Zincate Ions

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Facile Synthesis of Well-Defined Sodium Hydridoalkylzincates(II)**

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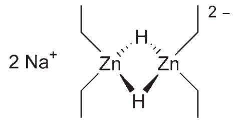
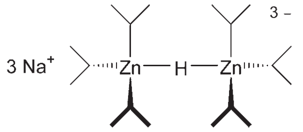
As described in a cover essay by Seyferth,[1] Edward Frankland first reported his discovery of diethylzinc in 1849.[2] In 1858,[3,4] J. Alfred Wanklyn, who was an assistant to Frankland in 1856,[1] discovered that diethylzinc reacts with sodium to form a crystalline compound, which he formulated as a "double compound of sodium-ethyl with zinc-ethyl".[4] The preparation of this compound, now known as sodium triethylzincate(II) according to modern "ate" terminology,[5] was communicated to the Royal Society of London by Frankland.[4b] Modern "ate" chemistry, including a historical overview, has recently been reviewed.[6] When repeating the reaction between sodium and neat diethylzinc (using the excess diethylzinc as solvent), we noticed that mild heating of the mixture resulted in gas evolution and the formation of a crystalline product. An X-ray crystal-structure determination[7] showed this to be sodium di-μ-hydridobis{diethylzincate(II)} (**1**), which contains a hitherto unknown dimeric hydride-bridged ethylzincate(II) anion (Figure 1). To examine the generality of this preparative approach, we decided to repeat the reaction with an alkyl group that is less prone to undergo β-elimination than ethyl, namely isopropyl. Thus, warming a mixture of sodium and neat diisopropylzinc gave sodium μ-hydridobis{tris(isopropyl)zincate(II)} (**2**). This compound also contains a new anion in which two $Zn(iPr)_3$ moieties are linked by a single hydride bridge (Figure 2).



$Na_2[Zn_2(C_2H_5)_4(\mu\text{-}H)_2]$ (**1**)



$Na_3[Zn_2(C_3H_7)_6(\mu\text{-}H)]$ (**2**)

Well-defined compounds containing base-free hydridoalkylzincate(II) anions do not appear to have been isolated previously, although the presence of hydridoalkylzincate(II) species in solution has been proposed from molecular weight measurements and ^1H NMR spectroscopic data.[8] These previous synthetic studies pioneered by Shriver and coworkers[8,9] utilized advanced high-vacuum line techniques (organozinc hydride complexes are notoriously difficult to handle) and solvents such as diethyl ether and dimethoxyethane. With diethyl ether as solvent, a precipitate of an ether adduct of $NaHZn(CH_3)_2$ was obtained.[8] With dimethoxyethane as solvent, very concentrated colorless solutions could be obtained but solvent removal in vacuo resulted in loss of dialkylzinc and precipitation of alkali metal hydride.[8] More recently, dialkylzinc hydride "ate" complexes have been generated in situ as active species for chemoselective, diastereoselective, and catalytic reductions.[10] Herein we describe the preparation and structural characterization of two crystalline compounds containing simple hydridoalkylzincate anions.

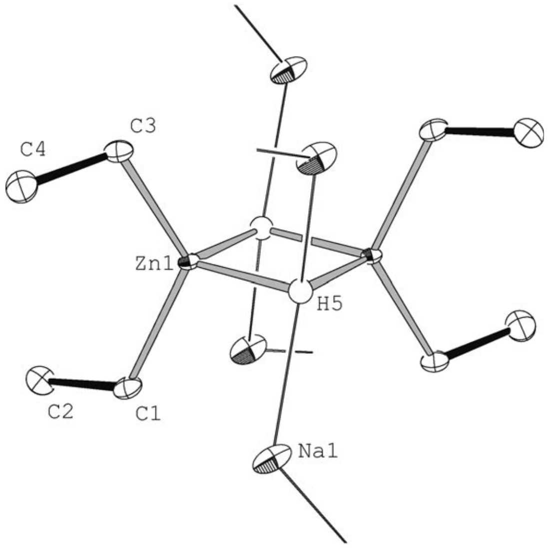


Figure 1. The di-μ-hydridobis{diethylzincate(II)} anions in **1** form layers through hydride–sodium interactions (thin "bonds") and sodium contacts with the α-carbon atoms C1 and C3 (not indicated for clarity). The midpoint of the dimeric anion is situated on a center of symmetry. The hydrogen atoms of the alkyl groups have been omitted. Thermal ellipsoids drawn at 50% probability. Selected interatomic distances [Å] and angles [°]: Zn1–C1 2.046(3), Zn1–C3 2.035(4), Zn–H5 1.83(4), Zn–H5^i 1.81(4), Na1–H5 2.33(4), Zn1···Zn1^i 2.6977(4); C1-Zn1-H5 105(1), C1-Zn1-H5^i 111(1), C3-Zn1-H5 113(1), C3-Zn1-H5^i 114(1), C1-Zn1-C3 122.6(1), H5-Zn1-H5^i 84(2), Zn1-H5-Zn^i 96(1). Symmetry code (i): $-x$, $1-y$, $2-z$.

Compound **1** can be seen as the product of β-elimination of triethylzincate(II) in the presence of sodium (Scheme 1). The structure of Wanklyn's crystalline solid[4] is unknown, but it is generally assumed to contain a trigonal-planar anion similar to that in $K(ZnMe_3)$.[11] The crystal structure[7] of sodium di-μ-hydridobis{diethylzincate(II)} (**1**) consists of di-μ-hydridobis{diethylzincate(II)} anions (Figure 1) in close contact with sodium cations. The zinc centers exhibit distorted tetrahedral coordination geometry with Zn–C bonds of

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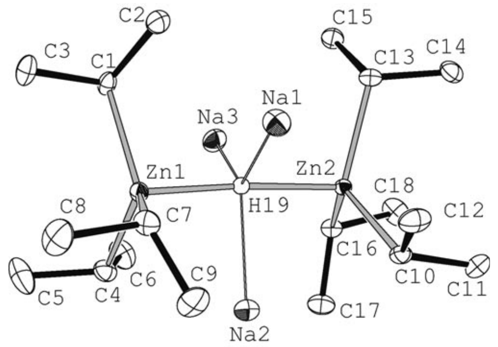
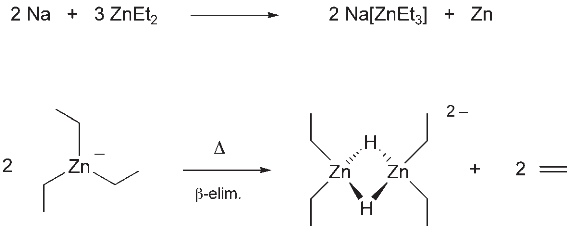


Figure 2. The μ-hydridobis{tris(isopropyl)zincate(II)} anion and sodium cations in **2** showing the crystallographic numbering. Hydride–sodium interactions are indicated by thin "bonds". The hydrogen atoms of the alkyl groups have been omitted for clarity. Thermal ellipsoids drawn at 50% probability. Selected interatomic distances [Å] and angles [°]: Zn1–C1 2.099(2), Zn1–C4 2.089(2), Zn1–C7 2.092(2), Zn2–C10 2.111(2), Zn2–C13 2.099(2) Zn2–C16 2.099(2), Zn1–H19 1.93(2), Zn2–H19 1.96(2), Na1–H19 2.27(2), Na2–H19 2.28(2), Na3–H19 2.19(2); C1-Zn1-C4 117.19(8), C1-Zn1-C7 116.01(7), C4-Zn1-C7 117.40(8), C1-Zn1-H19 99.2(7), C4-Zn1-H19 99.4(8), C7-Zn1-H19 102.4(7), C10-Zn2-C13 113.49(8), C10-Zn2-C16 116.11(7), C13-Zn2-C16 116.87(7), C10-Zn2-H19 105.3(7), C13-Zn2-H19 101.8(7), C16-Zn2-H19 100.3(7), Zn1-H19-Zn2 173(1).



Scheme 1. Formation of **1** by β-elimination of triethylzincate(II) in the presence of sodium.

2.046(3) and 2.035(4) Å and Zn–H bonds of 1.81(4) and 1.83(4) Å.

Only three hydride-bridged zinc compounds are known, namely [{[HC(CMeNAr)$_2$]Zn(μ-H)}$_2$] (Ar = 2,6-Me$_2$C$_6$H$_3$),[12] [Ar′Zn(μ-H)$_2$ZnAr′], and [Ar′Zn(μ-H)(μ-Na)ZnAr′] (Ar′ = 2,6-(2,6-*i*Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$).[13] The Zn⋯Zn separation of 2.6977(4) Å in **1** is longer than that in [{[HC(CMeNAr)$_2$]Zn-(μ-H)}$_2$] (Ar = 2,6-Me$_2$C$_6$H$_3$; 2.4513(9) Å), which was the first example of a zinc compound with bridging hydride ligands to be structurally characterized.[12] As expected, the Zn⋯Zn separation in **1** is also longer than the unsupported Zn–Zn bonds in [Zn$_2$(η^5-C$_5$Me$_5$)$_2$],[14,15] [{HC(CMeNAr)$_2$}ZnZn{HC-(CMeNAr)$_2$}] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[16] and Ar′ZnZnAr′.[13] Although [Ar′Zn(μ-H)$_2$ZnAr′] does not contain a Zn–Zn bond, its Zn⋯Zn separation is very similar to that in [Ar′ZnZnAr′][13] and is thus appreciably shorter than that in **1**. Hence, it seems unlikely that the Zn⋯Zn separation in the anion of **1** is indicative of a Zn–Zn bond.

The sodium ion in **1** is involved in eight short contacts with hydrogen (2.33(4)–2.69(3) Å), with the shortest being to the hydride ligand. It also has contacts of around 2.7–3.1 Å with C1 and C3 and around 3.2 Å with Zn1. As we can disregard any Na⋯Zn interaction, each sodium ion thus primarily coordinates to two α-carbon atoms and two hydride ligands. Short contacts between alkali metal cations and the α-carbon atoms of alkyl groups in zincates(II) have been noted previously.[17] Similarly, the H atoms on the α-carbon C3 exhibit short contact distances to sodium whereas those on C4 lack such anchoring effects. Cation⋯anion contacts in **1** lead to the formation of layers in the *bc* plane.

Compound **2** was prepared by gently heating sodium in an excess of neat diisopropylzinc. The X-ray crystal-structure determination of **2**[7] shows that it contains an [(*i*Pr)$_3$ZnHZn(*i*Pr)$_3$]$^{3-}$ ion (Figure 2) in which both zinc atoms exhibit coordination polyhedra that are distorted from tetrahedral towards trigonal pyramidal. The Zn–C distances in **2** (2.089(2)–2.111(2) Å) are slightly longer than those in **1**, whereas the Zn–H distances in **1** and **2** are very similar (1.81(4) and 1.83(4) Å in **1** and 1.92(2) and 1.96(2) Å in **2**) even though the hydrogen atoms participate in a double bridge in **1** but only a single bridge in **2**. Marginally shorter bridging Zn–H distances have been reported previously,[12,13] and a terminal Zn–H distance has been determined to be 1.618 Å by neutron diffraction.[18] Interestingly, the structure of the [H(Zn(*i*Pr)$_3$)]$^{3-}$ ion in **2** is analogous to that proposed previously for the H(ZnR$_2$)$_2^-$ ion in solution by Kubas and Shriver.[8]

The [(*i*Pr)$_3$ZnHZn(*i*Pr)$_3$]$^{3-}$ ion in **2** is closely associated with three sodium ions, with Na⋯H19 distances of 2.19(2)–2.28(2) Å. There are several other intramolecular Na⋯H contacts involving the isopropyl groups, but the shortest of these is still longer than those involving the hydride ion. The ZnNa$_3$HZn core can be described as a trigonal bipyramid with the hydride ligand at its center. The hydride ligand H19 lies approximately in the plane passing through Na1, Na2, and Na3, although it is displaced 0.05(2) Å from this plane towards Zn1. The Na⋯Zn separations spanning the edges of the trigonal bipyramid range from 2.915(1) to 3.058(1) Å and are shorter than the Na⋯Zn distance (3.113(4) Å) in [Ar′Zn-(μ-H)(μ-Na)ZnAr′].[13] There are intramolecular Na⋯C contacts as short as 2.840(1) Å involving the α-carbon atoms, and intermolecular Na⋯C contacts of 2.805(1) Å with the β-carbon atom on the next anion. These intermolecular cation⋯anion contacts in **2** lead to the formation of bands parallel to the *b* axis.

We have demonstrated that simple hydridoalkylzincate(II) anions can be prepared in essentially quantitative yield from mixtures of sodium and an excess of neat dialkylzinc reagent, which also acts as the solvent. Thus, sodium di-μ-hydridobis{diethylzincate(II)} (**1**) has been prepared by gently heating sodium in diethylzinc to initiate β-elimination of ethene. The reaction can be driven to completion simply by refluxing the reaction mixture for a few hours.

Determination of the yield of this reaction is not trivial because of the sensitivity of the product, but we were able to prepare a powder sample from the bulk product at low temperature[19] and record an X-ray diffractogram (Figure 3). This shows that the bulk product consists of almost exclusively one phase, namely **1**. Compound **2**, in which two trialkylzincate(II) fragments are joined by a single μ-hydrido bridge, can be considered as an intermediate in a slower β-elimination process. These facile reactions open up new,

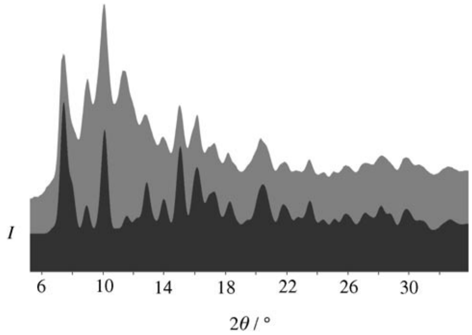


Figure 3. Calculated (dark gray) and measured (light gray) powder X-ray diffractograms for a bulk sample of **1**. The calculated diffractogram has been adjusted for instrument (R-Axis IIc image plate) broadening effects.

simple, and less-demanding routes to well-defined hydridoalkylzincates(II) for use as precursors in the preparation of new functionalized zinc hydride complexes and materials,[9,20] or as reducing agents in organic synthesis.[9,10] Catalytic asymmetric reduction[10] using optically active hydridoalkylzincates may now also become possible.

Experimental Section

Caution! The starting materials (sodium in diethylzinc) and reaction products (hydridoalkylzincates) are highly pyrophoric and must be handled with extreme care. All operations were carried out under nitrogen by using Schlenk or low-temperature[19] techniques. Commercial sodium, diethylzinc, isopropyl bromide, and isopropyl iodide were used without further purification. Diisopropylzinc was prepared according to a previously published procedure.[21]

Sodium (0.28 g, 12 mmol) was added to neat diethylzinc (5 mL, 48 mmol) in a Schlenk tube equipped with a reflux condenser. The mixture was heated gently to initiate the reaction and the diethylzinc was allowed to reflux slowly for 2 h to complete the reaction. The resulting suspension was allowed to cool to ambient temperature, which resulted in the formation of pyrophoric, colorless, plate-shaped crystals of **1**. Low-temperature powder X-ray diffraction analysis using the CrystalClear and AreaMax software packages (Figure 3) of a sample representative of the bulk product (the metallic zinc formed in the reaction is mainly deposited at the bottom of the reaction vessel) indicated that the yield is essentially quantitative.

Sodium (0.14 g, 6 mmol) was added to diisopropylzinc (1 mL, 9 mmol) in a Schlenk tube and the mixture was heated gently to initiate the reaction. A grayish precipitate separated out during the reaction and the mixture was then allowed to cool to ambient temperature. Pyrophoric, colorless, irregular-shaped crystals of **2** formed overnight.

Crystals[7] of **1** and **2** were selected and mounted under nitrogen in a glass capillary at low temperature[19] and transferred to a Rigaku R-AXIS IIc image plate system. Diffracted intensities were measured at 100(2) K, using graphite-monochromated $\mathrm{Mo}_{K\alpha}$ radiation from a RU-H3R rotating anode. The structures were solved and refined by using SHELX-97[22] in the WinGX program suite.[23,24]

CCDC-628679 (**1**) and CCDC-628680 (**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.

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[7] Crystal data for **1**: $C_8H_{22}Na_2Zn_2$, $0.30\times0.30\times0.10\ \mathrm{mm}^3$, $M_r = 295.0$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.261(2)$, $b = 7.464(2)$, $c = 8.209(2)$ Å, $\beta = 101.588(7)°$, $V = 615.9(2)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.591\ \mathrm{g\,cm}^{-1}$, $\mu = 3.916\ \mathrm{mm}^{-1}$. Refinement on F^2 for 87 parameters and 1030 reflections gave $R1 = 0.029$ and $wR2 = 0.069$ for $I > 2\sigma(I)$ (946 reflections); $R1 = 0.031$ and $wR2 = 0.070$ for all 1030 reflections. Residual electron density: $-0.45 < \Delta\rho < 1.02$ e Å^3. Na, Zn, and C atoms were refined with anisotropic thermal displacement parameters and the H atoms with isotropic parameters, except for those on C4, which were included as riding on their parent atom. Crystal data for **2**: $C_{18}H_{43}Na_3Zn_2$, $0.10\times0.10\times0.10\ \mathrm{mm}^3$, $M_r = 459.2$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.6403(6)$, $b = 11.2080(4)$, $c = 11.8372(12)$ Å, $\alpha = 81.19(2)°$, $\beta = 81.54(2)°$, $\gamma = 66.14(2)°$, $V = 1150.7(2)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.325\ \mathrm{g\,cm}^{-1}$, $\mu = 2.138\ \mathrm{mm}^{-1}$. Refinement on F^2 for 380 parameters and 4061 reflections gave $R1 = 0.028$ and $wR2 = 0.067$ for $I > 2\sigma(I)$ (3673 reflections); $R1 = 0.032$ and $wR2 = 0.068$ for all 4061 reflections. Residual electron density: $-0.40 < \Delta\rho < 0.42$ e Å^3. Na, Zn, and C atoms were refined with anisotropic thermal displacement parameters and the H atoms with isotropic thermal parameters.

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