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2022-05-23

John Wiley and Sons Ltd

http://hdl.handle.net/10138/355620

Mears, K L, Stennett, C R, Fettinger, J C, Vasko, P S P & Power, P P 2022, 'Inhibition of Alkali Metal Reduction of 1-Adamantanol by London Dispersion Effects', Angewandte Chemie (International Edition), vol. 134, no. 22, e202201318. https://doi.org/10.1002/ange.202201318

A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* **2022**, e202201318

Link to VoR: https://doi.org/10.1002/anie.202201318

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10.1002/anie.202201318

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Inhibition of Alkali Metal Reduction of 1-Adamantanol by London Dispersion Effects

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In memory of Professor Marilyn M. Olmstead

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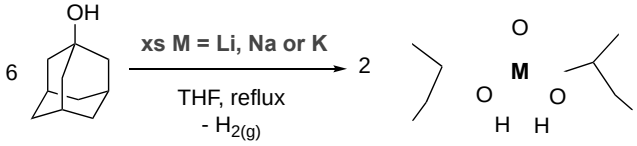
Abstract: A series of alkali metal 1-adamantoxide (OAd^1) complexes of formula $[M(OAd^1)(HOAd^1)_2]$, where M = Li, Na or K, was synthesised by reduction of 1-adamantanol with excess of the alkali metal. The syntheses indicated that only one out of every three $HOAd^1$ molecules was reduced. An X-ray diffraction study of the sodium derivative shows that the complex features two unreduced $HOAd^1$ donors as well as the reduced alkoxide (OAd^1), with the Ad^1 fragments clustered together on the same side of the NaO_3 plane, contrary to steric considerations. This is the first example of an alkali metal reduction of an alcohol that is inhibited from completion due to the formation of the $[M(OAd^1)(HOAd^1)_2]$ complexes stabilized by London dispersion effects. NMR spectroscopic studies revealed similar structures for the lithium and potassium derivatives. Computational analyses indicate that the decisive London dispersion effects are in the molecular structure are a consequence of the many C–H···H–C interactions between the OAd^1 groups.

London dispersion (LD) attractive interactions[1] continue to receive increasing recognition of their importance for the behavior of sterically crowded hydrocarbon molecules. These interactions had generally been overlooked in ligands[2] due to the weak individual energetic contribution from single H···H interactions (≤ 1 kcal mol^{-1}).[3] However, the combined total of multiple LD-interactions in larger molecules can generate significant stabilization of the order of tens of kcal mol^{-1}. The importance of these effects has been highlighted in several studies, aided by more efficient computational methods.[4a,b]

One way of installing many van der Waals (vdW) forces experimentally to effect dispersion stabilization is through the addition of multiple C–H moieties within a ligand framework, especially of rigid organic groups.[5] The 1-adamantoxide (OAd^1) ligand has been investigated previously for a range of transition-metal complexes, owing to their kinetic and thermally stabilizing properties,[6–9] nonetheless the LD contributions of these ligands were generally not discussed. The OAd^1 ligand was also employed in studies of unusual zinc complexes, which despite the bulk of the 1-adamantyl unit,[10] afforded a $[RZn(OAd^1)]_4$, R = -$CH_2(SiMe_3)$ tetrameric cubane-structure, featuring many intramolecular (but unremarked upon) close-contacts between C···H and H···H atoms of the adamantyl and trimethylsilyl groups. Schreiner and co-workers have employed adamantyl groups (and also, diamondoids or polymantanes)[11–13] to isolate hydrocarbons with exceptionally long (≥ 1.63 Å) C–C bonds. These are stabilized by attractive dispersion interactions between the H-atoms of these groups – which permits isolation of the otherwise strained and non-isolable hydrocarbons.[14,15] In addition, the same workers have recently developed systems to study dispersion effects[3b] in different chemical groups, including adamantyl-containing derivatives.[16–18] We have previously rationalized that the role of dispersion in various complexes we have isolated. These include mixed metal bonded complexes, low-coordinate species and solution stable multiply-bonded compounds.[19–22]

Here, we report the synthesis, characterization, and computational analysis through density functional theory (DFT) calculations of alkali metal 1-adamantoxides M = Li (**1**), Na (**2**) and K (**3**). The synthesis of the complexes was carried out by following the simple route illustrated in Scheme 1. We planned to develop a facile synthetic route to sodium adamantoxides of the putative formula $[Na(OAd^1)(THF)]_4$ - a typical tetrameric-cubane structure seen in alkali metal alkoxides - for use in subsequent salt metathesis reactions as an OAd^1 transfer agent. Instead, a complex of the formula $[Na(OAd^1)(HOAd^1)_2]$ (**2**) was obtained by refluxing excess metal with 1-adamantanol in THF and subsequent removal of all volatile components to yield a white powder. Manual separation of the excess metal followed by dissolution of the white powder in toluene, filtration, and cooling to ca. -30 °C afforded the alkoxide **2** as a crystalline solid.



Scheme 1. Synthetic route to alkali metal complexes $[M(OAd^1)(HOAd^1)_2]$, (**1**–**3**).

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Surprisingly, X-ray crystallography revealed that the sodium ion in **2** is complexed by three adamantyl-based ligands; only one of which had undergone reduction to form the sodium adamantoxide as originally planned. The two remaining ligands are datively coordinated $HOAd^1$ molecules which retain their protons, despite the use of excess Na. Furthermore, the less Lewis basic[23] $HOAd^1$ molecules were found to coordinate in preference to THF. We now describe experimental and computational data which show that LD-effects between the Ad^1 groups of the ligands play a key role in the limitation of the reduction and formation of this unprecedented structure.

The molecular structure of **2** is shown in Figure 1 and illustrates that, despite the size of the adamantyl cages, all Ad^1 groups cluster together on the same side of the NaO_3 plane. This is contrary to steric considerations and is likely due to the many (ca. 7) intramolecular short (< the sum of vdW radii of 2.4 Å) H···H contacts between the calculated positions of the hydrogen atoms of the Ad^1 groups (Figure 3). The complex features a mirror plane that lies parallel to the Na(1)–O(1) bond and the three Ad^1 substituents lie on one side of the NaO_3 unit which is essentially planar with $\Sigma°_{Na}$ = 359.58(2)°. This is the first example of a 3-coordinate sodium ion alkoxide complex that is not part of an extended (ring, chain, or cluster) structure. The O–H protons on the $HOAd^1$ molecules were located on a difference map. The closest approaches to the Na within the unit cell involve H-atoms on the Ad^1 groups. H-bonding (O···H = 1.682 Å) between the alkoxide O-atom in one molecule and H-atoms on the $HOAd^1$ fragments of a neighboring molecule were also apparent.

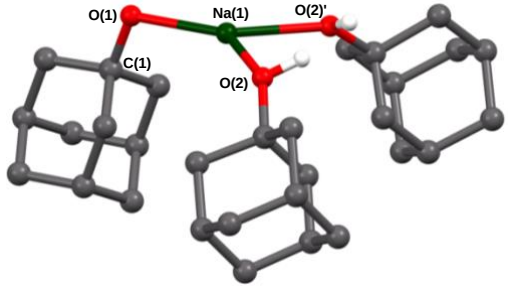

Figure 1. Molecular structure of **2** $[Na(OAd^1)(HOAd^1)_2]$. Thermal ellipsoids shown at 50% probability. Hydrogens (except those at the alcohol oxygens) are not shown for clarity. Key bond lengths (Å) and angles (°) include Na(1)–O(1) = 2.2580(18) Å, Na(1)–O(2) = 2.2811(15) Å, O(2)–Na(1)–O(1) = 136.02(4)°, O(2)–Na–O(2') = 87.54(9)°, C(1)–O(1)–Na(1) = 110.52(12)°, C(11)–O(2)–Na(1) = 110.65(12)°.

The Na(1)–O(1) and Na(1)–O(2) bond lengths (2.2580(18) Å and 2.2811(15) Å) in **2** are significantly shorter crystallographically (< 3σ) than those found in a similar 3-coordinate $[Na(THF)_3]$ counter ion isolated by Floriani and co-workers in $[Na(THF)_3]_2[Co(TPP)]$ (TTP = tetraphenylporphyrin),[24] which had Na–O bond lengths in the range of 2.313(5)–2.341(4) Å. The shorter Na–O bond lengths in complex **2**, despite the greater steric bulk of the Ad^1 substituent compared to the THF substituents in the TPP complex, further suggested that intramolecular attractive dispersion effects were present. ^{1}H NMR spectroscopy (SI) of **2** revealed overlapping environments at 298 K for the Ad^1 C–H moieties, indicating that the chemical shifts of the reduced OAd^1 ligand are similar to the datively coordinated $HOAd^1$ fragments. This further suggested that no dissociation of the $HOAd^1$ molecules occurred in solution. This was confirmed by diffusion order spectroscopy (DOSY) ^{1}H NMR spectroscopy which afforded a diffusion coefficient of 7.92 $\times 10^{-10}\, m^2 s^{-1}$, although the broadness of the Ad^1 signals implied highly fluxional solution-state behavior,[25] likely due to rotations of the Ad^1 groups around the C–O bond. The signals of the CH_2 groups of the Ad^1 molecules were found to be split into two distinct environments corresponded to those closest to the oxygen atom at δ = 1.64 ppm and δ = 1.48 ppm. The most downfield signal corresponding to the CH protons of the Ad^1 group at δ = 1.98 ppm. The signals most upfield at δ = 0.94 ppm are assigned to the O–H protons. The reaction of $HOAd^1$ with lithium metal in THF afforded a white powder that could not be redissolved in a range of solvents (including THF and toluene), though it proved sparingly soluble in benzene. We further attempted to obtain a crystalline sample of **1** from the reaction of $HOAd^1$ with ^{n}BuLi as the lithium source, but the same product, $[Li(OAd^1)(HOAd^1)_2]$ was generated (as determined by ^{1}H NMR spectroscopy). The reaction of excess potassium metal gave the potassium analogue $[K(OAd^1)(HOAd^1)_2]$ (**3**), which formed a white powder that was sparingly soluble in a toluene and THF (80:20) mixture. Attempts at crystallization from a mixture of these solvents yielded a colorless gel. DOSY NMR spectroscopy confirmed the isolation of **1** and **3**, which have diffusion coefficients of 7.88 $\times 10^{-10}\, m^2 s^{-1}$ and 8.02 $\times 10^{-10}\, m^2 s^{-1}$ respectively (SI). The similar diffusion coefficients of each species suggested that the complexes formed tris-coordinated structures analogous to that of **2** and have the formula $[M(OAd^1)(HOAd^1)_2]$ (M = Li, **1**; K; **3**).[26] This led to the conclusion that there is no change in coordination number with the size of the metal ion. The lack of other signals in the DOSY spectrum also confirmed that no dissociation of the $HOAd^1$ molecules occurred in solution at 298 K in C_6D_6 or THF-D_8 (SI). These two points further implied that LD-effects play a significant role in the solution-state behavior (similar systems by Schreiner and co-workers reported compounds that retained their structures in solution due to LD interactions)[27] of complexes **1**–**3** and provides a rationale for the inhibition of the deprotonation.

Computational studies on complex **2**, as well as the analogues with M = Li and K analogues (SI) using density functional theory (DFT) at the PBE1PBE-D3BJ/def2-TZVP level in the gas-phase, afforded an optimized geometry of complex **2**, in agreement with the observed experimental values. However, slightly stronger binding in the Na-O(1) bond is observed (2.043 Å in the computed structure using the PBE1PBE-D3BJ level of theory compared to 2.2580(18) Å in the molecular structure). In addition, the C–O–Na bond angles differ from the molecular structure obtained by X-ray diffraction (110.52(12)° in the molecular structure vs. 159.69° in the gas phase), potentially due to the lack of crystal-packing effects in the gas phase optimized structure or the ionic nature of the Na–O interaction (as interpreted from calculated natural charges and WBIs, Table S3).[27] Nevertheless, the computed bond parameters show an expected lengthening of the M–O(1) bond as the size of the group 1 metal increases (Table S1). Interestingly, the M–O(2) and M–O(3) bond lengths increase similarly and are longer than the respective covalent radii proposed by Pyykkö and Atsumi, as well as the extrapolated ionic radii of Shannon and Prewitt for a 3-coordinate alkali metal ion species.[28–30] This also suggests that there are significant stabilizing intramolecular interactions present between the OAd^1-ligands. If the three OAd^1 fragments are optimized without empirical dispersion correction, only minor changes in the calculated bond parameters are observed.

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Table 1. Calculated thermodynamic data (kcal/mol) for the dissociation of $[M(OAd^1)(HOAd^1)_2]$ into neutral $M(OAd^1)$ and 2 $HOAd^1$ fragments.

$[M(OAd^1)(HOAd^1)_2] \rightarrow M(OAd^1) + 2\ HOAd^1$

	M = Li		M = Na		M = K	
	PBE1PBE-D3BJ	PBE1PBE	PBE1PBE-D3BJ	PBE1PBE	PBE1PBE-D3BJ	PBE1PBE
Δ*E*	38.2	28.8	36.1	25.6	28.8	17.5
Δ*H*	39.4	30.0	37.3	26.8	29.9	18.7
Δ*G*	17.9	10.3	15.5	7.2	8.2	0.0

Our hypothesis that intramolecular dispersion effects help stabilize the structures of the complexes is further corroborated by the calculated dissociation energies given in Table 1. If the dissociation energies are calculated with dispersion correction, all three complexes $[M(OAd^1)(HOAd^1)_2]$ (M = Li, Na, K) are thermodynamically favored over the neutral fragments $[M(OAd^1)]$ and 2 $HOAd^1$. However, if the dispersion correction component is omitted from the calculation, the stabilization energies decrease, and for M = K, the Δ*G* is calculated at 0 kcal mol^{-1}. This energy profile is consistent with the difficulty in isolating **3**.

More detailed bonding analyses (Figure S21) were performed using the extended transition state method for energy decomposition analysis in combination with natural orbitals for chemical valence (ETS-NOCV). The results are summarized in Figure 2 (data from Table S2) and clearly showed that the electrostatic interactions and orbital contributions outweigh Pauli repulsion in all cases, despite our initial rationale that the effects of intermolecular H-bonding would sufficiently stabilize these complexes. We further carried out ETS-NOCV analysis using single-point energies (Table S4) which showed that dispersion contributions to the overall bonding remained roughly the same when comparing a gas-phase optimized structure or the crystallographic data (27% and 31% respectively). The crystal packing within the unit cell (Figure S26) shows that intermolecular H-bonding further facilitates intermolecular LD interactions between the Ad^1 groups.

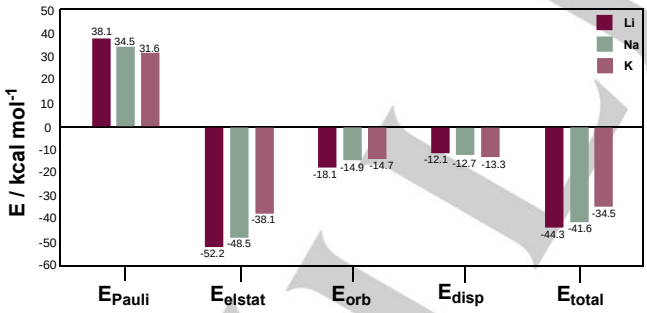

Figure 2. Summary of the energy decomposition analysis (EDA) results for $[M(OAd^1)(HOAd^1)_2]$ (M = Li, Na or K).

Approximately one third (M = Li, 28%; M = Na, 30%; M = K, 39%) of the calculated total bonding energies can be assigned to dispersion effects involving the C–H moieties of the Ad^1 fragments (Figure 3). To better understand the participation of LD-effects in the adamantyl-moiety, we tested the reduction of 2-adamantanol ($HOAd^2$) with excess sodium (Scheme 2) to see if a dispersion-dependent structure would be obtained. This reaction afforded a white powder which was not soluble in toluene (while **2** was

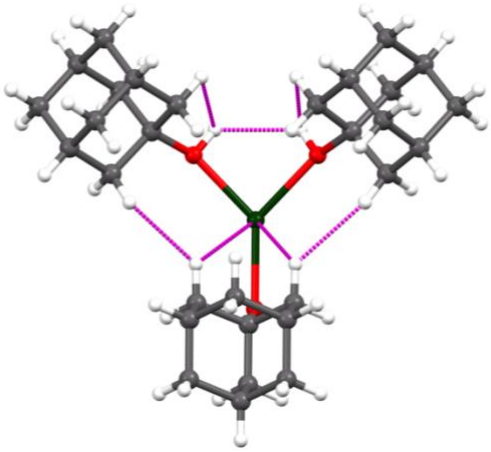

Figure 3. Molecular structure of **2**, illustrating the inter-ligand LD-induced close-contacts (< 2.4 Å, pink dashed lines).

soluble in toluene), though the addition of a small amount of THF (5 mL) to a saturated toluene solution did effect complete dissolution. Single crystals that proved to have the formula $[Na(OAd^2)(THF)]_4$ (**4**), and were suitable for X-ray analysis were obtained from a toluene:THF (95:5) solvent mixture after cooling to ca. -30 °C overnight. The molecular structure of **4** is shown in Figure 4.

The structure of **4** showed that use of $HOAd^2$ generates the more common tetrameric cubane-type alkali metal alkoxide structure[31–33] (28 other tetrameric cubane-type sodium alkoxide structures are reported in the Cambridge Structural Database). This showed that the bridgehead position of the $HOAd^1$ molecule is unique in generating the LD-effect of the structure of **2**. Furthermore, the reaction outlined in Scheme 2 proceeded to completion, showing that the reduction of the $HOAd^2$ was not inhibited. Typical bond lengths[31–33] between the Na and O atoms were found; for both the adamantoxide and datively coordinated THF molecules. The Na(1)–Na(1)' distance of 3.0556(16) Å and the Na(1)–O(1) bond length of 2.2718(16) Å in **4** were found to be shorter than those in other sodium alkoxides with similar steric profiles, such as Rheingold and co-workers' $[Na(OXyl)(THF)]_4$, Xyl = 2,6-dimethylphenyl.[32] The Na(1)–Na(1)' and Na(1)–O(1) distances in Rheingold's complex were found to be 3.208(2) Å and 2.309(2) Å respectively. In comparison to **2**, the Na(1)–O(1) bond length in **4** is significantly longer (2.2580(18) Å in **2**) and the O(2)–Na(1)–O(2) bond angle in **2** is narrower (87.54(9)°) compared to the Na(1)–O(1)–Na(1)' angle of 93.78(4)° in **4**. In the solution state, coordinated THF in **4** was found to dissociate dynamically at 298 K as evidenced by ^{1}H and DOSY NMR spectroscopy, and a molecular unit with a diffusion coefficient of 4.99 $\times\ 10^{-10}\ m^2 s^{-1}$ corresponding to the cluster **4** and two additional THF molecules.

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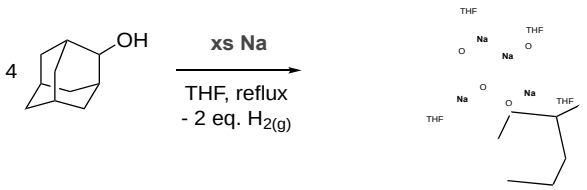

Scheme 2. Synthetic route toward the THF-complexed sodium 2-adamantoxide $[Na(OAd^2)(THF)]_4$, **4**.

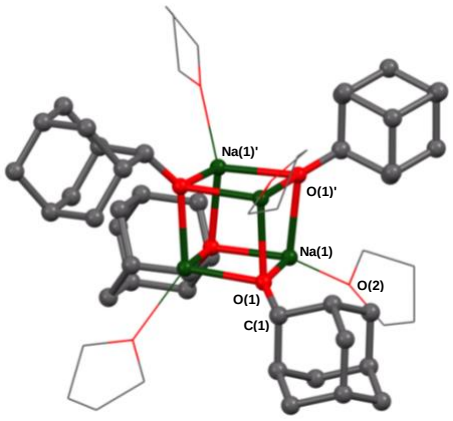

Figure 4. Molecular structure of **4**, $[Na(OAd_2)(THF)]_4$. Thermal ellipsoids shown at 50% probability. Hydrogens are not included and THF molecules are shown in wireframe for clarity. Key bond lengths (Å) and angles (°) include Na(1)–O(1) = 2.2718(16) Å, Na(1)–O(1)' = 2.2747(16), Na(1)–O(2) = 2.3718(17) Å, O(1)–(1) = 1.383(2) Å, Na(1)–O(1)–Na(1)' = 93.78(4)°, O(1)–Na(1)–O(2) = 148.82(6)°.[34]

In summary, we have shown that London dispersion effects play a crucial role in the reduction reactions of 1-adamantanol. Despite the use of excess alkali metal, dispersion effect stabilization resulted in the formation of 3-coordinate structures and prevented deprotonation of 2 $HOAd^1$ molecules in the complex. The molecular structures of the lithium (**1**) and potassium (**3**) analogues proved difficult to obtain because of their solubilities, but the sodium complex $[Na(OAd^1)(HOAd^1)_2]$ (**2**) afforded a molecular complex that is the first instance of a 3-coordinate sodium alkoxide which does not form a ring, chain or cluster extended structure. **2** clearly displays significant LD-effects including: many close intramolecular contacts between the C–H···H–C moieties of the ligands and an unusual clustering of the bulky adamantyl groups around the sodium center. The computational analyses further support the view that complexes **1**–**3** would not be isolable without LD-stabilization. Furthermore, the reduction of $HOAd^2$ with excess Na to yield **4**, the reduction was not impeded by LD-effects and the more common tetrameric cubane-type structure $[Na(OAd^2)(THF)]_4$ was obtained. This is the first example of LD-effects limiting the reduction of an alcohol and indicates that these interactions should be considered if similar dispersion-enhanced groups are being employed.

Acknowledgements

We gratefully acknowledge the U.S. National Science Foundation for their financial support (Grant CHE-1565501, C.R.S.) and for the acquisition of dual-source X-ray diffractometer (Grant CHE 0840444). We also thank the Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-FG02-07ER4675, K. L. M.) for support of this work. P. V. acknowledges the Academy of Finland for financial support (grant numbers 338271 and 346565) and CSC – IT Center for Science, Finland, for computational resources. Dr David J. Liptrot and Dr Michelle A. Faust are thanked for their early contribution to this work.

Conflicts of interest

The authors declare no conflicts.

Keywords: London Dispersion • Coordination Chemistry • Reduction • DFT • Alkoxides

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10.1002/anie.202201318

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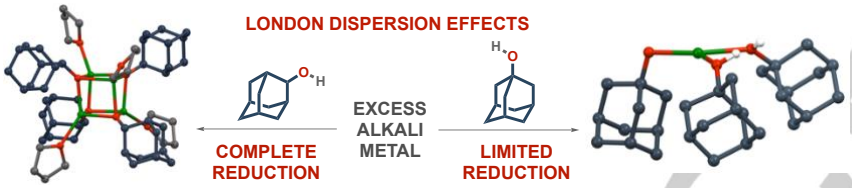

London dispersion (LD) effects limit the reduction of 1-adamantanol, despite the use of excess alkali metals Li, Na and K. An unusual sodium complex featuring the adamantoxide and two datively-coordinated 1-adamantanol molecules was isolated. This structure showed that the adamantyl moieties cluster together on one-side of the NaO_3 plane, and featured many intramolecular close contacts, as a result of the LD-effects present.

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