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Cryosynthesis, structure, and spectroscopic properties of aluminum chloride—cobalt(II) chloride complexes: experiment and calculations

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Products of co-condensation of aluminum chloride and cobalt(II) chloride vapors were studied by low-temperature (80—200 K) IR spectroscopy. In addition to 2 : 1 complexes, previously unknown equimolar associates were found and their IR spectra were investigated. Quantum-mechanical calculations were carried out including electron correlation with the use of the B3LYP and PBE density functionals. The geometric structures were optimized and harmonic vibrational frequencies of the molecules of aluminum chloride, cobalt chloride, and their complexes with different compositions were calculated. Under conditions of limited molecular mobility, the $(AlCl_3)_2 \cdot CoCl_2$ complexes can be stabilized in structures containing the Co atom in a tetrahedral or distorted octahedral environment. Their thermal stability limits were determined. It was found that labile ionic species are generated in the reactions of aluminum chloride complexes with cobalt chloride with different compositions at 120—170 K.

Key words: IR spectroscopy, molecular complex, aluminum chloride, cobalt(II) chloride, low temperature, quantum-mechanical calculation, density functional theory.

Aluminum chloride is of considerable current use as an acid catalyst. Catalytic systems, which include promoting additives (in particular, cobalt(II) halides) along with aluminum chloride, are of great interest. The introduction of such additives substantially increases the conversion and improves selectivity of many processes, for example, of isomerization of paraffins, alkylation of aromatic hydrocarbons, and cracking of heavy paraffins.[1—3] However, data on the compositions and structures of aluminum chloride complexes with transition metal salts are scarce.

Most of studies of interactions in $AlCl_3$—transition metal halide systems, including reviews,[4,5] were devoted to investigations in the gas phase at high temperatures (700—900 K).[6—10] Some other publications concerned investigations of the properties of crystalline binary salts of metal halides or their melts.[11—14] In particular, the crystal structure of the binary salt $CoAl_2Cl_8$, which was isolated after fusion of stoichiometric amounts of reagents, was established by X-ray diffraction analysis,[11,12] and the electronic spectra of its melt were investigated.[13] The coordination numbers of cobalt and aluminum in this salt are six and four, respectively. Dissolution of $CoCl_2$ in melts of the binary KCl—$AlCl_3$ salts gave rise to the ionic complexes $Co(Al_2Cl_7)_2$ and $Co(Al_2Cl_7)(AlCl_4)$, where the Co atom has a distorted octahedral coordination (according to the results of optical spectroscopy).[13] However, data on the structures of crystalline binary salts or compositions of their melts are insufficient for estimation of possible interactions between components of this system.

Data on the thermodynamics of gaseous mixtures of aluminum and transition metal halides provide evidence for the existence of several complexes containing from one to four $AlCl_3$ molecules per molecule of metal halide.[4] The spectroscopic characteristics are available primarily for binary complexes with composition $MCl_2 \cdot Al_2Cl_6$ (M = Co, Cu, Zn, Pd, *etc.*) and refer, as a rule, to the UV-Vis spectral region.[6—10] The structures of molecular complexes involving cobalt are still debated. The interpretation of electronic spectra of gaseous complexes presents difficulties because of the similarity of the spectroscopic characteristics of structurally different associates. In some studies, it was assumed that the cobalt atom is in a distorted octahedral environment.[6,7] Some researches are inclined to believe that these complexes have tetrahedral structures.[8,9] A number of investigators argued for the occurrence of these structures in dynamic equilibrium.[10] Recent quantum-mechanical calculations of the ground and excited states of the $CoAl_2Cl_8$ complexes using the density functional theory (DFT) are consistent with the latter assumption.[15]

The spectroscopic characteristics of 2 : 1 associates of aluminum and cobalt halides were investigated. The molar extinction coefficient of the adsorption band of the complex (≈630 nm) was found to depend on the temperature and pressure of aluminum chloride vapor.[6,9] This

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dependence was attributed[9] to the fact that the formation of the $CoAl_2Cl_8$ complexes is accompanied by the formation of the 1 : 4 associates with composition $Co(Al_2Cl_7)_2$. The formation of 1 : 1 complexes in the reactions of $CuCl_2$ with Al, Ga, and In halides in the gas phase was established by Raman spectroscopy.[16,17] These results were confirmed by quantum-mechanical calculations.[18] Data on vibrational spectra of aluminum chloride—cobalt halide complexes are lacking in the literature.

In the present study, intermolecular interactions in the aluminum chloride—cobalt chloride system were investigated by low-temperature IR spectroscopy and quantum-mechanical calculations. Labile complexes were stabilized at low temperatures in solid co-condensates of reagent vapors as well as by the matrix isolation method. Under conditions of limited molecular mobility, individual steps of complex formation can be distinguished and the sequence of transformations of associates can be revealed. Earlier, we have successfully used a combination of these methods for the detection and identification of aluminum chloride complexes with nitroalkanes and water.[19,20]

Experimental

Aluminum chloride of 99.99% purity (Aldrich) was sublimed *in vacuo* before preparation of samples. Anhydrous cobalt(II) chloride was prepared from the crystal hydrate $CoCl_2 \cdot 6H_2O$ (99.9%) by evacuation at 430 K for 3—4 h. Saturated hydrocarbons (HC) (*n*-octane, isooctane, and 2,4-dimethylheptane) were kept over sodium metal for several days and then distilled. The purity of the starting compounds was checked by IR spectroscopy and gas-liquid chromatography.

The IR spectra of solid samples were recorded in the 4000—400 cm^{-1} range on a Specord 75IR instrument in an optical cryostat described earlier.[19] Samples were prepared by co-condensation of reagent vapors *in vacuo* onto a mirrored surface of a copper block cooled to 80 K. Condensation of aluminum chloride was carried out by heating vapors to 343—353 K. To prepare $AlCl_3$ in the monomeric form, its vapor was additionally overheated to 1000—1100 K. Condensation of $CoCl_2$ vapors were performed after heating to 820 K. The rate of feeding of hydrocarbons was controlled using fine-adjustment needle valves. The condensation rate was 10^{14}—10^{16} molecule cm^{-2} s^{-1}. The film thickness was at most 4—15 μm. The temperature was maintained with an accuracy of ±1 K.

Results and Discussion

Spectroscopic studies

Starting reagents. Under the experimental conditions, aluminum chloride is condensed from a vapor phase primarily as the Al_2Cl_6 dimer. The IR spectrum of this dimer isolated in a hydrocarbon matrix shows bands at 616, 476, and 415 cm^{-1} belonging to ν(Al—Cl) stretching vibrations.[19,21] The IR spectrum of monomeric aluminum chloride in matrices of inert gases in the region of >400 cm^{-1} has the only band at 618 cm^{-1}.[20,22] Under conditions used in the present study and at the ratio HC : $AlCl_3$ = (10—100) : 1, the IR spectra virtually always show not only the band of the $AlCl_3$ monomer at 616 cm^{-1} but also the ν(Al—Cl) bands of the Al_2Cl_6 dimer. The intensities of the latter bands decrease compared to the intensity of the overall band of $AlCl_3$ and Al_2Cl_6 at 616 cm^{-1} as the degree of dilution ($HC/AlCl_3$) increases and the temperature of heating of aluminum chloride vapor is raised. There are no absorption bands of cobalt chloride in the IR spectral region under study, although stretching absorption bands of the $CoCl_2$ monomer and the Co_2Cl_4 dimer at 493 and 432 cm^{-1}, respectively, were observed in matrices of inert gases at the ratio Ar : $CoCl_2$ = (≈3000—1000) : 1.[23,24] Apparently, associates with more complex compositions are stabilized under the experimental conditions used in our study.

Co-condensates. Co-condensation of aluminum and cobalt chlorides was carried out in saturated hydrocarbon matrices with different compositions (*n*-octane, 2,2,4-trimethylpentane, and 2,4-dimethylheptane) at the

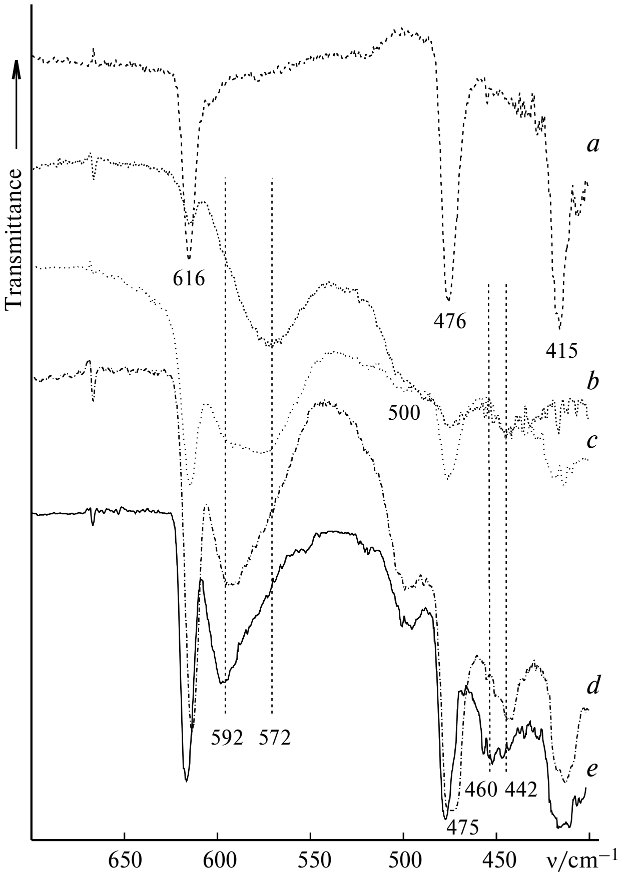


Fig. 1. IR spectra of Al_2Cl_6 (*a*) and the co-condensates of $AlCl_3/Al_2Cl_6$ with $CoCl_2$ in hydrocarbon matrices at 80 K and different ratios $n = AlCl_3/CoCl_2$: 0.8 (*b*), 1.8 (*c*), 3 (*d*), 4 (*e*).

$AlCl_3 : CoCl_2$ ratio varying from 0.3 : 1 to 10 : 1 and HC : $AlCl_3$ = (5—50) : 1. The spectra of the co-condensates are shown in Fig. 1. These spectra are not a result of a simple superposition of the spectra of the starting compounds, because the chemical reaction proceeds already at 80 K. The spectral pattern depends on the reagent ratio, the degree of dilution, and the temperature.

The region of ν_{Al-Cl} stretching vibrations of the spectra of co-condensates with a nearly equimolar composition ($n \approx 1$) (Fig. 1, *b*, *c*) has not only low-intensity bands of the aluminum chloride dimer (616, 476, and 415 cm^{-1}) but also new absorption bands, *viz.*, a broad band with a maximum at 572 cm^{-1} and bands at 500 and 442 cm^{-1}. An increase in the temperature to 100—120 K leads to the disappearance of the bands of free halide and an increase in the intensity of the new bands. An increase in the percentage of $CoCl_2$ ($n < 1$) in the co-condensates has only a slight effect on the spectral pattern.

An increase in the percentage of aluminum chloride ($n > 1$) leads to a change in the spectral pattern (Fig. 1, *d*, *e*). A new strong absorption band appears at 592 cm^{-1}, and its relative intensity (compared to the band at 572 cm^{-1}) increases as *n* increases. The spectrum also shows weak absorption at 460 cm^{-1} and a very strong band at 475 cm^{-1}. The frequency of the latter is identical to that of one of the stretching bands of the Al_2Cl_6 dimer. Hence, to estimate its intensity, it is necessary to subtract the spectrum of the dimer from the overall absorption spectrum. There is a qualitative correlation between the intensities of the bands at 592 and 475 cm^{-1}, which indicates that they belong to the same associate. The relative intensities of these bands increase as *n* increases. Apparently, 1 : 1 complexes of aluminum chloride with cobalt chloride (**1**), which prevail in equimolar specimens, and 2 : 1 associates (**2**), which are generated predominantly in an excess of aluminum halide, are generated in the system under study.

Generally, the degree of complexation of the reagents (α) upon condensation at 80 K is lower than 100%. Even the spectra of specimens containing an excess of cobalt halides have absorption bands of Al_2Cl_6 (see Fig. 1). This fact is typical of low-temperature syntheses. We have observed this phenomenon many times in other systems.[25] The parameter α depends on the rate of feeding of the starting compounds, the degree of dilution, the nature of the matrix, the temperature, *etc*. An increase in the temperature of co-condensates of aluminum chloride and cobalt chloride from 80 to 100—120 K leads to the additional complexation of the reagents.

The composition of the adducts is determined by the reagent ratio and the degree of dilution. Metal halides, which remain unconsumed at 80 K, react at 100—120 K to form predominantly complexes **1** at $n < 1$ and complexes **2** at $n > 3$. Both these processes often proceed simultaneously (at n = 1—3).

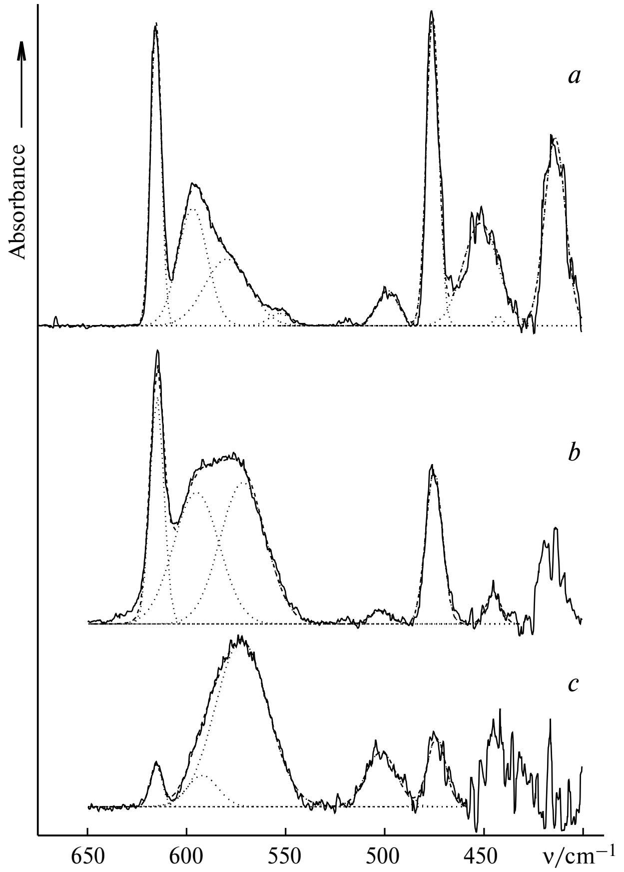


Fig. 2. IR spectra and their approximation by a superposition of Gaussian bands for co-condensates of $AlCl_3$ with $CoCl_2$ in hydrocarbon matrices at 80 K and n = 4 (*a*), 1.8 (*b*), 0.8 (*c*).

To make a more accurate assignment of IR bands to compositionally different complexes, we performed deconvolution of the spectra into individual components (Fig. 2). The assignments of vibrational frequencies, which were made based on experimental data, to compositionally different complexes are given in Tables 1 and 2. The 2 : 1 associates are stabilized at low temperatures, apparently, as structures **2a** and **2b**, which differ (according to the published data[6—10]) in coordination of the cobalt atom. The results of quantum-mechanical calculations allowed us to establish the structures of the complexes and assign the frequencies to particular types of normal vibrations.

Calculation methods and results

The structures of the $AlCl_3$, Al_2Cl_6, $CoCl_2$, and Co_2Cl_4 reagents and their 1 : 1 and 2 : 1 complexes as well as vibrational frequencies were calculated by quantum-mechanical methods including electron correlation with the use of the B3LYP[26] and PBE[27] density functionals. The full geometry optimization of the structures within the framework of relaxation models (without *a priori* restrictions on the structural parameters) was carried out and

Table 1. Experimental data (80 K, HC matrix) and the frequencies (ν/cm^{-1}) and intensities (I/km mol^{-1}) of stretching vibrations of the 1 : 1 aluminum chloride—cobalt chloride complexes calculated by the PBE and B3LYP/6-31G* methods

Experiment	Calculation				Assignement
	1a (C_{2v})		**1b** (C_{3v})		
	PBE	B3LYP	PBE	B3LYP	
572 s	588 (142)	602 (174)	608 (187)	612 (226)	ν(AlCl)^t
500 m	490 (138)	500 (157)	420 (101)	441 (119)	ν(AlCl)
			412 (83)	438 (117)	ν(AlCl)
442 m	432 (131)	437 (171)	411 (83)	424 (118)	ν(CoCl)
	367 (71)	373 (109)	340 (1)	351 (1)	ν(AlCl)^b
	318 (11)	328 (17)			ν(AlCl)^b
	276 (30)	276 (32)	226 (29)	231 (35)	ν(CoCl)
	245 (1)	241 (3)			

Note: s, strong; m, medium; ν(AlCl)^t and ν(AlCl)^b are stretching vibrations of the terminal and bridging bonds, respectively; ν(AlCl) are mixed stretching vibrations.

harmonic force fields were calculated by the B3LYP method with the 6-31G* basis set using the GAUSSIAN 94 program package.[28] The transformation of the calculated force fields from the Cartesian into internal coordinates, analysis of normal vibrations, and calculations of the potential energy distribution were performed with the use of the Spektr program package.[29] Calculations by the PBE method were carried out using the PRIRODA program.[30]

The equilibrium structures of the $AlCl_3$ complexes with $CoCl_2$ with 1 : 1 (**1**) and 2 : 1 (**2**) compositions and the geometric parameters, which were optimized at the B3LYP/6-31G* level of theory, are presented in Figs. 3 and 4. The calculated harmonic vibrational frequencies for these structures are given in Tables 1 and 2. The total energies of the molecules under study and their differences for the reactions of complex formation from the monomeric molecules (ΔE) with regard to dimerization of aluminum chloride ($\Delta E'$) are listed in Table 3.

Starting reagents. The structure of the $CoCl_2$ molecule was calculated in the low-spin (doublet) and high-spin (quartet) states. A stable virtually linear structure with the C_{2v} symmetry was obtained for the doublet ground state. The Co—Cl distance is 2.1508 Å, and the Cl—Co—Cl angle is 179.96°. The vibrational frequencies are 472 (ν^{as}(CoCl)), 341 (ν^{s}(CoCl)), and 50 cm^{-1} (α^{s}(ClCoCl)) (B3LYP). A more bent structure was demonstrated to be stable for the quartet state. The optimized geometric parameters of the latter are as follows: the Co—Cl distance is 2.0939 Å, the Cl—Co—Cl angle is 161.4°. The vibrational frequencies are 511 (ν^{as}(CoCl)), 360 (ν^{s}(CoCl)), and 84 cm^{-1} (α^{s}(ClCoCl)). The calculated IR spectra are consistent with the experimental data obtained for $CoCl_2$ isolated in an argon matrix (493 and 94 cm^{-1}).[23,24]

The results of calculations of the $AlCl_3$ and Al_2Cl_6 molecules using the B3LYP/6-31G* and PBE functionals are in satisfactory agreement with the empirical data on

Table 2. Experimental data (80 K, HC matrix) and the frequencies (ν/cm^{-1}) and intensities (I/km mol^{-1}) of stretching vibrations of the 2 : 1 aluminum chloride—cobalt chloride complexes calculated by the PBE and B3LYP/6-31G* methods

$(AlCl_3)_2 \cdot CoCl_2$							$Al_2Cl_6 \cdot CoCl_2$			
2a (C_2)			**2b** (C_{2h})			Assignement	**3** (C_{2v})			Assignement
Experiment	Calculation		Experiment	Calculation			Experiment	Calculation		
	PBE	B3LYP		PBE	B3LYP			PBE	B3LYP	
592 s	593 (138)	604 (171)	592 s	603 (0)	611 (0)	ν(AlCl)^t	616 s	614 (142)	620(256)	ν(AlCl)^t
	589 (138)	604 (171)		597 (442)	604 (496)	ν(AlCl)^t			607(62)	ν(AlCl)^b
500 w	491 (29)	503 (0.03)				ν(AlCl)^t	552 v.w	551 (61)	522(15)	ν(AlCl)^b
475 v.s	482 (359)	494 (402)	460 m.br	443 (142)	452 (215)	ν(AlCl)^t	520 w	521 (46)	492 (134)	ν(CoCl)
				432 (85)	450 (214)	ν(AlCl)^b	476 v.s	475 (358)	481(421)	ν(AlCl)
				426 (50)	426 (0)	ν(AlCl)^b	415 s	425 (181)	423(132)	ν(AlCl)^b
								419 (2)		
	369 (62)	372 (100)				ν(AlCl)^b		337 (21)	343 (6)	ν(CoCl)
	365 (62)	372 (100)		402 (2)	352 (0)	ν(AlCl)^b		327 (8)	333 (2)	ν(AlCl)^b
	340 (66)	332 (4)		346 (1)	350 (0,1)	ν(AlCl)^b		302 (21)	311 (87)	ν(AlCl)^t
	315 (1)	327 (0)		343 (1)	232 (0)	ν(AlCl)^b		270 (3)	270 (1)	ν(AlCl)^t
	305 (141)	308 (259)		233 (124)	223 (171)	ν(CoCl)		214 (4)	220 (0)	ν(AlCl)^b

Note: v.s, very strong; s, strong; m, medium; w, weak; br., broad; ν(AlCl)^t and ν(AlCl)^b are stretching vibrations of the terminal and bridging bonds, respectively; ν(AlCl) are mixed stretching vibrations.

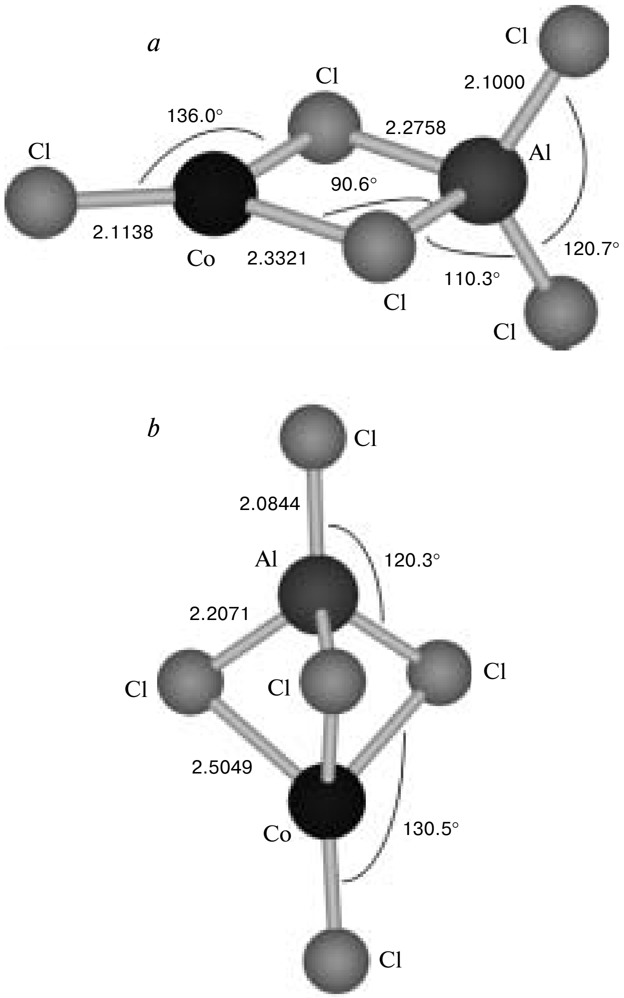


Fig. 3. Models of the 1 : 1 molecular complex $AlCl_3 \cdot CoCl_2$: *a*, **1a**; symmetry C_{2v}; *b*, **1b**, symmetry C_{3v} (B3LYP/6-31G*).

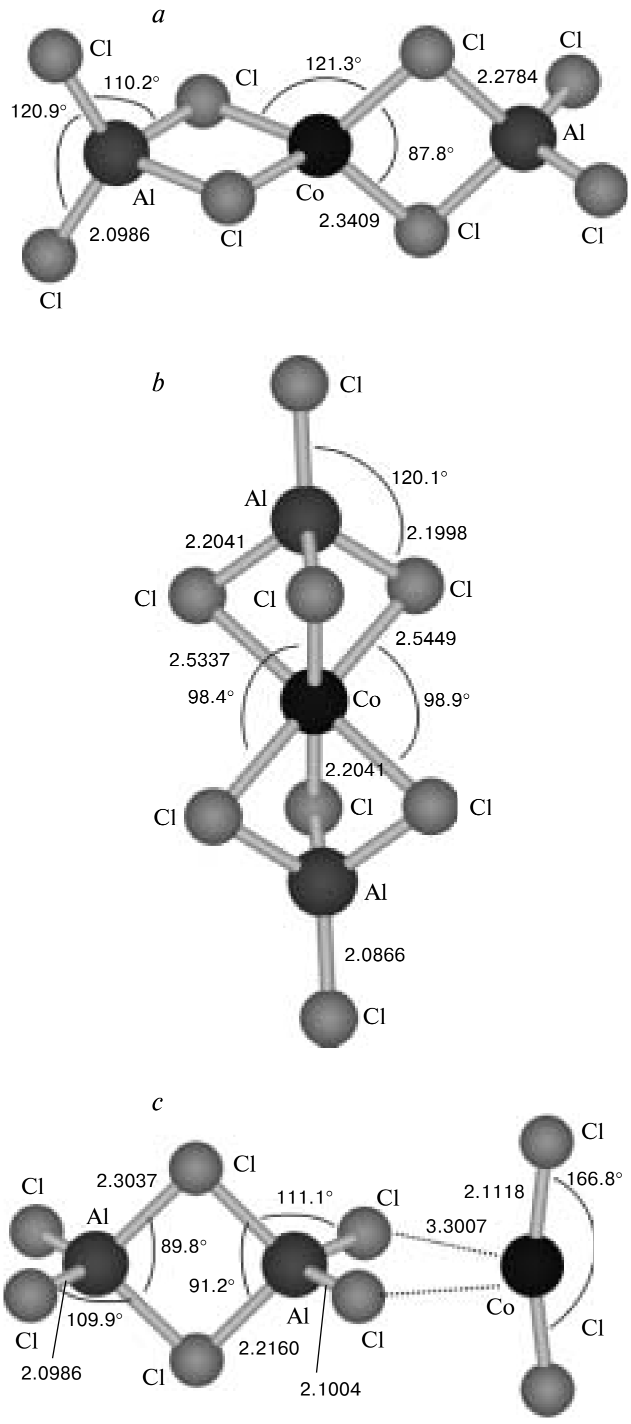


Fig. 4. Models of the 2 : 1 molecular complex of aluminum chloride with cobalt chloride: *a*, *b*, $(AlCl_3)_2 \cdot CoCl_2$ (**2a**, symmetry C_2 (*a*); **2b**, symmetry C_{2h} (*b*)); *c*, $Al_2Cl_6 \cdot CoCl_2$ (**3**) (B3LYP/6-31G*).

the structures and spectra[22] as well as with the results of calculations published in the literature.[31,32]

Complex with 1 : 1 composition. The results of quantum-mechanical calculations for the 1 : 1 complexes of aluminum chloride with cobalt chloride provide evidence for the possible existence of two stable structures in which the multiplicity of the cobalt atoms is 4 (see Table 3). For the doublet ground state of the Co atom, mixed associates are unstable. According to the results of calculations at the B3LYP/6-31G* level, structure **1a** with the C_{2v} symmetry is most stable (see Fig. 3, *a*); the energy of its formation is —27.3 kcal mol^{-1}. In this structure, the transition metal atom is linked to the aluminum atom through two bridging Cl atoms analogously to the coordination of the cobalt atoms in the Co_2Cl_4 dimer. Structure **1b** with the C_{3v} symmetry (Fig. 3, *b*), in which the cobalt atom has a coordination number of 4, is energetically less favorable. The energy of its stabilization is –24.7 kcal mol^{-1}. A substantial elongation of the bridging Co—Cl bonds in complex **1b** (≈2.5 Å) compared to the analogous bonds in complex **1a** (≈2.3 Å) can lead to higher lability of complex **1b**. According to the results of calculations using the

Table 3. Total energies (E) of aluminum chlorides, cobalt(II) chlorides, and their associates and the energies of complex formation from the starting molecules (ΔE) and with consideration for dimerization of aluminum chloride ($\Delta E'$) calculated by the B3LYP and PBE methods

Compound	χ_{Co}	$-E$/a.u.		$-\Delta E$		$-\Delta E'$	
				kcal mol^{-1}			
		PBE	B3LYP	PBE	B3LYP	PBE	B3LYP
$CoCl_2$	2	2302.75448	2303.109569	—	—	—	—
Co_2Cl_4	3	4605.494906	4606.215676	−8.8	−2.2		—
$AlCl_3$	—	1622.624719	1623.233267	—	—	—	—
Al_2Cl_6	—	3245.292449	3246.503237	27.0	23.0	—	—
$AlCl_3 \cdot CoCl_2$ (**1a**)	3	3925.424516	3926.386333	28.4	27.3	14.9	15.8
$AlCl_3 \cdot CoCl_2$ (**1b**)	4	3925.423780	3926.382338	28.0	24.8	14.5	13.3
$(AlCl_3)_2 \cdot CoCl_2$ (**2a**)	4	5548.102813	5549.666548	62.0	56.8	35.1	33.7
$(AlCl_3)_2 \cdot CoCl_2$(**2b**)	6	5548.095916	5549.652873	57.7	48.2	30.8	25.1
$A_2Cl_6 \cdot CoCl_2$ (**3**)	4	5548.053605	5549.619131	31.2	27.0	4.2	4.0

Note: χ_{Co} is the coordination number of cobalt.

PRIRODA program, complex **1a** appeared to be only slightly more stable than complex **1b** (see Table 3).

It should be noted that the formation of complexes **1** is energetically favorable even starting from dimeric aluminum chloride (reaction 2). In this case, the energy of stabilization is 13—15 kcal mol^{-1} (see Table 3).

$$AlCl_3 + CoCl_2 \longrightarrow AlCl_3 \cdot CoCl_2, \qquad (1)$$

$$1/2\ Al_2Cl_6 + CoCl_2 \longrightarrow AlCl_3 \cdot CoCl_2. \qquad (2)$$

Complex with 2 : 1 composition. Quantum-mechanical calculations for the 2 : 1 complexes predicted a possible existence of at least three relatively stable structures (Fig. 4), in which the ground state of the transition metal atom is also a quartet. The total energies of stabilization and the energies of complex formation are given in Table 3. According to the results of calculations at the B3LYP/6-31G* level of theory, complex **2a**, which has the C_2 symmetry and in which the central Co^{II} atom adopts a tetrahedral configuration typical of transition metal compounds, is most stable of all possible 2 : 1 complexes. Its energy of stabilization taking into account dimerization of aluminum chloride is −33.8 kcal mol^{-1}. Complex **2b**, which has the C_{2h} symmetry (Fig. 4, *b*) and in which the cobalt atom adopts a pseudooctahedral configuration, is less stable (by almost 9 kcal mol^{-1}).

Tetrahedral complex **3** with the C_{2v} symmetry (Fig. 4, *c*) in which the cobalt atom is in a nonequivalent environment appeared to have the energetically least favorable structure. The relatively low energy of its stabilization of (~4 kcal mol^{-1}) and the longer bridging Co—Cl bond (~3.3 Å) indicate that an unstable associate rather than a stable complex occurs in this case. Calculations by the PBE method led us to analogous conclusions.

On the whole, the calculated energies of stabilization indicate that the probability of detection of complexes **2b** and **3** is much lower than that of tetrahedral complex **2a**. However, the calculated data correspond to the gas phase. Under real experimental conditions, the co-existence of these structures is quite possible. According to the published data,[4,5] three-dimensional structures containing transition metal atoms with different coordination numbers can occur in equilibrium.

Interpretation of IR absorption spectra of the complexes

The experimental spectrum of the 1 : 1 complex, which has three absorption bands in the region of 600—400 cm^{-1} (at 572, 500 and 442 cm^{-1}), is in satisfactory agreement with the calculated vibrational spectrum of structure **1a** (see Table 1). The theoretical IR spectrum of associate **1b** differs from the spectrum of **1a** in that the high-frequency band is slightly shifted to shorter wavelengths and absorption in the region of 500 cm^{-1} is absent. The formation of this complex along with **1a** could explain the appearance of the band at 592 cm^{-1}. However, this is inconsistent with the observed dependence of the intensity of this band on the reagent ratio $n = AlCl_3/CoCl_2$. Besides, the absorbances of the bands at 500 and 442 cm^{-1} are directly proportional to each other (Fig. 5), *i.e.*, their relative intensities are invariant to the reagent ratio n, which indicates that these absorption bands belong to the same complex.

Therefore, the 1 : 1 complexes formed in the reaction of aluminum and cobalt chlorides in nearly equimolar ratios have predominantly structure **1a** in which the cobalt atom has a coordination number of 3. Earlier, a structurally similar complex has been found in the $AlCl_3$—$CuCl_2$ system.[16—18] The vibrational spectrum of this gaseous complex is similar to that of the $AlCl_3 \cdot CoCl_2$ compound.

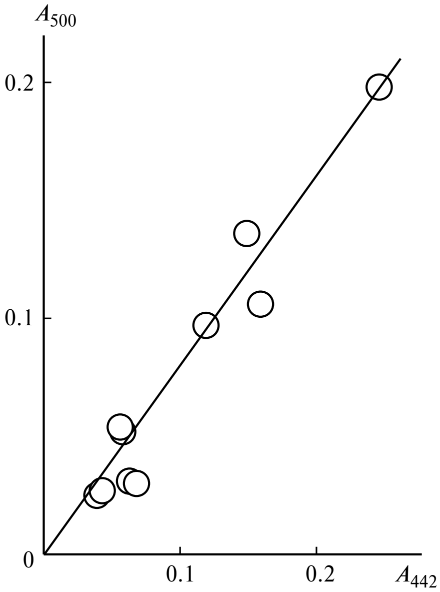


Fig. 5. Correlation between the absorption bands at 500 and 442 cm^{-1} in the co-condensates of $AlCl_3/Al_2Cl_6$ with $CoCl_2$ in hydrocarbon matrices at n = 0.5—4, HC : $AlCl_3$ = 5—30.

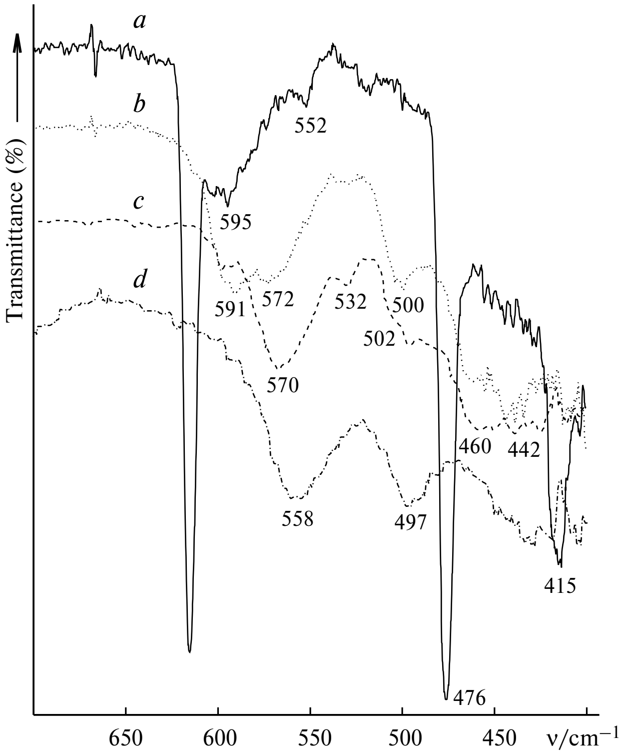


Fig. 6. IR spectra of co-condensates of aluminum chloride with cobalt chloride at different temperatures: 80 (*a*), 130 (*b*), 185 (*c*) and 220 K (*d*); $AlCl_3$: $CoCl_2$ = 1.5, HC : $AlCl_3$ = 15.

The vibrational frequencies of the structurally different 2 : 1 complexes calculated by two methods are given in Table 2 and are compared with the experimental frequencies assigned to complexes with different structures. The assignment was made based on analysis of the spectra of the co-condensates in a wide temperature range, at different reagent ratios, and for different matrices. Hence, under conditions of low molecular mobility in the solid phase at low temperatures, we succeeded in recording the IR spectra of the unstable $(AlCl_3)_2 \cdot CoCl_2$ complexes with different structures. Under an excess of aluminum chloride with respect to cobalt chloride, either complexes **2a** or complexes **2b** are generated depending on the degree of dilution of the reagents with a hydrocarbon matrix (HC). At low degrees of dilution (HC : $AlCl_3$ < 5), associate **2a** with the C_{2v} symmetry prevails. In this associate, the cobalt atom has a coordination number of 4 (Fig. 4, *a*). The theoretical data are in satisfactory agreement with both the experimental vibrational frequencies (592, 500, and 475 cm^{-1}) and their relative intensities.

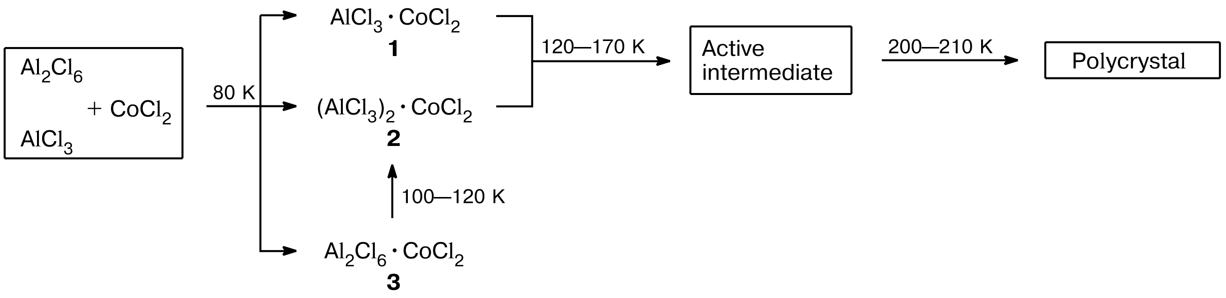
In more dilute specimens (HC : $AlCl_3$ > 10), the formation of less stable pseudooctahedral complex **2b** with the C_{2h} symmetry (Fig. 4, *b*) becomes possible. The IR frequencies of this complex (592 and 460 cm^{-1}) are similar to the corresponding frequencies for complex **2a**. However, the relative intensities for these complexes are strongly different. In the spectrum of **2a**, the most intense absorption band is observed at 475 cm^{-1}, whereas the analogous band at 460 cm^{-1} in the spectrum of **2b** is much weaker than the absorption band at 592 cm^{-1}, which is also consistent with the calculated intensities of the bands in the theoretical IR spectra (see Table 2).

Quantum-mechanical calculations predicted also the possibility of formation of the labile unsymmetrical $(AlCl_3)_2 \cdot CoCl_2$ associates containing cobalt with a coordination number of 4 (structure **3**). Actually, we succeeded in detecting such species at 80 K in a 2,4-dimethylheptane matrix at HC : $AlCl_3$ > 10 (see Table 2 and Fig. 6). The experimental results correlate satisfactorily with the calculated values.

Therefore, aluminum chloride forms at least four different complexes with cobalt chloride with 1 : 1 and 2 : 1 compositions, which differ in the structure and spectroscopic characteristics. In the present study, complex **1** was detected for the first time. Its synthesis appeared to be possible both from monomers and dimers of aluminum chloride (reactions (1) and (2), respectively) in contrast to the earlier studies, where it has been hypothesized that such equimolar associates can be generated only from monomeric aluminum chloride.[16—17]

The above-mentioned three different structures of complex **2** (two of which, *viz*., **2a** and **2b**, are similar in stability) are consistent with the conclusion[10,15] that the tetrahedral (distorted) and octahedral (distorted) aluminum chloride complexes with cobalt halide occur in equi-

Scheme 1



librium under the conditions of unlimited molecular mobility. In the solid phase, one of these structures can predominantly be stabilized depending on the conditions. Below are considered the conditions for the existence of the complexes and the limits of their thermal stability.

Thermal stability and interconversions of the complexes

Thermal stability of the complexes was studied in the temperature range of 80—290 K. Complex **3** proved to be the least stable of all the compounds under study, which is consistent with the results of calculations. This complex is transformed into complexes **1** and **2** already at 100—120 K, (see Fig. 6), which is accompanied by a decrease in the intensity of the bands at 616, 552, 476, and 415 cm^{-1} and an increase in the intensity of the bands at 572, 500, 442 cm^{-1} (**1**) and 592, 460 cm^{-1} (**2**). The detection of complex **3** became possible due to the use of the low-temperature synthesis, when the kinetic factors can play a decisive role in stabilization of particular structures. The influence of the kinetic factors was considered in-depth in the study.[25] It was demonstrated that condensation under specific conditions can give rise to a complex, which has the highest rate of formation regardless of its relative thermodynamic stability. In this case, the transformation into a more stable state occurs only at higher temperature.

The stability and transformation pathways of complexes **1** and **2** were demonstrated to depend on the molecular environment of the latter. If complexes are surrounded by molecules of a matrix devoid of free cobalt halides (in the case of **1**, $n < 1$) or aluminum halides (in the case of **2**, $n > 3$) and are isolated from associates with a different composition, they are stable up to 210—230 K. As the temperature is further raised, the hydrocarbon matrix loses its isolating properties and the complexes are transformed into polycrystalline associates. This process is accompanied by the appearance of two broad similar-intensity IR bands with maxima at 558 and 497 cm^{-1}.

A more complex temperature evolution occurs in samples containing simultaneously complexes **1** and **2** in an excess of hydrocarbon (n = 1—3). In this case, the spectra change already upon heating to 120—130 K. In the IR spectra (see Fig. 6, *c*), the intensities of absorption bands of complexes **1** and **2** decrease and new bands appear at 572, 532, 502, and 450 cm^{-1}. This spectral pattern is observed up to 210—230 K. Further heating leads to evaporation of a hydrocarbon matrix to form polycrystalline adducts (Fig. 6, *d*). These facts are indicative of the formation of previously unknown labile intermediate species, which are, apparently, ionic associates. The simultaneous presence of the $AlCl_3 \cdot CoCl_2$ and $(AlCl_3)_2 \cdot CoCl_2$ complexes in a hydrocarbon matrix at 120—170 K (n = 1—3) is a necessary condition for the formation of the above-mentioned ionic associates. The transformations occurring in the system are shown in Scheme 1.

To summarize, in the $AlCl_3$—$CoCl_2$ system, we detected not only relatively stable molecular complexes with different compositions but also labile intermediate species. The spectroscopic characteristics of the latter were revealed. It can be suggested that the observed intermediates serve as real catalysts for the conversion of paraffins in the presence of mixed metal halides. This assumption is confirmed by the data on low-temperature transformations of normal and branches alkanes, where the highest yields of the products and the best selectivity of isomerization were observed for the reagent ratios n close to 2.[33] The structures of ionic intermediates and their role in low-temperature catalytic transformations of hydrocarbons will be described elsewhere.

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