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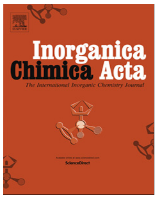

Research paper

Redox processes in the Cu/(*phen*)/$[B_{12}H_{12}]^{2-}$/solv system: Selective preparation of copper(I), copper(II), and heterovalent copper(I/II) compounds

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ABSTRACT

The complexation of copper and 1,10-phenanthroline (*phen*) in the presence of the $[B_{12}H_{12}]^{2-}$ anion is studied in organic solvents. The starting reagents contain copper(I) salts. The reactions are carried out in air and accompanied with oxidation of copper(I). Varying solvents and starting reagents, we succeeded in synthesizing selectively copper(I), copper(II), and heterovalent copper(I,II) complexes. Mononuclear, tetranuclear, and polymeric copper(II) complexes as well as a mononuclear copper(I) complex and a mixed cationic mononuclear copper(I)/copper(II) complexes are isolated and characterized by IR-spectroscopy and X-ray diffraction. The electronic structure of mononuclear copper(II) complex $[Cu^{II}(phen)_2Cl]_2[B_{12}H_{12}]$ $2CH_2I_2$ is studied by EPR.

1. Introduction

The boron cluster anions $[B_nH_n]^{2-}$ ($n = 6, 10, 12$) are electron-deficient structures characterized by high delocalization of the electron density over the boron cluster, 3D aromaticity, and relatively low charge [1–4]. It is known that redox transformations proceed in complexation of metals which have at least two non-zero stable oxidation states when *N*-donor organic ligands and boron clusters are present (in particular, $[B_{10}H_{10}]^{2-}$ possesses reduction activity) (e.g., iron [5], cobalt [6], and copper [7] complexation). Moreover, it was shown that copper and cobalt complexation reactions can be accompanied with the substitution of terminal hydrogen atoms in the decahydro-*closo*-decaborate anion to form metal complexes with substituted *closo*-decaborates [6–10].

Complexation processes in the $[Cu^I_2[B_{10}H_{10}]]$/L/solv systems, where L are *N*-donor ligands (1,10-phenanthroline (*phen*), 2,2′-bipyridyl (*bipy*), 2,2′-bipyridylamine (*bpa*), solv = CH_3CN, DMF, and DMSO) were studied systematically [7–15]. In these studies it was shown that one can obtain copper(I) complexes $[Cu^I_2L_2[B_{10}H_{10}]]$ with the inner-sphere position of the boron cluster, copper(II) complexes with the *closo*-decaborate anion as counterion (for example, $[Cu^{II}L_2][B_{10}H_{10}]$, L = *phen*), and heterovalent copper(I,II) complexes with different structures, namely cationic-anionic copper(I)/copper(II) complex $[Cu^I_2[B_{10}H_{10}]_3][Cu^{II}_4(OH_4)L_4]$ (L = *bipy* or *bpa*) and mixed cationic copper(I)/copper(II) complex $[Cu^IL_2][Cu^{II}L_3][B_{10}H_{10}]_2$ (L = *phen*). It was found that copper complexation can be accompanied with redox processes. When using copper(I) as the starting reagent, we can prepare copper(I) complexes in the presence of $[B_{10}H_{10}]^{2-}$ and L in acetonitrile (at room temperature in air when L = *bipy* and *phen*; at an inert atmosphere when L = *bpa*); copper(I,II) complexes in acetonitrile (on heating in air when L = *bipy* and *phen*; at −20 °C when L = *bpa*); and copper(II) complexes containing OH or CO_3 groups when DMSO or DMF were added to acetonitrile reaction solutions (L = *bipy* or *bpa*) or in air in acetonitrile for more reactive L = *bpa*.

When copper(II) was used as the starting reagent, copper(II) complexes can be synthesized in organic ligands (acetonitrile, DMF) and no redox transformation proceeds. It should be noted that redox processes $Cu^I \rightarrow Cu^{II}$ (because of air oxygen) or $Cu^{II} \rightarrow Cu^I$ (under the action of $[B_{10}H_{10}]^{2-}$ anion) can be realized at the reagent ratio M: L = 1: 1 or 1: 2, while the threefold excess of bidentate ligands prevents copper(II) cations to be reduced.

It is known that the $[B_{12}H_{12}]^{2-}$ has minor reaction ability among boron cluster anions $[B_nH_n]^{2-}$ ($n = 6–12$). As for redox properties, this anion it known to be stable in the presence of oxidizing agents,

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such as Fe(III) or Ce(IV). The *closo*-structure of the boron cluster is retained even on boiling in 30% hydrogen peroxide; in this case, the persubstituted $[B_{12}(OH)_{12}]^{2-}$ anion was formed in high yield [16]. Only addition of a reducing agent (Na_2SO_3 or SO_2) to an aqueous solution of Cu^{II} and $[B_{12}H_{12}]^{2-}$ salts allowed us to prepare Cu^{I} complexes $\{Cat[Cu^{I}[B_{12}H_{12}]]\}_n$ [17] while no reaction was observed to proceed between copper(II) salts and the $[B_{12}H_{12}]^{2-}$ anion in water. The high stability of $[B_{12}H_{12}]^{2-}$ compounds determines their application as polyfunctional materials including neutron-protective coatings [18].

Here, we study the copper(I)/copper(II) complexation reactions with *phen* in the presence of $[B_{12}H_{12}]^{2-}$ anion starting from copper (I) compounds. Taking into account redox processes that accompany copper complexation in air due to the nature of ligand L and solvent, the reaction conditions to prepare Cu(I), Cu(I/II), and Cu(II) compounds with the $[B_{12}H_{12}]^{2-}$ anion are determined.

2. Results and discussion

In copper complexation reactions we used $Cu^{I}Cl$, salts of the decahydro-*closo*-decaborate anion $Cs[Ag[B_{12}H_{12}]]$ or $Ph_4P[Cu^{I}[B_{12}H_{12}]]$, and *phen* as starting reagents (Table 1).

When the complexation reaction was carried out using copper (I) salts and *phen* in DMF in the presence of $[B_{12}H_{12}]^{2-}$, only copper(II) complexes **I** and **II** were formed (Table 1, reaction 1). The scheme of this reaction is shown in Scheme 1.

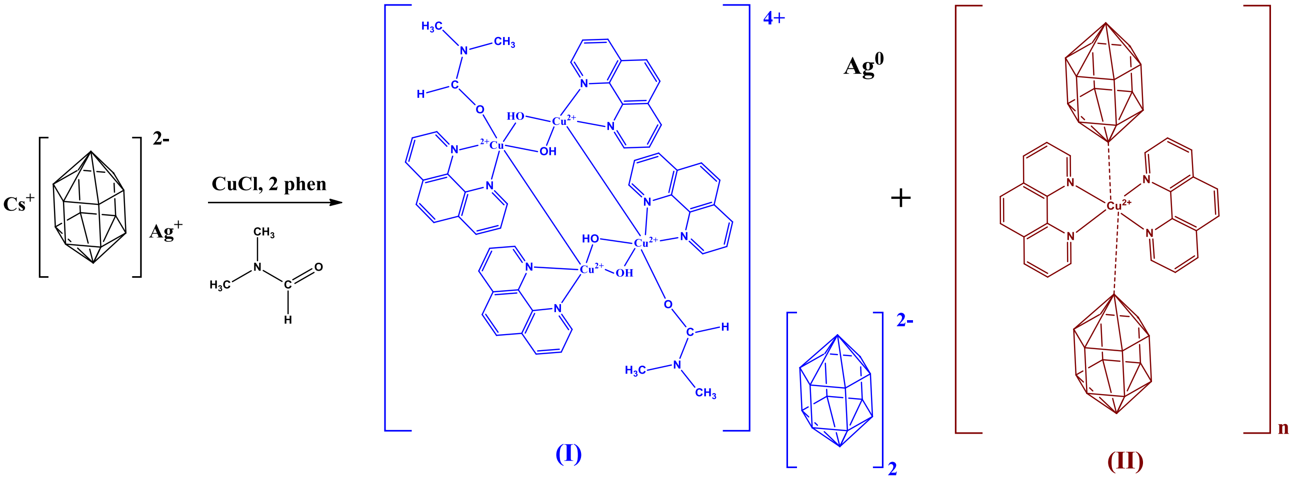
In this case, copper(I) is oxidized in air because both azaheterocyclic ligand L (*phen*) and solvent (DMF) stabilize copper(II) compounds. It should be noted that complexation reactions which proceed in the presence of silver salt $Cs[Ag[B_{12}H_{12}]]$ lead to simultaneous presence of two metals in the reaction solution, and in addition to the oxidation $Cu^{I} \rightarrow Cu^{II}$ because of L, the reduction $Ag^{I} \rightarrow Ag^{0}$ is observed. As a result of the redox transformations, tetramer **I** with the composition $[Cu^{II}_4(\mu\text{-}OH)_4(phen)_4(DMF)_2][B_{12}H_{12}]_2{\cdot}0.16H_2O$ was isolated from the reaction solution as the main product.

Structure **I** is built of centrosymmetric tetranuclear double-decker complex cations $[Cu^{II}_4(\mu\text{-}OH)_4(phen)_4(DMF)_2]^{4+}$, which are formed by two dinuclear complexes $[(Cu^{II}(phen)(OH)_2(Cu^{II}\text{-}PhenDMF)]^{2+}$, and $[B_{12}H_{12}]^{2-}$ anions (Fig. 1). Each deck consists of $[Cu^{II}(phen)]$ and $[Cu^{II}(phen)DMF]$ moieties connected by two OH-bridges. Two decks are bound through O(1)H groups which act as μ_3 bridges. The Cu(1) and Cu(2) atoms have distorted tetragonal pyramidal coordinations. The N_2O_2 bases of the pyramids are not quite planar: the CuN_2 and CuO_2 triangles are twisted by 12.1° for Cu(1) and 16.7° for Cu(2). Both hydroxo bridges between the Cu(1) and Cu(2) atoms are almost equilateral. The Cu—O bonds with the μ_2-O(2) atom (average, 1.926 Å) are shorter than those with the μ_3-O(1) atom (average, 1.974 Å). Although the range of Cu—N bonds is rather narrow (1.9993(16)–2.0307(16) Å), the bond with the nitrogen atom located trans to μ_3-O(1) is slightly shorter than the bond with the μ_2-O(2) atom for both copper atoms (Table S1). The apical Cu(1)—O(1)′ and Cu(2)—O(3) bonds are elongated to 2.3404(14) and 2.2191(15) Å, respectively. The four-membered Cu(1)O(1)Cu (1)′O(1)′ cycle is planar by symmetry. The Cu(1)O(1)Cu(2)O(2) cycle is folded by 16.7° along the O(1)...O(2) line or by 19.4° along the Cu (1)...Cu(2) line. The Cu(1)...Cu(2) distance of 2.9402(3) Å is the shortest copper–copper distance in the core of the complex cation. The Cu(1)...Cu(1)′ and Cu(1)...Cu(2)′ distances are 3.1609(3) and 3.6374(4) Å.

A search for tetranuclear dihydroxo-bridged copper(II) complexes with *phen* and O-ligands in the Cambridge Database [19] revealed several compounds with water molecules [20–29] and one compound with OH groups [29] acting as O-ligands. In all of them, complex cations have centrosymmetric structures close to that found in structure **I**. However, it is notable that in all of the related structures [20–29] the planes of phenanthroline molecules coordinating two copper atoms are almost parallel (2.7°–5.2°), whereas in structure **I** this angle is 25.0°. The large dihedral angle hampers π–π interactions between phenanthroline molecules, which were noted [21,24,27,29]. In structure **I** complex cations are packed into layers parallel to the *ac* plane (Fig. S1). The

Table 1
Schemes for the preparation of copper complexes with the $[B_{12}H_{12}]^{2-}$ anion and *phen*.

No	Solvent	Reagents	Products
1	DMF	$Cs[Ag[B_{12}H_{12}]]$ + CuCl + 2 *phen*	$[Cu^{II}_4(\mu\text{-}OH)_4(phen)_4(DMF)_2][B_{12}H_{12}]_2{\cdot}0.16H_2O$ **(I)** + $[[Cu^{II}(phen)_2][B_{12}H_{12}]]_n$ **(II)**
2	CH_3CN	$Ph_4P[Cu^{I}[B_{12}H_{12}]]$ + *phen*	$\{[Cu^{I}(phen)_2]_2[Cu^{II}(phen)_3]\}[B_{12}H_{12}]_2$ **(III)**
3	CH_3CN/CH_2I_2	$Ph_4P[Cu^{I}[B_{12}H_{12}]]$ + *phen*	**III** + $[Cu^{II}(phen)_3][B_{12}H_{12}]{\cdot}0.45(CH_2I_2){\cdot}1.55CH_3CN$ **(IV)**
4	$CH_3CN/CH_2I_2/C_6H_6$	$Ph_4P[Cu^{I}[B_{12}H_{12}]]$ + *phen* + $2Ph_3P$	$[Cu^{I}(phen)_2]_2[B_{12}H_{12}]{\cdot}C_6H_6$ **(V)**
5	CH_3CN/CH_2I_2	$Ph_4P[Cu^{I}[B_{12}H_{12}]]$ + $[Cu^{II}_2(phen)_4(\mu\text{-}CO)_3]Cl_2{\bullet}DMF{\bullet}H_2O$	$[Cu^{II}(phen)_2Cl]_2[B_{12}H_{12}]$ $2CH_2I_2$ **(VI)**



Scheme 1. Synthesis of complexes **I** and **II** (reaction 1 from Table 1).