CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201001374

Oxidative Perhydroxylation of [*closo*-$B_{12}H_{12}$]$^{2-}$ to the Stable Inorganic Cluster Redox System [$B_{12}(OH)_{12}$]$^{2-/\bullet-}$: Experiment and Theory**

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The icosahedral dodecahydro-*closo*-dodecaborate dianion, [*closo*-$B_{12}H_{12}$]$^{2-}$, is the most prominent member of the hydridoborate cluster family. Its stability,[1] as rationalized in most popular form by Wade's rules, has frequently been compared with that of planar "aromatic" compounds in hydrocarbon chemistry. In contrast to such quintessential organic systems, the [*closo*-$B_{12}X_{12}$]$^{2-}$ clusters exhibit three-dimensional electron delocalization,[2] and they normally lack two well-established kinds of features that characterize the chemistry of organic aromatic compounds: they are less easily functionalized and they usually do not undergo facile reversible electron transfer. However, recent studies to functionalize and substitute [*closo*-$B_{12}H_{12}$]$^{2-}$ have provided a variety of closomers.[3] With respect to the parent anion, [*closo*-$B_{12}H_{12}$]$^{2-}$, these closomers retain the icosahedral cage but incorporate variable additional properties relating to the geometrical and electronic structure, ionic charge, redox capability, paramagnetism, chromophoric features, or hydrophobicity. In terms of charge, the boron cage of most known closomers is isoelectronic to that of [*closo*-$B_{12}H_{12}$]$^{2-}$. However, some closomers can exist with less than the standard number of cage-bonding electrons and are described as [*hypocloso*-$B_{12}X_{12}$]^{n} ($n=-1$ for radical and $n=0$ for neutral forms). Several protected radical anions such as [*hypocloso*-$B_{12}Me_{12}$]$^{\bullet-}$ and [*hypocloso*-$B_{12}(OCH_2Ph)_{12}$]$^{\bullet-}$ have been reported in the literature up to date.[4,5] With one or two electrons removed, the symmetry is lower than I_h with its quadruply degenerate HOMO, resulting in a Jahn–Teller distortion. The lower electron density in the boron cage may be compensated by external donor substituents, involving π back-donation and inductive and electronegativity effects.[4,5] Of the known persubstituted 12-vertex boron radicals, the stabilization of [*hypocloso*-$B_{12}Me_{12}$]$^{\bullet-}$ may be attributed to steric crowding and the combined inductive effect, whereas π back-donation from the oxygen nonbonding electron pairs into the electron-deficient cage is the main reason for the persistence of [*hypocloso*-$B_{12}(OR)_{12}$]$^{\bullet-}$ intermediates of nanomolecular redox systems.[5c] Both of these air-stable radical compounds are persubstituted with hydrophobic organic substituents and were obtained by the one-electron oxidation of corresponding closomer dianions with oxidants such as Fe^{3+} or Ce^{4+}. Neither inorganic derivatives nor alternative methods of synthesis have been published to date. All reported closomers resulting from functionalization reactions of [*closo*-$B_{12}H_{12}$]$^{2-}$ were obtained in the -2 state.[3] The perhydroxylation of [*closo*-$B_{12}H_{12}$]$^{2-}$, for example, has been carried out in the oxidation with hydrogen peroxide, H_2O_2 (30 %). At temperatures ranging from 105 °C up to reflux, this reaction led only to $Cs_2[B_{12}(OH)_{12}]\cdot 2H_2O$ as the reaction product[5] despite the oxidizing power of H_2O_2. Efforts to obtain the perhydroxylated radical anion by one-electron oxidation of [*closo*-$B_{12}(OH)_{12}$]$^{2-}$ did not succeed.

In this work we describe how the use of hydrogen peroxide leads to the cesium salts of both the diamagnetic [*closo*-$B_{12}(OH)_{12}$]$^{2-}$ and the paramagnetic [*hypocloso*-$B_{12}(OH)_{12}$]$^{\bullet-}$,

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[**] The authors would like to thank Dr. Falk Lissner for performing the single-crystal X-ray data collection.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001374.

thus producing a B_{12} cluster redox system with an unprecedented potential for functionalization at the OH groups. Both the electron-transfer capacity and the possible functionalization through OH would be of interest for areas such as material science (spin-bearing oligoboranes) or medicine (boron neutron-capture therapy, BNCT).[6] The air-stable, paramagnetic, sparingly water-soluble, solvent-free radical compound $Cs[B_{12}(OH)_{12}]$ can be synthesized directly through perhydroxylation of $Cs_2[B_{12}H_{12}]$ with H_2O_2 (30 %) at 65 °C for six days.[7] Further increase in reaction temperature over 100 °C leads to the formation of diamagnetic $Cs_2[\textit{closo}\text{-}B_{12}(OH)_{12}]\cdot 2H_2O$, which has already been characterized.[5] This preparation process effected not only the hydroxylation but also a one-electron oxidation of the boron cage. Owing to its low solubility in water, the radical compound is easily separated in high purity from the reaction mixture. Complete hydroxylation of all B–H vertices of $[\textit{closo}\text{-}B_{12}H_{12}]^{2-}$ was achieved although the radical preparation reaction was carried out at rather low temperatures.

The electrospray mass spectrum (ESI-MS, negative mode) reveals the molecular ion peak of $[\textit{hypocloso}\text{-}B_{12}(OH)_{12}]^{\bullet-}$ at m/z: 336.1. The experimental and simulated mass spectra are shown in the Supporting Information. The radical anion exhibits an unresolved EPR signal at $g=2.0042$ (2.5 mT peak-to-peak distance) in the solid, which is close to the free-electron value of 2.0023 and not much different from the value of 2.0076 for $[\textit{hypocloso}\text{-}B_{12}Me_{12}]^{\bullet-}$.[9] The lack of EPR spectral resolution reflects the large number of theoretical lines calculated for the interaction of one unpaired electron with 12 ^{1}H and 12 ^{11}B nuclei and the presence of a vast number of different isotopomers (^{11}B: 80.2 %, $I=3/2$; ^{10}B: 19.8 %, $I=3$). Considering only the all-(^{11}B) combination one arrives at 481 lines (37×13), the other, partially more abundant $^{10}B/^{11}B$ combinations yield many more hyperfine lines. EPR measurements at higher frequencies (95, 190, and 285 GHz) showed no g factor anisotropy $\Delta g = g_1 - g_3$ for the solid radical at 5 K. At 285 GHz a very slight signal asymmetry could be associated with a Δg value of approximately 0.01. The DFT calculated[10] isotropic g value is 2.0098 and there is a small calculated anisotropy Δg of 0.006. The electron spin density is mainly delocalized over the slightly distorted B_{12} skeleton (see below and the Supporting Information).

The UV/VIS spectrum of $Cs[B_{12}(OH)_{12}]$ in acetonitrile shows an absorption maximum at $\lambda=477$ nm, which is in agreement with the TDDFT calculated most-intense transition at 474 nm (B_{12} framework centered), arising from fully occupied MOs to the singly occupied molecular orbital (SOMO) characterized above. We calculated two more, less-intense transitions at 463 and 457 nm (see the Supporting Information). The corresponding energy-level diagram, based on a slight B_{12} structural distortion from I_h symmetry affecting the quadruply degenerate MO by the Jahn–Teller effect, is also provided in the Supporting Information.

Single crystals of $Cs[B_{12}(OH)_{12}]$ were obtained from water and the crystal structure was determined from single-crystal X-ray diffraction.[11] In the radical compound, the B–B bond lengths fall in a small range from 179.1 to 180.3 pm, whereas the B–O bond lengths range between 143.3 and 144.4 pm (Figure 1). These bond lengths are only slightly different from those of the $[\textit{closo}\text{-}B_{12}(OH)_{12}]^{2-}$ dianion (B–O: 143.3–145.9 pm; B–B: 178–181 pm)[5] and from typical values for B–B and B–O bond lengths (177 and 144 pm, respectively). In contrast to the unusually short $Cs^{+}\cdots Cs^{+}$ separation of 397 pm in $Cs_2[B_{12}(OH)_{12}]\cdot 2H_2O$, there are no such interactions in $Cs[B_{12}(OH)_{12}]$ ($Cs^{+}\cdots Cs^{+}$ separations are 704 pm). The less-pronounced distortion of the anionic cluster in $Cs[B_{12}(OH)_{12}]$ as compared with $Cs_2[B_{12}(OH)_{12}]\cdot 2H_2O$ may be due to the diminished interactions between the cesium cations and the cluster through the oxygen atoms, and to the absence of hydrogen bonds by involving water molecules. Among $[\textit{hypocloso}\text{-}B_{12}X_{12}]^{\bullet-}$ radicals (X: OH, Me, and OCH_2Ph), the lengthening of the B–B bonds and the shortening of the B–O bonds in $[\textit{hypocloso}\text{-}B_{12}(OH)_{12}]^{\bullet-}$ is less pronounced than those in $[\textit{hypocloso}\text{-}B_{12}Me_{12}]^{\bullet-}$ (B–B: 178.5–180.5 pm; B–C: 159.8–145.9 pm)[9] and $[\textit{hypocloso}\text{-}B_{12}(OCH_2Ph)_{12}]^{\bullet-}$ (B–B: 176.8–184 pm; B–O: 139.8–141.9 pm).[5c] In the crystal structure of $Cs[B_{12}(OH)_{12}]$ with its rock salt-type related arrangement, six Cs^{+} cations surround each boron cage octahedrally and vice versa. The Cs–O distances (340–360 pm) are longer than those of the diamagnetic compound (307–352 pm). The Cs^{+} cations in $Cs[B_{12}(OH)_{12}]$ exhibit coordination number of 12 (Figure 2), whereas the coordination numbers of the Cs^{+} cations in $Cs_2[B_{12}(OH)_{12}]\cdot 2H_2O$ is only 10.

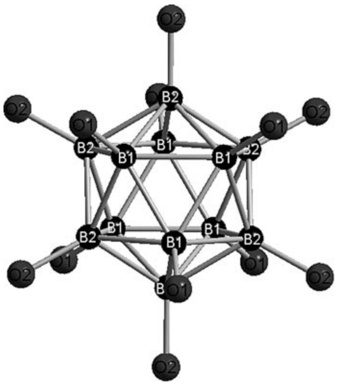

Figure 1. View of a $[\textit{hypocloso}\text{-}B_{12}(OH)_{12}]^{\bullet-}$ radical anion in the crystal structure of $Cs[B_{12}(OH)_{12}]$.

Electrochemical studies of the interconversion $[B_{12}(OH)_{12}]^{2-/\bullet-}$ were hampered by the poor solubility of $Cs[B_{12}(OH)_{12}]$. The best, reproducible results were obtained by using cyclic voltammetry with either a Pt electrode after extracting the solid into 0.2 M Bu_4NPF_6/CH_3CN solution for several hours at room temperature, or with a gold electrode at 75 °C in 0.1 M KNO_3/H_2O. Under those conditions, anodic oxidation of $[\textit{closo}\text{-}B_{12}(OH)_{12}]^{2-}$ was irreversible at slower scan rates but increasingly reversible above 1 V s^{-1}. Against ferrocenium/ferrocene as the internal standard, the half-wave potentials were determined as +0.45 V in CH_3CN and

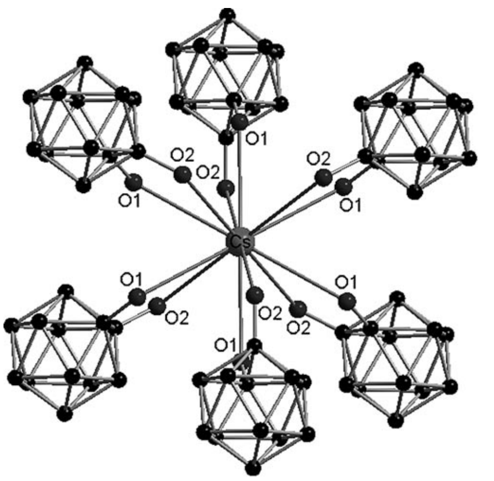

Figure 2. Coordination polyhedron of Cs^+ in the crystal structure of $Cs[B_{12}(OH)_{12}]$.

+0.75 V in water, reflecting the expected large difference for a polyhydroxy species in aprotic versus aqueous systems. Nevertheless, the twelvefold substitution of H in [*closo*-$B_{12}H_{12}]^{2-}$ by OH in [*closo*-$B_{12}(OH)_{12}]^{2-}$ lowers the oxidation potential through π back-donation sufficiently to allow for the generation of the one-electron oxidized [*hypocloso*-$B_{12}(OH)_{12}]^{\bullet-}$ as a stable radical anion and its isolation in the form of the anhydrous cesium salt.

An important stabilizing factor in *closo*-boranes are the highly diatropic electronic currents inside the cage, which can be quantified by the negative value of the NICS (nucleus independent chemical shift) index. These diatropic currents are interpreted as spherical aromaticity (3D). To assess the change in 3D aromaticity, the NICS indices were calculated for both members of the redox couple $[B_{12}(OH)_{12}]^{2-/\bullet-}$. The small difference between −28.96 ppm (2− anion) and −28.24 ppm (1− radical anion) suggest marginal diminishing of the aromaticity on one-electron oxidation.

In conclusion, a surprisingly straightforward reaction between $Cs_2[B_{12}H_{12}]$ and H_2O_2 (30%) yields both diamagnetic $Cs_2[B_{12}(OH)_{12}]\cdot 2H_2O$ and paramagnetic $Cs[B_{12}(OH)_{12}]$ as parts of a new structurally characterized oligoborane cluster redox system with a stable radical state[4] and the potential for functionalization at the OH groups.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft (Bonn), Fondecyt 1070345, Millennium Nucleus P07-006-F, UNAB-DI 09-09/I.

Keywords: borates • cage compounds • closomers • electron-deficient compounds • hydroxylation • radicals

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[7] For reacting $Cs_2[B_{12}H_{12}]$ with H_2O_2 at higher temperatures adequate precautions have to be taken. Hydrogen peroxide (30%, 12 mL) was added to $Cs_2[B_{12}H_{12}]$ (6.0 g, 14.7 mmol) and the mixture was heated to 65 °C with vigorous stirring. Additional H_2O_2 was added slowly in 4 mL portions until all $Cs_2[B_{12}H_{12}]$ was dissolved. The precipitation of the yellowish green anhydrous radical compound begins after 4 days and is completed after 6 days. $Cs[B_{12}(OH)_{12}]$ was collected by filtration in almost quantitative yield and dried under vacuo. Single crystals of the compound were obtained during recrystallization from water.

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[10] a) The relativistic DFT calculations were done by using the ADF 2008.01 code,[10b] incorporating both scalar and spin-orbit corrections through the two-component ZORA Hamiltonian.[10c,d] For the calculations we employed triple-ξ Slater basis set plus polarization function (STO-TZP). Geometry optimizations were done without any symmetry restrain, by an analytical energy- gradient method implemented by Verluis and Ziegler,[10e] within the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) approximation for the exchange and correlation potential.[10f,g] The nucleus-independent chemical shifts (NICS)[10h,i,j] were calculated by employing the GGA exchange expression proposed by Handy and Cohen[10k] and the correlation expression proposed by Perdew, Burke, and Ernzerhof[10g] (OPBE), incorporating both scalar and spin-orbit effects (OPBE/ZORA+SO); b) Amsterdam Density Functional (ADF) Code, Release, Vrije Universiteit, Amsterdam, **2008**; c) E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.* **1994**, *101*, 9783–9792; d) G. Te Velde, F. M. Bickelhaupt, S. J. A. van Gisberger, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931–967; e) L. Versluis, T. Ziegler, *J. Chem. Phys.* **1988**, *88*, 322–328; f) J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* **1996**, *54*, 16533–16539; g) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868; h) C.-G. Zhan, F. Zheng, D. A. Dixon, *J. Am. Chem. Soc.* **2002**, *124*, 14795–14803; i) A. E. Kuznetsov, A. I. Boldyrev, X. Li, L.-S. Wang, *J. Am. Chem. Soc.* **2001**, *123*, 8825–8831; j) A. I. Boldyrev, A. E. Kuznetsov, *Inorg. Chem.* **2002**, *41*, 532–537, and references therein; k) N. C. Handy, A. Cohen, *J. Mol. Phys.* **2001**, *99*, 403–412.

[11] Crystal data of Cs[$B_{12}(OH)_{12}$]: trigonal; space group $R\bar{3}m$ (no. 166); $a=929.85(6)$, $c=1364.78(9)$ pm; $c/a=1.468$; $V_m=205.136$ cm^3 mol^{-1}; $\rho_{calcd}=2.275$ g cm^{-3}; $Z=3$; $\mu(\mathrm{Mo}_{K\alpha})=2.78$ mm^{-1}; F(000) = 669; Nonius-κ-CCD diffractometer; $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda=71.069$ pm, graphite monochromator); $T=293$ K; 2877 measured reflections; 338 independent reflections; numerical absorption correction (HABITUS); $R_{int}=0.112$ ($R_\sigma=0.042$). The crystal structure (Cs at 3a: 0, 0, 0; B1 at 18h: 0.0645(2), $-x/a$, 0.5999(2); B2 at 18h: 0.1038(2), $-x/a$, 0.4767(2); O1 at 18h: 0.12213(14), $-x/a$, 0.68087(15); O2 at 18h: 0.19145(13), $-x/a$, 0.46085(16)) was solved by direct methods (SHELX-97) and was refined anisotropically with least-squares methods against F^2 with all data and 28 parameters to $R_1=0.056$, $wR_2=0.075$, and GOF = 1.056. The positions of the oxygen-bound hydrogen atoms could not be determined at room temperature. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: mailto:crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository number CSD-420713 for Cs[$B_{12}(OH)_{12}$].

Received: May 19, 2010