DOI: 10.1021/cg101272n

Lithium and Lead(II) Butyrates Binary System. Pure Compounds and an Intermediate Salt: From 2D to 3D Coordination Polymers

F. J. Martínez Casado,^{†,‡} M. Ramos Riesco,[§] I. da Silva,^{||} M. I. Redondo Yélamos,[§] A. Labrador,[†] and J. A. Rodríguez Cheda^{*,§}

[†]BM16-Laboratori de Llum Sincrotó (LLS), c/o ESRF, 38043 Grenoble, France, [‡]Laboratorio de Estudios Cristalográficos IACT, CSIC-UGR, Edificio Inst. López Neyra, Avenida del Conocimiento s/n, P.T. Ciencias de la Salud, E-18100 Armilla, Granada, Spain, [§]Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain, and ^BBM25-Spline, c/o ESRF, 38043 Grenoble, France

Received September 28, 2010; Revised Manuscript Received December 20, 2010



ABSTRACT: The binary phase diagram between lithium and lead(II) butyrates, $[x\text{LiC}_3\text{H}_7\text{CO}_2 + (1 - x)\text{Pb}(\text{C}_3\text{H}_7\text{CO}_2)_2]$ was determined by differential scanning calorimetry, in order to investigate the formation of intermediate salts. A complex or intermediate salt (with a 1:1 stoichiometry) was found during the solution of the phase diagram. Crystals of this salt, which melt incongruently at $T_{\text{fus}} = 443.2$ K, were obtained later by crystallization. The structures of the crystal phase of both pure compounds and the intermediate salt were solved by single crystal and powder X-ray diffraction, using synchrotron radiation. Lithium and lead(II) butyrates present a monoclinic unit cell ($P2_1/c$ and $P2_1/m$, respectively). Both pure salts show a bilayered arrangement, in a structure of 2D coordination polymers, as usually metal alkanoates do. Nevertheless, the complex forms a microporous 3D ionic network (tetragonal, $I4_1/a$), very atypical in this kind of organic salts. Binary phase diagrams are proved to be a powerful tool to detect and predict the formation of intermediate crystals.

1. Introduction

Metal alkanoates^{1–6} or metal soaps $(Me(Cn)_x)$ (where Me is the metal cation with charge +x and n is the total number of carbons in the alkanoate anion, from now on) are well-known not only for their properties as surfactants in solution but also for their *polymesomorphism* (liquid crystal, *rotator*⁷ or *condis*⁸ phases) and their varied *stepwise melting* processes; that is, all the transitions involved from the totally ordered crystal to the isotropic liquid.

The amphiphilic nature of pure metal soaps, with metal cations and linear alkanoate anions, makes them present a characteristic bilayered structure (usually 2D coordination polymers) in the crystal phase, with alternating ionic and lipidic layers,⁹ with some exceptions, as in the case of copper-(II) alkanoates that form 1D coordination polymers.^{10,11} To obtain a 3D ionic structure in this kind of salts is rather difficult due to the steric hindrance in the alkyl chains packing (hydrophobic nuclei), and it has been uniquely seen in some hydrated short alkanoates.^{15–18} In this sense, mixing short alkanoates with different metal cations may be the key to obtain 3D-MOFs (metal–organic frameworks) from bilayered organic salts.

The solution of binary phase diagrams of salts is one of the best methods for studying and obtaining intermediate compounds or complexes from pure salts. Obviously, to deal with real binary phase diagrams, the two salts need to have the same cation or anion, to avoid the formation of new components by metathesis of the ions. Plenty of binary systems with common cations or common anions formed by alkali alkanoates have been analyzed, and some of them were reviewed and critically evaluated.¹⁹ Originally, the main objective of these works had been to study the formation and stabilization of an ionic liquid crystal (ILC) phase, trying to decrease the melting point to have this phase at lower temperatures. Moreover, some studies have reported the formation of a homogeneous liquid crystal region in the phase diagram, by mixture of two nonmesogenic (but "potentially mesogenic") compounds. This formation is favored by mixing salts with different (the bigger the better) sized cations.²⁰ There are specifically some binary phase diagrams containing lithium butyrate, such as [LiC4 + NaC4],²¹ [LiC4 + RbC4],²² and [LiC4 + CsC4],²³ showing the formation of an ILC phase, and others, from short lithium alkanoates ([LiC3+TlC3] and [LiC5+TlC5]),²⁴ proving the stabilization of such phase, besides presenting the formation of intermediate salts or complexes. Another objective of the present work has been also to obtain an ILC phase from two "potentially mesogenic" salts, such as LiC4 and $Pb(C4)_2$.

Lithium or lead(II) butyrates were selected not only for the short chain length but also for the special characteristics of the metal cations: small size, high polarizability, and short bonds of lithium,²⁵ and complex coordination and low polarizability of lead(II).²⁶ The results of this study have been satisfactory, and the two components are good candidates to obtain MOFs.

On the one hand, lithium alkanoates (LiC*n*) have been widely studied for the last few decades,²⁷ by several techniques, such as adiabatic calorimetry,²⁸ DSC,²⁹ or XRD,^{30–32} among others. However, the molecular structure of some members of the series has been recently discovered for the first time: the ones for anhydrous lithium acetate and its hydrates,¹² forming 3D coordination polymers, and lithium propanoate and pentanoate (LiC3 and LiC5),³³ showing the typical bilayered structure of metal alkanoates. On the other

^{*}Corresponding author. Telephone: +91-3944306. Fax: +91-3944135. E-mail: cheda@quim.ucm.es.

Table 1.	Experimental	Parameters and	Main (Crystallographic	Data for t	he Studied	Compe	ounds

data	LiC4a	LiC4b	LiPb(C4) ₃ a	LiPb(C4) ₃ b
empirical formula	LiC ₄ H ₇ O ₂	LiC ₄ H ₇ O ₂	LiPbC ₁₂ H ₂₁ O ₆	LiPbC ₁₂ H ₂₁ O ₆
$M_{\rm r}({\rm g}\cdot{\rm mol}^{-1})$	94.04	94.04	475.42	475.42
λ (Å)	0.7514	0.7513	0.7379	0.7513
crystal system	monoclinic	monoclinic	tetragonal	tetragonal
space group	$P2_1/c$	$P2_1/c$	$I4_1/a$	$I4_1/a$
temp (K)	100(2)	298(2)	100(2)	298(2)
crystal size (mm)	$0.07 \times 0.05 \times 0.007$	$0.07 \times 0.05 \times 0.007$	$0.07 \times 0.04 \times 0.04$	$0.07 \times 0.05 \times 0.03$
a (Å)	11.800(2)	12.153(2)	18.052(3)	18.417(3)
$b(\mathbf{A})$	4.9110(10)	4.9280(10)	18.052(3)	18.417(3)
$c(\dot{A})$	8.8460(18)	8.9050(18)	19.523(4)	19.880(4)
β (deg)	91.41(3)	91.58(3)	90	90
$V(Å^3)$	512.47(18)	533.12(19)	6362.1(18)	6743.0(19)
Z	4	4	16	16
$D_{\rm c} (\rm g \cdot \rm cm^{-3})$	1.219	1.172	1.985	1.873
$\mu (\mathrm{mm}^{-1})$	0.09	0.09	10.63	11.45
F(000)	200	200	3616	3616
reflection collected	1657	1625	21328	50928
absorption correction			multiscan	multiscan
independent reflections/ R_{int}	975/0.085	941/0.035	3632/0.172	3572/0.115
reflections with $I > 2\pi(D)$	793	772	2772	3222
$\frac{20(1)}{\theta}$	27 50/08 20/	27 50/05 40/	28 60/00 00/	28 10/00 50/
data/restraints/	975/0/92	941/0/64	3632/7/182	3572/7/181
index ranges:				
h	$-14 \rightarrow 14$	$-14 \rightarrow 14$	$-23 \rightarrow 23$	$-23 \rightarrow 23$
k	$0 \rightarrow 6$	$0 \rightarrow 5$	$-23 \rightarrow 23$	$-22 \rightarrow 23$
1	$-10 \rightarrow 10$	$=10 \Rightarrow 10$	$\begin{array}{c} 23 \\ -25 \rightarrow 22 \end{array}$	$-25 \rightarrow 25$
hydrogen treatment	only H-atom coordinates refined	H-atom parameters not refined	H-atom parameters not refined	H-atom parameters not refined
goodness of fit	1.045	1.112	1.061	1.092
final <i>R</i> indices $[I > 2\sigma(I)]$: R1/wR2	0.075/0.220	0.0650/0.1862	0.0731/0.1949	0.0376/0.0991
<i>R</i> indices (all data): R1/wR2	0.088/0.2201	0.0805/0.2070	0.0864/0.2133	0.0405/0.1021
largest diff. peak and hole $(e \cdot Å^{-3})$	0.493/-0.366	0.302/-0.252	2.75/-2.30	1.300/-1.175
CCDC deposition number	793980	793981	794307	793984

hand, numerous similar studies have also been done in the lead(II) alkanoates series, $Pb(Cn)_2$.^{34–40} During the last few years, the short members of the series (Pb(C2)₂ to Pb(C4)₂) have also been synthesized and analyzed,⁴¹ and the nature of the intermediate phase as *rotator* has been discovered for members with $n \ge 5$,⁴² and also the formation of a *rotator* glass for Pb(C5)₂.⁴³ Although the members of the series point to be isostructural, only the structure of lead(II) heptanoate, also bilayered, had been solved and refined so far.⁴⁴

The study of the $[LiC4 + Pb(C4)_2]$ system demonstrated the formation of a 3D ionic network in an intermediate salt from 2D coordination polymers, and the absence of a ILC phase in this case. Moreover, solving binary phase diagrams predicts the intermediate compounds formation without having to isolate them by crystallization, and it could be used to design them.

2. Experimental Section

2.1. Sample Preparation. a. Pure Samples: LiC4 and Pb(C4)₂. The synthesis of LiC4 was described in the literature, 28b,29a using Li₂CO₃ and butyric acid, as reagents, with a slight excess of the latter, in deionized water. However, it was preferred to vary the method in order to avoid the formation of acid soaps or the presence of water. Thus, LiC4 was obtained by reaction between lithium hydroxide (LiOH \cdot H₂O, Fluka, \geq 99%), instead of lithium carbonate, and the butyric acid (Fluka, \geq 99.5%), using ethanol (Merck, \geq 99.8%) as solvent. The salt was recrystallized several times in methanol (Merck, 99.8%) and precipitated with 2-propanol (Panreac, 99%).

Pb(C4)₂ was prepared, as described in a previous work,⁴¹ by reaction between the same butyric acid, used for the preparation of LiC4, and lead(II) oxide (Aldrich, \geq 99.8) in ethanol, being later recrystallized again in ethanol and vacuum-dried.

The purity of the synthesized products determined by differential scanning calorimetry (DSC) was 99.97 and 99.63% for LiC4 and $Pb(C4)_{2}$, respectively.

Once both phase diagrams were solved, the complex LiPb(C4)₃ was prepared as pure compound. Stoichiometric amounts (1:1) of LiC4 and Pb(C4)₂ were dissolved in hot methanol, respectively. LiPb(C4)₃ crystallized by slow evaporation of solvents. The salt was washed with acetone (Merck, >99.5%) and vacuum-dried. The thermal behavior of the intermediate salt thus obtained is similar to that of the mixture with the same composition.

Crystals suitable for single crystal X-ray studies were grown up by slow evaporation from solutions of compounds in the aforementioned solvents, after trying with several of them. In the case of LiC4, in spite of the great difficulty, it was possible to obtain a single crystal. As can be inferred from the solved crystal, the structure is bilayered (ionic and lipidic layers). The joining between these latter layers is very weak, making good crystals difficult to obtain due to the ease of exfoliation. This feature makes lithium alkanoates grow into flake-shaped crystals, as was also found for LiC3 and LiC5. The same feature occurs for lead(II) alkanoates, with the same bilayered structure. Thus, no single crystals of Pb(C4)₂ could be obtained, so the structure was solved by powder X-ray diffraction. In the case of LiPb(C4)₃, with a 3D ionic structure, and a prismatic morphology, it was less complicated to found proper crystals, maybe due to its 3D coordination polymer condition. The sizes of the single crystals are given in Table 1.

b. Molar Fractions of the Binary System. Twelve different mixtures were prepared (of about 0.3 g each), apart from the pure compounds, covering the whole range of compositions of the

Table 2. Temperatures, Enthalpies, and Entropies of the Transitions and Glass Transition of the Pure Compounds

compd	transition	T/\mathbf{K}	$\Delta H/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	$\Delta S/\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1}$	$T_{\rm g}/{ m K}$
$LiC4Pb(C4)_2LiPb(C4)_3b$	SI–IL SI–IL incongruent fusion	$591.0 \pm 0.5 \\ 346.5 \pm 0.3 \\ 443.2 \pm 0.5$	$\begin{array}{c} 21.1 \pm 0.1 \\ 14.7 \pm 0.1 \\ 32.0 \pm 0.3 \end{array}$	35.7 ± 0.2 42.4 ± 0.3 72.2 ± 0.8	274.9 ± 0.3^a

^{*a*} Measured at 10 K \cdot min⁻¹. ^{*b*} Values referred to the intermediate salt as a pure compound.

 $[LiC4 + Pb(C4)_2]$ systems. The estimated error in the molar fraction x was at most (± 0.002).

As it was reported previously,⁴¹ lead(II) butanoate quenches into a glass state very easily from the isotropic liquid phase. For this reason, it was not possible to get homogeneous mixtures by reheating the mixtures up and down from solid to melt. The molar fractions were instead obtained by dissolving the corresponding amounts of the pure compounds in methanol, removing it later in a rotavapor.^{22,24} Despite this precaution, the method used here to prepare the mixtures also failed in the molar fractions between x(LiC4) = 0 and 0.5, due to glass formation: the quick removal of the solvent led to an amorphous phase and did not allow crystallization. Thus, leaving the mixtures settling at room temperature for at least one month was needed, until the recovery of the thermodynamically stable behavior. Of course, glass states were again formed after the first heating of the mixtures, with it being necessary to wait the same time for measuring the second or following heatings.

2.2. Differential Scanning Calorimetry. A TA Instruments DSC, Model Q10, was used to register all the thermograms. Tightly sealed aluminum volatile pans were utilized, in dry nitrogen, flowing at $50.0 \text{ mL} \cdot \text{min}^{-1}$. A MT5Mettler microbalance was used to weigh the samples, ranging between 3 and 10 mg (with an error of ± 0.001 mg). The calorimeter was calibrated in temperature using standard samples of In and Sn, supplied by TA (purity >99.999% and >99.9%, respectively), and of benzoic acid (purity >99.97%), supplied by the former NBS (lot 39i), and in enthalpy with the In and Sn standards already described.

All of the measurements were done at a heating rate of 5 $\text{K} \cdot \text{min}^{-1}$, except the specific ones for the glass transition. All the scans were usually explored from 200 K to the temperature corresponding to the isotropic liquid in each case (a maximum of 650 K).

2.3. Single Crystal X-ray Diffraction (SCXRD). X-ray diffraction measurements were conducted using synchrotron radiation (Table 1) at the BM16 Spanish beamline⁴⁵ at ESRF, making phi scans when collecting the data. Data sets of 360 (or 180) images were collected in a ADSCq210r CCD detector. The oscillation rage $(\Delta \varphi)$ used for each image was 1°. LiC4 and LiPb(C4)₃ were measured at two different temperatures: *a*, to refer to the case at low temperature (100 K), and *b*, for the measurements at room temperature (see Table 1). In the case of the complex, LiPb(C4)₃, different crystals were needed for collecting data each time, because they suffered severe radiation damage, only being possible to measure them once with a short exposure time (2 s with an oscillation range of 1° per image taking 180 images, in the case of *LiPb*(*C4*)₃*a*, and 360 images, for *LiPb*(*C4*)₃*b*).

The structures were solved by direct methods and subsequent Fourier syntheses using the SHELXS-97 program⁴⁶ and were refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for all non-hydrogen atoms with the SHELXL-97 program.⁴⁷ The treatment of the hydrogen atoms was different depending on the compounds and the quality of the crystals: the positions of the hydrogen atoms were refined only for *LiC4a*; for the rest of the structures, the hydrogen atoms were calculated at geometrical positions and refined as riding on the respective carbon atoms.

The main crystallographic data and some experimental details are shown in Table 1.

2.4. Powder X-ray Diffraction. High resolution powder diffraction (HRPD) measurement was performed at SpLine beamline (BM25A) of the Spanish CRG at the European Synchrotron Radiation Facility (ESRF, Grenoble) with a fixed wavelength of (0.8266 \pm 0.0001) Å, at room temperature. The powdered sample was placed inside a 0.5-mm-diameter glass capillary, which was rotated during exposure. Data collection was done in a 2 θ -step scan mode with 0.015° step and 5 s acquisition time per point.

2.5. Infrared Spectroscopy (FTIR). The infrared spectra were recorded at room temperature in a Perkin-Elmer Spectrum 100 FTIR spectrometer using the universal ATR sampling accessory.

3. Results and Discussion

3.1. Thermal Analysis. The thermal behavior of the pure compounds was studied in previous works, for LiC4^{22,29} and Pb(C4)₂,⁴¹ and the results here obtained are in total agreement with the reported ones. LiC4 and Pb(C4)₂ present only one solid phase (solid I phase, SI from now on), melting at $T_{\rm f} = 591.0 \pm 0.5$ K and $T_{\rm f} = 346.5$ K ± 0.3 K, respectively. The other thermal data for these salts are shown in Table 2.

Regarding the $[LiC4 + Pb(C4)_2]$ binary system, 14 different molar fractions, including the pure components, were prepared to study this system. DSC data were normalized to "*heat flow per mole of mixture*" in order to make thermograms comparable with each other and to build a 3D representation of heat flow/temperature/molecular fraction (Figure 1 A). The 2D projection of the former plot, showing the construction of the *T vs x* phase diagram, is also given in Figure 1 B.

A ΔH vs x phase diagram (Figure 2A), showing the evolution of transition energies with composition, was drawn following the Tammann's method, ^{22,24,48} to find the characteristic points (**E** and **P**, eutectic and peritectic, respectively), in the apex of the triangles formed in this diagram. Finally, the complete *T* vs x phase diagram is represented in Figure 2B. All the defined regions, except in the isotropic liquid phase (IL), correspond to two phase-separation regions.

The characteristic reactions of this binary system, also eutectic and peritectic reactions, are described in Scheme 1.

An intermediate salt appears with a composition (1:1), LiPb(C4)₃. This compound was later isolated by crystallization in methanol and studied by DSC. LiPb(C4)₃ has only a transition that corresponds to the incongruent fusion or the peritectic reaction. The enthalpy of this transition is $(32.0 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$ per mole of complex or $(16.0 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$ per mole of mixture (the value reported in the plot). Obviously, since the intermediate salt is actually a pure compound, its molecular mass is twice the average molecular mass of the mixture with the composition x(LiC4) = 0.5, that is, 475.42 and 237.71 g \cdot mol⁻¹, respectively. The full thermal data for LiPb(C4)₃ are shown in Table 2.

Vitreous Pb(C4)₂ can be obtained by cooling the melt fast (10 K · min⁻¹ or faster), as has been reported previously.⁴¹ Also, a glass transition has been detected for the mixtures with $0 \le x(\text{LiC4}) < 0.5$, that is, the ones with free Pb(C4)₂ (symbol \bigcirc and dotted line, in Figure 2B). Nevertheless, the glass was here obtained also by a quick removal of the solvent. The glass transition for Pb(C4)₂ appeared at 274.9 K, measured at a heating rate of 10 K · min⁻¹. The thermodynamically stable behavior is recovered in these mixtures after one month at room temperature.

3.2. Structural Analysis. The crystal structures of LiC4 and LiPb(C4)₃, by SCXRD (at several temperatures), and of



Figure 1. (A) 3D plot (heat flow vs composition vs temperature) for the $LiC4 + Pb(C4)_2$ system. (B) Contour plot (with z corresponding to the heat flow) of the diagram composition vs temperature.



Figure 2. (A) ΔH (per mole of mixture) *vs* composition plot for the LiC4 + Pb(C4)₂ system, for the following main transitions: (solid triangle pointing right) solubilization of the Pb(C4)₂; (\bigcirc) eutectic reaction; (\blacklozenge) solubilization of the intermediate salt (MS); (\square) peritectic reaction; (\blacklozenge) solubilization of the LiC4. (B) *T vs* composition plot for the LiC4 + Pb(C4)₂ system, showing the eutectic point (E), and the peritectic point (P). *SI* and *IL* correspond to the *solid I* phase of each indicated compound and the isotropic liquid phase, respectively. The (\bigcirc) symbols represent the T_g values for these molar fractions in the second heating when quenched at 10 K · min⁻¹, until 250 K.

Scheme 1. Description of the Eutectic and Peritectic Reactions for the LiC4 + Pb(C4)₂ System^a

Eutectic reaction:

0,042 LiC4 + 0,958 Pb(C4)₂
T =340,7 K
1 *liq.* [x(LiC4) = 0.042]
$$\xrightarrow{\Delta H = -12,8 \text{ kJ·mol}^{-1}}$$
 0.956 Pb(C4)₂ + 0.044 LiPb(C4)₃

Peritectic reaction:

 $1 \text{ LiC4} + 1 \text{ Pb(C4)}_2$

1

$$\downarrow LiPb(C4)_3 \xrightarrow{AH = 32,0 \text{ kJ-mol}^-}_{T = 443,2 \text{ K}} 0.919 \text{ lia. } [x(LiC4) = 0.456] + 0.081 \text{ LiC4}$$

^{*a*} All of the phases are solid, except the ones indicated by *liq*. (liquid) with the corresponding composition of LiC4.

 $Pb(C4)_2$, by HRPD, have been solved and refined in this study.

LiC4 is isostructural with LiC3 and LiC5,³³ as expected, with the symmetry $P2_1/c$. It presents also a bilayered arrange-



Figure 3. (A) Crystal structure for LiC4 in the *ac* projection at 100 K (*LiC4a*). (B) Asymmetric unit showing 50% probability ellipsoids for all non-H atoms, and the tetrahedral coordination of Li atoms.

ment (alternating ionic and lipidic layers), as shown in Figure 3A. Although the association between alkyl chains is weak, the strong bonds (due to their ionic nature) in a 2D-net between lithium and oxygen atoms explains the high value for the melting point. The lithium atoms present a tetrahedral coordination (Figure 3B), joined by μ_4 -carboxylates. The structure for this compound was analyzed at two temperatures, 100 and 298 K, and the main crystallographic data are shown Table 1.

Table 3. Crystallographic Data, Experimental Parameters, and Structure Refinement Data for Pb(C4)₂

Data Collection diffractometer specimen mounting data collection mode scan mode 2θ range (deg), step size (deg 2θ)

Refinement refinement method R_p , R_{wp} , R_{exp} R_F , R_{BRAGG} goodness-of-fit profile function no. of contributing reflections no. of parameters no. of restraints CCDC deposition number

Pb(C4)₂ was analyzed by HRPD, due to the impossibility of growing good single crystals. The 2θ positions of the first 20 peaks were determined using the *WinPLOTR*⁴⁹ program, and peak indexing was carried out with the *DicVOL06*⁵⁰ program, and a monoclinic cell was found. The *Expo2009*⁵¹ program was used to find the correct space group; after an automatic intensity extraction procedure, the statistical algorithm for finding the correct space group⁵² found, as the most probable, $P2_1/m$.

Structure solving of Pb(C4)₂ was achieved by means of Direct Methods, with the *Expo2009* program, within the P21/m space group. All the 12 non-H atoms were found on a default run of the program.

Rietveld refinement was performed with the *FullProf*⁵³ program, introducing the atomic coordinates previously found by *Expo2009*. The atomic coordinates of the 12 independent non-H atoms were fitted for Pb(C4)₂. Two different isotropic temperature factors were introduced: one for the Pb atom and one for the rest of the atoms. The positions of H atoms were then introduced at the last stage of the refinement, at their calculated positions.

Crystal data for these two compounds are given in Table 3, while in Figure 4 the result of the Rietveld refinement is shown.

Pb(C4)₂ is a 2D coordination polymer and its structure is bilayered, as expected from the ones known for other members of the series.^{41–44} Despite longer members belonging to another crystal system (triclinic, $P\overline{1}$), the molecular arrangement is the same in all of the cases. Thus, there are two kind of alkyl chains, corresponding to two existing types of carboxylates: (a) μ_3 -carboxylate (with both oxygens chelating and one of them also coordinating another Pb atom) and (b) μ_4 -carboxylate (with both oxygens bridging and chelating). The ligands present a hemidirected geometry, with seven being the coordination number of the Pb atom and with the O atoms forming a distorted monocapped trigonal prism. The structure of Pb(C4)₂ is shown in Figure 5. Some selected bond distances (Pb–O and Pb–Pb) are displayed in Table 4.







Figure 4. Rietveld refinement for $Pb(C4)_2$, showing the excellent agreement between the observed and calculated diffraction patterns, their difference, and Bragg positions.

Both LiC4 and Pb(C4)₂ present a very compact packing in the alkyl chains, according the values of the *cross-section area* (S').^{24,32} This can be calculated in bilayered compounds from the *area per polar head* (S), and on the torsion (tilt) of the plane of the chains with respect to the ionic plane (α), with the following equation: $S' = S \cos(\alpha)$. The torsion angles for the alkyl chains for Pb(C4)₂ are 4.5°, almost negligible, and 33° for LiC4. The values of S (and S') are 17.4 (17.3) and 21.7 (18.2) for Pb(C4)₂ and LiC4, respectively. These values of S' indicate the dense packing of the chains, showing that there is no possibility for them to present *gauche* defects before the fusion, in agreement with the fact that no phase transition exists prior to the melting points in both cases.

 $LiPb(C4)_3$ was measured by SCXRD in the same solid phase (SI) at three different temperatures (100, 160, and 298 K). The arrangement of the molecules in this complex is



Figure 5. (A) Crystal structure for $Pb(C4)_2$ in the *ab* projection. (B) Asymmetric unit showing the coordination polyhedron of the lead(II) atom (hemidirected geometry).

(Both at 298 K)					
atom 1	atom 2	count	distance/Å		
Pb2	O5	$1 \times$	2.470(21)		
	O4	$1 \times$	2.572(21)		
	01	$2\times$	2.579(10)		
	O1	$2 \times$	2.794(14)		
	O5	$1 \times$	3.066(19)		
Pb2	Pb2	$2 \times$	4.368(1)		
	Pb2	$2 \times$	4.801(3)		
	Pb2	$2 \times$	4.959(2)		
Pb1	O2	$1 \times$	2.356(4)		
	O5	$1 \times$	2.420(4)		
	O4	$1 \times$	2.464(4)		
	O6	$1 \times$	2.685(6)		
	O3	$1 \times$	2.770(5)		
	O1	$1 \times$	2.799(5)		
	O6	$1 \times$	2.898(6)		
Pb1	Lil	$1 \times$	3.396(9)		
	Lil	$1 \times$	3.866(9)		
	Lil	$1 \times$	3.917(9)		
	Pb1	$2 \times$	4.8811(7)		
	eta dom 1 Pb2 Pb2 Pb1 Pb1	(Both at 298 K) atom 1 atom 2 Pb2 O5 O1 O1 O1 O5 Pb2 Pb2 Pb2 Pb2 Pb1 O2 O4 O6 O3 O1 O6 Pb1 Li1 Li1 Li1 Pb1	atom 1 atom 2 count Pb2 O5 1× O1 2× O1 2× O1 2× O1 2× O5 1× Pb2 2× Pb2 Pb2 2× Pb2 2× Pb1 O2 1× O5 1× O6 1× O5 1× O6 1× O6 1× O6 1× O6 1× O6 1× O6 1× O1 1× O6 1× Pb1 Li1 1× D6 1× Pb1 Li1 1× Pb1 Ei1 1× Pb1 Li1 1× Pb1 Ei1 1× Pb1 2× Pb1 2× Pb1 2×		

Table 4. Pb–O and Pb–Metal Distances for Pb(C4)₂ and LiPb(C4)₃ (Both at 298 K)

much more complex than that in the pure compounds, as can be inferred from its structure. The orientations of the 3D structure through the *a* (similar to *b*) and *c* axes are plotted in parts A and B, respectively, of Figure 6. Lithium and lead(II) cations and carboxylate anions build a tetragonal microporous 3D-net, with the symmetry $I4_1/a$. The crystal data for this salt are given in Table 1. The coordination numbers are four for the Li atoms, in a tetrahedral coordination, and seven (hemidirected monocapped trigonal prism) for the Pb ones (as in the case of Pb(C4)₂). There are also two kinds of carboxylates: (a) μ_4 -carboxylates (two of them, with both oxygens bridging and chelating), and (b) one μ_3 -carboxylate (chelating the Pb atom, with one O coordinating also the Li atom). The asymmetric unit is represented in Figure 6C, showing the aforementioned arrangement.

The ionic structure of this intermediate salt can be represented in clusters, containing four Pb atoms each in the core, with each Pb being surrounded by three Li atoms. Four Li and four O atoms become the joints between these clusters (Figure 7), making the structure move up from 2D to 3D. Short Pb–O and Pb–Li, and Pb–Pb distances are shown in Table 4. In the case of Pb–O distances, these are comparable to the ones for Pb(C4)₂, as both compounds present similar coordination in the Pb atoms.



Figure 6. Crystal structure, indicating the unit cell, for LiPb(C4)₃ along the *b* and *c* axes, in A and B, respectively (the H and the C atoms, except the ones of the carboxylate anions, have been removed). (C) Asymmetric unit of LiPb(C4)₃ at 100 K (*LiPb*(*C4*)₃ *a*), showing 50% probability ellipsoids for all non-H atoms. Coordination polyhedra of Li and Pb atoms are included in blue and orange, respectively.

Four other mixed-metal alkanoates forming MOFs are known. All of these compounds contain calcium: Ca_2Pb - $(C3)_6$,¹⁵ $Ca_2Sr(C3)_6$,¹⁶ $Ca_2Ba(C3)_6$,¹⁷ and $Ca_2Ba(C4)_6$.¹⁸ Although the symmetry of LiPb(C4)₃ is similar to that of some of them (tetragonal), their ionic arrangements are very different. Three Li atoms surround each Pb atom, and vice versa, while, in the other cases, the big metal cation (Pb, Sr, or Ba) is located in the center of a distorted tetrahedron formed by four Ca ions; each of these is surrounded by six O atoms, forming a distorted octahedron. All of these calcium-based complexes present solid-to-solid transitions at low temperatures related to electrical properties (ferroelectricity and



Figure 7. View of the clusters of $LiPb(C4)_3$ along the *c* and *b* axes (A and B, respectively), highlighting the joining atoms (Li, purple; O, red) and showing the bonding direction in solid and dashed arrows (upward and downward, respectively).

paraelectricity).⁵⁴⁻⁵⁷ In the case of LiPb(C4)₃, no phase transitions were found above 180 K, apart form the incongruent fusion, as has been explained in section 3.1.

Other mixed-metal alkanoates recently discovered, Li₂Tl- $(C3)_3$ and Li₂Tl $(C5)_3$,²⁴ are 2D coordination polymers, as are most pure metal alkanoates. In those cases, the presence of two lithium atoms in the asymmetric unit makes the bilayered structure of lithium alkanoates remain.³³ Thus, the existence of an intermediate salt with the same stoichiometry, Li₂Tl $(Cn)_3$, can be predicted for any [LiCn + TlCn] system, since the salts present a bilayered structure with the same ionic arrangement. However, in the [LiCn + Pb $(Cn)_2$] systems, it is not possible to extrapolate the formation of complexes with the stoichiometry 1:1, LiPb $(Cn)_3$, at least not with the same structure, because large alkyl chains pointing into the pores of the net make it no longer stable for steric reasons.

Regarding the organic part of the molecule in the LiPb-(C4)₃, the alkyl chains partially occupy the pores, with room enough to present some kind of disorder. Thus, the thermal ellipsoid sizes of the β -, γ -, and δ -C atoms for the three chains are much bigger than those for the other atoms. This was observed at the three temperatures of measurement. The same feature was found for all of the calcium-based complexes, as in the case of Ca₂Ba(C3)₆,¹⁷ or Ca₂Ba(C4)₆,¹⁸ where even the position of these C atoms could not be defined.

The FTIR spectra of LiC4, Pb(C4)₂, and LiPb(C4)₃ are shown in Figure 8. As can be seen, the v_{as} COO⁻ vibration at 1504 cm⁻¹ in Pb(C4)₂ and at 1580 and 1561 cm⁻¹ (doublet) in LiC4 shifts to 1523 (singlet) in the complex LiPb(C4)₃ and the v_s COO⁻ bands at 1444 and 1397 cm⁻¹ in Pb(C4)₂ and 1439 and 1417 cm⁻¹ in LiPb(C4)₃ shift to a doublet at 1430 and 1400 cm⁻¹ in LiPb(C4)₃. It is remarkable that in the CH₂ wagging and rocking regions (1400–700 cm⁻¹) the spectra of the intermediate salt and the Pb(C4)₂ are almost coincident in the number and frequency of the different bands. Only bands at around 1309 cm⁻¹ and 805 cm⁻¹ corresponding to *gauche* conformations⁵⁸ present in the chain of the intermediate salt are observed in its spectrum.

Finally, no mesogenicity was observed in the [LiC4 + $Pb(C4)_2$] system, which was one of the aims of this work. In other phase diagrams studied, such as those for [LiC4 + RbC4],²² [LiC4 + CsC4],²³ or [LiC5 + TlC5],²⁴ a homogeneous ionic liquid crystal (ILC) phase is formed in a large range of composition. Another case to compare with is the



Figure 8. FTIR spectra at room temperature for LiC4, LiPb(C4)₃, and Pb(C4)₂ in black, red, and blue, respectively, in the ν (COO) region.

[LiC4 + NaC4] system, in which the ILC phase also appears but is less stabilized than in the previous ones, since the temperature range of existence decreases from the pure compound (NaC4) to the LiC4-NaC4 mixture. The ILC phase does not even appear in the case of the [LiC3 + TlC3]phase diagram.²⁴ The influence of the chain length and of the cation size has been deeply studied in several metal alkanoate series for the appearance of liquid crystal phases.^{1,2} The appearance of the liquid crystal phase in pure compounds starts from $n \ge 4$ for NaCn, from $n \ge 5$ for RbCn and TlCn, from $n \ge 6$ for CsCn and Pb(Cn)₂, and from $n \ge 12$ for LiCn (with n being the total number of carbon atoms of the shortest member forming this mesophase, the so-called *criti*cal length). The radius values for monovalent Li, Na, Rb, Cs, and Tl are 0.59, 1.02, 1.52, 1.67, and 1.50 Å, respectively, while the radius of divalent Pb(II) ion is smaller: 1.19 Å. Thus, it seems to be clear that series with intermediate-sized cations present an ILC phase with lower values of n,^{1,20} indicating that mixtures of alkanoates with different-sized cations at intermediate compositions (with average intermediate-size cations) should behave in the same way. This may be the reason why, with a certain chain length, systems mixing ions such as Li-Rb, Li-Cs, or Li-Tl present a stable ILC phase and other mixtures such as Li-Na or Li-Pb do not. Moreover, lead(II) as well as thallium(I) present low polarizability. Therefore, they form less ionic and weaker

bonds than the alkaline and alkaline earth cations. This explains the lower melting points of lead(II) alkanoates in comparison with those of the alkaline and alkaline earth ones.

4. Conclusions

The phase diagram of lithium and lead(II) butyrates, thoroughly studied by DSC, XRD, and FTIR, shows the formation of a complex with a 3D ionic arrangement (3D coordination polymer), totally different from the bilayered structure (2D) of both pure compounds and typical of most of the metal alkanoates and some mixed-metal alkanoates.

The transition from 2D to 3D coordination polymers found in this system can be extrapolated to other alkanoate mixtures, changing conveniently the metal cation. This would be a new method to find materials with interesting properties: such as magnetic (using transition metals) or porosity control. However, although the compounds used in these systems contain lead or thallium in their composition, which are poisonous, the nature of such atoms (peculiar coordination, low polarizability, etc.) makes these salts able to present interesting features, not only from the physical-chemical point of view but also to establish correlation rules to be extended to other materials with "green" components.

The formation of a stable ILC phase was not found in the $[\text{LiC4} + \text{Pb}(\text{C4})_2]$ system. However, similar binary phase diagrams between longer members of the lithium and lead(II) alkanoates series can produce a stable ILC phase, in a broad region of the phase diagram. Moreover, since longer lead(II) alkanoates present a *rotator* phase,⁴² with a considerable increase of its electrical conductivity, they could be used in binary systems to get high conductivity fluid phases, which could be even increased by doping them with small amounts of lithium due to its high mobility.

In summary, this method of solving binary phase diagrams has proved to be a very useful tool to detect and predict intermediate compounds prior to their isolation and crystallization, and in the same way, it could also be valid for studying cocrystallization processes between functionalized chemicals.

Acknowledgment. Partial support of this research by the *Beca de Especialización en Organismos Internacionales* (ES-2006-0024) and by the DGICYT of the Spanish *Ministerio de Ciencia e Innovación* (Project CTQ2008-06328/BQU) is gratefully acknowledged. The authors wish to thank BM16-LLS and BM25 (both Spanish beamlines at the ESRF, in Grenoble, France) for the use of their technical facilities.

Supporting Information Available: The structures reported in this paper may be obtained from the Cambridge Crystallographic Data Center, on quoting the depository numbers 793980 and 793981, for *LiC4a* and *LiC4b*, respectively, 793985 for $Pb(C4)_2$, and 794307 and 793984, for *LiPb*(*C4*)₃*a* and *LiPb*(*C4*)₃*b*, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

References

- Franzosini, P.; Sanesi, M. Thermodynamic and transport properties of organic salts; Pergamon Press: Oxford, 1980.
- (2) (a) Skoulios, A.; Luzzati, V. Acta Crystallogr. 1961, 14, 278–286. (b)
 Gallot, B.; Skoulios, A. Acta Crystallogr. 1962, 15, 826–831. (c)
 Abied., H.; Guillon, D.; Skoulios, A.; Weber, P.; Giroud-Codquin,
 A. M.; Marchon, J. C. Liq. Cryst. 1987, 2 (3), 269–279.
- (3) Giroud-Godquin, A. M. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, K. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, Chapter XIV, p 901.

- (4) Donnio, B. Curr. Opin. Colloid Interface Sci. 2002, 7, 371-394.
- (5) Donnio, B.; Guillon, D.; Deschenaux, R.; Bruce, D. W. Metallomesogens. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, 2003; Vol. 7, Chapter 7.9, pp 357–627.
- (6) Binnemans, K.; Görller-Walrand, C. Chem. Rev. 2002, 102 (6), 2303–2345.
- (7) Sirota, E. B.; King, H. E.; Singer, D. M.; Shao, H. H. J. Chem. Phys. 1993, 98 (7), 5809–5824.
- (8) Wunderlich, B.; Möler, M.; Grebowicz, J.; Baur, H. Conformational Motion and Disorder in Low and High Molecular Mass Crystals; In Advances in Polymer Science. Number 87; Höcker, H., Ed.; Springer-Verlag: Heidelberg, 1988.
- (9) (a) Vand, V.; Lomer, T. R.; Lang, A. Acta Crystallogr. 1949, 2, 214–220. (b) Lomer, T. R. Acta Crystallogr. 1952, 5, 11–14. (c) Lomer, T. R. Acta Crystallogr. 1952, 5, 14–17. (d) Dumbleton, J. H.; Lomer, T. R. Acta Crystallogr. 1965, 19, 301–307.
- (10) (a) Bird, M. J.; Lomer, T. R. Acta Crystallogr., B 1972, 28, 242–246.
 (b) Lomer, T. R.; Perera, K. Acta Crystallogr., B 1974, 30, 2912–2913.
 (c) Lomer, T. R.; Perera, K. Acta Crystallogr., B 1974, 30, 2913–2915.
- (11) Ramos Riesco, M.; Martínez Casado, F. J.; López-Andrés, S.; García Pérez, M. V.; Redondo Yélamos, M. I.; Torres, M. R.; Garrido, L.; Rodríguez Cheda, J. A. *Cryst. Growth Des.* 2008, 8 (7), 2547–2554.
- (12) Enders-Beumer, A.; Harkema, S. Acta Crystallogr., B 1973, 29, 682–685.
- (13) Cameron, T. S.; Mannan, K. M.; Rahman, M. O. Acta Crystallogr., B 1976, 32, 87–90.
- (14) Martínez Casado, F. J.; Ramos Riesco M.; Redondo, M. I.; López-Andrés, S.; Cheda, J. A. R. Cryst. Growth Des. DOI: 10.1021/ cg1010133.
- (15) Shaikh, A. M.; Dhar, V. J. Appl. Crystallogr. 1982, 15, 635-636.
- (16) (a) Maruyama, H.; Tomiie, Y.; Mizutani, I.; Yamazaki, Y.; Uesu, Y.; Yamada, N.; Kobayashi, J. J. Phys. Soc. Jpn. 1967, 23, 899. (b) Mizutani, I.; Yamazaki, Y.; Uesu, Y.; Yamada, N.; Kobayashi, J.; Maruyama, H.; Tomiie, Y. J. Phys. Soc. Jpn. 1967, 23, 900.
- (17) Stadnicka, K; Glazer, A. M. Acta Crystallogr., B 1980, 36, 2977.
- (18) Kiosse, G. A.; Razdbreev, I. M.; Malinowskii, T. I. Sov. Phys. Crystallogr. 1988, 33, 690.
- (19) Franzosini, P.; Ferloni, P. Molten Alkali Metal Alkanoates; IUPAC Solubility Data Series; Schiraldi, A., Spinolo, G., Eds.; Pergamon Press: Oxford, 1988; Vol. 33.
- (20) Mirnaya, T. A.; Volkov, S. V. Ionic Liquid Crystals as Universal Matrices (Solvents). Main Criteria for Ionic Mesogenicity; In Green Industrial Applications of Ionic Liquids; Rogers, R. D. et al., Eds.; NATO Science Series; Kluwer Academic Publishers: 2003; pp 439-456.
- (21) Prisyazhny, V. D.; Mirny, V. N.; Mirnaya, T. A. Ukr. Khim. Zh. 1983, 49, 668–669.
- (22) Martínez Casado, F. J.; Ramos Riesco, M.; Cheda, J. A. R. J. Term. Anal. Calorim. 2007, 87 (1), 73–77.
- (23) Mirnaya, T. A.; Yaremchuk, G. G.; Prisyazhnyi, V. D. Liq. Cryst. 1990, 8, 701–705.
- (24) Martínez Casado, F. J.; Ramos Riesco, M.; Da Silva, I.; Labrador, A.; Redondo, M. I.; García Pérez, M. V.; López-Andrés, S.; Cheda, J. A. R. J. Phys. Chem. B 2010, 114 (31), 10075–10085.
- (25) Olsher, U.; Izatt, R. M.; Bradshaw, J. S.; Dalley, N. K. Chem. Rev. 1991, 91 (2), 137–164.
- (26) Claudio, E. S.; Magyar, J. S.; Godwin, H. A. Fundamental Coordination Chemistry, Environmental Chemistry, and Biochemistry of Lead(II). *Prog. Inorg. Chem.* 2003, *51*, 1–144.
- (27) Ferloni, P.; Westrum, E. F. Pure Appl. Chem. 1992, 64 (1), 73-78.
- (28) (a) Franzosini, P.; Westrum, E. F. J. Chem. Thermodyn. 1984, 16, 81–90. (b) Franzosini, P.; Ngeyi, S. P.; Westrum, E. F. J. Chem. Thermodyn. 1986, 18 (7), 609–618. (c) Franzosini, P.; Ngeyi, S. P.; Westrum, E. F. J. Chem. Thermodyn. 1986, 18 (12), 1169–1181.
- (29) (a) Ferloni, P.; Sanesi, M.; Franzosini, P. Z. Naturforsch 1975, 30a (11), 1447–1454. (b) Ferloni, P.; Zangen, M.; Franzosini, P. Z. Naturforsch. 1977, 32a (6), 627–631. (c) Sanesi, M.; Ferloni, P.; Franzosini, P. Z. Naturforsch. 1977, 32a (10), 1173–1177. (d) Franzosini, P.; Sanesi, M.; Cingolani, A.; Ferloni, P. Z. Naturforsch. 1980, 35a (1), 98–102.
- (30) Gallot, B.; Skoulios, A.; Kolloid, Z. Z. Polymer 1966, 209 (2), 164– 169.
- (31) Vold, M. J.; Funakoshi, H.; Vold, R. D. J. Phys. Chem. 1976, 80 (16), 1753–1761.
- (32) Busico, V.; Ferraro, A.; Vacatello, M. J. Phys. Chem. 1984, 88 (18), 4055–4058.

- (33) Martínez Casado, F. J.; Ramos Riesco, M.; García Pérez, M. V.; Redondo Yélamos, M. I.; López-Andrés, S.; Cheda, J. A. R. *J. Phys. Chem. B* **2009**, *113* (39), 12896–12902.
- (34) Bazuin, C. G.; Guillon, D.; Skoulios, A.; Amorim da Costa, A. M.; Burrows, H. D.; Geraldes, C. F. G. C.; Teixeira-Dias, J. J. C.; Blackmore, E.; Tiddy, G. J. T. *Liq. Cryst.* **1988**, *3* (12), 1655–1657.
- (35) Schwede, J.; Koehler, L.; Grossmann, H. P.; Pietralla, M.; Burrows, H. D. Liquid Cryst. 1994, 16 (2), 267–276.
- (36) Ellis, H. A.; de Vries, J. W. C. Mol. Cryst. Liq. Cryst. 1988, 163, 133–139.
- (37) Amorim da Costa, A. M.; Burrows, H. D.; Geraldes, C. F. C. G.; Teixeira-Dias, J. J. C.; Bazuin, C. G.; Guillon, D.; Skoulios, A.; Blackmore, E.; Tiddy, G. J. T.; Turner, D. L *Liq. Cryst.* **1986**, *1* (3), 215–226.
- (38) Sánchez Arenas, A.; García, M. V.; Redondo, M. I.; Cheda, J. A. R.; Roux, M. V.; Turrión, C. *Liq. Cryst.* **1995**, *18*, 431–441.
- (39) Adeosun, S. A.; Sime, S. J. *Thermochim. Acta* 1978, *27*, 319–327.
 (40) Ekwunife, M. E.; Nwachukwu, M. U.; Rinehart, F. P.; Sime, S.
- J. Chem. Soc., Faraday Trans. 1 1975, 71 (7), 1432–1446.
 (41) Martínez Casado, F. J.; Sánchez Arenas, A.; García Pérez, M. V.; Redondo Yélamos, M. I.; López de Andrés, S.; Cheda, J. A. R. J. Chem. Thermodyn. 2007, 39 (3), 455–461.
- (42) Martínez Casado, F. J.; García Pérez, M. V.; Redondo Yélamos, M. I.; Cheda, J. A. R.; Sánchez Arenas, A.; López de Andrés, S.; García-Barriocanal, J.; Rivera, A.; León, C.; Santamaría, J. *J. Phys. Chem. C* 2007, *111* (18), 6826–6831.
- (43) Martínez Casado, F. J.; Ramos Riesco, M.; Sánchez Arenas, A.; García Pérez, M. V.; Redondo, M. I.; López-Andrés, S.; Garrido, L.; Cheda, J. A. R. J. Phys. Chem. B 2008, 112 (51), 16601–16609.

- (44) Lacouture, F.; Francois, M.; Didierjean, C.; Rivera, J. P.; Rocca, E.; Steinmetza, J. Acta Crystallogr., C 2001, 57, 530–531.
- (45) Juanhuix, J.; Labrador, A.; Beltran, D.; Herranz, J. F.; Carpentier, P.; Bordas, J. *Rev. Sci. Instrum.* **2005**, *76* (8), 086103.
- (46) Sheldrick, G. M. SHELXS 97; University of Göttingen: Germany, 1997.
- (47) Sheldrick, G. M. SHELXL 97; University of Göttingen: Germany, 1997.
- (48) Aragon, E.; Jardet, K.; Satre, P.; Sebaoun, A. J. Therm. Anal. Calorim. 2000, 62 (1), 211–225.
- (49) Roisnel, T.; Rodriguez-Carvajal, J. Mater. Sci. Forum 2002, 378–381, 118–126.
- (50) Boultif, A.; Louër, D. J. Appl. Crystallogr. 2004, 37, 724-731.
- (51) Altomare, A.; Camalli, M.; Cuocci, C.; Giacovazzo, C.; Moliterni, A.; Rizzi, R. J. Appl. Crystallogr. 2009, 42, 1197–1202.
- (52) Altomare, A.; Camalli, M.; Cuocci, C.; da Silva, I.; Giacovazzo, C.; Moliterni, A. G. G.; Rizzi, R. J. Appl. Crystallogr. 2005, 38, 760– 767.
- (53) (a) Rodríguez-Carvajal, J. *Physica B* 1993, 192, 55–69. (b) Rodriguez-Carvajal, J. Comm. Powder Diffr. (IUCr) Newsl. 2001, 26, 12–19.
- (54) Itoh, K.; Niwata, A.; Abe, W.; Kasatani, H.; Nakamura, E. J. Phys. Soc. Jpn. 1992, 61, 3593–3600.
- (55) Sawada, A.; Kikugawa, T.; Ishibashi, Y. J. Phys. Soc. Jpn. **1979**, 46, 871–875.
- (56) Oda, T.; Sakata, K.; Kondo, S. J. Chem. Phys. 1951, 19 (10), 1314.
- (57) Gesi, K. J. Phys. Soc. Jpn. 2003, 72, 1123-1126.
- (58) Kim, Y.; Strauss, H. L.; Snyder, R. G. J. Phys. Chem. 1989, 93, 7520–7526.
- (59) Shannon, R. D. Acta Crystallogr., A 1976, 32, 751-767.