

SOLID-PHASE LIGAND SUBSTITUTION PROCESSES BY OUTER-SPHERE ANIONS IN ISOMERIC MIXED-LIGAND HEXAMINE CHROMIUM(III) COMPLEXES

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The mixed-ligand complex compounds *cis*- and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) were synthesized. It was demonstrated by IR spectroscopy that the hydrogen atoms of the anions B₁₀H₁₀²⁻ carrying the negative charge interact with the proton of the amino group in the coordinated amine, forming the bond system N–H–H–B. The complex salts obtained have high densities ($d^{20} = 1.55 \text{ g/cm}^3$ and 1.47 g/cm^3 for the *cis* and *trans* isomer, respectively) and high thermal stability 230–250 °C.

At 250–270 °C both the *cis* and the *trans* compound dissociate, with simultaneous substitution of two methylamine molecules in the coordination sphere of the chromium(III) ion by the anions Br⁻ and B₁₀H₁₀²⁻. The process is described by the topochemical equation $f(\alpha) = (1 - \alpha)^{2/3}$ (reaction on the interface of the phases), and is characterized by high values of the kinetic parameters: $E_a = 510\text{--}524 \text{ kJ/mol}$, $\log A = 49.9\text{--}50.2$. We found that the value of E_a for the amine substitution process in the *cis* compound, determined by evolved gas analysis under non-isothermal conditions, decreases by 220 kJ/mol when the heating rate is increased from 5.0 to 7.5 deg/min. This finding can be explained in that when the heating rate is increased, the intervals in which the *cis-trans* isomerization and ligand substitution reactions proceed come closer to one another, and finally overlap; the activation energy of the isomerization process then compensates part of the energy required for activation of the ligand substitution process.

In earlier papers, the solid-phase substitution of ligands in hexamine complexes of chromium(III) and cobalt(III) by outer sphere anions was studied with the aims of elucidating the stoichiometry and of finding the conditions for carrying out such reactions [1, 2]. It was demonstrated [1] that for solid-phase substitution of ligands in the coordination sphere of a transition metal by borohydride anions in the outer sphere, it is necessary that the dissociation of the complex cation should take place in a temperature interval in which the borohydride ligand entering the coordination sphere does not undergo thermal decomposition, and also that at the temperature of the substitution process, the oxidation state of the central ion should not be changed by the leaving ligand or by the entering outer anion. In [2] it was demonstrated that

the stoichiometry and temperature interval of the ligand substitution process in hexamine mixed-ligand complexes of chromium(III) by bromide anions from the outer sphere depend both on the nature of the coordinated ligands and on their position in the coordination sphere of the metal ion.

In the present work we have studied the stoichiometry of solid-phase ligand substitution processes in the hexamine mixed-ligand coordination compounds *cis*- and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀); we have also measured the kinetic parameters of these reactions and discuss the possible reaction mechanisms.

Experimental

The compounds were synthesized by the reactions *cis*- and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br₃ · *n*H₂O, prepared as described in [2], with ammonium decahydridocarbonate(2-), synthesized as described in [3]. 1.2–1.5 g of the initial complex salt was dissolved in 50–60 ml water acidified with HBr to pH 2–4. To this solution, a concentrated solution of (NH₄)₂B₁₀H₁₀ (1 g salt in 5–10 ml water) was added in small portions, in an amount to give a 10–20% excess of (NH₄)₂B₁₀H₁₀ in the mixture. Immediately after addition of the first portions, precipitation of the complex salt to be synthesized began. Full precipitation was attained after cooling of the reaction mixture in an ice-bath. The crystals were separated, washed on the filter and dried in air. The yield was 80–85% relative to the initial hexamine salt.

To identify the compounds and the products of their thermal transformation, their Cr, C, N and H contents were determined by chemical analysis, and their IR and electron absorption spectra were recorded. Further, the densities of the compounds and the molar conductivities of aqueous solutions of the complex salts in concentrations of (1–2) · 10⁻³ mol/dm³ were measured.

IR spectra were recorded in KBr tablets on an IKS 29 (LOMO) spectrometer in the frequency range 400 to 4000 cm⁻¹. Control records were taken in vaseline oil and LiF tablets; coinciding results were obtained. The electronic spectra of the solid salts were recorded with an SF-20 (LOMO) spectrophotometer; the samples were prepared in the form of thin suspensions in silicone oil. The conductivities of the solutions were measured with an automated a. c. bridge instrument of R-5016 type.

The thermal transformations of the complex salts were studied in air at a flow rate of 100 cm³/min, in the temperature interval 20 to 500°, by thermoanalytical methods. T, DTA, TG, DTG, EGA and DEGA were recorded on an OD-103 derivatograph fitted an evolved gas analyzer (MOM, Budapest). Open conical crucibles (diam. 12 mm, height 16 mm) were used. The samples were prepared as follows: a 4–5 mm layer of alumina was placed on the bottom of the crucible; subsequently, the crucible was filled with a 6–8 layer of a 1:1 mixture of the salt to be investigated and alumina, in such a way that the junction of the thermocouple was located in the centre of this layer. For thermal analysis we took particle fractions of the compound

and of alumina in the range 20–50 μm and 150–200 μm , respectively. The evolved amine was titrated [4, 5] with 0.025 mol/l sulphuric acid at pH 5. To ensure the exact determination of the stoichiometry of the transformation processes, the initial compounds were kept isothermally in a thermostated cell at the temperature at which the reaction proceeds till constant mass was reached, i.e. total completion of the reaction. The kinetic parameters of the reactions were calculated from the derivative EGA (DEGA) curves and also from gas evolution curves obtained in the decomposition of the substance in a continuous reactor fitted with a conductometric detector, as described in [6]. The carrier gas was helium, at a flow rate of 100 cm^3/min . The sample mass was 10 mg.

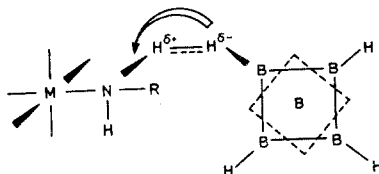
Results and discussion

The analysis results on *cis*- and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) in Table 1 compare well with each other and with the calculated values. However, the densities and molar electrical conductivities of their aqueous solutions differ. These data agree well with the results obtained in [2] for *cis*- and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br₃ · nH₂O, i.e. the initial compounds for the synthesis of the compounds investigated in this paper.

In the range 400–1600 cm^{-1} , the spectra of the *cis* and *trans* compounds are practically identical. Besides the absorption bands corresponding to the stretching and deformation vibrations of methylamine and ethylenediamine, deformation vibrations of the anion B₁₀H₁₀²⁻ (660–670, 1030–1080 cm^{-1}) are observed [1]. However, in contrast to hexamine chromium(III) complex salts with non-mixed ligands and containing the B₁₀H₁₀²⁻ anion in the outer sphere, a strong interaction arises between the anion B₁₀H₁₀²⁻ and the other ions of the crystal lattice, due to the structure of the complex salts studied in this paper. Such an interaction was observed earlier in solid hexamine complex salts of cobalt(III) [1].

The IR spectra of the synthesized compounds in the range 2000 to 3700 cm^{-1} are shown in Fig. 1. In this range, the N–H, C–H and B–H stretching vibrations of the coordinated amines and the anion B₁₀H₁₀²⁻ are observed. The splitting of the band corresponding to the B–H stretching vibrations is marked; it is stronger for the salts in which the complex cation has the *trans* structure. Simultaneously, a very intense absorption band appears at 3230 cm^{-1} , similarly as observed [1] in the spectra of the analogous hexamine complex cobalt(III) salts. In [1], the splitting of the band corresponding to the B–H stretching vibrations is explained by the interaction of the B₁₀H₁₀²⁻ in the outer sphere with the proton of the amino group of the coordinated ligand, resulting in the formation of an N—H—B bond system. Analysis of the IR spectra of the compounds studied in this paper and in [1] demonstrates that the intense band at 3230 cm^{-1} , shifted towards high frequencies relative to $\nu(\text{NH}_2)$, is observed only when splitting of the $\nu(\text{BH})$ band is significant. For compounds of this type, no other bands except those corresponding to the stretching vibrations of

the NH_2 groups are observed in the range $3100\text{--}3300\text{ cm}^{-1}$. We therefore assumed that this band might be a consequence of a bond formed between a terminal hydrogen atom of the $\text{B}_{10}\text{H}_{10}^{2-}$ and a proton of the amino group of the coordinated ligand:



Considering the hydride nature of the terminal hydrogen atom in the anion, the shift of $\nu(\text{NH}_2)$ towards high frequencies may be explained by the transfer of electron density along the $\text{H}\text{--}\text{H}$ bond of the $\text{--N}\text{--}\text{H}\text{--}$ bond.

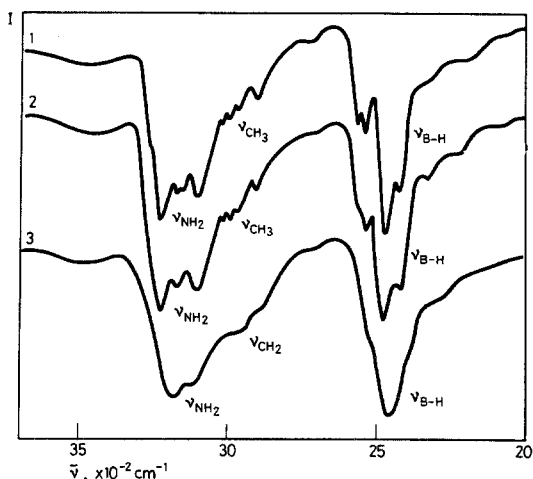


Fig. 1 Infrared spectra of the complex salts $\text{trans-}[\text{Cr}(\text{en})_2(\text{NH}_2\text{CH}_3)_2]\text{Br}(\text{B}_{10}\text{H}_{10})$ (1), $\text{cis-}[\text{Cr}(\text{en})_2(\text{NH}_2\text{CH}_3)_2]\text{Br}(\text{B}_{10}\text{H}_{10})$ (2) and $\text{trans-}[\text{Cr}(\text{en})_2\text{Br}(\text{B}_{10}\text{H}_{10})]$ (3)

The electronic spectra of the synthesized compounds include two symmetric absorption bands corresponding to the octahedral ligand field $d\text{--}d$ transitions $4A_2 \rightarrow 4T_1$ at $(27\text{--}30) \cdot 10^3\text{ cm}^{-1}$ and $4A_2 \rightarrow 4T_2$ at $(20\text{--}24) \cdot 10^3\text{ cm}^{-1}$. The positions of the maxima practically coincide with the data in [7] for solid cis- and $\text{trans-}[\text{Cr}(\text{en})_2(\text{NH}_2\text{CH}_3)_2]\text{Br}_3 \cdot n\text{H}_2\text{O}$.

Figure 2 presents the thermoanalytical curves of the studied hexamine complex compounds in a dynamic air atmosphere. The thermal stabilities of these compounds were unexpectedly high. Methylamine molecules were split off at initial temperatures of $227\text{--}247^\circ$, and the maximum of the DEGA curve corresponds to the temperature

interval 280–290°. These temperatures are the highest for all known hexamine complexes of chromium(III). For instance, *cis*- and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br₃ dissociate even at 100°, splitting off methylamine, and even the analogous tris(ethylenediamine) chromium(III) salts are less stable by 20–30°, although they

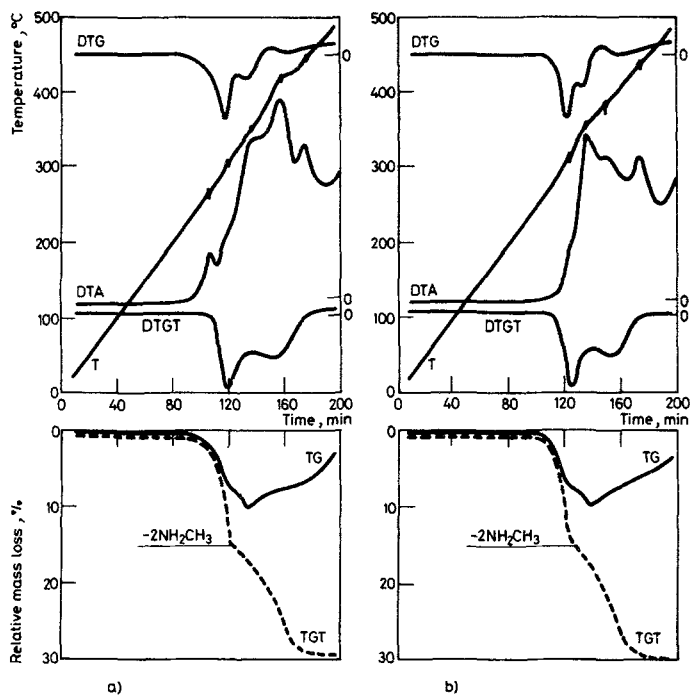


Fig. 2 Thermogravimetric (TG), derivative thermogravimetric (DTG), temperature (T), differential thermoanalytical (DTA), evolved gas analytical (EGA) and derivative evolved gas analytical (DEGA) curves for the salts *cis*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) (a) and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) (b). Sample mass 0.20 g, heating rate 2.5 deg/min

contain bidentate ligands only. Since the formation energies of the ions composing the lattice of the salts are practically identical [10], the data may be explained by the compounds having close to tightest ion packing. As a result, the highest possible lattice energy is attained, and no advantage could be gained from any intermediates being formed in the substitution of methylamine molecules by anions from the outer sphere. The high density of the compounds and their slight solubility in water are also in favour of this explanation. It is seen in Fig. 2 that the thermal transformations for the two isomeric compounds in the temperature interval between 20 and 500° differ essentially only in the transformation of the *cis* compound proceeding without mass loss and accompanied by a slight exothermic effect. Such processes

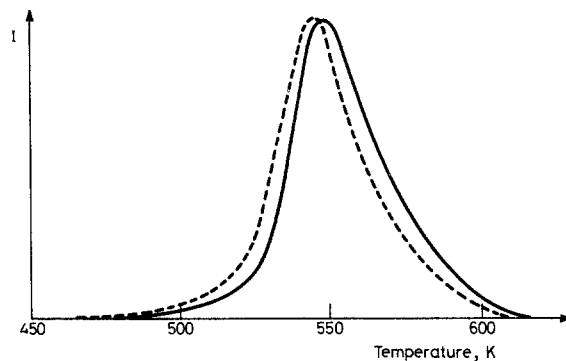
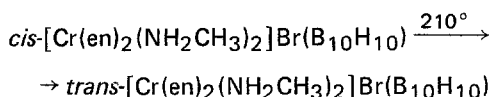


Fig. 3 Gas evolution curves recorded in a continuous reactor. — $trans$ -[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀), - - - cis -(Cr(en)₂(NH₂CH₃)₂)Br(B₁₀H₁₀)

Table 1 Elemental analysis, density and molar conductance of the studied chromium(III) compounds and their thermal decomposition products at 240 °C

| Compound | Composition, mass-% | | | | Colour | d^{20}_4 , g/cm ³ | λ^{20}_m , cm ² /Ωmol |
|---|---------------------|------|------|------|--------|-----------------------------------|---|
| | Cr | C | N | H | | | |
| cis -[Cr(en) ₂ (NH ₂ CH ₃) ₂]Br(B ₁₀ H ₁₀) | Found | 11.8 | 16.5 | 19.4 | 8.3 | yellow | 1.55 |
| | Calcd | 12.0 | 16.6 | 19.3 | 8.3 | | |
| $trans$ -[Cr(en) ₂ (NH ₂ CH ₃) ₂]Br(B ₁₀ H ₁₀) | Found | 11.9 | 16.4 | 19.5 | 8.1 | yellow | 1.47 |
| | Calcd | 12.0 | 16.6 | 19.3 | 8.3 | | |
| Decomposition product of the | | | | | | | |
| cis -salt: $trans$ -[Cr(en) ₂ Br(B ₁₀ H ₁₀)] | Found | 13.9 | 12.7 | 15.0 | 6.9 | reddish brown | 1.62 |
| | Calcd | 14.0 | 12.9 | 15.1 | 7.0 | | |
| Decomposition product of the | | | | | | | |
| $trans$ -salt: $trans$ -[Cr(en) ₂ Br(B ₁₀ H ₁₀)] | Found | 14.0 | 12.8 | 15.0 | 6.9 | reddish brown | 1.62 |
| | Calcd | 14.0 | 12.9 | 15.1 | 7.0 | | |

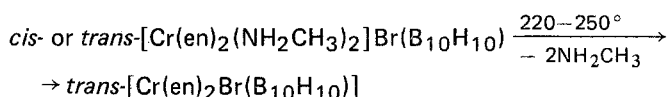
are characteristic of isomerization reactions of coordination compounds; in our case



In air, the ligand substitution reactions of hexamine chromium(III) complexes are accompanied by exothermic effects at temperatures exceeding 180–185°. The reason is that the exothermic oxidation processes of the gaseous products by air are superimposed on endothermic processes related to the splitting-off of the amine or to the dissociation of the borohydride anion [1, 2]. Methylamine is quantitatively determined up to 300–350° (DEGA curve), allowing the conclusion that the NH₂ groups of the

ligand are stable to oxidation at these temperatures. The titration data (DEGA curve) were therefore utilized to calculate the kinetic parameters of the substitution of amine molecules by outer sphere anions. To eliminate possible errors in kinetic parameter determinations, characteristic in thermoanalytical measurements, and also to eliminate distortion of the results due to side-reactions (ligand oxidation by atmospheric oxygen), we also recorded gas evolution curves in inert gas in a continuous reactor (Fig. 3).

The results of isothermal decomposition of both isomeric salts and identification of the products (Table 1) demonstrated that in the interval 220–250° both *cis*- and *trans*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) dissociate with substitution of two methylamine molecules in the coordination sphere by the outer sphere anions Br and B₁₀H₁₀²⁻. The reaction results in both cases in the formation of a brown compound insoluble in water:



The electronic spectrum of this solid compound in the range 10.000–35.000 cm⁻¹ contains three absorption bands of moderate intensity (up to 60–100), characteristic for the *d*–*d* transitions of the chromium(III) ion in the *D*_{4h} symmetry field [8, 9]: a band with maximum at 24.940 cm⁻¹ and two bands at 20.280 and 16.150 cm⁻¹, corresponding to the transitions from the basic term ⁴A₂ into ⁴E and ⁴B₂, obtained in the splitting of the term ⁴T₂. The identification results on the transformation products of the salts at 220–250° (Table 1, Fig. 1) indicate the formation of a direct bond between the chromium(III) ion and the B₁₀H₁₀²⁻. A comparison of the parameters of the crystalline field formed by the ligands in the *xy* plane and along the *z* axis, calculated from the electronic spectrum of the transformation product, viz. *Dq(xy)* = 2128 cm⁻¹ and *Dq(z)* = 1249 cm⁻¹, with the analogous characteristics for the complex *trans*-[Cr(en)₂Br₂]⁺, viz. *Dq(xy)* = 2180 cm⁻¹ and *Dq(z)* = 1170 cm⁻¹, allows the conclusion that the anion B₁₀H₁₀²⁻ creates a stronger field than that due to the bromide anion.

Table 2 lists the kinetic parameters of the studied reactions. These were calculated by the method described in [6]. For processes A_s → B_s + C_g, the rate of the reaction depends on the temperature and the conversion:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

The temperature-dependence is assumed to be identical with that of homogeneous reactions:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right)$$

Table 2 Kinetic parameters of the ligand substitution reactions in the complexes *trans*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) (I) and *cis*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) (II)

| Compound | Heating rate, deg/min | Temperature, K | | Conversion range used in calcul. | E_a , kJ/mol | log A | - log k, | |
|----------|-----------------------|----------------|------|----------------------------------|----------------|-------|-------------|------------|
| | | init. | max. | | | | $T_{init.}$ | $T_{max.}$ |
| I* | 2.5 | 505 | 557 | 5.6-49.2 | 524 ± 20 | 50.2 | 4.70 | 1.83 |
| I | 4.0 | 516 | 555 | 5.3-49.0 | 494 | 44.7 | 4.38 | 1.82 |
| I | 7.0 | 513 | 555 | 5.5-56.0 | 456 | 41.2 | 4.28 | 1.76 |
| II* | 2.5 | 518 | 558 | 5.8-47.6 | 510 ± 20 | 49.9 | 4.90 | 1.89 |
| II | 5.0 | 485 | 531 | 5.2-54.9 | 498 | 45.9 | 5.12 | 1.69 |
| II | 5.5 | 485 | 531 | 5.7-51.3 | 462 | 43.8 | 6.07 | 1.70 |
| II | 6.7 | 485 | 530 | 5.4-51.8 | 428 | 40.5 | 5.52 | 1.61 |
| II | 7.0 | 489 | 532 | 4.2-52.6 | 382 | 35.9 | 4.96 | 1.65 |
| II | 7.5 | 470 | 529 | 5.2-57.9 | 281 | 25.9 | 5.30 | 1.81 |

* Kinetic characteristics calculated from derivative evolved gas curves.

For the function $f(\alpha)$ characterizing the topochemical mechanism of the process, we chose the form $f(\alpha) = (1 - \alpha)^n$, corresponding to processes proceeding on the interface of the phases. From experimental data, the function

$$g(\alpha) = \int_{\alpha_1}^{\alpha_2} \frac{1}{f(\alpha)} d\alpha$$

was obtained, and the value of the exponent n was determined by reducing this function to the linear relationship of its logarithm vs. reciprocal temperature [6]. We found that, for the conversion range between 6 and 50%, the function $\log g(\alpha)$ changes linearly with $1/T$ if $f(\alpha) = (1 - \alpha)^{2/3}$ (shrinking sphere).

The activation energy values calculated from the DEGA curves are practically identical for the two isomeric compounds. The activation energy values for the *trans* compound, calculated from the gas evolution curves when the ligand substitution process takes place in helium, are, lower by 20-25 kJ/mol however. It was also established that the activation parameters depend on the heating rate in the case of the *cis* compound. At low heating rate up to 5.0 deg/min, these parameters are identical with those found for the *trans* compound. When the heating rate was increased from 5.5 to 7.5 deg/min, the parameter values decreased, slowly initially and subsequently sharply: the activation energy decreased by ≈ 20 kJ/mol. The explanation for this phenomenon was found when we compared the decrease in activation energy of the *cis* compound as a function of temperature with the activation energy of the *cis-trans* isomerization process for chromium(III) tetramine complexes [10]. The temperature interval in which solid-phase isomerization of *cis*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) into the *trans* salt proceeds is close to the

temperature of the subsequent ligand substitution process. At low heating rates, the isomerization process and the ligand substitution process proceed separately, and at such heating rates the measured activation parameters therefore correspond to the ligand substitution reaction into the *trans* compound, independently of the structure

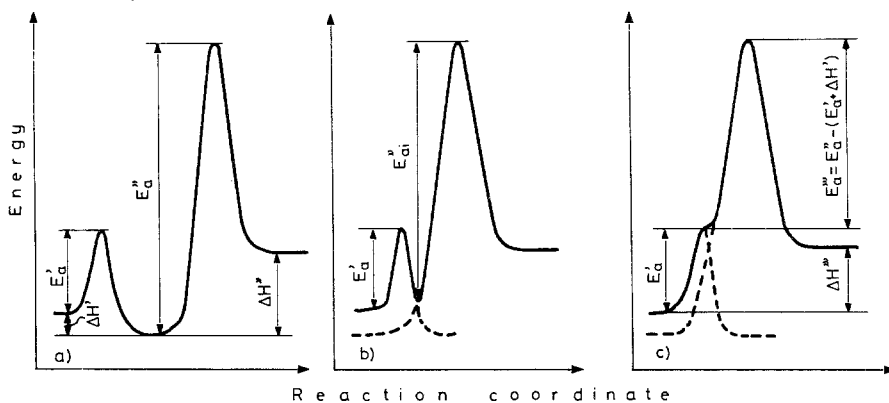


Fig. 4 Energy profiles of the solid-phase ligand substitution reaction and the isomerization reaction for the complex salt *cis*-[Cr(en)₂(NH₂CH₃)₂]Br(B₁₀H₁₀) at different heating rates. *a* - $\beta \leq 5.0$ deg/min; *b* - $5.0 < \beta < 7.5$ deg/min; *c* - $\beta \geq 7.5$ deg/min

of the initial salt. The energy profile of the reaction path in this case is presented in Fig. 4a.

As the heating rate increases, the temperature intervals of the isomerization reaction and the ligand substitution reaction approach each other and subsequently overlap, the rate of the isomerization reaction becoming comparable with and the less than the heating rate. The energy profiles for these cases are shown in Figs 4b and 4c. Gas evolution curves do not reflect energy consumption not connected with mass loss. Hence, the activation energy calculated from the gas evolution curves will be lower by the energy communicated to the complex for activation of the isomerization process, when the reaction path will be between those shown in Figs 4b and 4c.

Thus, the data obtained led to the establishment of the solid-state *iso-trans* isomerization of chromium(III) hexamine complex salts containing ligands of different denticity in the coordination sphere. Moreover, the fact that the isomerization process in the given case is connect with a change in position of the monodentate volatile ligands, when the bonds between the methylamine molecules and the metal ion are being split, is cogent proof of the mechanism of solid-phase *cis-trans* isomerization proceeding without splitting of the bond between the metal and the ligand, defended by one of the authors [10].

The measured activation parameters of the ligand substitution are higher by a factor of more than 5 as compared to the values for similar processes in solution [11]. This result is in agreement with the high densities and high thermal stabilities of the

compounds. Calculations have demonstrated [12] that ligand substitution in hexamine cobalt(III) cations to yield five-coordinated transition complexes by the dissociative mechanism requires (depending on the structure) up to 600 kJ/mol. When process takes place in solution, a major part of this energy is compensated through solvation. In the analogous process in the solid phase the solvent effect is absent. Moreover, if the reaction takes place by the dissociative path, the lattice energy of the complex salt must be significantly reduced in the transient state in order to increase the distance between the ions.

Since 700–800 kJ/mol is necessary to split one single chromium(III)–methylamine bond [10], and if this value is compared with the measured activation energy (Table 2), it may be concluded that in the given case the reaction does not follow a purely dissociative path. However, the high activation entropies ($\log A \approx 50$) of these processes (cf. Table 2) point to the dissociative path. If the associative reaction path could be realized, the activation energy would be of the order of 180–250 kJ/mol, while the Arrhenius frequency factor would be $A = 10^{15}–10^{25}$. It appears, therefore, that the structure of the initial complex salt is such that the interaction of Br^- with the chromium(III) hexamine complex is substantially reduced because of the large dimensions of $\text{B}_{10}\text{H}_{10}^{2-}$, while the formation of the seven-coordinated complex with the participation of $\text{B}_{10}\text{H}_{10}^{2-}$ is hindered by its bulk. These factors are obstacles to the associative mechanism in ligand substitution reactions of the studied complex compounds.

References

- 1 Yu. N. Shevchenko, N. I. Yashchina, K. B. Yatsimirsky, R. A. Svitsin and N. V. Egorova, *Zh. Neorg. Khim.* 28 (1983) 352.
- 2 Yu. N. Shevchenko and V. V. Sachok, *Zh. Obshch. Khim.*, 52 (1982) 1368.
- 3 E. L. Muetterties, J. H. Balthis, J. T. Chia, W. H. Knoth and H. C. Miller, *Inorg. Chem.*, 3 (1964) 444.
- 4 J. Paulik and F. Paulik, *Thermochim. Acta*, 3 (1971) 13.
- 5 F. Paulik and J. Paulik, *Thermochim. Acta*, 4 (1972) 189.
- 6 V. A. Logvinenko, *Thermal Analysis of Coordination Compounds and Clathrates*, Nauka, Novosibirsk, 1982 (in Russian).
- 7 Yu. N. Shevchenko, V. V. Sachok and V. Ya. Dudarev, *Zh. Obshch. Khim.* 52 (1982) 1224.
- 8 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam—London—New York, 1968.
- 9 A. B. P. Lever, *Coord. Chem. Rev.* 3 (1968) 119.
- 10 Yu. N. Shevchenko, *Teoret. i eksperim. khimiya*, 17 (1981) 844.
- 11 Yu. N. Shevchenko and V. V. Sachok, *Zh. Neorg. Khim.*, 28 (1983) 1973.
- 12 F. Basolo and R. Pearson, *Mechanisms of inorganic reactions*, Mir, Moscow, 1971 (Russian translation).

Zusammenfassung – Die Komplexverbindung *cis*- und *trans*- $[\text{Cr}(\text{en})_2(\text{NH}_2\text{CH}_3)_2]\text{Br}(\text{B}_{10}\text{H}_{10})$ wurden synthetisiert. IR-spektroskopisch konnte gezeigt werden, daß die die negative Ladung tragenden Wasserstoffatome des $\text{B}_{10}\text{H}_{10}^{2-}$ -Anions mit dem Proton der Aminogruppe des koordinativ gebundenen Amins unter Ausbildung des Bindungssystems N–H–H–B in Wechselwirkung treten. Die erhaltenen Komplexsalze weisen eine hohe Dichte ($d^{20} = 1.55 \text{ g/cm}^3$ für das *cis*-

Isomere und 1.47 g/cm^3 für das *trans*-Isomere) und eine hohe thermische Stabilität ($230\text{--}250^\circ$) auf. Bei $250\text{--}270^\circ$ dissoziieren sowohl die *cis*- als auch die *trans*-Verbindung unter gleichzeitiger Substitution von zwei Methylaminmolekülen in der Koordinationssphäre des Chrom(III)-Ions durch die Anionen Br^- und $\text{B}_{10}\text{H}_{10}^{2-}$. Der Prozeß wird durch die topochemische Gleichung $f(\alpha) = (1 - \alpha)^{2/3}$ (Reaktion an der Phasengrenzfläche) beschrieben und ist durch hohe Werte der kinetischen Parameter charakterisiert: $E_a = 510\text{--}524 \text{ kJ/mol}$, $\log A = 49.9\text{--}50.2$. Es wurde festgestellt, daß der durch Analyse der Gasentwicklung unter nichtisothermen Bedingungen bestimmte Wert von E_a um 220 kJ/mol abnimmt, wenn die Aufheizgeschwindigkeit von 5.0 auf 7.5 K/min erhöht wird. Dieser Befund kann damit erklärt werden, daß sich die Intervalle, in denen die *cis-trans*-Isomerisierung und die Ligandensubstituierung verlaufen, mit steigender Aufheizgeschwindigkeit einander nähern und schließlich überlappen; die Aktivierungsenergie des Isomerisierungsprozesses kompensiert dann einen Teil der für die Aktivierung der Ligandensubstituierung erforderlichen Energie.

Резюме — Синтезированы смешанно-лигандные комплексные соединения *cis*- и *trans*- $[\text{Cr}(\text{en})_2(\text{NH}_2\text{CH}_3)_2]\text{Br}(\text{B}_{10}\text{H}_{10})$. ИК спектроскопическим методом показано, что атомы водорода аниона $\text{B}_{10}\text{H}_{10}^{2-}$, несущие отрицательный заряд, взаимодействуют с протоном аминокруппы координированного амина с образованием связи $\text{N} - \text{H} \cdots \text{H} - \text{B}$. Полученные комплексные соли имеют высокую плотность ($d^{20} = 1.55 \text{ г/см}^3$ для *cis*-изомера и $d^{20} = 1.47 \text{ г/см}^3$ для *trans*-изомера) и обладают высокой ($230\text{--}250^\circ \text{C}$) термостабильностью.

При $250\text{--}270^\circ \text{C}$ как *cis*-, так и *trans*- $[\text{Cr}(\text{en})_2(\text{NH}_2\text{CH}_3)_2]\text{Br}(\text{B}_{10}\text{H}_{10})$ диссоциируют за счет реакции одновременного замещения двух молекул метиламина в координационной сфере иона хрома(III) внешнесферными анионами Br^- и $\text{B}_{10}\text{H}_{10}^{2-}$. Процесс описывается топохимическим уравнением $f(\alpha) = (1 - \alpha)^{2/3}$ (реакция на межфазной границе) и характеризуются высокими значениями кинетических параметров $E_a = 510\text{--}524 \text{ кДж/моль}$, $\log A = 49.9\text{--}50.2$. Найдено, что величина E_a для процесса замещения амина в *cis*- $[\text{Cr}(\text{en})_2(\text{NH}_2\text{CH}_3)_2]\text{Br}(\text{B}_{10}\text{H}_{10})$, измеряемая методом неизомерической кинетики по выделяющемуся газообразному лиганду, при увеличении скорости нагрева от 5.0 до 7.5 град/мин уменьшается на 220 кДж/моль . Этот результат объяснен тем, что при увеличении скорости нагрева температурные интервалы протекания реакций *cis-trans* изомеризации и замещения лигандов сближаются, а затем и перекрываются. При этом активация процесса изомеризации компенсирует часть энергии, необходимой для активации процесса замещения лигандов.