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DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

$M_2(H_2O)[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ ($M = \text{Ba}^{2+}, \text{Pb}^{2+}$) – Two Isotypic Three-Dimensional Coordination Polymers with a Layer-like Separation between Anions and Cations

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Keywords: Benzene-1,2,4,5-tetracarboxylate; Pyromellitate; Metal-organic-framework, Crystal structure

Abstract. Monoclinic single crystals of $\text{Ba}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**1**) and $\text{Pb}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]\cdot\text{H}_2\text{O}$ (**2**) have been obtained using the silica gel method. Space group $C2/c$ (no. 15), $Z = 4$; **1**: $a = 780.89(4)$, $b = 1756.19(8)$, $c = 914.80(5)$ pm, $\beta = 114.512(5)^\circ$; **2**: $a = 756.70(10)$, $b = 1772.8(2)$, $c = 890.2(2)$ pm, $\beta = 113.590(10)^\circ$. There are two crystallographically independent M^{2+} ions ($M = \text{Ba}, \text{Pb}$). $M(1)$ is surrounded by eight carboxylate oxygen atoms and one water molecule forming a tricapped trigonal

prism. $M(2)$ is coordinated by ten carboxylate oxygen atoms in the shape of a tetracapped octahedron. The connection between the $M(1)$ and $M(2)$ polyhedra leads to infinite layers parallel to (010) which are linked by $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anions to form a three-dimensional framework. The $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anion adopts a μ_{10} coordination mode. Compound **1** reveals short Ba–Ba contacts of 426.46(2) pm, whereas the Pb–Pb distance of 411.01(6) pm in **2** is larger than twice the van der Waals radius.

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A rational approach in synthesis requires systematic structural studies in order to shed light on the structure-directing principles. Dale et al. [33] reported on $\text{Ba}(\text{H}_2\text{O})_5[\text{C}_6\text{H}_2(\text{COO})_2(\text{COOH})_2]$ with a layer-like structure synthesized in an aqueous solution. Here we report on the crystal structure of $\text{Ba}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ and $\text{Pb}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$, which are characterized by a compact three-dimensional framework. Colourless single crystals were obtained using the silica gel method.

Introduction

The coordination of multi-dentate complexing agents, like the anions of benzenecarboxylic acids, with metal cations leads to coordination polymers with various structural features [1–13]. These coordination polymers attract great interest due to their structural variety and interesting properties. The carboxylate groups of benzenecarboxylic acids anions are able to coordinate metal ions in flexible modes. It has been shown that the coordination between the anion of benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid) and metal cations leads to coordination polymers with chain- and layer-like structures as well as to three-dimensional frameworks (so-called MOF's) [14–19]. The obtained crystal structures strongly depend on the reaction conditions. For instance, the reaction between Co^{2+} and benzene-1,2,4,5-tetracarboxylic acid results either in a one-dimensional structure (chain-like) [4], a two-dimensional layer-like structure [20] or in a three-dimensional framework [21–23]. Previous studies on benzene-1,2,4,5-tetracarboxylato complexes with main group metal ions like Mg^{2+} , Sr^{2+} and Al^{3+} reveal three-dimensional structures with zeolite-like features [24–26]. Moreover, metal-benzenecarboxylates show interesting magnetic, catalytic, luminescence and gas sorption properties [24–32].

Results and Discussion

In the isotypic coordination polymers $\text{Ba}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**1**) and $\text{Pb}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**2**) there are two crystallographically independent M^{2+} -ions ($M = \text{Ba}, \text{Pb}$) which are situated on a twofold crystallographic axis of space group $C2/c$ (Wyckoff position 4e). $M(1)$ is coordinated by eight carboxylate oxygen atoms ($2\times\text{O}(1)$, $2\times\text{O}(2)$, $4\times\text{O}(3)$) and one water molecule (Ow) forming a distorted tricapped trigonal prism (Fig. 1). Coordination number nine could also result from a distorted monocapped square antiprism, however, the distances and angles between the ligand atoms are more consistent with a tricapped trigonal prism. The $M(1)$ –O distances range from 265.4(2) to 294.0(2) pm for **1** and 255.2(7) to 282.4(8) pm for **2** (Tab. 1 and 2). The $M(1)$ polyhedra are connected by common edges ($\text{O}(3)$, $\text{O}(3')$) to form infinite chains along [001] (Fig. 2a). The coordination polyhedron around $M(2)$ can be best described as a tetracapped octahedron ($\text{CN} = 10$). The $M(2)$ -cations are surrounded by six carboxylate oxygen atoms in a distorted octahedral manner with $M(2)$ –O bond length of 278.2(2)–282.6(2) pm for **1** and 257.8(8)–276.9(8) pm for **2** (Tab. 1 and 2). Additionally, four oxygen atoms ($2\times\text{O}(3)$, $2\times\text{O}(1')$) with longer metal oxygen distances of

301.5(2)–309.0(2) pm for **1** and 292.3(8)–293.4(8) pm for **2** generate a second distorted tetrahedron-like coordination environment. Metal-cations with a tetracapped octahedral coordination mode have been found as well in $\text{SrV}_2(\text{P}_2\text{O}_7)_2$ [34] and in $\text{Pb}(\text{15-crown-5})(\text{CCl}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ [35]. The $M(2)$ polyhedra are also connected by common edges ($\text{O}(1)$, $\text{O}(1')$) resulting in infinite chains along [001]. Both zig-zag-like polyhedra chains ($M(1)$, $M(2)$) are linked by common corners and edges forming infinite layers parallel to (010) (Fig. 2a). These layers are stacked in ...ABAB... sequence along the [010] direction (Fig. 2b). In compound **2** the coordination polyhedra suggest that the lone electron pair of Pb^{2+} has no stereochemical influence on the crystal structure. A stereochemically active lone electron pair would cause a nonspherical charge distribution around the lead(II) cation resulting in a hemidirected coordination sphere, which was not found in compound **2**. As pointed out by Shimoni-Livny et al. [36] and Noshiranzadeh et al. [37] $\text{Pb}(\text{II})$ -compounds with coordination numbers of nine or ten favour a holodirected coordination sphere with an inactive lone electron pair. Employing the method of Brown [38] the bond order is calculated to 2.36 ($\text{Ba}(1)$), 1.96 ($\text{Ba}(2)$), 1.98 ($\text{Pb}(1)$), and 1.87 ($\text{Pb}(2)$), respectively. The Pb^{2+} The $\text{Ba}(1)$ – $\text{Ba}(2)$ distance with 426.46(2) pm is smaller than the one in metallic barium [39]. The $\text{Pb}(1)$ – $\text{Pb}(2)$ distance of 411.01(6) pm is larger than twice the van der Waals radius and is in the range of Pb – Pb distances found in metallic lead [40,41]. Short cation-cation contacts are also found in e.g. barium alkoxid derivatives [42], barium squarate [43], barium terephthalate [44], as well as in bis(diphenyldithiophosphinato)lead(II) [45] and lead(II) benzene-1,3,5-tricarboxylate [46].

Groeneman and Atwood [44] reported on a similar zig-zag-like connection between barium-oxygen polyhedra in barium terephthalate tetrahydrate. However, in this compound the barium coordination sphere is made up of four carboxylate oxygen atoms and six water molecules resulting in polyhedra chains linked by terephthalate anions to a two-dimensional network.

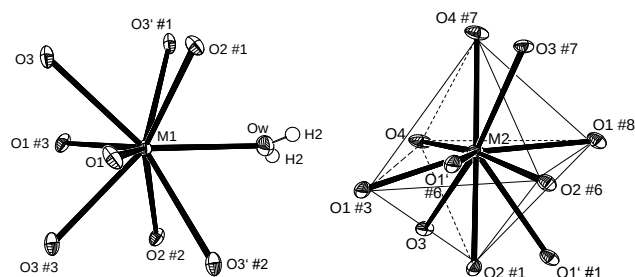


Figure 1. The coordination environments of M^{2+} ($M = \text{Ba}, \text{Pb}$). Ellipsoids are given for compound **1** at 50% probability, arbitrary radii for hydrogen atoms. Thin lines are guides to the eyes. The index (') indicates the longest M – O bond. Symmetry codes as in Tab. 1.

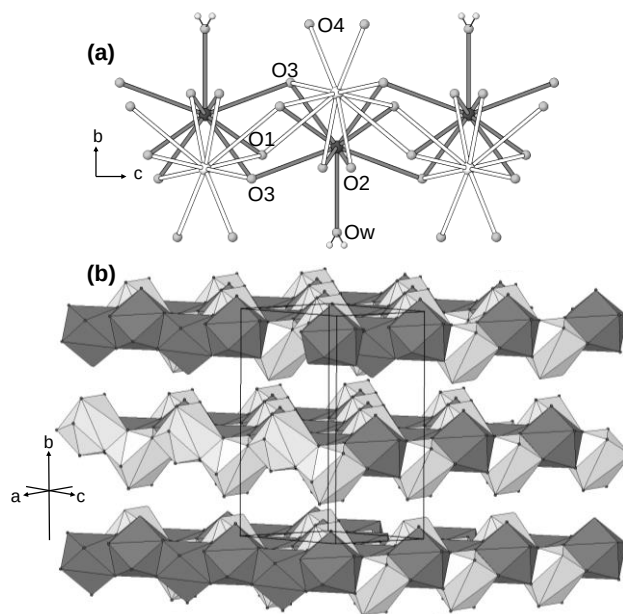


Figure 2. (a) The connection between the $M(1)$ and $M(2)$ polyhedra ($M = \text{Ba}^{2+}, \text{Pb}^{2+}$). (b) Stacking of the polyhedra layers along [010]. The $M(2)$ coordination sphere is drawn with open bonds and light polyhedra, respectively.

Table 1. The Coordination of Ba^{2+} in $\text{Ba}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**1**)

bond lengths (pm)			
$\text{Ba}(1)\text{-Ow}$	272.5(3)	$\text{Ba}(2)\text{-O}(2)^{\#1}$	278.2(2)
$\text{Ba}(1)\text{-O}(2)^{\#1}$	265.4(2)	$\text{Ba}(2)\text{-O}(2)^{\#6}$	278.2(2)
$\text{Ba}(1)\text{-O}(2)^{\#2}$	265.4(2)	$\text{Ba}(2)\text{-O}(1)^{\#3}$	287.5(2)
$\text{Ba}(1)\text{-O}(1)$	279.8(2)	$\text{Ba}(2)\text{-O}(1)^{\#8}$	287.5(2)
$\text{Ba}(1)\text{-O}(1)^{\#3}$	279.8(2)	$\text{Ba}(2)\text{-O}(4)$	282.6(2)
$\text{Ba}(1)\text{-O}(3)$	282.7(2)	$\text{Ba}(2)\text{-O}(4)^{\#7}$	282.6(2)
$\text{Ba}(1)\text{-O}(3)^{\#3}$	282.7(2)	$\text{Ba}(2)\text{-O}(1')^{\#1}$	309.0(2)
$\text{Ba}(1)\text{-O}(3')^{\#1}$	294.0(2)	$\text{Ba}(2)\text{-O}(1')^{\#6}$	309.0(2)
$\text{Ba}(1)\text{-O}(3')^{\#2}$	294.0(2)	$\text{Ba}(2)\text{-O}(3)$	301.5(2)
		$\text{Ba}(2)\text{-O}(3)^{\#7}$	301.5(2)
$\text{Ow-H}(2)$	75(4)	$\text{Ba}(1)\cdots\text{Ba}(2)$	426.46(2)
bond angles (°)			
$\text{O}(2)^{\#1}\text{-Ba}(1)\text{-O}(2)^{\#2}$	151.10(9)	$\text{O}(2)^{\#2}\text{-Ba}(1)\text{-Ow}$	75.55(5)
$\text{O}(2)^{\#2}\text{-Ba}(1)\text{-O}(1)$	68.99(6)	$\text{Ow-Ba}(1)\text{-O}(1)^{\#3}$	117.38(5)
$\text{Ow-Ba}(1)\text{-O}(3)$	136.21(4)	$\text{O}(2)^{\#1}\text{-Ba}(1)\text{-O}(3)$	69.93(7)
$\text{O}(3)\text{-Ba}(1)\text{-O}(3)^{\#3}$	87.58(9)	$\text{O}(1)^{\#3}\text{-Ba}(1)\text{-O}(3)$	74.00(6)
$\text{O}(1)\text{-Ba}(1)\text{-O}(3')^{\#2}$	128.57(6)	$\text{O}(2)^{\#2}\text{-Ba}(1)\text{-O}(3')^{\#2}$	64.09(9)
$\text{O}(2)^{\#2}\text{-Ba}(1)\text{-O}(1)^{\#3}$	126.01(7)	$\text{O}(3)\text{-Ba}(1)\text{-O}(3')^{\#2}$	144.99(7)
$\text{O}(1)\text{-Ba}(1)\text{-O}(3)$	67.15(6)	$\text{O}(2)^{\#2}\text{-Ba}(1)\text{-O}(3)$	134.70(6)
$\text{Ow-Ba}(1)\text{-O}(3')^{\#1}$	69.82(4)	$\text{O}(2)^{\#1}\text{-Ba}(1)\text{-O}(3')^{\#2}$	105.36(7)
$\text{O}(3)^{\#3}\text{-Ba}(1)\text{-O}(3')^{\#2}$	71.27(7)	$\text{O}(1)^{\#3}\text{-Ba}(1)\text{-O}(3')^{\#2}$	72.17(6)
		$\text{O}(3')^{\#2}\text{-Ba}(1)\text{-O}(3')^{\#1}$	139.65(8)
$\text{O}(2)^{\#1}\text{-Ba}(2)\text{-O}(1)^{\#3}$	66.19(6)	$\text{O}(2)^{\#6}\text{-Ba}(2)\text{-O}(1)^{\#3}$	98.57(6)
$\text{O}(2)^{\#1}\text{-Ba}(2)\text{-O}(4)$	109.70(6)	$\text{O}(1)^{\#8}\text{-Ba}(2)\text{-O}(4)$	110.20(7)
$\text{O}(1)^{\#3}\text{-Ba}(2)\text{-O}(4)$	83.40(7)	$\text{O}(2)^{\#6}\text{-Ba}(2)\text{-O}(1')^{\#6}$	44.21(6)
$\text{O}(1)^{\#3}\text{-Ba}(2)\text{-O}(1')^{\#6}$	59.99(7)	$\text{O}(4)\text{-Ba}(2)\text{-O}(1')^{\#6}$	141.55(7)

$\text{O}_{(2)}^{\#6}\text{-Ba}_{(2)}\text{-O}_{(2)}^{\#1}$	62.58(9)	$\text{O}_{(2)}^{\#6}\text{-Ba}_{(2)}\text{-O}_{(4)}$	169.72(7)
$\text{O}_{(4)}\text{-Ba}_{(2)}\text{-O}_{(4)}^{\#7}$	78.76(9)	$\text{O}_{(2)}^{\#6}\text{-Ba}_{(2)}\text{-O}_{(1')}^{\#1}$	67.93(6)
$\text{O}_{(1)}^{\#3}\text{-Ba}_{(2)}\text{-O}_{(1')}^{\#1}$	108.03(6)	$\text{O}_{(4)}\text{-Ba}_{(2)}\text{-O}_{(1')}^{\#1}$	101.84(6)
$\text{O}_{(1)}^{\#8}\text{-Ba}_{(2)}\text{-O}_{(3)}$	111.86(6)	$\text{O}_{(4)}^{\#7}\text{-Ba}_{(2)}\text{-O}_{(3)}$	123.19(6)
$\text{O}_{(1)}^{\#8}\text{-Ba}_{(2)}\text{-O}_{(3)}^{\#7}$	70.11(6)	$\text{O}_{(4)}^{\#7}\text{-Ba}_{(2)}\text{-O}_{(3)}^{\#7}$	44.42(6)
$\text{O}_{(2)}^{\#6}\text{-Ba}_{(2)}\text{-O}_{(3)}$	126.76(6)	$\text{O}_{(1')}^{\#1}\text{-Ba}_{(2)}\text{-O}_{(3)}$	121.64(6)
$\text{O}_{(2)}^{\#1}\text{-Ba}_{(2)}\text{-O}_{(3)}$	65.54(6)	$\text{O}_{(1')}^{\#1}\text{-Ba}_{(2)}\text{-O}_{(3)}$	67.26(6)
$\text{O}_{(1)}^{\#3}\text{-Ba}_{(2)}\text{-O}_{(1)}^{\#8}$	162.86(9)	$\text{O}_{(3)}\text{-Ba}_{(2)}\text{-O}_{(3)}^{\#7}$	167.61(8)
		$\text{O}_{(1')}^{\#6}\text{-Ba}_{(2)}\text{-O}_{(1')}^{\#1}$	100.52(8)

The index (') indicates the longest M–O bond.

#1: -x;-y+1;-z+2, #2: x;-y+1;z-0.5, #3: -x;y;-z+1.5, #6: x-1;-y+1;z-0.5, #7: -x-1;y;-z+1.5, #8: x-1;y;z

Table 2. The Coordination of Pb^{2+} in $\text{Pb}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (2)

bond lengths (pm)			
$\text{Pb}_{(1)}\text{-Ow}$	261(1)	$\text{Pb}_{(2)}\text{-O}_{(2)}$	257.8(8)
$\text{Pb}_{(1)}\text{-O}_{(2)}$	255.2(7)	$\text{Pb}_{(2)}\text{-O}_{(2)}^{\#5}$	257.8(8)
$\text{Pb}_{(1)}\text{-O}_{(2)}^{\#1}$	255.2(7)	$\text{Pb}_{(2)}\text{-O}_{(1)}^{\#2}$	275.6(7)
$\text{Pb}_{(1)}\text{-O}_{(1)}^{\#2}$	271.6(8)	$\text{Pb}_{(2)}\text{-O}_{(1)}^{\#6}$	275.6(7)
$\text{Pb}_{(1)}\text{-O}_{(1)}^{\#3}$	271.6(8)	$\text{Pb}_{(2)}\text{-O}_{(4)}^{\#3}$	276.9(8)
$\text{Pb}_{(1)}\text{-O}_{(3)}^{\#2}$	277.5(8)	$\text{Pb}_{(2)}\text{-O}_{(4)}^{\#7}$	276.9(8)
$\text{Pb}_{(1)}\text{-O}_{(3)}^{\#3}$	277.5(8)	$\text{Pb}_{(2)}\text{-O}_{(1')}^{\#5}$	293.4(8)
$\text{Pb}_{(1)}\text{-O}_{(3')}^{\#1}$	282.4(8)	$\text{Pb}_{(2)}\text{-O}_{(1')}^{\#5}$	293.4(8)
$\text{Pb}_{(1)}\text{-O}_{(3')}^{\#1}$	282.4(8)	$\text{Pb}_{(2)}\text{-O}_{(3)}^{\#3}$	292.3(8)
		$\text{Pb}_{(2)}\text{-O}_{(3)}^{\#7}$	292.3(8)
		$\text{Pb}_{(1)}\cdots\text{Pb}_{(2)}$	411.01(6)
bond angles (°)			
$\text{O}_{(2)}^{\#1}\text{-Pb}_{(1)}\text{-O}_{(2)}$	154.3(4)	$\text{O}_{(2)}\text{-Pb}_{(1)}\text{-Ow}$	77.1(2)
$\text{O}_{(2)}\text{-Pb}_{(1)}\text{-O}_{(1)}^{\#2}$	66.5(2)	$\text{Ow-Pb}_{(1)}\text{-O}_{(1)}^{\#3}$	116.4(2)
$\text{Ow-Pb}_{(1)}\text{-O}_{(3)}^{\#2}$	135.6(2)	$\text{O}_{(2)}^{\#1}\text{-Pb}_{(1)}\text{-O}_{(3)}^{\#2}$	68.3(2)
$\text{O}_{(3)}^{\#2}\text{-Pb}_{(1)}\text{-O}_{(3)}^{\#3}$	88.7(3)	$\text{O}_{(1)}^{\#3}\text{-Pb}_{(1)}\text{-O}_{(3)}^{\#2}$	74.6(2)
$\text{O}_{(1)}^{\#2}\text{-Pb}_{(1)}\text{-O}_{(3')}^{\#3}$	129.3(2)	$\text{O}_{(2)}\text{-Pb}_{(1)}\text{-O}_{(3')}^{\#3}$	67.1(2)
$\text{O}_{(2)}\text{-Pb}_{(1)}\text{-O}_{(1)}^{\#3}$	126.6(2)	$\text{O}_{(3)}^{\#2}\text{-Pb}_{(1)}\text{-O}_{(3')}^{\#3}$	143.6(2)
$\text{O}_{(1)}^{\#1}\text{-Pb}_{(1)}\text{-O}_{(3)}^{\#2}$	68.3(2)	$\text{O}_{(2)}\text{-Pb}_{(1)}\text{-O}_{(3)}^{\#2}$	133.2(2)
$\text{Ow-Pb}_{(1)}\text{-O}_{(3')}^{\#3}$	70.8(2)	$\text{O}_{(2)}^{\#1}\text{-Pb}_{(1)}\text{-O}_{(3')}^{\#3}$	104.1(2)
$\text{O}_{(3)}^{\#3}\text{-Pb}_{(1)}\text{-O}_{(3')}^{\#3}$	70.4(3)	$\text{O}_{(1)}^{\#3}\text{-Pb}_{(1)}\text{-O}_{(3')}^{\#3}$	70.1(2)
		$\text{O}_{(3')}^{\#3}\text{-Pb}_{(1)}\text{-O}_{(3')}^{\#1}$	141.7(3)
$\text{O}_{(2)}\text{-Pb}_{(2)}\text{-O}_{(1)}^{\#2}$	65.5(2)	$\text{O}_{(2)}\text{-Pb}_{(2)}\text{-O}_{(1)}^{\#6}$	99.8(2)
$\text{O}_{(2)}^{\#5}\text{-Pb}_{(2)}\text{-O}_{(4)}^{\#7}$	110.5(2)	$\text{O}_{(1)}^{\#2}\text{-Pb}_{(2)}\text{-O}_{(4)}^{\#7}$	108.6(2)
$\text{O}_{(1)}^{\#2}\text{-Pb}_{(2)}\text{-O}_{(4)}^{\#3}$	84.8(2)	$\text{O}_{(2)}\text{-Pb}_{(2)}\text{-O}_{(1')}^{\#7}$	47.0(2)
$\text{O}_{(1)}^{\#6}\text{-Pb}_{(2)}\text{-O}_{(1')}^{\#5}$	59.3(3)	$\text{O}_{(4)}^{\#7}\text{-Pb}_{(2)}\text{-O}_{(1')}^{\#7}$	140.7(2)
$\text{O}_{(2)}\text{-Pb}_{(2)}\text{-O}_{(2)}^{\#5}$	65.1(3)	$\text{O}_{(2)}\text{-Pb}_{(2)}\text{-O}_{(4)}^{\#7}$	170.8(2)
$\text{O}_{(4)}^{\#7}\text{-Pb}_{(2)}\text{-O}_{(4)}^{\#3}$	75.1(3)	$\text{O}_{(2)}^{\#5}\text{-Pb}_{(2)}\text{-O}_{(1')}^{\#7}$	70.9(2)
$\text{O}_{(1)}^{\#2}\text{-Pb}_{(2)}\text{-O}_{(1')}^{\#7}$	109.7(2)	$\text{O}_{(4)}^{\#3}\text{-Pb}_{(2)}\text{-O}_{(1')}^{\#7}$	100.1(2)
$\text{O}_{(1)}^{\#2}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#7}$	110.6(2)	$\text{O}_{(4)}^{\#3}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#7}$	120.1(2)
$\text{O}_{(1)}^{\#2}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#3}$	71.7(2)	$\text{O}_{(4)}^{\#3}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#3}$	45.0(2)
$\text{O}_{(2)}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#7}$	128.9(2)	$\text{O}_{(1')}^{\#7}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#7}$	124.4(2)
$\text{O}_{(2)}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#3}$	65.8(2)	$\text{O}_{(1')}^{\#7}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#3}$	65.8(2)
$\text{O}_{(1)}^{\#6}\text{-Pb}_{(2)}\text{-O}_{(1)}^{\#2}$	163.4(4)	$\text{O}_{(3)}^{\#7}\text{-Pb}_{(2)}\text{-O}_{(3)}^{\#3}$	165.1(3)
		$\text{O}_{(1')}^{\#7}\text{-Pb}_{(2)}\text{-O}_{(1')}^{\#5}$	106.5(3)

The index (') indicates the longest M–O bond.

#1: -x+2;y;-z-0.5, #2: x;-y+1;z-0.5, #3: -x+2;-y+1;-z, #5: -x+1;y;-z-0.5, #6: -x+1;-y+1;-z, #7: x-1;-y+1;z-0.5

The $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anion (Fig. 3) is situated on an inversion centre and is almost planar with respect to the carbon skeleton. The largest deviation from a plane fitted to the carbon atoms in **1** and **2** is 4.0 pm and 4.2 pm (C(5)), respectively. The carboxylate groups with C(1) are twisted against the C_6 -ring by 83.8° for **1** and 84.6° for **2**, while the carboxylate group with C(2) is almost coplanar to the C_6 -ring (max. torsion angle 3.3°). The C–O bond lengths range from 124.5(4) to 128.4(3) for **1** and 124(1) to 128(1) pm for **2** (Tab. 3). All oxygen atoms from the anion are involved in the M^{2+} coordination. The shortest C–O bonds are formed by O(4) which is only involved in the coordination sphere of one M(1), whereas the longest C–O bonds are with O(1) and O(3) which belong to the polyhedra of three M^{2+} cations. Each centrosymmetric benzene-1,2,4,5-tetracarboxylate anion connects ten metal-ions and adopts a μ_{10} coordination mode (Fig. 3a). The carboxylate group with C(1) is coordinated to four metal-ions in a $\mu_4\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1$ connection mode, whereas the carboxylate group with C(2) is bonded to three metal-ions in a $\mu_3\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1$ mode [47]. The anions are stacked along [001], however a π – π interaction between the aromatic C_6 -rings can be excluded, because of their large distances, which corresponds to the crystallographic c-axis [48,49] (Fig. 3b).

Table 3. Selected Bond Lengths (pm) and Angles (°) of the Benzene-1,2,4,5-tetracarboxylate anion in **1** and **2**

$\text{Ba}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (1)					
$\text{C}_{(1)}\text{-C}_{(3)}$	151.0(4)	$\text{C}_{(3)}\text{-C}_{(4)}$	139.5(4)	$\text{O}_{(2)}\text{-C}_{(1)}$	125.9(3)
$\text{C}_{(2)}\text{-C}_{(4)}$	151.4(4)	$\text{C}_{(5)}\text{-C}_{(4)}$	139.8(4)	$\text{O}_{(3)}\text{-C}_{(2)}$	128.4(3)
$\text{C}_{(3)}\text{-C}_{(5)}$	138.9(4)	$\text{O}_{(1)}\text{-C}_{(1)}$	126.2(4)	$\text{O}_{(4)}\text{-C}_{(2)}$	124.5(4)
				$\text{C}_{(5)}\text{-H}_{(1)}$	72(4)
$\text{C}_{(5)}\text{-C}_{(3)}\text{-C}_{(4)}$	120.3(3)			$\text{O}_{(1)}\text{-C}_{(1)}\text{-C}_{(3)}$	118.6(3)
$\text{C}_{(5)}\text{-C}_{(3)}\text{-C}_{(1)}$	116.7(3)			$\text{O}_{(3)}\text{-C}_{(2)}\text{-C}_{(4)}$	117.8(3)
$\text{C}_{(5)}\text{-C}_{(4)}\text{-C}_{(3)}$	118.0(3)			$\text{O}_{(1)}\text{-C}_{(1)}\text{-O}_{(2)}$	124.2(3)
$\text{C}_{(3)}\text{-C}_{(4)}\text{-C}_{(2)}$	122.8(2)			$\text{O}_{(3)}\text{-C}_{(2)}\text{-O}_{(4)}$	122.3(3)
$\text{C}_{(4)}\text{-C}_{(5)}\text{-C}_{(3)}$	121.7(3)			$\text{C}_{(3)}\text{-C}_{(5)}\text{-H}_{(1)}$	120(4)
$\text{Pb}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (2)					
$\text{C}_{(1)}\text{-C}_{(3)}$	150(1)	$\text{C}_{(3)}\text{-C}_{(4)}$	141(1)	$\text{O}_{(2)}\text{-C}_{(1)}$	128(1)
$\text{C}_{(2)}\text{-C}_{(4)}$	151(1)	$\text{C}_{(5)}\text{-C}_{(4)}$	139(1)	$\text{O}_{(3)}\text{-C}_{(2)}$	126(1)
$\text{C}_{(3)}\text{-C}_{(5)}$	137(1)	$\text{O}_{(1)}\text{-C}_{(1)}$	127(1)	$\text{O}_{(4)}\text{-C}_{(2)}$	124(1)
				$\text{C}_{(5)}\text{-H}_{(1)}$	93
$\text{C}_{(5)}\text{-C}_{(3)}\text{-C}_{(4)}$	121(1)			$\text{O}_{(1)}\text{-C}_{(1)}\text{-C}_{(3)}$	121(1)
$\text{C}_{(5)}\text{-C}_{(3)}\text{-C}_{(1)}$	118(1)			$\text{O}_{(3)}\text{-C}_{(2)}\text{-C}_{(4)}$	119(1)
$\text{C}_{(5)}\text{-C}_{(4)}\text{-C}_{(3)}$	118(1)			$\text{O}_{(1)}\text{-C}_{(1)}\text{-O}_{(2)}$	122(1)
$\text{C}_{(3)}\text{-C}_{(4)}\text{-C}_{(2)}$	122(1)			$\text{O}_{(3)}\text{-C}_{(2)}\text{-O}_{(4)}$	122(1)
$\text{C}_{(4)}\text{-C}_{(5)}\text{-C}_{(3)}$	121(1)			$\text{C}_{(3)}\text{-C}_{(5)}\text{-H}_{(1)}$	119(1)

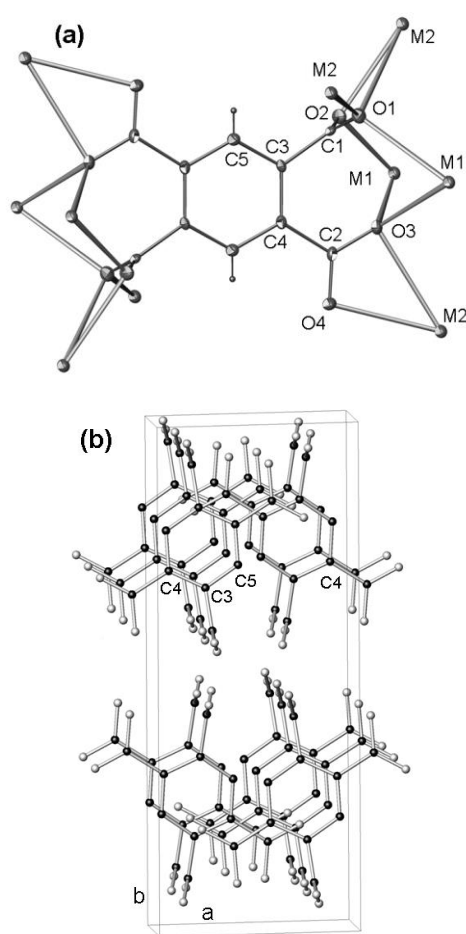


Figure 3. (a) The connection between the $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anion and the M^{2+} -cations ($M = \text{Ba}, \text{Pb}$) (ellipsoids are given at 50% probability, arbitrary radii for hydrogen atoms). (b) The arrangement of the equivalent $[\text{C}_6\text{H}_2(\text{COO})_4]^{4-}$ anions (hydrogen atoms are omitted).

The coordination between the benzene-1,2,4,5-tetracarboxylate anions and the M^{2+} -cations forms a compact three-dimensional framework with a layer-like separation between the anions and cations with respect to the $[010]$ direction (Fig. 4). The carboxylate groups show monodentate and asymmetric chelate coordination modes and act as bridging ligands between the metal ions. The coordination to $M(2)$ forms four-membered chelate rings ($\text{C}(1)\text{--O}(2)\text{--}M(2)\text{--O}(1')$, $\text{C}(2)\text{--O}(3)\text{--}M(2)\text{--O}(4)$) (Fig. 3a).

Three-dimensional structures with layer-like separation of anions and cations were also found in e.g. aluminum-, magnesium-, and strontium- as well as in gadolinium-potassium-, and some transition-metal benzene-1,2,4,5-tetracarboxylato complexes [24–26,50–52].

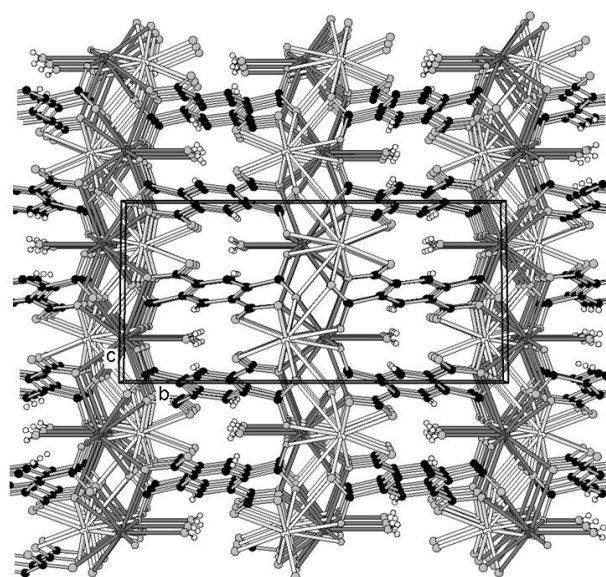


Figure 4. Perspective projection of the crystal structure of $M_2(H_2O)[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ ($M = \text{Ba}^{2+}, \text{Pb}^{2+}$) viewed from $[100]$. $M(2)$ polyhedra are drawn with open bonds.

Only one hydrogen bond between the water molecule (Ow), which is placed on the Wyckoff position $4e$, and the carboxylate oxygen atom O(4) is formed. The $\text{O}\cdots\text{O}$ distance and the $\text{O}\cdots\text{H}\cdots\text{O}$ angle for **1** is 280.4 pm and 155° indicating a hydrogen bond of medium strength. In **2** the $\text{O}\cdots\text{O}$ distance is 277.7 pm (the position of the hydrogen atom could not be determined).

The IR spectra of compounds **1** and **2** are shown in Fig. 5. The broad band with maxima at $3420/3318\text{ cm}^{-1}$ (**1**) and $3380/3286\text{ cm}^{-1}$ (**2**) reflects the $\text{O}\text{--H}$ symmetric and asymmetric stretching vibrations [53]. The $\text{H}\text{--O}\text{--H}$ bending mode appears at 1684 cm^{-1} (**1**) and 1674 cm^{-1} (**2**), respectively. The bands between 1550 and 1350 cm^{-1} represent $\text{C}\text{=C}$ and $\text{C}\text{=O}$ stretching vibrations. The in-plane rocking vibration of the $\text{C}\text{--H}$ group is manifested at 1136 cm^{-1} for **1** and 1138 cm^{-1} for **2**, while the out-of-plane rocking mode appears at 925 cm^{-1} (**1**) and 933 cm^{-1} (**2**), respectively [54].

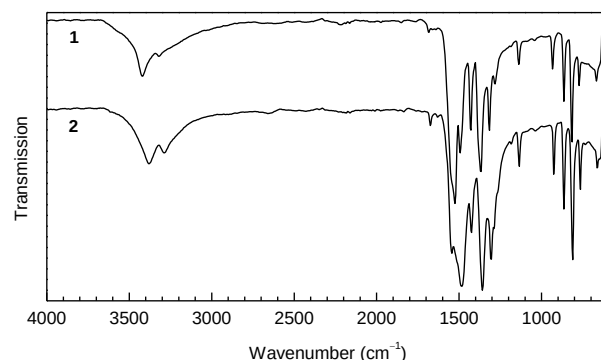


Figure 5. IR spectra (ATR technique) of $\text{Ba}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**1**) and $\text{Pb}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**2**).

TGA/DTA studies (Fig. 6) were carried out in air from room temperature to 1000°C at a heating rate of 10 K/min. With **1** a continuous weight loss of 7.2 % up to 510°C can be observed. The release of coordinated water would cause a weight loss of only 3.3 %. The observed significantly higher weight loss indicates that the dehydrated sample is not stable and further decomposition processes lead to a continuous weight loss. Further heating shows a strong exothermic signal ($T_{\text{on}} = 525^\circ\text{C}$) and the decomposition process results in a total weight loss of 28.8 % (calc. 27.3 %). The residue contained BaCO_3 identified by X-ray powder diffraction. The weak endothermic processes with onset temperatures of 805 and 964°C are obviously caused by the two phase transitions of BaCO_3 from the orthorhombic to the hexagonal form and from the hexagonal to the cubic one [55]. With **2** a first endothermic weight loss of 3.0% between 250 and 310°C corresponds to the loss of coordinated water (calc. 2.6 %). The dehydrated sample was stable up to 360 °C. The following decomposition processes up to 1000 °C caused a total weight loss of 33.7 % (calc. 34.6 %). A last endothermic signal with an onset temperature of 860 °C is associated to the melting of PbO [56]. The orange-yellow residue contained orthorhombic PbO .

The thermoanalytic measurements showed that the dehydrated sample of **1** was not stable in contrast to compound **2**. It may be assumed that in **2** the thermal stability of the dehydrated compound is caused by the lone electron pair of Pb^{2+} , which might stabilize the Pb(1) coordination sphere when $\text{CN} = 9$ is lowered to $\text{CN} = 8$ during the loss of the coordinated water molecule.

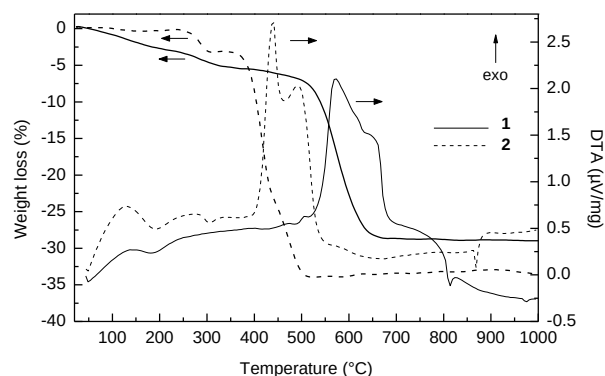


Figure 6. Thermal analysis of compounds **1** and **2**.

Conclusions

In summary, we reported on the synthesis and crystal structures of barium benzene-1,2,4,5-tetracarboxylate monohydrate (**1**) and lead benzene-1,2,4,5-tetracarboxylate monohydrate (**2**). The connection between the metal cations and the benzene-1,2,4,5-tetracarboxylate anions leads to a three-dimensional framework which layer-like separation between the anions and the cations. Short metal–metal

contacts of 426.46(2) pm were found in **1**, whereas the metal–metal distance in **2** (411.01(6) pm) is more than twice the van der Waals radius.

Experimental Section

Single crystals of $\text{Ba}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**1**) and $\text{Pb}_2(\text{H}_2\text{O})[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ (**2**) were grown in a silica gel matrix. To a mixture of 10 ml 2M HNO_3 , 5 ml water, and 10 ml 0.1M sodium benzene-1,2,4,5-tetracarboxylate solution an aqueous 2M $\text{Na}_2\text{H}_2\text{SiO}_4$ solution was added until a pH value of 5 was reached. Then the mixture was placed in a test tube and within 24 h it turned to a high viscous gel. An aqueous solution of 0.05 M $\text{Ba}(\text{NO}_3)_2$ for **1** and $\text{Pb}(\text{NO}_3)_2$ for **2** was placed on the top of the gel, respectively. The test tubes were kept at 60°C in a drying oven and after several days colourless rods appeared.

Results of elemental analysis: **1**: (molecular weight 542.81) C 19.77 (calc. 22.13); H 0.80 (0.74)%. **2**: (molecular weight 682.51) C 17.64 (calc. 17.60); H 0.81 (0.59)%.

The lower carbon value found in **1** is due to the formation of BaCO_3 during the analysis which is stable even at high temperatures.

IR-ATR (cm^{-1}): **1**: 3421(m), 3318(w), 1684(w), 1526(s), 1494(m), 1430(m), 1368(s), 1317(m), 1283(w), 1138(m), 933(m), 864(s), 816(s), 772(m), 667(m), 614(m). **2**: 3380(m), 3286(m), 1674(w), 1544(m), 1484(s), 1426(m), 1359(s), 1306(m), 1136(m), 925(m), 864(s), 812(s), 765(m), 662(m), 618(m).

Thermoanalytic measurements were performed in flowing air using a Netzsch STA429 device. ATR Fourier transformed infrared (IR-ATR) measurements were carried out at room temperature using a Bio-rad FTS 25. X-ray single crystal structure determination was performed on a Siemens P4 four-circle diffractometer (MoK α , graphite monochromator) in a theta range up to 30.00° and 27.00°, respectively. Numerical absorption corrections have been applied. Extinction effects have been compensated for by introduction of an extinction parameter. The phase problem was solved by direct methods. Full matrix least squares refinement employing $|F|^2$ made use of the SHELXTL program suite [57]. Difference Fourier maps revealed the hydrogen atom positions of **1**. They were allowed to refine individually with isotropic displacement parameters. For **2** only the position of the carbon bound H atom was included in the final cycles of refinement with a fixed isotropic displacement parameter. Crystallographic data are given in Table 4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1045552 (Ba-compound) and CCDC-1045553 (Pb-compound). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>)

Table 4. Crystallographic Data

	1	2
Empirical formula	$C_{10}H_4Ba_2O_9$	$C_{10}H_4Pb_2O_9$
Crystal system	monoclinic	
Space group	C2/c (No.15)	
Lattice constants	a=780.89(4) pm b=1756.19(8) pm c=914.80(5) pm $\beta=114.512(5)^\circ$	a=756.70(10) pm b=1722.8(2) pm c=890.2(2) pm $\beta=113.590(10)^\circ$
Cell volume	1.14149(10) nm ³	1.0635(3) nm ³
Formulas in unit cell	4	
Formula weight	542.81 g·mol ⁻¹	682.51 g·mol ⁻¹
Density (calc.)	3.159 g·cm ⁻³	4.263 g·cm ⁻³
Wavelength	71.073 pm	
Absorption coefficient	6.907 mm ⁻¹	31.672 mm ⁻¹
numerical absorption correction	min./max. transmittance	min./max. transmittance
	0.6484/0.7896	0.0278/0.2919
Temperature	293 K	
Crystal size (mm)	0.08 x 0.16 x 0.20	0.04 x 0.18 x 0.90
F (000)	992	1200
Θ -range	2.32° – 30.00°	3.17° – 27.00°
Limiting indices	<i>h</i> -1/+10 <i>k</i> -1/+24 <i>l</i> -12/+12	<i>h</i> 0/+9 <i>k</i> 0/+22 <i>l</i> -11/+10
Reflections collected	2109	1246
Independent reflections	1658 ($R_{int}=0.0199$)	1161 ($R_{int}=0.0173$)
Structure solution	Direct methods	
Structure refinement	Full-matrix least-squares on $ F ^2$	
Refined parameters	106	98
Extinction parameter	0.00124(5)	0.0025(2)
Final mean shift/esd	0.006	0.002
Goodness-of-fit on $ F ^2$	1.621	1.706
Residuals (all data)	$R_1 = 0.0225$, $wR_2 = 0.0446$	$R_1 = 0.0479$, $wR_2 = 0.1062$
Max. features in last difference Fourier synthesis	800 / -806 e·nm ⁻³	3414 / -4925 e·nm ⁻³

Acknowledgement

We are grateful to Mrs Christina Apfel for recording the thermoanalytical data.

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R. Köferstein and C. Robl, $M_2(H_2O)[\mu_{10}\text{-C}_6\text{H}_2(\text{COO})_4]$ ($M = \text{Ba}^{2+}, \text{Pb}^{2+}$) – Two Isotypic Three-Dimensional Coordination Polymers with a Layer-like Separation between Anions and Cations, *Z. Anorg. Allg. Chem.* 641 (2015) 1150–1155. (DOI: 10.1002/zaac.201500050)