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OCBBCO: A Neutral Molecule with Some Boron–Boron Triple Bond Character

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It is generally known that the bond order between two p-block main group elements is always lower than the number of element valence electrons in known compounds.^{1–3} Recently, a gallyne Na₂[Mes*₂C₆H₃–GaGa–C₆H₃Mes*₂] (Mes* = 2,4,6-i-Pr₃C₆H₂) was synthesized and characterized as the first example of a triple bond between group 13 metals.⁴ Each Ga atom in this dianion holds four valence electrons. The triple bond assignment has been questioned, and this stimulated several theoretical investigations and hot discussions.^{5–11} Molecules containing boron–boron multiple bonds are extremely rare due to the electron-deficient nature of boron. Boron–boron double-bonded species such as diborate dianions have been synthesized,^{12,13} and a boron–boron double-bonded model molecule, HBBH, has also been characterized experimentally in matrices.¹⁴ In this report, we present experimental and theoretical evidence for a neutral boron–boron multiply bonded molecule: OCBBCO.

Matrix isolated OCBBCO molecules were produced by co-deposition of laser vaporized boron atoms with CO in excess argon at 8 K and investigated using Fourier transformed infrared spectroscopy.¹⁵ With the aid of the isotopic substitution technique, matrix isolation infrared absorption spectroscopy can provide unique structural information on ground-state molecules. Recent studies have shown that matrix isolation infrared spectroscopy combined with quantum chemical calculation is very powerful in investigating the spectrum, structure, and bonding of novel species.¹⁶

The BCO molecule is the primary reaction product observed after sample deposition.¹⁷ New product absorptions were produced on sample annealing (Table 1). The absorptions at 2014.2, 1100.2, 1086.1, and 517.1 cm^{–1} can be grouped together on the basis of their growth/decay characteristics measured as a function of changes of experimental conditions. The spectra in the 1150–1050 cm^{–1} region using different isotopic substituted CO are shown in Figure 1. The spectra clearly demonstrated that the new product molecule involves two equivalent B and two equivalent CO subunits and is assigned to an OCBBCO molecule. The band at 2014.2 cm^{–1} is due to the CO stretching mode (σ_u).¹⁸ The bands at 1100.2 and 1086.1 cm^{–1} in experiments with natural abundance boron target are assigned to the BC stretching mode (σ_u) of OC¹⁰B¹¹BCO and OC¹¹B¹⁰BCO molecules. The OC¹⁰B¹⁰BCO counterpart is observed at 1116.5 cm^{–1} with a ¹⁰B-enriched target. This band is very weak in experiments with a natural abundance boron target (about 1/16 the intensity of OC¹¹B¹¹BCO. With natural abundance boron, a vibrational mode which involves two equivalent boron atoms will split into three absorptions with approximately 1:8:16 relative intensities.) Absorption at 517.1 cm^{–1} is due to BCO bending vibration (π_u).

Table 1. Observed and Calculated (B3LYP) Vibrational Frequencies (cm^{–1}) and Isotopic Frequency Ratios for the OC¹¹B¹¹BCO Molecule

| | freq ^a | | ¹⁰ B/ ¹¹ B | | ¹² C/ ¹³ C | | ¹⁶ O/ ¹⁸ O | |
|------------|-------------------|------------------|----------------------------------|--------|----------------------------------|--------|----------------------------------|--------|
| | calc ^b | obs ^c | calc | obs | calc | obs | calc | obs |
| σ_u | 2107 | 2014.2 | 1.0013 | 1.0011 | 1.0261 | 1.0255 | 1.0183 | 1.0176 |
| σ_u | 1091 | 1086.1 | 1.0338 | 1.0280 | 1.0017 | 1.0080 | 1.0160 | 1.0123 |
| π_u | 540 | 517.1 | 1.0088 | 1.0083 | 1.0276 | 1.0274 | 1.0076 | 1.0076 |

^a Only the IR active vibrational modes are listed: antisymmetric CO stretching (σ_u), B–C stretching (σ_u), and BCO bending (π_u). ^b The calculated IR intensities of the three modes are 3495, 48, and 29 km/mol, respectively. ^c Two matrix trapping sites were observed, and only the major site absorptions are listed. The relative intensities of the three modes are approximately 1:0.016:0.009.

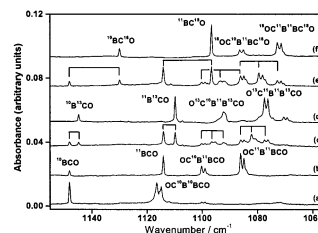


Figure 1. Infrared spectra in the 1155–1055 cm^{–1} region from co-deposition of laser evaporated boron atoms with CO in excess argon. (a) B-10 enriched (97%) target, 0.1% ¹²C¹⁶O; (b)–(f) natural abundance boron target: (b) 0.1% ¹²C¹⁶O, (c) 0.1% ¹²C¹⁶O + 0.1% ¹³C¹⁶O, (d) 0.1% ¹³C¹⁶O (containing 12% ¹³C¹⁸O), (e) 0.1% ¹²C¹⁶O + 0.1% ¹²C¹⁸O, and (f) 0.1% ¹²C¹⁸O.

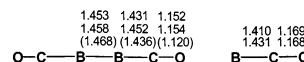


Figure 2. Optimized structures of singlet OCBBCO and quartet BCO at (U)B3LYP/6-311+G(d), (U)CCSD(T)/6-311+G(d), and CAS(4, 4)/6-311+G(d) (in parentheses) levels of theory. Bond lengths are given in Å.

To support the experimental assignment and to provide insight into the structure and bonding in OCBBCO, we turn to quantum chemical calculations.¹⁹ The calculation shows that the RHF wave function of singlet OCBBCO has an internal RHF/UHF instability. Therefore, we perform DFT calculations using the broken-symmetry unrestricted wave function (Figure 2). The linear triplet state OCBBCO was calculated to be about 20.5 kcal/mol higher in energy than the linear singlet. The structure with two bridging CO's was predicted to have a triplet ground state and is about 42.7 kcal/mol less stable than the linear singlet at the (U)B3LYP/6-311+G(d) level of theory. The calculated vibrational frequencies and isotopic frequency ratios (Table 1) are in excellent agreement with the experimental values.

The multireference-based CASSCF approach is used to describe the singlet OCBBCO molecule. At the CAS(4,4)/6-311+G(d) level, the dominant configuration of the singlet ground-state OCBBCO

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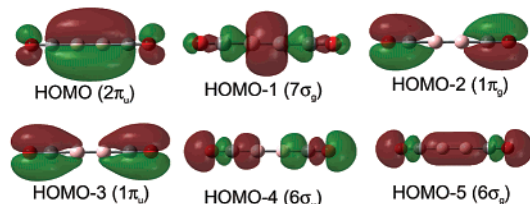


Figure 3. Molecular orbital pictures of singlet OCBBCO, showing the HOMO ($2\pi_u$) down to the fifth valence molecular orbital from the HOMO. HOMO, HOMO-2, and HOMO-3 each consist of two degenerate pairs, and only one of them was plotted.

is (core) $(6\sigma_g)^2 (6\sigma_u)^2 (1\pi_u)^4 (1\pi_g)^4 (7\sigma_g)^2 (2\pi_u)^4$.²⁰ The molecule can be viewed as the interaction of a closed-shell excited-state B_2 in $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (1\pi_u)^4 (2\sigma_u)^0 (3\sigma_g)^0$ configuration and two CO's. Figure 3 shows the one-electron molecular orbital pictures from HOMO down to the fifth valence molecular orbital from the HOMO of the dominant configuration. The doubly degenerate HOMO is the B–B π bonding orbitals, which comprise $B_2 1\pi_u \rightarrow CO \pi^*$ back-bonding. The HOMO-1 is a B–B σ bonding orbital. The doubly degenerate HOMO-2 and HOMO-3 are primary C–O π bonding orbitals. The HOMO-4 and the HOMO-5 comprise $5\sigma \rightarrow B_2 2\sigma_u$ and $3\sigma_g$ donation, which are B–B antibonding and bonding in character, respectively. Therefore, singlet OCBBCO exhibits some boron–boron triple bond character. The Lewis structure can be drawn as $O \equiv C - B \equiv B - C \equiv O$, which satisfies the octet rule.

The OCBBCO molecule was calculated to have a very short B–B bond length. At the (U)B3LYP/6-311+G(d) level of theory, the B–B bond length was predicted to be 1.453 Å, significantly shorter than the B–B double bond experimentally characterized (1.57–1.59 Å).^{12,13} Calculations at (U)CCSD(T)/6-311+G(d) and CAS(4,4)/6-311+G(d) levels gave a slightly longer B–B bond length (1.458 and 1.468 Å). Comparison calculations were done on the HBBH model molecule, which has been characterized to have a $^3\Sigma_g^-$ ground state with a typical B–B double bond.^{14,21} The B–B bond length was calculated to be 1.507 Å with B3LYP and 1.519 Å with CCSD(T), 0.054 or 0.061 Å longer than that of the OCBBCO molecule. The $^3\Sigma_g^-$ ground-state B_2 was calculated to have a B–B bond length of 1.571 Å (B3LYP) and 1.603 Å (CCSD(T)), compatible with the experimental value of 1.590 Å.²²

Upon annealing to 25 K, BCO increased markedly, and $B(CO)_2$ and OCBBCO were formed. BCO decreased, while $B(CO)_2$ and OCBBCO kept increasing on further stepwise annealing. BBCO was also observed, but only in high ablation laser energy experiments. This implies that OCBBCO was formed by BCO dimerization and not via B_2 reactions. The BCO molecule has been well studied to have a $^4\Sigma^-$ ground state with the three spins predominantly on the boron atom.²³ The formation of quartet BCO from ground-state B and CO requires $B 2s \rightarrow 2p$ promotion. The growth of BCO and OCBBCO on annealing indicates that little or no activation energy is required for both $B(^2P) + CO \rightarrow BCO (^4\Sigma^-)$ and $2BCO (^4\Sigma^-) \rightarrow OCBBCO$ reactions. The dimerization process involves the formation of one B–B σ bond and two π bonds. The binding energy of OCBBCO with respect to two ground-state BCO molecules was calculated to be 143.5 kcal/mol with B3LYP. At the same theoretical levels, the binding energy of $^3\Sigma_g^-$ HBBH with respect to two ground-state BH molecules was predicted to be 113.0 kcal/mol.

In contrast to boron, the remaining group 13 metal carbonyls prefer to form dibridged $M_2(\mu^2-CO)_2$ molecules.^{24,25} No metal–metal-bonded linear molecules have been observed. Therefore, formation of a linear molecule with some boron–boron triple bond character seems to be unique for boron.

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Supporting Information Available: Experimental observed and calculated isotopic frequencies; calculated total energies and structural parameters of the aforementioned species (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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