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# First steps towards a stable neon compound: observation and bonding analysis of $[B_{12}(CN)_{11}Ne]^{-\ddagger}$

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**Noble gas (Ng) containing molecular anions are much scarcer than Ng containing cations. No neon containing anion has been reported so far. Here, the experimental observation of the molecular anion  $[B_{12}(CN)_{11}Ne]^{-}$  and a theoretical analysis of the boron–neon bond is reported.**

Binding to noble gases – the most unreactive elements – has fascinated chemists since their discovery.<sup>1</sup> Today, a diverse Xe chemistry is established<sup>2</sup> and several stable Kr compounds are known.<sup>3</sup> Extreme pressures can force even He to form chemical bonds, ( $Na_2He$  is stable at pressures  $> 100$  MPa),<sup>4</sup> but evidence for stable compounds containing the light noble gases at ambient or lower pressures are extremely rare. The neutral compound HArF has been shown to exist in a cryogenic matrix.<sup>5</sup> Some other interactions, which exceed the strength of van-der-Waals attractions, have been detected between the atoms of cryogenic noble gas matrices and embedded molecules.<sup>6</sup> Stable Ne and He compounds are unknown at ambient pressure conditions. On the other hand, isolated cations in the gas phase, containing small noble gases, are long known.<sup>7</sup> Therefore, it may be assumed that ionic compounds formed with small noble gas containing molecular ions, may have a chance to exist.

Noble gases have a negative electron affinity and do therefore not exist as an atomic anion.<sup>8</sup> They are also unable to accept

electrons provided by nucleophiles. The only way to form a localized, directed bond with a noble gas is by abstracting electron density from the noble gas atom. Therefore, spontaneous binding of noble gases is the sole privilege of the strongest electrophiles, which are usually cationic. Complex polyatomic cations containing Ar have been discovered.<sup>9</sup> Schröder and Roithová detected a Ne-containing molecular dication by the endothermic substitution of  $F^{\bullet}$  in  $SiF_3^{2+}$  with Ne.<sup>10</sup> Although the strongest bonds with noble gas atoms have been found for cations, they bear an intrinsic problem for the formation of stable compounds in the condensed phase: a cation needs to be paired with an anion. A negatively charged ion always competes with the noble gas for the highly electrophilic binding site in the cation (see Fig. 1a). The noble gas atom will be replaced by the anion due to its stronger nucleophilic character. In contrast, a noble gas containing anion may be a more promising ionic building block for condensed phase material:<sup>11</sup> A carefully chosen counteranion should not compete with a noble gas for the electrophilic binding site, enabling the formation of stable ion pairs (Fig. 1b). Unfortunately, most anions do not possess a sufficiently strong electrophilic binding site to form a stable noble gas bond.

Chemical intuition may suggest a consistent trend in the periodic table row so that He is the most unreactive element. However, theoretical investigations predict that binding of Ne

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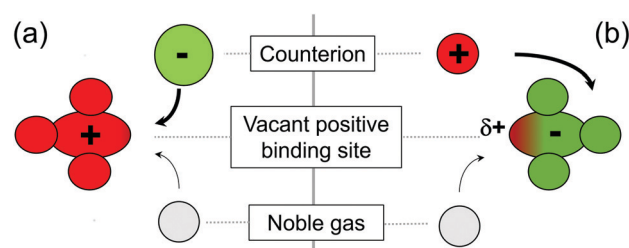
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**Fig. 1** Visualization of the concept that strongly electrophilic cations have an intrinsic problem for noble gas binding if paired with a counteranion (a). In contrast, an anion with a positive binding site capable to bind noble gases avoids the problem (b).

to a reactive molecule can be substantially less favorable than binding of He.<sup>12–14</sup> In contrast to He, Ne contains occupied p-orbitals which results in higher orbital repulsion during formation of a  $\sigma$ -bond between Ne and a reactive atom. Often, this disadvantage overcompensates the higher polarizability of Ne compared to He. Therefore, with respect to chemical bonding, Ne may actually be ranked as the stubbornest element in the periodic table. Molecular anions containing He and Ne have not been observed experimentally so far. While some anionic species such as  $[\text{FHeX}]^-$  ( $X = \text{O}, \text{S}, \text{Se}$ ) have been theoretically predicted to be metastable, the equivalent Ne anions were shown to be unbound.<sup>11,15</sup> In particular for Ne, the above-mentioned concept (molecular noble gas anions as building blocks for salts) remains purely hypothetical because no Ne containing anions have been observed or even predicted so far.

The presence of a strongly electrophilic binding site within an anion represents a critical key aspect of the discussed concept. We have recently reported on the exceptional reactivity of the  $[\text{B}_{12}(\text{CN})_{11}]^-$  anion,<sup>16</sup> a fragment of the highly stable *closo*-dodecaborate dianion  $[\text{B}_{12}(\text{CN})_{12}]^{2-}$ .<sup>16,17</sup> The monoanion  $[\text{B}_{12}(\text{CN})_{11}]^-$ , although being overall negatively charged, possesses a free boron atom with a significant positive partial charge which behaves as a strong electrophile.  $[\text{B}_{12}(\text{CN})_{11}]^-$  even binds Ar spontaneously at room temperature. Although spontaneous Ne-binding was not observed, we believe that  $[\text{B}_{12}(\text{CN})_{11}]^-$  is the most promising candidate for the observation of a bound Ne-containing anion, which may exist at lower temperatures. Here, we communicate the first steps towards the generation of an ionic compound based on a Ne-containing molecular anion:

(1) We report an improved synthetic procedure based on a photochemical approach, which enables a room-temperature and metal-free synthesis of  $[\text{B}_{12}(\text{CN})_{12}]^{2-}$ . An easy and cost-efficient synthesis of the precursor constitutes the baseline for potential applications of the  $[\text{B}_{12}(\text{CN})_{11}]^-$  anions.

(2) We experimentally probe the binding properties of  $[\text{B}_{12}(\text{CN})_{11}]^-$  towards the small noble gases He and Ne and perform a complementary theoretical bonding analysis of the B-Ne bond.

In our first study on  $[\text{B}_{12}(\text{CN})_{11}]^-$ , its precursor  $[\text{B}_{12}(\text{CN})_{12}]^{2-}$  was generated only as a side product in a reaction mixture<sup>16</sup> by irradiation of an aqueous solution of  $\text{K}_2[\text{B}_{12}\text{I}_{12}]$  and KCN with a 150 W medium pressure mercury lamp. Very recently, a new synthesis procedure was published enabling generation of  $[\text{B}_{12}(\text{CN})_{12}]^{2-}$  based on Pd-catalyzed cross coupling in a high temperature microwave reaction on a small scale.<sup>18</sup> The advanced synthesis procedure of the percyano-*closo*-dodecaborate anion reported here is based on a photochemical reaction, which exchanges iodine substituents in  $[\text{B}_{12}\text{I}_{12}]^{2-}$  with CN groups. This approach was mentioned first by Trofimenko in 1965, but yielded only products with a maximum of 8–9 CN groups.<sup>19</sup> Our improved procedure consists of the use of  $\text{Na}^+$  as a counter cation instead of  $\text{K}^+$  and reducing the amount of the solvent water, which produces a soluble fraction and a white precipitate. The soluble fraction contains  $[\text{B}_{12}(\text{CN})_{12-x}(\text{OH})_x]^{2-}$  ( $x = 0-3$ ) ions, while the precipitate consists of an approximately 1:1 mixture of  $[\text{B}_{12}(\text{CN})_{12}]^{2-}$  and

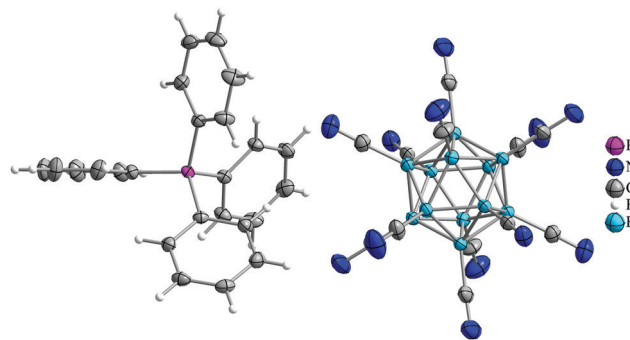


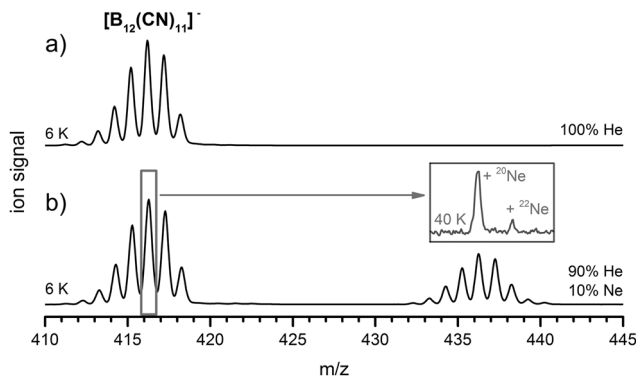
Fig. 2 Part of the crystal structure of  $[\text{PPh}_4]_2[\text{B}_{12}(\text{CN})_{12}]$ . The disordered iodine atoms and the second  $[\text{PPh}_4]^+$  cation were omitted for clarity. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are shown with arbitrary radii. The averaged B–C (1.541 Å, *cf.* 1.541 Å in ref. 18 and 1.538 Å on the B3LYP/def2-QZVPP level) and C≡N bond lengths (1.130 Å) in the free  $[\text{B}_{12}(\text{CN})_{12}]^{2-}$  anion are in accord with those in the very recently published Cu-complex  $(\text{CH}_3\text{CN})_3\text{Cu}[\mu-\text{B}_{12}(\text{CN})_{12}]\text{Cu}-(\text{CH}_3\text{CN})_3$  (1.134 and 1.549 Å)<sup>18</sup> and quantum chemically predicted values using the B3LYP/def2-QZVPP method (1.150 and 1.538 Å).

$[\text{B}_{12}(\text{CN})_{11}\text{I}]^{2-}$ . From the latter product single crystals of the solid solution of  $[\text{B}_{12}(\text{CN})_{12}]^{2-}$  and  $[\text{B}_{12}(\text{CN})_{11}\text{I}]^{2-}$  as  $[\text{PPh}_4]^+$  salt could be obtained (Fig. 2). For details on synthesis and characterization see ESI.†

For a first orientation, we performed high-level computational investigations to obtain a reasonable estimate of the binding energy of He and Ne to  $[\text{B}_{12}(\text{CN})_{11}]^-$ . Details of the calculations can be found in the ESI.† Based on dispersion-corrected B3LYP/def2-QZVPP and on an SCS-MP2 basis-set limit approach, 0 K attachment enthalpies of around 0 to  $-2 \text{ kJ mol}^{-1}$  for He and  $-6$  to  $-9 \text{ kJ mol}^{-1}$  for Ne binding are found. This means that the existence of  $[\text{B}_{12}(\text{CN})_{11}\text{Ne}]^-$  should in principle be possible.

Observation of spontaneous binding of a reagent to a reactive ion in the gas phase requires several preconditions, even if the bond formation is energetically favorable. Energy from the collision event is redistributed within the internal degrees of freedom of the molecular ion, making the ion ‘hot’. Cooling by collisions with cold background gases can stabilize the product, however, very weak bonds do often not survive the necessary timeframe for collisional cooling. Here, we used an ion trap cryogenically cooled to  $\sim 6 \text{ K}$ .<sup>20</sup> The internal temperature of captured ions under these conditions is typically estimated to be slightly higher which can be rationalized by absorption of infrared blackbody radiation, radiofrequency heating and inefficient energy transfer.<sup>21</sup> Generation and isolation of  $[\text{B}_{12}(\text{CN})_{11}]^-$  was performed following previously described procedures.<sup>16</sup> He gas was introduced as a buffer gas for cooling of the ions. Even at the lowest temperatures amenable in our experiments, spontaneous He binding to this ion was not observed (Fig. 3a). However, when we mixed the He gas with 10% of Ne, a signal 20 mass units higher than  $[\text{B}_{12}(\text{CN})_{11}]^-$  was observed, see Fig. 3b. The ion trap temperature was heated in steps of 5 K. The additional signal was clearly visible up to an ion trap temperature of 45 K. At around 50 K, the intensity dropped below a signal to noise ratio of 3:1 using our standard experimental settings (see ESI†). At 40 K ion trap





**Fig. 3** Mass spectrum observed after isolation of  $[B_{12}(CN)_{11}]^-$  in a cryogenic ion trap (a) filled with pure He and (b) filled with a gas mixture of Ne and He. The inset shows the product signal observed after isolation of ions with boron isotopic combination  $^{10}B_2^{11}B_{10}$  at  $m/z$  416 which have added Ne.

temperature, we isolated all ions with  $m/z$  416 (width of one mass unit, marked grey in Fig. 3b). These ions of the composition  $[^{10}B_2^{11}B_{10}(CN)_{11}]^-$  lead to the ions  $[^{10}B_2^{11}B_{10}(CN)_{11}^{20}Ne]^-$  and  $[^{10}B_2^{11}B_{10}(CN)_{11}^{22}Ne]^-$  after reaction with Ne gas. The two product signals, which reflect the natural isotopic distribution of Ne (inset in Fig. 3b), evidence that the observed signal indeed corresponds to the Ne-bound product. This constitutes the first observation of a thermodynamically bound Ne containing anion.

Remarkably, calculated attachment enthalpies and experimental results show consistently that Ne-binding is substantially preferred over He-binding in the case of  $[B_{12}(CN)_{11}]^-$ . As discussed above, this is in contrast to many theoretical investigations on other highly reactive binding sites which have shown that the dative bond to Ne is weaker than to He.<sup>12–14</sup> Thus, other interactions than the direct Ne–B bond may be of critical relevance. Electrostatic and dispersion forces play a significant role for the binding properties of the electrophilic anions of type  $[B_{12}X_{11}]^-$ .<sup>16</sup> The positive binding site lies in a “crater” of negatively charged substituents. Compared with He, the better polarizability of Ne results in stronger dispersion interactions. This hypothesis is corroborated by a complementary bonding analysis (Table 1). The B–Ne bond (2.09 Å) is predicted to be significantly longer than the B–He bond (1.59 Å) and even longer than the B–Ar bond with 1.98 Å.<sup>16</sup> Natural population analysis (NPA)<sup>22</sup> predicts a positive

charge of +0.1e for the bound Ne, while the atomic charge of the bound He is more than doubled (+0.2e). This indicates that He has provided more electron density to the positive boron in the anion than Ne, although He is less polarizable. A Quantum Theory of Atoms in Molecules (QTAIM)<sup>23</sup> analysis shows that the electron density  $\rho$  and the energy density  $H$  at the bond critical point (bcp) are smaller in the case of the B–Ne bond compared to the B–He bond. Also, the delocalization index  $\delta$ , which is often discussed as a measure of covalent bond order, is significantly lower in the case of Ne. This indicates consistently that the direct interaction is indeed weaker for B–Ne than for B–He. It follows that the stronger binding of Ne must have another origin.

We performed an energy decomposition analysis (EDA)<sup>24</sup> to partition the interactions between the two binding partners  $[B_{12}(CN)_{11}]^-$  and Ne/He into orbital interactions, electrostatics, Pauli repulsion and dispersion forces, see Table 1. The total interaction energy calculated by this method is higher for Ne than for He. We note that this quantity is not directly comparable to the previously discussed 0 K attachment enthalpies, because (i) optimization of the separated binding partners is not part of the EDA and (ii) different base functions are used for the calculation (see details in the ESI†). All contributions with the exception of dispersion are significantly lower in their absolute number for Ne than for He. In particular, the contribution of the orbital interaction, which can be associated with the directed B–Ne bond, is smaller. Note that also the Pauli repulsion is smaller due to the large bond length, which significantly contributes to the higher interaction energy with Ne.

The upper temperature limit of the  $[B_{12}(CN)_{11}Ne]^-$  detection in our instrument (50 K) is remarkable, because it lies significantly above the Ne condensation temperature of 25 K.<sup>25</sup> We note that so-called low temperature “tagging” of ions with small noble gas atoms is a common process used in spectroscopy<sup>26</sup> and was observed in similar instrument for Ne and some cations at roughly 10 K.<sup>26</sup> In contrast, to the best of our knowledge, Ne tagging to anions has not been reported. This underlines that the observed binding of Ne is not a low temperature condensation effect but the result of a significant chemical interaction.

To study the influence of a counteranion, a  $Na^+$  cation was positioned at several different locations on the surface of the

**Table 1** Attachment enthalpy of Ng (He, Ne) to  $[B_{12}(CN)_{11}]^-$  and bonding analysis of the B–Ng bonds (B3LYP-GD3BJ/def2-QZVPP) and EDA results (B3LYP-GD3BJ/AUG/ATZP) for details, see text

Ng		He	Ne
Ng attachment enthalpy (0 K), $\text{kJ mol}^{-1}$		–1.3	–8.9
Bond length, Å		1.59	2.09
$\rho_{\text{bcp}}$ , $e \text{ \AA}^{-3}$		0.27	0.16
$H_{\text{bcp}}/\rho_{\text{bcp}}$ , $\text{Ha } e^{-1}$		–0.45	–0.22
$\delta$		0.20	0.14
$Q_{\text{NPA}}$ bound Ng, $e$		+0.22	+0.11
Energy components (EDA)	Orbital interaction, $\text{kJ mol}^{-1}$	–75.0	–33.0
	Electrostatics, $\text{kJ mol}^{-1}$	–23.3	–17.1
	Pauli repulsion, $\text{kJ mol}^{-1}$	+93.4	+44.8
	Dispersion, $\text{kJ mol}^{-1}$	–5.7	–8.0
	Total interaction energy, $\text{kJ mol}^{-1}$	–10.6	–13.2



$[\text{B}_{12}(\text{CN})_{11}\text{Ne}]^-$  anion. Substitution of the Ne atom is not favorable, since the  $\text{Na}^+$  cation has no binding tendency towards the positive boron site, which binds the Ne atom. Instead the energetically lowest lying configuration was found by positioning the  $\text{Na}^+$  cation close to the most negatively charged surface of the anion, which lies on the backside of the Ne binding site, see ESI.† The counterion further polarizes the anion and attracts its electron density. This increases the positive charge of the reactive boron atom and therefore the calculated 0 K attachment enthalpy of Ne by nearly 30%. Further information on the energy of different  $\text{Na}^+$  position isomers, changes in QTAIM and NPA parameters in comparison to the free anion can be found in the ESI.† We conclude that in contrast to noble gas binding cations, the presence of a counterion strengthens the boron–neon bond and does not lead to dissociation confirming a recent theoretical study.<sup>27</sup>

The practical realization of condensed phase salts like  $\text{Na}[\text{B}_{12}(\text{CN})_{11}\text{Ne}]$  still bears significant challenges: no synthesis procedures exists to generate the key anion  $[\text{B}_{12}(\text{CN})_{11}]^-$  outside a mass spectrometer. However, molecular ion deposition methods have recently shown significant progress in the generation of condensed phase material layers on surfaces.<sup>28</sup> Very recently new experimental setups were introduced which enable high frequency switching between anion and cation deposition.<sup>29</sup> This allows salt formation from combined gaseous cations and anions. This method may be combined with an ultrahigh vacuum approach allowing deposition on a cryogenically cooled target in the presence of an introduced Ne background atmosphere. Then, the formation of the mentioned type of salts may be possible.

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## Conflicts of interest

There are no conflicts to declare.

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