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Reactions of 2-chlorobutane with polynuclear bimetallic aluminum and cobalt chloride complexes: low-temperature synthesis and structure of adducts

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Co-condensation of aluminum and cobalt chlorides and 2-chlorobutane leads to the formation of triple complexes. Density functional method PBE was used for the quantum chemical calculations of structures and harmonic vibration frequencies. The structures of associates were established by the comparison of experimental and theoretical IR spectra. Introduction of cobalt chloride into the system 2-chlorobutane—aluminum chloride leads to the formation of a triple molecular associate, in which coordination of the organic substrate with the bimetallic complex is accomplished through the transition metal atom. The triple complex is stable in the temperature range 80—240 K and in contrast to the binary complex of butyl chloride with aluminum halide is not capable of self-ionization to form *sec*-butyl cation.

Key words: IR spectroscopy, carbocations, molecular complexes, aluminum chloride, cobalt chloride, 2-chlorobutane, low temperatures, quantum chemical calculations, density functional theory.

Aluminum chloride is one of the widely used acid catalysts, its action is the most efficient in the presence of promoting additives. Transition metal salts, which exhibit synergism with Lewis acids in the processes of isomerization and cracking of alkanes, alkylation of unsaturated and aromatic compounds, cracking of heavy parafins[1—4] are of special interest among them. An increase in the acidity of a Lewis acid, in particular aluminum halide, in the presence of a transition metal is accepted as a principal cause for the synergism.[1,2,5] At the same time, a number of experimental facts indicate a possibility of direct interaction of transition metal cations with organic substrates, for example, for the reactions of ions in the gas phase[6,7] or in catalytic transformations of alkanes on zeolites modified with transition metal ions.[8,9] Product compositions of the low-temperature conversion (170—220 K) of parafins C_7—C_{10}, for the first time accomplished by us on a promoted aluminum chloride, is also an evidence.[10] Nontypical for the traditional acid catalysts, alkanes of normal structure with the number of carbon atoms less by one unit as compared to the starting number were obtained in high yields along with alkanes of the isostructure in the presence of transition metal halide, including cobalt chloride.[10] Here, the fraction of cracking products does not exceed 5% as compared to 70—80% for the aluminum chloride both individual or promoted with organic halo derivatives. Such an influence of transition metal salts on selectivity of the processes in the presence of Lewis acids was observed in the liquid-phase conversion of parafins as well.[1,4]

One of prospective approaches to the understanding mechanism of catalytic action of Lewis acids consists in the study of intermolecular interactions at low temperatures under conditions of restricted molecular mobility. In this case, each step of the complexation can be separated and the sequence of the associate transformations can be followed. This approach has been applied by us earlier for the detection and identification of aluminum chloride complexes with cobalt halides[11,12] and alkyl halides.[13] As a result, a possibility of stabilization of a secondary butyl cation in the reaction of 2-chlorobutane and aluminum chloride has been shown for the first time. Earlier, ion pairs involving this cation have been registered only in the presence of the strongest Lewis acids, for example, in the SbF_5 matrix (see Ref. 14). As it was expected, secondary cations are less stable as compared to the tertiary and are registered only in the limited temperature range. If tertiary butyl cations t-Bu^+ are stable in the presence of aluminum chloride at temperatures of 80—295 K, the secondary carbenium ions s-Bu^+ are stable only at temperatures of 130—180 K (see Ref. 13). At the same time, in the matrix of stronger Lewis acid, SbF_5, stability of ion pairs involving s-Bu^+ is higher, and they are registered up to temperature of 233 K.[14] Due to the correlation indicated, a possi-

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bility of formation and stability of the secondary butyl cation can be used for the comparison of the Lewis acid strengths on a qualitative level.

As it has been already mentioned above, the data on the change in the aluminum chloride acidity in the reaction with transition metal derivatives are of principal importance for the understanding the promotion mechanism. In the case if the Lewis acidity increases, the promotion effect is well explained from the point of view of generally accepted carbocationic mechanism; if the Lewis acidity decreases, there is reason to suppose a direct involvement of the transition metal ion, for example, of cobalt, into the reaction with an organic substrate. In the present work, the acidities of binary bimetallic polynuclear complexes of aluminum and cobalt chlorides were evaluated based on the product compositions of their reactions with 2-chlorobutane at low temperatures. Complexes of various compositions were obtained by co-condensation of the halide vapors taken in different proportions. *n*-Alkanes were used as a matrix for stabilization of the complexes. The complex structures and their evolution were studied by low-temperature IR Fourier-spectroscopy *in situ* in combination with quantum chemical calculations.

Experimental

Aluminum chloride containing 99.99% of the principal substance (Aldrich) was distilled *in vacuo* before preparation of samples. Anhydrous cobalt chloride was obtained from the hydrate $CoCl_2 \cdot 6H_2O$ (99.9%) by evacuation over 3—4 h at 430 K. 2-Chlorobutane (2-ClBu) (purity 99+%, Aldrich) was used as purchased. Purity of starting substances was controlled by IR spectroscopy and gas-liquid chromatography.

IR spectra of solid samples were recorded on an optical cryostat described earlier.[11] The samples were prepared by co-condensation of the reagent vapors *in vacuo* (the pressure of $\sim 10^{-2}$ Pa) on a copper block mirror surface cooled to 80 K. To obtain compositionally homogeneous samples, the condensation was accomplished in the regime of molecular beams.[15] The condensation rate was 10^{14}—10^{16} molecules cm^{-2} s^{-1}. Evaporation of aluminum and cobalt chlorides was accomplished at 343—353 K and 800—850 K, respectively. The supply rate of 2-chlorobutane was controlled by a needle valve of fine adjustment. The films were 2—10 μm thick. The sample temperatures were varied in the range 80—250 K and kept with accuracy ±1 K.

IR transmission spectra of solid samples were recorded in the reflecting regime with the double transmission of the beam through the sample film. IR spectra in the region 5000—380 cm^{-1} were obtained on a Infralum FT-801 IR Fourier-spectrometer.

Calculation Methods

Earlier,[7] we have applied methods of the density functional theory with the use of the B3LYP (see Ref. 16) and PBE (see Ref. 17) functionals for the quantum chemical calculations of structures and vibration frequencies of $AlCl_3$, Al_2Cl_6, $CoCl_2$, and Co_2Cl_4 molecules and their 1 : 1 and 2 : 1 molecular complexes. The results obtained are in satisfactory accord between each other and with experimental data. Earlier,[13] the structure and vibration spectra of solid 2-ClBu and its molecular and ionic complexes with aluminum chloride have been studied as well. In the present work, calculations of structures and vibration frequencies of triple complexes with allowance for the correlation of electrons were performed by the PBE density functional (see Ref. 17) using the PRIRODA program package (see Ref. 18). For expansion of the one-electron wave functions, the TZ2*p* atomic basis sets of the grouped Gaussian function type were used: for H atoms of the form (311/1), for C atoms of the form (611111/411/11), for Al and Cl atoms of the form (6111111111/611111/11), and for Co atoms of the form (611111111111/511111111/5111). Full optimization of geometry and calculation of harmonic force fields were performed.

Results and Discussion

Starting compounds. Samples obtained by co-condensation are homogeneous in composition optically transparent films. The use of the regime of molecular beams for their preparation provides phase homogeneity of the system close to homogeneous media, that is confirmed by the registration of those states of the molecules on a cooled support, in which they were in the vapor phase at the evaporation temperature. The regularities indicated have been repeatedly observed earlier for various molecular systems,[15] including molecular systems based on aluminum chloride as well.[11—13] Structural studies of the aluminum chloride solid films under conditions of various matrix surroundings[19,20] showed that on the condensation of aluminum halide from the gas phase, a metastable molecular structure of dimers Al_2Cl_6 is preserved in the solid films obtained, and the content of the dimers is from 40 to 100% depending on the extent of dilution with the second component. Transition to the crystalline state occurs only at temperatures of 95—150 K. Vibration spectra of molecular and polycrystalline forms of aluminum halides are different.

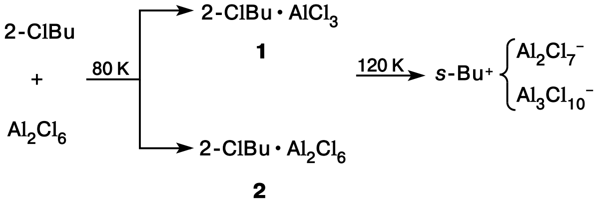
Aluminum chloride under conditions of this experiment condenses from the vapor phase as a dimer Al_2Cl_6, whose IR spectrum in the hydrocarbon matrix exhibits bands at 617, 478, and 417 cm^{-1} related to the stretching vibrations ν(Al—Cl) (see Refs 19—21). The IR spectrum of the aluminum chloride monomer in the inert gas matrices in the region $\nu > 400$ cm^{-1} contains the only band at 618 cm^{-1} (see Ref. 21). The IR spectrum of polycrystalline aluminum chloride contains intensive broad bands at 605 and 503 cm^{-1} (see Refs 19 and 20).

No absorption bands of cobalt chloride are observed in the region of the spectrum under study, though in the inert gas matrices for dilutions in the proportion ~3000—1000 : 1, absorption bands of stretching vibrations of monomer $CoCl_2$ and dimer Co_2Cl_4 are found at 493 and 432 cm^{-1}, respectively.[22,23] Under conditions of our experiment, associates of more complex composition are apparently stabilized.

2-Chlorobutane condenses from the gas phase as three conformers $S_{\mathrm{CH}'}$, $S_{\mathrm{HH}'}$, and $S_{\mathrm{H}'\mathrm{H}'}$, that is reflected in the IR spectra by splitting a number of bands to three components. The splitting mentioned is clearly seen in the region 700—600 cm^{-1}, which corresponds to the stretching vibrations of the C—Cl bond. The proportion of the band intensities for different conformers is similar to their distribution in the spectra of 2-chlorobutane, liquid or isolated in the argon matrix,[24,25] with predominance of the most stable $S_{\mathrm{H}'\mathrm{H}'}$ configuration. The ratio of conformers does not virtually depend on temperature. The presence of various conformational states of 2-chlorobutane in the condensates obtained, in contrast to the only conformer observed in the crystalline state,[24] can be considered as an additional evidence that condensates obtained by us are close to the homogeneous systems.

Molecular complexes. The system aluminum chloride—2-chlorobutane. The co-condensation of aluminum chloride with 2-chlorobutane leads to the emergence of new absorption bands in the IR spectra, which are absent in the spectra of starting reagents. Earlier,[13] study of the spectra of binary co-condensates has been performed in details in a wide range of the reagent proportions and temperatures (80—250 K), as well as using partial isolation in the alkane matrices. It was established that in the binary co-condensates of aluminum chloride with 2-ClBu, molecular and ionic complexes are formed; conditions for their formation and interconversions are shown in Scheme 1.

Scheme 1



According to Ref. 13, the reaction of Al_2Cl_6 with 2-ClBu at 80 K mainly leads to molecular complexes 2-ClBu • $AlCl_3$ (**1**). When aluminum chloride is in excess amount, the 1 : 2 complexes 2-ClBu • Al_2Cl_6 (**2**) are also formed along with complexes **1**. Transformation of complexes **1** and **2** to ionic associates is observed at temperatures above 120 K. The IR spectra of 2-ClBu and its complex **1** are given in Table 1. As it is seen from the data in Table 1, the formation of molecular associates is accompanied by the extinction of a number of absorption bands of the starting reagents (for example, 1298, 1237, 1076, 993, 617, 603 cm^{-1}) and emergence of new bands (1282, 1224, 1069, 991, 563, 551 cm^{-1} for **1** or 1280, 1224, 1067, 989, 596, 570, 555 cm^{-1} for **2** (see Ref. 13)).

The system aluminum chloride—cobalt chloride—2-chlorobutane. Similar picture is also characteristic of the IR spectrum of the three-component co-condensate of aluminum and cobalt halides and 2-ClBu at the ratio of reagents ~1 : 1 : 1. The IR spectra of the organic halide in the free state and in the three-component system 2-ClBu • $CoAlCl_5$ are shown in Fig. 1. It is seen that when the triple complex is formed, absorption bands of the starting 2-ClBu disappear and new bands appear, for example, at 1292, 1282, 1229, 1069, 990, 564, 503, 470 cm^{-1}. Vibration frequencies of the three-component system are given in Table 1. A comparison of the IR spectra of complex 2-ClBu • $CoAlCl_5$, binary complex **1**, and the starting reagents shows that the vibration frequencies of 2-chlorobutane in the triple system are close to those observed in the spectrum of 2-ClBu • $AlCl_3$, the deviations, as a rule, do not exceed 5 cm^{-1}. Note that the IR spectra of complexes **1** and **2** are close enough as well.[13]

However, in the low-frequency region of the spectrum (700—400 cm^{-1}) where metal—chlorine stretching vibrations are found (Fig. 2), considerable differences in the binary (Fig. 2, *1* and *2*) and triple (see Fig. 2, *3*) systems are present already at 80 K. In this case, no bands at 563 and 551 cm^{-1} typical of complex **1** (see Fig. 2, *1*) are observed, with broad intensive bands at 566, 502, 470, and 446 cm^{-1} emerging instead (Fig. 2, *3*). The frequencies recorded for the triple systems do not agree with the spectra of binary complexes $AlCl_3$ • $CoCl_2$ either (Fig. 2, *2*), which were found earlier[11,12] during study of co-condensates of aluminum and cobalt chlorides for wide ranges of the reagent ratios (from 0.3 to 10) and temperatures (80—250 K). Among associates of various composition and structure revealed in works,[11,12] complexes $AlCl_3$ • $CoCl_2$ and $(AlCl_3)_2$ • $CoCl_2$ have spectral characteristics the closest to those observed for the triple co-condensates. The superposition of spectra of these complexes exhibiting at 574, 504, 444 cm^{-1} and at 594, 467 cm^{-1}, respectively, is shown in Fig. 2, *2*. From Fig. 2, it is seen that a possible

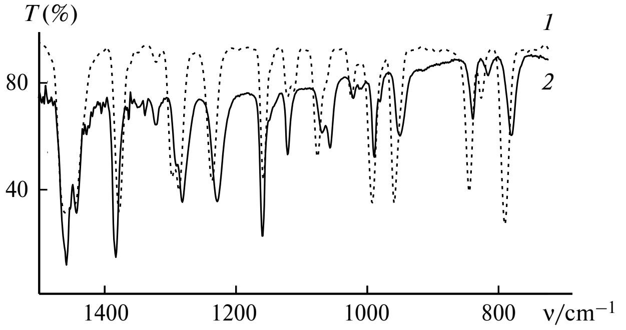


Fig. 1. IR spectra of 2-chlorobutane (*1*) and co-condensates of 2-chlorobutane with aluminum chloride and cobalt chloride of the form 2-ClBu • $CoAlCl_5$ (*2*) at 80 K.

Table 1. Experimental (80 K) and calculated by the DFT/PBE/3z method wave numbers (cm^{-1}) and intensities[a] (km mol^{-1}) in the IR spectra of 2-chlorobutane and its molecular complexes with aluminum chloride and aluminum and cobalt chlorides

2-ClBu		2-ClBu · AlCl$_3$ (**1**)		2-ClBu · CoAlCl$_5$			Assignment[b]
Experiment	Calculation	Experiment	Calculation	Experiment	Calculation		
					3A	**3B**	
2972 s	3062 (16)	2975 s	3075 (3)	2978 s	3069 (6)	3075 (3)	$\nu(\mathrm{Me})$
	3045 (30)		3056 (16)		3055 (20)	3057 (18)	
2938 s	3039 (31)	2939 s	3050 (21)	2939 s	3048 (17)	3050 (14)	$\nu(\mathrm{Me})$
	3035 (26)		3044 (5)		3044 (9)	3046 (2)	
2929 s	3014 (2)	2926 m	2989 (6)	2925 s	3000 (6)	2993 (5)	$\nu(\mathrm{CH_2})$
2917 m	2999 (5)	2917 w	3028 (1)	2914 w	3030 (2)	3028 (0)	$\nu(\mathrm{CH})$
2878 m	2970 (23)	2878 m	2979 (12)	2879m	2977 (16)	2978 (11)	$\nu(\mathrm{Me})$
	2965 (15)		2971 (11)		2972 (8)	2973 (5)	
2846 w	2971 (13)	2847 w	2944 (11)	2849 m	2949 (9)	2944 (8)	$\nu(\mathrm{CH_2})$
1461 s	1465 (7)	1460 s	1455 (15)	1458 s	1457 (11)	1455 (13)	$\delta(\mathrm{Me})$
	1454 (7)		1450 (13)		1452(13)	1450(14)	
1455 s	1450 (6)	1455 s	1446 (7)	1452 s	1442 (2)	1444 (2)	
1443 s	1444 (13)	1440 s	1432 (8)	1442 s	1434 (11)	1430 (12)	
1432 m.sh	1435 (1)		1416 (2)		1413(4)	1408 (4)	$\delta(\mathrm{CH_2})$
1378 s	1359 (11)	1381 s	1373 (6)	1383 s	1368 (8)	1371 (8)	$\delta(\mathrm{Me})$
1362 w	1352 (6)		1361 (14)		1361(12)	1363 (14)	
1321 vw	1330 (1)	1323 vw	1348 (1)	1321 w	1351 (3)	1354 (1)	$\chi(\mathrm{CH})$
1298 s	1303 (3)	1282 s	1277 (14)	1282 s	1279 (1)	1277 (10)	$\mathrm{w(CH_2)}$
1287 s	1251 (1)	1287 s	1266 (6)	1292 m	1267 (20)	1262 (14)	$\mathrm{sc(CH_2)}$, $\chi_\mathrm{i}(\mathrm{CH})$
1237 s	1214 (19)	1224 s	1215 (9)	1229 s	1208 (16)	1202 (16)	$\chi_\mathrm{i}(\mathrm{CH})$
1158 s	1143 (13)	1160 s	1143 (15)	1160 s	1144 (17)	1143 (23)	$\nu(\mathrm{CC})$
1122 m	1125 (1)	1122 m	1108 (3)	1121 m	1106 (2)	1108 (2)	$\nu(\mathrm{CC})$
1076 s				1069 m			$\nu(\mathrm{CC})$, $\mathrm{r(Me)}$
1063 m	1045 (12)	1069 s	1054 (8)	1057 m	1050 (10)	1048 (7)	
1025m	1002 (6)	1024 m	1015 (6)	1021 w	1014 (8)	1013 (9)	$\nu(\mathrm{CC})$
993 s	958 (5)	991 s	972 (16)	990 s	974 (17)	972 (14)	$\mathrm{r(Me)}$
959 s	935 (9)	950 s	937 (11)	950 m	934 (8)	929 (13)	$\mathrm{r(Me)}$
844 s	831 (9)	839 m	825 (6)	839 m	826 (10)	826 (11)	$\nu(\mathrm{CC})$
791 s	767 (4)	778 s	765 (18)	781 s	757 (20)	753 (22)	$\mathrm{r(CH_2)}$
607 vs	652 (29)	—[c]	512 (22)	—[c]	511 (31)	502 (80)	$\nu(\mathrm{CCl})$
	408 (1)	—[c]	443 (2)	—[c]	444 (1)	445 (2)	$\gamma(\mathrm{CCC})$
618[d]		563 s.br	568 (147)	565 vs	574 (144)	569 (178)	$\nu(\mathrm{AlCl})$
		551 s.br	545 (131)	503 s	489 (210)	491 (10)	$\nu(\mathrm{AlCl})$, $\nu(\mathrm{CCl})$
				470 s			
			362 (33)	444 s	389 (68)	410 (103)	$\nu(\mathrm{AlCl})$, $\nu(\mathrm{CoCl})$
				420 w	380 (67)	382 (80)	
				387 w			

[a] Given in parentheses.

[b] ν are stretching, δ, γ — bending, χ and χ_i — out-of-plane and in-plane deformation, respectively, r — rocking, sc — scissoring, w — wagging deformation vibrations.

[c] Overlap with the $\nu(\mathrm{Al—Cl})$ vibrations.

[d] For monomer AlCl$_3$ in the region above 400 cm^{-1} in the Ar matrix.[21]

formation of the associates mentioned during co-condensation of AlCl$_3$, CoCl$_2$ and 2-ClBu should not lead to the spectrum shown in Fig. 2, *3*. First of all, this is related to the most intensive band at 566 cm^{-1} belonging to the stretching vibrations $\nu(\mathrm{Al—Cl})$, whereas similar vibrations in complexes AlCl$_3$ · CoCl$_2$ are found at 574—594 cm^{-1} of the IR spectra. Additional evidence for the formation of a new associate in the triple system is its thermal stability. It turned out that the elevation of temperature from 80 to 240 K produces no considerable changes in the IR spectrum of the triple co-condensate in contrast to the spectra of various binary co-condensates studied earlier,[11—13] in which the complex transformations causing a sharp change in the spectral picture occur already at 130—170 K.

To sum up, spectrum of the triple co-condensate of 2-ClBu, aluminum chloride, and cobalt chloride on the

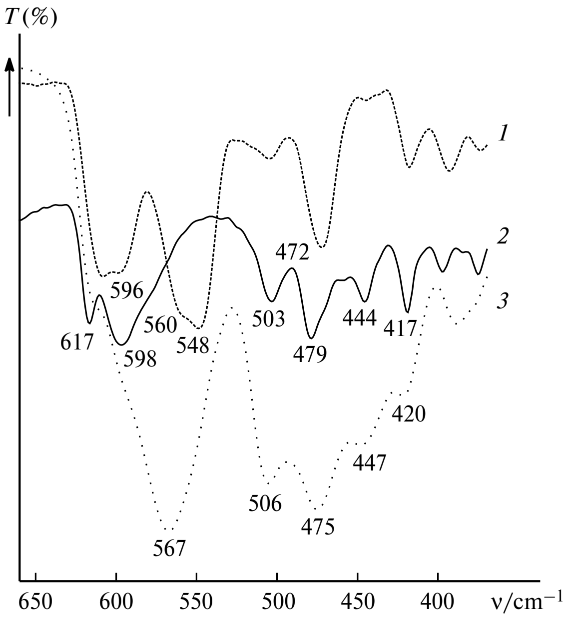


Fig. 2. Low-frequency IR spectra of binary co-condensates of aluminum chloride with 2-chlorobutane (*1*) and cobalt chloride (*2*) and triple co-condensate 2-ClBu • $CoAlCl_5$ (*3*) at 80 K.

whole cannot be described by superposition of spectra of the in-pair interactions. Therefore, a new associate is formed, by all appearances, a triple molecular complex. Quantum chemical calculations for the vibration spectra of possible triple associates performed confirmed this suggestion.

Quantum chemical calculations performed using the PBE/3z density functional predict formation of two isomeric 1 : 1 : 1 complexes 2-ClBu • $AlCl_3$ • $CoCl_2$ (**3**) (Fig. 3). In the isomeric complex **3A**, coordination of the 2-ClBu molecule is accomplished through the cobalt atom, in the complex **3B**, through the aluminum atom. The experimental and calculated vibration spectra of the triple co-condensate of aluminum and cobalt chlorides and 2-ClBu are given in Table 1.

As it is seen from the data in Table 1, the experimental spectrum of 2-ClBu observed in the three-component complexes is in satisfactory accord with the calculated vibration frequencies of complexes **3A** and **3B**. In this case, the spectra of complexes **3A** and **3B** are close to each other in the high-frequency region and differ little from the calculated spectrum of the binary associate **1**. On the contrary, in the low-frequency region, in which the metal—chlorine vibrations are found, differences are obvious. The experimental spectrum of the triple system cannot be already described by the spectrum of complex **1**, rather it satisfactorily agrees with the spectra of complexes **3A** and **3B**. Close positions of the vibration frequencies does not allow us to make an unambiguous conclusion on the site of coordination of 2-ClBu in the triple system. Relative intensities of the experimental bands of the complex in the low-frequency region agrees better with those calculated for complex **3A**. More substantiated conclusion can be drawn from the comparison of energies of formation of the complexes from starting reagents.

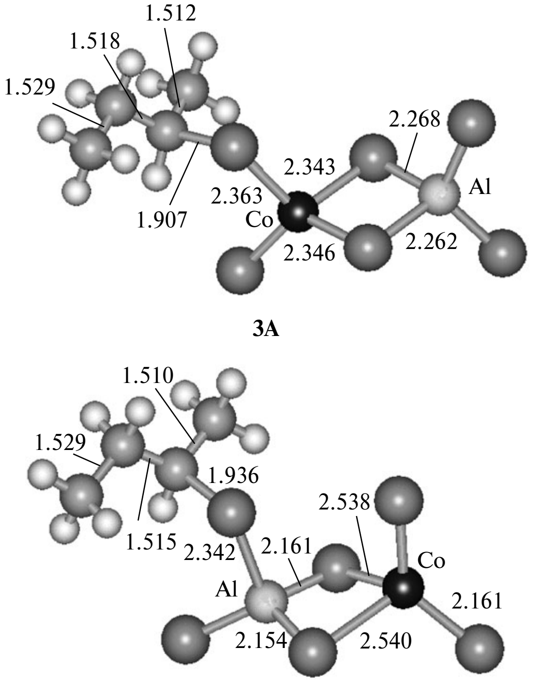


Fig. 3. Models of triple complexes of 2-chlorobutane, aluminum chloride, and cobalt chloride calculated by the PBE/3z method.

Figure 4 shows the diagram of the energy changes during complexation. It is seen that the gain in energy for the formation of complex **3A** (–46.5 kcal mol^{-1}) from the starting halides is much higher than in the case of complex

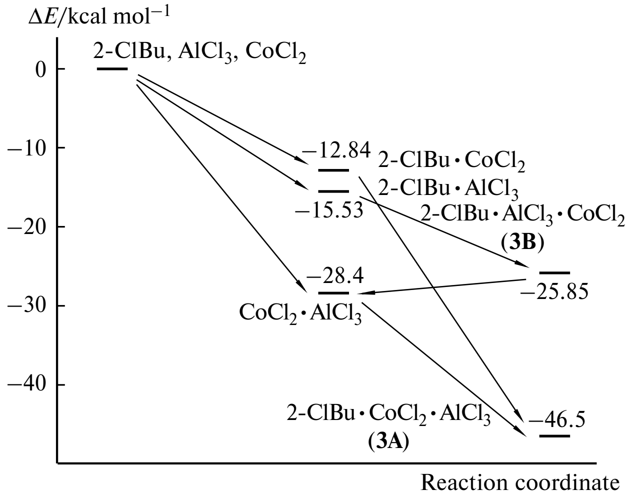


Fig. 4. Energy diagram for the formation of complexes of 2-chlorobutane with metal halides according to the data calculated by the PBE/3z method.

3B (–25.9 kcal mol^{-1}). In addition, the latter value is less than the energy of formation of the double complex $CoCl_2 \cdot AlCl_3$ by 2.5 kcal mol^{-1}. Therefore, according to the calculated data the formation of complex **3B**, in which coordination of 2-chlorobutane occurs at the aluminum atom, is energetically unfavorable.

To sum up, the reaction of 2-ClBu with aluminum and cobalt halides leads to the triple molecular complex $2\text{-ClBu} \cdot CoCl_2 \cdot AlCl_3$ of the structure **3A**, in which coordination of 2-chlorobutane is accomplished through the cobalt atom. Let us now consider whether ionization of such associates with the formation of carbocations is possible, as it happens with the binary complexes $2\text{-ClBu} \cdot AlCl_3$.

A possibility of formation of ionic complexes in the system $2\text{-ClBu} \cdot CoCl_2 \cdot AlCl_3$. Formation of *sec*-butyl cation in the binary systems is accomplished, as we have already mentioned, by self-ionization of molecular complexes **1** or **2** at temperatures above 120 K (see Scheme 1). Figure 5, *1* shows the IR spectrum of the corresponding ionic complex $s\text{-Bu}^+[Al_3Cl_{10}]^-$, which has been studied by us in details earlier.[13] Very close spectrum has been obtained for $s\text{-Bu}^+$ in the SbF_5 matrix as well.[14] The spectrum of the triple co-condensate $2\text{-ClBu} \cdot CoCl_2 \cdot AlCl_3$ (ratio of reagents ~1 : 1 : 1) recorded after heating to 150 K is also shown in Fig. 5. It is seen that the spectrum of 2-chlorobutane in the triple co-condensate contains no bands characteristic of $s\text{-Bu}^+$: there are absent, for example, bands at 1269, 1207, 1051, and 836 cm^{-1}. No considerable changes are observed either in the low-frequency region upon temperature elevation from 80 to 150 K (*cf.* Fig. 2 and 5). The IR spectrum of the triple complex **3** remains unchanged upon further heating up to 240 K. The indicated facts gave an evidence that only molecular complexes stable in a wide range of temperatures are formed in the triple system containing 2-chlorobutane and aluminum and cobalt halides.

Comparison of two systems (Scheme 2) shows that the processes of complexation in them considerably differ.

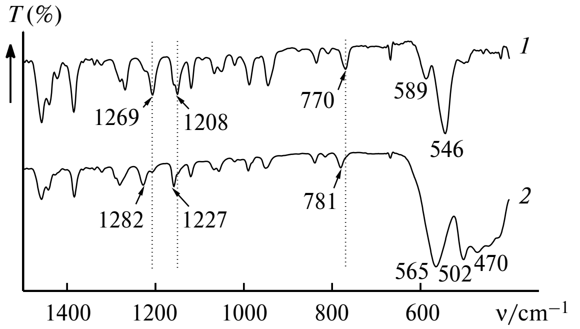


Fig. 5. IR spectra of the ionic complex $s\text{-Bu}^+[Al_3Cl_{10}]^-$ (*1*) and the triple system of the form $2\text{-ClBu} \cdot CoAlCl_5$ (*2*) at 150 K. Vertical lines represent frequencies of the ionic complex absent in the triple co-condensate.

Scheme 2

$$2\text{-ClBu} + AlCl_3 \xrightarrow{80\text{ K}} 2\text{-ClBu} \cdot AlCl_3 \xrightarrow{120\text{ K}} s\text{-Bu}^+ \cdot [Al_nCl_{3n+1}]^-$$

$$2\text{-ClBu} + AlCl_3 + CoCl_2 \xrightarrow{80\text{ K}} 2\text{-ClBu} \cdot CoAlCl_5 \overset{80\text{—}240\text{ K}}{\not\longrightarrow} s\text{-Bu}^+$$

Molecular complexes (for example, $BuCl \cdot AlCl_3$) formed by co-condensation (80 K) of 2-chlorobutane with aluminum chloride undergo transformation at ~120 K to the ionic structures containing *sec*-butyl cation and polychloroaluminate anion. The condensation of 2-ClBu with aluminum and cobalt halides at 80 K leads to the triple molecular complex $2\text{-ClBu} \cdot CoAlCl_5$ stable in the temperature range 80—240 K and undergoing no ionization to form *sec*-butyl cation.

In conclusion, a suggestion made earlier in the literature that the addition of transition metal compounds to aluminum chloride increases electron-withdrawing properties of the Lewis acid[1,2,5] found no confirmation, at least, in this case. Introduction of cobalt chloride to the system 2-chlorobutane—aluminum chloride leads to the formation of stable triple complex, capable of no self-ionization with the formation of *sec*-butyl cation. Moreover, in the triple complex the transition metal ion, rather than aluminum ion, is the center, which is involved into the interaction with the organic substrate. Apparently, the main part should belong to this ion in the reactions with alkanes as well. This conclusion is in complete agreement with the results of quantum chemical calculation by a density functional method for the complexes of aluminum and cobalt halides (components of the catalytic system) with propane.[26] In the triple complexes, the interaction with propane is accomplished through the transition metal atom, rather than through the stronger Lewis center, the aluminum atom. In this case, a strong polarization of the CH bonds takes place, the direction of which is opposite to that occurring upon the action of typical Lewis acids, including aluminum halide. According to the calculation, the reaction of alkane with aluminum chloride decreases negative charge on the carbon atom. At the same time, the reaction of an alkane with molecular or ionic bimetallic complexes leads to the opposite effect: electron density on the carbon atom increases, that promotes formation of metal-alkyl compounds, in which organic radical has a carbanionic character.

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