

# Structural Studies of Donor-Free and Donor-Solvated Sodium Carboxylates

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Focusing mainly on sodium 2-ethylhexanoate, this study reveals that the carboxylate exists as a dimer in MeOD solution as evidenced by Diffusion Ordered NMR Spectroscopy (DOSY). Two crystalline varieties with distinct polymeric structures have been synthesised and crystallographically characterised. A mixed 1,10-phenanthroline–water solvate  $[\{(C_5H_{10})(C_2H_5)COONa.(H_2O)[1,10-phen]\}_2]_{\infty}$  contains dimeric  $[Na(OH_2)_2]$  subunits, which propagate through hydrogen bonds between O atoms of the carboxylate and OH water bonds. Adjacent polymeric chains interdigitate with each other through  $\pi$ – $\pi$  interactions between 1,10-phen rings. Solvent-free sodium 2-ethylhexanoate has five-coordinate cations comprising one bidentate chelating and three monodentate carboxylate oxygen atoms. Here, the packing arrangement is different with the central hydrophilic  $(NaO_2)_{\infty}$  core surrounded by a wrapping of disordered alkyl groups. A similar polymeric structure is observed for the crystalline DMSO-solvated sodium valproate  $[\{(C_3H_7)(C_4H_8)COONa.(DMSO)\}]_{\infty}$ . This adopts a layered arrangement comprising alternating sodium carboxylate hydrophilic layers and hydrophobic organic bilayers.

reagent at some point in their preparation.<sup>[2]</sup> Organolithium compounds were introduced by Schlenk in 1917,<sup>[3]</sup> though perhaps surprisingly given the comparative lack of development, organosodium chemistry actually began even earlier, dating back to the reactions of alkyl halides with sodium metal in the 1840s and 1850s studied by Wanklyn.<sup>[4]</sup> Research into organosodium chemistry has been relatively limited, due mainly to the success of their lighter congeners since organolithium compounds in general exhibit higher solubility in commonly used organic solvents, are more stable, have the presence of NMR active lithium isotopes which lends themselves to solution state characterisation and are easier to handle than the heavier sodium congeners.<sup>[5]</sup> However, recently there has been an upsurge of interest in organosodium chemistry. This was partly driven by the higher reactivity of the heavier alkali metals when compared to lithium but also by increased focus within the chemical sciences on sustainability. Sodium is the most abundant alkali metal in the earth's crust and oceans, as well as being the sixth most abundant element on earth overall. Sodium also contains several other advantages from a sustainability point of view, such as being non-toxic and inexpensive.<sup>[6]</sup> There is therefore an understandable drive towards reducing the reliance on comparatively rare elements such as lithium with more sustainable alternatives such as sodium,<sup>[7]</sup> especially given lithium's burgeoning use in the widespread field of lithium-ion batteries,<sup>[8]</sup> the subject of the 2019 Nobel Prize in Chemistry,<sup>[9]</sup> which further incentivises the development of other alkali metals in areas such as sodium ion batteries<sup>[10]</sup> and catalysis. Of particular note in the latter area is the recent breakthrough by Takai *et al.* who showed that cross-coupling reactions such as Negishi and Suzuki-Miyaura could be carried out catalytically by organosodium compounds.<sup>[6,11]</sup> This study showed that these cross-coupling reactions could be accomplished in a one pot-reaction starting from inexpensive aryl chlorides, which is attractive from an industrial scale viewpoint.<sup>[11]</sup> Insight has also been gained into cyclisation reactions of alkylnols, which proceed sluggishly using a mixed lithium magnesiate, but worked more efficiently using a sodium magnesiate and best of all using a potassium based system, showing the potential advantages of investigating heavier alkali metals further.<sup>[12]</sup> A catalytic system looking at hydrophosphorylation of nitriles and alkenes has also been developed utilising simple alkali metal HMDS complexes (HMDS is 1,1,1,3,3,3-hexamethyldisilazide), which show superior performance when moving to the heavier alkali metals, again highlighting the advantages that sodium and potassium can offer.<sup>[13]</sup> In a final example, a NaHMDS catalyst system has also been found to

## Introduction

Of vital importance in the toolbox of the synthetic chemist are organolithium reagents such as lithium alkyl and lithium amide compounds, both classes of which are widely utilised throughout synthetic chemistry.<sup>[1]</sup> Collum put the extent of this utilisation into some perspective by pointing out that in excess of 95% of natural product syntheses rely upon a lithium based

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perform aminobenylation of aldehydes with toluenes in excellent yields while tolerating a wide variety of functional groups.<sup>[14]</sup> Clearly the field of sodium and organosodium chemistry in particular offers a vast untapped scope.

Considering structural studies, our research group has long been fascinated with the structural diversity and variation of sodium-containing complexes. It is known that the structures of alkali metal complexes can vary depending upon the identity of the alkali metal, which in turn can have a profound effect on the outcome of reactions. For example, in the context of trans-metal trapping it has recently been discovered that replacing LiTMP with NaTMP (TMP is 2,2,6,6-tetramethylpiperidide) has a significant effect on the onward reactivity of the trapped species, showing potential advantages in terms of replacement of lithium with sodium as a metallating agent.<sup>[15]</sup> We have also shown that changing the alkali metal can unlock fascinating structures depending on the identity of the alkali metal chosen, with the ligand system *trans*-calix[2]benzene[2]pyrrolides showing diverse structural motifs ranging from monomers to tetramers depending on which alkali metal partners them.<sup>[16]</sup>

Our recent reported work in the field of small molecule activation, particularly on the fixation of CO<sub>2</sub> using alkali metal complexes,<sup>[17]</sup> piqued our interest in sodium carboxylate chemistry since they can be produced by such reactions.<sup>[18]</sup> Sodium carboxylates are also an industrially important class of compound. For example, the sodium salt of 2-(2-dodecoxyethoxy)acetic acid or laureth-11 is often used in eyeliner products. Carboxylates are also found in shampoos as primary detergents, owing to the fact that they are both anionic and inexpensive, both considered important factors in the cosmetics industry.<sup>[19]</sup> Many other carboxylate ligands are used as linkers in metal-organic frameworks or MOFs, which are used in a wide range of fields including gas storage and purification, as well as heterogeneous catalysis.<sup>[20]</sup> Given that many non-alkali metal carboxylates are soluble in organic solvents, they have also been utilised as stabilisers in the polymer industry, particularly those carboxylates of tin, used to stabilise polyvinylchloride.<sup>[21]</sup> Examples of sodium carboxylates have also been utilised in the stabilisation of nanoparticles, indicating the many areas of chemistry these molecules are useful in.<sup>[22]</sup> Interestingly, however, there is also a gap in the literature with regard to the solid state structures of long chain examples (see below).

Sodium carboxylates also have their downsides in an industrial setting. When forming within diesel engines they are thought to be responsible for a myriad of issues such as poor engine operation, a decrease in the ability to drive using the engine as well as making it impossible to cold-start the engine.<sup>[23]</sup> The presence of these sodium carboxylate deposits is due to interaction between sources of sodium such as sodium hydroxide<sup>[24]</sup> and acidic molecules present in the diesel. These acidic molecules are generally long chain examples which are added to the diesel by engine manufacturers in order to improve some aspect of the engine performance. These long chain acids include dodecanyl succinic acid, that is introduced as a corrosion inhibitor and oleic acid, which is used as a lubricity improver to reduce metal on metal contact. The issue is when these acids interact with residual sodium in the diesel,

sodium carboxylates form, which block the engines components and contribute to the previously described issues.<sup>[25]</sup> Despite the industrial importance of understanding the effect of these deposits, a paucity of general research has been carried out into the structures of long chain examples of sodium carboxylates.<sup>[26]</sup> This is accounted for mainly by the long chain nature of these compounds, which makes their crystallisation extremely challenging and instead they exist as gels or micro-crystalline material which do not lend themselves to single crystal X-ray diffraction study.<sup>[27]</sup> Indeed, a search of the Cambridge Structural Database (CSD) shows that while there are 11,840 hits for a sodium containing complex, there are only 295 hits for sodium carboxylates, with long chain examples containing a chain of four or more carbons numbering only 45.<sup>[28]</sup> Moreover, limiting the elements present to only carbon, hydrogen, oxygen and sodium reveals a meagre 11 hits for a chain length of four or more carbons. Indeed, hitherto the longest chain example of a donor- and stabilising interaction-free alkali metal carboxylate within the CSD is lithium pentanoate, characterised by single crystal X-ray diffraction as recently as 2009,<sup>[29]</sup> with the longer chain examples ranging from 8–19 carbon atoms characterised only by powder X-ray diffraction studies or containing stabilising interactions such as hydrogen bonds.<sup>[30]</sup>

Here, in this contribution we present our results in studying long chain sodium carboxylates, with emphasis on obtaining structural insight into the architectures such compounds adopt in the solid state. We show that changing the nature of the Lewis base donor added can lead to a variety of distinct structural motifs, among which we present the longest chain example (numbering eight carbons in total) of a donor-free sodium carboxylate whose structure has been determined by single crystal X-ray diffraction.

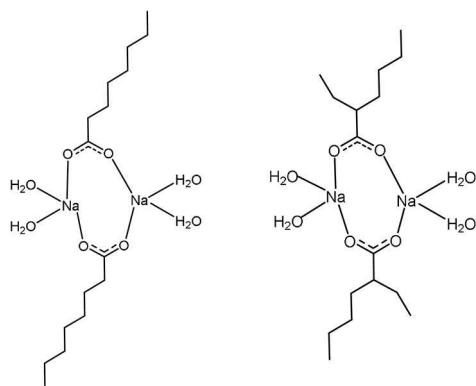
## Results and Discussion

The poverty of available literature on structurally characterised long chain examples of sodium carboxylates, as well as the industrial relevance of such compounds, prompted us to focus our efforts on obtaining relevant crystal structures. The carboxylic acids chosen were 2-ethylhexanoic acid and octanoic acid. Both are representative of the type of acids found in diesel fuel, whilst their relatively moderate chain lengths offer greater opportunity for crystallisation. In order to obtain samples of the sodium salts, the acids were reacted with ethanolic solutions of NaOH in a 1:1 ratio, to produce white powders. These powders proved to be insoluble in many apolar, organic solvents, requiring the use of MeOD for <sup>1</sup>H NMR characterisation. The spectra for both reaction products showed the deprotonation reaction had been successful in each case, with the absence of a resonance at about 12 ppm indicative of lack of a carboxyl proton (See ESI). In order to extract more information on their solution state structures, a Diffusion Ordered Spectroscopy (DOSY) NMR study was carried out, using tetramethylsilane (TMS) as an internal standard. DOSY NMR takes advantage of the fact that different molecular species within a solution will

have different diffusion coefficients, which are related to both the shape and size of the molecular species itself.<sup>[31]</sup> By plotting these diffusion coefficients, which are measured during the physical NMR experiment, it can be ascertained how many different species are present within the solution. Using software from Stalke *et al.* it is then also possible to estimate the molecular weight of these species and thereby predict the aggregation state and structure that may be adopted by such species in solution.<sup>[32]</sup> Carrying out the DOSY NMR on a sodium octanoate sample, it was seen that there was only one major species present in solution, which had a log diffusion value of  $-9.0825 \text{ m}^2/\text{s}$ . This estimates a molecular weight of 433 g/mol, which appears too large a value to represent a monomeric complex of only 166 g/mol. A dimeric sodium carboxylate species, comprising two sodium cations, two carboxylate anions and four solvating water molecules would have a calculated molecular weight of 404 g/mol. This value is within the error limits (an error of only  $-7\%$  between the theoretical and calculated molecular weight) of the DOSY software, which suggests that in polar solvents, sodium octanoate is likely to form a dimeric species as shown in Scheme 1.

Carrying out a DOSY analysis on a sample of sodium 2-ethylhexanoate also showed the presence of only one major species in solution, which had a log diffusion value of  $-9.1840 \text{ m}^2/\text{s}$ . This estimates a molecular weight value of 404 g/mol, again being found to be consistent with a dimeric structure containing solvating water molecules with an error of 0% (Scheme 1).

There is some literature precedent for such dimeric structures of alkali-metal carboxylates. For instance, Collum *et al.*, in their studies of lithium enolates, noted how previously it had been difficult to characterise such lithium structures due to their tendency to aggregate in solution and the lack of observed coupling between the oxygen and lithium atoms.<sup>[33]</sup> In order to study such lithium species in solution,  $^6\text{Li}$  NMR investigations of lithium carboxylates paired with lithium enolates was carried out.<sup>[33]</sup> It was suggested using such statistical analysis, that TMEDA-solvated lithium carboxylates



**Scheme 1.** ChemDraw representation of predicted dimeric structure of sodium octanoate (LHS) and sodium 2-ethylhexanoate (RHS), as implied by DOSY NMR analysis.

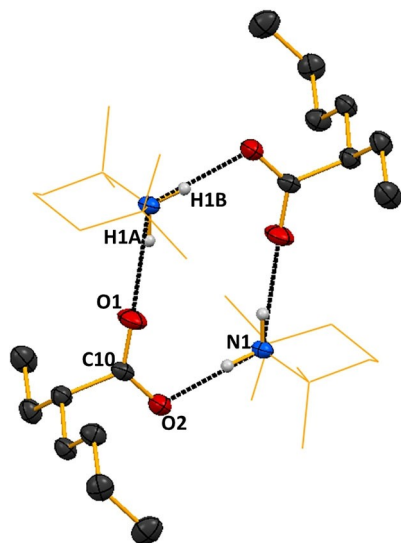
may form a dimer, though significantly they also noted that “crystallographic guidance is surprisingly absent.”

To try and redress this lack of information, we attempted to prepare examples of long chain sodium carboxylates that could be analysed *via* single crystal X-ray diffraction. Initial experiments were carried out using sodium 2-ethylhexanoate, with a range of common Lewis base donors such as *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), 2,2'-bipyridine (2,2'-bipy) and 4,4'-bipyridine (4,4'-bipy). These donor molecules could in theory have stabilised the sodium carboxylate *via* dative interactions with the sodium cation, allowing for the formation of solvated crystalline products. All nitrogen donors, they range from bidentate rigid species such as 2,2'-bipy to the tridentate PMDETA. Each donor was added to a suspension of sodium 2-ethylhexanoate in hexane, and the mixture was left stirring overnight. Dissolution was never apparent, with the solvent subsequently removed and the powder residue analysed using  $^1\text{H}$  NMR spectroscopy. Perhaps surprisingly,  $^1\text{H}$  NMR evidence suggested no metal coordination of any donor molecule regardless of the ratio of donor : acid used. This was evidenced from the non-movement of the donor resonances in the spectra of the product compared to those of the free donor, indicative that free, uncoordinated donor is still present (See ESI). This suggests that such donor intervention cannot break down the strong Na–O bonding within the parent sodium carboxylate.

Next, we visited the reaction between 2-ethylhexanoic acid and the secondary amide sodium tetramethylpiperidide (NaTMP), anticipating that this strong base would deprotonate the acid, producing the sodium carboxylate as well as concomitantly forming a bulky TMP(H) donor, which may interact with the sodium carboxylate as it forms and aid a potential crystallisation. To this end NaTMP [synthesised *in situ* from BuNa and TMP(H)]<sup>[34]</sup> was suspended in hexane and two equivalents of 2-ethylhexanoic acid were then added to obtain a yellow solution. This solution was concentrated and placed in a freezer at  $-30^\circ\text{C}$ , depositing colourless crystals identified by X-ray crystallography as the contacted ion pair complex  $[\{\text{TMP}(\text{H})_2\}^+ \{\text{C}_5\text{H}_{10}(\text{C}_2\text{H}_5)\text{COO}\}^-]_2$  (**1**) (Figure 1).

This sodium-free structure is a hydrogen-bonded dimer, containing a 2,2,6,6-tetramethylpiperidinium cation and a 2-ethylhexanoate carboxylate anion. Graph set notation describes the hydrogen bonding as R(4,4)12.<sup>[35]</sup> A potential explanation for the absence of the metal is that adventitious hydrolysis had occurred leading to formation of TMP(H) and NaOH, with the former in turn reacting with, and consuming, all the available acid to produce **1**. Alternatively, the remainder of the sodium carboxylate may stay in solution, as **1** was originally obtained fortuitously in a small yield of 16%. Repeating the reaction rationally using a 1:1 ratio of TMP(H) and 2-ethylhexanoic acid gave a much improved 67% yield.

A metric feature of note in the structure of **1**, is the C–O bonds, which are intermediate in length between single and double bonds [C10–O1, 1.237(3) Å and C10–O2, 1.253(2) Å]. This is indicative of the total resonance in the carboxylate group. The O1–C10–O2 bond angle also indicates total resonance, lying at  $124.3(2)^\circ$  which is consistent with the

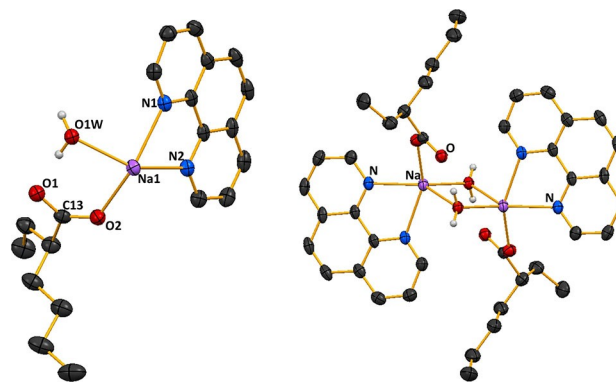


**Figure 1.** Extended molecular structure of  $[\{(\text{TMP}(\text{H})_2)^+\} \{(\text{C}_5\text{H}_{10}(\text{C}_2\text{H}_5)\text{COO})^-\}_2]$  (1). Hydrogen atoms except those of the  $\text{NH}_2$  groups are omitted and the organic TMP scaffold is shown as wire frame for clarity. Hydrogen bonds are represented by dashed black lines. Thermal ellipsoids are displayed at 40% probability level. Symmetry transformations used to generate equivalent atoms: 1-x,1-y,1-z.

literature value for the carboxylate group in sodium formate ( $124^\circ$ ).<sup>[36,37]</sup> Searching within the CSD for literature precedent of such dimeric structures uncovered only 13 hits for carboxylate groups with  $\text{TMP}(\text{H})_2^+$  related cations.<sup>[38,39]</sup> These were found to be generally short chain carboxylates such as acetates, with the long chain examples generally co-crystallising with a  $\text{TMP}(\text{H})$  derivative containing hydroxyl substituents rather than just the parent  $\text{TMP}(\text{H})$  itself.<sup>[39]</sup> A further search of the CSD showed only 12 hits for a 2-ethylhexanoate anion, with no examples of a 2-ethylhexanoate complex with a  $\text{TMP}(\text{H})_2^+$  counter ion. Attempts to obtain the corresponding octanoate salt were unsuccessful; hence we switched our attention towards obtaining examples of sodium 2-ethylhexanoate complexes.

We reasoned the use of another nitrogen donor molecule, specifically 1,10-phenanthroline (1,10-phen), may help stabilise the sodium carboxylate. While  $\text{TMP}(\text{H})$  is bulkier in terms of overall steric factors, it is only a unidentate donor, whereas 1,10-phen is bidentate, with the potential for both nitrogen atoms to coordinate to the same sodium cation given the fact they are 'locked' into one position by the inflexibility of the aromatic 1,10-phen ligand. To this end, one equivalent of 1,10-phen was added to a suspension of sodium 2-ethylhexanoate in hexane and the mixture was stirred overnight. The white powder formed was recrystallised upon addition of THF and gentle warming to give the polymer  $[\{(\text{C}_5\text{H}_{10}(\text{C}_2\text{H}_5)\text{COONa}(\text{H}_2\text{O})[1,10\text{-phen}]\}_2]_\infty$  (2) as colourless crystals (Figure 2).

Polymer 2 adopts a centrosymmetric dimeric coordination substructure comprising two molecules of sodium 2-ethylhexanoate, two molecules of 1,10-phen which chelate the sodium through the nitrogen atoms, and two water molecules that bridge the sodium atoms. The five-coordinate nature of each sodium centre comprises bonding to one carboxylate



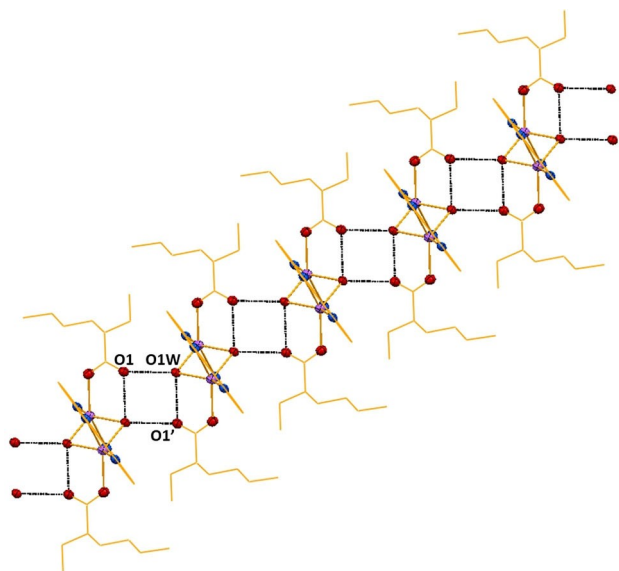
**Figure 2.** (LHS) Contents of the asymmetric unit of  $[\{(\text{C}_5\text{H}_{10}(\text{C}_2\text{H}_5)\text{COONa}(\text{H}_2\text{O})[1,10\text{-phen}]\}_2]_\infty$  (2). Hydrogen atoms except those of water and disorder in the alkyl chains are omitted for clarity. (RHS) Dimeric coordination unit that is the major structural motif of the hydrogen bonded polymeric structure of 2. Thermal ellipsoids are displayed at 40% probability level. Symmetry transformations used to generate equivalent atoms: 1-x,1-y,-z.

oxygen, two oxygen atoms of water molecules and two nitrogen atoms from 1,10-phen. This gives sodium a distorted trigonal bipyramidal geometry, as seen in the bond angles subtended at sodium, ranging from  $148.16(7)^\circ$  at  $\text{N1-Na1-O2}$  (which would be  $180^\circ$  in an idealised trigonal bipyramidal geometry) to  $86.07(6)^\circ$  at  $\text{O1W-Na1-O1W}$ , which would be  $90^\circ$  otherwise.

The solvating water presumably originates from the commercially obtained sodium 2-ethylhexanoate, which was used as received. Presumably, this is made industrially using the parent acid and  $\text{NaOH}$ , possibly explains the presence of trace amounts of water. In any case, the water proves to be vital to the architecture of the structure. The water molecule bridges to two sodium cations to create the dimer, while hydrogen bonding between  $\text{O1W}(\text{H})$  and  $\text{O1}$  of adjacent units [ $\text{O1W}\dots\text{O1}$   $2.786(2)$  Å and  $\text{O1W}\dots\text{O1}'$   $2.713(2)$  Å] forms a rather attractive polymeric structure, composed of linked dimers of 2 (Figure 3).

Crystallographically, these hydrogen bonded chains propagate through translation along the  $a$  direction. This polymer interacts with neighbouring polymers *via*  $\pi$ - $\pi$  interactions between 1,10-phen rings (centroid...centroid bond lengths between 1,10-phen rings are on average between 3.45 Å and 3.6 Å). Thus adjacent polymeric chains interdigitate with each other. The overall packing is a layered structure with hydrophobic bilayers composed of disordered alkyl groups alternating with layers containing the hydrophilic atoms and the aromatic groups. These layers lie parallel to the crystallographic  $ab$  plane.

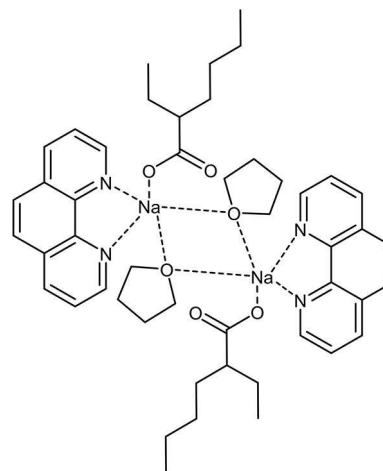
In order to ascertain whether this structure was maintained in solution, a DOSY NMR spectroscopic study was carried out on crystals of 2 in  $d_8$ -THF solvent, with TMS as an internal standard. This revealed two distinct species. One species corresponds to a 1:1 mixture comprising free 1,10-phen and THF with an error of  $\sim 3\%$  between the theoretical and calculated molecular weights of 252.32 g/mol and 259 g/mol respectively, while the other appears to be a 2:2:2 complex comprising a 1,10-phen solvated sodium 2-ethylhexanoate dimer, bonded THF, and free



**Figure 3.** (Top) Fivefold section of the polymeric structure of  $[[{(C_5H_{10})(C_2H_5)COONa.(H_2O)[1,10-phen]]}_2]_{\infty}$  (**2**) showing hydrogen bonding between dimer units as a black dashed line and (bottom) fivefold section of two interdigitating polymeric chains of  $[[{(C_5H_{10})(C_2H_5)COONa.(H_2O)[1,10-phen]]}_2]_{\infty}$  (**2**). These are connected by  $\pi$ - $\pi$  contacts. Hydrogen atoms are omitted, and organic groups are shown as wire frame for clarity. Thermal ellipsoids are displayed at 40% probability level.

THF corresponding to an error of 5% between theoretical and calculated molecular weights (Scheme 2). The DOSY suggests a loss of water (from crystalline **2**) and replacement with bridging THF molecules, which though rare have previously been observed crystallographically.<sup>[40]</sup> The loss of water leads to an absence of hydrogen bonding, meaning a molecular structure such as that in Scheme 2 is more likely to be present rather than the polymer witnessed in the solid state.

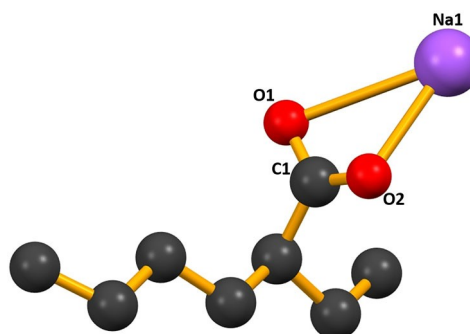
With these results in hand, we pondered whether crystals of a donor-free example of sodium 2-ethylhexanoate could be realised. We therefore attempted several different methods including layering techniques and slow diffusion type reactions with many different solvent systems, all of which were



**Scheme 2.** ChemDraw representation of the proposed sodium species present in a solution of **2** as implied by DOSY NMR analysis.

unsuccessful, producing only viscous oils or amorphous solids. Success finally came with the slow diffusion of acetonitrile into an acetone solution of sodium 2-ethylhexanoate that produced a few small crystals suitable for X-ray structural determination. This established their composition to be  $[[{(C_5H_{10})(C_2H_5)COO.Na}]_{\infty}$  (**3**) (Figure 4).

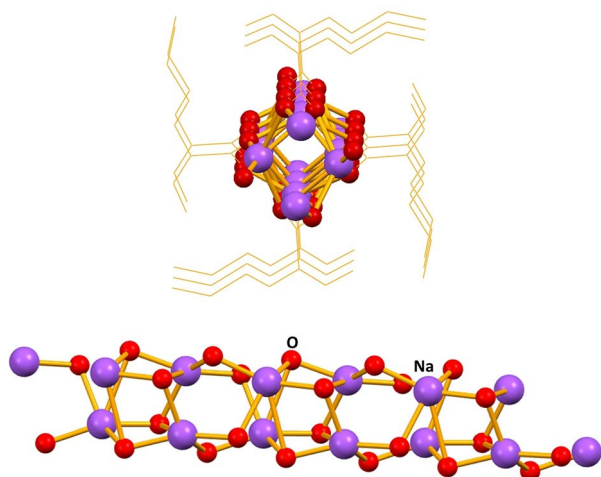
The structure of **3** is revealed to be a unique polymeric form of sodium 2-ethylhexanoate, which is both solvent-free and donor-free. Unfortunately, disorder throughout the long chain backbone rules out a detailed discussion of bond lengths and bond angles; however, the molecular connectivity of the polymer is unambiguous. An infinite chain is observed, with the polymer propagating by action of the  $4_1$  screw axis parallel to the crystallographic  $c$ -direction. Sodium cations within the structure are five-coordinate, made up of two oxygen atoms that attach in a bidentate chelating fashion, and to one carboxylate oxygen atom from three separate carboxylate anions. The long 2-ethylhexanoate chains rotate around a central 'core' composed of sodium cations. Unlike the solvated examples **2** and **4**, the packing arrangement is not a simple layering of hydrophobic and hydrophilic groups. Instead, the hydrophilic polymeric  $NaO_2$  core is surrounded by a wrapping



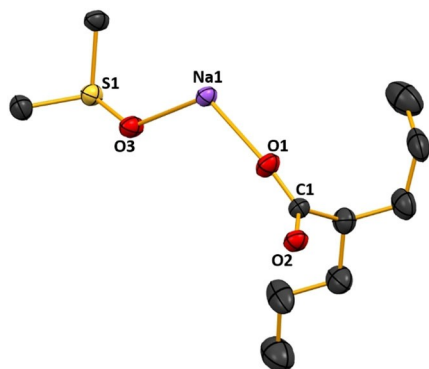
**Figure 4.** Contents of the asymmetric unit of  $[[{(C_5H_{10})(C_2H_5)COO.Na}]_{\infty}$  (**3**). Hydrogen atoms are omitted for clarity.

of disordered alkyl groups (Figure 5). This result is unique since to our knowledge it reveals the longest chain alkali metal carboxylate characterised *via* single crystal X-ray diffraction. The solid-state structure of sodium 2-ethylhexanoate also contrasts with the structure predicted by DOSY, which suggests that of a dimer. This would make sense given the fact that polar solvents such as water and methanol are likely to deaggregate the structure seen in **3** to that of a simpler dimeric structure.

Following these successful results, we then decided to investigate whether such complex architectures could be formed using similarly branched sodium carboxylates. We came across valproic acid as a potential interesting molecule to investigate, as its sodium salt (sodium valproate) and the parent acid are used as Active Pharmaceutical Ingredients (API) to treat a variety of medical disorders such as epilepsy, bipolar disorder and migraines.<sup>[41]</sup> To this end, sodium valproate was suspended in 2 ml of a 1:1 mixture of DMF and DMSO and heated until a solution was obtained. This solution was cooled slowly in a hot



**Figure 5.** (Top) Central Na–O core of **3** with hydrogen atoms omitted, sodium and oxygen atoms drawn as spheres for clarity and organic groups drawn as wire frame for clarity. (Bottom) Side-on view of central Na–O core showing coordination of sodium cations with hydrogen atoms and organic groups omitted and sodium and oxygen atoms drawn as spheres for clarity.



**Figure 6.** Contents of the asymmetric unit of  $[(C_3H_7)(C_4H_9)COONa.(DMSO)]_\infty$  (**4**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are displayed at 40% probability level.

water Dewar flask over a few days to afford colourless crystals, identified as the solvated polymer  $[(C_3H_7)(C_4H_9)COONa.(DMSO)]_\infty$  (**4**) (Figure 6).

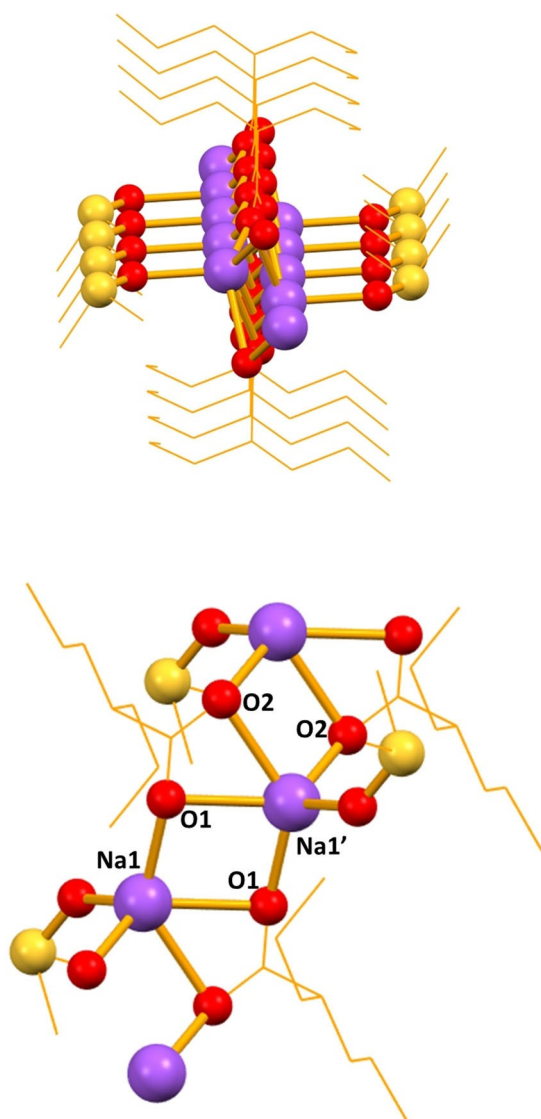
Complex **4** adopts a polymeric structure in the solid state, composed of the long chain sodium carboxylate with the sodium solvated by DMSO. Each sodium cation is five-coordinate, sitting in a markedly distorted square pyramidal geometry. There are also two near perfect squares present in **4**, with each square formed from two sodium cations and two oxygens of two different bidentate chelating carboxylates [ $Na_1-O_2-Na_1'$ , 91.11(7)°;  $O_2-Na_1'-O_2$ , 88.89(7)°;  $O_1-Na_1-O_1$ , 85.08(7)°;  $Na_1-O_1-Na_1'$ , 94.92(8)°]. The sodium interacts with two carboxylate unit oxygen atoms in a unidentate manner, one carboxylate unit oxygen atoms in a bidentate chelating manner and one oxygen of DMSO. The C–O bond lengths again confirm the presence of the carboxylate group, with lengths intermediate between single and double bonds [ $C_1-O_1$ , 1.249(3) Å and  $C_1-O_2$ , 1.252(3) Å]. Once again, the  $O_1-C_1-O_2$  bond angle also indicates total resonance within the carboxylate group lying at 123.7(2)°, which is consistent with the literature value of carboxylate groups.<sup>[37]</sup> A rather attractive polymeric chain structure is seen (Figure 7), with each chelated carboxylate NaOCO unit bridging to two adjacent sodium cations. Each polymeric motif propagates through translation parallel to the crystallographic *a* axis. This gives a layered structure with hydrophilic, coordination layers and hydrophobic organic bilayers alternating along the *c* direction.

## Conclusions

This study has given a glimpse of the vast array of structures that can be adopted by relatively simple alkali metal carboxylate species in the solid state. Reacting TMP(H) with a long chain branched acid results in the formation of a dimeric hydrogen bonded product, consistent with the predicted structure of sodium carboxylates within polar solvents, as predicted by DOSY NMR.

On reacting sodium 2-ethylhexanoate with 1,10-phenanthroline, a dimeric structure is obtained, with water bridges between the monomer units. This water is crucial to the integrity of the structure, as it provides the means of hydrogen bonding which forms a polymer of dimers featuring interdigitating polymeric chains composed *via*  $\pi$ - $\pi$  contacts. DOSY NMR analysis suggests the loss of this water in the solution state and its replacement by THF, to construct a molecular structure as opposed to the polymer seen in the solid state.

Moving to donor free sodium 2-ethylhexanoate, the solid-state structure of this revealed a remarkable polymeric arrangement, composed of a central core of hydrophilic sodium cations with the long, disordered alkyl chains wrapping around this core. This is in stark contrast to the simpler layers of hydrophobic and hydrophilic groups one might expect and is to the best of our knowledge the longest donor-free straight chain alkali metal carboxylate analysed *via* single crystal X-ray diffraction. Finally, we were able to show that similar polymer structures are obtained using donor molecules such as DMSO,



**Figure 7.** (Top) Central Na–O core of **4** with hydrogen atoms omitted, sodium and oxygen atoms drawn as spheres for clarity and organic groups drawn as wire frame for clarity. (Bottom) Repeating polymeric core of **4** showing two fused four-membered rings with hydrogen atoms omitted, sodium and oxygen atoms drawn as spheres for clarity and organic groups drawn as wire frame for clarity.

with the API sodium valproate also forming a core-based polymer consisting of sodium cations bridged by chelating carboxylates.

Shedding light on metallo structures containing long chain oxygen-based ligands could aid the development and understanding of the use of such ligands in synthetic chemistry. In that regard it is noteworthy that the Knochel group has recently introduced the 2-ethylhexanol derived ligand [sBuMgOR.LiOR], where R is 2-ethylhexyl, into halogen-magnesium exchange methodologies,<sup>[42]</sup> while sodium 2-ethylhexanoate itself has recently been shown to be a key activator in iron catalysed hydroboration reactions<sup>[43]</sup> It will be of future interest to ascertain how such structures modify on replacing sodium by

potassium given the profound changes in both structure and reactivity that can occur in alkali metal mediation chemistry.<sup>[44]</sup>

## Experimental Section

Full experimental characterisation and synthetic procedures are described in the Supporting Information.

Deposition Numbers 1984053 (for **1**), 1984054 (for **2**) 1984055 (for **3**), and 1984056 (for **4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformati-onszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Alkali metals · Carboxylate ligands · Sodium · Structure elucidation

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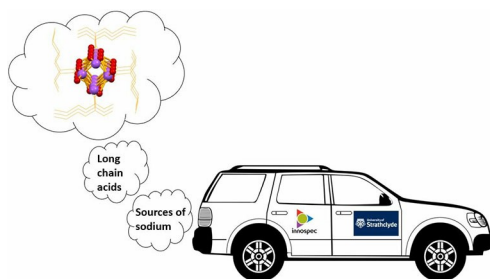
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# COMMUNICATIONS

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**Characterising the Culprits:** Industrially important; but also problematic in the operation of diesel engines, long chain sodium carboxylates have been notoriously difficult to crystallographically characterise. Here, successful

crystallisation and structural determination of three sodium carboxylates and a sodium-free variant highlights the structural complexity and diversity in this area.

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**Structural Studies of Donor-Free  
and Donor-Solvated Sodium Carboxylates**

