Boron Coordination

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The $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ Complexes Featuring the Smallest π-Aromatic Species B_3^+

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Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday

Abstract: *We report the spectroscopic identification of the $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ complexes, which feature the smallest π-aromatic system B_3^+. A quantum chemical bonding analysis shows that the adducts are mainly stabilized by L→$[B_3L_2]^+$ σ-donation.*

Much progress has been made in recent years in the synthesis of one- and two-center boron species that exhibit unusual chemical bonds. A tricoordinated borylene complex CAAC→B(H)←CAAC, where boron atom is a Lewis base that is stabilized by carbene ligands (CAAC = cyclic alkyl amino carbene), was synthesized by Bertrand and co-workers.[1] The related dicarbonyl complex OC→B(R)←CO (R = bulky aryl group) was recently reported by Braunschweig et al.[2] The same group isolated diatomic B_2 in the NHC→B≡B←NHC (NHC = N-heterocyclic carbene) complex, which features a boron–boron triple bond.[3,4a] They also synthesized the related adducts NHC^s→B≡B←NHC^s (NHC^s = saturated NHC)[4b] and CAAC→B≡B←CAAC.[4c] The variation of the π-acceptor strength of the carbene ligands L modulates the L←B≡B→L π-backdonation, and correlates nicely with the B–B bond lengths in the complexes[4] which supports the model of dative bonding.[5] Prior to this, the dicarbonyl complexes OC→B≡B←CO and [OB→B≡B←BO]$^{2-}$, which are molecules with all-triple bonds,[6] have been experimentally observed.[7]

We now report the extension of stabilizing one- and two-center boron species L→B_n←L with donor-ligands L to three-center cyclic boron complexes $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ where the cyclic B_3^+ cation is ligated by three N_2 and CO ligands, respectively. The eight valence-electron species B_3^+ has two π-electrons which are delocalized over the three-membered ring and thus, it is the smallest π-aromatic system that has been spectroscopically characterized. The related NHC complex $[B_3(NHC)_3]^+$ was the subject of a previous theoretical study,[8] but it was not observed until now. The molecules $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ are the first three-center complexes of main-group atoms that are stabilized through dative bonds by CO and N_2. Heavier group-13 homologues of gallium have been synthesized as salt compounds $[Ga_3R_3][M_2]$ (M = Na, K; R = bulky aryl group), which were the first cyclogallanes that were structurally characterized.[9] The related aluminum systems $[Al_3R_3][M_2]$ have also been isolated.[10] Theoretical studies of the parent systems $[E_3H_3]^{2-}$ (E = B, Al, Ga) showed that the dianions are 2π-aromatic species,[9b,11] similar to the cation $[B_3L_3]^+$. The $[E_3R_3][M_2]$ (E = Al, Ga) systems have E-R electron-sharing bonds, while $[B_3L_3]^+$ has donor–acceptor bonds. Figure 1 displays the bonding situation in $[E_3R_3]^{2-}$ and $[B_3L_3]^+$.

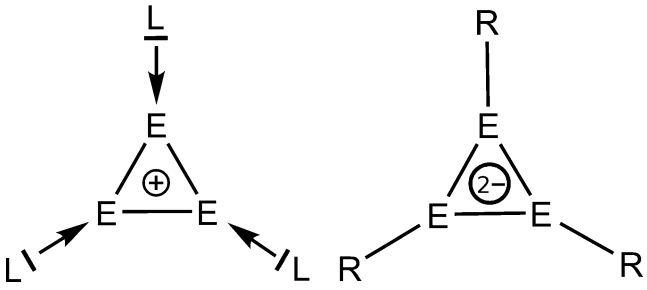

Figure 1. Representation of the bonding situation in a) cyclic group-13 cation complex $[E_3L_3]^+$ which has L→E dative bonds, and b) cyclic group-13 dianion which has R-E electron-sharing bonds. Both systems are 2π-aromatic species.

The boron–dinitrogen and boron–carbonyl cation complexes were generated in the gas phase using a pulsed laser vaporization/supersonic expansion ion source, and were studied by infrared photodissociation spectroscopy in the ligand-stretching vibrational frequency region as described previously.[12] A typical mass spectrum of boron dinitrogen cation complexes produced using a ^{11}B target in the *m*/*z* range of 60–160 is shown in Figure 2a. The spectrum is dominated by mononuclear BN_n^+ (n = 5–10) cation complexes. Peaks owing to $[B_2(NN)_3]^+$ and $[B_3(NN)_3]^+$ are the most intense multinuclear species in the mass spectra. The $[B_3(NN)_3]^+$

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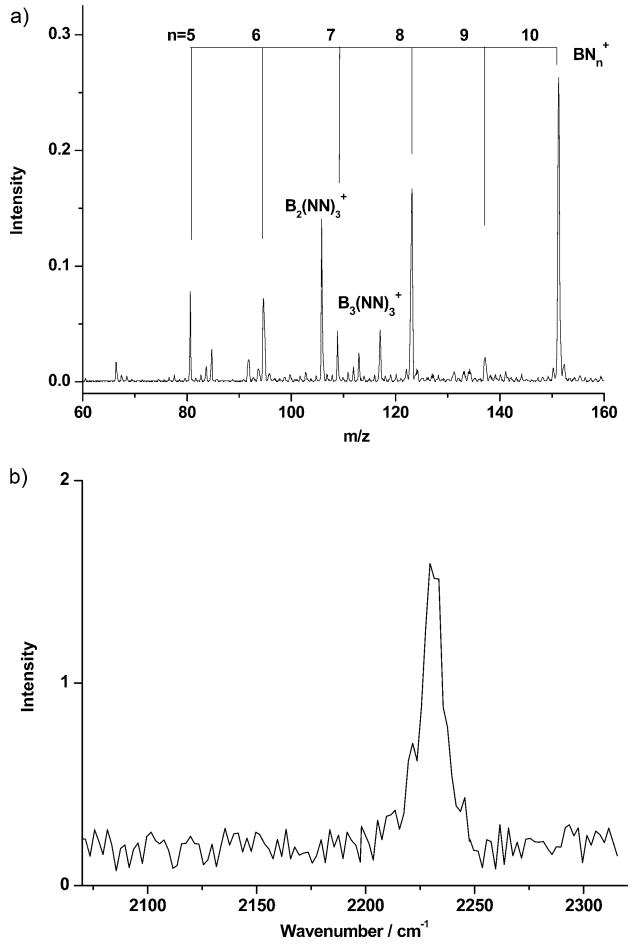

Figure 2. a) Mass spectrum of the boron–nitrogen cation complexes. The cations are formed by pulsed laser vaporization of a boron-11 target in an expansion of helium doped with dinitrogen. b) Experimental IR spectrum of the $[B_3(NN)_3]^+$ cation complex. The spectrum is measured by monitoring the N_2 fragmentation channel leading to the formation of $[B_3(NN)_2]^+$.

cation is mass-selected for infrared photodissociation. When the infrared laser is on resonance with one of the vibrational fundamentals of the cation complex, it photodissociates by losing one N_2 ligand with low efficiency (less than 2%). The signal detected is likely due to a multiphoton process, which is not expected to be very efficient at the low laser pulse energies used here (about 2 mJ/pulse). The resulting infrared photodissociation spectrum of $[B_3(NN)_3]^+$ is shown in Figure 2b. The experimental spectrum exhibits a single band centered at 2232 cm^{-1}, indicating a high symmetric structure. The band position is shifted by 98 cm^{-1} to the red from the frequency of gas phase N_2 (2330 cm^{-1}).[13]

The mass spectrum of boron-carbonyl cation complexes in the *m*/*z* range of 60–160 is shown in Figure S1. The most intense peaks correspond to $[B(CO)_3]^+$ and $[B_2(CO)_4]^+$, suggesting that these cations are formed preferentially. The $[B_3(CO)_3]^+$ cation complex is also formed with appreciable intensity. It dissociates by losing a CO ligand when excited with infrared light around the 2190 cm^{-1} frequency region, but the dissociation efficiency (less than 0.5%; Supporting Information, Figure S2) is too low to achieve an effective spectrum, indicating that this cation has a higher binding energy than that of $[B_3(NN)_3]^+$. Nevertheless, the recorded signal of 2190 cm^{-1} for the C–O stretching mode suggests a blue shift of 47 cm^1 relative to free CO (2143 cm^{-1}).[13]

We carried out high-level ab initio calculations of $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ using coupled-cluster theory at the CCSD(T)/cc-pVTZ level[14] to validate the identity of the cations and to analyze their electronic structure. Figure 3a shows the theoretically predicted geometries of the two complexes and the fragments (X^1A_1') B_3^+, N_2, and CO. The calculated bond lengths of the diatomic species agree very well with experimental data. Previous theoretical studies showed that B_3^+ has a D_{3h} equilibrium geometry and an X^1A_1' electronic ground state.[15] Alexandrova and co-workers

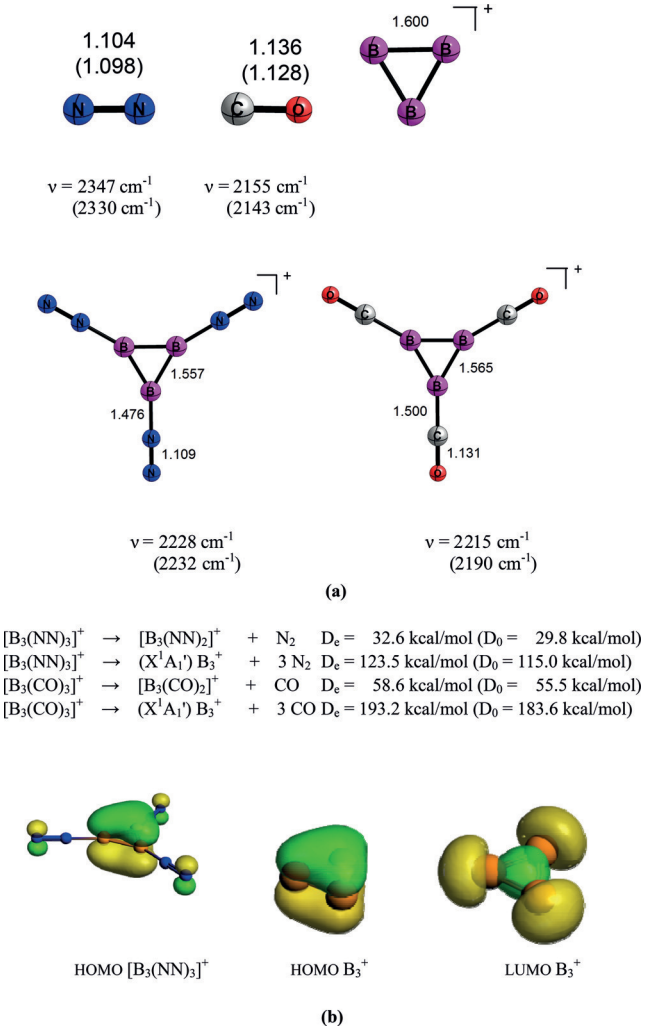

Figure 3. a) Calculated (experimental) equilibrium geometries of the complexes $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ and the fragments (X^1A_1') B_3^+, N_2, and CO at CCSD(T)/cc-pVTZ. Bond lengths are given in Å. Calculated (experimental) vibrational frequencies of the N–N and C–O stretching modes at LCCSD(T)/cc-pVTZ. Experimental values for N_2 and CO were taken from Ref. [13]. Calculated bond dissociation energies D_e and D_o at CCSD(T)/cc-pVTZ. The zero-point energy corrections were taken from LCCSD(T)/cc-pVTZ calculations. b) Plot of molecular orbitals at BP86/TZ2P+: HOMO of $[B_3(NN)_3]^+$, HOMO of (X^1A_1') B_3^+ and LUMO of (X^1A_1') B_3^+.

mention in a review about neutral and charged all-boron clusters B_n^q ($n=2$–6) that B_3^+ is a 2π-aromatic species.[16]

The calculations suggest that the B–B lengths in the complexes $[B_3L_3]^+$ are significantly shorter (1.557 Å for L = N_2 and 1.565 Å for L = CO) than in free B_3^+ (1.600 Å). Also, the N–N bonds in $[B_3(NN)_3]^+$ (1.109 Å) are a bit longer than in N_2 (1.104 Å), while the C–O bond in $[B_3(CO)_3]^+$ becomes a bit shorter (1.131 Å) compared with CO (1.136 Å). We calculated the vibrational spectra of the complexes using local coupled-cluster theory at the LCCSD(T)/cc-pVTZ level,[14] because frequency calculations at CCSD(T)/cc-pVTZ are not feasible for us. The optimized geometries of the molecules at LCCSD(T)/cc-pVTZ are very similar to the CCSD(T)/cc-pVTZ structures (Supporting Information). The computed stretching modes at LCCSD(T)/cc-pVTZ are in agreement with the changes of the bond lengths in $[B_3L_3]^+$: a red shift of the highest-lying IR active N–N stretching mode[17] of $\Delta\nu = 119\ cm^{-1}$ for $[B_3(NN)_3]^+$, while the C–O stretching frequency of $[B_3(CO)_3]^+$ exhibits a blue-shift by $\Delta\nu = 60\ cm^{-1}$ (Figure 3). The excellent agreement of the size and the direction of the C–O and N–N frequency shifts $\Delta\nu$ strongly supports the assignment of the complexes $[B_3(NN)_3]^+$ and $B_3(CO)_3^+$ to the spectroscopic data. The complete data of the calculated vibrational frequencies are given in the Supporting Information (Table S1). Figure 3 also shows the calculated bond dissociation energies (BDEs) for loss of one or three ligands L from $[B_3L_3]^+$. The calculations suggest that the CO ligands are more strongly bonded than N_2, which agrees with the smaller efficiency of the photodissociation.

Figure 3b shows a plot of the highest occupied molecular orbital (HOMO) of $[B_3(NN)_3]^+$ which resembles the undisturbed HOMO of naked (X^1A_1') B_3^+ that is also shown. The equivalent HOMO of $[B_3(CO)_3]^+$ looks very similar (Supporting Information, Figure S3). The shape of the HOMO indicates that the all-boron systems B_3^+ and $[B_3L_3]^+$ are two π-electron aromatic species. We estimated the aromaticity in the molecules with the nuclear independent chemical shift (NICS) method[18] and compared it with the classical two π-electron aromatic cyclopropenyl cation $C_3H_3^+$. The calculated NICS(1) values, which were suggested as reliable indicators of aromaticity in non-fused cyclic systems,[19] predict that all-boron cations possess significant aromatic character with decreasing order B_3^+ (−18.4 ppm) > $C_3H_3^+$ (−14.6 ppm) > $[B_3(CO)_3]^+$ (−13.2 ppm) > $[B_3(NN)_3]^+$ (−11.6 ppm).[20]

Figure 3b shows the lowest unoccupied molecular orbital (LUMO) of naked (X^1A_1') B_3^+, which is perfectly suited for $L_3 \rightarrow B_3^+$ σ-donation. We analyzed the nature of the donor–acceptor bonds of $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ with the energy decomposition analysis with natural orbitals of chemical valence (EDA-NOCV)[21] method.[22] The numerical results are given in Table 1. The strongest attraction between the ligand and the remaining fragment $L \rightarrow [B_3L_2]^+$ comes from the orbital interactions ΔE_{orb}. The largest contribution to ΔE_{orb} arises from the σ-donation of the lone-pair orbitals of the ligands N_2 and CO to the LUMO of (X^1A_1') B_3^+. This is nicely shown in Figure 4 which depicts the deformation

Table 1: Energy decomposition analysis of $[B_3L_3]^+$ at the BP86/TZ2P+ level using CCSD(T)/cc-pVTZ optimized geometries. Energy values are given in kcal mol^{-1}.

Fragments	$[B_3(NN)_2]^+ + N_2$	$[B_3(CO)_2]^+ + CO$
ΔE_{int}	−50.7	−76.9
ΔE_{Pauli}	171.6	202.4
ΔE_{elstat} [a]	−79.3 (35.6%)	−100.2 (35.9%)
ΔE_{orb} [a]	−143.0 (64.3%)	−179.1 (64.1%)
ΔE_{orb} (1)[b] $L \rightarrow [B_3(L)_2]^+$ σ-donation	−83.6 (58.5%)	−112.3 (62.7%)
ΔE_{orb} (2)[b] $L \leftarrow [B_3(L)_2]^+$ $\pi_{\parallel}$-backdonation	−20.3 (14.2%)	−26.7 (14.9%)
ΔE_{orb} (3)[b] $L \leftarrow [B_3(L)_2]^+$ $\pi_{\perp}$-backdonation	−18.5 (12.9%)	−19.6 (10.9%)
ΔE_{orb}(rest)[b] polarization	−20.6 (14.4%)	−20.5 (12.2%)

[a] The value in parentheses gives the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] The value in parentheses gives the percentage contribution to the total orbital interactions ΔE_{orb}.

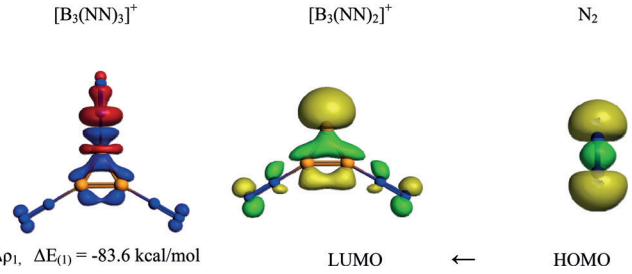

Figure 4. Plot of the deformation densities $\Delta\rho$ of the pairwise orbital interactions between $[B_3(NN)_2]^+$ and N_2 in $[B_3(NN)_3]^+$ and associated stabilization energies ΔE in kcal mol^{-1}. The color code of the charge flow is red→blue. Shape of the most important interacting orbitals of $[B_3(NN)_2]^+$ and N_2.

density $\Delta\rho$ that is associated with the σ-donation NN→$[B_3(NN)_2]^+$ in the dinitrogen complex. The color code for the charge flow is red→blue. The connected donor and acceptor orbitals of the fragments N_2 and $[B_3(NN)_2]^+$ are also shown in Figure 4. The shape of the deformation densities and the associated orbitals reveal that the NN→$[B_3(NN)_2]^+$ σ-donation enhances also the B–B bonding in the ring which explains the bond shortening with respect to free (X^1A_1') B_3^+. Note that the L←$[B_3L_2]^+$ π-backdonation (Table 1) which comes from the in-plane $\pi_{\parallel}$ orbital is stronger (−20.3 kcal mol^{-1} for L = N_2 and −26.7 kcal mol^{-1} for L = CO) than the contribution of the out-of-plane $\pi_{\perp}$ MO (−18.5 kcal mol^{-1} for L = N_2 and −19.6 kcal mol^{-1} for L = CO) which is the source of the aromaticity. The deformation densities $\Delta\rho$ and the associated fragments orbitals for the L←$[B_3(NN)_2]^+$ π-backdonation and the donation and backdonation in $[B_3(CO)_3]^+$ are shown in the Supporting Information (Figure S4).

The elongation of the N–N bonds in the complex $[B_3(NN)_3]^+$ relative to free N_2 can be explained with the N–N bonding nature of the σ-donor orbital and the antibonding π*-acceptor orbital of dinitrogen. The bond-shortening of the C–O bond in non-classical carbonyl complexes,[23] where CO is mainly a σ-donor, has been shown to come from the change in the polarization of the orbitals when electronic charge is withdrawn from the carbon atom.[24] A similar effect has recently been observed in the complex $[OC(BeCO_3)]$, where the origin of the C–O bond shortening was discussed in detail.[22] The atomic partial charges of the NBO method[25

agree with the strong σ-donation in the complexes. The partial charge at the cyclic B_3 moiety is −0.06 e in $[B_3(NN)_3]^+$, which indicates that the positive charge of the cation is completely localized at the more electronegative dinitrogen ligands. Even stronger donation $3\,CO \rightarrow B_3^+$ is found in the tricarbonyl complex $[B_3(CO)_3]^+$, where the partial charge of B_3 is −0.38 e.

It is illuminating to compare the bonding situation in B_3^+ and $[B_3L_3]^+$ with B_3^-. The latter anion has two more electrons than the cation, and thus the LUMO of B_3^+ (Figure 3b) is occupied in B_3^- where it becomes the HOMO. The latter orbital has been declared as the source of σ aromaticity, because it is a delocalized 2σ electron system that apparently agrees with the $4n+2$ rule.[16,26] Therefore, it is claimed that B_3^- is a double (σ and π) aromatic species, while B_3^+ exhibits 2π aromaticity but no σ aromaticity.[16,27] It may now be argued that $[B_3L_3]^+$ also possesses some σ aromaticity, because the L→B interaction leads to partial occupation of the LUMO of B_3^+. We refrain from discussing the possible degree of σ aromaticity in $[B_3L_3]^+$ because we are not convinced that the stabilization has a genuine aromatic origin. There is no doubt that there is some stabilization in the B_3^+ fragment of the complex that comes from the partial occupation of the delocalized LUMO of the cation. This can be seen from the shortening of the B–B bonds. However, delocalization does not automatically indicate aromaticity. The B_3^- has a total of four doubly occupied σ orbitals, which makes it an 8 σ electron system that would be an antiaromate according to the Hückel rule. It is somewhat artificial to discard the three lower-lying σ orbitals and to declare it a 2 σ aromate. But there is no doubt that $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$ are genuine 2 π aromatic species.

After this manuscript was submitted, a work by Braunschweig and co-workers appeared that reported the synthesis of the triboracyclopropenyl dianion $[B_3(NCy)_3]^{2-}$ (Cy = *cyclo*-C_6H_{11}) which was isolated as the dimeric salt ($Na_4[B_3(NCy)_3]_2\cdot 2\,DME$) where DME = 1,2-dimethoxyethane.[28] The molecule is the boron analogue of the heavier systems $[E_3R_3][M_2]$ (E = Al, Ga).[9,10] The bonding analysis gave clear evidence that $[B_3(NCy)_3]^{2-}$ is a Hückel 2π aromate. The latter dianion and the $[B_3L_3]^+$ cations that are reported here exhibit the bonding situations that are shown in Figure 1. They are examples of the lightest possible main-group element Hückel π aromate.[29] It is interesting that the 2π aromaticity is found in both the eight-electron cation B_3^+ and in the eleven-electron dianion B_3^{2-}.

In summary, we report the first spectroscopic identification of the complexes $[B_3(NN)_3]^+$ and $[B_3(CO)_3]^+$, which feature the smallest π-aromatic system B_3^+. A quantum chemical bonding analysis shows that the adducts are mainly stabilized by $L \rightarrow [B_3L_2]^+$ σ-donation. The results may be considered as exploration of a new field of ligand-stabilized boron complexes B_3L_3, which may be extended to main-group adducts E_nL_n with other atoms and ligands and larger cycles.

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