

Concept Paper

# Gold(III) Complexation in the Presence of the Macropolyhedral Hydridoborate Cluster $[B_{20}H_{18}]^{2-}$

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**Abstract:** Gold(III) complexation with the octadecahydro-eicosaborate anion  $[B_{20}H_{18}]^{2-}$  was studied for the first time. It was found that when gold(III) complexes  $[Au(L)Cl_2]BF_4$  (L = bipy, phen) reacted with  $[B_{20}H_{18}]^{2-}$ , complexes  $[Au(L)Cl_2]_2[B_{20}H_{18}]$  were isolated. The compounds consisted of a cationic gold(III) complex  $[Au(L)Cl_2]^+$  and the hydridoborate cluster as a counterion. X-ray diffraction studies revealed weak B–H...Au interactions for both compounds. Note that more reactive anions  $[B_nH_n]^{2-}$  ( $n = 10, 12$ ) in similar reactions with gold(III) complexes resulted in gold mirror reactions.

**Keywords:** hydridoborates; boron clusters; mixed-ligand complexes; X-ray diffraction; gold



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## 1. Introduction

Higher polyhedral boron dianions  $[B_nH_n]^{2-}$  ( $n = 6–12$ ) [1–5] (n.b., hydridoborate is the new IUPAC recommended name for this class of compounds [6]) are fascinating ligands in coordination chemistry of transition metals. On the one hand, due to their 3D aromaticity [7–11] and low charge density, they are typical soft Lewis bases, which form numerous stable complexes with the soft metal acids including copper(I) and silver(I) [12–15], zinc(II) and cadmium(II) [16–19], and lead(II) ([20] and references therein). In addition, the boron cluster anions form compounds with metal(II) complex cations acting as counterions, e.g., Cu(II), Fe(II), Co(II), Ni(II), and Mn(II) [15,21–26]. In the presence of metals(III) complexes, the boron cluster anions act as reducing agents being oxidized to oxidoborates [27–29]. On the other hand, boron clusters form numerous products of the substitution of terminal hydrogen atoms by various functional groups keeping the initial *closo*-structure [30–34].

The *closo*-decaborate anion  $[B_{10}H_{10}]^{2-}$  can be easily oxidized in the presence of Fe(III) or Ce(IV) salts to form a macropolyhedral boron cluster  $[trans-B_{20}H_{18}]^{2-}$  [35,36], and the coordination chemistry of the latter began to be studied only a few years ago. A number of silver(I) compounds with the coordinated macropolyhedron and  $Ph_3P$  ligand were isolated and characterized by X-ray diffraction; the single-crystal-to-single-crystal transformations initiated with UV radiation and high temperature were studied [37,38]. First lead(II) complexes with coordinated Bipy and  $[B_{20}H_{18}]^{2-}$  were synthesized and characterized by IR spectroscopy and X-ray diffraction [38]. *Tris*-chelate manganese complex  $[Mn(Bipy)_3][B_{20}H_{18}]$  [39] and iron(II) complex  $[CpFe(Cp-CH_2-NMe_2Et_2)][B_{20}H_{18}]$  [40] with the boron clusters in the outer sphere are also known.

A number of gold compounds with boron clusters were synthesized and characterized. In particular, the gold(I) complex with triphenylphosphine and the hexahydrido-*closo*-hexaborate anion  $\{\text{Au}_2(\text{Ph}_3\text{P})_4[\text{B}_6\text{H}_6]\}$  was reported [41]. The compound is a binuclear complex containing a *closo*-hexaborate anion as a bridging ligand coordinated to the gold(I) atoms via opposite  $\text{B}_3$  faces. The complex with a direct metal–boron bond  $\{\text{Au}_3(\text{Ph}_3\text{P})_3[\text{B}_{10}\text{H}_9]\}$  [42] was obtained by the reaction of  $[\text{Au}(\text{Ph}_3\text{P})\text{Cl}]$  with  $\{\text{Ag}_2[\text{B}_{10}\text{H}_{10}]\}$  in the acetonitrile/benzene system. A triangular  $\text{Au}_3$  fragment can be considered as a substituent in the apical position of the boron cluster.

Gold(I) compounds with an outer-sphere coordination of the boron clusters were also described. Complexes  $[\text{Au}(\text{Ph}_3\text{P})_x]_2[\text{B}_{12}\text{Hal}_{12}]$  (Hal = F, Cl, Br, I;  $x = 2, 3$ ) with perhalogenated boron clusters in the outer sphere were isolated [43] from the electrochemically assisted reactions of  $(\text{H}_3\text{O})_2[\text{B}_{12}\text{Hal}_{12}]$  acids with  $\text{Au}^0$  in the presence of  $\text{Ph}_3\text{P}$ . Structures of mononuclear gold(I) complexes  $[(\text{CH}_3\text{CN})_2\text{Au}][\text{B}_{12}\text{Cl}_{11}(\text{Me}_3\text{N})]\cdot\text{CH}_2\text{Cl}_2$  and  $[(\text{Ph}_3\text{P})_2\text{Au}_2\text{Cl}][\text{B}_{12}\text{Cl}_{11}(\text{Me}_3\text{N})]$  [44], as well as binuclear gold(I) complex  $[\text{Ph}_3\text{PAuClAuPh}_3\text{P}][\text{B}_{12}\text{Cl}_{11}(\text{Me}_3\text{N})]$  [45] with a substituted *closo*-dodecaborate anion  $[\text{B}_{12}\text{Cl}_{11}(\text{Me}_3\text{N})]^-$ , were also reported. In addition, polymeric chain complex  $[\text{Au}(\text{Ph}_3\text{P})_2][\text{Ag}[\text{B}_{12}\text{H}_{12}]]_n$  was isolated [46].

It is noteworthy that the reaction of  $[\text{Au}(\text{Ph}_3\text{P})\text{Cl}]$  with  $\{\text{Ag}_2[\text{B}_{12}\text{H}_{12}]\}$  gave a gold complex  $[\text{Au}_9(\text{PPh}_3)_8][\text{B}_{24}\text{H}_{23}]$  [42]. The nine-vertex gold cluster  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  is a cationic part of the compound, while the  $[\text{B}_{24}\text{H}_{23}]^{3-}$  trianion with a linear B–H–B' bridge is a counterion and shows a centrosymmetric structure.

Complexes of metals in a high oxidation state are extremely rare. Usually, metals(III) are reduced to metals(II) because of reducing properties of boron clusters. As far as we know, a few examples of iron(III) and cobalt(III) complexes have been reported. Binuclear iron(III) complex  $\{[(\eta^5\text{-Cp})(\text{dppe})\text{Fe}]_2[\mu^2\text{-}1,10\text{-NC}[\text{B}_{10}\text{H}_8(\text{CN})]]\}\cdot\text{H}_2\text{O}$  was isolated with disubstituted 1,10-derivative  $[\text{B}_{10}\text{H}_8(\text{CN})_2]^{2-}$ , which acts as a bridge ligand between two metal complexes with cyclopentadienyl and phosphine ligands [47]. In addition, the cobalt(III) complex with the least reactive *closo*-dodecaborate anion  $[\text{Co}^{\text{III}}(\text{Phen})_3][\text{B}_{12}\text{H}_{12}]\text{NO}_3\cdot 2\text{DMF}\cdot 4\text{H}_2\text{O}$  was isolated [48].

Here, we describe the results of our study of gold(III) complexation in the presence of a  $[\text{B}_{20}\text{H}_{18}]^{2-}$  anion. First, gold(III) complexes with boron cluster anions were isolated and characterized.

## 2. Experimental

### 2.1. Synthesis

All reactions were carried out in air. Acetonitrile (HPLC grade), ethanol (95%), bipy (98%), and  $\text{Ph}_3\text{P}$  (98%) were purchased from Sigma-Aldrich.  $(\text{Et}_3\text{NH})_2[\text{B}_{10}\text{H}_{10}]$  was synthesized from decaborane(14) according to the known procedure [49].  $(\text{Et}_3\text{NH})_2[\textit{trans}\text{-B}_{20}\text{H}_{18}]$  was prepared by oxidation of aqueous  $(\text{Et}_3\text{NH})_2[\text{B}_{10}\text{H}_{10}]$  with  $\text{FeCl}_3$  according to the procedure reported [35,50]. The obtained solid was dissolved in a  $\text{CH}_3\text{CN}/\text{water}$  mixture followed by the addition of aqueous  $\text{Ph}_4\text{PCl}$  in the reaction solution resulting in the quantitative precipitation of  $(\text{Ph}_4\text{P})_2[\text{B}_{20}\text{H}_{18}]$ .  $[\text{Au}(\text{bipy})\text{Cl}_2]\text{BF}_4$  and  $[\text{Au}(\text{phen})\text{Cl}_2]\text{BF}_4$  were prepared according to the known procedure [51].

*Synthesis of  $[\text{Au}(\text{L})\text{Cl}_2]_2[\text{B}_{20}\text{H}_{18}]$  (1: L = bipy, 2: L = phen)*

A solution of  $[\text{Au}(\text{L})\text{Cl}_2]\text{BF}_4$  (0.2 mmol) in acetonitrile was added with stirring to a solution of  $(\text{Ph}_4\text{P})_2[\text{B}_{20}\text{H}_{18}]$  (0.1 mmol) in acetonitrile (10 mL). The formation of dark-orange crystals was observed within 5–10 min. The crystals were filtered off and dried in air. The yield was ~90%. Single crystals **1**·2 $\text{CH}_3\text{CN}$  and **2**·2 $\text{CH}_3\text{CN}$  suitable for X-ray diffraction study were taken from the reaction solutions.

**Anal. calcd.** for  $\text{Au}_2\text{C}_{20}\text{H}_{34}\text{N}_4\text{Cl}_4\text{B}_{20}$  (**1**): C, 22.2; H 3.2; N, 5.2; B 20.0. Found, %: C 22.3; H 3.1; N, 5.1; B 19.9. **IR** (NaCl,  $\nu$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{BH})$  2540, 2515, 2501, 2470;  $\nu(\text{CN})_{\text{CH}_3\text{CN}}$  2355, 2335;  $\delta(\text{BBH})$  1029; 1605w, 1507w, 1456, 1377, 1320, 1249w, 1113w, 1077w, 1047w; 771. **NMR**  $^{11}\text{B}$  (dms- $d_6$ , ppm):  $-30.7$  (d, 2 $\text{B}_{\text{ap}}$ ),  $-16.2$  (s, 2 $\text{B}$ ,  $\text{B}_2$ ,  $\text{B}_2'$ ),  $-6.0$  (d, 2 $\text{B}_{\text{eq}}$ ),  $-11.7$  (d, 4 $\text{B}_{\text{eq}}$ ),  $-15.3$  (d, 4 $\text{B}_{\text{eq}}$ ),  $-18.8$  (d, 4 $\text{B}_{\text{eq}}$ ),  $-25.1$  (d, 2 $\text{B}_{\text{ap}}$ ).

Anal. calcd. for  $\text{Au}_2\text{C}_{24}\text{H}_{34}\text{N}_4\text{Cl}_4\text{B}_{20}$  (**2**): Au, 34.8; C, 25.5; H 3.0; N, 5.0; B 19.1. Found, %: Au, 34.3; C 24.8; H 2.9; N, 5.0; B 19.0. **IR** ( $\text{NaCl}$ ,  $\nu$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{BH})$  2530, 2490;  $\nu(\text{CN})_{\text{CH}_3\text{CN}}$  2360, 2332;  $\delta(\text{BBH})$  1030; 1602w, 1518w, 1461s, 1432, 1377, 1221w, 1153w, 954w, 871w; 847, 823w, 748w, 723w, 701w, 673w. **NMR**  $^{11}\text{B}$  ( $\text{dmsO}-d_6$ , ppm):  $-31.0$  (d,  $2\text{B}_{\text{ap}}$ ),  $-16.9$  (s,  $2\text{B}$ ,  $\text{B}_2$ ,  $\text{B}_2'$ ),  $-5.9$  (d,  $2\text{B}_{\text{eq}}$ ),  $-11.6$  (d,  $4\text{B}_{\text{eq}}$ ),  $-15.2$  (d,  $4\text{B}_{\text{eq}}$ ),  $-18.7$  (d,  $4\text{B}_{\text{eq}}$ ),  $-24.9$  (d,  $2\text{B}_{\text{ap}}$ ).

## 2.2. Materials and Methods

**Elemental analysis** for carbon, hydrogen, and nitrogen was performed using a Carlo ErbaCHNS-3 FA 1108 automated elemental analyzer. Boron and metal contents were determined on an iCAP 6300 Duo ICP emission spectrometer with inductively coupled plasma. Samples were dried in air to constant mass; thus, solvent-free samples **1** and **2** were used.

**IR spectra** of compounds were recorded with a Lumex Infracum FT-02 FTIR-spectrometer in the range of  $4000\text{--}600\text{ cm}^{-1}$  at a resolution of  $1\text{ cm}^{-1}$ . Samples were prepared as Nujol mulls;  $\text{NaCl}$  plates were used. Fresh crystals containing solvent molecules were used in measurements.

**$^{11}\text{B}$  NMR spectra** of solutions of compounds in  $\text{dmsO}-d_6$  were recorded with a Bruker AC 200 spectrometer at a frequency of 64.297 MHz using  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as an external standard.

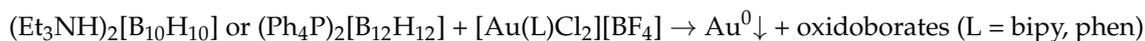
**X-ray powder diffraction** studies of crystals  $1 \cdot 2\text{CH}_3\text{CN}$  were carried out on a Bruker D8 Advance X-ray diffractometer at the Shared Research Center of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences. The measurements were performed using  $\text{CuK}\alpha$  radiation in low-background cuvettes with a substrate of an oriented silicon single crystal in the  $2\theta$  angle range of  $5^\circ\text{--}80^\circ$  with a step of  $0.01125^\circ$ . To obtain diffraction patterns, the samples were carefully triturated in an agate mortar. Before the measurements, the samples were dried to constant weight to remove solvent molecules. X-ray powder diffraction patterns of compound  $1 \cdot 2\text{CH}_3\text{CN}$  are shown in Figure S1. The data obtained verify the purity of the compound.

**X-ray diffraction studies** of single crystal  $1 \cdot 2\text{CH}_3\text{CN}$  were performed with a Bruker Apex DUO diffractometer ( $\text{MoK}\alpha$  radiation, respectively); crystal  $2 \cdot 2\text{CH}_3\text{CN}$  was studied using a Bruker Smart Apex II diffractometer ( $\text{MoK}\alpha$  radiation). The structures were solved by the SHELXT method [52] and refined by the full-matrix least squares method against  $F^2$  of all data using SHELXL-2014 [53] and OLEX2 [54] software. Nonhydrogen atoms were found on difference Fourier maps and refined with anisotropic displacement parameters. The positions of hydrogen atoms were calculated and included in the refinement in isotropic approximation by the riding model with the  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups and  $1.2U_{\text{eq}}(\text{C})$  for the other atoms, where  $U_{\text{eq}}(\text{C})$  are equivalent thermal parameters of parent atoms. Crystal data, details of data collection, and results of structure refinement are summarized in Table S1. The crystallographic data were deposited with the Cambridge Crystallographic Data Center as supplementary publications under CCDC nos. 2126248 and 2153860. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures) (accessed on 17 June 2022). Molecular views of compounds are shown in Figures S2 and S3.

## 3. Results and Discussion

Here, we studied the reactions of gold(III) complexes  $[\text{Au}(\text{L})\text{Cl}_2]^+$  containing chelating N,N-ligands ( $\text{L} = \text{bipy}$ ,  $\text{phen}$ ) with the boron cluster anions. Earlier, it was found that iron(III) and cobalt(III) salts react with  $[\text{B}_n\text{H}_n]^{2-}$  anions ( $n = 10, 12$ ) in the presence of bipy and phen, giving metal(II) compounds [55] with the boron clusters as counterions or even with substituted derivatives of the *closo*-decaborate anion with OH or Phen substitutes [56,57]. In the case of less reactive  $[\text{B}_{12}\text{H}_{12}]^{2-}$ , it was possible to isolate the cobalt(III) complex  $[\text{Co}(\text{phen})_3][\text{B}_{12}\text{H}_{12}]\text{NO}_3$  [44].

First, we carried out reactions of  $[\text{Au}(\text{L})\text{Cl}_2][\text{BF}_4]$  with the  $[\text{B}_{10}\text{H}_{10}]^{2-}$  and  $[\text{B}_{12}\text{H}_{12}]^{2-}$  anions in acetonitrile or acetonitrile/water solutions. However, it was found that both boron cluster anions reduce gold(III) to  $\text{Au}^0$  decomposing to oxidoborates.



The reaction solutions became black for a few seconds and a thin layer of gold formed on the flask wall, indicating that a gold mirror reaction took place.  $^{11}\text{B}$  NMR spectra of the reaction solutions showed the only peak at +20 ppm related to oxidoborates. In the IR spectra, a broad band at 1300–1200  $\text{cm}^{-1}$  is also observed assigned to  $\nu(\text{BO})$  of oxidoborates. No bands were found around 2500  $\text{cm}^{-1}$ , which is a typical range for  $\nu(\text{BH})$ .

Then, we studied the reactions of  $[\text{Au}(\text{L})\text{Cl}_2][\text{BF}_4]$  with  $[\text{B}_{20}\text{H}_{18}]^{2-}$  in acetonitrile and found that in such a case, gold(III) complexes  $[\text{Au}(\text{L})\text{Cl}_2]_2[\text{B}_{20}\text{H}_{18}]$  (**1**: L = bipy, **2**: L = phen) precipitate immediately as solvates  $[\text{Au}(\text{L})\text{Cl}_2]_2[\text{B}_{20}\text{H}_{18}] \cdot 2\text{CH}_3\text{CN}$  (**1**·2 $\text{CH}_3\text{CN}$  or **2**·2 $\text{CH}_3\text{CN}$ ). The complexes start to precipitate from the reaction solutions as dark orange needles (**1**·2 $\text{CH}_3\text{CN}$ ) or prisms (**2**·2 $\text{CH}_3\text{CN}$ ) as soon as solutions of reagents were mixed in acetonitrile.

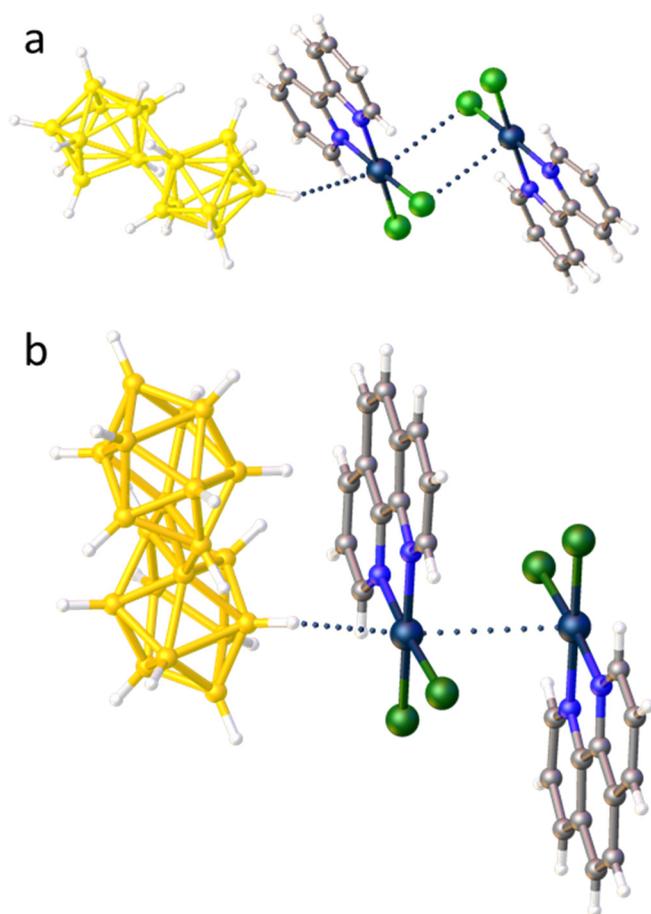


Successful formation of the gold(III) complexes with the  $[\text{B}_{20}\text{H}_{18}]^{2-}$  anion is most probably due to a lower reduction ability of the macropolyhedral boron cluster compared to  $[\text{B}_n\text{H}_n]^{2-}$  ( $n = 10, 12$ ) boron clusters.

A crystallographically independent part of the orthorhombic and triclinic unit cells of complexes **1**·2 $\text{CH}_3\text{CN}$  (*Pbca*) and **2**·2 $\text{CH}_3\text{CN}$  (*P-1*) contains the  $[\text{Au}(\text{L})\text{Cl}_2]^+$  cationic complex, half an anion, and a solvate molecule of acetonitrile, thus having the composition of  $[\text{Au}(\text{Bipy})\text{Cl}_2]_2[\text{B}_{20}\text{H}_{18}] \cdot 2\text{CH}_3\text{CN}$  or  $[\text{Au}(\text{Phen})\text{Cl}_2]_2[\text{B}_{20}\text{H}_{18}] \cdot 2\text{CH}_3\text{CN}$ . The anion in both cases also realizes the *trans*-configuration. The metal atom of the cations realize the square geometry with the gold(III) atom situated in the center of the  $\text{AuCl}_2\text{N}_2$  polyhedron (the shift in metal atom from the center is equal to 0.042(3) Å and 0.043(3) Å, respectively). The Au–N and Au–Cl distances are 2.016(8)–2.064(7) Å and 2.265(5)–2.278(4) Å for **1**, and 2.051(7)–2.060(6) Å and 2.270(3)–2.283(3) Å for **2**, respectively. In the structures of **1**·2 $\text{CH}_3\text{CN}$  and **2**·2 $\text{CH}_3\text{CN}$ , additional intermolecular interactions of the gold(III) atom can be observed (Figure 1). These are the B–H...Au interaction with the anion ( $r(\text{Au}\dots\text{B}8) = 3.89(1)$  Å,  $\text{AuHB} = 138.1(6)^\circ$ , and  $\text{NAuH} = 72.4(2)$ – $91.2(2)^\circ$  for **1** and  $r(\text{Au}\dots\text{B}9) = 3.55(1)$  Å,  $\text{AuHB} = 123.7(5)^\circ$ , and  $\text{NAuH} = 73.4(2)$ – $93.9(2)^\circ$  for **2**) and a long Au...Cl bond ( $r(\text{Au}\text{--}\text{Cl}) = 3.406(5)$  Å,  $\text{AuClAu} = 88.2(2)^\circ$ , and  $\text{NAuCl} = 82.8(2)$ – $87.7(2)^\circ$ ) in **1** and Au...Au bond ( $r(\text{Au}\text{--}\text{Au}) = 3.586(4)$  Å and  $\text{AuAuN} = 86.6(2)$ – $102.6(2)^\circ$ ) in **2**. Crystal packings of both compounds are shown in Figures S4 and S5. One of the equatorial BH groups interacts with the gold(III) atom in both structures.

In the IR spectra of complexes **1**·2 $\text{CH}_3\text{CN}$  and **2**·2 $\text{CH}_3\text{CN}$ , a strong splitting of the band of stretching vibrations  $\nu(\text{BH})$  is observed near 2500  $\text{cm}^{-1}$ , which is explained by weak interactions found in the structure. A narrow intensive band of bending vibrations of the BH group with respect to the boron cage  $\delta(\text{BBH})$  is observed near 1030  $\text{cm}^{-1}$ . Bands  $\nu(\text{CN})$  assigned to  $\text{CH}_3\text{CN}$  molecules are observed near 2300  $\text{cm}^{-1}$ . In addition, bands corresponding to coordinated Bipy and Phen ligands are observed in the region of 1600–700  $\text{cm}^{-1}$ .

At room temperature, complexes **1**·2 $\text{CH}_3\text{CN}$  and **2**·2 $\text{CH}_3\text{CN}$  are stable both in DMF solutions (at least for few days) and as solids (for some weeks) following our experimental data. We did not expose it to higher temperatures; however, based on our previous data for closely related compounds, we can expect them to show reasonable thermal stability. Note that cobalt and nickel compounds of the general formula  $[\text{ML}_6][\text{B}_{10}\text{H}_{10}]$  ( $\text{M} = \text{Co}, \text{Ni}$ ; L = DMF,  $\text{H}_2\text{O}$ ,  $1/2\text{N}_2\text{H}_4$ ) were used for low-temperature synthesis of metal borides [58–61]; they contain solvent molecules that can be easily removed when heating. Thermal stability data of gold complexes obtained here could be interesting because gold complexes contain metal in a more oxidized form (gold(III)), and in the presence of boron clusters that act as reducing agents, the obtained compounds should be more power-consuming compounds.



**Figure 1.** Gold(III) intermolecular interactions in the crystal of 2·2CH<sub>3</sub>CN (a) and 2·2CH<sub>3</sub>CN (b).

#### 4. Conclusions

We studied the reactions of gold(III) complexes [Au(L)Cl<sub>2</sub>]<sup>+</sup> (L = bipy, phen) with hydridoborate anions [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>, [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup>, and the macropolyhedral hydridoborate anion [B<sub>20</sub>H<sub>18</sub>]<sup>2-</sup>. The first gold(III) complexes with a hydridoborate cluster anion [Au(L)Cl<sub>2</sub>]<sub>2</sub>[B<sub>20</sub>H<sub>18</sub>] (L = bipy, phen) were isolated and characterized. In the structures of the compounds, the B–H...Au interactions were observed above the plane of the square-planar AuN<sub>2</sub>Cl<sub>2</sub> coordination polyhedron.

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**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/inorganics10070099/s1>, Figure S1: Calculated (orange) and experimental (black) X-ray powder diffraction patterns of complex 1·2CH<sub>3</sub>CN, Figure S2: Molecular view of 1·2CH<sub>3</sub>CN in representation of atoms with thermal ellipsoids (*p* = 50%), Figure S3: Molecular view of 2·2CH<sub>3</sub>CN in representation of atoms with thermal ellipsoids (*p* = 50%), Figure S4: Crystal packing of 1·2CH<sub>3</sub>CN, Figure S5: Crystal packing of 2·2CH<sub>3</sub>CN, Table S1: Crystal structure data and refinement details for 1·2CH<sub>3</sub>CN and 2·2CH<sub>3</sub>CN.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Muettterties, E.L.; Knoth, W.H. *Polyhedral Boranes*; Dekker: New York, NY, USA, 1968.
2. Greenwood, N.N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Elsevier: Oxford, UK, 1997.
3. Hosmane, N.S. *Boron Science: New Technologies and Applications*; Hosmane, N.S., Ed.; CRC Press: Boca Raton, FL, USA, 2012.
4. Boustani, I. *Boron Clusters, Molecular Modelling and Synthesis of Nanomaterials*; Springer Series in Materials Science; Springer: Cham, Switzerland, 2020; Volume 290, pp. 113–254. [[CrossRef](#)]
5. Duttwyler, S. Recent advances in B–H functionalization of icosahedral carboranes and boranes by transition metal catalysis. *Pure Appl. Chem.* **2018**, *90*, 733–744. [[CrossRef](#)]
6. Beckett, M.A.; Brellocks, B.; Chizhevsky, I.T.; Damhus, T.; Hellwich, K.-H.; Kennedy, J.D.; Laitinen, R.; Powell, W.H.; Rabinovich, D.; Viñas, C.; et al. Nomenclature for boranes and related species (IUPAC Recommendations 2019). *Pure Appl. Chem.* **2019**, *92*, 355–381. [[CrossRef](#)]
7. King, R.B. Three-Dimensional Aromaticity in Polyhedral Boranes and Related Molecules. *Chem. Rev.* **2001**, *101*, 1119–1152. [[CrossRef](#)] [[PubMed](#)]
8. Chen, Z.; King, R.B. Spherical Aromaticity: Recent Work on Fullerenes, Polyhedral Boranes, and Related Structures. *Chem. Rev.* **2005**, *105*, 3613–3642. [[CrossRef](#)] [[PubMed](#)]
9. Ren, L.; Han, Y.; Hou, X.; Ni, Y.; Wu, J. All are aromatic: A 3D globally aromatic cage containing five types of 2D aromatic macrocycles. *Chem* **2021**, *7*, 3442–3453. [[CrossRef](#)]
10. Poater, J.; Viñas, C.; Bennour, I.; Escayola, S.; Solà, M.; Teixidor, F. Too Persistent to Give Up: Aromaticity in Boron Clusters Survives Radical Structural Changes. *J. Am. Chem. Soc.* **2020**, *142*, 9396–9407. [[CrossRef](#)]
11. Núñez, R.; Tarrés, M.; Ferrer-Ugalde, A.; De Biani, F.F.; Teixidor, F. Electrochemistry and Photoluminescence of Icosahedral Carboranes, Boranes, Metallacarboranes, and Their Derivatives. *Chem. Rev.* **2016**, *116*, 14307–14378. [[CrossRef](#)]
12. Avdeeva, V.V.; Malinina, E.A.; Sivaev, I.B.; Bregadze, V.I.; Kuznetsov, N.T. Silver and Copper Complexes with *closo*-Polyhedral Borane, Carborane and Metallacarborane Anions: Synthesis and X-ray Structure. *Crystals* **2016**, *6*, 60. [[CrossRef](#)]
13. Malinina, E.A.; Avdeeva, V.V.; Goeva, L.V.; Kuznetsov, N.T. Coordination compounds of electron-deficient boron cluster anions  $B_nH_n^{2-}$  ( $n = 6, 10, 12$ ). *Russ. J. Inorg. Chem.* **2010**, *55*, 2148–2202.
14. Avdeeva, V.V.; Buzanov, G.A.; Malinina, E.A.; Kuznetsov, N.T.; Vologzhanina, A.V. Silver(I) and Copper(I) Complexation with Decachloro-*Closo*-Decaborate Anion. *Crystals* **2020**, *10*, 389. [[CrossRef](#)]
15. Avdeeva, V.; Malinina, E.; Kuznetsov, N. Boron cluster anions and their derivatives in complexation reactions. *Coord. Chem. Rev.* **2022**, *469*, 214636. [[CrossRef](#)]
16. Korolenko, S.E.; Malinina, E.A.; Avdeeva, V.V.; Churakov, A.V.; Nefedov, S.E.; Kubasov, A.S.; Burlov, A.S.; Divaeva, L.N.; Zhizhin, K.Y.; Kuznetsov, N.T. Zinc(II) and cadmium(II) complexes with the decahydro-*closo*-decaborate anion and phenyl-containing benzimidazole derivatives with linker N N or C N group. *Polyhedron* **2020**, *194*, 114902. [[CrossRef](#)]
17. Korolenko, S.E.; Kubasov, A.S.; Goeva, L.V.; Avdeeva, V.V.; Malinina, E.A.; Kuznetsov, N.T. Features of the formation of zinc(II) and cadmium(II) complexes with the inner-sphere and outer-sphere position of the decahydro-*closo*-decaborate anion in the presence of azaheterocyclic ligands. *Inorg. Chim. Acta* **2021**, *520*, 120315. [[CrossRef](#)]
18. Korolenko, S.E.; Zhuravlev, K.P.; Tsaryuk, V.I.; Kubasov, A.S.; Avdeeva, V.V.; Malinina, E.A.; Burlov, A.S.; Divaeva, L.N.; Zhizhin, Y.K.; Kuznetsov, N.T. Crystal structures, luminescence, and DFT study of mixed-ligand Zn(II) and Cd(II) complexes with phenyl-containing benzimidazole derivatives with linker C = N or N = N group. *J. Lumin.* **2021**, *237*, 118156. [[CrossRef](#)]
19. Zhang, Z.; Zhang, Y.; Li, Z.; Jiao, N.; Liu, L.; Zhang, S.  $B_{12}H_{12}^{2-}$ -Based Metal ( $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ) complexes as hypergolic fuels with superior hypergolicity. *Eur. J. Inorg. Chem.* **2018**, *2018*, 981–986. [[CrossRef](#)]
20. Malinina, E.A.; Goeva, L.V.; Kuznetsov, N.T. Multicenter interactions in lead(II) coordination compounds with  $B_nH_n^{2-}$  ( $n = 6, 10, 12$ ) cluster anions and their derivatives. *Russ. J. Inorg. Chem.* **2009**, *54*, 417–424. [[CrossRef](#)]
21. Teixidor, F.; Vinas, C.; Démonceau, A.; Nuñez, R. Boron clusters: Do they receive the deserved interest? *Pure Appl. Chem.* **2003**, *75*, 1305–1313. [[CrossRef](#)]
22. Avdeeva, V.V.; Malinina, E.A.; Zhizhin, K.Y.; Kuznetsov, N.T. Structural Diversity of Cationic Copper(II) Complexes with Neutral Nitrogen-Containing Organic Ligands in Compounds with Boron Cluster Anions and Their Derivatives (Review). *Russ. J. Inorg. Chem.* **2020**, *65*, 514–534. [[CrossRef](#)]
23. Avdeeva, V.V.; Vologzhanina, A.V.; Malinina, E.A.; Zhizhin, K.Y.; Kuznetsov, N.T. Boron Cluster Anions  $[B_{10}X_{10}]^{2-}$  ( $X = H, Cl$ ) in Manganese(II) Complexation with 2,2'-Bipyridyl. *Russ. J. Coord. Chem.* **2019**, *45*, 295–300. [[CrossRef](#)]
24. Belov, A.S.; Voloshin, Y.Z.; Pavlov, A.A.; Nelyubina, Y.V.; Belova, S.A.; Zubavichus, Y.V.; Avdeeva, V.V.; Efimov, N.N.; Malinina, E.A.; Zhizhin, K.Y.; et al. Solvent-induced encapsulation of cobalt(II) ion by a boron-capped tris-pyrazoloximate. *Inorg. Chem.* **2020**, *59*, 5845–5853. [[CrossRef](#)]
25. Shakirova, O.G.; Daletskii, V.A.; Lavrenova, L.G.; Trubina, S.V.; Erenburg, S.B.; Zhizhin, K.Y.; Kuzhetsov, N.T. Iron(II) *closo*-borate complexes with 1,2,4-triazole derivatives: Spin crossover in the iron(II) *closo*-borate complexes with tris(pyrazol-1-yl)methane. *Russ. J. Inorg. Chem.* **2013**, *58*, 650–656. [[CrossRef](#)]
26. Ivanova, A.D.; Lavrenova, L.G.; Korotaev, E.V.; Trubina, S.V.; Sheludyakova, L.A.; Petrov, S.A.; Zhizhin, K.Y.; Kuznetsov, N.T. High-Temperature Spin Crossover in Complexes of Iron(II) *closo*-Borates with 2,6-Bis(benzimidazol-2-yl)pyridine. *Russ. J. Inorg. Chem.* **2020**, *65*, 1687–1694. [[CrossRef](#)]

27. Avdeeva, V.V.; Malinina, E.A.; Vologzhanina, A.V.; Sivaev, I.B.; Kuznetsov, N.T. Formation of oxidopolyborates in destruction of the  $[B_{11}H_{14}]^-$  anion promoted by transition metals. *Inorg. Chim. Acta* **2020**, *509*, 119693. [[CrossRef](#)]
28. Kubasov, A.S.; Novikov, I.V.; Starodubets, P.A.; Avdeeva, V.V.; Zhizhin, K.Y.; Kuznetsov, N.T. Formation of Polyborates during Dimerization of the *closo*-Decaborate Anion and Isomerization of the Octadecahydroeicosaborate Anion. *Russ. J. Inorg. Chem.* **2022**, *67*, 984. [[CrossRef](#)]
29. Kozerozhets, I.; Panasyuk, G.; Semenov, E.; Voroshilov, I.; Avdeeva, V.; Buzanov, G.; Danchevskaya, M.; Kolmakova, A.; Malinina, E. A new approach to the synthesis of nanosized powder CaO and its application as precursor for the synthesis of calcium borates. *Ceram. Int.* **2021**, *48*, 7522–7532. [[CrossRef](#)]
30. Sivaev, I.; Bregadze, V.I.; Kuznetsov, N. Derivatives of the *closo*-dodecaborate anion and their application in medicine. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **2002**, *51*, 1362–1374. [[CrossRef](#)]
31. Zhizhin, K.Y.; Zhdanov, A.P.; Kuznetsov, N. Derivatives of *closo*-decaborate anion  $[B_{10}H_{10}]^{2-}$  with exo-polyhedral substituents. *Russ. J. Inorg. Chem.* **2010**, *55*, 2089–2127. [[CrossRef](#)]
32. Sivaev, I.B.; Prikaznov, A.V.; Naoufal, D. Fifty years of the *closo*-decaborate anion chemistry. *Collect. Czechoslov. Chem. Commun.* **2010**, *75*, 1149–1199. [[CrossRef](#)]
33. Sivaev, I.B.; Bregadze, V.I.; Sjöberg, S. Chemistry of *closo*-Dodecaborate Anion  $[B_{12}H_{12}]^{2-}$ : A Review. *Collect. Czechoslov. Chem. Commun.* **2002**, *67*, 679–727. [[CrossRef](#)]
34. Avdeeva, V.V.; Garaev, T.M.; Malinina, E.A.; Zhizhin, K.Y.; Kuznetsov, N.T. Physiologically Active Compounds Based on Membrantropic Cage Carriers—Derivatives of Adamantane and Polyhedral Boron Clusters (Review). *Russ. J. Inorg. Chem.* **2022**, *67*, 28–47. [[CrossRef](#)]
35. Kaczmarczyk, A.; Dobrott, R.D.; Lipscomb, W.N. Reactions of  $B_{10}H_{10}^{2-}$  ion. *Proc. Natl. Acad. Sci. USA* **1962**, *48*, 729–733. [[CrossRef](#)] [[PubMed](#)]
36. Hawthorne, M.F.; Shelly, K.; Li, F. The versatile chemistry of the  $[B_{20}H_{18}]^{2-}$  ions: Novel reactions and structural motifs. *Chem. Commun.* **2002**, *6*, 547–554. [[CrossRef](#)] [[PubMed](#)]
37. Avdeeva, V.V.; Buzin, M.I.; Malinina, E.A.; Kuznetsov, N.T.; Vologzhanina, A.V. Reversible single-crystal-to-single-crystal photoisomerization of a silver(i) macropolyhedral borane. *CrystEngComm* **2015**, *17*, 8870–8875. [[CrossRef](#)]
38. Avdeeva, V.V.; Buzin, M.I.; Dmitrienko, A.O.; Dorovatovskii, P.V.; Malinina, E.A.; Kuznetsov, N.T.; Voronova, E.D.; Zubavichus, Y.V.; Vologzhanina, A.V. Solid-State Reactions of Eicosaborate  $[B_{20}H_{18}]^{2-}$  Salts and Complexes. *Chem.—A Eur. J.* **2017**, *23*, 16819–16828. [[CrossRef](#)] [[PubMed](#)]
39. Il'inchik, E.A.; Polyanskaya, T.M.; Drozdova, M.K.; Myakishev, K.G.; Ikorskii, V.N.; Volkov, V.V. Geometric, Spectroscopic, and Magnetic Characteristics of  $[Tris(1,10\text{-phenanthroline)manganese}(2+), 1,2;1',2'\text{-trans-Bis[nonahydro-closo-decaborate]}(2-)] Bis(dimethylformamide)$ . *Russ. J. Gen. Chem.* **2005**, *75*, 1545–1552. [[CrossRef](#)]
40. Sirivardane, U.; Chu, S.S.C.; Hosmane, N.S.; Zhu, H.; Zhang, G. Bis[ethyl(ferrocenylmethyl)dimethylammonium] octadecahydroeicosaborate(2-). *Acta Cryst.* **1989**, *C45*, 333–336.
41. Schaper, T.; Preetz, W. Hexahydro-*closo*-hexaborate as a ligand in coordination compounds: Syntheses and crystal structure of  $[M_2(PPh_3)_2B_6H_6]$  (M = Cu, Au). *Chem. Ber. Recueil.* **1997**, *130*, 405–408. [[CrossRef](#)]
42. Malinina, E.A.; Drozdova, V.V.; Bykov, A.Y.; Belousova, O.N.; Polyakova, I.N.; Zhizhin, K.Y.; Kuznetsov, N.T. Complexes of gold clusters with the *closo*-borate anions  $B_{10}H_2-10$  and  $B_{12}H_2-12$ . *Dokl. Chem.* **2007**, *414*, 137–139. [[CrossRef](#)]
43. Exner, R.M.; Jenne, C.; Wegener, B. Electrochemical Synthesis of Triphenylphosphine Coinage Metal Complexes stabilized by *closo*-Dodecaborates  $[B_{12}X_{12}]^{2-}$  (X = H, F, Cl, Br, I). *Z. Anorg. Allg. Chem.* **2021**, *647*, 500–506. [[CrossRef](#)]
44. Jenne, C.; Wegener, B. Silver Salts of the Weakly Coordinating Anion  $[Me_3NB_{12}Cl_{11}]^-$ . *Z. Anorg. Allg. Chem.* **2018**, *644*, 1123–1132. [[CrossRef](#)]
45. Wegener, M.; Huber, F.; Bolli, C.; Jenne, C.; Kirsch, S.F. Silver-Free Activation of Ligated Gold(I) Chlorides: The Use of  $[Me_3NB_{12}Cl_{11}]^-$  as a Weakly Coordinating Anion in Homogeneous Gold Catalysis. *Chem.—Eur. J.* **2015**, *21*, 1328–1336. [[CrossRef](#)] [[PubMed](#)]
46. Avdeeva, V.V.; Malinina, E.A.; Belousova, O.N.; Goeva, L.V.; Polyakova, I.N.; Kuznetsov, N.T. Behavior of dodecahydro-*closo*-dodecaborate anion  $B_{12}H_{12}^{2-}$  in reaction with  $Au(Ph_3P)Cl$ . *Russ. J. Inorg. Chem.* **2011**, *56*, 524–529. [[CrossRef](#)]
47. Guschlbauer, J.; Shaughnessy, K.H.; Pietrzak, A.; Chung, M.-C.; Sponsler, M.B.; Kaszyński, P.  $[closo-B_{10}H_8-1,10-(CN)_2]^{2-}$  as a conduit of electronic effects: comparative studies of  $Fe \cdots Fe$  communication in  $[(\eta^5-Cp)(dppe)Fe]_2[\mu^2-(NC-X-CN)]_n^+$  ( $n = 0, 2$ ). *Organometallics* **2021**, *40*, 2504. [[CrossRef](#)]
48. Avdeeva, V.V.; Vologzhanina, A.V.; Goeva, L.V.; Malinina, E.A.; Kuznetsov, N.T. Reactivity of boron cluster anions  $[B_{10}H_{10}]^{2-}$ ,  $[B_{10}Cl_{10}]^{2-}$  and  $[B_{12}H_{12}]^{2-}$  in cobalt(II)/cobalt(III) complexation with 1,10-phenanthroline. *Inorg. Chim. Acta* **2015**, *428*, 154–162. [[CrossRef](#)]
49. Miller, H.C.; Miller, N.E.; Muetterties, E.L. Synthesis of Polyhedral Boranes. *J. Am. Chem. Soc.* **1963**, *85*, 3885–3886. [[CrossRef](#)]
50. Chamberland, B.L.; Muetterties, E.L. Chemistry of Boranes. XVIII. Oxidation of  $B_{10}H_{10}^{2-}$  and Its Derivatives. *Inorg. Chem.* **1964**, *3*, 1450–1456. [[CrossRef](#)]
51. Akhmadullina, N.S.; Churakov, A.V.; Retivov, V.M.; Sandu, R.A.; Shishilov, O.N. Gold(III) chloride and acetate complexes with bipyridine and phenanthroline. *Russ. J. Coord. Chem.* **2012**, *38*, 589–595. [[CrossRef](#)]
52. Sheldrick, G.M. SHELXT-Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71*, 3–8. [[CrossRef](#)]
53. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.

54. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [[CrossRef](#)]
55. Avdeeva, V.V.; Malinina, E.A.; Kuznetsov, N.T. Coordination chemistry of iron triad metals with organic N-donor ligands and boron cluster anions  $[B_{10}H_{10}]^{2-}$ ,  $[B_{12}H_{12}]^{2-}$ , and  $[B_{10}Cl_{10}]^{2-}$ : Complexation and accompanying processes. *Russ. J. Inorg. Chem.* **2017**, *62*, 1673–1702. [[CrossRef](#)]
56. Avdeeva, V.V.; Polyakova, I.N.; Churakov, A.V.; Vologzhanina, A.V.; Malinina, E.A.; Zhizhin, K.Y.; Kuznetsov, N.T. Complexation and exopolyhedral substitution of the terminal hydrogen atoms in the decahydro-*closo*-decaborate anion in the presence of cobalt(II). *Polyhedron* **2019**, *162*, 65–70. [[CrossRef](#)]
57. Malinina, E.A.; Korolenko, S.E.; Zhdanov, A.P.; Avdeeva, V.V.; Privalov, V.I.; Kuznetsov, N.T. Metal-Promoted Exopolyhedral Substitution of Terminal Hydrogen Atoms in the *Closo*-Decaborate Anion  $[B_{10}H_{10}]^{2-}$  in the Presence of Copper(II): Formation of the Substituted Derivative  $[2-B_{10}H_9OH]^{2-}$ . *J. Clust. Sci.* **2020**, *32*, 755–763. [[CrossRef](#)]
58. Avdeeva, V.V.; Polyakova, I.N.; Vologzhanina, A.V.; Goeva, L.V.; Buzanov, G.A.; Generalova, N.B.; Malinina, E.A.; Zhizhin, K.Y.; Kuznetsov, N.T.  $[Co(solv)_6][B_{10}H_{10}]$  (solv = DMF and DMSO) for low-temperature synthesis of borides. *Russ. J. Inorg. Chem.* **2016**, *61*, 1125–1134. [[CrossRef](#)]
59. Malinina, E.A.; Goeva, L.V.; Buzanov, G.A.; Retivov, V.M.; Avdeeva, V.V.; Kuznetsov, N.T. Synthesis and Thermal Reduction of Complexes  $[NiL_n][B_{10}H_{10}]$  (L = DMF,  $H_2O$ ,  $n = 6$ ; L =  $N_2H_4$ ,  $n = 3$ ): Formation of Solid Solutions  $Ni_3C_{1-x}B_x$ . *Russ. J. Inorg. Chem.* **2020**, *65*, 126–132. [[CrossRef](#)]
60. Malinina, E.A.; Goeva, L.V.; Buzanov, G.A.; Avdeeva, V.V.; Efimov, N.N.; Kozerozhets, I.V.; Kuznetsov, N.T. Synthesis and Physicochemical Properties of Binary Cobalt(II) Borides. Thermal Reduction of Precursor Complexes  $[CoL_n][B_{10}H_{10}]$  (L =  $H_2O$ ,  $n = 6$ ;  $N_2H_4$ ,  $n = 3$ ). *Russ. J. Inorg. Chem.* **2019**, *64*, 1325–1334. [[CrossRef](#)]
61. Malinina, E.A.; Goeva, L.V.; Buzanov, G.A.; Avdeeva, V.V.; Efimov, N.N.; Kuznetsov, N.T. A New Method for Synthesis of Binary Borides with Desired Properties. *Dokl. Chem.* **2019**, *487*, 180–183. [[CrossRef](#)]