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# Assembly of ethylzincate compounds into supramolecular structures

## Anna Hedström<sup>a</sup>, Anders Lennartson<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, University of Gothenburg, SE-412 96 Gothenburg, Sweden <sup>b</sup> Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

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### ABSTRACT

Sodium and potassium triethylzincate were isolated by Wanklyn in 1858, and are corner stones in the history of organometallic chemistry. Crystallisation of organozincates from neat dialkylzinc, in the absence of a coordinating solvent, can be expected to result in assembly of supramolecular structures, rather than formation of discrete molecules in the crystalline state. This inspired us to reinvestigate Wanklyn's classical compounds. Crystallisation of sodium triethylzincate from benzene led to metallation of benzene and the formation of diethylphenylzincate anions. The compound is a two-dimensional network where Na<sup>+</sup> ions link the zincate anions by coordination to both ethyl- and phenyl groups. We have also, accidently, isolated crystals of the two-dimensional coordination network [ $K_2(ZnEt_2)_4O_{ln}$ , displaying a rare oxo-centred core with an octahedral oxide ion surrounded by four zinc atoms and two potassium atoms.

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#### 1. Introduction

The discovery of diethylzinc and dimethylzinc by Edward Frankland in 1848 [1–4] marks the birth of modern organometallic chemistry. Diethylzinc and dimethylzinc were not only the first organozinc compounds to be prepared, but were also the first alkylmetal compounds, and the first main group organometallic compounds. The isolation of organozinc compounds promoted research on organometallic derivatives of other metals, and ten years later I. Alfred Wanklyn found that diethylzinc reacts with metallic sodium forming a white crystalline and highly reactive compound [5.6]. Wanklyn described his new compound as a "double compound between sodium-ethyl and zinc-ethyl" but it is now known to be sodium triethylzincate. The target for Wanklyn's synthetic attempts, ethylsodium, was first prepared by Schlenk and Holtz in 1917 [7]. Wanklyn noted that zincates were useful in the synthesis of carboxylic acids, since Na[ZnEt<sub>3</sub>] react with carbon dioxide to give propionic acid [5,8]. Since the late 1970's, zincates have attracted more and more attention in organic synthesis, and are today extensively used in conjugate addition to enones, halogen-zinc exchange reactions, nucleophilic additions to ketones and ring-opening of epoxides [9]. Even though Wanklyn's synthetic approach has been successfully used to crystallise other zincates [10], still today, no crystal structures of Wanklyn's historically important compounds, Na

\* Corresponding author. E-mail address: lennartson@ifk.sdu.dk (A. Lennartson).

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[ZnEt<sub>3</sub>] and K[ZnEt<sub>3</sub>], are found in the Cambridge Structural Database [11]. We recently reinvestigated Wanklyn's synthesis, and found that heating metallic sodium in an excess of diethylzinc led to a violent reaction with evolution of gas and deposition of metallic zinc. On cooling to ambient temperature, crystals of Na<sub>2</sub>[Zn<sub>2</sub>Et<sub>4</sub>( $\mu$ -H)<sub>2</sub>] were obtained [12]. Although hydridoalkylzincates [13–17] and related compounds [18] have gained considerable interest, this was the first synthetic route to well-defined hydridodialkylzincates. We continued the studies of Wanklyn's compounds, and in this paper we describe the crystal structures of the supramolecular networks [NaZnEt<sub>2</sub>Ph]<sub>n</sub> and [K<sub>2</sub>(ZnEt<sub>2</sub>)<sub>4</sub>O]<sub>n</sub>.

#### 2. Results and discussion

We have repeated Wanklyn's original synthesis several times in order to determine the crystal structure of the product. We were, however, unable to obtain single-crystals of X-ray quality of Wanklyn's compound Na[ZnEt<sub>3</sub>] through crystallisation from neat diethylzinc; neither cooling solutions to -40 °C or -80 °C, nor layering solutions with hexane was successful. Even crystals having the visual appearance of single-crystals, were found to be multi-component congeries, resisting all attempts of indexing the reflections. Recrystallisation from a coordinating solvent, such as tetrahydrofuran, would most probably give crystals with solvent molecules coordinated to Na<sup>+</sup> [19], and was therefore not considered. Na[ZnEt<sub>3</sub>] is insoluble in alkane solvents, but has been reported to be soluble in benzene [20], and recrystallisation of Wanklyn's compound from benzene was attempted. It was found that crystallisation of Na



Note



[ZnEt<sub>3</sub>] from benzene led to metallation of benzene by the strongly basic zincate (Scheme 1), and crystals of the coordination network  $[NaZnEt_2Ph]_n$ , **1** (Fig. 1), were isolated. Compound **1** is built up by Na<sup>+</sup> and [ZnEt<sub>2</sub>Ph]<sup>-</sup> ions, and there seems to be only two previous structures of zincate-like species with ethyl ligands in the Cambridge Structural Database. These two structures are very different from **1**. since they display functionalised R-groups and additional neutral ligands [21,22]. Both of these two compounds were, like 1, obtained by metallation of aromatic substrates. Other recent studies of zincation of aromatic compounds by zincate species include the zincation of toluene [23] and anisol [24]. Deprotonative metallation (and polymetallation) by ate compounds was recently reviewed [25]. Recrystallisation from other aromatic solvents was not attempted. The species present in solution may be difficult to assign, since zincates show highly dynamic behaviours in solution, even at low temperatures, and the NMR-spectra are therefore frequently difficult interpret [26–28]. The <sup>1</sup>H NMR spectrum of **1** in THF-d<sub>8</sub> shows a set of broad signals, indicating a dynamic behaviour in solution.

The zincate anion in **1** displays trigonal planar coordination geometry, as expected (for bond angles and distances, see Table 1). Each [ZnEt<sub>2</sub>Ph]<sup>-</sup> anion coordinates three Na<sup>+</sup> ions, and each Na<sup>+</sup> ion, consequently, coordinates three zincate ions. The coordination of the zincate ions to Na<sup>+</sup> occur both through the ethyl groups and through the phenyl groups; each Na<sup>+</sup> ion coordinates three ethyl groups and two phenyl groups. Within the asymmetric unit, Na1 forms a bond to C9, the  $\alpha$ -carbon atom in one of the ethyl groups, to C1, the *ipso*-carbon and to the two *m*-carbon atoms C2 and C6. The other face of the phenyl ring is coordinated to Na1(*x*, 1/2 - *y*, 1/2 + *z*), in a similar η<sup>3</sup> fashion. The other  $\alpha$ -carbon atom, C7, is coordinated to Na1(2-*x*, 1/2 + *y*, 1/2 - *z*). As a result, compound **1** is a coordination network forming infinite layers in the *bc*-plane (Fig. 2). There are no directed interactions, such as CH/ $\pi$  [29,30] or  $\pi$ - $\pi$  interactions, between these layers (Fig. 3).

The supramolecular aspect of organometallic chemistry is an important field, which has been thoroughly treated in a book by Haiduc and Edelmann [31]. There are only a limited number of crystal structures of Lewis base free organozinc compounds in the Cambridge Structural Database, and these structures show large variations from a supramolecular point of view. Dicyclopentadienylzinc, for example, gives rise to polymeric zigzag chains, which are interconnected through  $CH/\pi$ -interactions into a three-dimensional network [32]. Bis(2,3,4,5-tetramethylcyclopentadienyl)zinc forms similar chains, but there is no evidence of  $CH/\pi$ -interactions, and no network is formed [33]. In di(2-methylallyl)zinc, a three-dimensional supramolecular network is obtained through coordination of four methylallyl groups to each zinc; two through primarily covalent Zn–C  $\sigma$ -bonds, and two additional methylallyl ligands from adjacent molecules coordinate to the zinc atom through their  $\pi$ systems [34]. This structure is more similar to 1, since it is entirely based on metal-carbon bonds rather than weak hydrogen bonds. Still it is different, since the carbon atoms bearing the negative charge coordinate to one zinc atom only, and supramolecular linking is caused by a second functionality of the ligand in contrast to 1. In rubidium tetra(ethynyl)zincate, four ethynyl-groups radiate linearly from a tetrahedral zinc atom [35]. Each ethynyl ligand is surrounded by three Rb<sup>+</sup> ions coordinated to the ethynyl  $\pi$ -systems.



Scheme 1. Metallation of benzene by Na[ZnEt<sub>3</sub>]



**Fig. 1.** Molecular structure of **1** displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

This results in a three-dimensional network structure comparable to that of di(2-methylallyl)zinc. Lithium tetramethylzincate gives rise to a three-dimensional network structure, with tetrahedral coordination geometries around both lithium and zinc atoms [36]. Here, the network is constructed from alkali metal-carbon bonds and zinc-carbon bonds like in 1. Among the structures most similar to 1 is potassium tri(cyclopentadienyl)zincate which forms a twodimensional layered structure that was recently published by Carmona and co-workers [19]. The two zincates potassium trineopentylzincate benzene solvate and sodium trineopentylzincate, on the other hand, does not give rise to supramolecular assemblies [10]. Introduction of Lewis base ligands may give an even richer variety of structures. For instance, di-tert-butylzinc form discrete linear molecules in the crystalline state, but upon coordination of 1,2-di (4-pyridyl)ethane, it forms a one-dimensional polymer that gives rise to a two-dimensional nanofabric [37].

Crystals of compound **2**,  $[K_2(ZnEt_2)_4O]_n$  (Table 2), were accidently isolated in low yield in an attempt to prepare  $K[ZnEt_3]$  from metallic potassium and diethylzinc. Compound **2** is built up from a  $[K_2(ZnEt_2)_4O]$  tecton (Fig. 4) that has not been characterised previously in the solid state.

The most striking feature of this unit is the central oxide ion surrounded by a square planar array of four zinc atoms with two K<sup>+</sup> ions completing an octahedral coordination geometry. A search in the Cambridge Structural Database reveals that oxygen atoms

Selected bond distances (Å) and angles (°) for <b>1</b> .		
Zn1-C1	2.075(2)	
Zn1–C7	2.028(2)	
Zn1-C9	2.043(2)	
Na1–C1	2.654(2)	
Na1–C2	3.331(2)	
Na1-C6	3.055(2)	
Na1–C7	2.717(2)	
Na1-C9	2.861(2)	
Na1 <sup>i</sup> —C1	2.633(2)	
Na1 <sup>i</sup> —C2	2.780(2)	
Na1 <sup>i</sup> —C6	2.955(2)	
C1–Zn1–C7	119.90(7)	
C1-Zn1-C9	118.14(7)	
C7–Zn1–C9	121.90(7)	

Symmetry code: (i) x, 1/2 - y, 1/2 + z.

Table 1

Table 2



**Fig. 2.** Compound **1** forms a two-dimensional coordination network in the solid state. The zincate anions are linked *via* ethyl- and phenyl groups by the Na<sup>+</sup> counter ions into layers in the *bc*-plane. All hydrogen atoms have been omitted for clarity.

surrounded by six metal atoms is not a common motif except in molybdenum, vanadium, tungsten, tantalum and niobium chemistry; there are only six structures involving zinc atoms. One complex displays a Li<sub>4</sub>Zn<sub>2</sub>( $\mu_6$ -O) core with two zinc atoms in a *cis*-arrangement [38] and one complex a *fac*-Li<sub>3</sub>Zn<sub>3</sub>( $\mu$ <sub>6</sub>-O) core [39]. There are three complexes displaying double-cubane cores comprising  $K_2Zn_4(\mu_6-0)$ and  $C_{2}Zn_{4}(\mu_{6}-0)$  motifs [40]. These are guite dissimilar to **2**, having the two alkali metal ions in a *cis*-configuration, for example. The compound showing most similarities with 2 is  $[Ba_2Zn_4(Me)_2(O)]$ (PSiMe<sub>3</sub>)<sub>4</sub>(thf)<sub>6</sub>] (Fig. 5), isolated and characterised by Westerhausen and co-workers [41]. The two compounds share the  $M_2Zn_4(\mu_6-0)$ core with the two M atoms in a trans-arrangement, but apart from this core, the two structures are quite different. In 2, the four zinc atoms are chemically equivalent, displaying distorted trigonal planar geometries. The zinc atoms coordinate two ethyl groups and the central oxygen atom. In [Ba<sub>2</sub>Zn<sub>4</sub>(Me)<sub>2</sub>(O)(PSiMe<sub>3</sub>)<sub>4</sub>(thf)<sub>6</sub>], on the other hand, there are two types of zinc atoms. One type is threecoordinated with a T-shaped coordination geometry. These two zinc atoms coordinates two phosphide ligands and the central oxygen atom, while the other two zinc atoms are four-coordinated and coordinate two phosphide ligands, the central oxygen atom and one bridging methyl group. Another difference is the Ba<sup>2+</sup> ions which



**Fig. 3.** The layers in **1** are stacked along the crystallographic b-axis, without any indications of directed interactions between the layers. All hydrogen atoms have been omitted for clarity.

Selected Dolld distances (A) and angles (*) for 2.		
K1-C1	3.169(3)	
K1–C1 <sup>ii</sup>	3.169(2)	
K1-C7	3.123(3)	
K1–C7 <sup>ii</sup>	3.123(2)	
K1-O1	2.814(2)	
K2-C3	3.341(3)	
K2–C3 <sup>ii</sup>	3.341(3)	
K2-C5	3.173(3)	
K2–C5 <sup>ii</sup>	3.173(3)	
K2-01	2.707(2)	
Zn1–C1	2.001(2)	
Zn1–C3	2.022(2)	
Zn1-01	2.076(4)	
Zn1 <sup>ii</sup> –O1	2.0763(4)	
Zn201	2.0831(4)	
Zn2 <sup>ii</sup> –O1	2.0830(4)	
Zn2–C5	2.006(2)	
Zn2–C7	2.025(2)	
C1–Zn1–C3	138.3(1)	
C1-Zn1-O1	109.86(9)	
C3-Zn1-O1	111.74(9)	
C5-Zn2C7	136.5(1)	
C5-Zn2-O1	112.51(9)	
C7-Zn2-O1	110.89(9)	
K1-01-K2	180.0	
Zn1-01-K1	88.77(6)	
Zn1-01-K2	91.23(6)	
Zn1 <sup>ii</sup> –O1–Zn1	177.5(1)	
Zn1-01-Zn2	94.20(2)	
Zn2-01-K1	89.08(6)	
Zn2-01-K2	90.92(6)	
$Zn1-O1-Zn2^{n}$	85.76(2)	
Zn2 <sup>III</sup> -O1-Zn2	178.2(1)	

d hand distances (Å) and smales (a) for 7

Symmetry code: (ii) 2 - x, y, 1/2 - z.

coordinate THF molecules. Since **2** was crystallised from neat diethylzinc, no coordinating solvent is available for the two K<sup>+</sup> ions, and a coordination network is formed rather than discrete molecules. Each K<sup>+</sup> ion coordinates six ethyl groups, four within the [K<sub>2</sub>(ZnEt<sub>2</sub>)<sub>4</sub>O] tecton, and two ethyl groups from two different adjacent tectons. K1 forms bonds to C1, C7, C1(2 - *x*, *y*, 1/2 - *z*) and C7 (2 - *x*, *y*, 1/2 - *z*) within the tecton and two additional bonds to C3(1/ 2 + *x*, -1/2 + *y*, *z*) and C3(3/2 - *x*, -1/2 + *y*, 1/2 - *z*). K2 is chemically equivalent to K1 and forms bonds to C3, C5, C3(2 - *x*, *y*, 1/2 - *z*), C5 (2 - *x*, *y*, 1/2 - *z*), C7(-1/2 + *x*, -1/2 + *y*, *z*) and C7(5/2 - *x*, 1/2 + *y*, 1/ 2 - *z*). This means that that there are two types of ethyl groups; the negative charge on  $\alpha$ -carbon atoms C3 and C7 is shared between one



**Fig. 4.** Molecular structure of the tecton in **2** displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and all hydrogen atoms have been omitted for clarity.



**Fig. 5.** Comparison between the tecton in **2** (left) and  $[Ba_2Zn_4(Me)_2(O)(PSiMe_3)_4(thf)_6]$  (right) with the common features highlighted.

zinc atom and two K<sup>+</sup> ions, while the negative charge on  $\alpha$ -carbon atoms C1 and C5 is shared between one zinc atom and one K<sup>+</sup> ion. The linking of [K<sub>2</sub>(ZnEt<sub>2</sub>)<sub>4</sub>O] units results in a two-dimensional network structure composed of infinite layers stacked parallel to the *c*-axis (Fig. 6). Both faces of these layers are dominated by hydrophobic ethyl groups, and there are no indications of directed interactions between these layers. The <sup>1</sup>H NMR spectrum in THF-d<sub>8</sub> shows only one set of signals from the ethyl groups.

The most probable source of the central oxide ion in **2** is water rather than dioxygen, which would more likely give rise to alkoxide complexes. We have previously reported an octanuclear ethyl(oxo) zinc complex with a cubane core, which forms upon addition of water to a solution of diethylzinc and pyridine in hexane [42], and a zincphenoxide complex obtained by exposure of a solution of diphenylzinc in diethyl ether to air [43]. Due to the potential explosion hazard, we have not attempted to deliberately add water in any form to the reaction mixture of potassium in neat diethylzinc.

In conclusion, two new supramolecular zincate structures have been prepared, one of which displays a rare  $\mu_6$ -oxo-centred zincate tecton. The determination of the crystal structure of Wanklyn's original compounds, however, still remains a challenge.

#### 3. Experimental

*Caution*! Diethylzinc and alkylzincates are highly pyrophoric, ignite instantaneously upon contact with air, and react explosively with water. Sodium and potassium should be handled with care.



**Fig. 6.** Like **1**, compound **2** gives rise to a two-dimensional supramolecular network structure. This figure displays four vertical layers viewed along the *b*-axis; there are no directed interactions between the layers. All hydrogen atoms have been omitted for clarity.

#### 3.1. General

All experiments were performed under nitrogen atmosphere using Schlenk technique. All glass equipment was dried at 130 °C over night. Benzene was distilled from sodium/benzophenone shortly prior to use; hexane was distilled from sodium/benzophenone/tetraglyme shortly prior to use. Diethylzinc (Aldrich), 15% diethylzinc solution in hexane (Acros Organics), sodium (E. Merck) and potassium (Aldrich) were used as received. NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer.

#### 3.2. [Na Zn(Et)<sub>2</sub>Ph] (1)

Diethylzinc solution (50 ml, 15% in hexane, 60 mmol) was evaporated until 1/3 of the solution remained. Sodium (0.8 g, 33 mmol) was added in small pieces under stirring. The mixture was heated until the sodium started to melt and the mixture was stirred over night. The solution was withdrawn, the grey solid residue was washed with hexane ( $2 \times 5$  ml) and extracted with benzene (10 ml). The mixture was centrifuged (2 min, 2500 rpm) and the resulting clear, orange/brown solution was placed at 4 °C. After a few days, **1** had crystallised in colourless, irregular-shaped crystals. Yield: 2.3 g (30%). <sup>1</sup>H NMR (400.12 MHz, THF-d<sub>8</sub>):  $\delta = 8.05$  (s, Ph), 7.87 (s, Ph), 7.04 (s, Ph), 6.91 (s, Ph), 1.39 (s, CH<sub>3</sub>), 0.00 (s, CH<sub>2</sub>). <sup>13</sup>C NMR (100.62 MHz, THF-d<sub>8</sub>):  $\delta = 142$  (Ph), 141 (Ph), 129 (Ph), 126 (Ph), 125 (Ph), 123 (Ph), 15.6 (CH<sub>3</sub>), 6.95 (CH<sub>2</sub>).

#### 3.3. [K<sub>2</sub>(ZnEt<sub>2</sub>)<sub>4</sub>O] (2)

A small piece of potassium (*c*. 50 mg) was added to diethylzinc (2 ml) in a Schlenk tube. A white precipitate formed immediately. The mixture was stirred at ambient temperature over night, and placed at -35 °C. A few colourless needles were isolated after approx. 3 months. <sup>1</sup>H NMR (400.12 MHz, THF-d<sub>8</sub>):  $\delta = 1.09$  (m, CH<sub>3</sub>), -0.09 (q, CH<sub>2</sub>). <sup>13</sup>C NMR (100.62 MHz, THF-d<sub>8</sub>):  $\delta = 13.41$  (CH<sub>3</sub>), 4.29 (CH<sub>2</sub>).

#### 3.4. X-ray crystallography

The crystals of **1** and **2** were carefully selected using microscope at low-temperature [44]. Data were recorded at 100 K using

Table 3Crystal and refinement data for compounds 1–3.

Parameter	1	2
Empirical formula	NaZnC <sub>10</sub> H <sub>15</sub>	K <sub>2</sub> Zn <sub>4</sub> C <sub>16</sub> H <sub>40</sub> O
Μ	223.58	588.16
<i>T</i> (K)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c
a/Å	8.3949(17)	9.3390(18)
b/Å	13.298(3)	13.845(3)
c/Å	9.408(2)	18.098(4)
$\alpha /^{\circ}$	90	90
$\beta I^{\circ}$	92.947(9)	91.063(10)
γ/° _	90	90
V/Å <sup>3</sup>	1048.9(4)	2339.6(8)
Ζ	4	4
$D_c/g \text{ cm}^{-3}$	1.416	1.670
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	2.326	4.408
Crystal size/mm <sup>3</sup>	$0.3 \times 0.2 \times 0.2$	$0.3\times0.15\times0.15$
$\theta$ Range/°	2.65 - 25.50	3.71-25.00
Reflections collected	6446	6958
Unique reflections, R <sub>int</sub>	1873	1840
No. of parameters	111	110
Final $R_1(F)^{\mathrm{a}}(I > 2\sigma(I))/wR_2(F^2)^{\mathrm{b}}$	0.0253/0.0629	0.0264/0.0631
$R_1^{\rm a}/wR_2(F^2)^{\rm b}$ (all data)	0.0281/0.0639	0.0309/0.0644

<sup>a</sup>  $R_1(F) = \Sigma(||F_o| - |F_c||) / \Sigma |F_o|.$ 

<sup>b</sup>  $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}.$ 

a Rigaku R-AXIS IIc area detector with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) from a Rigaku RU-H3R rotating anode, operating at 50 kV and 90 mA. 90 oscillation photos with a rotation angle of 2° were collected. Data were processed using the CrystalClear software package [45], and an empirical absorption correction was applied using the REQAB program. The structures were solved using the program SIR-92 [46] and refined using fullmatrix least squares calculations on F<sup>2</sup> using the SHELXL-97 program [47]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions and refined using a riding model. Structures were drawn using ORTEP3 [48] for Windows and Pluton [49,50]. SIR-92, SHELXL-97, Pluton and ORTEP3 were enclosed in the WinGX-software package [51]. Crystal and refinement data are given in Table 3.

#### Appendix A. Supplementary material

CCDC 790585 (1) and 790586 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

#### Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.12.001.

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