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## Powder X-ray diffraction, infrared and $^{13}\text{C}$ NMR spectroscopic studies of the homologous series of some solid-state zinc(II) and sodium(I) *n*-alkanoates

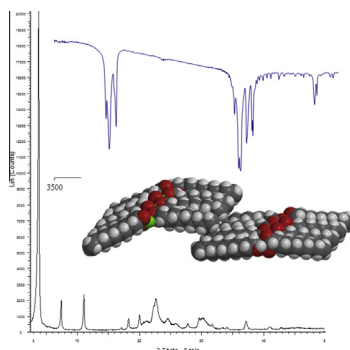
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### HIGHLIGHTS

- Comparative study of solid-state structures for series of zinc and sodium *n*-alkanoates.
- FT-IR, solid-state  $^{13}\text{C}$  NMR spectroscopy and PXRD carried out.
- Zn-OOC: bridging bidentate and Na-OOC: chelating bidentate coordination.
- Packing differences responsible for different levels of Van der Waals effects in the lattices.
- Packing differences arise from different electronic structure of metal ions.

### GRAPHICAL ABSTRACT

Basic solid state structures of zinc and sodium carboxylates.



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### ABSTRACT

A comparative study of the room temperature molecular packing and lattice structures for the homologous series of zinc(II) and sodium(I) *n*-alkanoates adduced from Fourier transform infrared and solid-state  $^{13}\text{C}$  NMR spectroscopic data in conjunction with X-ray powder diffraction measurements is carried out. For zinc carboxylates, metal-carboxyl bonding is via asymmetric bridging bidentate coordination whilst for the sodium adducts, coordination is via asymmetric chelating bidentate bonding. All compounds are packed in a monoclinic crystal system. Furthermore, the fully extended *all-trans* hydrocarbon chains are arranged as lamellar bilayers. For zinc compounds, there is bilayer overlap, for long chain adducts ( $n_c > 8$ ) but not for sodium compounds where methyl groups from opposing layers in the lamellar are only closely packed. Additionally, the hydrocarbon chains are extended along the *a*-axis of the unit cell for zinc compounds whilst for sodium carboxylates they are extended along the *c*-axis. These packing differences are responsible for different levels of Van der Waals effects in the lattices of these two series of compounds, hence, observed odd–even alternation is different. The significant difference in lattice packing observed for these two series of compounds is proposed to be due to the difference in metal-carboxyl coordination mode, arising from the different electronic structure of the central metal ions.

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## Introduction

The quest for new materials, for technological applications, possessing diversity in properties whilst being environmentally friendly, relatively cheap, recyclable and easy to manufacture continues to pose major challenges. Hence, the chemistry of metal carboxylates has, for several decades, been investigated by various groups, resulting in the publication of several hundred articles. However, in recent times there has been a resurgence of research interest in these compounds, mainly because they exhibit diverse coordination and solid-state molecular packing characteristics which significantly affect their physico-chemical properties [1–4]. For example, the luminescence properties of some metal carboxylates point to possible application in luminescence display devices. Taniguchi and coworkers [5] showed that the lamellar lanthanide surfactants of cerium(III), lanthanum(III) and yttrium(III) exhibited interesting luminescence properties with quantum yield of up to 90%. Luminescence on lead(II) decanoate reported by Burrows [6] showed emission maxima at 420 nm and excitation maxima at 258 nm. Unfortunately, the effects of chain length on these and other excitation and emission properties were not reported in that study. Selivanova and coworkers [7] reported on the luminescence properties of some lyotropic europium(III) and terbium(III) *n*-alkanoate liquid crystals highlighting the versatility of these compounds. In that study, several techniques were employed to show that these systems formed hexagonal mesophases in which luminescence is two-fold of that observed in the lamellar phase.

Also of interest is the fact that some metal carboxylates transition through a number of pre-melting phases, some of which are solid–solid whilst others are liquid crystalline phases of diverse physico-chemical properties when heated from the room temperature solid to the melt [4,8–10]. Some metal carboxylates tend to form liquid crystals of the smectic C, SmC [11,12], type hence, they find application in Liquid Crystal Display devices, LCDs. Such phases offer considerable advantages over currently applied liquid crystals; that is, they offer shorter switch times, higher complexity and larger field of view relative to conventional nematic and twisted-nematic devices [13–14]. Furthermore, they are environmentally friendly, easy and relatively cheap to prepare [15–17]. Unfortunately, these compounds form thermotropic liquid crystals; that is, they exist as liquid crystals at elevated temperature (>298 K), hence, their application in LCDs is limited. Nonetheless, several decades of research has shown that their phase properties are controlled by their solid-state molecular packing and lattice structures [18–21]. This means that their liquid crystalline properties can be designed and controlled. However, a comprehensive knowledge of their room temperature packing and lattice structure is required for such structural engineering; that is, accurate structural characterization is of major significance. Hence, our lab has dedicated a number of years to the study of these compounds. For example, we have shown that for a homologous series zinc(II) carboxylates, molecular packing and lattice structure is chain length dependent; that is, short chain compounds are packed differently from the long chain adducts [22–24]. Therefore, liquid crystalline phases were only observed for the long chain adducts where a balance between electrostatic and Van der Waals forces was easily achievable by heating. Indeed, we were successful in proposing molecular models to account for odd–even alternation observed in various physical parameters [23]. The effect of chain structure and packing was also explored through the study of some geometric isomeric zinc(II) alkynoates which showed low temperature liquid crystalline transitions [25]. Interestingly, as expected, the texture and properties of the phases observed were dependent on the position of the triple bond in the chain.

Significant investigations have also been carried out, by our group, on lithium(I), sodium(I), potassium(I) and silver(I) *n*-alkanoates

[8,26–28]. Interestingly, none of the compounds in these homologous series showed liquid crystalline transitions. However, they all exhibited odd–even alternation and showed different structural properties based on chain length, hence, molecular models were proposed to account for these properties. Furthermore, their thermo-chemical properties were correlated with their structural features. Since the long chain adducts form crystals that are either twinned or too thin for single crystal analysis, powder X-ray diffraction (PXRD) in conjunction with solid-state Fourier-Transform Infrared (FT-IR) and <sup>13</sup>C NMR spectroscopies were used in their structural elucidation [8,26–28]. Interestingly, despite the relative simplicity of sodium carboxylates not many investigations have been carried out on their molecular and lattice structures; that is, the majority of studies published on these compounds were focused on their phase properties. The studies on the structural work were not able to definitively propose molecular packing within the lattices, highlighting the structural factors responsible for their phase behavior. As a consequence of this limited understanding of the lattice structures of the sodium(I) alkanoates of an extended series, Nelson and Ellis were able to publish on their structures in recent times [28]. Nonetheless, Bui [29] in his Masters thesis presented a basic but relevant spectroscopic analysis of some sodium carboxylates. However, to the best of our knowledge no cross-homologous series studies have been carried out on these compounds to assess the main factor(s) controlling their molecular packing and hence, phase behavior.

Therefore, in this paper we report a cross-homologous series study on some zinc(II) as sodium(I) *n*-alkanoates to correlate the structural features of both series of compounds to their infrared and powder X-ray diffraction properties so as to establish the dominant structural features responsible for their lattice packing. The compounds are studied via solid-state FT-IR and <sup>13</sup>C NMR spectroscopies in conjunction with PXRD with the aim of elucidating structural similarities and difference between both series.

## Experimental

### Synthesis and FT-IR spectroscopy

All compounds were prepared and their purities verified as mentioned elsewhere [8,22]. Infrared spectra were recorded from grounded samples, deposited on a germanium window, using a Bruker Tensor 37 FT-IR spectrometer, in the range of 4000–400 cm<sup>-1</sup> at a resolution of ±1 cm<sup>-1</sup>.

### Powder X-ray diffraction

Powder X-ray diffractograms were collected on a Bruker D5005 Diffractometer with nickel filtered Cu K $\alpha$ , radiation ( $\lambda = 1.54056 \text{ \AA}$ ) from ungrounded samples, finely deposited on standard plastic holders, specially designed to minimize preferred orientation. The X-ray tube was operated at 45 kV and 35 mA at a time/step of 2 s for 2 h between  $2\theta$  of 2–60°.

### Solid-state <sup>13</sup>C NMR spectroscopy

High resolution solid-state spin decoupled spectra were collected at room temperature using a Bruker Avance 200 MHz spectrometer. Measurements were carried out at 50.32 MHz using CP and MAS with high-power <sup>1</sup>H decoupling for 3.6  $\mu$ s pulse intervals and a 5.0 s recycle time using a 7 mm probe. Typically, 1024 scans were collected with a sweep width of 21.93 kHz in 0.05 s. For acquisition, processing and plotting of the spectra, XWin NMR 3.5 computer software was used. TMS was used as reference at 0 ppm.

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