

## Synthesis and Structure of New Water-Soluble Ag(I) and Pb(II) Complexes with Sulfonyl-Substituted Derivatives of the *closo*-Decaborate Anion

E. A. Malinina<sup>a,\*</sup>, S. E. Korolenko<sup>a</sup>, L. V. Goeva<sup>a,\*\*</sup>, and Academician N. T. Kuznetsov<sup>a</sup>

Received June 26, 2018

**Abstract**—The reactivity of sulfonyl-substituted *closo*-decaborate derivatives (the  $[2-B_{10}H_9SH]^{2-}$  and  $[2-B_{10}H_9S(CH_2C(O)NH_2)_2]^-$  anions) in the complexation of Ag(I) and Pb(II), Pearson soft acids, in the presence of competitive organic ligands has been studied. The substituted derivatives act as bridging ligands to form silver(I) binuclear complexes  $[(Ag(bipy)_2)_2(2-B_{10}H_9SH)]$  and  $[(Ag(bipy)_2)_2(2-B_{10}H_9S(CH_2C(O)NH_2)_2)NO_3]$ ; the  $[2-B_{10}H_9SH]^{2-}$  anion is involved in the lead(II) coordination polyhedron in the  $[Pb(2-B_{10}H_9SH)]$  and  $[Pb(bipy)_2(2-B_{10}H_9SH)]$  complexes; in  $[Pb(bipy)_2][2-B_{10}H_9S(CH_2C(O)NH_2)_2]_2$ , the substituted decaborate derivative acts as a counterion. The solubility of the mixed-ligand complexes is different due to the variety of their structures. The synthesized complexes are the first water-soluble lead and silver compounds with the *closo*-decaborate anion.

DOI: 10.1134/S0012500818120042

Cluster boron anions with exopolyhedral B–S bond are of great practical importance for boron neutron capture therapy (BNCT) of malignant tumors [1]. The BNCT principle is based on the nuclear reaction of the stable boron-10 isotope with thermal neutrons. The generated alpha particles and recoil nuclei have a high linear energy loss and a small free path commensurate with the diameter of a single cell. In the case of selective boron-10 accumulation in tumor cells, a local radiation effect can be achieved. Therefore, nowadays, the major challenge is to create boron-containing drugs that can selectively deliver a therapeutic amount of boron-10 to malignant tumor cells, ensure its optimal microdistribution, and remain in the cells for the time required for irradiation. Currently, the most well-known and widely used compounds are those of the sulfonyl-substituted *closo*-dodecaborate anion,  $[B_{12}H_{11}SH]^{2-}$ . However, the task of obtaining drugs with high chemical and biological stability, a high boron content in the molecule, low toxicity, and high water solubility has not been completely solved, so research in this area continues and is relevant.

Substituted derivatives of cluster boron anions are of fundamental interest since they form a series of weakly coordinating ligands [2–6]. The formation of substituted derivatives can occur with both persistence

of the system charge and its decrease, up to the formation of neutral substituted derivatives. The decrease in the charge of substituted anions significantly suppresses their coordination ability. Synthesis of metal complexes based on sulfonyl derivatives of the  $[B_{10}H_{10}]^{2-}$  anion can undoubtedly significantly extend the practical use of such compounds because of the possibility of using their combined properties potentially inherent in the cationic and anionic parts of a compound. It should be noted that the high solubility of such compounds in water is a decisive factor and greatly facilitates the solution of the tasks [7].

The only lead(II) complex with a sulfonyl-substituted derivative— $Pb(bipy)_2[1-B_{10}H_9SMe_2]_2$ —has been described in the literature [8], where its synthesis is reported and its structure is discussed. Single-crystal X-ray diffraction has demonstrated that the Pb(II) coordination polyhedron is formed, in addition to the heterocycle nitrogen atoms, by the BH group of the cluster anion.

The present study deals with the reactivity of the sulfonyl-substituted *closo*-decaborate anion derivatives in the complexation of Ag(I) and Pb(II), including reactions in the presence of soft bases as competitive ligands. Conditions of formation of intra-sphere complexes have been formulated; the solubility of metal salts and complexes based on sulfonyl-substituted derivatives of the  $[B_{10}H_{10}]^{2-}$  anion has been estimated.

The starting reagents were tetrabutylammonium salts  $((C_4H_9)_4N)_2[2-B_{10}H_9SH]$  and  $(C_4H_9)_4N[2-$

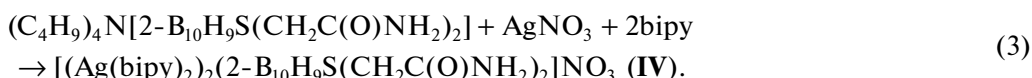
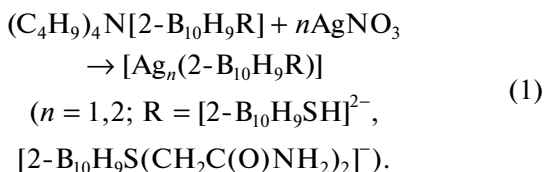
<sup>a</sup>Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia

\*e-mail: malinina@igic.ras.ru

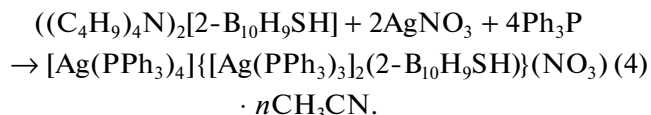
\*\*e-mail: lyudmila.goeva@mail.ru

$B_{10}H_9S(CH_2C(O)NH_2)_2$ , metal salts  $AgNO_3$  and  $Pb(NO_3)_2$ , and triphenylphosphine ( $Ph_3P$ ) and 2,2'-bipyridine as competitive ligands.

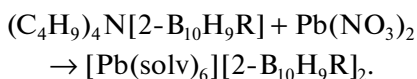
The reaction of  $((C_4H_9)_4N)_2[2-B_{10}H_9SH]$  or  $(C_4H_9)_4N[2-B_{10}H_9S(CH_2C(O)NH_2)_2]$  with  $AgNO_3$  in acetonitrile or  $H_2O$  gives  $[Ag_2(2-B_{10}H_9SH)] \cdot nsolv$  (**I**) or  $[Ag(2-B_{10}H_9S(CH_2C(O)NH_2)_2)] \cdot nsolv$  (**II**). The reaction in the general form is



The reaction of  $(Bu_4N)_2[2-B_{10}H_9SH]$  with  $AgNO_3$  and  $Ph_3P$  in a  $CH_3CN/C_6H_6$  mixture leads to the anionic complex  $[Ag(PPh_3)_4]\{[Ag(PPh_3)_3]_2(2-B_{10}H_9SH)\}(NO_3) \cdot nCH_3CN$  (**V**) irrespective of the reagent ratio (4):



The reaction of  $((C_4H_9)_4N)_2[2-B_{10}H_9SH]$  or  $(C_4H_9)_4N[2-B_{10}H_9S(CH_2C(O)NH_2)_2]$  with  $Pb(NO_3)_2$  in acetonitrile or  $H_2O$  gives  $[Pb(2-B_{10}H_9SH)]$  (**VI**) (bright yellow) or  $[Pb(solvent)_6][2-B_{10}H_9S(CH_2C(O)NH_2)_2]_2$ . The scheme of complexation is shown below:



The introduction of 2,2'-bipyridine (bipy) into the reaction solution containing  $((C_4H_9)_4N)_2[2-B_{10}H_9SH]$  or  $(C_4H_9)_4N[2-B_{10}H_9S(CH_2C(O)NH_2)_2]$  and  $Pb(NO_3)_2$  in acetonitrile leads to the  $[Pb(bipy)_2(2-B_{10}H_9SH)]$  (**VIII**) or  $[Pb(bipy)_2][2-B_{10}H_9S(CH_2C(O)NH_2)_2]_2$  (**IX**) complexes; complex **VIII** is rich colored.

Complexes **I–IX** were identified using elemental analysis<sup>1</sup> and IR spectroscopy data<sup>2</sup> (Table 1). The IR

<sup>1</sup> Elemental analysis on carbon, hydrogen, and nitrogen was performed on a Carbo Erba CHNS-3 FA 1108 Elemental Analyzer. Boron was quantified by atomic absorption spectroscopy on a Perkin-Elmer Model 2100 spectrometer with an HGA-700 electrothermal atomizer [9]; Ag was determined on an AAS-303 in an acetylene–air flame.

<sup>2</sup> IR spectra were recorded on a Lumex Infracum FT-02 spectrophotometer as Nujol mulls, NaCl plates, 4000–400  $cm^{-1}$ , resolution 1  $cm^{-1}$ .

The resulting complexes are brightly colored and are fairly soluble in water and organic solvents. It should be noted that the solubility of analogous complexes with the  $[B_{10}H_{10}]^{2-}$  and  $[B_{12}H_{12}]^{2-}$  anions is essentially lower, since the silver compounds of the  $[Ag_2B_nH_n]$  composition ( $n = 10, 12$ ) are the weighing forms ( $SP \sim 10^{-24}$ ) and are used in analytical determinations.

The introduction of 2,2'-bipyridine into the reaction solution containing  $((C_4H_9)_4N)_2[B_{10}H_9SH]$  or  $(C_4H_9)_4N[2-B_{10}H_9S(CH_2C(O)NH_2)_2]$  and  $AgNO_3$  in acetonitrile leads to the formation of fine crystalline precipitates of  $[(Ag(bipy)_2)_2(2-B_{10}H_9SH)]$  (**III**) or  $[(Ag(bipy)_2)_2(2-B_{10}H_9S(CH_2C(O)NH_2)_2)]NO_3$  (**IV**). The reactions are described by schemes (2) and (3):

spectra provide much information, which makes it possible to determine, at the first stage of studies, the participation of sulfanyl-substituted derivatives in the formation of metal coordination cores. In particular, for the complexes with the substituent group coordinated to the metal atom, the B–S stretching vibration band  $\nu(BS)$  at 960  $cm^{-1}$  is informative; for coordination by BH groups of the polyhedron, the B–H stretching vibration band  $\nu(BH)$  at 2340  $cm^{-1}$  is informative (Table 1).

The IR spectra of compounds **I–IV** show, in the BH stretching vibrations, two broad overlapping bands with maxima at about 2460 and 2320  $cm^{-1}$ , due to the  $\nu(BH)$  and  $\nu(BH)_{MHB}$  vibrations. The presence of the low-frequency band at 2320  $cm^{-1}$  points to the coordination of sulfanyl-substituted derivatives through the BH groups of the polyhedron to the Ag(I) or Pb(II) atoms. The spectrum of **VII** shows no low-frequency band at 2320  $cm^{-1}$ , which is evidence of the outer-sphere position of the  $[2-B_{10}H_9S(CH_2C(O)NH_2)_2]^-$  anion in the aqua complex. The coordinated water molecules in **VII** give rise to the  $\nu(OH)$  stretching vibration band in the range 3600–3400  $cm^{-1}$  and  $\delta(OH)$  bending vibration band at 1640  $cm^{-1}$ . The IR spectra of **I**, **VI**, and **VIII** allow us to conclude that the sulfur atom is involved in contacts with metal atoms, since the spectra show characteristic changes in the range of  $\nu(BS)$  vibrations 700–900  $cm^{-1}$ , which are absent in the spectra of the initial sulfanyl-substituted derivatives.

In the range of BH stretching vibrations, the IR spectrum of **V** shows the broadened strong  $\nu(BH)$  band of “free” BH groups at 2460  $cm^{-1}$  and the moderate  $\nu(BH)_{MHB}$  band at about 2330  $cm^{-1}$ , which

**Table 1.** Maxima of selected absorption bands in the IR spectra of compounds I–IX ( $\nu$ ,  $\text{cm}^{-1}$ )

Compound	$\nu(\text{BH})$	$\nu(\text{BH})_{\text{MHB}}$	$\delta(\text{BBH})$	$\nu(\text{BS})$
$\text{Cs}_2[2\text{-B}_{10}\text{H}_9\text{SH}]$	2451	–	1011	956
$((\text{C}_4\text{H}_9)_4\text{N})_2[2\text{-B}_{10}\text{H}_9\text{SH}]$	2441	–	1015	960
$((\text{C}_4\text{H}_9)_4\text{N})[2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2]$	2475	–	1002	927
$[\text{Ag}_2(2\text{-B}_{10}\text{H}_9\text{SH})] \cdot \text{nsolv}$ (I)	–	2320	941	873, 828, 790
$[\text{Ag}(2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2)] \cdot \text{nsolv}$ (II)	2505	2372	1005	925
$[(\text{Ag}(\text{bipy})_2)_2(2\text{-B}_{10}\text{H}_9\text{SH})]$ (III)	2492	2349	1012	935
$[(\text{Ag}(\text{bipy})_2)_2(2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2)]\text{NO}_3$ (IV)	2536, 2504	2356	1012	935
$[\text{Ag}(\text{PPh}_3)_4]\{[\text{Ag}(\text{PPh}_3)_3]_2(2\text{-B}_{10}\text{H}_9\text{SH})\}(\text{NO}_3) \cdot n\text{CH}_3\text{CN}$ (V)	2464	2329	998	971, 944, 917
$[\text{Pb}(2\text{-B}_{10}\text{H}_9\text{SH})]$ (VI)	2458	–	946	866, 825, 795
$[\text{Pb}(\text{H}_2\text{O})_6][2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2]_2$ (VII)	2470	–	1008	932
$[\text{Pb}(\text{bipy})_2(2\text{-B}_{10}\text{H}_9\text{SH})]$ (VIII)	2474	–	1011	935
$[\text{Pb}(\text{bipy})_2][2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2]_2$ (IX)	2468	–	1006	942

For V:  $\nu(\text{NO})_{\text{NO}_3} = 1308$ ;  $\nu(\text{Ph}_3\text{P}) = 1600\text{--}700$ ;  $\pi(\text{CH}) = 744, 694$ ;  $\nu(\text{C}\equiv\text{N}) = 2249 \text{ cm}^{-1}$ ; for III, IV, and V:  $\nu_{\text{cycle}} = 1700\text{--}700 \text{ cm}^{-1}$ .

indicates the coordination of the substituted derivative  $[2\text{-B}_{10}\text{H}_9\text{SH}]^{2-}$  through BH groups of the polyhedron to form three-center two-electron (3c2e) metal–H–B (MHB) bonds. The spectrum of this complex also shows changes in the range of B–S bond vibrations: instead of one moderate  $\nu(\text{BS})$  band at  $954 \text{ cm}^{-1}$ , the spectrum displays a broadened and very weak band with maxima at 972, 945, and  $915 \text{ cm}^{-1}$ , which can reflect the participation of the thio group of the sulfanyl-substituted derivative in contacts with metal atoms. The presence of the broadened strong  $\nu(\text{NO})$  band at about  $1350 \text{ cm}^{-1}$  corresponds to the presence of the  $\text{NO}_3$  group in the complex. The spectrum also shows a full set of vibrations of coordinated triphenylphosphine molecules in the range  $1500\text{--}700 \text{ cm}^{-1}$ .

The IR spectra of complexes III, VII, VIII, and IX show, in addition to  $\nu(\text{BH})$  and  $\nu(\text{BH})_{\text{MHB}}$  stretching vibration bands (III and VII), a full set of absorption bands of coordinated 2,2'-bipyridine molecules in the range  $1600\text{--}700 \text{ cm}^{-1}$ .

It should be noted that the high solubility of the initial alkylammonium salts of sulfanyl-substituted  $[\text{B}_{10}\text{H}_{10}]^{2-}$  derivatives is inherent in the synthesized Ag(I) and Pb(II) complexes with the corresponding substituted derivatives.

Thus, the synthesized Ag(I) and Pb(II) complexes with sulfanyl derivatives of the *closo*-decaborate anions— $[2\text{-B}_{10}\text{H}_9\text{SH}]^{2-}$  and  $[2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2]^{-}$ —and competitive soft bases are the first examples of water-soluble complexes with cluster boron anions and their substituted derivatives. The high solubility of the  $[\text{Ag}(2\text{-B}_{10}\text{H}_9\text{R})]_n$  ( $n = 1, 2$ ),  $\text{Pb}[2\text{-B}_{10}\text{H}_9\text{SH}]$ , and

$[\text{Pb}(\text{solv})_6][2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2]_2$  complexes, comparable with the solubility of alkali metal and alkylammonium salts with the corresponding anions, makes them good candidates for using in BNCT. The solubility of the synthesized mixed-ligand complexes is different and is likely caused by the diversity of their structures. In particular, in the binuclear  $[(\text{Ag}(\text{bipy})_2)_2(2\text{-B}_{10}\text{H}_9\text{SH})]$  and  $[(\text{Ag}(\text{bipy})_2)_2(2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2)]\text{NO}_3$  complexes, the substituted derivatives act as bridging ligands; in the  $[\text{Pb}(2\text{-B}_{10}\text{H}_9\text{SH})]$  and  $[\text{Pb}(\text{bipy})_2(2\text{-B}_{10}\text{H}_9\text{SH})]$  complexes, the  $[2\text{-B}_{10}\text{H}_9\text{SH}]^{2-}$  anion is involved in the formation of the Pb(II) coordination polyhedron (the coordination occurs only through the SH group of the substituted derivative); in  $[\text{Pb}(\text{bipy})_2][2\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_2\text{C}(\text{O})\text{NH}_2)_2]_2$ , the sulfanyl-substituted derivative acts as a counterion.

#### ACKNOWLEDGMENTS

This work was supported by the Council of the President of the Russian Federation for State Support of Leading Scientific Schools (project no. NSh-2845.2018.3).

#### REFERENCES

- Sivaev, I.B. and Bregadze, V.V., *Eur. J. Inorg. Chem.*, 2009, vol. 11, p. 1433.
- Ivanov, S.V., Ivanova, S.M., Miller, S.M., Anderson, O.P., Solntsev, K.A., and Strauss, S.H., *Inorg. Chem.*, 1996, vol. 35, p. 6914.
- Avdeeva, V.V., Polyakova, I.N., Vologzhanina, A.V., Malinina, E.A., Zhizhin, K.Yu., and Kuznetsov, N.T., *Polyhedron*, 2017, vol. 123, p. 396.

4. Zhizhin, K.Yu., Vovk, O.O., Malinina, E.A., Mustyatsa, L.V. Goeva, L.V., Polyakova, I.N., and Kuznetsov, N.T., *Russ. J. Coord. Chem.*, 2011, vol. 27, no. 9, pp. 653–658.
5. Zhizhin, K.Yu., Malinina, E.A., Polyakova, I.N., Lisovskii, M.V., et al., *Russ. J. Inorg. Chem.*, 2002, vol. 47, no. 8, pp. 1158–1167.
6. Zhizhin, K.Yu., Mustyatsa, V.N., Malinina, E.A., Matveev, E.Yu., et al., *Russ. J. Inorg. Chem.*, 2005, vol. 50, no. 2, pp. 203–209.
7. Zhizhin, K.Yu., Malinina, E.A., Goeva, L.V., Chernyavskii, S.A., Ivanov, S.V., Luk'yanets, E.A., Solntsev, K.A., and Kuznetsov, N.T., *Dokl. Akad. Nauk*, 1997, vol. 357, no. 2, p. 206.
8. Orlova, A.M., Sivaev, I.B., Lagun, V.L., Solntsev, K.A., and Kuznetsov, N.T., *Koord. Khim.*, 1993, vol. 19, p. 116.
9. Ochertyanova, L.I., Mustyatsa, V.N., Belousova, O.N., Zhizhin, K.Yu., and Kuznetsov, N.T., *Inorg. Mater.*, 2004, vol. 40, no. 2, pp. 144–146.

*Translated by G. Kirakosyan*