

Bonding Analysis

International Edition: DOI: 10.1002/anie.201907089
German Edition: DOI: 10.1002/ange.201907089Realization of Lewis Basic Sodium Anion in the NaBH_3^- Cluster

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Abstract: We report a $\text{Na}^- \rightarrow \text{B}$ dative bond in the NaBH_3^- cluster, which was designed on the principle of minimum-energy rupture, prepared by laser vaporization, and characterized by a synergy of anion photoelectron spectroscopy and electronic structure calculations. The global minimum of NaBH_3^- features a $\text{Na}-\text{B}$ bond. Its preferred heterolytic dissociation conforms with the IUPAC definition of dative bond. The lone electron pair revealed on Na and the negative Laplacian of electron density at the bond critical point further confirm the dative nature of the $\text{Na}-\text{B}$ bond. This study represents the first example of a Lewis adduct with an alkali as the Lewis base.

Metals normally act as Lewis acids (LA), given the prevalence of metal-ligand compounds in which the empty orbitals of the Lewis acidic metals accept pairs of electrons from Lewis basic ligands. Intriguingly, some transition metals can conversely provide their lone electron pairs and form directional dative bonds to electron deficient molecules, that is, act as Lewis bases. The concept of metal Lewis basicity was recognized by Shriver,^[1] and developed as a synthetic methodology by Vaska, Werner, and others.^[2] Later structural assignments, however, casted doubt on these complexes with negative results on metal-LA interaction.^[3] It was not until 1999 that the first structural confirmation of a $\text{M} \rightarrow \text{B}$ dative bond was reported.^[4] Then, metal Lewis basicity has seen a prosper of research activity, and numerous novel Lewis pairs have been prepared featuring the interaction between Lewis basic transition metals and Lewis acidic ligands.^[5] Compared to classic metal-ligand bond, this weak yet electronically reverse metal \rightarrow LA interaction holds the promise for a novel type of metal-ligand cooperativity in catalytic reactions,^[6] and

open doors to many applications involving H_2 storage and activation, olefin hydrogenation, CO_2 fixation, etc.^[7-16]

The metal Lewis basicity, however, has only been demonstrated for transition metals.^[5] Main group metals have only shown Lewis acidity.^[5c] Intuitively, among all main group metals, alkali metals are the least appropriate candidates for Lewis base. The lack of an electron pair requires them to form the extremely reducing alkalides (alkali metal anions) before forming dative bonds with LA. While alkalides have been found in a handful of examples, their interaction with the surroundings is ionic.^[17]

Within this context, we aimed to design an unusual Lewis acid/base adduct in which the Lewis base is an alkali. Two requirements are to be fulfilled: the alkali needs to form a direct chemical bond with the LA, and this bond needs to be dative, i.e., the electron pair needs to derive from the alkali. The latter requirement is better interpreted using the minimum-energy rupture principle,^[18] which is adapted by IUPAC as the standard for differentiating dative bond from covalent or ionic bond.^[19] Specifically, this principle analyses the energies of the homolytic and heterolytic bond breakage in the gas phase: if homolytic bond rupture requires less energy, the bond is considered covalent or ionic; if heterolytic bond rupture is energetically favored, the bond is considered dative. This implies a strategy for designing the alkali \rightarrow LA Lewis adduct: choose a weak LA whose electron affinity is much lower than alkali, and prepare an anionic alkali-LA complex where the alkali moiety forms a direct chemical bond with the LA moiety, i.e., $(\text{alkali-LA})^-$. Such $(\text{alkali-LA})^-$ complex would prefer a heterolytic bond rupture into alkali and LA, fulfilling the above-mentioned requirements for being a Lewis adduct with an alkali as the base. The choice of LA is thus critical. Being electron deficient in nature, some LA have surprisingly low EA. For example, the EA of the prototype LA, BH_3 , is only 0.038 eV,^[20] which is much lower than the EA of all alkali metals. Here, we show that the designer $(\text{Na-BH}_3)^-$ cluster possesses a unique $\text{Na}^- \rightarrow \text{BH}_3$ dative bond, representing the first observation of a Lewis pair in which the base is an alkali.

The $(\text{Na-BH}_3)^-$ was generated with a laser vaporization source by focusing an intense beam of Nd:YAG laser (532 nm, 60 mJ) onto a NaBH_4 coated rod. The laser caused dissociation of the $\text{B}-\text{H}$ bond in NaBH_4 . The resulting mass spectrum is presented in Figure 1 A, along with the expected isotopic mass distribution of $(\text{Na-BH}_3)^-$ in its top panel. The overall agreement between the experimental and expected mass patterns verifies the existence of $(\text{Na-BH}_3)^-$. Dissociation of multiple $\text{B}-\text{H}$ bonds is possible during the laser vaporization of borohydride.^[21] Thus, the small mass peak at 35 amu suggests the formation of NaBH_2^- via the breakage of two $\text{B}-\text{H}$ bonds. The peak at 37 amu was selected for anion

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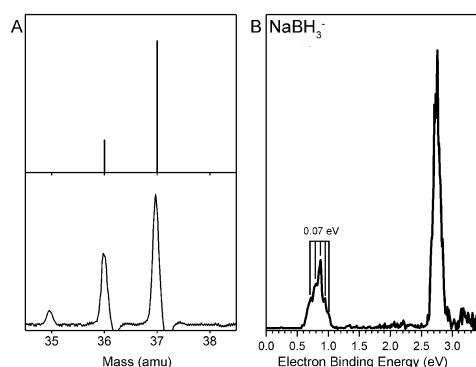


Figure 1. A) The expected (top panel) and experimental (bottom panel) mass spectra of $(\text{Na-BH}_3)^-$, and B) the anion photoelectron spectrum of NaBH_3^- taken with 355 nm (3.496 eV) photons.

photoelectron spectroscopic study as it was solely comprised of $(\text{Na-BH}_3)^-$.

Anion photoelectron spectroscopy can interpret the bonding picture of $(\text{Na-BH}_3)^-$ via directly probing the electronic structure and intramolecular interaction.^[22] The photoelectron spectrum of $(\text{Na-BH}_3)^-$ (Figure 1B) exhibits two fairly sharp transitions peaked at electron binding energies (EBE) of 0.87 and 2.74 eV. The two EBE values are assigned as the vertical detachment energies (VDE), respectively corresponding to transitions with maximized Franck-Condon overlaps from the ground state of anion, to the ground and to the first excited electronic state of neutral. Potentially, the Na moiety could exist in three different structures: (i) Na forms chemical bonds with multiple B and H atoms, (ii) Na^- weakly interacts with the H atoms in BH_3 molecule, that is, physically “solvated” by BH_3 , resulting in $\text{Na}^-(\text{BH}_3)$, and (iii) Na^- directly interacts with the electron-deficient B atom, forming a $[\text{Na}^-(\text{BH}_3)]$ complex. Only structure (iii) holds the promise for a Lewis adduct. The photoelectron spectrum of NaBH_3^- resembles that of Na^- ,^[23] suggesting the existence of a Na^- moiety in NaBH_3^- as the chromophore for photodetachment. Though the spectrum appears to be a shift of the Na^- spectrum to higher EBE, which is a common fingerprint of physical solvation effect,^[24,25] two spectral features strongly suggest the formation of chemical bond between the Na^- and BH_3 moieties: a) the spacing between the two peaks, 1.87 eV, is smaller than the expected spacing for solvation complex, 2.10 eV (the Na D-line), implying a change in electronic structure induced by chemical interaction; b) the observed vibrational progression spaced at ≈ 0.07 eV in the lower EBE peak is not a characteristic frequency of BH_3 ; thus, this progression is likely due to a Na–B vibrational mode, implying the formation of a Na–B chemical bond.

Isolated and well-defined gas-phase systems are ideally suited for simulations employing state-of-the-art quantum theoretical methods. To find the most thermodynamically stable structure of $(\text{Na-BH}_3)^-$, which was expected to be the main contributor of the photoelectron spectrum, we performed an unbiased GM search of 5000 randomly generated structures on both singlet and triplet potential energy surfaces. All the geometries were initially optimized using

DFT-level PBE0/6–31 + G*.^[26] The low-lying singlet and triplet structures were subsequently reoptimized with CCSD(T)/aug-cc-pVTZ.^[27] Then single-point energy calculations were performed using CCSD(T)/aug-cc-pCVQZ accounting for full electron correlation.^[28] Structures were then ranked based on their relative energies. The GM of NaBH_3^- exhibits a C_{3v} structure, features a Na–B bond of 2.72 Å between Na and the slightly distorted BH_3 , and has a singlet electronic configuration of $1a_1^2 1e_1^4 2a_1^2$.

The B–H–B \angle is 119.4°, while the overall distortion measured as the \angle between $\text{H}_1\text{–H}_2\text{–H}_3$ plane and B atom is 8.7°. The most stable triplet structure has a C_s symmetry with a $1a'^2 1a''^2 3a'^2 4a''^1 5a'^1$ electronic configuration, and is less stable than the GM by 5.9 kcal mol^{−1} (Figure 2).

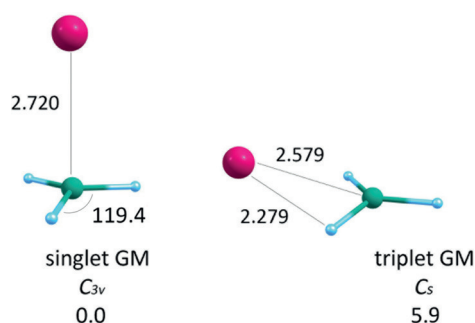


Figure 2. The lowest energy singlet and triplet structures of $(\text{Na-BH}_3)^-$. No other structures were found within 20 kcal mol^{−1}. Bond lengths are given in Å. Point groups are given in italic. Bottom values refer to the relative energy including ZPE correction at CCSD(T)/aug-cc-pCVQZ level.

Though being a simple cluster, pronounced multireference character in $(\text{Na-BH}_3)^-$ is revealed by CASSCF(8,14)/aug-cc-pwCVQZ.^[29] To verify that the calculated GM of $(\text{Na-BH}_3)^-$ describes the experimental spectrum, the VDEs were computed at the coupled cluster and CASSCF levels of theory. As shown in Table 1, for the singlet GM, the calculated VDEs are in excellent agreement with the experimental VDEs, validating the calculations for accurately describing the energetics of this system. An A1 symmetric umbrella inversion with a frequency of 0.078 eV (629 cm^{−1}) is also revealed (Supporting Information, Table S1), which is in accordance with the vibrational progression observed in the

Table 1: Experimental and calculated VDEs for lowest-energy singlet and triplet $(\text{Na-BH}_3)^-$ at different levels of theory. For all calculations aug-cc-pCVQZ basis set was used.

| Anion state ∇ | Neutral configuration | VDE [eV] | | |
|----------------------|-----------------------------------|----------|-------------------|------------------|
| | | EXPT. | CC ^[a] | CAS(8,14)NEVPT2 |
| Singlet GM | $1a_1^2 1e_1^4 2a_1^1 3a_1^0$ | 0.87 | 0.88 | 0.81 |
| | $1a_1^2 1e_1^4 2a_1^0 3a_1^1$ | 2.74 | 2.64 | — ^[b] |
| Triplet | $1a'^2 1a''^2 3a'^2 4a''^1 5a'^1$ | 0.87 | 0.79 | — |
| | $1a'^2 1a''^2 3a'^2 4a''^1 5a'^1$ | 2.74 | 1.54 | — |

[a] CC stands for coupled-cluster theory. For the first VDEs CCSD(T) method was used while the second ones were calculated with EOM-CCSD.^[30] [b] This VDE cannot be obtained at this level of theory.

photoelectron spectrum. For the triplet $(\text{Na-BH}_3)^-$, however, while its 1st calculated VDE matches the experiment, the absence of the 2nd one in experimental spectrum makes its existence unlikely. This thus confirms the singlet GM structure of $(\text{Na-BH}_3)^-$, which possesses a Na-B chemical bond, as the major species observed in experiment.

Since the EA of Na ($12.64 \text{ kcal mol}^{-1}$) is significantly higher than that of BH_3 ($0.88 \text{ kcal mol}^{-1}$), the heterolytic breakage of $(\text{Na-BH}_3)^-$ into Na^- and BH_3 should be favored by approximately ($12.64 - 0.88 = 11.76$) kcal mol^{-1} over the homolytic breakage into Na^\cdot and $\cdot\text{BH}_3^-$. As shown in Table 2, the calculated heterolytic bond dissociation energy

Table 2: BDEs calculated at the CCSD(T)/aug-cc-pCVQZ level of theory including ZPE corrections. The energies are given in kcal mol^{-1} .

| Dissociation pathway | BDE |
|---|-------|
| $(\text{Na-BH}_3)^- \rightarrow \text{Na}^- + \text{BH}_3$ | 17.8 |
| $(\text{Na-BH}_3)^- \rightarrow \text{Na}^\cdot + \cdot\text{BH}_3^-$ | 30.1 |
| $(\text{Na-BH}_3)^- \rightarrow \text{Na}^+ + \cdot\text{BH}_3^{2-}$ | 248.7 |
| $\text{H}_3\text{N-BH}_3 \rightarrow \cdot\text{NH}_3 + \text{BH}_3$ | 26.0 |

(BDE) is $17.8 \text{ kcal mol}^{-1}$, while the calculated homolytic BDE is $30.1 \text{ kcal mol}^{-1}$. The calculated BDE difference, $12.3 \text{ kcal mol}^{-1}$, is close to the expected value, $11.76 \text{ kcal mol}^{-1}$, validating the calculated BDEs. For reference, the BDE of the prototype Lewis adduct, $\text{H}_3\text{N-BH}_3$, was also calculated. Our result is consistent with previous study.^[31] Dissociation into ionic fragments Na^+ and $\cdot\text{BH}_3^{2-}$ is much less favored due to the instability of $\cdot\text{BH}_3^{2-}$. Therefore, the Na-B bond in $(\text{Na-BH}_3)^-$ favors the heterolytic dissociation, making it satisfy the IUPAC definition of dative bond; $(\text{Na-BH}_3)^-$ can be described as a $\text{Na}^- \rightarrow \text{BH}_3$ Lewis acid/base adduct.

The Lewis adduct nature of $(\text{Na-BH}_3)^-$ is also demonstrated by the charge distribution change on the potential energy surface along the Na-B coordinate. Figure 3 shows that when Na and BH_3 moieties are completely separated, all the negative charge localizes on Na, that is, the formation of

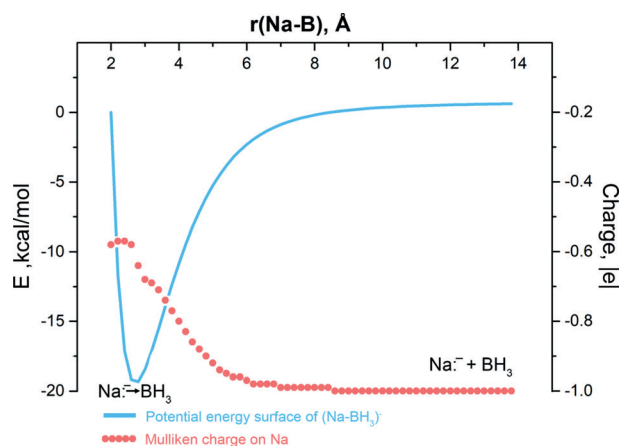


Figure 3. Potential energy surface of $(\text{Na-BH}_3)^-$ along the Na-B coordinate (blue curve) and the Mulliken charge on Na at corresponding $r(\text{Na-B})$ (red dotted curve).

$(\text{Na-BH}_3)^-$ complex starts from Na^\cdot and BH_3 . The charge on Na moiety gradually reduces as Na approaches BH_3 , suggesting charge transfer from Na to BH_3 when forming $\text{Na}^- \rightarrow \text{BH}_3$ bond. These curves comply with the classic picture of dative bond formation.

The nature of this $\text{Na}^- \rightarrow \text{BH}_3$ dative bond is further investigated using Adaptive Natural Density Partitioning (AdNDP), which analyses chemical bonding patterns based on the concept of electron pair,^[32] and the Quantum Theory of Atoms in Molecules (QTAIM), which interprets chemical bonds based on topological analysis of electron density.^[33] According to AdNDP, there are three fully localized 2c-2e B-H σ -bonds with an occupation number (ON) equal to $1.96 |e|$. The $\text{Na}^- \rightarrow \text{BH}_3$ bond is a pure 2c-2e σ -bond with $\text{ON} = 1.76 |e|$ (Figure 4A). AdNDP also allows us to locate an s lone pair on Na as an alternative to the 2c-2e Na-B bond in order to evaluate the Na contribution. The recovered lone pair has an ON of $1.28 |e|$ (Figure 4B), indicating that Na acquires extra electron and has doubly occupied orbital. Moreover, the ON value of the s lone pair suggests it the primary component of the Na-B bond. The QTAIM results for $(\text{Na-BH}_3)^-$ are shown in Figure 4C. The negative $\nabla^2\rho$ values at the B-H bond critical points (BCPs) indicate shared interaction, in accordance with the covalent nature of the B-H bonds. The positive $\nabla^2\rho$ value at the Na-B BCP indicates closed shell interaction, which is one main feature of a dative bond. The

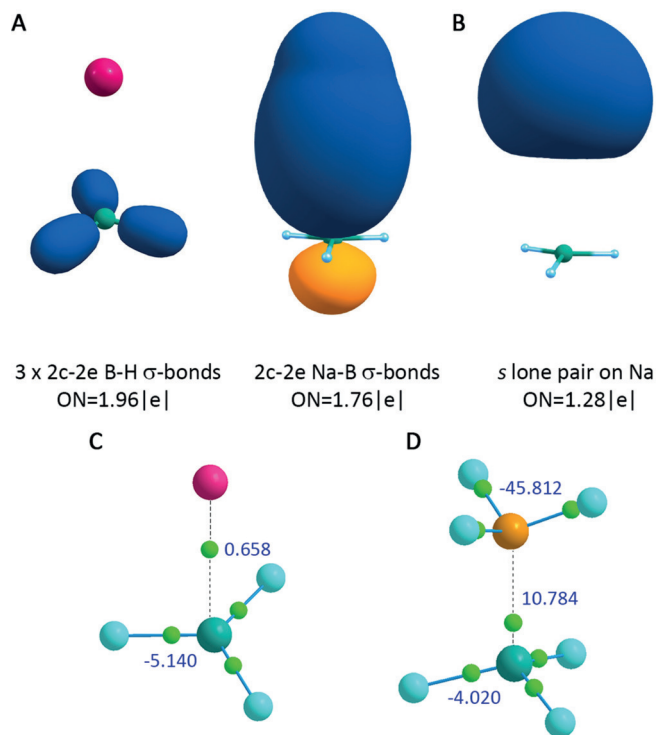


Figure 4. AdNDP and QTAIM chemical bonding patterns. A) AdNDP full bonding picture of $(\text{Na-BH}_3)^-$, B) AdNDP recovered s -type lone electron pair on Na, C) QTAIM results of $(\text{Na-BH}_3)^-$, and D) QTAIM results of $\text{H}_3\text{N-BH}_3$. Na is purple, B is dark green, N is orange, H is blue. QTAIM calculated BCPs are represented by light green spheres. The numbers in blue besides BCPs are the Laplacians of electron density, $\nabla^2\rho$, in $\text{e}^- \text{Å}^{-5}$.

electron density of Na–B bond is comparable to that of a strong hydrogen bond.^[34] For comparison, we also performed QTAIM on H₃N–BH₃ as an example of a classic dative interaction^[35] (Figure 4D). The QTAIM results of (Na–BH₃)[−] and H₃N–BH₃ are similar: both dative Na–B and N–B bonds have positive $\nabla^2\rho_{(\text{BCP})}$ values, while the $\nabla^2\rho_{(\text{BCP})}$ of all covalent B–H bonds are negative. Therefore, the QTAIM results further corroborate the dative nature of the Na–B bond. These results comply with the AdNDP analysis.

Lastly, we analyzed an isolated hypothetical [Na–B(CN)₃][−] complex, which derives from the solid-phase Na₂B(CN)₃, a salt comprised of Na⁺ and B(CN)₃^{2−} dianion.^[36] For [Na–B(CN)₃][−], its homolytic dissociation into Na[•] and •B(CN)₃[−] requires 60.3 kcal mol^{−1} less in energy than the heterolytic dissociation into Na[−] and B(CN)₃ (Table S3). This is consistent with the high EA of B(CN)₃ (78.9 kcal mol^{−1}). Dissociation into Na⁺ and [B(CN)₃]^{2−} has a much higher BDE, because [B(CN)₃]^{2−} is not a stable species when isolated. According to the IUPAC guidance, the Na–B bond in [Na–B(CN)₃][−] can be characterized as covalent or ionic. AdNDP reveals that the Na moiety bears an ON of only 0.49 |e|, while NBO suggests a positive charge of +0.23 |e| on Na. These indicate a near-neutral configuration of Na, and that the Na–B bond is a polar covalent bond (Figure S1). The [Na–B(CN)₃][−] can thus be written as Na⁰[B(CN)₃][−]. While this result seems counter-intuitive to the condensed-phase characterization of [Na–B(CN)₃][−] as Na⁺[B(CN)₃]^{2−}, it is consistent with numerous studies on anions of isolated salts (M⁺X[−])[−], which have shown that the excess electron goes to the cation to form M⁰X[−].^[37] Therefore, this hypothetical [Na–B(CN)₃][−] serves as a contrasting example of (Na–BH₃)[−], emphasizing the importance of using weak Lewis acid for the design of alkali → LA Lewis adduct.

To summarize, we have designed a (Na–BH₃)[−] cluster featuring a non-trivial Na[−] → BH₃ dative bond, representing the first example of a Lewis adduct with an alkali as the base. Anion photoelectron spectroscopy reveals a negatively charged Na moiety and its direct chemical bond with BH₃. The excellent agreement between the experimental and calculated VDEs confirms the optimized structure. The dative nature of the Na–B bond is confirmed by *minimum energy rupture*, AdNDP and QTAIM analyses. The realization of this unprecedented Na[−] → B dative bond, together with several recent studies showing alkali metals can form covalent bond as ligands^[38] and electronically transmute Al to form Al–Al multiple bonds,^[39] demonstrates the unusual versatility of alkali metals in contributing to various types of chemical bonds. This study extends our understanding on Lewis acid/base, a fundamental concept in chemistry, and opens the door for synthesizing novel Lewis adducts.

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Conflict of interest

The authors declare no conflict of interest.

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