Single crystal growth of lead (II) *n*-octa-, *n*-nona- and *n*-decanoate

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Abstract

Single crystals of lead (II) *n*-octa ($Pb(C_8)_2$), *n*-nona ($Pb(C_9)_2$), and *n*-decanoate ($Pb(C_{10})_2$) have been obtained by using a silica gel technique. These crystals have been identified by polarizing light microscopy, X-ray diffraction, Raman spectroscopy, and scanning electron microscopy. The crystals show polyhedral morphology bounded by flat (001) faces and non-flat striated faces. Cleavage lines can be observed in the (001) faces. This cleavage can be related with the bilayer structure of these compounds. Two kinds of crystals with different internal cleavage angle have been found in $Pb(C_9)_2$ and $Pb(C_{10})_2$. The value of this angle is 90° in one of them and ~ 120° in the other one. This fact can be explained by taking into account the polymorphism and polytypism in the lead (II) alkanoates series.

The lead (II) alkanoates series ($Pb[CH_3(CH_2)_{n-2})COO]_2$, where n is the number of the carbon chains, with the carboxylic group included) has been broadly studied in the last years. This series belongs to the family of the so-called organic salts, formed by an alkylic chain with a polar carboxylate anion and a lead (II) cation. Its interest is due both to its *polymorphism* and thermo- and lyotropic *polymesomorphism*, and to the ease for "moving" a particular physical property to a desired condition by changing the size or shape of the organic ions and/or those of the inorganic counterion. We may cite Franzosini and Sanesi's book [1] and Mirnaya et al.'s review [2], where important industrial applications of these ionic crystals are claimed. Particularly interesting of the lead (II) alkanoates series is the large size of the lead (II) cation; since when mixturing two mesogenic salts, the resulting lyotropism decreases with temperature when increasing the difference in size of the counterions of the binary mixture [2].

Moreover, this series of compounds presents polytypism. A different thermal behaviour when registering the thermogram, and also differences in the Raman spectra of the crystalline and premelted samples, have been observed [3].

These compounds were obtained by metathesis of potassium (I) by lead (II) from the corresponding organic salt, previously obtained by an acid–base reaction between the organic acid and potassium hydroxide, in ethanolic solution [3,4].

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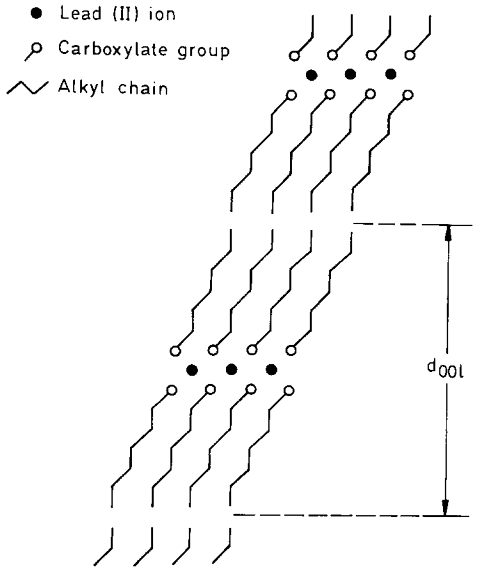

Fig. 1. Schematic representation of the bilayer structure of lead (II) *n*-alkanoates.

Several crystallizations in ethanol were followed until a high purity sample was obtained.

The lead (II) *n*-alkanoates are arranged in bilayers with the chain axes parallel to each other with a characteristic tilt angle between the chain and the ionic surface, as schematically shown in Fig. 1. The layers, which are electrically neutral and form stable structure units parallel to (001), are joined to each other by Van der Waals forces. In general, *n*-alkanoates can occur in more than one crystalline form. Depending on their structural characteristics these forms are classified as polytypes or polymorphs. Polytypism is caused by different stacking sequences of the layers, while keeping the two-dimensional arrangements within the individual layer unchanged. Polymorphism is attributed to different combinations of all the possible molecular interactions. The representative interactions occur through CH_3 end groups between adjacent layers, and through hydrocarbon planes inside individual layer.

However, in the case of lead (II) *n*-alkanoates serious discrepancies among the different authors were found, not only in the nature and amount of the different phases (one or two liquid crystal phases in one compound) [5–7], but also in the crystal Bragg spacings for some members of the series, and about the tilt angle of the chains with respect of the layers of the crystal [5,8].

In an attempt to solve these discrepancies, we have obtained single crystals of several members of the lead (II) series by a double diffusion–reaction system [9]. In this system, two reagents diffuse through a silica hydrogel column (9 mm diameter and 280 mm long) to generate the corresponding lead(II) *n*-alkanoate as a reaction product.

Silica hydrogel has been prepared by the acidification of a Na_2SiO_3 solution (Merck, density: 1.059 g/cm^3, pH = 11.2) with a 1M HCl solution, until the desired pH level (5.5 in all the experiments). The source reservoirs have been filled with a 0.5M sodium octanoate or 0.05M potassium nona- or decanoate solutions, and lead(II) nitrate solutions (similar concentration as that of the organic salts). The temperature was 25° C in all the experiments.

The waiting period (the time taken for the first crystallites to be observed under a magnification of ×500) was 60 days in all the experiments. After the growth process the crystals were removed from the gel, and cleaned several times with ethanol. The obtained crystals were colourless and extremely fragile during manipulation. The single crystals were identified by polarizing light microscopy, X-ray diffraction, Raman spectroscopy, and scanning electron microscopy (SEM).

The crystals obtained show polyhedral morphologies bounded by flat (001) faces and non-flat striated faces. Such morphologies involve a growth rate controlled by a spiral growth mechanism. Fig. 2 shows a scanning electron micrograph of a tabular crystal of lead (II) *n*-nonanoate. In this picture, the (001) face and the cleavage lines parallel to (001) can be observed. The cleavage is related with the structure of lead (II) *n*-alcanoates. In these structures the layers are joined to each other by van der Waals interactions. Since these interactions are weak we may expect such crystals to have excellent cleavage. In Fig. 2 it can be seen that the internal angle between the two cleavage directions is approximately 90° (Type I).

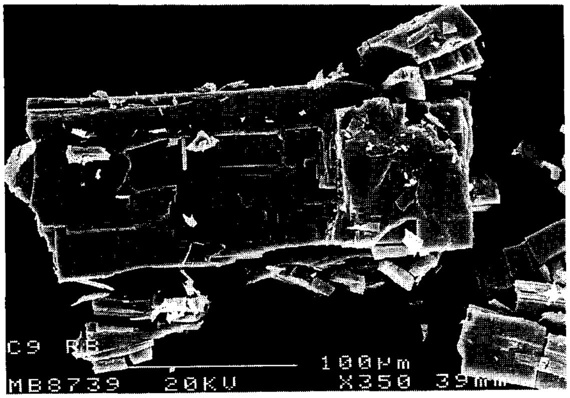

Fig. 2. Scanning electron micrograph of a single crystal of lead (II) *n*-nonanoate with cleavage lines with an angle of 90° with respect to each other.

In the cases of lead (II) *n*-nonanoate and *n*-decanoate, another kind of crystal has been found in the crystals grown by the gel technique. Fig. 3 shows cleavage lines on the (001) face with an angle between them of ~ 120° (Type II). These two kinds of lead (II) *n*-nonanoate crystals can be explained by taking into account the polymorphism and polytypism in this compound.

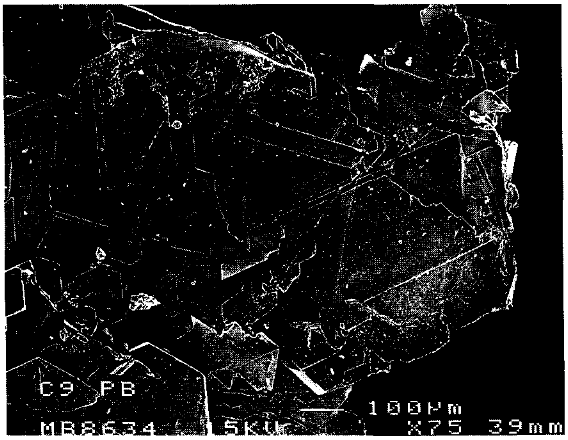

Fig. 3. SEM of a lead (II) *n*-nonanoate crystal showing two cleavage directions with an angle of 120° with respect to each other.

Table 1
X-ray data of single crystals

l	d/l (Å)	I/I_0	d (Å)
$Pb(C_8)_2$			
1	24.660	100	24.660
2	12.600	59	25.200
3	8.455	58	25.565
4	6.355	46	25.420
5	5.088	46	25.440
6	4.251	18	25.506
$Pb(C_9)_2$ (Type I)			
1	27.247	100	27.247
2	13.799	56	27.598
3	9.273	62	27.819
4	6.970	18	27.880
5	5.590	19	27.950
$Pb(C_9)_2$ (Type II)			
1	26.612	100	26.612
2	13.598	57	27.196
3	9.118	38	27.354
4	6.810	40	27.240
5	5.471	45	27.355
6	4.576	20	27.456
7	3.922	24	27.454
8	3.430	13	27.440
9	3.050	15	27.450
10	2.739	9	27.390
$Pb(C_{10})_2$ (Type II) [a]			
1	28.049	100	28.049
2	14.489	50	28.978
3	9.772	47	29.316
4	7.406	18	29.624
5	5.946	19	29.730
6	4.942	7	29.652
7	4.240	8	29.680

[a] Only X-ray data of type II because crystals of type I are scarce.

Powder diffraction patterns were obtained by using copper Kα radiation, and a graphite monochromator. The main reflections, shown in Table 1, are in agreement with the ASTM cards numbers 5-332, and 9-615. These diffraction patterns have similar characteristics as other alkanoates: in the region of low Bragg angle ($2\theta <$ 20°) a series of strong reflections can be observed. These reflections correspond to different divisors of the "long spacing", d_{001} (25.455 Å for $Pb(C_8)_2$, 27.766 and 27.403 Å for $Pb(C_9)_2$, and 29.581 Å for $Pb(C_{10})_2$), and can be indexed as

(00l); their intensity decreases, in general, as "l" increases. For higher Bragg angles, the reflections have lower intensity. These reflections correspond to "side spacings" resulting from the side attachment between alkylic chains. Therefore, X-ray powder data confirm a lamellar structure for these kinds of alkanoates.

The thermodynamics and structural properties of these isolated polytypes will be discussed in detail in a later publication.

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