N–O Bond Cleavage During the Deprotonation of *N,O*-Bis(trimethylsilyl)hydroxylamine

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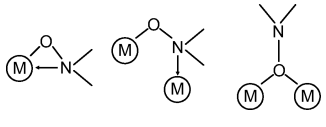
The reaction of *N,O*-bis(trimethylsilyl)hydroxylamine with potassium hydride in pentane affords a product of the formula $\{K_6[OSiMe_3]_4[ON(SiMe_3)_2]_2\}$, resulting from deprotonation followed by N–O bond cleavage and 1,2-silyl-shift. The compound was characterised by elemental analysis and by single crystal X-ray diffraction. The aggregate consists of a K_3O_3 bis-cubane core, with $N(SiMe_3)_2$ groups at the oxygen atoms shared by the two cubes, and Me_3Si groups attached to the four O vertices. Two weak K···N interactions are also detected in the solid state structure.

Key words: Potassium, Hydroxylamine, Aggregate, Bond Cleavage, Crystal Structure

Introduction

Hydroxylamide ligands show a surprisingly large variety of binding modes in their complexes of various elements in the Periodic Table, which is due to the presence of two adjacent donor atoms of different nature. The main three motifs can be described as displayed in Scheme 1 as η^2, μ^2-(*O,N*) and μ^2-(*O,O*) [1]. These binding modes may be further combined in the presence of more than one or two metal atoms, *i. e.* in polynuclear aggregates.

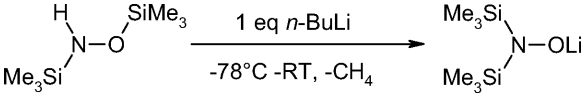


Scheme 1.

For the preparation of such hydroxylamide compounds, alkane elimination reactions using OH functional hydroxylamines and metal alkyls have been the preferred routes. Only recently we reported the preparation of hydroxylamide yttrates and samarates [2], which were obtained by salt elimination reactions from hydroxylamine potassium salts. Employing these reagents was hampered so far, as no defined compounds were known, except for a few lithium salts [3, 4], which have the drawback of leading to lithium halides as accompanying products in salt elimination reactions, with the disadvantage of being soluble in ethers and therefore difficult to separate. We then got hold of defined potassium salts of $HONMe_2$, HON^iPr_2 and $HONBz_2$ by deprotonation with potassium hydride. In the latter case indeed a molecular hexameric $[KONBz_2]_6$ with a double-cube aggregation motif was obtained, but the first two potassium salts are insoluble in any solvents, apart from the hydroxylamines themselves that lead to adducts of the formulae $[(KONMe_2)(HONMe_2)]$ and $[(KON^iPr_2)(HON^iPr_2)(THF)]$, which crystallize as polymeric aggregates and with different coordination numbers of the K atoms [5].

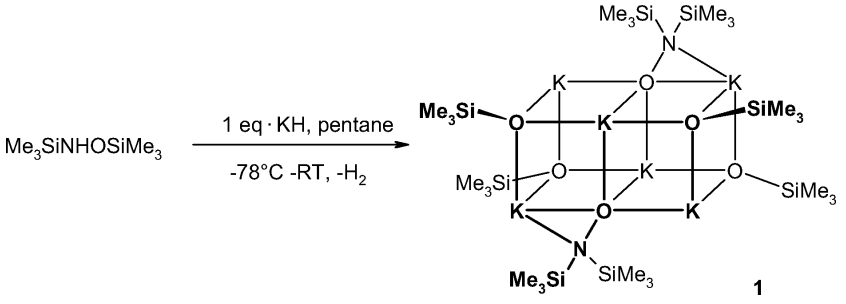
Results and Discussion

In this contribution we describe the product of a reaction of KH with *N,O*-bis(trimethylsilyl)hydroxylamine. Our intention was to deprotonate *N,O*-bis(trimethylsilyl)hydroxylamine with potassium hydride to get *N,N*-bis(trimethylsilyl)hydroxylaminato potassium as a reagent for salt elimination reactions. The occurrence of an 1,2-shift of the trimethylsilyl group from the O to the N atom is known from the deprotonation reaction of *N,O*-bis(trimethylsilyl)hydroxylamine with *n*-butyl lithium, which results in the formation of *N,N*-bis(trimethylsilyl)hydroxylaminato lithium [3] (Scheme 2).



Scheme 2. Deprotonation of *N,O*-bis(trimethylsilyl)hydroxylamine with *n*-butyl lithium.

However, a mixed silylhydroxylamide/silanolate complex of potassium was isolated, when *N,O*-bis (trimethylsilyl)hydroxylamine was treated with 1 eq. of KH in pentane at −78 °C and warmed up to r. t. In this reaction more than one product is formed, but only one is pentane-soluble. This solu-



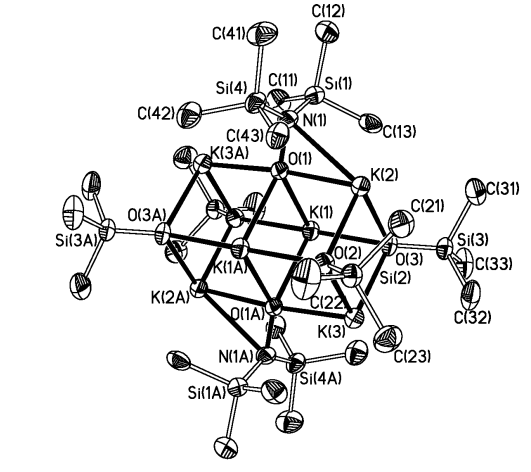
Scheme 3. Reaction of *N,O*-bis (trimethylsilyl) hydroxylamine with potassium hydride.

ble product could be crystallised and characterised to be $\{K_6[OSiMe_3]_4[ON(SiMe_3)_2]_2\}$ (**1**) (Scheme 3). The pentane-insoluble product may possibly contain $KON(SiMe_3)_2$ and some amide species, but this could not be proven, as this part turned out to be also insoluble in the usual hydrocarbon or ethereal solvents.

The cleavage of the O–N bond could possibly be the result of an initial deprotonation of $Me_3Si(H)N–OSiMe_3$ with KH to give the intermediate $Me_3Si(K)N–OSiMe_3$, which then undergoes either an extrusion of silylnitrene ($Me_3Si–N$) to leave $KOSiMe_3$ or a rearrangement by 1,2-silyl shift to give $(Me_3Si)_2N–OK$. This and $KOSiMe_3$ in a ratio 2 : 4 would then lead to the formation of **1**. The nitrene formation from silylhydroxylamines is a known reaction, which was employed on a preparative scale in organic synthesis [6].

Compound **1**, $K_6[ON(SiMe_3)_2]_2[OSiMe_3]_4$, crystallises in the triclinic crystal system, space group $P\bar{1}$, as a molecular entity. The structure consists of two K_4O_4 cubes sharing a common face (Fig. 1). The middle of this central K_2O_2 unit is the crystallographic inversion centre. The asymmetric unit thus contains three potassium atoms, one $ON(SiMe_3)_2$ group and two $OSiMe_3$ groups. There are three types of potassium atoms. Two belonging to the central K_2O_2 unit have the coordination number four and a bisphenoidal coordination geometry of four O atoms, two of them belong to $ON(SiMe_3)_2$ groups. Two potassium atoms at the vertices of the double cube have a coordination number of only three (trigonal pyramidal), which is only possible due to the steric shielding of the voluminous $SiMe_3$ groups. There exist a number of relatively short contacts between the $SiMe_3$-hydrogen atoms and these potassium atoms.

Two other potassium atoms, also at the vertices of the double cube, are similarly coordinated as the latter, but receive further weak donating interactions from the nitrogen atoms of the $ON(SiMe_3)_2$ groups. The distance N1–K2 is 2.919(7) Å, which is longer than in $[(KONMe_2)(HONMe_2)]$ (2.810 and 2.892 Å) and also in $[(KONBz_2)_6]$ (2.773 – 2.827 Å), which crystallises



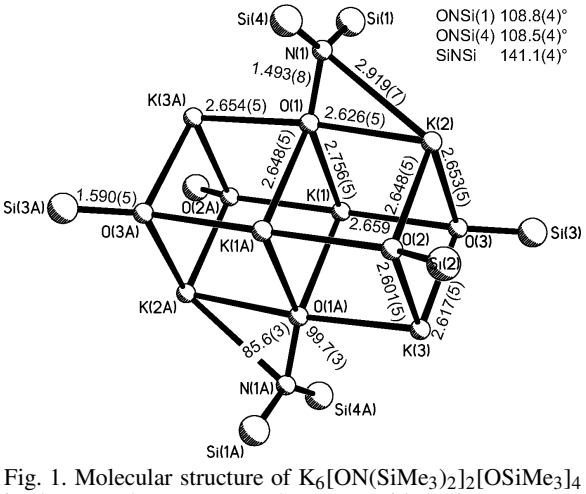


Fig. 1. Molecular structure of $K_6[ON(SiMe_3)_2]_2[OSiMe_3]_4$ in the crystal. Upper part: Structure with hydrogen atoms omitted, displacement ellipsoids drawn at the 50 % probability level and labelling scheme; lower part: C and H atoms omitted, with selected bond lengths (in Å) and angles (in deg).

in a similar molecular double-cube aggregation motif [5]. This might be rationalised by the weaker basicity of silylated nitrogen atoms as compared with alkylated ones [7], which is also obvious from the almost planar coordination (sum of angles about N: 358.4°), with the extremely large Si–N–Si angle of 141.1(4)° worth noting. The weakness of this contact leads to only a small deviation of a perpendicular arrangement of the N–O bond relative to the K–O–K edge of the double cube, characterised by one smaller K–O–N angle 85.6(3)° involving the interacting K and N atoms and a larger K–O–N angle [99.7(3)°] involving the other. The respective longer K···N distance to this K atom, to which we have assigned three-coordination, is 3.257(6) Å and shows that the assignment of coordination numbers is of course somewhat arbitrary.

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk techniques. The elemental analysis was carried out on a Vario E1 III CHNS instrument. $Me_3SiNHOSiMe_3$ was prepared according to a literature procedure [5].

Potassium hydride (0.401 g, 10.0 mmol) was suspended in 30 mL of *n*-pentane. The mixture was cooled to −78 °C. A solution of $Me_3SiNHOSiMe_3$ (1.79 g, 10.0 mmol) in 15 mL of *n*-pentane was added dropwise to this suspension. The reaction mixture was allowed to attain r. t. The solvent was removed under vacuum to leave a colourless powder. This product was extracted with pentane, the extract filtered and cooled to −26 °C, which led to the crystallisation of **1**. The pentane insoluble residue was not soluble in any other hydrocarbon or ethereal solvent. Yield for **1**: 0.46 g (29 %). Elemental analysis (%): calcd. for $C_{24}H_{27}N_2O_6Si_8K_6$ (944.28): C 30.52, H 7.70, N 2.96; found C 30.19, H 7.49, N 2.73.

Crystal structure determination. A Stoe IPDS-1 X-ray diffractometer was used to collect the scattering intensities for the single crystal of **1**. A crystal was selected and prepared under perfluoropolyether and mounted in a drop of it onto the tip of a glass fibre on the goniometer head of the diffractometer. The structure was solved by Direct Methods and refined with full-matrix least-squares methods against F^2 (SHELXTL) [8]. Formula $C_{12}H_{36}NO_3Si_4K_3$, M_r = 236.04, crystal size 0.1 × 0.1 × 0.1 mm, crystal system triclinic, space group $P\bar{1}$, a = 10.489(2), b = 11.337(2), c = 11.953(2) Å, α = 100.81(2), β = 111.36(2), γ = 95.14(2)°, V = 1285.4(4) Å^3, T = 163(2) K, Z = 2, ρ_{calc} = 1.220 g cm^{-3}, λ = 0.71073 Å, μ = 0.726 mm^{-1}. 20245 scattering intensities were collected of which 5288 were independent and 2368 met the observation criterion. R_1 = 0.082, wR_2 = 0.162 for 2368 scattering intensities with $I \geq 2\sigma(I)$, and wR_2 = 0.209 for all data. $\Delta\rho_{fin}$ = 0.52 / −0.56 e Å^{-3}.

CCDC 661260 contains 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.

Acknowledgements

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