An Alkali Metal Phenoxide with an Unusual Dimeric Crystal Structure: $[Na(OC_6H_3Bu^t\text{-}2,6)(\mu\text{-}Me_2SO)(Me_2SO)]_2$

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Metallic sodium reacts with 2,6-di-*tert*-butylphenol to yield bis(2,6-di-*tert*-butylphenoxo)bis(μ-dimethyl sulfoxo)-bis(dimethyl sulfoxo)disodium **1** when Me_2SO is used as recrystallization medium; the crystal structure of compound **1** shows an unusual feature, where the solvent molecule acts as the bridging group; usually in alkali metal phenoxides the bridge is formed by the bulky phenoxo ligand.

One of the main uses of alkali metallated organic compounds (*e.g.* alkali metal alkoxides) is in the synthesis of corresponding organotransition metal complexes.[1,2] Alkali metal alkoxides are also interesting from a purely structural point of view,[3,4] and tend to oligomerize by the formation of oxygen bridges between metal atoms. The size of oligomers can be controlled by the choice of the alkyl group in the alkoxo ligand.[5] When a very bulky alkoxo ligand is used (*e.g.* 2,6-*tert*-butylphenoxide) the alkali metal alkoxo in alkanes, more polar solvents are used in their recrystallisation. Lithium dimers contain usually three-coordinate lithium with only one solvent molecule bonded to both lithium atoms. With heavier alkali metals the increased coordination number requirements in dimeric compounds are satisfied by coordination of extra solvent molecules.[8,11] Thus dimeric sodium alkoxides contain four-coordinate sodium with two solvent molecules bonded to the metal atoms. So far, in all dimeric alkali metal alkoxide structures determined, the alkoxo ligand acts as a bridging group.[6–11] Only one report on a potassium dimer exists where both the solvent molecule (THF) and the bulky phenoxo ligand form bridges between potassium atoms.[8]

Here, we report the synthesis and the X-ray crystal structure of a dimeric sodium alkoxide, in which only the solvate molecule (Me_2SO) forms bridges, *via* its oxygen atoms, between the sodium ions. The bulky phenoxo ligand is terminally bound.

$[Na(OC_6H_3Bu^t\text{-}2,6)(\mu\text{-}Me_2SO)(Me_2SO)]_2$ **1** was formed by refluxing metallic sodium and 2,6-di-*tert*-butylphenol in toluene. The resulting white solid was recrystallised from Me_2SO to obtain suitable crystals for an X-ray diffraction study.[†] The manipulation of the air-sensitive crystals was carried out as described by Hope.[12] The X-ray diffraction data was collected at −120 °C. Fig. 1 shows the ORTEP view of **1**. The significant feature in the structure is that the coordinated solvent molecule forms a bridge between the sodium ions and that the phenoxo ligand is terminal. To our knowledge this has not been reported previously.[13] In the analogous lithium dimer the phenoxo ligand is bridging and one terminal Me_2SO molecule is coordinated to each metal atom.[10] The solvent molecule can act as a bridging group when the size of the alkali metal increases. In the cases of potassium even the relatively poor polar solvent THF forms bridges between metal ions.[8]

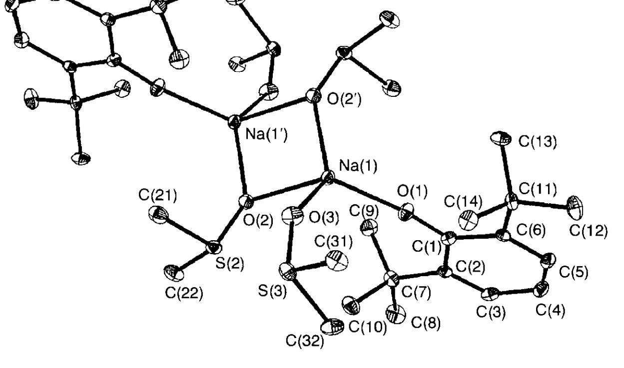

Fig. 1 Structure of compound **1** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Na(1)–O(1) 2.144(5), Na(1)–O(3) 2.257(5), Na(1)–O(2) 2.366(5), Na(1′)–O(2) 2.284(5), O(1)–C(1) 1.292(7), O(2)–Na(1)–O(2′) 84.5(2), Na(1)–O(2)–Na(1′) 95.5(2).

The coordination sphere of sodium is distorted tetrahedral. The bridging Me_2SO ligand is slightly asymmetrically coordinated to the sodium atoms, as indicated by the difference in bonds Na(1)–O(2) [2.366(5) Å] and Na(1′)–O(2) [2.284(5) Å]. The Na_2O_2 unit is planar, with the planes of the bulky phenoxo ligands almost perpendicular [110.3(3)°] to it. One terminal Me_2SO molecule is also bound to each sodium atom and the complex has a centre of symmetry.

According to the results of this study and earlier work it can be concluded that the nature of the bridging in dimeric alkali metal alkoxides can be affected by the polarity of the solvent and the size of the alkali metal. Solvent molecules can act as bridging groups when the metal is larger than lithium. When the polarity of the solvent increases (*e.g.* from THF to Me_2SO) the more likely it is that it will act as the bridging unit, even to the extent that the bulky alkoxo ligand loses its bridging capability.

Received, 4th November 1994; Com. 4/06761D

Footnote

[†] *Crystal data* for compound **1**: $C_{36}H_{66}Na_2O_6S_4$, M = 769.1, monoclinic, space group $P2_1/n$, a = 9.218(3), b = 16.180(7), c = 14.420(3) Å, β = 90.59(2)°, V = 2150.6(1) Å^3, $F(000)$ = 832, Z = 2, D_c = 1.188 g cm^{-3}, μ = 2.80 cm^{-1}, crystal size 0.30 × 0.20 × 0.09 mm, 5516 total (4086 independent) reflections, R = 0.075 and R_w = 0.071 from 2392 reflections with $F > 4\sigma(F)$ (250 variables, observations/variables 9.6) maximum peak in final Fourier difference synthesis 0.41 e Å^{-3}. Maximum final Δ/σ = 0.016. Data were collected at −120 °C on a Rigaku AFC-7S diffractometer using graphite-monochromated Mo-Kα radiation (2θ–ω scan mode, θ_{max} = 27.5°). Corrections were made for Lorentz and polarization effects as well as an empirical ψ-scan correction for absorption.[14] The structure was solved by direct methods and refined by the full-matrix least-squares technique. All hydrogen atoms were placed in calculated positions. In the final refinement all non-hydrogen atoms were anisotropically refined and H-atoms isotropically refined (riding model, C–H = 0.96 Å). Crystallographic calculations were carried out using the SHELXTL/PC program package.[15] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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