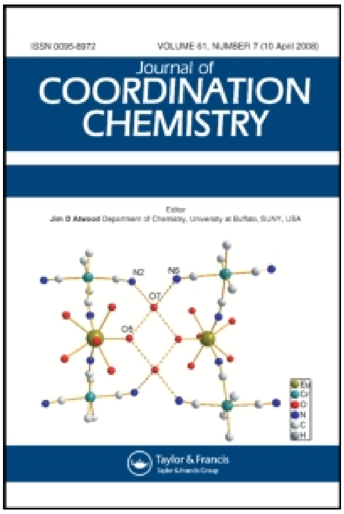

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CRYSTAL STRUCTURE OF DIMERIC OCTAAQUABIS(μ-2,6-DICHLOROBENZOATO O,O,O′) TETRAKIS (2,6-DICHLOROBENZOATO O) DILANTHANIDE(III) DIHYDRATES

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New lanthanide(III) complexes of formula $[Ln_2(C_7H_3O_2Cl_2)_6 \cdot 8H_2O] \cdot 2H_2O$, where Ln = Ce(III), Pr(III), Nd(III), Tb(III) and Dy(III) crystallize in the triclinic system, space group $P\bar{1}$. The structure of the isomorphous complexes has been determined using X-ray diffraction methods. The two lanthanide(III) ions in the molecule are held together in a dimeric unit by two carboxylate groups of the organic ligands and each lanthanide(III) ion is further bonded to two 2,6-dichlorobenzoate ligands and four water molecules. Two molecules of water are in the outer coordination sphere $Ln—O_{(carboxylate)}$ distances are in the range 2.323(3)–2.986(5), $Ln—O_{(water)}$ 2.328(5) to 2.539(2) and Ln—Ln 4.420(1) to 4.625(1) Å.

Keywords: lanthanides; 2,6-dichlorobenzoic acid; complexes; X-ray structure

INTRODUCTION

The majority of structural data on chlorobenzoates refer to monochlorobenzoates of transition metals, and only a few structural data referring to dichlorobenzoates have been published.[1–3] In the known chlorobenzoate complexes, coordination of metal ions occurs by the carboxylic oxygen atoms. The carboxylate group of organic ligands may act in a different way in coordination with lanthanide ions. When the carboxylate group is of the bidentatechelating or monodentate character, monomeric complexes are formed. A great variety of coordination modes

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is found in the case of dimeric or polymeric carboxylate complexes. Oxygen atoms of carboxylate groups may form bidentate *syn-syn*, *syn-anti*, *anti-anti* or terdentate chelating-bridging structures, which unite the metal ion in a dimer or polymer. The most common coordination number (8 or 9) in the dimeric or polymeric complexes is achieved by lanthanide ions through additional coordination of organic ligands or water molecules. The mode of coordination influences the Ln—Ln distance in dimeric or polymeric complexes. The smallest Ln—Ln distances, about 4Å, are observed when lanthanide(III) ions are connected by a few bi- or terdentate bridging carboxylate groups of the *syn-syn* type.[4] When the carboxylate bridges are *syn-anti* or *anti-anti*, the Ln—Ln distance increases to above 6Å.[5–7] The aim of the present study on a series of lanthanide 2,6-dichlorobenzoates was to investigate how 2,6-dichlorobenzoate ions are coordinated with the lanthanide ions and how the Ln—O and Ln—Ln bond lengths change with decreasing metal ionic radius in the lanthanide series.

EXPERIMENTAL

Crystals of 2,6-dichlorobenzoates of cerium(III), praseodymium(III), neodymium(III), terbium(III) and dysprosium(III) were obtained by recrystallization of the compounds described in a previous paper[8] from aqueous solutions. The crystals for measurement were cut from larger ones. Densities were measured by flotation in $CCl_4/C_2H_4Br_2$ mixtures. Approximate unit cell dimensions were determined from rotation and Weissenberg photographs. Resulting lattice constants and physical constants are summarized in Table I. The diffraction data were collected with MoK_{α}, graphite-monochromated radiation on a KUMA-4 diffractometer at 295 K. Reflections were measured under the conditions listed in Table I. Crystallographic data and refinement procedures are given also in Table I. Intensities were corrected for Lorentz and polarization effects, but not for extinction or absorption. Three selected reflections monitored in every 100 showed no significant variation during data collection. The structure determination was based on reflections with $I > 3\sigma(I)$. Structures were solved by the heavy-atom method using SHELXS-86[9] and refined by full-matrix least-squares methods using SHELXL-93[10] programs. H-atoms in the complex molecules were found from Fourier difference syntheses and kept fixed during refinement. Several cycles of refinement of the coordinates and anisotropic thermal parameters for non-hydrogen atoms led to final R values in the range 0.024 to 0.032. Final positional and thermal parameters for non-hydrogen atoms are given in Table II. Selected bond distances and angles are listed in Table III and the geometries of hydrogen bonds are given in Table V.

TABLE I Crystallographic data, structure refinement details and experimental conditions forcerium(III), praseodymium(III), neodymium(III), terbium(III) and dysprosium(III), 2,6-dichlorobenzoates: $[M_2(C_7H_3O_2Cl_2)_6 \cdot 8H_2O] \cdot 2H_2O$ (M = Ce, Pr, Nd, Tb, Dy) triclinic, space group $P\bar{1}$, Z = 1

M	*Ce*	*Pr*	*Nd*	*Tb*	*Dy*
F.W.	1600.36	1601.94	1608.60	1637.96	1645.12
a(Å)	11.335(2)	11.295(2)	11.265(2)	11.153(2)	11.125(2)
b(Å)	12.533(3)	12.504(3)	12.531(3)	12.631(3)	12.629(3)
c(Å)	12.972(3)	12.938(3)	12.898(3)	12.838(3)	12.794(3)
α(°)	111.30(3)	111.28(3)	111.33(3)	111.72(3)	109.10(3)
β(°)	114.82(3)	114.85(3)	114.77(3)	114.32(3)	114.19(3)
γ(°)	95.97(3)	95.90(3)	95.86(3)	95.60(3)	98.59(3)
V(Å^3)	1484.9(6)	1472.9(6)	1468.6(6)	1462.8(6)	1463.3(6)
D_c[Mg / m^3]	1.790	1.806	1.819	1.859	1.867
D_m [Mg / m^3]	1.80	1.80	1.82	1.86	1.86
abs.coeff. [mm^{-1}]	2.125	2.151	2.367	3.019	3.154
F (000)	786	788	790	800	802
crystal size [mm]	0.35 × 0.35 × 0.40	0.34 × 0.30 × 0.40	0.32 × 0.30 × 0.40	0.30 × 0.30 × 0.40	0.15 × 0.15 × 0.30
theta range [°]	2.02–26.07	2.03–27.56	2.04–25.05	2.06–25.05	2.05–23.60
refl.coll.	5534	6533	5194	5160	4056
refl.unique	4973	5799	4602	4706	3487
final *R*	0.0244	0.0245	0.0308	0.0312	0.0322
R_W	0.0654	0.0681	0.0793	0.0825	0.0923

TABLE II Fractional atomic coordinates (×10^4) for non-hydrogen atoms and temperature factors (Å^2×10^3) with esd' in parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	*Atom*	*x/a*	*y/b*	*z/c*	U_{eq}
Ce	834(1)	4603(1)	3674(1)	22(1)	Pr	834(1)	4600(1)	3674(1)	21(1)
Cll(11)	1829(1)	2815(1)	6940(1)	60(1)	Cl(11)	1832(1)	2821(1)	6942(1)	58(1)
Cl(12)	−2832(1)	1113(1)	2531(1)	95(1)	Cl(12)	−2837(1)	1126(1)	2534(1)	94(1)
Cl(21)	5203(1)	7493(1)	8902(1)	66(1)	Cl(21)	5187(1)	7476(1)	8897(1)	64(1)
Cl(22)	4314(1)	2907(1)	5769(1)	65(1)	Cl(22)	4309(1)	2893(1)	5755(1)	64(1)
Cl(31)	1268(1)	1787(2)	−246(1)	79(1)	Cl(31)	1291(1)	1801(2)	−236(1)	77
Cl(32)	−3712(1)	1173(1)	−702(1)	82(1)	Cl(32)	−3705(1)	1172(1)	−702(1)	80(1)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	*Atom*	*x/a*	*y/b*	*z/c*	U_{eq}
O(11)	466(3)	2617(2)	3829(2)	38(1)	O(11)	458(2)	2635(2)	3826(2)	36(1)
O(12)	−154(2)	3898(2)	5013(2)	30(1)	O(12)	−158(2)	3906(2)	5022(2)	29(1)
O(21)	2762(2)	5103(2)	5806(2)	35(1)	O(21)	2751(2)	5088(2)	5796(2)	34(1)
O(22)	4713(2)	5891(3)	5964(2)	48(1)	O(22)	4705(2)	5882(3)	5954(2)	47(1)
O(31)	−183(2)	2897(2)	1521(2)	37(1)	O(31)	−168(2)	2906(2)	1535(2)	36(1)
O(32)	−1179(3)	3370(2)	−62(2)	52(1)	O(32)	−1174(3)	3370(2)	−55(2)	53(1)
O(1)	2587(2)	3923(2)	3118(2)	43(1)	O(1)	2581(2)	3922(2)	3121(2)	41(1)
O(2)	−1751(2)	4046(2)	2552(2)	42(1)	O(2)	−1726(2)	4043(2)	2564(2)	40(1)
O(3)	131(3)	5440(2)	2122(2)	48(1)	O(3)	132(3)	5427(2)	2130(2)	47(1)
O(4)	2651(2)	6501(2)	4435(2)	42(1)	O(4)	2648(2)	6482(2)	4432(2)	40(1)
O(5)	2033(3)	7385(3)	2577(3)	58(1)	O(5)	2017(3)	7377(3)	2574(3)	56(1)
C(11)	−585(3)	1909(3)	4794(3)	33(1)	C(11)	−578(3)	1921(2)	4800(3)	30(1)
C(12)	189(4)	1836(3)	5904(3)	39(1)	C(12)	196(4)	1842(3)	5903(3)	37(1)
C(13)	−288(5)	974(4)	6180(4)	55(1)	C(13)	−287(5)	971(4)	6180(4)	54(1)
C(14)	−1572(6)	173(4)	5325(5)	65(1)	C(14)	−1563(5)	184(4)	5334(5)	63(1)
C(15)	−2377(5)	208(4)	4206(5)	63(1)	C(15)	−2374(5)	217(4)	4204(5)	63(1)
C(16)	−1858(4)	1078(3)	3956(4)	48(1)	C(16)	−1864(4)	1080(3)	3945(4)	47(1)
C(17)	46(3)	2866(2)	4524(3)	27(1)	C(17)	−47(3)	2878(2)	4528(2)	26(1)
C(21)	4821(3)	5171(3)	7429(3)	37(1)	C(21)	4810(3)	5154(3)	7419(3)	36(1)
C(22)	5415(3)	6089(4)	8664(3)	47(1)	C(22)	5401(3)	6080(4)	8662(3)	46(1)
C(23)	6172(5)	5913(5)	9710(4)	69(1)	C(23)	6169(4)	5907(5)	9712(4)	66(1)
C(24)	6338(5)	4801(6)	9522(5)	77(2)	C(24)	6337(5)	4803(6)	9528(5)	77(2)
C(25)	5770(5)	3877(5)	8330(5)	67(1)	C(25)	5766(5)	3863(5)	8323(5)	65(1)
C(26)	5013(4)	4067(4)	7286(4)	47(1)	C(26)	*5005(4)*	4058(4)	7276(4)	46(1)
C(27)	4048(3)	5412(3)	6311(3)	33(1)	C(27)	4034(3)	5397(3)	6298(3)	32(1)
C(31)	−1267(3)	1357(3)	−571(3)	33(1)	C(31)	−1247(3)	1365(3)	−561(3)	33(1)
C(32)	−373(4)	880(3)	−926(3)	45(1)	C(32)	−347(4)	885(3)	−918(3)	43(1)
C(33)	−739(6)	−279(4)	−1821(4)	66(1)	C(33)	−712(6)	−275(4)	−1811(4)	63(1)
C(34)	−2049(8)	−979(4)	−2393(5)	85(2)	C(34)	−2011(7)	−978(4)	−2386(4)	77(2)
C(35)	−2984(6)	−571(4)	−2082(4)	75(2)	C(35)	−2959(6)	−565(4)	−2072(4)	75(2)
C(36)	−2573(4)	612(3)	−1146(3)	50(1)	C(36)	−2563(4)	614(3)	−1151(3)	48(1)
C(37)	−839(3)	2652(3)	374(3)	32(1)	C(37)	−829(3)	2657(3)	384(3)	30(1)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	*Atom*	*x/a*	*y/b*	*z/c*	U_{eq}
Nd	836(1)	4598(1)	3674(1)	21(1)	Tb	868(1)	4594(1)	3628(1)	23(1)
Cl(11)	1833(1)	2825(1)	6943(1)	57(1)	Cl(11)	1799(2)	2853(1)	6960(1)	58(1)
Cl(12)	−2837(2)	1131(2)	2528(2)	92(1)	Cl(12)	−2847(2)	1167(2)	2490(2)	93(1)
Cl(21)	5175(1)	7462(1)	8893(1)	64(1)	Cl(21)	51 03(2)	7388(2)	8872(2)	65(1)
Cl(22)	4305(2)	2883(1)	5742(2)	64(1)	Cl(22)	4244(2)	2846(2)	5680(2)	63(1)
Cl(31)	1314(2)	1812(2)	−229(1)	75(1)	Cl(31)	1403(2)	1829(2)	−217(2)	76(1)
Cl(32)	−3694(2)	1172(2	698(2)	79(1)	Cl(32)	−3660(2)	1152(2)	−721(2)	80(1)
O(11)	455(3)	2649(2)	3827(3)	35(1)	O(11)	395(3)	2792(3)	3841(3)	35(1)
O(12)	−160(3)	3919(2)	5036(2)	30(1)	O(12)	−232(3)	3962(3)	5132(3)	34(1)
O(21)	2742(3)	5076(3)	5785(3)	34(1)	O(21)	2674(3)	5024(3)	5710(3)	33(1)
O(22)	4700(3)	5874(3)	5951(3)	45(1)	O(22)	4672(3)	5843(4)	5929(4)	46(1)
O(31)	−155(3)	2907(2)	1539(2)	35(1)	O(31)	−109(3)	2912(3)	1546(3)	34(1)
O(32)	−1176(4)	3368(3)	−54(3)	52(1)	O(32)	−1153(5)	3351(3)	−67(3)	53(1)
O(1)	2580(3)	3928(3)	3133(3)	41(1)	O(1)	2573(3)	3899(3)	3118(3)	41(1)
O(2)	−1710(3)	4042(3)	2574(3)	39(1)	O(2)	−1622(3)	4058(3)	2612(3)	35(1)
O(3)	135(3)	5425(3)	2145(3)	44(1)	O(3)	182(4)	5369(3)	2125(3)	46(1)
O(4)	2626(3)	6470(3)	4427(3)	41(1)	O(4)	2633(3)	6388(3)	4373(4)	43(1)
O(5)	2019(4)	7361(3)	2567(3)	54(1)	O(5)	1997(5)	7350(4)	2585(4)	55(1)
C(11)	−583(4)	1928(3)	4797(4)	30(1)	C(11)	−615(5)	1964(4)	4782(5)	31(1)
C(12)	196(5)	1847(4)	5909(4)	37(1)	C(12)	170(6)	1868(4)	5890(5)	38(1)
C(13)	−291(6)	979(5)	6172(5)	53(1)	C(13)	−306(7)	980(5)	6146(6)	52(2)
C(14)	−1569(7)	190(5)	5326(7)	66(2)	C(14)	−1574(8)	186(6)	5270(8)	62(2)
C(15)	−2378(6)	229(5)	4208(6)	61(1)	C(15)	−2378(7)	242(6)	4149(8)	62(2)
C(16)	−1855(5)	1093(4)	3950(5)	45(1)	C(16)	−1869(6)	1118(5)	3910(6)	47(1)
C(17)	−50(4)	2884(3)	4531(3)	25(1)	C(17)	−106(4)	2965(4)	4566(4)	27(1)
C(21)	4800(4)	5147(4)	7411(4)	36(1)	C(21)	4733(4)	5092(5)	7367(5)	35(1)
C(22)	5392(4)	6059(5)	8657(4)	45(1)	C(22)	5335(5)	5993(6)	8619(5)	47(1)
C(23)	6153(6)	5889(7)	9695(5)	67(2)	C(23)	6115(6)	5819(8)	9664(6)	66(2)
C(24)	6345(6)	4783(8)	9513(6)	77(2)	C(24)	6309(7)	4728(9)	9461(7)	77(2)
C(25)	5764(6)	3858(6)	8317(7)	67(2)	C(25)	5727(7)	3809(7)	8257(8)	65(2)
C(26)	4996(5)	4039(5)	7267(5)	45(1)	C(26)	4937(5)	3995(6)	7215(6)	46(1)
C(27)	4018(4)	5385(4)	6286(4)	32(1)	C(27)	3968(4)	5336(4)	6249(4)	30(1)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	*Atom*	*x/a*	*y/b*	*z/c*	U_{eq}
C(31)	−1235(4)	1371(3)	−557(4)	33(1)	C(31)	−1178(5)	1365(4)	−563(4)	33(1)
C(32)	−332(5)	897(4)	−909(4)	43(1)	C(32)	−237(6)	904(5)	−904(5)	43(1)
C(33)	−684(7)	−267(5)	−1808(5)	61(2)	C(33)	−567(9)	−251(6)	−1787(6)	62(2)
C(34)	−1993(9)	−975(5)	−2375(6)	76(2)	C(34)	−1872(1)	−978(6)	−2369(6)	69(2)
C(35)	−2929(7)	−565(5)	−2065(5)	72(2)	C(35)	−2844(8)	−567(6)	−2059(7)	73(2)
C(36)	−2541(5)	618(4)	−1141(4)	48(1)	C(36)	−2471(6)	608(5)	−1148(5)	49(1)
C(37)	−817(4)	2664(3)	393(3)	30(1)	C(37)	−775(5)	2657(4)	387(4)	32(1)
Dy	878(1)	4595(1)	3611(1)	25(1)	C(13)	−320(10)	964(7)	6133(8)	50(2)
Cl(11)	1782(2)	2859(2)	6964(2)	58(1)	C(14)	−1591(11)	176(8)	5262(10)	60(3)
Cl(12)	−2851(3)	1165(3)	2473(3)	95(1)	C(15)	−2360(9)	230(7)	4159(10)	61(2)
Cl(21)	5096(2)	7386(2)	8866(2)	64(1)	C(16)	−1878(8)	1114(7)	3904(8)	48(2)
Cl(22)	4223(2)	2837(2)	5671(2)	63(1)	C(17)	−121(6)	2974(5)	4575(6)	26(1)
Cl(31)	1408(2)	1830(3)	−222(2)	76(1)	C(21)	4720(6)	5091(7)	7359(7)	37(2)
Cl(32)	−3668(2)	1144(3)	−733(3)	81(1)	C(22)	5321(7)	5982(8)	8604(7)	45(2)
O(11)	381(5)	2822(4)	3850(4)	34(1)	C(23)	6099(9)	5808(10)	9644(8)	62(3)
O(12)	−252(5)	3966(4)	5162(4)	35(1)	C(24)	6295(10)	4732(13)	9459(11)	82(4)
O(21)	2662(4)	5018(4)	5691(4)	33(1)	C(25)	5720(9)	3812(9)	8255(11)	64(3)
O(22)	4669(5)	5852(5)	5938(5)	49(1)	C(26)	4925(7)	3999(8)	7213(8)	47(2)
O(31)	−105(4)	2909(4)	1541(4)	31(1)	C(27)	3962(7)	5339(6)	6236(6)	33(2)
O(32)	−1155(6)	3346(5)	−70(5)	55(2)	C(31)	−1172(7)	1368(6)	−562(6)	33(2)
O(1)	2596(4)	3898(4)	3139(5)	41(1)	C(32)	−239(8)	894(7)	−906(7)	43(2)
O(2)	−1599(4)	4062(4)	2620(4)	39(1)	C(33)	−567(12)	−260(9)	−1787(9)	59(2)
O(3)	195(5)	5370(4)	2123(5)	47(1)	C(34)	−1852(15)	−965(8)	−2357(9)	71(3)
O(4)	2635(5)	6375(4)	4356(5)	43(1)	C(35)	−2838(11)	−583(8)	−2071(9)	71(3)
O(5)	2013(6)	7362(5)	2593(5)	58(2)	C(36)	−2478(8)	604(7)	−1150(7)	45(2)
C(11)	−621(7)	1959(6)	4769(6)	31(2)	C(37)	−781(7)	2647(6)	378(6)	33(2)
C(12)	156(8)	1862(6)	5882(6)	36(2)					

TABLE III Selected bond lenghts (Å) and bond angles (°) in dimeric Ce(III), Pr (III), Nd (III), Tb (III) and Dy (III) 2,6-dichlorobenzoates

	Ce	*Pr*	*Nd*	*Tb*	*Dy*
M—M	4.445(1)	4.433(1)	4.420(1)	4.534(1)	4.625(1)
M—O12i	2.469(2)	2.451(2)	2.429(3)	2.323(3)	2.378(5)
M—O12	2.756(2)	2.755(2)	2.759(3)	2.969(4)	2.986(5)
M—O11	2.574(2)	2.542(2)	2.529(3)	2.425(3)	2.372(4)
M—O21	2.490(2)	2.472(2)	2.457(3)	2.403(3)	2.393(4)
M—O31	2.480(3)	2.459(2)	2.452(3)	2.406(3)	2.446(5)
M—OW1	2.512(2)	2.493(2)	2.472(3)	2.396(3)	2.428(4)
M—OW2	2.539(2)	2.506(2)	2.487(3)	2.422(3)	2.383(4)
M—OW3	2.481(2)	2.455(2)	2.437(3)	2.365(4)	2.328(5)
M—OW4	2.538(3)	2.518(3)	2.500(3)	2.428(4)	2.354(5)
C17—O12	1.262(3)	1.257(3)	1.268(4)	1.255(5)	1.298(8)
C17—O11	1.232(4)	1.231(3)	1.228(5)	1.237(5)	1.245(8)
C27—O21	1.266(4)	1.258(3)	1.249(5)	1.258(5)	1.247(8)
C27—O22	1.232(4)	1.235(4)	1.236(5)	1.248(5)	1.200(8)
C37—O31	1.246(4)	1.246(3)	1.239(5)	1.248(6)	1.255(8)
C37—O32	1.239(4)	1.234(4)	1.234(5)	1.239(6)	1.235(9)
C17—C11	1.506(4)	1.500(4)	1.497(5)	1.499(6)	1.458(9)
C27—C21	1.507(4)	1.506(4)	1.506(5)	1.501(6)	1.500(9)
C37—C31	1.505(4)	1.501(4)	1.505(5)	1.513(6)	1.529(10)
C12—Cl 11	1.731(4)	1.724(4)	1.724(5)	1.724(6)	1.703(8)
C16—Cl 12	1.731(4)	1.717(4)	1.721(5)	1.725(6)	1.732(8)
C22—Cl 21	1.733(4)	1.720(4)	1.732(5)	1.736(7)	1.770(9)
C26—Cl 22	1.729(4)	1.731(4)	1.729(5)	1.731(7)	1.777(9)
C32—Cl 31	1.728(5)	1.724(4)	1.730(5)	1.726(6)	1.698(8)
C36—Cl 32	1.735(5)	1.735(4)	1.736(6)	1.741(6)	1.764(9)
Mi—O12—M	116.5(7)	116.6(1)	116.7(1)	117.6(1)	118.7(1)
O12—M—O11	48.3(7)	48.4(1)	48.5(1)	46.5(1)	48.1(2)
O11—C17—O12	122.4(3)	122.4(3)	122.1(3)	122.3(4)	125.0(6)
O21—C27—O22	125.5(3)	125.6(3)	126.2(4)	124.9(4)	124.6(6)
O31—C37—O32	126.4(3)	126.3(3)	127.0(4)	126.8(4)	125.0(7)
Ligand 1*	82.3(1)	82.0(1)	82.9(1)	79.5(1)	78.4(1)
Ligand 2	82.1(1)	82.1(1)	81.8(1)	80.7(1)	82.1(1)
Ligand 3	80.4(1)	80.2(1)	80.0(1)	79.6(1)	78.0(1)

* Carboxylic group plane phenyl ring plane; Symmetry code: i = $-x$; $-y + 1$; $-z + 1$

TABLE IV The values of Δ for coordination polyhedra of lanthanide ions in the complexes with 2,6-dichlorobenzoic acid

	Ce	*Pr*	*Nd*	*Tb*	*Dy*
TCTP	0.1140	0.1116	0.1098	0.1364	0.1392
SCAP	0.1072	0.1078	0.1092	0.1115	0.1007

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

D - H ... A	*Ce*	*Pr*	*Nd*	*Tb*	*Dy*
O1W-H(2) ... O(22)*i*					
D - H	0.89	0.88	0.76	0.88	0.93
H ... A	1.86	1.85	1.98	1.86	1.79
D ... A	2.755(4)	2.727(4)	2.728(4)	2.730(6)	2.698(8)

TABLE V (*Continued*)

D - H ... A	*Ce*	*Pr*	*Nd*	*Tb*	*Dy*
<D - H ... A	163	171	168	171	167
O2W - H(3) ... O(21)*ii*					
D - H	0.87	0.85	0.86	0.88	0.73
H ... A	1.90	1.93	1.91	1.94	2.15
D ... A	2.764(4)	2.771(3)	2.770(4)	2.804(5)	2.878(7)
<D - H ... A	173	170	177	164	170
O3 - H(5) ... O32					
D - H	0.71	0.81	0.82	0.80	0.73
H ... A	2.03	1.97	1.96	2.00	2.03
D ... A	2.700(4)	2.687(4)	2.695(4)	2.671(5)	2.714(8)
<D - H ... A	159	147	149	141	158
O3 - H(6) ... O5					
D - H	0.86	0.83	0.86	0.87	0.83
H ... A	1.93	1.97	1.94	1.94	1.88
D ... A	2.780(5)	2.774(5)	2.776(6)	2.764(7)	2.697(9)
<D - H ... A	170	164	165	159	170
O4 - H(7) ... O(5)					
D - H	0.75	0.86	0.75	0.89	0.97
H ... A	2.18	2.06	2.19	2.02	1.92
D ... A	2.866(5)	2.865(4)	2.863(5)	2.853(9)	2.817(9)
<D - H ... A	152	157	151	155	153
O4 - H(8) ... O(22)					
D - H	0.75	0.94	0.79	0.93	0.97
H ... A	2.04	1.80	1.98	1.80	1.84
D ... A	2.750(4)	2.725(4)	2.731(5)	2.687(6)	2.687(8)
<D - H ... A	156	169	159	160	163
O5 - H ... O(32)*iii*					
D - H	0.97	0.87	0.96	0.89	0.83
H ... A	1.76	1.85	1.76	1.83	1.91
D ... A	2.719(4)	2.720(4)	2.709(5)	2.707(6)	2.732(9)
<D - H ... A	169	171	166	168	180

Symmetry code: i = l–Mx, 1–y, 1–z; ii = –x, 1–x, 1–z; iii = –x, 1–y, –z.

Lists of observed and calculated structure factors, atom coordinates and anisotropic thermal parameters for the nonhydrogen atoms can be obtained from the authors on request.

RESULTS AND DISCUSSION

Figure 1 shows the structure of the octaaqua*bis* (μ -2,6-dichlorobenzoato *O,O,O′*) *tetrakis*-(2,6-dichlorobenzoato*O*) dipraseodymium(III) dihydrate, as one of the series of isomorphous lanthanide complexes and gives the numbering of the atoms. The structure of the complex consists of centrosymmetric dimers in which lanthanide(III) ions are connected by two ligands through the carboxylate groups. The carboxylate groups of both ligands are terdentate, chelating-bridging. The carboxylate groups chelate to one metal ion and simultaneously bridge two lanthanide(III) ions forming centrosymmetric dimers. The Ln—Ln distance is 4.420(1)Å for the cerium(III) complex and increases in the series of dimers to 4.625(1)Å for the dysprosium(III) one; this can be explained by the change of ionic radius in the lanthanide series. The fact that lanthanide ions are bridged by two chelating-bridging carboxylate groups causes smaller Ln—Ln distances in comparison with other dimeric carboxylate complexes. One of the shorter Ln—Ln distances, 3.926(1)Å, is observed in the terbium(III) benzoate, where metal ions are connected by four bridging carboxylate groups[4] one of the longest, 6.530(1)Å, is in the benzeno-1,2,4-tricarboxylate, where neodymium(III) ions are bridged by one *syn-anti* carboxylate ligand.[7] In the investigated series, lanthanide(III) ions form nine metal-oxygen bonds (Table III). One, M—O12, is considerably long and increases in the lanthanide series from 2.756(2)Å for cerium(III) to 2.986(5)Å for dysprosium(III). At the same time, remaining metal-oxygen bond distances are significantly shorter and their distance decreases from about 2.5Å for light to below 2.4Å for heavy lanthanide(III) complexes. One thus expects a change of coordination number to 8 for 2,6-dichlorobenzoates of lanthanides heavier than dysprosium(III). The geometry of the anions with the carboxylate group closely situated to chlorine atoms probably influences the Ln—O bond distances, and the carboxylate group position in relation to the phenyl ring plane. Steric crowding in the primary coordination sphere and crystal packing forces are the reason for the market carboxylate group rotation from the phenyl ring plane. The angles are a maximum in the cerium(III) complex, being 82.3(1)°, 82.1(1)° and 80.4(1)° and at a minimum for the dysprosium(III) complex, 78.4(1)°, 82.1(1)° and 78.0(1)°. Coordination polyhedra, may be described as distorted, tricapped trigonal prisms or as capped square antiprisms (Figure 2) with Δ values collected in Table IV. In $\Delta = \sum_{i=1}^{i=n} d_i^2/9$ the value d_i is the distance between the real position of the i-th atom and the relevant vertex in the ideal, least-squares-fitted polyhedron. The oxygen atoms of carboxylate groups of ligands, as well as water molecule oxygens may be assumed to be vertices of bases (O12^{i}, O2, O3; O11, O21, O1) and caps (O12, O31, O4) in the tricapped trigonal prism, TCTP, or as vertices of bases (O12^{i}, O21, O1, O3; O12, O11, O31, O2) and O4 as a cap in the capped square antiprism, CSAP. Almost the same values of Δ for both polyhedrons around Ce(III), Pr(III), Nd(III) ions and slightly different ones for Tb(III) and Dy(III) ions are evidence for fluent transitions between different polyhedrons, characteristic for CN=9.

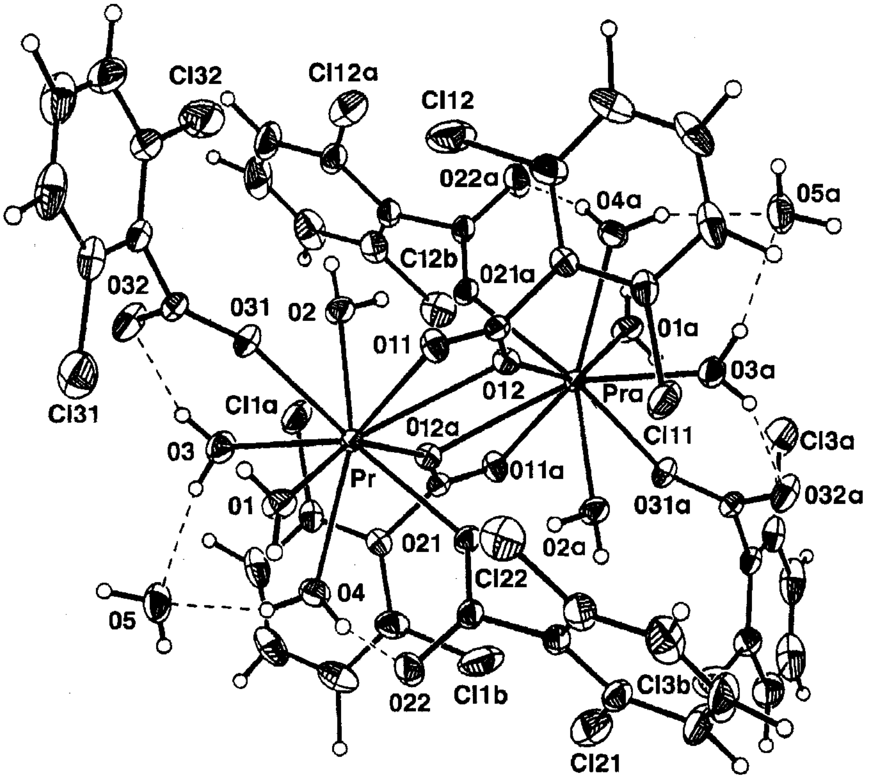
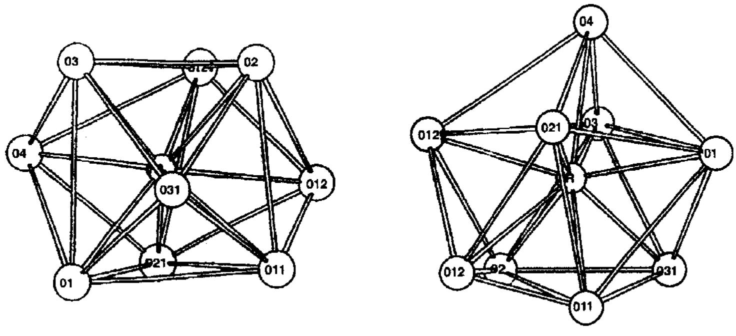


FIGURE 1 The molecular structure of the dimer octaaqua*bis*(μ-2,6-dichlorobenzoat°*O,O,O′*)-*tetrakis* (2,6-dichlorobenzoato*O*)dipraseodymium(III) dihydrate.



TCTP

CSAP

FIGURE 2 The coordination polyhedron formed by oxygen atoms about Pr(III) ion can be described as a tricapped trigonal prism, TCTP, with $\Delta = 0.1116$ or as a capped square antiprism, CSAP, with $\Delta = 0.1072$.

The corresponding bond distances and angles within the two crystallographically independent 2,6-dichlorobenzoate ligands are not significantly different and are comparable with those observed in Co (II), Ni (II)[2] and Cu (II)[3] 2,6-dichlorobenzoate complexes. Phenyl rings are planar and C—C distances and C—C—C angles are on the average 3.390(5)Å and 119.9°, respectively. C—Cl bond lengths have values in the range 1.698(8)–1.777(9) Å. C_{phenyl}—$C_{carboxyl}$ bond distances have values about 1.50Å, as in free benzoic acids.

In the carboxylate groups, C—O distances differ significantly; in the monodentate carboxylate group coordination of the metal ion causes lengthening of C—O (1.266(4)–1.247(8)Å) in comparison to uncoordinated ligand (1.232(4)–1.200(8)Å). Simultaneously, in the terdentate carboxylate group, one can observe longer C—O distances, 1.262(5)–1.298(8) Å, when the oxygen atom coordinates two lanthanide(III) ions C17—O12 (Table III), compared to C17—O11, when oxygen coordinates only to one metal ion in the dimer (1.228(4)–1.245(8)Å). The angles O1—C7—O2 in the terdentate chelating-bridging carboxylate groups are about 122° for the Ce—Tb complexes 125.0(6)° for the Dy(III). These are characteristic for bridging COO groups. When carboxylate groups coordinate to metal ion by only one oxygen atom, the O—C—O angles have much greater values in all complexes, reaching a maximum of 127.0(4)° for Nd(III).

The crystal structure consists of discrete units of neutral, dimeric complexes and molecules of water of crystallization. All four coordinated water molecules and the two free water molecules are proton donors in strong and nearly linear hydrogen bonds to the carboxylate groups of the dimer (O22, O32) as well as to carboxylate groups of neighbouring units ($O22^{i}$, $O21^{ii}$ and $O32^{ii}$) and lattice water molecule (O5). The chlorine atoms do not participate in hydrogen bond formation (Table V). The equilibrium reached between intra- and intermolecular forces in the 2,6-dichlorobenzoate water system leads to the formation of isostructural complexes from Ce to Dy. Similarly, long series of isostructural lanthanide benzoates are formed with 3-aminobenzoic,[11] and 3,5-diaminobenzoic[12] acids, but difficulties in obtaining suitable crystals do allow structure determinations in these cases.

References

[1] K. Nakatani, J. Sletten, S. Halut-Desporte, S. Jeannin, Y. Jeannin and O. Kahn, *Inorg. Chem.*, **30**, 164 (1991).

[2] W. Brzyska, W. Wołodkiewicz, Z. Rzączyńska and T. Głowiak, *Polish J. Chem.*, **69**, 1392 (1995).

[3] W. Brzyska, W. Wołodkiewicz, Z. Rzączyńska and T. Głowiak, *Mh. Chem.*, **126**, 285 (1995).

[4] DuanZhi-Bang, JinZhong-Sheng, HuNing-Hai and NiJia-Zan, *J. Struct. Chem.*, **8**, 168 (1989).

[5] L.A. Aslanov, I.D. Kiekbaev, I.D. Abdul'minev and M.A. Poray-Koshits, *Kristallogr.*, **19**, 170 (1974).

[6] I.R. Amiraslanov, Kh.S. Mamedov and E.M. Movsumov, *Zh. Strukt. Khim.*, **22**, 113 (1981).
[7] JinZhong-Sheng, DuanZhi-Beng, Wei GeCheng and NiJia-Zan, *J. Struct. Chem.*, **9**, 69 (1990).
[8] W. Brzyska and E. Świta, *Thermochim. Acta*, **225**, 191 (1995).
[9] G.M. Sheldrick, SHELXS 86, Program for crystal Structure solution, (University of Göttingen, F.R.G., 1986).
[10] G.M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, (University of Göttingen, Germany, 1994).
[11] A.E. Kozioł, B. Klimek, K. Stepniak, Z. Rzączyńska, W. Brzyska, O.I. Bodak, L.G. Akselrud, W.W. Pawliuk and V.A. Tafeenko, *Zeitschr. Kristallogr.*, **25**, 200 (1992).
[12] Z. Rzączyńska, *Polish J. Chem.*, **65**, 1531 (1991).