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# COMMUNICATION

## Crystal structure of sodium ethoxide (C$_2$H$_5$ONa), unravelled after a 180 years

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**As early as 1837, Liebig synthesised solid C$_2$H$_5$ONa. Today, C$_2$H$_5$ONa is one of the standard bases in organic synthesis. Here, we report the identification of different solid phases and the crystal structures and phase transformations of C$_2$H$_5$ONa and C$_2$H$_5$ONa · 2 C$_2$H$_5$OH.**

Sodium ethoxide (sodium ethanolate, C$_2$H$_5$ONa, **1**) is a very common base in organic synthesis.[1] In the laboratory, it is generally synthesised *in situ* from sodium and excess ethanol and used as a solution or a suspension. Solid C$_2$H$_5$ONa was synthesised by Liebig as early as 1837, see Fig. 1. [2] Surprisingly, the structure of solid sodium ethoxide has not been determined hitherto.

When a solution of C$_2$H$_5$ONa in ethanol is evaporated to dryness *in vacuo* at room temperature, a metastable, white residue remains, which turns into a liquid after a few minutes of storage under argon. Further evaporation results in a residue, which again liquidifies under argon after a few minutes. Finally, the evaporation leads to a white, hygroscopic solid which is stable under argon. We investigated this solid by X-ray powder diffraction. A mixture of two phases was found, which turned out to be sodium ethoxide (C$_2$H$_5$ONa, **1**) and sodium ethoxide ethanol disolvate



Liebig (1837)

Wenn man Kalium oder Natrium in absoluten Alkohol bringt, so wird das Hydratwasser des Alkohols zerlegt, denn es entwickelt sich reines Wasserstoffgas; durch eine schwache Erwärmung, nicht über 50°, geht diese Zerlegung rasch vor sich, die neue Verbindung löst sich bei dieser Temperatur auf, und wenn man soviel Kalium oder Natrium eingetragen hat, dass der noch nicht zerlegte Alkohol damit gesättigt ist, so scheiden sich, wenn man noch mehr von diesen Metallen hineinbringt, weisse durchsichtige, bei dem Natrium gross-blättrige Krystalle ab, zu denen die ganze Flüssigkeit erstarrt, wenn man sie bei diesem Zeitpunkte erkalten lässt. Diese Krystalle sind eine Verbindung von Aether (Aethyloxyd) mit wasserfreiem Kalium- oder Natriumoxyd; sie lassen sich unter einer Glocke mit concentrirter Schwefelsäure völlig trocken erhalten und nachher bis zu 80° erhitzen, ohne dass sie etwas Flüchtiges abgeben oder ihre Beschaffenheit verändern.

Translation

If one adds potassium or sodium to absolute alcohol, the hydrate water of the alcohol is decomposed, because pure hydrogen gas evolves; with gentle heating, not more than 50°C, this decomposition occurs rapidly, the new compound dissolves at this temperature, and if one has added so much potassium or sodium, that the non-decomposed alcohol is saturated with them, and if one adds even more of these metals, then white, transparent, in the case of sodium large plate-shaped crystals precipitate, into which the entire liquid solidifies, if it is allowed to cool at this moment. These crystals are a composition of ether (ethyl oxide) with anhydrous potassium or sodium oxide; they can be obtained entirely dry under a bell jar with concentrated sulfuric acid, and heated afterwards to 80°C without causing them to release any volatiles or to change their nature.

**Figure 1.** Original description of the synthesis of C$_2$H$_5$ONa by Liebig (1837) [2], from the paper "Über die Äthertheorie" ("On the theory of ether"). Liebig assumed that ethanol is the hydrate of ether – which is not completely far fetched: (C$_2$H$_5$)$_2$O · H$_2$O corresponds to 2 C$_2$H$_5$OH. Consequently, Liebig postulated that the reaction product of ethanol and sodium is an adduct of diethyl ether and sodium oxide – which actually matches the correct stoichiometry: (C$_2$H$_5$)$_2$O · Na$_2$O corresponds to 2 C$_2$H$_5$ONa.

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(C$_2$H$_5$ONa · 2 C$_2$H$_5$OH, **2**). This mixture is formed, when the excess ethanol is distilled off at ambient pressure, or the ethanol is removed at room temperature *in vacuo*. Pure C$_2$H$_5$ONa is obtained upon further evaporation *in vacuo* at 50 °C. We determined the solid-state structures and phase transitions of both phases, C$_2$H$_5$ONa and C$_2$H$_5$ONa · 2 C$_2$H$_5$OH.

We could not obtain single crystals of C$_2$H$_5$ONa. Therefore, its crystal structure was determined by X-ray powder diffraction. The powder pattern could be indexed with DICVOL[3] resulting in a tetragonal unit cell, which contains two formula units of C$_2$H$_5$ONa. The structure was solved with the real-space method with the program DASH[4] and Rietveld-refined [5] with TOPAS[6]. The Rietveld plot is shown in Fig. 2. Crystallographic data are given in Table 1.

C$_2$H$_5$ONa crystallises in the tetragonal space group $P\overline{4}2_1m$.‡ The structure does not contain discrete complexes, but consists of layers. The Na$^+$ ions form a square planar lattice. The oxygen atoms are situated at the centres of all meshes, alternatingly shifted above and below the Na$^+$ layer by 0.734(3) Å (Fig. 3a). Correspondingly, every Na$^+$ ion is coordinated to four oxygen atoms in a squeezed tetrahedron. The oxygen atoms have five neighbours, which arrange in a square pyramid: the four Na$^+$ ions on the corners and the ethyl group on top of the pyramid, see Fig. 3b+c. The ethyl groups are disordered on two orientations.
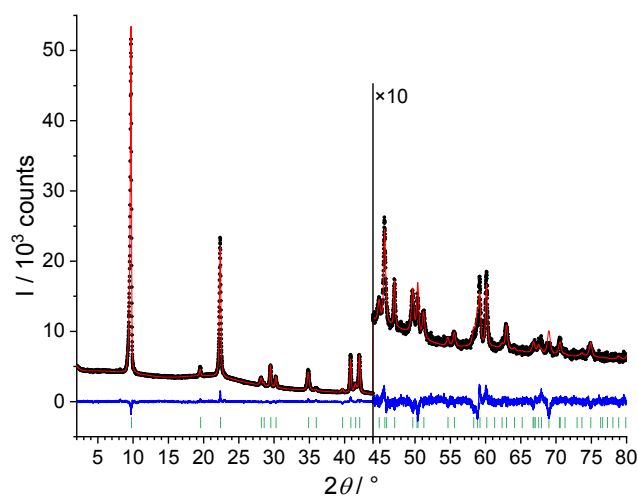
**Table 1.** Crystallographic data of C$_2$H$_5$ONa and C$_2$H$_5$ONa · 2 C$_2$H$_5$OH.

| | C$_2$H$_5$ONa (**1**) | C$_2$H$_5$ONa · 2 C$_2$H$_5$OH (**2**) |
|---|---|---|
| Crystal structure determined from | powder data | single crystals |
| CCDC number | 1943793 | 1943794 |
| MW /g·mol$^{-1}$ | 68.05 | 160.18 |
| Crystal system | tetragonal | monoclinic |
| Space group (No.) | $P\overline{4}2_1m$ (113) | $P2_1/c$ (14) |
| $a$ /Å | 4.41084 (4) | 11.622 (6) |
| $b$ /Å | 4.41084 (4) | 5.1926 (9) |
| $c$ /Å | 9.06779 (17) | 17.682 (6) |
| $\alpha$ /° | 90 | 90 |
| $\beta$ /° | 90 | 104.03 (3) |
| $\gamma$ /° | 90 | 90 |
| $V$ /Å$^3$ | 176.418 (5) | 1035.0 (7) |
| $Z$, $Z'$ | 2, 1/4 | 4, 1 |
| $D_{calc}$ /Mg·m$^{-3}$ | 1.281 | 1.028 |
| Crystal size (mm) | powder | 0.8 × 0.08 × 0.02 |
| $T$ /K | 298 (3) | 238 (2) |
| Radiation type | Cu-$K\alpha_1$ | Cu-$K\alpha$ |
| $\lambda$ /Å | 1.5406 | 1.5418 |
| $2\theta$ range /° | 2-80 | 4.14-59.9 |
| $R_p$ /% | 2.33 | - |
| $R_{wp}$ /% | 3.39 | - |
| $R1$ /% | - | 16.88 |
| w$R2$ /% | - | 27.10 |
| *GOF* | 1.58 | 0.979 |
| Site symmetry of Na, O and C atoms | $\overline{4}$.., 2.*mm*, ..*m* | 1, 1, 1 |



**Figure 2.** Rietveld refinement of C$_2$H$_5$ONa. Experimental powder pattern (black dots), calculated pattern (red line through the dots), difference curve (blue line below) and reflection positions (vertical green dashes).

The Na and O atoms exhibit the same arrangement as the O$^{2-}$ and Pb$^{2+}$ ions in red PbO (litharge, see Fig. 3d). The ethyl groups in C$_2$H$_5$ONa are in the same positions as the lone pairs of the Pb$^{2+}$ ions in PbO[7]. Hence, the structure of C$_2$H$_5$ONa could be described as an "anti-PbO type".

The methyl derivatives, sodium methoxide[8] and lithium methoxide[9], exhibit a layer structure similar to **1**. In contrast, sodium *tert*-butoxide does not crystallise in layers, but forms hexamers and nonamers in the solid state. [10]
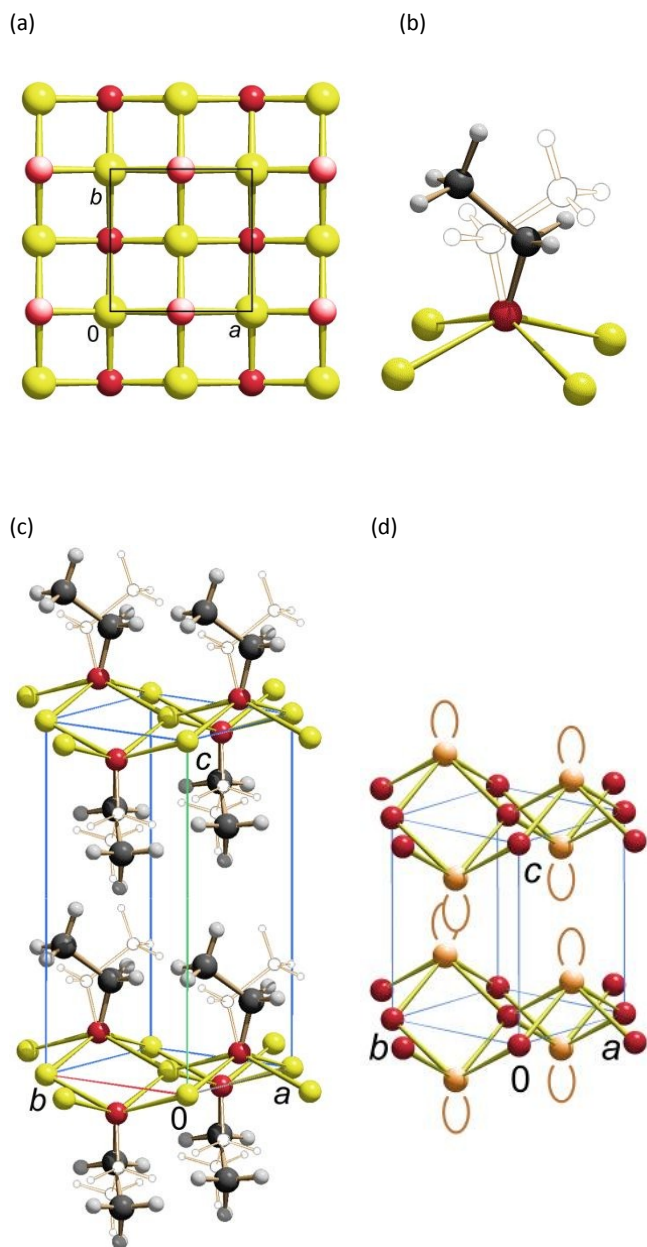
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(a)    (b)

(c)    (d)

**Figure 3.** Crystal structure of $C_2H_5ONa$. (a) Layer of Na cations and O atoms. The Na⁺ ions (yellow) are situated in the paper plane, the light red O atoms above and the dark red O atoms below it. (b) Coordination of the ethoxide group by four Na⁺ ions. The ethyl moiety is disordered on two orientations with 50 % occupancy each. (c) Crystal structure of $C_2H_5ONa$. (d) Crystal structure of red PbO. Na yellow, O red, C black, H white, Pb light brown. Empty circles in (b) and (c) denote the second orientation of the disordered ethyl groups. Brown arcs in (d) indicate the position of the lone pairs of the $Pb^{2+}$ ions. Drawings were made with SCHAKAL [11].

As mentioned by Liebig, the addition of an excess of sodium to ethanol at 50 °C leads to a termination of the H₂ evolution with left-over sodium. Upon cooling to room temperature, the mixture solidifies. In contrast to Liebig's observation, we did not obtain "grossblättrige Krystalle" (large plate-shaped

crystals), but obtained a gel. From this gel, we isolated needle-shaped colourless single crystals of $C_2H_5ONa \cdot 2 C_2H_5OH$ (**2**) after three months. A phase composed of $C_2H_5ONa \cdot 2 C_2H_5OH$ was already observed in 1895 in composition-dependent vapour-pressure measurements.[12]

The crystal structure of $C_2H_5ONa \cdot 2 C_2H_5OH$ (**2**) was determined by single-crystal X-ray diffraction‡. In the structure of **2**, the Na⁺ ions are tetrahedrally coordinated to two ethoxide ions and two ethanol molecules. The ethoxide ions bridge two Na⁺ ions resulting in a helical chain. The chain is additionally stabilised by hydrogen bonds, see Fig. 4a. The chains are arranged in a distorted hexagonal pattern (Fig. 4b). Neighbouring chains are connected by van der Waals interactions between the ethyl groups only (Fig. 4b). This structure explains the observed needle-like morphology of the crystals.

The crystal structures of **1** and **2** agree with the X-ray powder data published in 1976 by Blanchard [13], and with the unit cell parameters of $C_2H_5ONa$ published by Chandran *et al.* [14]. The lithium methoxide analogue of **2**, $CH_3OLi \cdot 2 CH_3OH$, does not form chains, but tetramers [15].
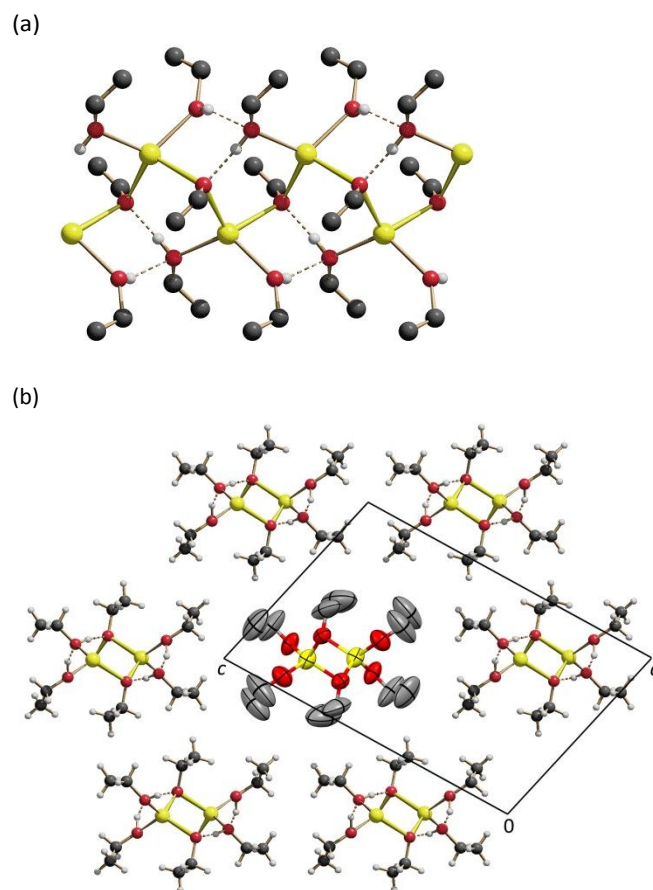
(a)

(b)

**Figure 4.** Crystal structure of $C_2H_5ONa \cdot 2 C_2H_5OH$ (**2**). (a) Helical chain (yellow) composed of Na⁺ and ethoxide ions with terminal ethanol molecules. View direction [3 0 2]. (b) Arrangement of the chains. View along the chains, view direction [0 -1 0]. The central chain is shown with anisotropic displacement parameters with a 50 % probability level.

In C$_2$H$_5$ONa, the ionic Na-O layers are surrounded by non-polar ethyl groups on both sides. Neighbouring layers are connected by van der Waals contacts only (Fig. 3c). Thus, a non-polar solvent, such as toluene, could penetrate between the layers, and eventually exfoliate the layers, but cannot break the ionic layers themselves. The large layers will remain intact, which explains the observed low solubility of C$_2$H$_5$ONa in non-polar solvents.

In polar solvents, especially with solvent molecules containing oxygen atoms, the layers are easily destroyed by the solvent. The crystal structure of C$_2$H$_5$ONa · 2 C$_2$H$_5$OH resembles the first step in the dissolution of C$_2$H$_5$ONa by ethanol: The Na-O layers of C$_2$H$_5$ONa are reduced to Na-O chains, which are surrounded by ethanol molecules. Further solvation leads to a molecular complex in solution.

Apart from the phases **1** and **2**, we observed two additional phases, **3** and **4**. They occured together with **1** and **2** in varying amounts in several experiments upon the evaporation of an ethanolic solution of C$_2$H$_5$ONa, depending on the applied conditions (For details, see ESI). However, we could neither isolate the phases **3** or **4**, nor grow single crystals. Hitherto, all our attempts to determine the crystal structures of **3** and **4** from X-ray powder data of the phase mixtures were to no avail. Correspondingly, the chemical composition and the crystal structures of **3** and **4** remain obscure.

The disolvate **2** is stable only in the presence of ethanol vapours. The crystals decompose upon contact with dry air or dry nitrogen. Under vacuum at 50 °C , **2** converts to the solvent-free **1**, too. In reverse, **1** reacts with moisture from the air to a mixture which contains all four phases **1-4** in varying amounts. This complex phase behavior, and the absence of single crystals of C$_2$H$_5$ONa might be the reason why the crystal structure of sodium ethoxide was not determined earlier.

In conclusion, this work reveals that the standard base sodium ethoxide exhibits a layer structure of the "anti-PbO type" in the solid state, which explains the limited solubility of C$_2$H$_5$ONa in non-polar solvents. The disolvate C$_2$H$_5$ONa · 2 C$_2$H$_5$OH, which apparently precipitates first on synthesis, forms a chain structure, which resembles the first step of the dissolution of C$_2$H$_5$ONa with ethanol. Thus, the crystal structures of these simple compounds were finally unravelled – a 180 years after their first synthesis.

Conflicts of Interests
There are no conflicts of interest to declare.

## Notes and references

‡ CCDC-1943793 and 1943794 contain the crystallographic data of **1** and **2**.

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