



## Note

## 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

## ARTICLE INFO

## Article history:

Received 31 August 2010

Received in revised form

24 November 2010

Accepted 1 December 2010

## Keywords:

Organozinc

Zincate

Supramolecular chemistry

Metallation

Diethylzinc

## 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  $\text{Na}^+$  ions link the zincate anions by coordination to both ethyl- and phenyl groups. We have also, accidentally, isolated crystals of the two-dimensional coordination network  $[\text{K}_2(\text{ZnEt}_2)_4\text{O}]_n$ , displaying a rare oxo-centred core with an octahedral oxide ion surrounded by four zinc atoms and two potassium atoms.

© 2010 Elsevier B.V. All rights reserved.

## 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 J. 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  $\text{Na}[\text{ZnEt}_3]$  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,  $\text{Na}[\text{ZnEt}_3]$  and  $\text{K}[\text{ZnEt}_3]$ , 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  $\text{Na}_2[\text{Zn}_2\text{Et}_4(\mu\text{-H})_2]$  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  $[\text{NaZnEt}_2\text{Ph}]_n$  and  $[\text{K}_2(\text{ZnEt}_2)_4\text{O}]_n$ .

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  $\text{Na}[\text{ZnEt}_3]$  through crystallisation from neat diethylzinc; neither cooling solutions to  $-40^\circ\text{C}$  or  $-80^\circ\text{C}$ , 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  $\text{Na}^+$  [19], and was therefore not considered.  $\text{Na}[\text{ZnEt}_3]$  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  $\text{Na}[\text{ZnEt}_3]$  and  $\text{K}[\text{ZnEt}_3]$ , 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  $\text{Na}_2[\text{Zn}_2\text{Et}_4(\mu\text{-H})_2]$  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  $[\text{NaZnEt}_2\text{Ph}]_n$  and  $[\text{K}_2(\text{ZnEt}_2)_4\text{O}]_n$ .

## 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  $\text{Na}[\text{ZnEt}_3]$  through crystallisation from neat diethylzinc; neither cooling solutions to  $-40^\circ\text{C}$  or  $-80^\circ\text{C}$ , 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  $\text{Na}^+$  [19], and was therefore not considered.  $\text{Na}[\text{ZnEt}_3]$  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  $\text{Na}[\text{ZnEt}_3]$  and  $\text{K}[\text{ZnEt}_3]$ , 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  $\text{Na}_2[\text{Zn}_2\text{Et}_4(\mu\text{-H})_2]$  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  $[\text{NaZnEt}_2\text{Ph}]_n$  and  $[\text{K}_2(\text{ZnEt}_2)_4\text{O}]_n$ .

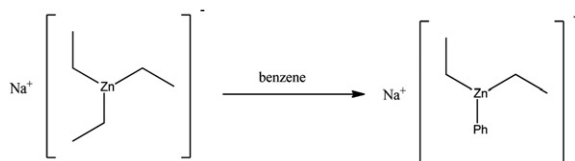
\* Corresponding author.

E-mail address: [lennartson@ifk.sdu.dk](mailto:lennartson@ifk.sdu.dk) (A. Lennartson).

[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<sub>2</sub>Ph]<sub>n</sub>, **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 to 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 α-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 α-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/π [29,30] or π-π 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 Edlmann [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/π-interactions into a three-dimensional network [32]. Bis(2,3,4,5-tetramethylcyclopentadienyl)zinc forms similar chains, but there is no evidence of CH/π-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 σ-bonds, and two additional methylallyl ligands from adjacent molecules coordinate to the zinc atom through their π-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 π-systems.



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

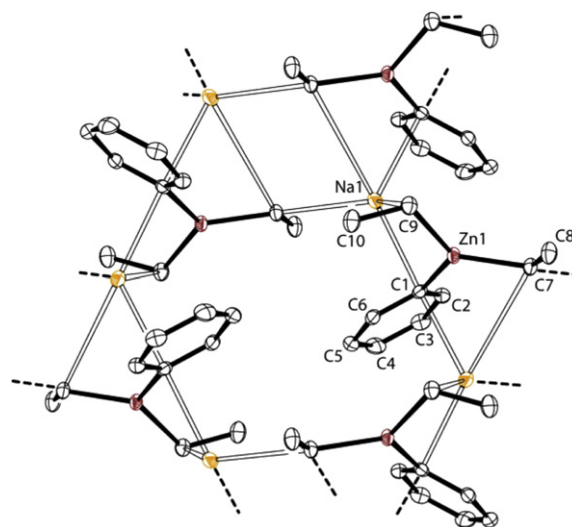


Fig. 1. Molecular structure of **1** displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

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 two-dimensional 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<sub>2</sub>(ZnEt<sub>2</sub>)<sub>4</sub>O]<sub>n</sub> (Table 2), were accidentally isolated in low yield in an attempt to prepare K[ZnEt<sub>3</sub>] from metallic potassium and diethylzinc. Compound **2** is built up from a [K<sub>2</sub>(ZnEt<sub>2</sub>)<sub>4</sub>O] 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

Table 1  
Selected bond distances (Å) and angles (°) for **1**.

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*.

Download English Version:

<https://daneshyari.com/en/article/1326664>

Download Persian Version:

<https://daneshyari.com/article/1326664>

[Daneshyari.com](https://daneshyari.com)