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Potassium Hydroxylamine Complexes

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Potassium complexes of *N,N*-dialkylhydroxylamines [$KONR_2$, R = Me (**1a**), ^iPr (**2a**), $CH_2C_6H_5$] were synthesized by the deprotonation of the corresponding *N,N*-dialkylhydroxylamines with KH. **1a** and **1b** [$(KONMe_2)(HONMe_2)$] dissolve in THF under the addition of an additional equiv of the parent hydroxylamine to give **1b** and [$(KON^iPr_2)(HON^iPr_2)(THF)$] **2b**. **1b**, **2b** and [$(KONBn_2)_6(THF)_4$] (**3**) were characterized by NMR and IR spectroscopy, by elemental analyses, and by X-ray diffraction of single crystals. **1b** and **2b** crystallize as polymers, whereby compound **1b** with smaller groups leads to higher coordination numbers at the potassium atoms (CN = 7) and double-stranded more complex ladder-type aggregates, whereas **2b** with the larger ^iPr groups contains potassium atoms with a coordination number of 5 and is a single-stranded polymer. The compound {$[KON(CH_2C_6H_5)_2]_6(THF)_4$} (**3**) exists in a hexameric bis-cubane-based form in the solid state. Quantum chemical calculations were undertaken to examine the nature of the hydrogen bonding in the ($R_2NO\cdots H\cdots ONR_2$) units of **1b** and **2b**, which is asymmetric in the first and symmetric in the second case.

Introduction

Alkali-metal alkoxides have been known for several decades. There is a considerable amount of data on their synthetic and structural aspects.[1–5] They have been utilized as precursors for MOCVD processes[6] as well as reagents or catalysts in chemical transformations.[7–9]

Alkali-metal complexes of hydroxylamines are closely related to the alkoxides, except they possess an extra nitrogen donor atom adjacent to the oxygen atom. However, little is known about the alkali metal complexes of hydroxylamines,[10–12] although they could be useful precursors in the preparation of other hydroxylamine metal compounds, which have so far mostly been prepared by alkane elimination reactions from metal alkyls and OH functional hydroxylamines.[13] The introduction of this extra nitrogen donor atom in addition to the oxygen atom leads to a variety of aggregation modes depending on the type of the substituents on the hydroxylamine as compared to the corresponding alkoxides.

The chemistry featuring alkali-metal complexes of (organo)hydroxylamines is so far restricted to lithium compounds in the literature.[10–12] Up to now, there is no report of any hydroxylaminato potassium complex. In this article, we

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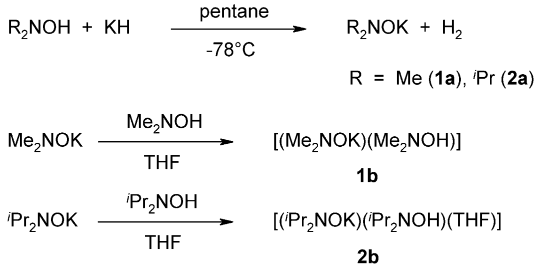
Scheme 1



$$R_2NOH + KH \xrightarrow[-78°C]{pentane} R_2NOK + H_2$$

R = Me (**1a**), ${}^iPr$ (**2a**)

$$Me_2NOK \xrightarrow[THF]{Me_2NOH} [(Me_2NOK)(Me_2NOH)]$$

1b

$${}^iPr_2NOK \xrightarrow[THF]{{}^iPr_2NOH} [({}^iPr_2NOK)({}^iPr_2NOH)(THF)]$$

2b

present the synthesis and structural characterization of such potassium complexes of *N*,*N*-difunctionalized hydroxylamines with different substituents on the hydroxylamines. These complexes prove to be useful starting materials for the synthesis of new hydroxylamine compounds in salt-elimination reactions with element halides.[14] Under such conditions, the potassium hydroxylamides lead to the formation of potassium halides, which are insoluble in ethereal solvents, whereas the lithium analogues lead to the formation of soluble halides, which are difficult to separate.

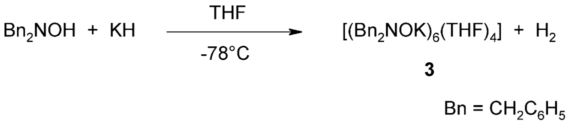
Results and Discussion

Preparation and Characterization. We obtained the potassium salts of *N*,*N*-dialkylhydroyxlamines ($KONR_2$, R = Me, ${}^iPr$) by treatment of R_2NOH with potassium hydride in pentane at −78 °C (Scheme 1).

As our original intention was to use them as reagents for the preparation of rare-earth hydroxylamine complexes by reacting them with anhydrous rare-earth halides,[14] we were first satisfied with such insufficiently identified intermediate products **1a** and **2a**. These were found to be insoluble in all hydrocarbon and ethereal solvents, and thus neither a spectroscopic identification by NMR in solution nor crystallization from solution was possible. At first sight, surprisingly we found out that the above-described reactions gave soluble products if we applied the H-functional hydroxylamines in excess. Consequently, we tried to dissolve the insoluble primary products in THF under addition of a further equivalent of H-functional hydroxylamine $HONMe_2$ and HON^iPr_2. Crystallization from concentrated THF solutions led to the formation of the coordination polymers $[(Me_2NOK)(Me_2NOH)]$ **1b** (devoid of THF) and $[({}^iPr_2NOK)({}^iPr_2NOH)(THF)]$ **2b** (containing one THF molecule coordinated to each potassium atom). A combination of **1** with ${}^iPr_2NOH$ did not lead to a compound of the expected composition $[(Me_2NOK)({}^iPr_2NOH)]$. **1b** and **2b** were characterized by elemental analyses, ${}^1H$ and ${}^{13}C$ NMR spectroscopy, IR spectroscopy, and single-crystal X-ray crystallography.

1b of the composition $[(Me_2NOK)(Me_2NOH)]$ shows only one single signal for the protons of the methyl groups in the ${}^1H$ NMR at 2.50 ppm and likewise only one signal in the ${}^{13}C$ NMR spectrum (52.3 ppm) for these groups. Thus, a rapid exchange of the OH proton between two Me_2NO units must occur in solution at ambient temperature. This OH proton is observed in the ${}^1H$ NMR as a resonance at 12.7 ppm. **2b** with a composition $[({}^iPr_2NOK)({}^iPr_2NOH)(THF)]$ shows a similar behavior in solution to that of **1b**. The isopropyl groups give only one set of signals in both the ${}^1H$ and ${}^{13}C$ NMR spectra. The OH function is observed as a resonance at 10.4 ppm in the ${}^1H$ NMR spectrum.

Scheme 2



$$Bn_2NOH + KH \xrightarrow[-78°C]{THF} [(Bn_2NOK)_6(THF)_4] + H_2$$

3

$Bn = CH_2C_6H_5$

The solid state IR spectrum of **1b** shows a shoulder (at the band of CH stretching) in the region of 3160 cm^{-1}. This value is indicative of a strongly hydrogen-bonded hydrogen atom.[15] It also indicates the bonding situation for this proton to differ markedly from that in **2b**, which does not show any OH stretching mode in the region above those of the CH stretching bands. This finds its explanation in the structure discussed below in more detail.

3 was prepared by the addition of a THF solution of *N*,*N*-dibenzylhydroxylamine to a suspension of 1 equiv of potassium hydride at −78 °C. It was crystallized as THF adduct by layering pentane on a concentrated THF solution (Scheme 2).

3 is soluble in toluene and THF and could thus be characterized by ${}^1H$ NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction experiments. An attempt to prepare a compound of the composition $[(Bn_2NOK)(Bn_2NOH)]$ in analogy to **1b** and **2b** by combining **3** with Bn_2NOH did not lead to an isolable product.

Crystal Structure Determinations. $[(Me_2NOK)(Me_2NOH)]$ (**1b**). **1b** crystallizes in the monoclinic system, space group $P2_1/c$. The compound forms a polymeric ladder-type structure (Figure 1). The ladder is made up by the bonds between K1 and O1 and symmetry equivalents as shown in Figure 1, which link two strands of vertex-sharing K_2O_2 rhombs (Figure 2 for a subsection with dimensions), which are extended with NMe_2 groups at both oxygen atoms. These two nitrogen atoms are arranged in a way that each makes a contact to a different potassium atom at either side of the K_2O_2 rhomb. In this way, each potassium atom is coordinated by two nitrogen atoms of different rhomb units. The total coordination number at potassium is seven.

An alternative description is that of an arrangement of pseudo-K_3O_4-cubes with one vertex (a potassium atom) missing. These pseudo cubes are fused by shared faces, whereby each pseudo cube shares two adjacent faces with two neighboring pseudo cubes.

The composition $[(Me_2NOK)(Me_2NOH)]$ with one deprotonated (anionic) and one OH functional hydroxylamine unit together with a potassium cation leads to a charge balanced system. An alternative description is that both hydroxylamine units share one common hydrogen atom between the two oxygen atoms, that is, a hydrogen bonded $[Me_2NO{-}H{-}ONMe_2]$ anion is formed. These anions have their

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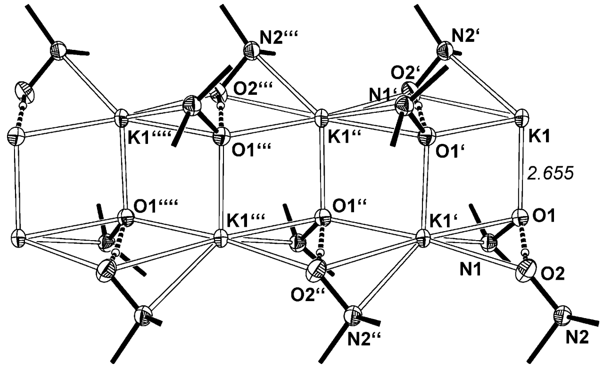

Figure 1. Crystal structure of $[(\text{Me}_2\text{NOK})(\text{Me}_2\text{NOH})]$ (**1b**) as obtained by low-temperature X-ray crystallography. The thermal ellipsoids are drawn at the 50% probability level. The distance K1−O1 is given in angstroms, and the N−O distances are N1−O1 1.452(2) and N2−O2 1.449 (2) Å. Further structural parameters are given in Figure 2, showing a subset of this representation. The hydrogen atoms of the methyl groups have been omitted for clarity, and carbon atoms are drawn in stick mode.

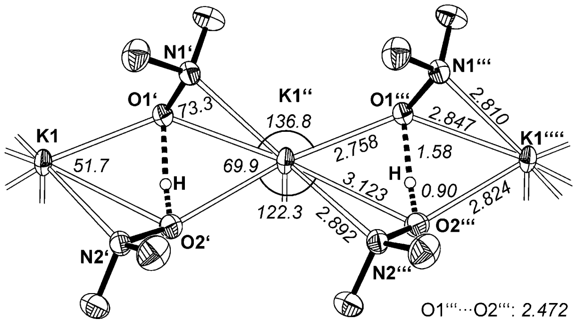

Figure 2. Subsection of the ladder structure of $[(\text{Me}_2\text{NOK})(\text{Me}_2\text{NOH})]$ (**1b**). Selected distances are given in angstroms, and angles are in degrees. The hydrogen bond can be described by the following parameters: O2−H 0.90(3), O1···H 1.58(3), O1···O2 2.473(2) Å, O−H···O 172(3)°.

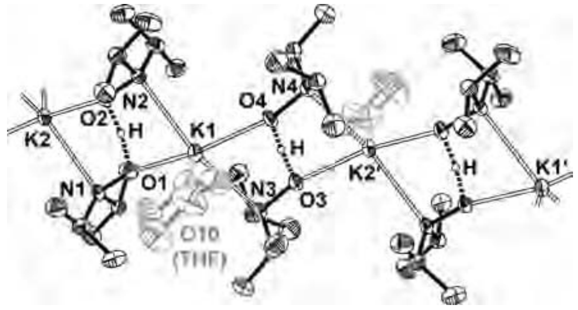

Figure 3. Crystal structure of $[(^i\text{Pr}_2\text{NOK})(^i\text{Pr}_2\text{NOH})(\text{THF})]$ (**2b**) as obtained by low-temperature X-ray crystallography. The thermal ellipsoids are drawn at the 50% probability level. Selected structural parameters are given in Figure 4, showing a subset of this representation. The distance K1−O4 is 2.530(2) Å, the angles about the atom K1 are O1−K1−N2 67.7(1), O1−K1−O4 148.0(1), O1−K1−N3 101.0(1), N2−K1−O4 102.1(1), O4−K1−N3 69.5(1), O10−K1−O1 111.6(1), O10−K1−O4 100.4(1)°. The hydrogen atoms of the isopropyl groups have been omitted and the THF units are drawn in faint color for clarity.

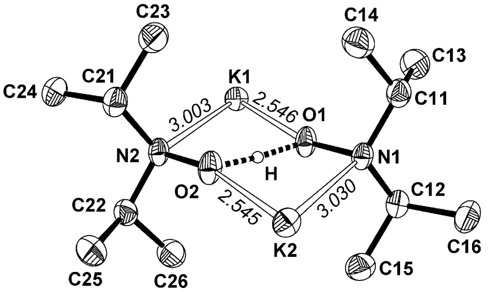

Figure 4. Part of the polymeric structure of $[(^i\text{Pr}_2\text{NOK})(^i\text{Pr}_2\text{NOH})(\text{THF})]$ (**2b**). Selected distances are given in angstroms. The position of the proton was restrained to equal distances to both oxygen atoms. The O···O distance is 2.434 Å. According to the results of the calculations, the hydrogen-bonded hydrogen atoms were included with the constraints of being equally distant to both oxygen atoms.

O−H−O linkage located across one of the pseudocube faces, which is spanned up by these two oxygen and two potassium atoms, all interacting with one another by K−O links measuring between 2.758(2) and 3.123(1) Å (such a broad range of K−O distances is commonly observed also for potassium alkoxides).[2] The two longest edges of these K_2O_2 rhombs are those bridged by the nitrogen atoms linked to the oxygen atoms of the hydroxylamine units, whereby the two nitrogen atoms of one $\text{Me}_2\text{NO}-\text{H}-\text{ONMe}_2$ unit bind to two different potassium atoms of the K_2O_2 rhomb. These K_2O_2 rhombs have smaller angles at the potassium atoms (51.7 and 69.9°) than the exocyclic O−K−O angles (122.3 and 136.6°).

With respect to only the potassium atoms, there are two types of Me_2NO ligands. One is μ_3-bridging (rhomb and chain formation) and simultaneously η^2-coordinating (formation of three-membered KON rings); these Me_2NO ligands have oxygen atoms with a coordination number of 5 if the hydgrogen atoms they are hydrogen bonded to are taken into account. The other type of Me_2NO ligands bearing these hydrogen atoms with a primary OH bond, is linked to one nitrogen and two potassium atoms, and has thus a coordination number of 4. In both cases, this leads to unusual coordination geometries at oxygen. Regarding these hydrogen atoms, one can say that there are two pseudocube faces that contain no hydrogen atoms, and these are the faces shared by different cubes along the chain. The pseudocube faces that share potassium vertices along the chain contain hydrogen atoms. This hydrogen atom could be located in the difference Fourier maps and refined. It defines an asymmetric hydrogen bridge O−H···O with an O−H distance of 0.90(3) Å and an O···O distance of 2.473(2) Å. It can be expected that the hydrogen atom could change its primary binding partner and thus flip between the two oxygen atoms. As refining the hydrogen position from the X-ray diffraction experiment can be expected to be not of utmost reliability in the presence of the heavy potassium atoms, we verified this position independently by DFT calculations (below).

$[(^i\text{Pr}_2\text{NOK})(^i\text{Pr}_2\text{NOH})(\text{THF})]$ (**2b**). **2b** crystallizes in the tetragonal space group $P4_1$. It consists of chain aggregates of six-membered $K_2O_2N_2$ rings, sharing potassium vertices to form the chains. Each potassium atom bears one additional THF ligand bonded through its oxygen atom so that the total coordination number of the potassium atoms is 5. As in **1b**, there is one hydrogen atom shared between two $^i\text{Pr}_2\text{NO}$ units, leading to formal $[^i\text{Pr}_2\text{NO}-\text{H}-\text{ON}\,^i\text{Pr}_2]$ anions alternating in chains with [K(THF)] cations.

In contrast to **1b**, each oxygen atom of a hydroxylamine unit makes only one contact to a potassium atom. In other words, in **1b** the Me_2NO ligands are μ_3-bridging three potassium atoms and simultaneously η^2-coordinating (three-membered KON rings), and the oxygen atoms are involved in hydrogen bonding and thus reach a coordination number of 4 or 5, respectively, whereas in **2b** the coordination number at the oxygen atoms is 3 and can be described as distorted T-shaped. Obviously, the higher steric demand of the ^{i}Pr groups is responsible for these changes from a double-stranded aggregate of chains of K_2O_2 rhombs to a single-stranded aggregate of $K_2O_2N_2$ six-membered rings.

The reduced coordination number at the oxygen atom is not compensated, but the potassium atoms saturate their demand for more donor contacts by coordination to the THF molecules, (which is not observed in **1b** despite this compound was also crystallized from THF).

In the very center of one of the two crystallographically independent $K_2O_2N_2$ rings a residual peak was found, but this could not be freely refined to represent the hydrogen atom. This is on the first sight not surprising in the presence of the heavy potassium atoms in the structure. Independent proof for the presence of these hydrogen atoms stems from the NMR spectroscopy data discussed above. To obtain more structural evidence for their positions, we performed DFT calculations on these systems, which are described below. The result of these calculations was that a symmetric hydrogen bridge exists with a very shallow potential for hydrogen atom movement between the two oxygen atoms. For completion of the structure, we therefore included hydrogen atom positions with constraints of being equally distant from the two oxygen atoms into the refinement.

$[(Bn_2NOK)_6(THF)_4]$ (**3**). **3** crystallizes in the monoclinic system, space group *C*2/*c*. The structure consists of a double cube (two face-sharing cubes) of six alternating potassium and six oxygen atoms. These oxygen atoms are those of the Bn_2NO groups. Within the cubes, there is a distribution of K−O distances between 2.562(2) and 2.812(2) Å, but this distribution is uneven, without a pattern easy to recognize. Each oxygen atom of the double cube bears one adjacent nitrogen atom also bound to the potassium atoms. All such K−N distances fall over a range between 2.743(3) and 2.828(3) Å, except K(1)−N(4), which is far longer at 3.178(3) Å. All four potassium vertices of the double cube are further coordinated to the oxygen atoms of THF molecules.

Defining these K−O and K−N contacts as the primary coordination sphere of the potassium atoms, the double cube contains potassium atoms of different coordination numbers. The vertices of the double cube are K(1) and K(2) on one side and K(3) and K(4) on the other side. The vertices on one side, K(1) and K(2), are six-coordinate (three K−$ONBn_2$ contacts, two K−N contacts, and one THF ligand), whereas K(3) and K(4), the other two vertices, are five-coordinate (three K−$ONBn_2$ contacts, one K−N contact, and one THF ligand). The face-shared potassium atoms of the double cube adopt a coordination number of 4 and the coordination sphere of the four anionic hydroxylamide ligands is highly asymmetric.

In contrast, the known lithium analogue $(LiONBn_2)_6$ crystallizes as a solvent-free hexamer and as a drumlike aggregate with a core of two stacked $(OLi)_3$ rings and an even distribution of the metal−nitrogen interactions. The formation of two additional K−O contacts is connected with the uneven distribution of K−N interactions in **3**. The formal difference between the drumlike aggregate of $(LiONBn_2)_6$ and the double cube aggregate of **3** is thus the establishing of a link between two M−O units at opposite−sites of the drum of $(LiONBn_2)_6$.

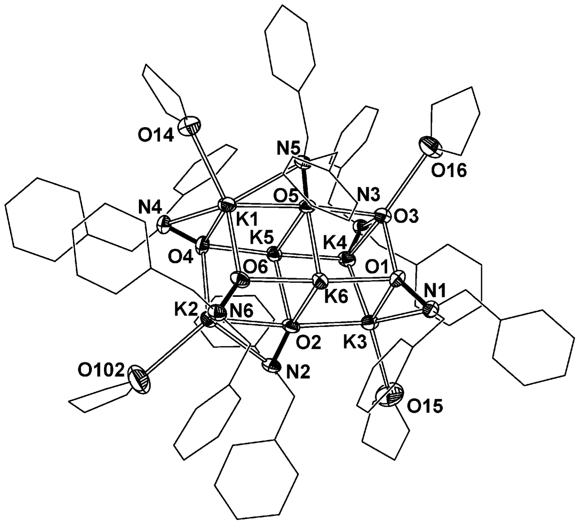

Figure 5. Crystal structure of $[(Bn_2NOK)_6(THF)_4]$ (**3**) as obtained by low-temperature X-ray crystallography. The thermal ellipsoids are drawn at the 50% probability level. Selected structural parameters are given in Figure 6, showing a subset of this representation. The hydrogen atoms have been omitted, and the carbon atoms are drawn as a wire-frame model for clarity.

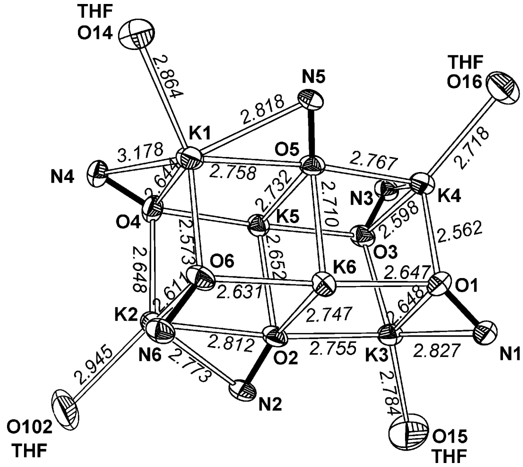

Figure 6. Part of the polymeric structure of $[(Bn_2NOK)_6(THF)_4]$ (**3**). Selected distances are given in angstroms.

Additionally, further reaching contacts of the potassium atoms in **3** to the hydrogen and carbon atoms of THF of benzyl groups are present. The shortest of these contacts involving carbon atoms (the hydrogen atoms were introduced in calculated positions are therefore neglected in this discussion) are those to the low-coordinate potassium atoms K(5) and K(6) and the aromatic systems of the benzyl groups: K(5)···C(36) 3.126(3) Å and K(6)···C(102) 3.283(3) Å. Further on, there is a number of longer K···C contacts ranging from 3.3 to 3.4 Å.

Quantumchemical Calculations. Strategy and Methods. **1b** and **2b** show hydrogen bridges according to the X-ray

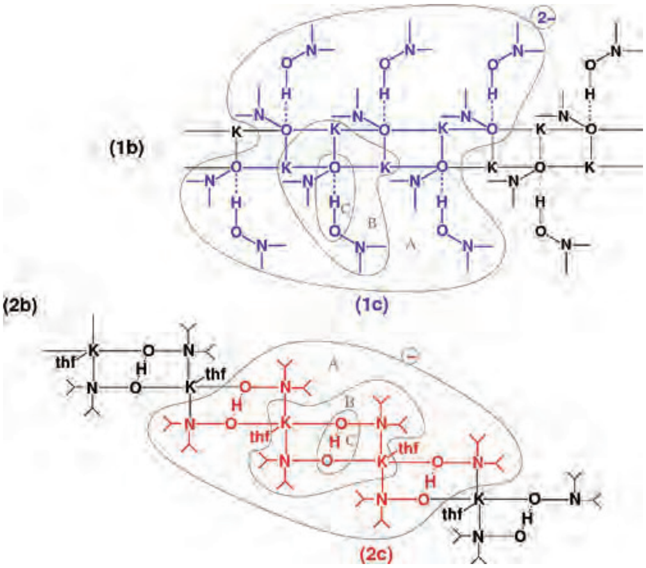

Figure 7. Definitions of the parts of the polymeric structures of **1b** and **2b**, which were used as models for the quantumchemical calculations (notation of the models: **1c** and **2c** as shown above).

structure analysis. From both crystal structures and IR spectra, it has to be concluded that the binding mode of the bridging hydrogen atoms is substantially different in the two compounds. To gain more insight into the nature of these hydrogen bonds, we performed a DFT study of two model systems. Thereby, we focused on two questions:

1. Is the location of the hydrogen atom positions in crystal structures of **1b** and **2b** valid?
2. Is there a possibility of flipping between different hydrogen positions in the solid state?

Both questions can be answered satisfactorily, knowing the potential energy curves along the O−H stretching coordinate connected with the hydrogen bonds.

In Figure 7, the model dianion $[K_4H_6(ONMe_2)_{12}]^{2-}$ (**1c**) as a substructure of the solid state structure of **1b** is depicted in a simplified way, where only the dominating interactions are shown. Similarly, also the model anion $[K_2H_3(ON^iPr_2)_6]^{-}\cdot 2$ thf (**2c**) is shown in figure 7. In both model species, one O−H−O group of interest is embedded in a larger framework, which is present in the solid state. Coordinatively unsaturated potassium atoms are avoided. **1c** bears a net charge of −2, and thus one has to bear in mind that self-interaction errors of the common DFT functionals might play a role. However, there were no positive eigenvalues of KS orbitals observed, and moreover the effect on the potential energy surface is expected to be small.

The calculations of the potential curves describing the linear motion of a hydrogen atom along the connecting line of the two hydrogen bond-accepting oxygen atoms (which is a close approximation to the corresponding O−H stretching frequency) were performed in two steps:

1. Preoptimization of the model species with an efficient and fast method.
2. Variation of only one hydrogen atom position in the preoptimized structures followed by single point energy calculations using a more accurate method.

For step 1, in both cases (**1b** and **2b**) the respective substructures of the crystal structures were used as the start geometries of **1c** and **2c** (Figure 7).

All of the calculations were carried out using the *Turbomole*[15] program package, version 5.7. The preoptimization step was performed using Density Functional Theory (DFT) with the Becke−Perdew local density functional[16] and employing *Turbomole's RI-DFT*[17−19] program deck, which is utilizing the 'RI two-electron-integral' evaluation routine.[20] All-electron SV(P) basis sets[21] for all elements including because were employed because relativistic effects are expected to be small. DFT calculations were done with a standard grid of m3 size.[22]

Whereas the optimization of the model species **2c** converged to a stationary point that closely resembles the solid-state structure of **2b**, there was a major rearrangement of the dimethyl hydroxylaminate ligands in case of **1c**. This may indicate a primary importance of interactions between the chain aggregates in solid **1b**, whereas such effects may be secondary for the formation of solid **2b**. However, for the consideration of the hydrogen bonding potential in the solid state, a close structural similarity of the model species and the solid state structure is desirable. For that reason in the preoptimization of **1c**, all non-hydrogen atom positions were fixed at their positions in **1b** with the exception of the central $H[K(ON^iPr_2)]_2$ substructure, containing the hydrogen bridge of interest, which was fully optimized. Consequently, all hydrogen atom positions were also optimized to correct for the deficiencies of X-ray crystallography in the determination of hydrogen-atom positions.

To generate the structures for the single-point calculations, the hydrogen atoms were placed onto the connecting line of two hydrogen bond accepting oxygen atoms (above) and the energies of these configurations of the model species **1c** and **2c** where calculated using the PBE0 hybrid functional[23] in connection with a hierarchy of basis sets ranging from SV(P) for the more distant atoms (subsets A in Figure 7) of the hydrogen bridge over TZVP[24] for closer atoms (subsets B in Figure 7) to TZVPP[24] for the O−H−O group (subsets C in Figure 7).

Calculation Results. The resulting potential curves for the O−H stretching modes within the hydrogen bridges of **1c** and **2c** are given in Figure 8. Both cases represent completely different cases of hydrogen bonding. Whereas

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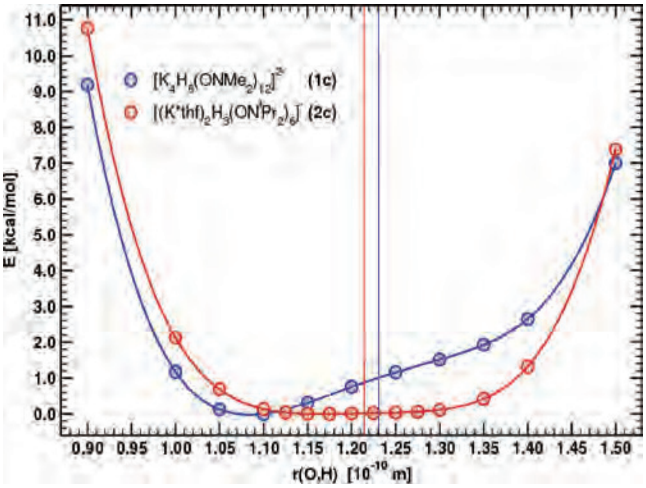

Figure 8. Potential curves of the position of the hydrogen atoms on the O···O vector as a function dependent on the distance of one oxygen atom for the model structures **1c** and **2c**. The middle point between the two oxygen atom positions is marked as a vertical line for both cases.

in **1c** the protons distinctly prefer coordination to one of the two different hydroxylamine substituents, namely those that are weaker coordinated by potassium atoms, in **2c**, two more or less equivalent hydroxylamine groups share the proton in a fair-minded way.

Consequently, the answer to question 1 is: Within its limitations, the qualitative assignment from X-ray crystallography of the hydrogen atoms, which are involved in hydrogen bonds in **1b** and **2b**, is fully confirmed by the DFT calculations.

Regarding question 2: Because of the absence of a second minimum in both O−H stretching mode potential curves, the possibility of a flipping of hydrogen atoms between two hydroxylamine groups in **1b** or **2b** can be excluded on the basis of the DFT calculations.

The most striking feature of the O−H stretching mode potential curve of **2c**, is its extreme shallowness. Within this picture, one has to conclude that the hydrogen atom can move freely within a distance of approximately 1.1 to 1.3 Å from one of the two oxygen atoms. These data are consistent with those of a symmetric hydrogen bridge found in [K(^{t}BuO···H···O^{t}Bu)],[3] which has an O−H distance of 1.23 Å. The data are also consistent with the fact that all calculated vibrational frequencies of model species **2c** containing hydrogen atom vibrational contributions (all are coupled with molecular core vibrational modes) are occurring in a very low energy range from 600 to 1200 cm^{-1}. This result may cast doubts about the validity of the Born−Oppenheimer approximation for the description of the hydrogen bonds in **2b**.

Conclusion

The potassium salts of three different *N*,*N*-dialkylhydroxylamines have been prepared and structurally examined. Large variations in the aggregation behavior depending on the alkyl substituents have been found. Some structural motifs found for **1b** and **3** are reminiscent of those of lithium amide aggregates concerning ring stacking and laddering principles.[25] For the larger benzyl substituents, a defined molecular aggregate [(Bn$_2$NOK)$_6$](THF)$_4$] (**3**) is formed, which is soluble even in toluene. A well characterized compound without OH functions could thus be obtained by crystallization. In the case of the smaller substituents Me and ^{i}Pr, the solubility of the pure potassium salts is very low − even in THF. After the addition of additional equivalents of the OH functional hydroxylamines, these insoluble precipitates dissolve to form chain aggregates containing formal [R$_2$NO−H−ONR$_2$] anions upon crystallization. These anions are linked by different O−H−O hydrogen bridges depending on Me and ^{i}Pr substituents, namely an asymmetric O−H···O bridge in the first case (Me groups) and a symmetric O···H···O bridge in the latter (^{i}Pr groups). These differences stem from the different role of the oxygen atoms and the fact that smaller Me substituents allow for a higher aggregation and in particular a higher coordination number at the potassium and oxygen atoms. In contrast, the larger ^{i}Pr groups at nitrogen lead to a lower degree of aggregation and subsequently to equal oxygen sites and symmetric hydrogen bridges. It is interesting to note that just recently the concept of hydrogen bridging in alkoxide aggregates of a related structure to **3** has been utilized for the inclusion of water molecules in alkali-metal host aggregates.[26] This demonstrates that such aggregates as well as the alkali-metal hydroxylamides are interesting substrates for creating new motifs in hydrogen bonding.

Knowing the structures and compositions, we have now three defined potassium hydroxylamide salts in our hands, capable of being employed beneficially as starting materials in stoichiometrically controlled reactions.

Experimental Section

All manipulations were performed under a rigorously dry inert atmosphere of nitrogen or argon using standard Schlenk techniques. THF and pentane were dried with sodium/benzophenone and freshly condensed from LiAlH$_4$ before using for the reactions. NMR solvents THF-*d*$_8$ and Tol-*d*$_8$ were dried over Na/K alloy. NMR measurements were made with a Bruker Avance 400 spectrometer. Elemental analyses were performed with a Vario E1 III CHNS instrument. HONMe$_2$ and HONiPr$_2$ were synthesized according literature.[27,28] *N*,*N*-Dibenzylhydroxylamine was purchased from Aldrich. Potassium hydride was washed with dry pentane and dried in vacuum before use.

Preparation of 1b. KH (0.80 g, 20.0 mmol) was suspended in 30 mL pentane. It was cooled to −78 °C. A solution of HONMe$_2$ (1.22 g, 20.0 mmol) in 15 mL pentane was added dropwise to this suspension. The reaction mixture was allowed to attain room temperature. The solvent was removed under vacuum to yield 1.96 g of a white powder (**1a**) (yield 99%), which was directly used for the further transformation. This powder (**1a**, 0.49 g, 5.0 mmol) was

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Table 1. Crystal and Experimental Data for the Structures of **1b**, **2b**, and **3**

compound	**1b**	**2b**	**3**
formula	$C_8H_{26}N_4O_4\ K_2$	$C_9H_{20.5}NO_{1.75}K_{0.50}$	$C_{832}H_{992}N_{48}O_{88}K_{48}$
fw (g mol^{-1})	320.53	190.31	14 949.54
cryst syst	monoclinic	tetragonal	monoclinic
space group	$P2_1/c$	$P4_1$	$C2/c$
a [Å]	10.176(2)	10.536(1)	56.511(6)
b [Å]	5.210(1)	10.536(1)	14.517(2)
c [Å]	16.274(3)	41.326(8)	26.289(3)
β [deg]	93.910(4)	90	112.013(2)
V [Å^3]	860.8	4587.2	19995
Z	2	16	1
D_{calcd} [g cm^{-3}]	1.237	1.102	1.242
μ [mm^{-1}]	0.561	0.251	0.322
F(000)	344	1680	7936
cryst size [mm]	0.12 × 0.10 × 0.05	0.14 × 0.24 × 0.36	0.29 × 0.20 × 0.14
θ_{max} [deg]	30.05	30.05	30.03
reflns collected	9362	52460	112823
reflns unique	2504	13335	29074
R(int)	0.0429	0.1134	0.1063
completeness [%]	99.1	99.7	99.4
reflns with $I > 2\sigma(I)$	2026	7872	15031
refined params	128	449	1183
absolute structure params		0.05(3)	
R1 [$I > 2\sigma(I)$]	0.0375	0.0587	0.0795
wR2 [$I > 2\sigma(I)$]	0.0855	0.1190	0.1583
R1 [all data]	0.0510	0.1055	0.1646
wR2 [all data]	0.0909	0.1307	0.1907
ρ_{fin} max/min [e Å^{-3}]	0.37/−0.22	0.46/−0.29	0.95/−0.50

suspended in 10 mL THF. $HONMe_2$ (0.30 g, 5.0 mmol) was added and stirred until a clear solution was obtained. Colorless crystals were obtained from this solution at room temperature. Yield 0.72 g (90%). ^{1}H NMR (THF-d_8, 400 MHz): $\delta = 2.50$ (s, 12H, C*H*$_3$), 12.7 (s, 1H, *H*ON$(CH_3)_2$); ^{13}C NMR (100 MHz): $\delta = 52.3$ (CH_3); Elemental analysis (%) calcd for $C_4H_{13}N_2O_2K$ (160.27) C 29.98, H 8.18, N 17.48; found C 29.52, H 7.82, N 16.95.

Preparation of 2b. KH (0.80 g, 20.0 mmol) was suspended in 30 mL pentane. The mixture was cooled to −78 °C. A solution of HON^iPr_2 (2.34 g, 20.0 mmol) in 15 mL pentane was added dropwise to this suspension. The reaction mixture was allowed to attain room temperature. The solvent was removed under vacuum to yield 3.05 g of a colorless powder (**2b**) (yield 98%). This material was directly used for further transformation. This material (**2a**, 0.46 g, 3.0 mmol) was suspended in 10 mL THF. HON^iPr_2 (0.35 g, 3.0 mmol) was added, and the mixture was stirred until a clear solution was obtained. Colorless crystals were obtained from this solution at room temperature. Yield 0.73 g (89%). ^{1}H NMR (THF-d_8, 400 MHz): $\delta = 1.00$ (d, $J = 6.3$ Hz, 24H, CH(C*H*$_3$)$_2$), 2.87 (sept, $J = 6.3$ Hz, 4H, C*H*(CH$_3$)$_2$), 10.4(s, 1H, *H*ON(CHMe$_2$)$_2$); ^{13}C NMR (100 MHz): $\delta = 20.2$ (CH(*C*H$_3$)$_2$), 53.7 (*C*H(CH$_3$)$_2$); Elemental analysis (%) calcd for $C_{16}H_{38}N_2O_3K$ (272.53) C 55.66, H 11.01, N 8.11; found C 55.27, H 10.87, N 7.94.

Preparation of 3. A solution of *N*,*N*-dibenzylhydroxylamine (2.13 g, 10.0 mmol) in THF (15 mL) was added dropwise to a suspension of KH (0.40 g, 10.0 mmol) in 20 mL of THF at −78 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The solvents were removed under vacuum, and the product was washed with pentane to afford 4.81 g of a raw product. This was recrystallized by layering pentane on a concentrated THF solution at room temperature to obtain. Yield of **3**: 4.63 g (86%). ^{1}H NMR (toluene-d_8, 400 MHz): $\delta = 1.46$ (s, 16H, THF), 3.50 (s broad, 24H, C*H*$_2$), 3.56 (s, 16H, THF), 7.12(m, 12H, *p*-Ph), 7.24(t, $J = 7.2$ Hz, 24H, *m*-Ph), 7.35 (d, $J = 7.2$ Hz 24H, *o*-Ph); Elemental analysis (%) calcd for $C_{100}H_{116}N_6O_{10}K_6$ (1795.60) C 66.88, H 6.46, N 4.68; found C 66.02, H 6.03, N 4.43

X-Ray Structural Analyses. Single crystals of **1b, 2b**, and **3** were obtained as described above. For the diffraction measurements, they were prepared under cooling (ca. −40 °C) and mounted on the tip of a glass fiber with a minimum amount of silicone grease in the cryostream of the diffractometer measurements. These were carried out on an Apex Smart CCD diffractometer (Bruker) with Mo Kα radiation. These structures were solved by Direct methods (*SHELXS-86*, *SIR-92/97*) and refined by full-matrix least-squares (*SHELXL-97*).[29] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were placed in calculated positions and were refined using a riding model, with $U_{iso} = 1.2$ or 1.5 U_{eq} of the parent atom. The position of the OH hydrogen atom in **1b** was refined. Crystal and refinement data are collected in Table 1.

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Supporting Information Available: Tables of crystal structure details including atom coordinates, full listing of bond lengths and angles, and displacement factors for **1b**, **2b**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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