

Influence of substituents on selectivity and efficiency of chiral separations of anions containing single *nido*-7,8-dicarbaundecaborane cluster with α -cyclodextrin

Hana Horáková^{a,b,*}, Radim Vespalec^a

^a Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, 602 00 Brno, Czech Republic

^b Department of Analytical Chemistry, Faculty of Sciences, Palacky University Olomouc, Czech Republic

Received 27 September 2006; received in revised form 20 December 2006; accepted 22 December 2006

Available online 29 December 2006

Abstract

In background electrolyte (BGE) with the optimal methanol concentration of 30% (v/v), the ion with $-NCS$ group bonded to a cluster boron atom exhibits the strongest interaction with α -cyclodextrin and the highest separation selectivity. Interaction of ions with alkyl or thioalkyl group weakens with the increasing substituent size. The ion with phenyl group exhibits the weakest interaction. Bonding of a group to boron atom weakens the ion interaction with α -cyclodextrin. Second substituent further weakens the interaction with α -cyclodextrin. Separation efficiency is lower at the presence of α -cyclodextrin than at its absence. This separation efficiency loss, amounts up to 90%.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Capillary electrophoresis; Boron cluster compounds; Chiral separations; Cyclodextrins

1. Introduction

Tendency of boron atoms to mutual bonding is analogical to such tendency of carbon or silicon atoms [1]. Purely synthetic chemical clusters of boron atoms are three-dimensional. Boron has only three valence electrons for four valence orbitals. This deficiency of one bonding electron considering the number of boron valence orbitals is counterbalanced by formation of the three-centre two-electron bond in synthetic boron cluster compounds. Single pair of valence electrons binds three atoms in the bond. Accumulation of the bonds increases total deficiency of valence electrons in boron clusters to such an extent that they may exist only if electron pairs from individual bonds are delocalized over whole clusters. Statistically uniform distribution of delocalized electrons is easier attainable in symmetric systems. Symmetry is therefore, feature-supporting stability of boron cluster compounds. The most symmetric boron cluster species is the divalent anion of *closo*-dodecaborane (Fig. 1). Its

dipotassium salt melts at approximately 810 °C without decomposition [1,2].

Delocalization of cluster bonding electrons cannot compensate for their overall deficiency. This holds even if cluster boron atoms are partly replaced with other atoms, e.g., C, N, P or Co. The most straightforward way of suppressing the deficiency is including an σ -electron pair, which binds an *exo*-skeletal hydrogen atom, among delocalized electrons. This step requires splitting off of the hydrogen as proton. Tendency for increasing the number of delocalized electrons is so strong that at least one *exo*-skeletal proton splits at dissolution of boron cluster compound in organic solvents like methanol or acetonitrile. Chemical clusters based on boron atoms are extremely acidic from this reason and respective compounds behave as “superacids”. *Exo*-skeletal basic groups bind split protons and compounds bearing basic groups become zwitterionic [2].

Higher number of delocalized electrons weakens their attraction with cations of the cluster forming elements. The cluster size and shape depends therefore on the number of delocalized electrons too. The most closed clusters of n atoms have $(2n + 2)$ delocalized electrons and create *closo*-structural type. Clusters with $(2n + 4)$, $(2n + 6)$ and $(2n + 8)$ delocalized bonding electrons create *nido*-, *arachno*- and *hypho*-structural types, respectively

* Corresponding author at: Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, 602 00 Brno, Czech Republic. Tel.: +420 532290 142; fax: +420 541212 113.

E-mail address: horakova@iach.cz (H. Horáková).

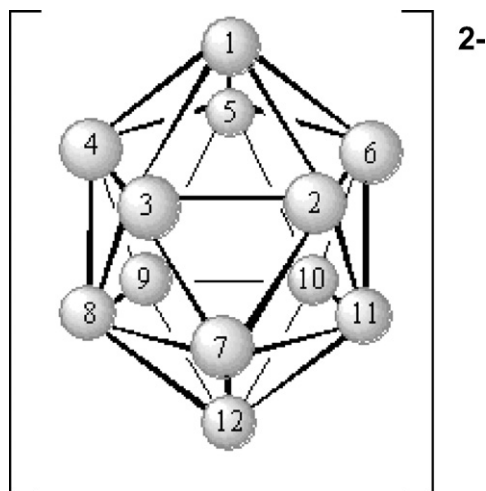


Fig. 1. Divalent anion of *closo*-dodecaborane.

[1,3]. Chemical reaction of boron cluster compound requires preliminary affection of its delocalized electrons. The higher is the number of delocalized electrons, the easier is the affection. Chemical reactivity of boron cluster compounds therefore increases, and chemical stability decreases, from the *closo*- to the *hypho*-type. The *nido*-structural type is usually best compromised for chemical reactivity and stability [1,4]. Majority of practically utilized and promising compounds belongs to this structural type [2,3].

The simplest boron cluster compounds, cluster boranes, consist only of the cluster-forming boron atoms and of *exo*-skeletal hydrogen atoms. Substitution of both skeletal boron atoms and *exo*-skeletal hydrogen atoms decreases symmetry of reaction products. Other synthetic steps usually have the same effect. Reaction products consecutively lose symmetry and become structurally chiral in this way even if they are free of discrete centres of chirality. Majority of synthesized boron cluster compounds is therefore chiral [5,6]. It makes methods for their chiral analyses highly desirable.

Cyclodextrins are chiral selectors of first choice in chromatography and electrophoresis [7,8]. β -Cyclodextrin and its derivatives proved powerful selectors in chiral liquid chromatography separations and preparations of zwitterionic boron cluster compounds [5,6]. However, these selectors failed in chiral separations of boron cluster anions that are much more attractive reactants in synthetic reactions. Surprisingly, β -cyclodextrin proved effective chiral selector for a set of randomly chosen boron cluster anions if capillary electrophoresis was the separation technique [9]. Our research shows since this finding [10–13] that analytical properties and behaviour of compounds with chemical clusters of boron, which are based on the three-centre two-electron bond, are different from properties and behaviour of naturally occurring compounds and their synthetic analogues, which are based on the two-centre two-electron bond. Validity of knowledge and rules obtained by experiments with compounds built up on the latter type of bond cannot be a priori expected for species containing chemical species based on three-centre two-electron bonds and vice versa to our experience.

Recently, we have investigated applicability of native α -, β - and γ -cyclodextrins for chiral separations of boron cluster anions of four structural types [12]. This electrophoretic study proved in accordance with expectation that structural type, size and number of *exo*-skeletal substituents strongly affect separation selectivity of boron cluster anions with β -cyclodextrin (β -CD). However, the influence of type, size and number of substituents on separation selectivity differed from their reported influence in chiral liquid chromatography separations of zwitterionic boron cluster compounds with various chemically bonded cyclodextrins [6]. Therefore, the question arises if this difference is observed with other native cyclodextrin too. γ -Cyclodextrin is not proper chiral selector for chiral separations of boron cluster anions [12]. Number and structural variety of ions separable with α -CD in [12] was very low for answering this question. Thus, we repeated investigation on separability of boron cluster anions by α -CD with the set of anions completed with anions having two substituents and two different bulky substituents. It allowed finding out if existing substituents that preclude from chiral separations of ions were derived from single *nido*-7,8-dicarbundecaborane cluster. Ions with this cluster are frequent intermediates in targeted syntheses of boron cluster compounds. Replacing of sodium cations in BGE [12] with Tris cations made possible finding out if and how much the Tris cations affect separation selectivity. Adverse effect of the added α -CD on separation efficiency, which was found in [12], was observed too. Wide range of α -cyclodextrin concentrations had to be used for generation of measurable separation selectivity for majority of ions. Rich set of accumulated mobility data made possible check on applicability of the 1:1 interaction model [14–16], which holds for chiral separations of organic compounds almost without exceptions.

2. Experimental

2.1. Instrumentation

Laboratory electrophoretic set-up is described in [9]. Its main parts are the switchable high voltage power supply Spellman CZE 100 R (Plainview, NY, USA) and the UV–vis spectrophotometer JASCO 875 (Tokyo, Japan) for liquid chromatography adapted for experiments with liquid thermostated and radially illuminated fused silica capillaries. Optimal detection wavelength ranged from 200 to 210 nm for analytes given in Table 1. Detector output was monitored, evaluated and stored by the integrator CSW 1.7 (DataApex, Praha, Czech Republic). The fused silica capillary (Composite Metal Services Ltd., Ilkley, UK) of 360 μm I.D., 75 μm O.D., 64.5 cm total length and 53 cm separation length, coated with polyacrylamide [17], was thermostated to 25 ± 0.1 °C with streaming liquid. The freshly coated capillary was cleaned overnight in the background electrolyte (BGE) by the applied voltage of -6 kV in order to minimize the baseline drift and noise. Stabilized capillary was briefly flushed with BGE before the sample injection. The capillary flushing was 5 min after a change in the α -cyclodextrin concentration. The current of 6 μA flows through the capillary filled with BGE, whose composition is given in Section 2.2, at the -20 kV driv-

Download English Version:

<https://daneshyari.com/en/article/1211162>

Download Persian Version:

<https://daneshyari.com/article/1211162>

[Daneshyari.com](https://daneshyari.com)