ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

UDC 546.273'16

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RESEARCH OF COMPOSITION AND STRUCTURE OF COMPLEX Cd(II) TETRAFLUOROBORATES WITH PHENYLENEDIAMINES

М.В. Шестакова, О.М. Чеботарьов. **Вивчення складу і будови комплексних тетрафтороборатів Cd(II) з фенілен діамінами.** Тетрафтороборна кислота і різні її продукти, наприклад, комплексні тетрафторобораты металів знаходять широке застосування в електрохімічних процесах при рафінуванні металів, при отриманні паяльних флюсів. Цікавою особливістю тетрафтороборатних комплексів металів з органічними лігандами є те, що в цих з'єднаннях група BF_4^- має різний характер зв'язування. ***Мета:*** Метою дослідження є підтвердження встановленої раніше залежності між основністю органічного ліганду і складом координаційної сфери тетрафтороборатного комплексу. ***Матеріали і методи:*** Препаративним шляхом синтезовано комплексні тетрафторобораты Cd(II) з ізомерними о-, м-, п-фенілендіамінами (ФДА). За допомогою ряду фізико-хімічних методів дослідження визначено склад і будову синтезованих комплексних сполук. У відповідності з результатами елементного, титриметричного й атомно-абсорбційного аналізів незалежно від способу синтезу для м- і п-ізомерів реалізуються сполуки $[CdФДА_4](BF_4)_2$. У випадку о-ФДА при синтезі без розчинника було отримано комплекс $[Cd(о\text{-}ФДА)_2](BF_4)_2$. ***Результати:*** Результати вимірів молярної електропровідності розчинів сполук у диметилформаміді свідчать, що комплекси є триіонними електролітами загального складу $[CdФДА_4](BF_4)_2$, а у випадку о-ФДА — $[Cd(о\text{-}ФДА)_2](BF_4)_2$. Центри координації органічних лігандів та зовнішньосферний характер зв'язку тетрафторобораt-іона встановлено за допомогою ІЧ спектроскопії. Відмічено вплив положення аміногруп у молекулі діаміну на склад і будову комплексів. ***Висновки:*** Встановлений склад координаційної сфери тетрафторборатних комплексів Cd(II) з ізомерними фенілендіамінами дає можливість зробити висновок про їх тетраедричну конфігурацію, оскільки саме така будова координаційного вузла характерна для даного металу-комплексоутворювача з координаційним числом 4.
Ключові слова: комплексні тетрафторобораты, фенілендіамін, координація, тетрафторобораt-іон.

M.V. Shestakova, O.M. Chebotarev. **Research of composition and structure of complex Cd(II) tetrafluoroborates with phenylenediamines.** Borofluoric acid and its various products, for example complex metals tetrafluoroborates, become widely used in electrochemical processes at refinement of metals, when receiving soldering fluxes. An interesting feature of tetrafluoroborate complexes of metals with organic ligands is that in these compounds the BF_4^- group has various nature of bond. ***Aim:*** The aim of this work is to confirm the established earlier dependence between basicity of organic ligand and structure of the coordination sphere of tetrafluoroborate complex. ***Materials and Methods:*** By preparative way the complex tetrafluoroborates Cd(II) with isomeric o-, m-, p-phenylenediamine (PD) are synthesized. The composition and the structure of the synthesized complex compounds are defined by series of physical and chemical methods of research. According to results of elemental, titrimetric and nuclear-absorbing analyses and without dependency on way of synthesis for m- and p-isomers the $[Cd(PD)_4](BF_4)_2$ bindings are implemented. In case of OPD use at synthesis without solvent the $[Cd(OPD)_2](BF_4)_2$ complex has been received. ***Results:*** Measurements results of solutions molar conductivity of bonds in dimethyl formamide demonstrate that complexes are the three-ionic electrolytes of the general structure of $[Cd(PD)_4](BF_4)_2$, and in case of OPD use — the $[Cd(OPD)_2](BF_4)_2$. Coordination centers of organic ligands and outer-sphere nature of tetrafluoroborate ion bond are defined by IR spectroscopy. Influence of provision of amino groups in diamine molecule on composition and structure of complexes is noted. ***Conclusions:*** The established structure of the coordination sphere of the Cd(II) tetrafluoroborate complexes with isomeric phenylenediamines allows to draw conclusion about their tetrahedral configuration as such structure of coordination node is characteristic for this metal as complexing agent with 4 as coordination number.
Keywords: complex tetrafluoroborates, phenylenediamine, coordination, tetrafluoroborate ion.

Introduction. Borofluoric acid and its various products, for example complex metals tetrafluoroborates, become widely used in electrochemical processes at refinement of metals, when receiving soldering fluxes [1]. Interesting feature of tetrafluoroborate complexes of metals with organic ligands (L) is that in these compounds the BF_4^- group has various nature of. As the BF_4^- ion represents regular tetrahedron in which the boron atom is covalently saturated, it is fair to assume mainly ionic character of BF_4^- in complex bonds. At the same time, tetrafluoroborate ion can act as mono- or bidentate ligand or to be in transient state between covalent-bonded and ionic, got its name of "semi-

DOI 10.15276/opu.1.48.2016.17

coordination" in literature [2, 3]. It should be noted that coordination binding of tetrafluoroborate ion in such complexes is implemented due to electron-donor atoms of fluorine, and organic ligands are the spatially unhindered compounds of rather simple structure, in particular the nitrogen-containing organic bases of amines (Am) class.

Earlier it is established by us [4…6] that for state of tetrafluoroborate ion in coordination bonds in case of two-charging metals the electron-donor ability (basicity) of Am has the paramount importance. Operating of this factor is linked with number of the molecules of organic ligand which are taking part in coordination which in its turn defines the nature of tetrafluoroborate ion binding. Thus, for rather weak organic bases which pK_a value does not exceed five, the six molecules of organic ligand are the part of the internal sphere according to coordination number of complexing agent metal. If the pK_a of Am values lie in the range of 5…7, the structure of complex bonds can be presented as $ML_4(BF_4)_2$. Formation of diverse ligand complexes which internal coordination sphere contains two molecules of organic ligand and two groups of BF_4^- takes place in case of rather strong bases which pK_a value exceeds 8 [4].

The aim of this work is to receipt the additional experimental acknowledge for the dependency received earlier between basicity of organic ligand and structure of the coordination sphere of tetrafluoroborate complex.

Materials and Methods. To solve this problem, the complex Cd(II) tetrafluoroborates with isomeric phenylenediamines were synthesized and investigated: o-phenylenediamine (OPD, pK_a=4.57), m-phenylenediamine (MPD, pK_a=5.11), p-phenylenediamine (PPD, pK_a=6.31). The choice of these diamines allowed to receive additional experimental confirmations to consistent patterns determined earlier.

Synthesis, and also elemental, IR-spectroscopic and titrimetric analyses, measurement of solutions bindings conductivity were carried out according to the techniques given in works [5, 7]. Content of metal and boron was determined by nuclear and absorbing and titrimetric methods. Identity of bindings is confirmed with the data of the X-ray phase analysis.

Results. According to results of the analyses the synthesized tetraftoroborate compounds have the structure provided in table 1. As it seen of the received results, irrespective of synthesis way (with solvent or without it) the $[CdPD_4](BF_4)_2$ compounds are implemented for m- and p-isomers. In case of OPD use at synthesis without solvent with ratio of components 1:6 the $[Cd(OPD)_2](BF_4)_2$ complex has been received. The specified structure of the one is undoubtedly linked with bidentate character of OPD that will be confirmed during IR-spectroscopic researches and it will be shown below.

The considered compounds represent steady on air products of white color and restrictedly water soluble. The measurements results of solutions molar conductivity of μ synthesized compounds in dimethylformamide (DMF) demonstrate that complexes are three-ionic electrolytes of the general structure $[CdPD_4](BF_4)_2$, and in case of OPD — $[Cd(OPD)_2](BF_4)_2$.

Table 1

Structure and some physical and chemical properties of complex Cd(II) tetrafluoborates with isomeric phenylenediamines

Compound	Atomic absorption analysis, %		Titrimetric analysis, %	μ, $Ohm^{-1}\cdot cm^2\cdot mol^{-1}$
	Cd (calculated/computed)	B (calculated/computed)	Cd (computed)	
$[Cd(OPD)_2](BF_4)_2$	22.38/22.73	4.30/4.83	22.29	160
$[Cd(MPD)_4](BF_4)_2$	15.64/15.50	3.01/3.38	15.97	155
$[Cd(PPD)_4](BF_4)_2$	15.64/15.91	3.01/3.32	15.33	150

Results of IR spectroscopy research are provided to table 2, where references of the main absorption bands of organic ligands and tetrafluoroborate ion vibrations are given in spectra of the synthesized complexes.

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

In the spectra of initial amines, the absorption bands with maxima in the ranges of 1450…1630 cm^{-1} caused by vibrations of benzene ring are observed; ranges of 1230…1310 cm^{-1} fit with valent vibrations of C–N bond; the set of bands in the range of 3000…3065 cm^{-1} is connected with valent vibrations of C–H of bonds, and strips at 670…760 cm^{-1}, 962…1015 cm^{-1} are connected with extra plane deformation vibrations of C–H of bonds. Fluctuations of in-coordinate amino group are fit with absorption bands at 3290…3300 cm^{-1} (symmetric valent vibration — ν_s) and 3390…3400 cm^{-1} (asymmetric valent vibration — ν_{as}); 1590…1610 cm^{-1} — plane deformation vibration of $\beta(NH_2)$ and 845…850 cm^{-1} — extra plane deformation vibration of $\gamma(NH_2)$ of free amino group.

In IR spectrums of complex tetrafluoroborates the greatest changes are fixed in the field of valent fluctuations of organic ligands amino groups. Shift values to the low-frequency area of valent asymmetric fluctuations bands of $\nu_{as}(NH_2)$ (Δ 180 cm^{-1}) and valent symmetric fluctuations of $\nu_s(NH_2)$ (Δ 150 cm^{-1}) along with noticeable low-frequency shift in the range of 1590…1610 cm^{-1} allow to speak about bidentate character of OPD in complex of $[Cd(OPD)_2](BF_4)_2$. In case of complexes with p- and m-isomers of PDA the splitting and low-frequency shift of absorption bands of amino groups and the presence of the bands related to free amino groups demonstrates coordination of cadmium on nitrogen atom only of one of NH_2-groups.

Lowering of valent fluctuations frequencies of C–N bond confirm weakening of this bond that is also result of complex formation.

Table 2

The main characteristic frequencies in IR spectrums complex Cd(II) tetrafluoroborates[*]

Compound	ν_{as} (NH_2)	ν_s (NH_2)	ν (rings)	$\nu_3(BF_4^-)$	$\nu_4(BF_4^-)$	ν(Cd–N)
OPD	3390 s	3290 m	1500 s 1600 m			
$[Cd(OPD)_2](BF_4)_2$	3210 m	3140 m	1490 m 1605 m	1015 vs	515 m 525 m	245 w
MPD	3400 s	3300 s	1500 s 1600 s			
$[Cd(MPD)_4](BF_4)_2$	3310 m	3240 m	1490 m 1590 m	1050 vs	525 m	275 m
PPD	3390 m	3300 m	1510 s 1600 w			
$[Cd(PPD)_4](BF_4)_2$	3300 m	3220 m	1500 m 1570 m	1070 vs	520 m	280 m

In IR spectra of the studied complexes also the absorption bands characteristic of valent and deformation fluctuations tetrafluoroborate ion are identified. Free tetrafluoroborate ion of T_d symmetry has 9 oscillatory degrees of freedom distributed between four normal fluctuations: full-symmetric valent $\nu_1(A_1)$ (760 cm^{-1}) and doubly degenerated antisymmetric deformation ν_2 (E) (360 cm^{-1}), and also three times degenerated antisymmetric valent $\nu_3(F_2)$ (1100 cm^{-1}) and deformational $\nu_4(F_2)$ (530 cm^{-1}). All these fluctuations are active in spectra of combinational dispersion while in IR spectrums only ν_3 and ν_4 are active. However, immixture of BF_4^--ion even in very weak interactions of various character causes lowering of this anion symmetry that leads to removal of degeneration and bans of oscillatory transitions. Owing to this, the absorption bands of active vibrations are split in IR spectrum, and inactive vibrations become active.

In IR spectrums of all Cd tetrafluoborates there are new bands caused by vibrations of tetrafluoroborate ion. Thus, in spectra of $[Cd(OPD)_2](BF_4)_2$ compound several changes of oscillatory characteristics of BF_4^- — splitting of deformation vibration band $\nu_4(BF_4^-)$, give the grounds to assume

[*] s = strong, m = medium, w = weak, vs = very strong, vw = very weak

about inclusion of BF_4^- anion in system of hydrogen bonds. For other compounds the character of the main tetrafluoroborate ion absorption bands position demonstrates that BF_4^- acts as antiion. It is confirmed by absence of absorption bands of $\nu_1(BF_4^-)$ and $\nu_2(BF_4)$ in IR spectrums, and also not unsplitted structure of absorption bands of $\nu_3(BF_4^-)$ and $\nu_4(BF_4^-)$, that demonstrates preservation of T_d of symmetry of this anion inherent in tetrahedral configuration of this anion, and, therefore, and its outer-sphere coordination.

Formation of Cd←N coordinate bonds in all received complexes is confirmed by availability of absorption bands in spectra of long-wave band ν(Cd-N) (245…280 cm^{-1}).

The established structure of the coordination sphere of the Cd(II) tetrafluoroborate complexes with isomeric phenylenediamines allows to draw conclusion about their tetrahedral configuration as such structure of coordination node is characteristic for this metal as complexing agent with 4 as coordination number. As one would expect, the spacious arrangement of amino groups in ligand defines its denticity and structure of the internal sphere of complex.

Conclusions. It is established that in case of complex Cd(II) tetrafluoroborates with organic ligands with average values pK_a the binds with coordination number of Cd equal to four of general formula $[CdL_4](BF_4)_2$ in case of monodentate and $[CdL_2](BF_4)_2$ in case of bidentate organic ligands are implemented. In all cases tetrafluoroborate ion does not join in coordination. Thus, the conducted research in general confirms the dependence established earlier [4].

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Received January 25, 2016
Accepted March 25, 2016