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Electrochemistry of *closo*-dodecaborate dianion and its simple *exo*-skeletal derivatives at carbon electrodes in aqueous phosphate buffers

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It is pleasure for R.V. to dedicate this article to Prof. Petr Boček.

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ABSTRACT

The principle building blocks of fully synthetic boron cluster compounds are electron deficient chemical clusters, which consist only of boron and hydrogen atoms and their derivatives are characterized by exo-skeletal substituents. Unique medical promises of these compounds and their use as biomarkers cause the need for systematic investigation of their physico-chemical properties, particularly those utilizable in efficient analytical methods suitable for their characterization and determination, including electrochemical activity of the boron cluster species in water. The water soluble *closo*-dodecaborate divalent anion and its seven simple derivatives have been chosen for introductory study with pyrolytic and glassy carbon graphite electrodes. All anions exhibited electrochemical activity that has shown dependence on atoms and functional groups bonded to the cage boron atoms of the *closo*-dodecaborane cluster. The most water soluble derivative with one hydroxy group exhibited the best pronounced electrochemical behavior, and was therefore chosen for a basic electrochemical characterization.

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1. Introduction

Vast majority of compounds existing in nature as well as their man-made analogues are typically based on two-centre two-electron bonds. In such compounds, usually each bonded atom furnishes one valence electron into one two-centre bond. Dissimilarities among the two-centre bonds result from their bonds polarity and multiplicity. From the viewpoint of the electron saturation, two centre bonds are electron exact (saturated), multiple two-electron bonds are electron rich. In contrast, fully synthetic cluster boron compounds contain three-centre two-electron bonds involved in the inner cluster bonding scheme [1,2] to which each boron contributes by three valence orbitals and only by two electrons. Number of bonding valence electrons $2n + 2$ (where n = number of vertices) involved in *closo*-cages leads to divalent negative charge observed for the most boranes with closed cages. In addition, two-centre bonds are also involved in the binding scheme and are most frequently represented by these interconnecting one hydridic hydrogen atom to each boron, or eventually substituent pointing outside of the cage. The three-centre bonds are the reason why the cluster is composed from triangular facets, in contrast to the linear or planar ring geometry observed for compounds based on electron exact two-centre bonds. Electron delocalization over the three-centre bond system in the cage causes rigid structures and three-dimensional space geometries. The delocalization of electron causes superaromaticity of the cluster [3,4], completely delocalized negative charge over the cluster surface, i.e. existence of phenomena never reported for compounds occurring in nature. The electrons superaromaticity markedly contributes to the fact that the cluster structures are decisive for many properties of boron cluster compounds (BCCs) including the electrochemical ones [5].

In the past, differences in electrochemical activity of newly synthesized BCCs were utilized for their characterization and identification via application of electrochemistry in addition to other analytical techniques. Plenty of BCCs belonging to various structural types have been analyzed by this way [5]. Platinum working electrode was the most frequently used electrode for the BCCs studies in non-aqueous electrolytes [5,6]. In a few cases, use of carbon electrodes was also reported [7,8]. Use of Pt electrodes for electrochemical modification of the BCCs was reported in Ref. [9]. Electronegativity of boron is lower than that of hydrogen. Exo-skeletal hydrogen atoms, which are bonded to the cluster boron atoms by standard two-centre bonds, have therefore partially hydridic nature. This nature prevents the cage surface from interaction with water molecules by forming classical hydrogen bonds, thus can only interact via the recently described non-classical

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dihydrogen bonds [10,11]. This effect makes surface of boron cluster species rather hydrophobic. The water solubility are then governed by the charge of the cluster, a counteractions present in the salts. According to recent theoretical study of $B_{12}H_{12}^{2-}$ system, hydratation can be grossly influenced by the substituent [11]. Recent studies have show that even the bulkier divalent anions tend to aggregate upon aging in aqueous solutions [12,13]. Polar organic solvents or their water solutions have been therefore used in majority of electrochemical experiments and in all studies with cluster species containing up to 12 boron atoms, see, e.g. Ref. [5]. However, water is predominant solvent in biochemistry, biology and the only acceptable solvent for medicine. Medical promises of BCCs [14–22], and their utilization as markers in biochemical and biophysical studies [23] thus generates demand for analytical techniques applicable in aqueous media. Rules and pieces of knowledge extracted from studies conducted in non-aqueous solvents may have low relevance for bioanalysis without verification of their validity for aqueous solutions, which has motivated us to perform the present electrochemical study. Behavior of various boron cluster species in aqueous media, and influence of their substitutions on electrochemical properties will be the main goal of this study. The later knowledge practically does not exist in the literature. Indeed, substitution of boron cluster compounds by organic and inorganic functional groups plays important role in the currently proceeding design and development of boron-based building blocks applied further in the synthesis of compounds for bio-medicinal applications. Synthetic studies evidence that chemical properties and physicochemical characteristics of organic and inorganic exo-skeletally bound functional groups are grossly affected due to binding to electron deficient clusters. Considering aqueous solutions, the influence on the electrochemical properties by substitution with various groups has not been previously investigated, although some consequences have been scarcely mentioned in existing literature on electrochemical properties of boron cluster compounds. It increases the need for their systematic consideration in subsequent electrochemical studies motivated by better understanding of solution phenomena connected with biological activity of these species. To ensure unequivocal correlation between chemical composition and structure of investigated species and their electrochemical properties, a set of seven water soluble cluster anions [24–26] (listed in Table 1) based on the basic *closo*-dodecaborane framework (Fig. 1) had been utilized for this study. The divalent *closo*-dodecaborane anion is the cornerstone of many intermediates on the way to practically attractive or promising compounds. Further, it belongs to clusters with most elaborated substitution chemistry in boron area. This simplest and most symmetrical icosahedral *closo*-dodecaborane anion composed of 12 BH units, is free from perturbation by other endohedral atoms or groups, and due to its double charge is sufficiently water soluble, despite of water repulsion behavior of its exo-skeletal hydrogen atoms. Its electrochemical properties can thus serve as a reference. Experiments revealed that the double charge provides a satisfactory solubility of all compounds under study inclusive the investigated halogen derivatives. Hydroxyl group and protonated amino group belong to hydrophilic exo-skeletal substituents, which markedly increase water solubility of the resulting anions.

Table 1
Systematic formulas of precipitated salts (as synthesized) of investigated boron cluster anions.

Systematic formula	Charge of the anion	Shortcut in the text	Molecular weight of the salt anion
closo-$B_{12}H_{12}(Et_3NH)_2$	2−	*B12*	141.82
1,7-Cl_2-*closo*-$B_{12}H_{10}(Bu_4N)_2$-	2−	*B12Cl2*	210.71
1-Br-*closo*-$B_{12}H_{11}(Bu_4N)_2$	2−	*B12Br*	220.72
1,7-Br_2-*closo*-$B_{12}H_{10}(Bu_4N)_2$	2−	*B12Br2*	299.62
1-I-*closo*-$B_{12}H_{11}(Bu_4N)_2$	2−	*B12I*	267.72
1,7-I_2-*closo*-$B_{12}H_{10}(Bu_4N)_2$	2−	*B12I2*	393.61
1-OH-*closo*-$B_{12}H_{11}Cs_2$	2−	*B12OH*	157.82
1-H_3N-*closo*-$B_{12}H_{11}(Me_3NH)$	1−	*B12NH3*	157.84

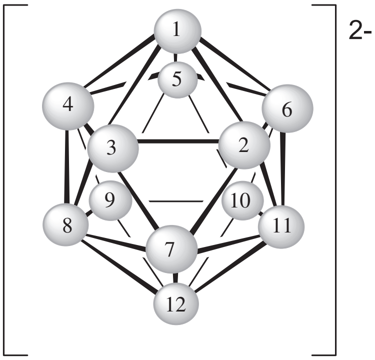

Fig. 1. The numbering scheme for the cage of the *closo*-$B_{12}H_{12}^{2-}$ anion. For clarity, the hydrogen atoms bonded to boron atoms by standard two-centre two-electron bonds are omitted.

To our knowledge, electrochemistry of BCCs has rarely been investigated with carbon electrodes which are otherwise widely applied in bioanalytical electrochemistry as cheap, in some variants disposable sensors. Polarographic data for $B_nH_n^{2-}$ polyhedral anions [27–30] and for some halogen derivatives of B_{10} and B_{12} cages [31] identified the *closo*-dodecaborate as the oxidative most stable member of the family of *closo*-boranes. The previous study [6] revealed the *closo-B12* cage to be inert towards electrochemical oxidation. Here we show a remarkable electrochemical activity, reflected in well pronounced anodic current signals, of the B_{12} cluster and its derivatives bearing various substituents.

2. Material and methods

BCCs were synthesized in the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Husinec-Řež, by previously published procedures [24–26]. Cations specified in Table 1 served for precipitation of investigated anions from reaction mixtures. In order to unify cation of studied salts, and enhance their solubility in water, the tetrabutyl ammonium and cesium were exchanged for sodium using standard ion exchange methods on Amberlite CG-120 (Fluka) ion-exchange resin. The ion exchange was first step in all electrochemical experiments described here. Other used chemicals purchased from Sigma–Aldrich were of the highest available purity. Common three electrode system was used for electrochemical experiments. An Ag|AgCl|3 M KCl reference electrode and a platinum wire (1 mm diameter) auxiliary electrode were used. All measurements were carried out at room temperature in a conventional electrochemical cell. An Autolab potentiostat pgstat 302 (Ecochemie, The Netherlands) was used for all electrochemical measurements. VA stand 663 (Metrohm, Switzerland) was used to perform measurements on rotating electrode with rotation speed (according to manufacturer) of 3200 rpm. The differential pulse voltammetry (DPV) was applied with the pulse amplitude of 0.025 V, pulse width of 50 ms, and scan rate of 0.008 V s^{-1}.

Glassy carbon electrode (GCE, Metrohm, Switzerland) and pyrolytic graphite electrodes in edge (PGEe) or basal plane (PGEb) orientations (Momentive performance materials, USA) were used as the working electrodes. Current values were normalized to the surface area of used electrodes. Torr-seal (Varian, Palo Alto, USA) epoxy resin was used for electrodes mounting. Electrodes were prepared for measurements as follows. The electrodes (GCE and

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