Angewandte Chemie International Edition

**Boron Clusters**

DOI: 10.1002/anie.201004755

# Oxidation of *closo*-$[B_{12}Cl_{12}]^{2-}$ to the Radical Anion $[B_{12}Cl_{12}]^{\bullet-}$ and to Neutral $B_{12}Cl_{12}$**

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Compounds containing boron atoms as spin carriers have recently received attention.[1] The icosahedral *closo*-dodecaborate ion $[B_{12}H_{12}]^{2-}$ is the archetypal boron cluster, and thus of special interest. Whereas the parent cluster $[B_{12}H_{12}]^{2-}$ undergoes an irreversible one-electron oxidation with the formation of $[B_{24}H_{23}]^{3-}$,[2] the methylated cluster $[B_{12}Me_{12}]^{2-}$ is oxidized at $+0.44$ V vs. $Ag/Ag^+$ to the air-stable blue radical anion $[B_{12}Me_{12}]^{\bullet-}$.[3] Alkoxy-substituted ions $[B_{12}(OR)_{12}]^{2-}$ are oxidized at an even lower potential and even neutral $B_{12}(OR)_{12}$ could be prepared.[4] Very recently, the perhydroxylated radical $[B_{12}(OH)_{12}]^{\bullet-}$ has been prepared and structurally characterized.[5] Smaller perhalogenated polyborane cluster radical anions $[B_nX_n]^{\bullet-}$ (X = H, Cl, Br, I; $n = 6$, 8–10), which are derived by one-electron oxidation from the corresponding *closo* clusters have been prepared and characterized by chemical and electrochemical methods.[6] Halogen substitution and an increasing cluster size significantly increase the resistance to oxidation and consequently the perhalogenated dodecaborates $[B_{12}X_{12}]^{2-}$ (X = halogen) are much more difficult to oxidize. Oxidation of dodecaborates $[B_{12}X_{12}]^{2-}$ (X = H, F, Cl, Br) to give the corresponding radical anions $[B_{12}X_{12}]^{\bullet-}$ has been investigated theoretically[7] and by electrochemical methods.[8] The stability of $[B_{12}X_{12}]^{2-}$ to oxidation is not only of fundamental interest, but is also gaining importance for possible applications of $Li_2[B_{12}X_{12}]$ in lithium-ion batteries.[9,10] The fluorinated cluster $[B_{12}F_{12}]^{2-}$ undergoes a quasi reversible oxidation at 1.85 V vs. $Ag/Ag^+$ (1.9–2.0 V vs. NHE) to the radical anion $[B_{12}F_{12}]^{\bullet-}$ in ethylene carbonate/dimethyl carbonate solution,[9] whilst in earlier electrochemical investigations, the derivatives containing heavier halogens (X = Cl, Br) did not have a well-defined oxidation wave in acetonitrile.[2a,11] In a recent review, Kaim et al. stated that "*Although the oxidation of $[B_{12}X_{12}]^{2-}$ (X=halogen) via radical anion intermediates $[B_{12}X_{12}]^{\bullet-}$ has been considered, this process is highly irreversible in electrochemical experiments even at low temperatures.*"[1] To date, no $[B_{12}X_{12}]^{\bullet-}$ (X = halogen) radical anions have been isolated and characterized as pure compounds. However, as long ago as 1985, a pale violet color, which rapidly diminished upon contact with air, was observed during dehydration of $H_2B_{12}Cl_{12}\cdot 8H_2O$ and attributed to the radical anion $[B_{12}Cl_{12}]^{\bullet-}$.[12]

In the course of our investigations into the perchlorinated *closo*-dodecaborate $[B_{12}Cl_{12}]^{2-}$ as a weakly coordinating dianion,[13] we prepared, simultaneously with and independently of Reed et al.,[14] the diprotic superacid $H_2B_{12}Cl_{12}$ by reaction of the silylium salt $(Et_3Si)_2B_{12}Cl_{12}$ with gaseous HCl. The reaction proceeds, in agreement with similar investigations by Willner et al., according to Equation (1) (see Supporting Information, Figure S4 for an IR spectrum of the gaseous by-products).[15]

$$(Et_3Si)_2B_{12}Cl_{12} + 8\,HCl \rightarrow H_2B_{12}Cl_{12} + 6\,C_2H_6 + 2\,SiCl_4 \qquad (1)$$

Solutions of $H_2B_{12}Cl_{12}$ in liquid $SO_2$ are stable for a few days at −40 °C, but turn dark-blue within a few minutes above 0 °C. Whilst $H_2B_{12}Cl_{12}$ in liquid $SO_2$ at low temperature shows the typical $^{11}B$ NMR spectrum for the $[B_{12}Cl_{12}]^{2-}$ dianion, the blue solution does not exhibit an $^{11}B$ NMR signal at all (Supporting Information, Figure S5). After removal of the solvent and exposure to air, the $^{11}B$ NMR signal of $[B_{12}Cl_{12}]^{2-}$ reappears (Supporting Information, Figure S8). Thus, we attribute the blue color to the radical anion $[B_{12}Cl_{12}]^{\bullet-}$, which is formed by oxidation of the $[B_{12}Cl_{12}]^{2-}$ dianion by $H^+$ [Eq. (2)]. Furthermore, the successful recovery of the $[B_{12}Cl_{12}]^{2-}$ dianion after hydrolysis, as shown by $^{11}B$ NMR spectroscopy, indicates that the oxidation is reversible.

$$H_2B_{12}Cl_{12} \xrightarrow{SO_2} HB_{12}Cl_{12} + {}^1\!/_2\,H_2 \qquad (2)$$

We then looked for a synthetically straightforward route to the radical anion $[B_{12}Cl_{12}]^{\bullet-}$. The much higher oxidation potential of the halogenated boron clusters compared to $[B_{12}H_{12}]^{2-}$,[2] $[B_{12}Me_{12}]^{2-}$,[3] and $[B_{12}(OR)_{12}]^{2-}$ (OR = OH,[5]

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[**] We are grateful to the Deutsche Forschungsgemeinschaft (DFG) and the Universität Freiburg for financial support, and Prof. Ingo Krossing for support of this work. Prof. Dage Sundholm and Prof. Caroline Röhr are thanked for helpful discussions. M.R. thanks the Deutsche Akademische Austauschdienst (DAAD) for a scholarship and S.R. thanks the Fonds der Chemischen Industrie (FCI) for financial support. Work in Canada was supported by the Natural Sciences and Engineering Research Council (NSERC) and the University of Lethbridge.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004755.

alkoxy[4]) argues against using conventional organic solvents such as acetonitrile.[8] However, the successful generation of $[B_{12}Cl_{12}]^{\bullet-}$ from $H_2[B_{12}Cl_{12}]$ in $SO_2$ suggests that liquid sulfur dioxide might be a suitable solvent. Sulfur dioxide has a very large electrochemical window from −1.1 V to +3.3 V vs. $Fc^{0/+}$ (Fc = ferrocene).[16] Indeed, reactions of the alkali metal salts $M_2[B_{12}Cl_{12}]$ (M = Li, Na, K, Cs) in liquid $SO_2$ with a large excess of the strong oxidizer $AsF_5$ yield dark-blue solutions owing to the presence of $[B_{12}Cl_{12}]^{\bullet-}$ [Eq. (3)].[17]

$$2\,M_2[B_{12}Cl_{12}] + 3\,AsF_5 \xrightarrow{SO_2} 2\,M[B_{12}Cl_{12}] + 2\,M[AsF_6] + AsF_3 \qquad (3)$$

Filtration of the insoluble side-product $M[AsF_6]$ and subsequent removal of the solvent and all volatiles yielded $M[B_{12}Cl_{12}]$, containing the radical anion $[B_{12}Cl_{12}]^{\bullet-}$, as dark-blue solids in essentially quantitative yields. Solid $M[B_{12}Cl_{12}]$ samples are air-sensitive and discolor on exposure to air within less than one minute. The radical anion $[B_{12}Cl_{12}]^{\bullet-}$ is itself a strong oxidizer and may be used for the oxidation of other substrates: For example, the reaction of $[B_{12}Cl_{12}]^{\bullet-}$ with elemental sulfur gives $S_8[B_{12}Cl_{12}]$, which contains the $[S_8]^{2+}$ cation, as shown by Raman spectroscopy. Vibrational spectra of $M[B_{12}Cl_{12}]$ show splitting of the typical signals for the icosahedron, which is in agreement with a reduced symmetry of the boron cluster. Theoretical calculations predict a distortion from $I_h$ to either $T_h$ or $D_{3d}$ symmetry.[7] Solid $M[B_{12}Cl_{12}]$ has an EPR signal that is centered at $g = 2.06$ with a 3.9 mT peak-to-peak line width (Figure 1), thus confirming the presence of an unpaired electron. The large number of theoretical hyperfine lines predicted for the interaction of the unpaired electron spin with the spins of twelve boron and twelve chlorine nuclei (taking into account a vast number of isotopomers) overlap to an inhomogeneously broadened unresolved line. Furthermore, hyperfine anisotropies that persist in the frozen state contribute to line broadening. Concentrated solutions of $M[B_{12}Cl_{12}]$ in liquid $SO_2$ show a very broad $^{11}B$ NMR resonance shifted to high field by about $\delta = 200$ ppm (Supporting Information, Figure S7), the position of which varies depending on temperature and concentration.

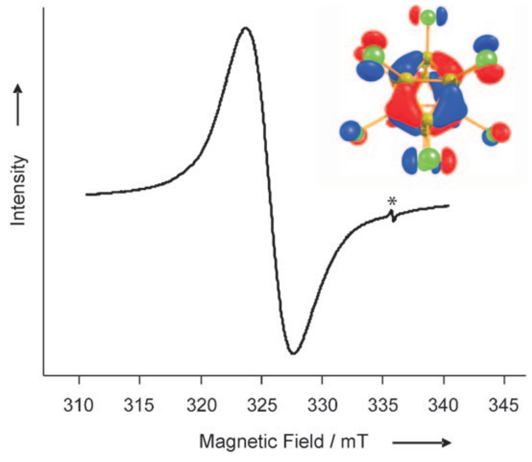

***Figure 1.*** Continuous-wave X-band (9.410 GHz) EPR signal (first derivative with respect to the magnetic field) of solid $Li[B_{12}Cl_{12}]$. Experimental conditions: temperature 15 K, microwave power 12.63 mW, modulation frequency 100 kHz, modulation amplitude 0.1 mT. The asterisk marks a signal of an unknown impurity. The insert in the right top corner represents the SOMO of $[B_{12}Cl_{12}]^{\bullet-}$ in $T_h$ symmetry.

Previous attempts to study the electrochemical behavior of $[B_{12}Cl_{12}]^{2-}$ by cyclic voltammetry (CV) in the organic solvents $CH_2Cl_2$[18] and $CH_3CN$[11] indicated the absence of well-defined waves, whereas differential pulse voltammetry in $CH_3CN$ revealed a well-shaped oxidation wave at +2.34 V vs. $Ag/Ag^+$.[11] In this work, we used liquid sulfur dioxide as solvent for cyclic voltammetry and obtained consistent anodic oxidation potentials for the entire series of $[B_{12}X_{12}]^{2-}$ anions (X = H, F, Cl, Br) under identical conditions for the first time. The midpoint potential for the oxidation of $[B_{12}Cl_{12}]^{2-}$ in liquid $SO_2$ was observed at +2.11 V vs. $Fc^{0/+}$ by CV, in good agreement with the square-wave voltammogram (SWV) peak potential of +2.14 V (Supporting Information, Table S1). As a consequence of both the large potential range and small dielectric constant of $SO_2$, a second oxidation of the radical anion $[B_{12}Cl_{12}]^{\bullet-}$ to neutral $B_{12}Cl_{12}$ is observed at 2.67 V vs. $Fc^{0/+}$ (Figure 2). Whereas the first oxidation is quasi reversible, the second oxidation appears highly irreversible under these conditions, possibly as a result of the strong electrode absorption effects encountered throughout this investigation. That the CV is thereby excessively distorted in the second process is suggested by the SWV, for which the peak currents of the two processes appear quite similar. Going from $[B_{12}F_{12}]^{2-}$ to $[B_{12}I_{12}]^{2-}$, the stability against oxidation is increased, as shown by CV measurements and calculated gas-phase ionization potentials (IPs; Table 1). This contradicts the trend of the electronegativities of the halogens and may be explained by decreasing π back-donation from the halogen to the boron cluster on going from fluorine to the heavier halogens.

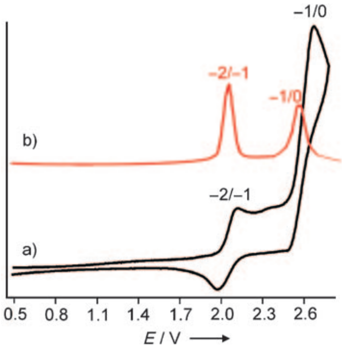

***Figure 2.*** a) Cyclic voltammogram of $Na_2[B_{12}Cl_{12}]$ in $SO_2$ (0.1 M $[nBu_4N][PF_6]$, 200 mV s$^{-1}$, 224 K). b) Square-wave voltammogram obtained on the same solution, illustrating the similarity in peak currents for the −2/−1 and −1/0 processes. The potential scales (E) are referenced to (external) $Fc^{0/+}$.

The experimental UV/Vis spectrum of $Li[B_{12}Cl_{12}]$ in liquid $SO_2$ shows two intense bands at 398 and 674 nm (Supporting Information, Figure S9). The latter has a very broad shoulder at approximately 550 nm. Calculations of the absorption spectrum of the $[B_{12}Cl_{12}]^{\bullet-}$ radical anion on the CC2/def2-TZVPP level give two intensive bands at 462 nm and 642 nm,

***Table 1:*** Calculated (PBE0/def2-TZVPP) ionization potentials [kJ mol$^{-1}$] and experimental anodic peak potentials [V] for $[B_{12}X_{12}]^{2-}$ (X = H, F, Cl, Br, I).

| Anion | $IP_{calcd}$ [kJ mol$^{-1}$] | $E_p^{a1}$ [V][a] |
|---|---|---|
| $[B_{12}I_{12}]^{2-}$ | +274 | NA[b] |
| $[B_{12}Br_{12}]^{2-}$ | +256 | 2.31 |
| $[B_{12}Cl_{12}]^{2-}$ | +229 | 2.15 |
| $[B_{12}F_{12}]^{2-}$ | +131 | 1.78 |
| $[B_{12}H_{12}]^{2-}$ | +92 | 1.66[c] |

[a] Cyclic voltammetry in $SO_2$ vs. $Fc^{0/+}$: platinum working and auxiliary electrodes, silver wire quasi reference electrode; details are given in the Supporting Information. [b] Not applicable. [c] Irreversible.

which is in accord with the experimental spectrum. The broad shoulder at approximately 550 nm can be explained by the presence of smaller quantities of neutral $B_{12}Cl_{12}$, for which an absorption maximum at 569 nm has been calculated.

Therefore, cyclic voltammetry of $[B_{12}Cl_{12}]^{2-}$ in $SO_2$ and the UV/Vis spectrum of $[B_{12}Cl_{12}]^{\bullet-}$ in $SO_2$ both give evidence for the existence of neutral $B_{12}Cl_{12}$ under these conditions. To confirm this possibility, Born–Haber–Fajans cycles for both steps of the oxidation of $K_2[B_{12}Cl_{12}]$ by $AsF_5$ were constructed (Supporting Information, Figure S12). These calculations show that the first oxidation to the radical anion $[B_{12}Cl_{12}]^{\bullet-}$ and the second oxidation to give neutral $B_{12}Cl_{12}$ are both thermodynamically favored. $B_{12}Cl_{12}$ had previously been identified by $^{11}B$ NMR spectroscopy and mass spectrometry as a by-product of the thermal disproportionation of $B_2Cl_4$.[19]

A single-crystal X-ray diffraction study on a blue cubic crystal obtained from a reaction designed to give $K[B_{12}Cl_{12}]$ resulted in the structure determination of neutral $B_{12}Cl_{12}$ (Figure 3). The $B_{12}Cl_{12}$ molecules are packed in a cubic closed-packing in the lattice (Supporting Information, Figure S13).[20] The B–B bonds (181.2(2)–185.5(3) pm) are longer and the B–Cl bonds (174.2(2)–174.8(2) pm) are shorter than those in *closo*-$[B_{12}Cl_{12}]^{2-}$ (B–B 178.7 pm, B–Cl 178.9 pm)[13a]. The singly occupied HOMO of the $[B_{12}Cl_{12}]^{\bullet-}$ radical anion, which is B–B-bonding and B–Cl-antibonding, is shown in Figure 1. Removal of an electron from this orbital should lead to a lengthening of the B–B bonds and a shortening of the B–Cl bonds, which is in accordance with the experimental results.

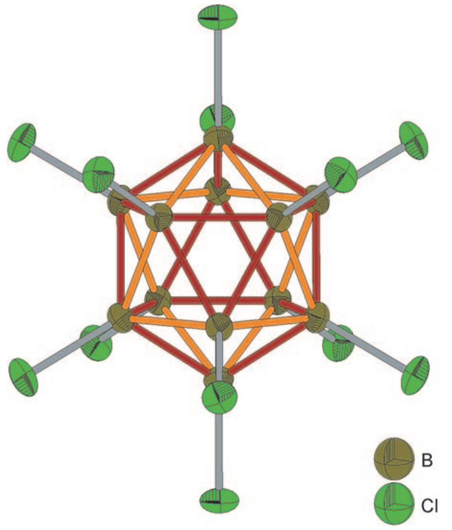

***Figure 3.*** Section of the crystal structure of $B_{12}Cl_{12}$. Light-brown B–B bonds represent long contacts (185.2(3)–185.5(3) pm) and dark-brown B–B bonds represent short contacts (181.2(2)–181.8(3) pm). B–Cl bonds are in the range 174.2(2)–174.8(2) pm. Thermal ellipsoids are set at 50% probability.

$B_{12}Cl_{12}$ has only *n* skeleton electron pairs, in constrast to the $n+1$ skeleton pairs for a *closo* structure according to Wade's rules.[21] The term *hypercloso* has frequently been used to describe similar electron-deficient systems.[22] The HOMO of the parent cluster $[B_{12}Cl_{12}]^{2-}$ is fourfold-degenerate and therefore removal of one or two electrons from this orbital should result in a Jahn–Teller distortion. Two different isomers having $D_{3d}$ symmetry and one isomer having $T_h$ symmetry were calculated (Supporting Information, Section S5). All three isomers are very close in energy, with the $T_h$ isomer being the global minimum. Note that all of the structurally characterized $B_{12}(OR)_{12}$ (OR = alkoxy) clusters exhibit $D_{3d}$ symmetry.[4b] The same holds for the experimental structure of $B_{12}Cl_{12}$, which has a symmetry very close to $D_{3d}$. The electronic situation in $[B_{12}X_{12}]^{n-}$ ($n = 0, 1$) clusters merits further theoretical investigations in the future.

In conclusion, chemical or electrochemical oxidation of the dianion $[B_{12}Cl_{12}]^{2-}$ in liquid sulfur dioxide can produce both the radical anion $[B_{12}Cl_{12}]^{\bullet-}$ and neutral $B_{12}Cl_{12}$, which were identified by various spectroscopic and physical methods. Electrochemical investigations indicate that similar behavior may be found for other $[B_{12}X_{12}]^{2-}$ (X = F, Br) clusters. Whether this is actually the case is part of ongoing investigations.

Received: July 31, 2010
Published online: November 30, 2010

**Keywords:** boron · cyclic voltammetry · Jahn–Teller distortions · oxidation · radical ions

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[17] Synthesis of M[$B_{12}Cl_{12}$] (M = Li, Na, K): $M_2$[$B_{12}Cl_{12}$] (prepared by reaction of [$NEt_3H$]$_2$[$B_{12}Cl_{12}$] with two equivalents of MOH in aqueous solution)[13a] was charged into a H-shaped Schlenk vessel equipped with a G4 frit and J. Young Teflon-in-glass valves. $SO_2$ (10 mL) and a large excess (four- to sevenfold, scavenger for traces of impurities) of $AsF_5$ (prepared from $AsF_3$ and $F_2$: D. R. Aris, C. Knapp, J. Passmore, X. Wang, *J. Fluorine Chem.* **2005**, *126*, 1368 – 1372) were condensed at −196 °C onto the solid and the solution was stirred at ambient temperature overnight. Subsequently, the dark-blue reaction mixture was filtered through the frit and the insoluble residue (M[$AsF_6$] according to IR and $^{19}$F NMR spectroscopy) was washed several times with $SO_2$ until it became almost colorless. All volatiles were removed in vacuum, yielding M[$B_{12}Cl_{12}$] as a dark-blue solid in quantitative yield.

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[20] The single-crystal X-ray structure determination was carried out on a Rigaku R-AXIS Spider image plate diffractometer using $Mo_{K\alpha}$ (0.71073 Å) radiation. The crystal was selected at −30 °C and mounted onto a cryo-loop using fluorinated oil and frozen in the cold nitrogen stream of the goniometer. The structure was solved by direct methods. Subsequent least-squares refinement on $F^2$ located the positions of the remaining atoms in the electron density maps (G. M. Sheldrick, SHELX-97 Programs for Crystal Structure Analysis, Institut für Anorganische Chemie der Universität Göttingen, **1997**). All atoms were refined anisotropically. The data were corrected for absorption (semi-empirical from equivalents). $B_{12}Cl_{12}$: $M_r = 555.12$, cubic, $Pa\bar{3}$, $a = b = c = 1244.98(12)$ pm, $V = 1.9297(3)$ nm$^3$, $Z = 4$, $\mu = 1.703$ mm$^{-1}$, $T = 115(2)$ K, 10279 reflections measured, 737 independent ($R_{int} = 0.0565$), $R1 = 0.0253$ ($I > 2\sigma(I)$), $wR2 = 0.0595$ (all data). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421891.

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