№ 12111-6251/131

“УТВЕРЖДАЮ”
Директор ИНЭОС РАН
чл.-корр. А. А. Трифонов

4 апреля 2022

ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

Руководитель-эксперт Федерального государственного бюджетного учреждения науки Института элементоорганических соединений им. А.Н.Несмеянова Российской академии наук, рассмотрев *статью* V.V. Avdeeva, A.V. Vologzhanina, S.E. Korolenko, L.V. Goeva, E.A. Malinina, N.T. Kuznetsov «**Polymeric anionic silver(I) complexes $\{Cat[Ag[B_{10}H_{10}]]\}_n$ (Cat = Pr_4N^+, Ph_4P^+, Ph_4As^+) with facial and edge-facial coordination of the boron cluster**», подготовленную для печати в журнале *Polyhedron*, подтверждает, что в материале *не содержатся* сведения, предусмотренные Постановлением Правительства РФ №1233 от 30.11.1994г. и на публикацию материала *не следует* получать разрешение *Минобрнауки и/или Президиума РАН*

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(ф. и. о., должность)

Polyhedron 223 (2022) 115932

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Polymeric anionic silver(I) complexes $\{Cat[Ag[B_{10}H_{10}]]\}_n$ (Cat = Pr_4N^+, Ph_4P^+, Ph_4As^+) with facial and edge-facial coordination of the boron cluster

Varvara V. Avdeeva [a,*], Anna V. Vologzhanina [b], Svetlana E. Korolenko [a], Lyudmila V. Goeva [a], Elena A. Malinina [a], Nikolay T. Kuznetsov [a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow 119991 Russia*
[b] *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str. 28, Moscow 119991 Russia*

ARTICLE INFO

Keywords:
Boron clusters
Decahydro-*closo*-dodecaborate
Hirshfeld surface
Coordination compounds
Silver
X-ray diffraction

ABSTRACT

The reaction between $Cat_2[B_{10}H_{10}]$ (Cat = Pr_4N^-, Ph_4P^+ and Ph_4As^+) and $AgNO_3$ in acetonitrile afforded solids $\{Cat[Ag[B_{10}H_{10}]]\}_n$ (**1**–**3**, respectively) which have been isolated and characterized by IR spectroscopy and X-ray diffraction. According to the X-ray diffraction data obtained, these compounds are 1D coordination polymers built of alternating silver atoms and *closo*-decaborate anions. The chains are packed parallel and separated by cations Cat. The *closo*-decaborate anion is coordinated by the silver atom via two equatorial BBB faces (in **1**) and through an equatorial face and an equatorial edge of the boron cage anion (in **2**). These types of coordination have not been previously observed in polymeric anionic silver(I) compounds with the boron clusters. In compound **3**, the boron cluster anion is disordered over four positions and the type of coordination cannot be determined unambiguously. Overall, the Ag–H and Ag–B distances vary from 2.423(4) to 2.762(4) and from 2.09 to 2.81 Å, respectively.

1. Introduction

Boron clusters anions $[B_nH_n]^{2-}$ (n = 6–12) and related carboranes [1–8] are fascinating objects for coordination chemistry. They provide chemists to vary their electronic and geometric structure, size and charge, which results in different properties and application [9–12].

Due to their 3D aromaticity [13–16], boron cluster anions participate in reactions of electrophilic, nucleophilic and radical substitution of the terminal hydrogen atoms to form a great number of substituted derivatives with various functional groups added to the boron cage [17–21]. At the same time, boron clusters form a great number of complexes [22,23] with different coordination mode of the boron cage to the metal atom (via three-centered two-electron (MHB) bonds, three-centered two-electron bonds through the hydrogen bridge M–H–M, bonds M–B(H) with hydrogen non interacting in the bonding, and B–M bonds with M substituting the corresponding terminal hydrogen atom).

The boron anion $[B_{10}H_{10}]^{2-}$ forms a large series of structurally characterized silver(I) complexes deposited to the Cambridge Structural Database (see, for example, review [22]). In the majority of them, the *closo*-decaborate anions are coordinated by metal atoms forming the (AgHB) three-centered two-electron bonds.

Among molecular complexes, mononuclear complex $[Ag(Ph_3P)_4][Ag(PPh_3)_2[B_{10}H_{10}]]$ [24] and two positional isomers of binuclear complex $[Ag_2(Ph_3P)_4[B_{10}H_{10}]]$ were reported [25–27]. First examples of binuclear $[Ag_2L_2[B_{10}H_{10}]]$ and polymeric $\{Ag_2L[B_{10}H_{10}]\}_n$ compounds with azaheterocyclic ligands L = 2,2′-bipyridyl and 1,10-phenanthroline were synthesized [28]. For dimeric boron cluster $[B_{20}H_{18}]^{2-}$, a number of isomeric mixed-ligand binuclear silver complexes with Ph_3P were reported [29,30]. Structures of a number of related silver complexes with carboranes were also reported [31–34]; the majority of them are polymeric.

In the absence of ligands in the reaction solution, solvent molecules can act as ligands. Thus, the structures of polymeric complexes $\{Ag_2(DMF)[B_{10}H_{10}]\}_n$ [35] and $\{[Ag(CH_3CN)_3]_2[Ag[2\text{-}B_{10}H_9F]]_2\}_n$ [36] were reported.

The present work concerns anionic silver complexes with the *closo*-decaborate anion. Synthesis of compounds $\{Cat[M[B_{10}H_{10}]]\}_n$ (M = Cu, Ag) with bulky cations Cat = K^+, Cs^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+, and R_4N^+

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* Corresponding author.
E-mail address: avdeeva.varvara@mail.ru (V.V. Avdeeva).

https://doi.org/10.1016/j.poly.2022.115932
Received 7 April 2022; Accepted 19 May 2022

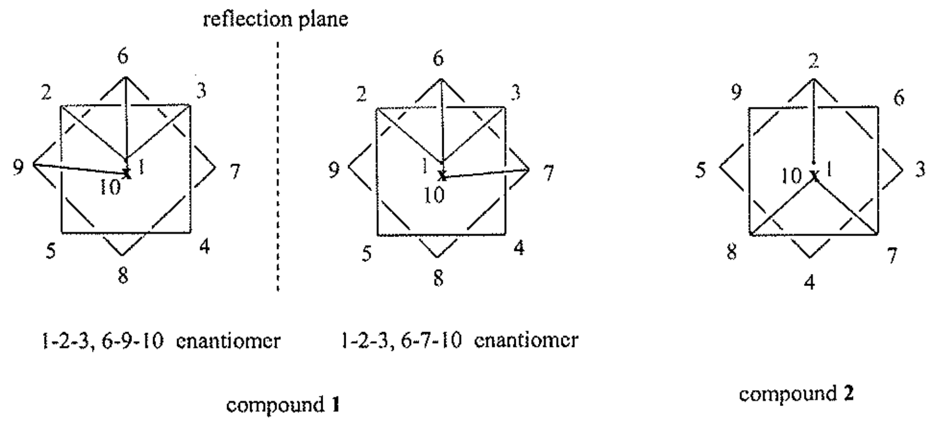

Fig. 4. Schematic representation of the co-crystallizing enantiomers in compound **1** and structure of compound **2**.

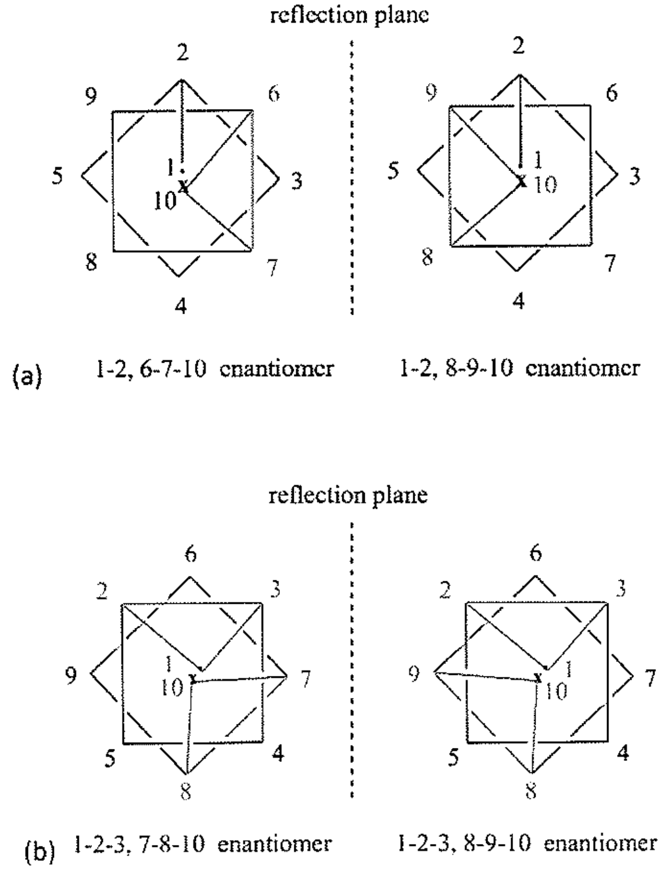

Fig. 5. Schematic representation of enantiomers co-crystallizing in binuclear complexes (a) [$Cu_2(Bipy)_2B_{10}H_{10}$] and (b) [$Cu_2(Phen)_2B_{10}H_{10}$] with (a) edge-facial and (b) facial coordination of the boron cluster [47,48].

[58–62]. However, in general, the metal cations of the environment do not affect the distribution of the electron density in the boron cluster anion (see [56] for copper), it is too uniform to make any one position preferable; this fact explains the existence of many types of coordination in complexes formed.

4. Conclusions

The silver(I) complexation reactions with the decahydro-*closo*-dodecaborate anion $[B_{10}H_{10}]^{2-}$ in acetonitrile have been studied. Polymeric compounds $\{Cat[Ag[B_{10}H_{10}]]\}_n$, where Cat = Pr_4N^+ (**1**), Ph_4P^+ (**2**), and Ph_4As^+ (**3**) have been isolated and characterized by IR spectroscopy and X-ray diffraction. The compounds are built of indefinite chains formed by alternating silver atoms and the *closo*-decaborate anions, while cations are located between the chains. First facial coordination of the boron cluster has been found for anionic compounds: the 10-vertex boron polyhedron is coordinated by two apical faces in **1** and by an apical face and an apical edge in **2**.

Funding

This work was supported by the Ministry of Science and Higher Education of the Russian Federation as part of the State Assignment of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences and the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences in the field of fundamental research.

CRediT authorship contribution statement

Varvara V. Avdeeva: Investigation, Writing – review & editing, Visualization. **Anna V. Vologzhanina:** Formal analysis, Visualization, Writing – original draft. **Svetlana E. Korolenko:** Formal analysis, Writing – original draft. **Lyudmila V. Goeva:** Formal analysis. **Elena A. Malinina:** Conceptualization, Methodology. **Nikolay T. Kuznetsov:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2022.115932.

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