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Crystal structure of a polymeric complex of lead(II) with 2,6-dihydroxybenzoic acid

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Abstract

The complex $Pb_2(DHB)_4 \cdot 3H_2O$ (DHB = 2,6-dihydroxybenzoate(−1)) has been prepared and characterized using single-crystal X-ray diffraction. The compound consists of a polymeric network which accommodates two types of lead ions. The coordination polyhedron around the first of them can be described as a distorted pentagonal bipyramid, where four carboxylate and one phenolic oxygens are the basal coordinating atoms, while the water molecule and a second phenolic group are in the apical positions. The second lead atom is involved in a dimeric Pb–Pb unit (metal–metal distance: 4.23 Å) bridged by two water molecules lying at distances of 2.59 and 2.61 Å, respectively. The coordination at each atom of this dimeric entity is completed by a bidentate carboxylate, a monodentate carboxylate, a water molecule and two phenolic groups resulting in a heavily distorted square antiprismatic stereochemistry. The Cd(II) complex is likely to have the same structure as the lead complex.

Introduction

Soil metal ions are predominantly bound to the complex humic and fulvic matter originating from the decomposition of natural organic substances. Really, these ligands are composed of a limited number of rather simple aromatic molecules, bearing mainly carboxyl and phenolic substituents, held together by secondary bonds. Metal ions can contribute to the aggregation processes, e.g. by coordinating the phenolic and carboxylic donor groups of different monomeric ligands and thus acting as crosslinks in the complex humic structure.

A number of studies performed on the transition metal complexes formed by simple humic models showed several metal coordination modes both in solution and in the solid state [1–9]. For instance, in the case of salicylic-like ligands, an outer-sphere complexation type, e.g. based on the interaction between hydrated aquaions and ligands deprotonated at the carboxyl groups, was observed in solid compounds isolated from acidic solutions [1]. Complexes involving carboxylate coordination are formed at higher pH [1–6]. Nevertheless, the salicylate-like chelation through *ortho* carboxylate and phenolate donors is the predominant complex formation process above pH 5 [5, 6].

With ligands provided with couples of *ortho* phenolic groups, the catecholic coordination type prevails, although mixed salicyclic–catecholic coordination may be a competitive bonding mode, at least for ligands having suitable combinations of such donor groups [6, 7].

We are also investigating the possibility that the coordination of metal ions to these simple molecules can yield directly polymeric compounds with structures comparable to those of metal–humic aggregates. Oligo- or polynuclear species may be obtained when more than one donor set, e.g. salicylic/carboxylic or catecholic/carboxylic, is available for coordination in the same ligand molecule [6, 7]. A bridging behaviour may be observed when phenolate and carboxylate groups are distant and thus excluded from chelation, e.g. in 3-methoxy-4-hydroxy-benzoic acid or their analogues [9]. In addition, linear-chain polymeric species can also be obtained where, although the ligand behaves as a monodentate carboxylic donor, water molecules bridge the metal ions and the whole structure is stabilized by stacking interactions between adjacent chains [8, 9].

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This study reports the crystal structure of a complex formed by lead(II) with 2,6-dihydroxybenzoic acid (HDHB), having formula $Pb_2(DHB)_4 \cdot 3H_2O$, where some of the metal-coordination modes for this type of ligand are exemplified. The polymeric structure, where several donors are involved, makes this compound a reliable example of a metal humic-like complex.

Experimental

Synthesis

$Pb(CH_3COO)_2 \cdot 3H_2O$ or $CdCl_2$ and the ligand (1:2 molar ratio) were dissolved in water at pH *c.* 4. Crystals were formed by slow evaporation at room temperature. The Pb complex was satisfactorily analysed as $Pb_2(DHB)_4 \cdot 3H_2O$ (**I**). *Anal.* Calc. for $C_{28}H_{20}O_{16}Pb_2 \cdot 3H_2O$: C, 31.11; H, 2.42; H_2O, 5.0. Found: C, 31.10; H, 2.58; H_2O, 5.0% (by thermogravimetry). The crystalline Cd complex initially exhibited $Cd(DHB)_2 \cdot 10H_2O$ stoichiometry, but it was readily transformed into a powder-like compound $Cd(DHB)_2 \cdot 1.5H_2O$ (**II**) with an empirical formula analogous to that of **I**. *Anal.* Calc. for $C_{14}CdH_{10}O_8 \cdot 1.5H_2O$: C, 37.73; H, 2.94; H_2O, 6.1. Found: C, 38.46; H, 3.03; H_2O, 6.4% (by thermogravimetry).

Instruments

IR spectra were recorded with a FT Bruker IFS-66 interferometer using KBr disks (4000–600 cm^{-1}) or powdered samples spread on NaCl plates (1700–1200 cm^{-1}). Thermogravimetric data were obtained with a Perkin-Elmer TGS-2 apparatus under a nitrogen flow.

Crystallographic studies

A crystal of approximate dimensions 0.18 × 0.18 × 0.25 mm was mounted on a Syntex $P2_1$ computer-controlled four-circle diffractometer. Data were collected using the θ–2θ procedure with 2θ limit = 52° and graphite monochromated Mo Kα radiation. A total of 5306 unique reflections was measured, giving 3711 with $I \geq 3.5\sigma(I)$. Two standard reflections, monitored after every 50 data measurements, showed only random fluctuations of ±5%.

Crystal data

$Pb_2(DHB)_4 \cdot 3H_2O$. $C_{28}H_{26}O_{19}Pb_2$, $M = 1080.89$, triclinic, $a = 7.540(2)$, $b = 14.014(3)$, $c = 15.030(3)$ Å, $\alpha = 83.06(3)$, $\beta = 85.15(3)$, $\gamma = 83.72(3)°$, $U = 1563.0(6)$ Å^3, Mo Kα radiation ($\lambda = 0.710\ 69$ Å), space group $P1$, $Z = 2$, $D_m = 2.30(1)$ g cm^{-3}, by flotation in $CCl_4/CHBr_3$, $D_c = 2.297$ g cm^{-3}, $F(000) = 1020$. μ(Mo Kα) = 106.97 cm^{-1}.

Structure analysis and refinement

The structure was solved by direct methods using the SHELX-76 set of programs [10] and refined by full-matrix least-squares with anisotropic parameters for all non-hydrogen atoms. All H atoms were placed at computed positions, as determined from the successive Fourier difference maps. The refinement of coordinates and thermal parameters (anisotropic for non-hydrogen and isotropic for hydrogen atoms) converged at $R = 0.031$, $R_w = 0.034$, with $R = \Sigma(|F_0| - |F_c|)/\Sigma(|F_0|)$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(|F_0|)^2]^{1/2}$. The function minimized was $[w = 1/\sigma^2(F_0)]$, $\Sigma w(|F_0| - |F_c|)^2$. The final S value, $[\Sigma w(|F_0| - |F_c|)^2/(n-p)]^{1/2}$, was 1.787. $(\Delta/\sigma)_{max} = 0.01$ and $(\Delta\rho)_{max} = 0.73$ e Å^{-3}. Absorption correction was introduced by DIFABS procedure [11]. The minimum and maximum of transmission was 0.748 and 1.317, respectively. Sources of neutral atomic scattering factors for all atoms are given in ref. 12. Computations were performed with a PC/AT computer using the Syntex XTL/XTLE computation package [13].

The final atomic positional parameters are listed in Table 1, and bond distances and angles related to lead coordination geometry are given in Table 2.

Discussion

Structure of the complex $Pb_2(C_7H_5O_4)_4 \cdot 3H_2O$

As shown by single-crystal X-ray diffraction data, the structure of the complex consists of a polymeric network which accommodates two types of lead ions (Fig. 1). The first of them, labelled as Pb(1), is seven-coordinated (Fig. 2(a)). Two carboxylate groups chelate this metal ion, one of them, [O(21)–C(21)–O(22)], more asymmetrically than the other one, [O(11)–C(11)–O(12)]. The respective Pb–O(carboxylate) distances are 2.35 and 2.97 and 2.42 and 2.65 Å, for the more and less asymmetrically bonded groups, respectively. The coordination at this lead atom is completed by a water molecule (2.35 Å) and two long contacts from phenolic oxygens belonging to adjacent complex molecules (distances of 2.72 and 3.06 Å), all the Pb–O distances being shorter than the sum of the van der Waals radii (1.76 + 1.40 Å). The overall geometry around the metal is that of a heavily distorted pentagonal bipyramid, where four carboxylate and one of the phenolic oxygens are the basal coordinating atoms, while the water molecule and the second phenolic group are in the apical positions. The five equatorial oxygens O(11), O(12), O(14)^{ii}, O(21) and O(22) are deviated from the mean plane by 0.014(7), 0.126(8), −0.123(8), −0.302(8) and 0.267(8) Å, respectively. However the O(14)^{ii} and O(22) atoms, which occupy adjacent corners of the basal plane, are considerably more distant from lead compared to the others.

TABLE 1. Positional and thermal (Å^2) parameters, with e.s.d.s. in parentheses

	x	y	z	B_{eq}
Pb(1)	0.1321(1)	0.1022(1)	0.0772(1)	3.0(1)
Pb(2)	0.1216(1)	0.3654(1)	0.4644(1)	2.3(1)
O(11)	0.4105(9)	0.1542(5)	0.1140(4)	2.9(4)
O(12)	0.1999(8)	0.1880(6)	0.2170(5)	3.3(4)
O(13)	0.2733(9)	0.2118(5)	0.3738(5)	3.2(4)
O(14)	0.7404(9)	0.1383(6)	0.1478(5)	3.4(4)
O(21)	0.3400(10)	0.0817(6)	−0.0466(5)	3.9(5)
O(22)	0.0931(10)	0.0996(6)	−0.1173(5)	3.9(5)
O(23)	0.6455(9)	0.0577(6)	−0.1292(5)	3.5(5)
O(24)	0.1096(10)	0.1094(6)	−0.2891(5)	4.0(5)
O(31)	0.3348(9)	0.3605(6)	0.6005(4)	3.1(4)
O(32)	0.1290(9)	0.3836(6)	0.7124(5)	3.5(4)
O(33)	0.6556(9)	0.3215(5)	0.6301(4)	3.0(4)
O(34)	0.2114(9)	0.3545(6)	0.8724(5)	3.9(5)
O(41)	−0.0127(8)	0.3658(6)	0.3172(5)	2.9(4)
O(42)	−0.2180(9)	0.3980(5)	0.4226(4)	2.6(4)
O(43)	−0.0813(9)	0.3744(6)	0.1545(5)	4.1(5)
O(44)	−0.5464(8)	0.4344(5)	0.3853(4)	2.7(4)
W(1)	0.0507(11)	0.2638(6)	0.0209(5)	4.3(5)
W(2)	0.9720(9)	0.2241(5)	0.5580(4)	3.4(4)
W(3)	0.0796(8)	0.5491(5)	0.4125(4)	2.1(4)
C(11)	0.3659(13)	0.1744(7)	0.1921(7)	2.4(5)
C(12)	0.4977(12)	0.1749(7)	0.2571(6)	1.9(5)
C(13)	0.4500(13)	0.1920(7)	0.3459(6)	2.2(5)
C(14)	0.5731(14)	0.1863(8)	0.4099(7)	2.8(6)
C(15)	0.7497(13)	0.1640(8)	0.3844(7)	2.8(6)
C(16)	0.8008(15)	0.1470(9)	0.2961(8)	3.7(7)
C(17)	0.6800(13)	0.1530(7)	0.2335(6)	2.4(5)
C(21)	0.2590(14)	0.0886(8)	−0.1189(6)	2.9(6)
C(22)	0.3718(12)	0.0833(7)	−0.2043(6)	2.4(5)
C(23)	0.5596(13)	0.0662(7)	−0.2063(7)	2.4(5)
C(24)	0.6626(14)	0.0579(7)	−0.2859(8)	3.1(6)
C(25)	0.5770(16)	0.0647(9)	−0.3654(7)	3.7(7)
C(26)	0.3911(15)	0.0819(8)	−0.3663(7)	3.3(6)
C(27)	0.2933(14)	0.0930(8)	−0.2881(7)	3.0(6)
C(31)	0.2886(12)	0.3625(7)	0.6829(6)	2.4(5)
C(32)	0.4245(13)	0.3361(7)	0.7493(6)	2.3(5)
C(33)	0.6078(13)	0.3155(7)	0.7202(7)	2.4(6)
C(34)	0.7349(14)	0.2921(8)	0.7810(7)	3.0(6)
C(35)	0.6842(15)	0.2875(8)	0.8715(7)	3.4(7)
C(36)	0.5104(14)	0.3074(8)	0.9020(7)	3.0(6)
C(37)	0.3807(3)	0.3327(7)	0.8412(7)	2.5(6)
C(41)	−0.1727(12)	0.3892(7)	0.3411(6)	2.0(5)
C(42)	−0.3080(12)	0.4032(7)	0.2740(6)	1.7(5)
C(43)	−0.2584(14)	0.3954(7)	0.1823(7)	2.7(6)
C(44)	−0.3817(14)	0.4088(8)	0.1201(7)	3.2(6)
C(45)	−0.5559(15)	0.4311(8)	0.1452(7)	3.5(7)
C(46)	−0.6174(13)	0.4395(8)	0.2364(7)	3.0(6)
C(47)	−0.4909(13)	0.4262(7)	0.2987(6)	2.2(5)

TABLE 2. Bond distances (Å) and angles (°) with their e.s.d.s in parentheses

Pb(1)–O(11)	2.423(7)	Pb(2)–Pb(2)^{i}	4.227(1)
Pb(1)–O(12)	2.654(7)	Pb(2)–O(13)	2.775(7)
Pb(1)–O(14)^{ii}	3.062(7)	Pb(2)–O(31)	2.696(6)
Pb(1)–O(21)	2.353(7)	Pb(2)–O(41)	2.510(7)
Pb(1)–O(23)^{iii}	2.968(7)	Pb(2)–O(42)	2.666(6)
Pb(1)–W(1)	2.354(7)	Pb(2)–O(44)	2.892(6)
		Pb(2)–W(2)	2.592(7)
		Pb(2)–W(3)	2.591(6)
		Pb(2)–W(3)^{i}	2.612(6)
O(11)–C(11)	1.251(12)	O(21)–C(31)	1.262(11)
O(12)–C(11)	1.276(12)	O(32)–C(31)	1.263(12)
O(13)–C(13)	1.371(12)	O(33)–C(33)	1.367(12)
O(14)–C(17)	1.362(12)	O(34)–C(37)	1.338(12)
O(21)–C(21)	1.280(12)	O(41)–C(41)	1.249(11)
O(22)–C(21)	1.242(13)	O(42)–C(41)	1.260(11)
O(23)–C(23)	1.362(12)	O(43)–C(43)	1.376(13)
O(24)–C(27)	1.380(13)	O(44)–C(47)	1.348(11)
O(11)–Pb(1)–O(12)	50.5(2)	Q(13)–Pb(2)–O(31)	103.1(2)
O(11)–Pb(1)–O(14)^{ii}	134.4(2)	O(13)–Pb(2)–O(41)	68.4(2)
O(11)–Pb(1)–O(21)	72.9(3)	O(13)–Pb(2)–O(42)	106.3(2)
O(11)–Pb(1)–O(22)	115.4(2)	O(13)–Pb(2)–O(44)	77.9(2)
O(11)–Pb(1)–O(23)^{iii}	71.7(2)	O(13)–Pb(2)–W(2)	79.6(2)
O(11)–Pb(1)–W(1)	87.3(3)	O(13)–Pb(2)–W(3)	130.8(2)
O(12)–Pb(1)–O(14)^{ii}	84.6(2)	O(13)–Pb(2)–W(3)^{i}	156.6(2)
O(12)–Pb(1)–O(21)	123.0(2)	O(31)–Pb(2)–O(41)	167.3(2)
O(12)–Pb(1)–O(22)	152.5(2)	O(31)–Pb(2)–O(42)	143.1(2)
O(12)–Pb(1)–O(23)^{iii}	91.8(2)	O(31)–Pb(2)–O(44)	73.6(2)
O(12)–Pb(1)–W(1)	80.9(3)	O(31)–Pb(2)–W(2)	87.1(2)
O(14)^{i}–Pb(1)–O(21)	148.0(2)	O(31)–Pb(2)–W(3)	101.1(2)
O(14)^{i}–Pb(1)–O(22)	101.0(2)	O(31)–Pb(2)–W(3)^{i}	75.6(2)
O(14)^{i}–Pb(1)–O(23)^{iii}	124.5(2)	O(41)–Pb(2)–O(42)	49.5(2)
O(14)^{i}–Pb(1)–W(1)	76.4(2)	O(41)–Pb(2)–O(44)	95.0(2)
O(21)–Pb(1)–O(22)	47.0(2)	O(41)–Pb(2)–W(2)	100.1(2)
O(21)–Pb(1)–O(23)^{iii}	74.7(2)	O(41)–Pb(2)–W(3)	79.2(2)
O(21)–Pb(1)–W(1)	91.3(3)	O(41)–Pb(2)–W(3)^{i}	116.1(2)
O(22)–Pb(1)–O(23)^{iii}	106.4(2)	O(42)–Pb(2)–O(44)	134.3(2)
O(22)–Pb(1)–W(1)	74.4(2)	O(42)–Pb(2)–W(2)	76.8(2)
O(23)^{iii}–Pb(1)–W(1)	157.3(3)	O(42)–Pb(2)–W(3)	75.9(2)
		O(42)–Pb(2)–W(3)^{i}	68.5(2)
		O(44)–Pb(2)–W(2)	146.0(2)
		O(44)–Pb(2)–W(3)	68.9(2)
		O(44)–Pb(2)–W(3)^{i}	122.7(2)
		W(2)–Pb(2)–W(3)	143.9(2)
		W(2)–Pb(2)–W(3)^{i}	77.0(2)
		W(3)–Pb(2)–W(3)^{i}	71.3(2)
		Pb(2)–W(3)–Pb(2)^{i}	108.7(2)
Hydrogen bonding			
O(11)···O(14)	2.561(9)	O(32)···O(34)	2.509(10)
O(12)···O(13)	2.535(10)	O(41)···O(43)	2.527(10)
O(21)···O(23)	2.532(10)	O(42)···O(44)	2.568(9)
O(22)···O(24)	2.561(10)	O(43)···W(1)	2.738(11)
O(31)···O(33)	2.486(9)		

Symmetry code: (i) $-x$, $1-y$, $1-z$; (ii) $-1+x$, y, z; (iii) $1-x$, $-y$, $-z$.

The second lead atom Pb(2) is involved in a dimeric Pb–Pb unit bridged by two water molecules lying at distances of 2.59 and 2.61 Å, respectively, from the metal. The coordination at each atom of this dimeric entity (Fig. 2(b)) is completed by a bidentate carboxylate (with Pb–O distances of 2.51 and 2.67 Å), a monodentate carboxylate (2.70 Å), a water oxygen (2.59 Å). and two phenolic groups, O(13) and O(44), from adjacent complex molecules (2.77 and 2.89 Å, respectively). The resulting eight-coordinated stereochemistry is severely distorted from the square antiprisma, with the atoms O(13), O(44), O(31) and that of non-bridging water W(2) being approximately in the upper plane, and the

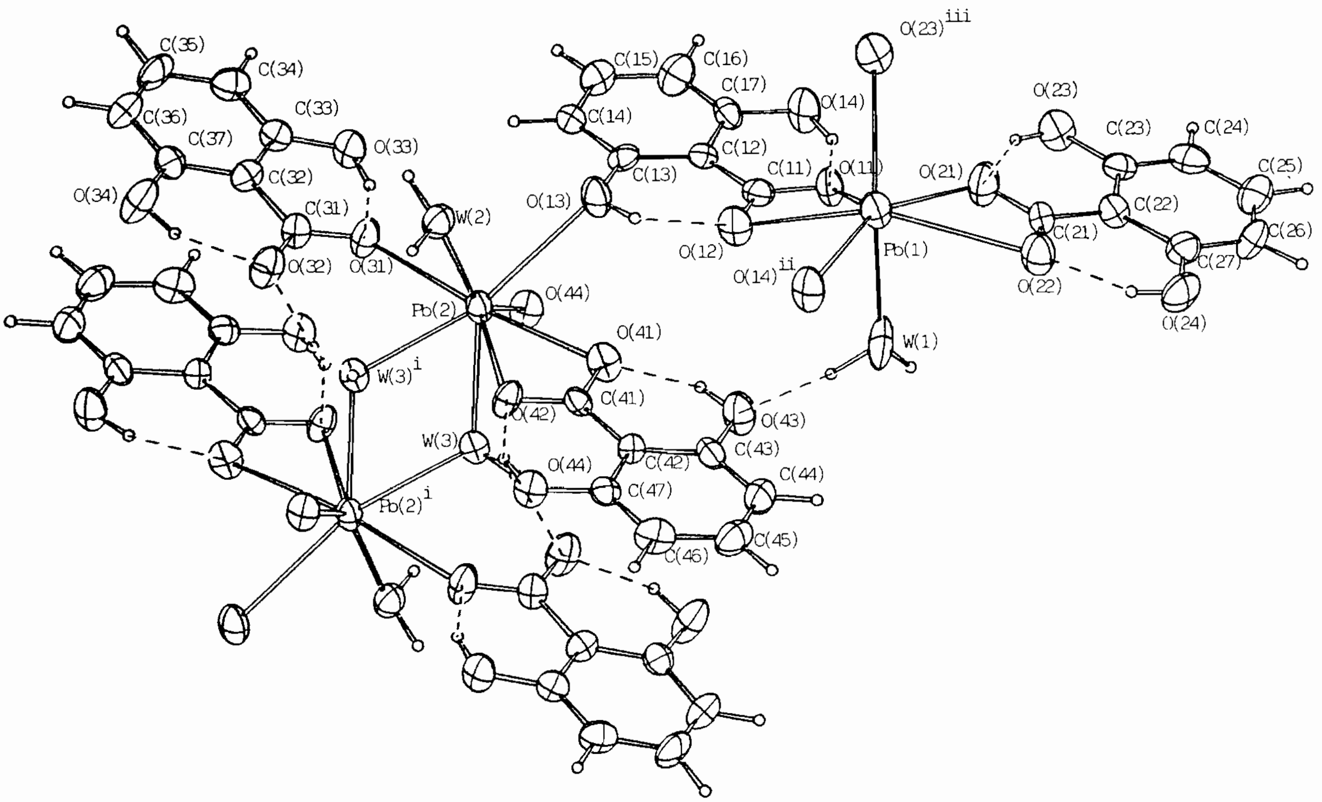

Fig. 1. Perspective view of the complex $Pb_2(DHB)_4 \cdot 3H_2O$.

remaining oxygens in the lower one. In the metal coordination polyhedron the angles subtended by couples of adjacent oxygens at the Pb atom are in the range 68–106° except that between O(41) and O(42) (49.5°). The coordination polyhedra of the two lead atoms share an edge, yielding a dimeric unit where the water-bridged metal ions are 4.23 Å distant from each other.

On the whole, this structure bears resemblance to that of the EDTA complex which also comprises a dimeric unit, where two carboxylate groups act as bridges and the metal is eight-coordinated, together with a monomeric seven-coordinate lead atom [14]. Also the metal–oxygen distances measured for the DHB complex are in the same range of those found in the EDTA and other carboxylate complexes [15].

Among the peculiarities of the complex structure it should be stressed that all C–O distances are uniform (1.36±0.03 Å for phenolic groups and 1.26±0.02 Å for carboxylic ones) regardless of the type of bonding to lead. In particular, the asymmetry of coordination for the monodentate carboxylate groups is not reflected by different C–O bond lengths. Since all the carboxylic oxygens, either coordinated or not, are hydrogen bound to *ortho* phenolic groups, it may be concluded that hydrogen bonding is as much effective as the metal coordination in determining the C–O bond distance.

Hydrogen bonding contacts, in which carboxylates, phenolic groups and water molecules take part, complete the structure (Table 2) and seem to play a very important role in building up and stabilizing the polymeric network.

Spectroscopic and thermogravimetric data

To get a comparison with the analogous complexes formed by the same ligand with other divalent metal ions, the spectral and thermal properties of the lead(II) and cadmium(II) complexes were also examined. The IR spectra of $Pb_2(DHB)_4 \cdot 3H_2O$ and those of the Cd analogue are very similar, suggesting the same structure for both the complexes. The absorption bands conform well to those described previously for other 2,6-dihydroxybenzoate complexes [1–4]. Broad absorption bands at 1577 and 1391 cm^{-1} are attributed to carboxylate groups, although they cannot be considered indicative enough of the coordination mode of the carboxylate groups. Actually, four different carboxylates exist in the Pb complex and, as discussed above, their involvement in hydrogen bonding interactions makes the situation even more complicated. Bands at 3572, 3476, 3047 and 3020 cm^{-1} are assigned to the stretching modes of phenolic groups and water molecules, as confirmed by examination of the compound prepared in D_2O, where these bands are shifted to 2646, 2575, 2257 and 2237 cm^{-1}, respectively. Dehydration of the

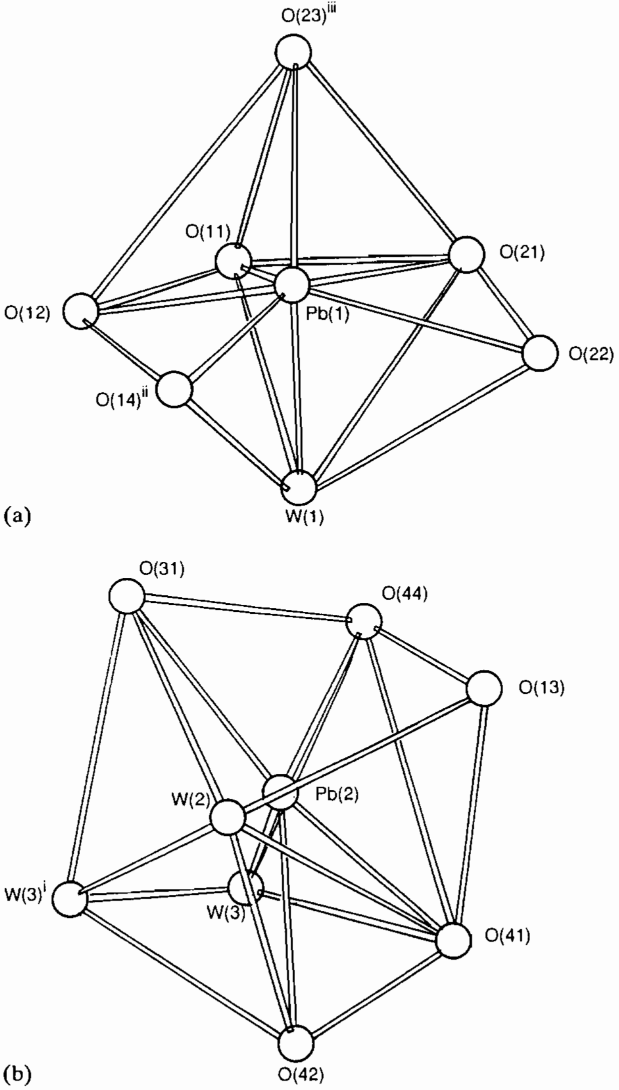

Fig. 2. Coordination polyhedra of the two different lead(II) ions in $Pb_2(DHB)_4 \cdot 3H_2O$.

compound allowed the stretches at 3572, 3476 cm^{-1} (absent in the anhydrous compound) to be attributed to water molecules and those at 3047 and 3020 cm^{-1} (replaced, after dehydration, by a series of multiple absorptions in the range 2940–2740 cm^{-1}) to phenolic groups. An intense band at 931 cm^{-1} (653 cm^{-1}, after deuteriation) is due to the rocking mode of water [16]. This absorption is tentatively assigned to the bridging molecules because usually non-bridging molecules yield bands around 830–860 cm^{-1}.

The thermal decomposition of the compounds follows a mechanism analogous to that reported previously for the other complexes [17]. Namely, after removal of the water molecules, anhydrous compounds with $M(DHB)_2$ stoichiometry are formed. These decompose around 190 (Cd) or 230 (Pb) °C by releasing a molecule of ligand which decarboxylates to resorcinol (1,3-dihydroxybenzene), analogously as observed for the free ligand at the same temperature. Resorcinol was isolated from the gas effluent and identified by elemental analysis, IR and NMR. After release and decomposition of this DHB molecule, a complex with the 1:1 ligand-to-metal molar ratio is formed in the residue, as substantiated by elemental analysis. In the Cd residue the metal is bound to a 2,6-dihydroxybenzoate(−2) ligand, which, being deprotonated at both the carboxylate and the phenolic groups, acts as a bidentate chelator of the salicylic-like type. Accordingly, this undecomposed DHB ligand can be recovered by acidification of an aqueous solution of the residue. Moreover, stretching modes indicative of a metal-bound carboxylate (1578 and 1400 cm^{-1}) and an undissociated phenolic group (3180 cm^{-1}) are distinguished by IR spectroscopy. In the case of lead(II), since decomposition to yield the 1:1 complex occurs at temperature higher than for Cd, also the DHB molecule remaining in the residue undergoes CO_2 loss and, after decarboxylation, the ligand binds the metal ion through the phenolic groups. Therefore, the residue is a polymeric complex of resorcinol with a 1:1 ligand-to-metal ratio, as confirmed by analytical and IR spectral data, which, for instance, rule out the presence of carboxylic and undissociated phenolic groups.

Supplementary material

Tables of H-atom coordinates, thermal parameters and remaining bond lengths and angles, as well as a listing of observed and calculated structure factors, are available from the authors on request.

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