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SOLID-PHASE LIGAND SUBSTITUTION REACTIONS BY BOROHYDRIDE ANIONS IN CHROMIUM(III) AND COBALT(III) AMINE COMPLEXES

I. I. Yashina and *Yu. N. Shevchenko*

INSTITUTE OF PHYSICAL CHEMISTRY, ACADEMY OF SCIENCES OF THE
UKRAINIAN S. S. R., KIEV, U. S. S. R.

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The kinetic and thermodynamic characteristics of solid-phase ligand substitution reactions were determined for chromium(III) and cobalt(III) amine complexes with $B_{10}H_{10}^{2-}$ and $C_2B_9H_{12}^-$ in the outer sphere. The kinetic equation of the topochemical process was found to be of the form $f(\alpha) = (1-\alpha)^{2/3}$, corresponding to a reaction proceeeding on the interface between the phases (shrinking sphere).

Two types of solid-phase ligand substitution reactions were found: endothermic and exothermic reactions taking place either through thermal activation of the metal-ligand bond (in substitution reactions by the anion $B_{10}H_{10}^{2-}$), or through the acid-base proton-exchange reaction between the anion $C_2B_9H_{12}^-$ entering the coordination sphere and the amine leaving it; in this case the process proceeds without mass loss.

It could be demonstrated that the reactions occurring in crystalline complex salts cannot proceed by purely dissociative or associative mechanisms; depending on the structure of the crystal lattice, mutually adapted dissociative or associative mechanisms are feasible. Reactions proceeding by the first mechanism have $E_a = 300$–500 kJ/mol and $\log A = 30$–50; the values for reactions proceeding by the second mechanism are $E_a = 180$–250 kJ/mol and $\log A = 15$–25.

The basic method for synthetizing transition metal complexes with borohydrides is substitution of the ligands in the coordination sphere of the metal by borohydrides in various solvents. Reaction conditions must be selected for each individual case. However, it is indispensable to apply low temperatures (0 to 100°) [1, 2]. Methods have been reported for stabilizing such complexes by introducing (together with the borohydride) π-donor or π-acceptor ligands (CO, phosphines, stilbines, π-cyclopentadiene etc.) [3]. Stabilization of transition metal complexes with borohydrides by purely kinetic hindrance has also been reported, i.e. by introducing bulky ligands into the coordination sphere of the transition metal. For instance, stable complex salts $NiA(BH_4)_2$ were obtained (A being a cyclic or acyclic tetramine) [4].

Our earlier studies [5–8] demonstrated that stable complex compounds of transition metals with borodydrides can be synthetized by utilizing the solid-phase substitu-

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tion of the ligands in the coordination sphere of the metal ion by borohydride anions in the outer sphere:

$$[L_{n-1}M-(L)]^{z*}\ B_nH_m^{x-}\rightarrow[L_{n-1}MB_nH_m]^{(z-x)-}+L$$

Solid-phase reactions have recently been applied increasingly to synthetize new complex compounds [9, 10]. The implementation of such reactions has particular features, however. It must be considered, for instance, that the chemical reaction takes place between the central atom, the ligands and the cations or anions in the outer sphere, all of these already being packed in a tight crystal lattice. The transformation process is heterogeneous, therefore and proceeds within the crystal space. No solvent molecules are present that could enter the coordination sphere and stabilize certain intermediates. Translational and rotational motions of the ions and molecules in the crystal are largely restrained by virtue of the small distances between them. Hence, solid-phase reactions involving the inner coordination sphere depend to a great extent on the external environment [10].

Although much experimental material has been accumulated on solid-phase ligand substitution reactions, it is impossible to generalize and to predict conditions for some reaction. Further, this type of reaction has not been studied much for transition metal complexes with borohydrides.

In this paper we report measurements of the kinetic and thermodynamic characteristics of solid-phase ligand substitution reactions within chromium(III) and cobalt(III) complexes with borohydride anions; such reactions are classified and the possible mechanisms are studied.

Experimental

The compounds

$$[Cr(NH_2CH_3)_6]Br(B_{10}H_{10})\cdot 2\,H_2O,\ [Cr(NH_2CH_3)_5Br](C_2B_9H_{12})_2,$$

$$[Co(NH_2CH_3)_6]Br(C_2B_9H_{12})_2 \text{ and } trans\text{-}[Cr(NH_2CH_3)_2(en)_2]Br(B_{10}H_{10})$$

were synthetized and identified as described in [5–8]. These compounds were chosen for investigation since the borohydride anions in the outer sphere are capable of acting, when substituted for the ligands in the coordination sphere, both as monodentate and as multidentate ligands [11]. They can coordinate, to the complexing ion through σ-bonds $M-B<$, three-centre bonds $\overset{M}{B\curlywedge B}$ or three-centre bridge bonds $M-H-B$ [1, 2, 12]. Further $C_2B_9H_{12}^-$, after losing a proton at position 3, is capable of bond formation through overlapping of the π-orbital with the *d* orbital of the transition metal [13]. On the other hand, an indispensable condition for solid-state ligand substitution reactions is satisfied in these compounds [8]: in the temperature interval in which the bond between the metal and the emerging ligand is split, the borohydride anion entering the coordination sphere is stable: in this temperature interval, the complexing ion is not reduced either by the leaving ligand, or by the entering borohydride anion.

An OD-103 derivatograph, manufactured by MOM, Hungary, was used to record T, DTA, TG and DTG curves. The instrument was calibrated for measuring enthalpies of reaction [9] via the heats of melting of potassium thiocyanide and urea. In the experiments for measuring the activation characteristics of the reaction through the DTA curve, the experimental arrangement was taken into account as in studying thermolysis kinetics under non-isothermal conditions [10]. The experiments were carried out in open conical crucibles, and the volatiles formed were continuously removed at a rate of 100 cm^3/min. To study the sequence of stages in the ligand substitution by anions from the outer sphere, the initial salts were subjected to preliminary dehydration and/or desamination under isothermal conditions. The respective temperatures were chosen so as to allow dehydration only, or dehydration and splitting-off of one methylamine molecule. In these operations the crystals of the initial salt disintegrated into particles of 10 to 100 μm. To observe equal conditions for the thermal transformation, we chose a fraction of 20–50 μm for further investigation. At such particle sizes, the effect on the kinetic parameters is practically negligible. To eliminate the effect of diffusion processes on the ligand substitution reaction, the sale samples were diluted with alumina (particle size 100–200 μm), and any volatiles evolved were removed rapidly. The sample was prepared in the following manner: on the bottom of the crucible (diam. 12 mm, height 16 mm) a 4–5 mm deep layer of alumina was placed; this was followed by a 6–8 mm deep layer of a 1 : 1 mixture of the substance being investigated and alumina; the junction of the thermocouple was located in the centre of this layer. The correctness of the selected experimental conditions is proved by the fact that the kinetic parameters measured with sample masses varying from 50 to 150 mg were unchanged.

Results and discussion

For reaction of the type $A_s \rightarrow B_s + C_g$, the rate of the process depends on the temperature and the conversion. The rate equation for such reactions has the general form [10]

$$\frac{d\alpha}{dT} = f(\alpha)\frac{A}{\varphi}\exp\left(-\frac{E_a}{RT}\right)$$

where α is the conversion, $d\alpha/dT$ is the rate of change of α, K^{-1}, φ is the heating rate, $K\ s^{-1}$, A is the frequency factor in the Arrhenius equation, and $f(\alpha)$ is the kinetic equation of the topochemical process.

The dependence of α on T was determined experimentally from DTA and DTG curves, and the entropy and activation energy values were calculated as described in [10]. For the reaction studied, $f(\alpha) = (1-\alpha)^{2/3}$ is valid, corresponding to the reaction proceeding on the interface of the phases (shrinking sphere). We calculated the activation energy by the method described in [14, 15], without taking into account the particular features of the topochemical process.

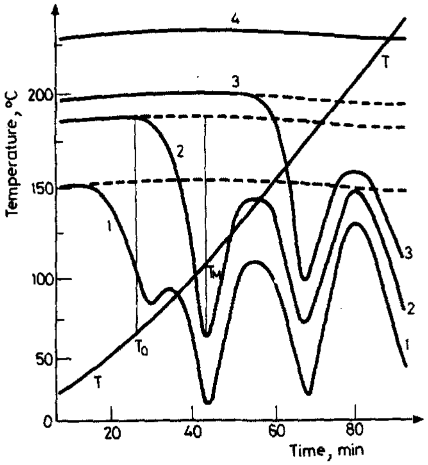


Fig. 1 DTA curves of complex chromium(III) salts. 1 – $[Cr(NH_2CH_3)_6]Br(B_{10}H_{10}) \cdot 2\,H_2O$, 2 – $[Cr(NH_2CH_3)_6]Br(B_{10}H_{10})$, 3 – $[Cr(NH_2CH_3)_5Br](B_{10}H_{10})$, 4 – zero line of the instrument, recorded with identical amounts (1.0 g) of Al_2O_3 in the crucible for the sample and in the crucible for the reference material. Sample mass of the complex salts: 150–160 mg

Figure 1, curve 1 is the DTA curve obtained on heating

$$[Cr(NH_2CH_3)_6]Br(B_{10}H_{10}) \cdot 2\,H_2O$$

in the temperature interval 20–250°. We earlier [8] demonstrated that the first endothermic effect corresponds to the loss of the two water molecules, and the two following effects to the stages of replacement of methylamine ligands by anions from the outer sphere. A comparison of the DTA curve with the zero line (curve 4) shows that in this case it is impossible to calculate the activation energy of methylamine substitution in the chromium(III) hexamine complex from the DTA curve, due to the positions of the thermal effects corresponding to dehydration and to ligand substitution in this temperature interval. For this reason we carried out preliminary isothermal decomposition of the initial salt. Decomposition temperatures were chosen so as to attain either dehydration only, or dehydration and substitution of the first methylamine molecule. The DTA curves for

$$[Cr(NH_2CH_3)_6]Br(B_{10}H_{10})$$

(curve 2) and

$$[Cr(NH_2CH_3)_5Br](B_{10}H_{10})$$

(curve 3) allowed calculation of the activation parameters of the reactions from the portions of the curve corresponding to the onset and to the maximum rate of dehydration and of methylamine substitution by Br^-. The temperatures for calculating the activation parameters were determined from the *T* curve recorded on the sample itself and not on an inert substance, as described in [15].

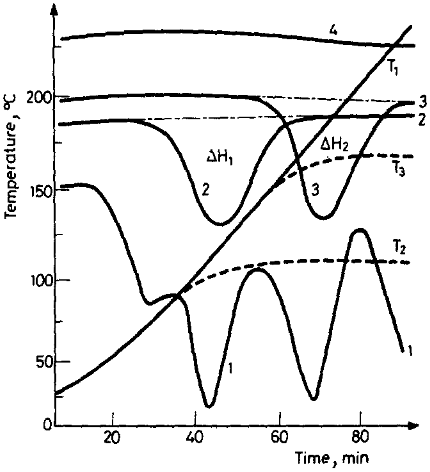


Fig. 2 DTA curves of complex chromium(III) salts recorded at stopped heating. 1 – $[Cr(NH_2CH_3)_6]Br(B_{10}H_{10}) \cdot 2\,H_2O$, 2 – $[Cr(NH_2CH_3)_6]Br(B_{10}H_{10})$, 3 – $[Cr(NH_2CH_3)_5Br](B_{10}H_{10})$, 4 – Zero line of the instrument. Sample mass of the complex salts: 150–160 mg

To separate the individual thermal effects in measuring ΔH, besides preliminary isothermal decomposition of the initial complex salts, we used the thermal curves recorded when heating was stopped as soon as the sample had reached the temperature at which ligand substitution takes place (Fig. 2). The enthalpies of the reactions studied were calculated by comparison of the areas confined by the thermal effects with the areas obtained under similar conditions with reference materials.

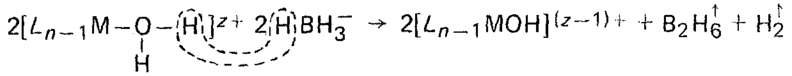
The experimentally found values for enthalpy ΔH, activation energy E_a, $\log A$ and other characteristics of the ligand substitution reactions are listed in Table 1 (the data are mean values from 6 to 8 parallel experiments). When the ligand substitution processes in amine complexes of chromium(III) and cobalt(III) were investigated by DTA using large sample masses (exceeding 150 mg) and the gas phase evolved was not removed, activation energy values higher by 100–150 kJ/mol were obtained than when the sample mass was 50–60 mg and the gas phase was removed. We demonstrated in [10] that the increased activation energy in this case is connected with the hindered diffusion of the gas evolved through the sample layer to the surface, and also with the reversibility of the solid-phase ligand substitution reaction, with transition of the amine from the coordination sphere of the metal ion into the gas phase.

Hence, by reducing the mass of sample applied and with the forced removal of the methylamine evolved in the reaction, the errors due to the above causes could be eliminated.

The second type of substitution whose energetic characteristics are listed in the Table is a solid-state acid-base reaction, involving proton-exchange between the anions $C_2B_9H_{12}^-$ in the outer sphere and the coordinated amine molecules. The π-(3)-dicarbolyl anion $C_2B_9H_{11}^{2-}$ enters the coordination sphere of the metal, while the protonated amine, as counter-ion, is accommodated in the outer sphere [5–7]. These ligand substitution reactions proceed without mass loss.

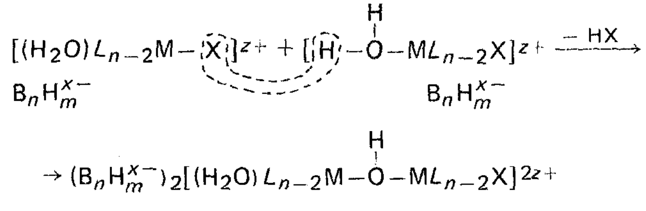
Besides ligand substitution reactions based on proton-exchange between the ligands leaving and entering the coordination sphere, and proceeding without mass loss, processes have been described [9] in which the coordinated ligands are expelled by proton-exchange with the entering anions from the outer sphere, and as a result of the reaction a volatile compound is formed. A general rule for this type of solid-phase ligand substitution might be as follows: ligand substitution through an acid-base reaction is possible only when the basicity of the ligand split off from the transition metal is significantly higher than that of the protonated ligand entering the coordination sphere.

Besides the positive effect leading to the substitution reaction and formation of the coordinate bond between the transition metal and the borohydride, the acid-base properties of the ligands may in certain cases hinder this process. It is well known, for instance, that the acidity of the protons of water, ammonia and other ligands is sharply increased when they are coordinated to a transition metal ion [16]. For this reason, aqua complexes of transition metals with borohydride anions in the outer sphere, and particularly with the most reactive anions BH_4^- and $B_3H_8^-$, are unstable and will decompose, evolving gaseous borohydrides and hydrogen, e.g.



$$2[L_{n-1}M-\underset{\displaystyle H}{\underset{|}{O}}-H]^{z+}\;2HBH_3^- \rightarrow 2[L_{n-1}MOH]^{(z-1)+} + B_2H_6\uparrow + H_2\uparrow$$

It is possibly for these reasons that amine complexes of nickel(II) with BH_4^- in the outer sphere decompose during storage, while tetrahydridoborates of chromium(III) amine complexes decompose at temperature above 100–120° [17, 19]. Aquahalide complexes are unstable too, since in this case heating may yield polynuclear complexes in which the transition metal ions are bonded through hydroxo-bridges, and gaseous hydrogen halides are evolved [19] which destroy the borohydride anions. For example:



$$\underset{B_nH_m^{x-}}{[(H_2O)L_{n-2}M-X]^{z+}} + \underset{B_nH_m^{x-}}{[H-\overset{\displaystyle H}{\overset{|}{O}}-ML_{n-2}X]^{z+}} \xrightarrow{-HX}$$

$$\rightarrow (B_nH_m^{x-})_2[(H_2O)L_{n-2}M-\overset{\displaystyle H}{\overset{|}{O}}-ML_{n-2}X]^{2z+}$$

Table 1 Energetic characteristics of solid-phase ligand substitution reactions in Cr(III) and Co(III) amine complexes

Reaction	T_i, K	T_{max}, K	ΔH kJ/mol	E_a, kJ/mol according to [15]	E_a, kJ/mol according to [10]	log A	$-\log K_{T_i}$	$-\log K_{T_{max}}$
$[Cr(NH_2CH_3)_5Br](C_2B_9H_{12})_2 \to$ $\to [Cr(NH_2CH_3)_3Br(C_2B_9H_{11})_2](NH_2CH_3)_2$	364	384	-60 ± 5	—	—	—	—	—
$[Co(NH_2CH_3)_5Br](C_2B_9H_{12})_2 \to$ $\to [Co(NH_2CH_3)_3Br(C_2B_9H_{12})_2](NH_2CH_3)_2$	346	358	-89 ± 5	—	—	—	—	—
$[Co(NH_2CH_3)_6]Br(B_{10}H_{10}) \to$ $\to [Co(NH_2CH_3)_5Br](B_{10}H_{10}) + NH_2CH_3^{\uparrow}$	323	339	196 ± 15	255 ± 25	245 ± 20	35.4	4.91	2.40
$[Cr(NH_2CH_3)_6]Br(B_{10}H_{10}) \to$ $\to [Cr(NH_2CH_3)_5Br](B_{10}H_{10}) + NH_2CH_3^{\uparrow}$	374	401	185 ± 10	284 ± 25	276 ± 20	34.1	4.10	1.89
$[Cr(NH_2CH_3)_5Br](B_{10}H_{10}) \to$ $\to [Cr(NH_2CH_3)_4Br(B_{10}H_{10}(] + NH_2CH_3^{\uparrow}$	401	428	187 ∓ 15	427 ± 30	416 ± 20	49.1	4.81	1.78
trans-$[Cr(en)_2(NH_2CH_3)_2]Br(B_{10}H_{10}) \to$ $\to$ *trans*-$[Cr(en)_2Br(B_{10}H_{10})] + 2\ NH_2CH_3^{\uparrow}$	506	557	—	536 ± 25	524 ± 20	50.2	4.70	1.83

In this work, in order to determine the possible mechanisms of solid-phase ligand substitution reactions, we investigated the energetics of the successive elementary stages of the process, involving the rearrangement of atoms and molecules in the crystal lattice in the thermal activation of the bonds. For instance, the reactions studied (listed in Table 1) may be grouped as endothermic and exothermic reactions. Let us divide each process into a series of elementary acts, their sum yielding the ligand substitution process with an endothermic or exothermic effect, depending on the established stoichiometric equation. A common feature of all the processes studied is splitting of the bond between the metal and the ligand leaving the coordination sphere ($\Delta H_{\mathrm{M-L}}$), and formation of a new bond between the metal and the borohydride anion entering the coordination sphere ($\Delta H_{\mathrm{M-B}_n\mathrm{H}_m^{x-}}$). In addition, the overall balance will include the energy change of the complex salt lattice (ΔU_k), by reason of the changes in the number of ions composing the lattice, their charges and radii [20]. The studied exothermic reactions include proton-exchange acid-base reactions. The amount of heat evolved is equal to the proton affinity of the amine leaving the coordination sphere (ΔH_{prot}) minus the energy required to split the proton off the borohydride anion entering the coordination sphere ($\Delta H_{\mathrm{B}_n\mathrm{H}_m^{x-}-H^+}$). Consequently, for endothermic reactions

$$\Delta H = \Delta H_{\mathrm{M-L}} - \Delta H_{\mathrm{M-B}_n\mathrm{H}_m^{x-}} + \Delta U_k$$

while for the studied exothermic reactions

$$\Delta H = 2\,\Delta H_{M-L} - 2\,\Delta H_{M-B_nH_m^{x-}} - 2\,\Delta H_{\mathrm{prot}} + 2\,\Delta H_{B_nH_m^{x-}-H^+} + \Delta U_k$$

The proton affinity of methylamine is $\Delta H_{\mathrm{prot}} = 883$ kJ/mol [21], while the energy required to split the $\mathrm{Cr}^{3+}\text{—}\mathrm{NH_2CH_3}$ bond, calculated as 1/6 of the formation energy of $[\mathrm{Cr(NH_2CH_3)_6}]^{3+}$ [22] is 797 kJ/mol. Obviously, ligand substitution is promoted by the appreciable reduction of the energy of the system due to protonation of the ligand leaving the coordination sphere. This is supported by the fact that, independently of the strength of the bond between the metal and the amine, the substitution processes proceed in practically the same temperature interval of 100–140° [5–7].

Attention should be paid to the high activation energies found for the studied reactions, several times exceeding the thermal effects (cf. Table 1) and over five times higher than the activation energies for analogous processes in solution [23]. These high activation energies suggest that the process takes place by the dissociative path. In [16] it was demonstrated for hexamine cations of cobalt(III) that when pentacoordinated transition complexes are formed by ligand substitution, energies up to 600 kJ/mol are required, depending on the structure. In solution, a large part of the energy is compensated by solvation. In the solid phase, however, solvents are absent, and moreover, to proceed by the dissociative path, a substantial reduction of the lattice energy of the complex salt in the transition state (ΔU_k^*) is necessary, due to the increase of the distance between the ions. In the studied endothermic reactions, therefore, assuming that the process occurs purely by the dissociative path, the activation energy will be expressed by the relationship

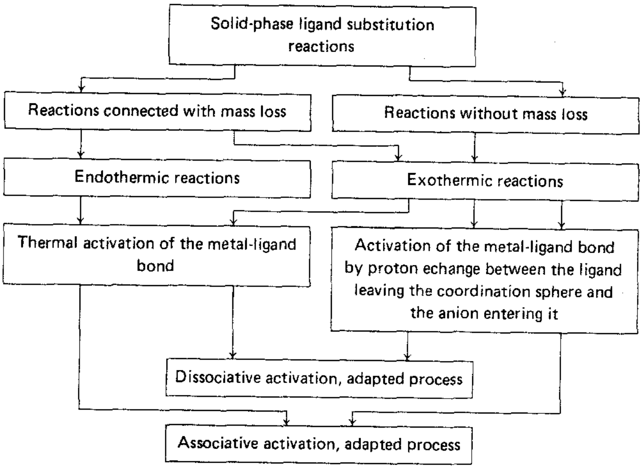
$$E_a = \Delta H^*_{M-L} + \Delta U^*_k$$

Since ΔH^*_{M-L} must have a value of 700–800 kJ/mol in the given case, it may be concluded that the pure dissociative mechanism does not take place. On the other hand, the high values of $\log A$ found for these reactions (cf. Table 1) indicate the dissociative path.

This sharp increase of entropy may be eliminated if the reaction proceeds by the associative path in this temperature interval. The energy of formation of a semi-coordinated complex is substantially lower [16], while the change of the lattice energy in the transient state ΔU^*_k will not be so high if substitution proceeds by the associative mechanism with a preliminary slight dissociative activation of the metal-ligand bond. For reactions of this type, activation energies of the order of 180–250 kJ/mol and Arrhenius frequency factors $A = 10^{15}$–10^{25} may be excepted. However, the associative mechanism may be impeded by the nature of the anion entering the coordination sphere from the outer sphere. Obviously, the large dimensions of $B_{10}H_{10}^{2-}$ will lead to an ionic crystal structure in which the interaction of Br^- with the chromium(III) or cobalt(III) hexamine complex will be significantly weakened, but the formation of a semi-coordinated complex with the participation of $B_{10}H_{10}^{2-}$ will be hindered by reason of steric non-conformity.

An answer to these problems will presumably be found if the kinetic and thermodynamic parameters of this type of ligand substitution in solid complex compounds of transition metals are studied in more detail.

The data obtained in this work and reported in the literature [9–10] regarding the stoichiometry, kinetics and thermodynamics of ligand substitutions in complexes of transition metals demonstrate that the reactions may be classified as follows:



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References

1 T. J. Marks and J. R. Kolb, Chem. Rev., 77 (1977) 263.
2 N. N. Greenwood and M. Ward, Chem. Soc. Rev., 3 (1974) 231.
3 A. Davison, D. D. Traficante and S. S. Wreford, J. Am. Chem. Soc., 96 (1974) 2802.
4 N. F. Curtis, J. Chem. Soc., (1965) 964.
5 Yu. N. Shevchenko, N. K. Davidenko, R. A Svitsin, N. I. Yashchina and N. B. Egorova, Zh. Neorg. Khim., 25 (1980) 2180.
6 Yu. N. Shevchenko, N. I. Yashchina, R. A. Svitsin and N. V. Egorova, Zh. Obshch. Khim., 51 (1981) 1258.
7 Yu. N. Shevchenko and N. I. Yashchina, Zh. Obshch. Khim., 51 (1981) 2582.
8 Yu. N. Shevchenko, N. I. Yashchina, K. B. Yatsimirsky, R. A. Svitsin and N. B. Egorova, Zh. Neorg. Khim., 28 (1983) 416.
9 Yu. N. Kukushkin, V. F. Budanova and G N. Sedova, Thermal transformations of coordination compounds in the solid phase, Izv. Leningradskogo Universiteta, Leningrad, 1981, p. 176 (in Russian).
10 V. A. Logvinenko, Thermal analysis of coordination compounds and clathrates, Izd. Nauka, Sibirian Division, Novosibirsk, 1982, p. 128 (in Russian).
11 L. J. Todd, Metalloborone derivatives with ligand-metal single bonds, Inorg. Compounds with Unusual Properties, Washington, D. D., 1976, p. 302 (in Russian).
12 R. D. Dobrott and W. N. Lipscomb, J. Chem. Phys., 37 (1962) 1779.
13 R. Grimes, Carboranes, Izd. Mir, Moscow, 1974, p. 264 (Russian translation).
14 A. A. Fotiev and V. V. Mochalov, Zh. Neorg. Khim., 13 (1968) 3174.
15 A. F. Zatsepin, A. A. Fotiev and I A. Dimtriev, Zh. Neorg. Khim., 18 (1973) 2883.
16 F. Bassolo and R. Pearson, Mechanisms of inorganic reactions, Izd. Mir, Moscow, 1971, p. 592 (Russian translation).
17 E. Zirngiebl and A. Burger, USA, Pat. No. 3.298.798.
18 Yu. N. Shevchenko, N. K. Davidenko, K. B Yatsimirsky, R. A. Svitsin and V. S. Khain, Izv. AN SSSR, Neorg. materiali, 14 (1978) 1747.
19 Yu. N. Shevchenko and N. I. Yashchina, Zh. Neorg. Khim., 27 (1982) 1441.
20 A. F Kapustinsky and K. B Yatsimirsky, Zh. Obshch. Khim., 26 (1956) 941.
21 V. N. Kondrateva, Splitting energies of chemical bonds. Ionization potentials and electron affinity, Izd. Nauka, Moscow, 1974, p. 351 (in Russian).
22 Yu. N. Shevchenko, Synthesis and investigation of cobalt(III) and chromium(III) amine complexes, Abstract of thesis for the C. Sc. degree, Kiev, 1977, p. 27 (in Russian).

Zusammenfassung — Die kinetischen und thermodynamischen Kennwerte der Ligandensubstitutionsreaktionen in fester Phase bei Chrom(III)- und Kobalt(III)-Aminkomplexen mit $B_{10}H_{10}^{2-}$ und $C_2B_9H_{12}^-$ als Anionen in der externen Sphäre wurden untersucht. Die kinetische Gleichung des topochemischen Prozesses hat die Form $f(\alpha) = (1 - \alpha)^{2/3}$, was einer an der Grenzfläche zwischen zwei Phasen verlaufenden Reaktion entspricht. Zwei Typen von Ligandsubstitutionsreaktionen in fester Phase wurden gefunden: endotherme und exotherme Reaktionen verlaufen entweder infolge thermischer Aktivierung der Metall-Ligand-Bindung (in Substitutionsreaktionen des Anions $B_{10}H_{10}^{2-}$) oder durch Protonenaustausch zwischen dem in die Koordinationssphäre eintretende Anion $C_2B_9H_{12}^-$ und dem daraus austretenden Amin; in diesem Falle verläuft der Prozeß ohne Massenverlust. Es konnte gezeigt werden, daß die in kristallinen Komplexsalzen vor sich gehenden Reaktionen nicht nach einem rein dissoziativen oder assoziativen Mechanismus verlaufen können;

abhängig von der Struktur des Kristallgitters ist ein wechselseitig angepasster dissoziativer oder assoziativer Mechanismus wahrscheinlich. Die nach dem ersten Mechanismus verlaufenden Reaktionen weisen für E_a Werte von 300 500 kJ/mol und für $\log A$ von 30–50 auf, während bei nach dem zweiten Mechanismus verlaufenden Reaktionen die entsprechenden Werte zwischen 180 und 250 kJ/mol bzw. 15 und 25 liegen.

Резюме — Измерены кинетические и термодинамические характеристики твердофазных реакций замещения лигандов в аминных комплексах хрома(III) и кобальта(III) борогидридными анионами $B_{10}H_{10}^{2-}$ и $C_2B_9H_{12}^-$ во внешней сфере. Найдено, что для изученных реакций кинетическое уравнение топохимического процесса имеет вид $f(\alpha) = (1-\alpha)^{2/3}$, что соответствует развитию реакции на межфазной границе (сжимающаяся сфера).

Установлены два типа твердофазных реакций замещения лигандов: реакции с эндо- и экзотермическим эффектом, которые могут осуществляться либо за счет термической активации связи металл-лиганд (реакция замещения анионом $B_{10}H_{10}^{2-}$), либо за счет кислотно-основной реакции обмена протоном между вступающим в координационную сферу анионом $C_2B_9H_{12}^-$ и уходящим амином; причем процесс протекает без потери массы.

Показано, что чисто диссоциативный или чисто ассоциативный механизмы для реакций в кристаллических комплексных солях не реализуются. В зависимости от строения кристаллической решетки соли возможны диссоциативный или ассоциативный взаимосогласованные механизмы. Реакции, протекающие по первому механизму, будут иметь величины $E_a = 300–500$ кДж/моль и $\log A = 30–50$, по второму — $E_a = 180–250$ кДж/моль и $\log A = 15–25$.