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Cryosynthesis, structure, and IR spectra of aluminum chloride—nitromethane molecular complexes

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The products of codeposition of aluminum chloride and nitromethane were studied by low-temperature IR spectroscopy (80—200 K). Density functional (B3LYP/6-31G* and B3LYP/6-31+G**) quantum-chemical calculations of the geometry and vibrational frequencies of aluminum chloride, nitromethane, and $AlCl_3 \cdot MeNO_2$ and $2AlCl_3 \cdot MeNO_2$ complexes were carried out. Comparison of the experimental and calculated IR spectra suggests that the preferred geometry of the $2AlCl_3 \cdot MeNO_2$ complex is such that one $AlCl_3$ molecule is coordinated to an O atom of the nitro group, while the other $AlCl_3$ molecule forms an Al...Cl bridge.

Key words: IR spectroscopy, molecular complex, aluminum chloride, nitromethane, nonempirical quantum-chemical calculations, density functional theory.

Aluminum halide complexes with nitro compounds are known to be catalysts of many organic reactions, *e.g.*, alkylation and isomerization of aromatic hydrocarbons.[1,2] Recently, a number of polynuclear aluminum halide complexes with organic ligands were found to possess the properties of aprotic superacids.[3] To gain a better insight into the mechanism of catalysis, it is essential to know the composition, structure, and properties of such complexes. Our recent studies of the $AlCl_3$—$MeNO_2$ system[4—6] revealed the existence of two previously unknown types of molecular complexes, namely, $AlCl_3 \cdot 2MeNO_2$ (1 : 2) and $2AlCl_3 \cdot MeNO_2$ (2 : 1), differing in spectral characteristics and thermal stabilities in addition to the known 1 : 1 associates.[7—10] The structure and vibrational spectra of $AlCl_3 \cdot MeNO_2$ (1 : 1) and $AlCl_3 \cdot 2MeNO_2$ (1 : 2) complexes were considered earlier.[5] The results of quantum-chemical calculations were found to be in reasonable agreement with the experimental data. Taking into account considerable interest in the chemical and catalytic properties of the complexes with excess aluminum halide, in this work we carried out a more detailed experimental and theoretical study of the $2AlCl_3 \cdot MeNO_2$ (2 : 1) molecular complexes. To provide the possibility of rigorous interpretation of experimental vibrational spectra, we also calculated the geometry and spectral characteristics of the $AlCl_3 \cdot MeNO_2$ (1 : 1) molecular complexes using the density functional theory (DFT) approach at the B3LYP/6-31G* and B3LYP/6-31+G** levels.

Experimental

Aluminum chloride (Aldrich, 99.99% purity) was vacuum distilled prior to the preparation of samples. Nitromethane (NM) was purified using standard procedures. Purity of initial substances was monitored by IR spectroscopy and GLC.

Infrared spectra of solid samples were recorded on a Specord IR-75 instrument in the range 4000—400 cm^{-1} using an optical cryostat described elsewhere.[4] Samples were prepared by codeposition of the reagents *in vacuo* on a mirror surface of a copper plate cooled down to 80 K. Aluminum chloride was condensed by heating the vapor to 343—353 K. The NM feed rate was controlled by needle valves. The condensation rate was 10^{14} to 10^{16} molecules cm^{-2} s^{-1} and the film thickness did not exceed 2—5 μm. The temperature was maintained with an accuracy of ±1 K.

Quantum-chemical calculations of the molecules of reagents, $AlCl_3$ and $MeNO_2$, and $AlCl_3 \cdot MeNO_2$ (1 : 1) and $2AlCl_3 \cdot MeNO_2$ (2 : 1) complexes were carried out using the density functional approach with the three-parameter B3LYP functional,[11] inclusion of electron correlation, and the 6-31G* basis set using the GAUSSIAN-94 program package[12] on VAX-4090 and IBM RS-6000/560 computers at the Wisconsin-Madison University (USA). The geometries were optimized without imposing *a priori* restrictions on the structural parameters. Harmonic force fields were also calculated. Transformations of the calculated quantum-chemical force fields from Cartesian coordinates to internal coordinates were carried out using the "SPEKTR" program package.[13]

Results and Discussion

Vibrational spectra of complexes. The spectra of all the three types of molecular complexes of aluminum chloride with NM were first reported in our earlier publications.[4—6] The differences between the IR spectra of the complexes $AlCl_3 \cdot MeNO_2$ (**1**) and $2AlCl_3 \cdot MeNO_2$ (**2**) were found to be insignificant as compared to the changes in the spectrum of NM upon the equimolar complex formation. This required a more detailed study of the dependence of the IR spectra on the reagent ratio.

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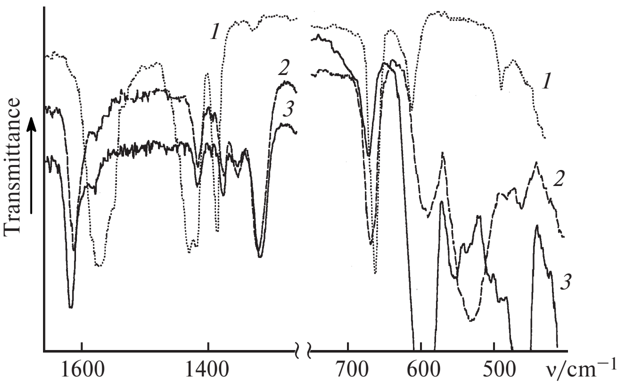

Fig. 1. IR spectra of nitromethane (*1*) and its codeposites with aluminum chloride (*2*, *3*) at 80 K. The reagent ratio, $n = AlCl_3 : MeNO_2$, was 1.3 (*2*) and 5 (*3*).

The IR absorption spectra of NM and its codeposites with $AlCl_3$ are shown in Fig. 1. The vibrational frequencies of the initial compounds, $MeNO_2$ and $AlCl_3$, and the complexes are listed in Table 1. In the experiment, aluminum chloride deposited from the vapor phase occurs mainly in the form of Al_2Cl_6 dimer. In this case, the ν(Al—Cl) stretching bands in the IR spectra are observed at 603, 467, and 413 cm^{-1}. The behavior of the Al_2Cl_6 dimer in the solid phase and in different matrices has been studied in detail.[15,16]

Codeposition of the reagents leads to shifts of particular bands in the spectra of the initial compounds and to the appearance of new absorption bands (see Fig. 1). It was found that the spectral pattern depends on the reagent ratio, $n = AlCl_3 : MeNO_2$. If the components are taken in nearly equimolar ratio (n ~ 1), the experimental spectrum corresponds to that of the 1 : 1 complex.[4,5]

Two bands, at 1617 and 1317 cm^{-1}, in the IR spectra of the samples with excess $AlCl_3$ can be assigned to the ν^{as}(N—O) and ν^{s}(N—O) vibrations, respectively. These bands appear to be even more distant from those of free NM than the corresponding bands in the spectrum of the 1 : 1 complex. In addition, the spectral pattern in the region 400—600 cm^{-1} becomes more complicated as compared to the spectrum of the 1 : 1 complex. This spectral region is characteristic of the bands corresponding to the ν(Al—Cl) vibrations and rocking deformation vibrations of the NO_2 group, ρ(NO_2). Here, new bands with absorption maxima at 588, 563, 542, and 432 cm^{-1} are observed in addition to the very strong vibrational bands of free Al_2Cl_6 (see Fig. 1, Table 1). These changes in the spectra of $AlCl_3$—NM codeposites are thought to be due to the formation of the 2 : 1 complexes.[4,6] The fact that the ν(N—O) frequency shifts in the spectra of both complexes **2** and **1** change with respect to the spectrum of NM in a similar manner suggests that two $AlCl_3$ molecules in the former complex are coordinated to one O atom of the nitro group analogously to the 1 : 1 complex.

Comprehensive interpretation of the IR absorption spectra of the codeposition products of $AlCl_3$ with $MeNO_2$ and establishment of their geometries were carried out using the results of quantum-chemical calculations.

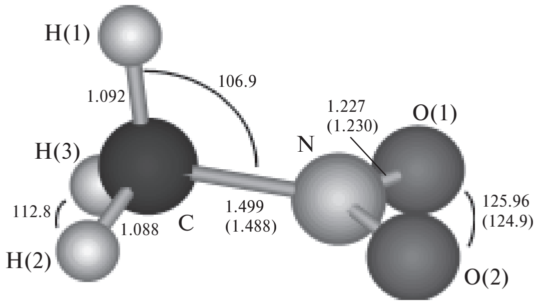

Fig. 2. Molecular geometry of nitromethane obtained from B3LYP/6-31G* density functional calculations. Selected bond lengths (in Å) and angles (in deg) are shown. The experimental values[17] are given in parentheses.

Calculations of $MeNO_2$ and $AlCl_3$ molecules. The results of our B3LYP/6-31G* calculations of NM molecule were found to be in reasonable agreement with those of experimental structural and spectral studies[17—21] and with the published data of quantum-chemical calculations.[22—24] Selected geometric parameters of the NM molecule are listed in Fig. 2.

We also compared the results of our calculations of $AlCl_3$ molecule with the available data on its structure and spectra and with the results of previous quantum-chemical calculations.[14,25,26] It was found that B3LYP/6-31G* calculations allow correct reproduction of peculiarities of the molecular geometry and IR spectrum.

$AlCl_3 \cdot MeNO_2$ (1 : 1) and $2AlCl_3 \cdot MeNO_2$ (2 : 1) complexes. Selected geometric parameters of complexes **1** and **2** obtained in this work from B3LYP/6-31G* calculations are presented in Figs. 3 and 4.

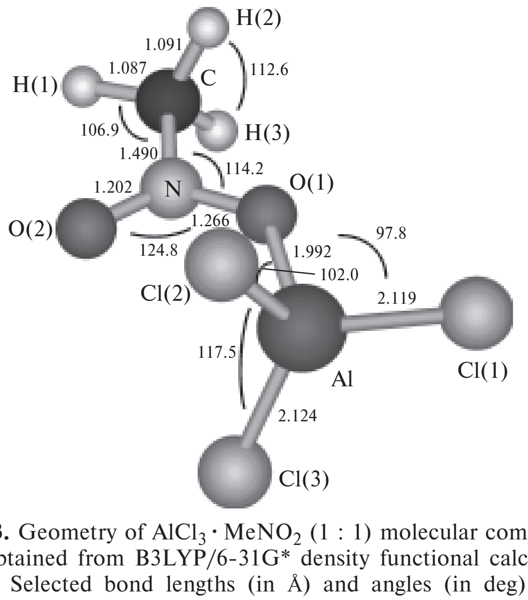

Fig. 3. Geometry of $AlCl_3 \cdot MeNO_2$ (1 : 1) molecular complex (**1**) obtained from B3LYP/6-31G* density functional calculations. Selected bond lengths (in Å) and angles (in deg) are shown.

Table 1. Experimental (80 K) and calculated (B3LYP/6-31G*) IR spectra (ω/cm^{-1}) of nitromethane, aluminum chloride, and complexes $AlCl_3 \cdot MeNO_2$ and $2AlCl_3 \cdot MeNO_2$

Assignment[a]	Free reagents $MeNO_2$ and $AlCl_3$		$AlCl_3 \cdot MeNO_2$ (**1**)				$2AlCl_3 \cdot MeNO_2$					
							Calculations[b]				Experiment	
	Calculations[b], ω	Experiment, ω	Calculations[b]		Experiment		**2a**		**2b**			
			ω	Δω[c]	ω	Δω[c]	ω	Δω[c]	ω	Δω[c]	ω	Δω[c]
ν(CH)	3226 (0.1)	3073 m	3240 (3)	+14	3075 m	+2	3239 (3)	+13	3243 (16)	+17	3072 m	−1
ν^{as}(CH)	3195 (2)	3040 w	3197 (2)	+2	3035 w	−5	3197 (2)	+2	3155 (22)	−40	3038 w	−2
ν^{s}(CH)	3102 (1)	2957 w	3105 (2)	+3	2950 w	−7	3106 (1)	+4	3075 (43)	−27	2956 w	−1
$\nu^{as}(NO_2)$	1679 (335)	1560 vs, 1550 vs	1695 (173)	+16	1610 s	+50	1692 (187)	+13	1607 (403)	−72	1617 s	+57
δ (CH_3)	1502 (13)	1435 w	1489 (16)	−13	1435 vw	0	1491 (16)	−11	1480 (150)	−22	1435 vw	0
δ (CH_3)	1490 (44)	1420 s	1486 (24)	−4	1415 m	−5	1486 (23)	−4	1476 (14)	−4	1414 m	−6
$\nu^{s}(NO_2)$	1444 (53)	1403 m	1397 (170)	−47	1325 s	−78	1402 (186)	−42	1406 (59)	−38	1317 s	−86
δ (CH_3)	1419 (43)	1378 m	1434 (25)	+15	1373 m	−5	1436 (30)	+17	1458 (12)	+39	1373 m	−5
$\rho(CH_3)$	1144 (1)	1120 w	1150 (0.6)	+6	1120 w	0	1150 (0.6)	+6	1154 (1)	+10	1120 w	0
$\rho(CH_3)$	1119 (12)	1105 s	1131 (33)	+12	1100 s	−5	1131 (32)	+12	1141 (14)	+22	1105 s	0
ν(CN)	929 (10)	916 m	931 (9)	+2	905 m	−11	934 (8)	+5	946 (4)	+17	903 m	−13
$\gamma(NO_2)$	663 (18)	656 s	676 (51)	+13	673 s	+17	672 (44)	+9	678 (34)	+15	678 s	+22
$\chi(NO_2)$	607 (5)	605 m	614 (12)	+7	603 m	−2	618 (25)	+11	605 (7)	−2	601 m	−4
ν(AlCl)	616	619[d] s	565 (167), 563 (179)	−51 −53	546 m.sh, 535 s	−73 −84	594 (316), 586 (0.1), 523 (134), 468 (150)	−22 −30 −93 −148	605 (179), 584 (162), 584 (215), 559 (104)	−11 −32 −32 −57	588 m 563 s 542 s 432 w	−31 −56 −77 −188
$\rho_r(NO_2)$	480 (1)	480 w	529 (24)	+53	—[e]		512 (47)	+32	512 (18)	+32	—[e]	
ν(AlCl), ν(AlO)			384 (57)		408 w		385 (124)		380 (9)		408 m	

[a] Notations of vibrations: ν is stretching, δ and γ are bending, ρ is rocking deformation, χ is out-of-plane deformation, and τ is torsional vibration.

[b] Absorption band intensities (in km mol^{-1}) are given in parentheses.

[c] The frequency difference between the complex and free reagent.

[d] For $AlCl_3$ monomer in the spectral region above 400 cm^{-1} in Ar matrix.[14]

[e] The corresponding band is overlapped with the ν(AlCl) band.

The calculated equilibrium structure of complex **1** virtually corresponds to the point symmetry group C_s and is characterized by "eclipsed" configuration of NM, in which one C—H bond is projected on the free N—O bond. Such a geometry of this complex is in agreement with the results of MP2/6-31G [5] and X-ray diffraction studies.[10] This serves as additional argument in support of the fact that the computational method employed in this work is adequate to the problem under study.

Two stable structures were located for the $2AlCl_3 \cdot MeNO_2$ (2 : 1) complexes. The distinctive features of the first structure (**2a**) are coordination of both $AlCl_3$ molecules to one O atom of the nitro group and retention of one bridging bond typical of the Al_2Cl_6 dimer, whereas the second structure (**2b**) is characterized by coordination of the acceptor to both O atoms of the nitro group (see Fig. 4). The energy difference between structures **2a** and **2b** is ~3 kcal mol^{-1}, the

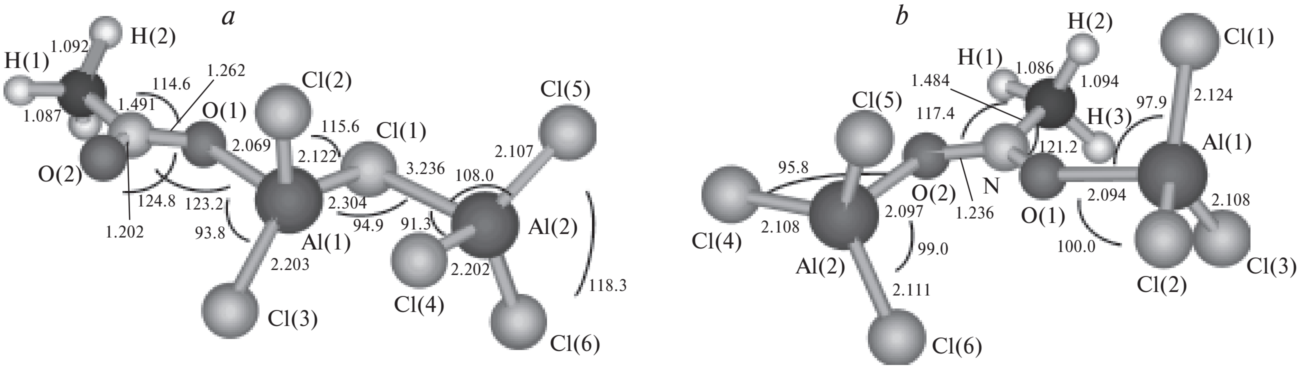

Fig. 4. Two types of the geometry of the molecular complex **2** obtained from B3LYP/6-31G* density functional calculations: $Al_2Cl_6 \cdot MeNO_2$ (**2a**) (*a*) and $(AlCl_3)_2 \cdot MeNO_2$ (**2b**) (*b*). Selected bond lengths (in Å) and angles (in deg) are shown.

Table 2. Calculated vibrational frequencies (ω) and potential energy distribution (PED) in $AlCl_3 \cdot MeNO_2$ (1 : 1) complex (**1**)

Vibration number	B3LYP/6-31G*		B3LYP/6-31+G**	
	ω/cm^{-1}	PED (%)	ω/cm^{-1}	PED (%)
1	3240	100CH	3228	100CH
2	3197	100CH	3185	100CH
3	3105	100CH	3090	100CH
4	1695	89NO	1673	88NO
5	1489	90*A*,10*B*	1471	88*A*,10*B*
6	1486	87*A*,10*B*	1468	82*A*,14*B*
7	1434	49*B*,46*A*	1421	46*B*,44*A*
8	1397	62NO,10CN,8ONO	1391	60NO,9CN,7ONO
9	1150	78*B*,10*A*,12*X*(NO)	1139	76*B*,10*A*,12*X*(NO)
10	1131	75*B*,11NO,7*A*	1122	74*B*,11NO,8*A*
11	931	44CN,28NO,17ONO	926	44CN,27NO,17ONO
12	676	41CN,31ONO,16CNO	671	41CN,32ONO,17CNO
13	614	76*X*(NO),11*B*,11*T*(NO)	612	82*X*(NO),12*B*
14	565	94AlCl	560	94AlCl
15	563	94AlCl	557	95AlCl
16	529	65CNO,21O...Al	525	66CNO,20O...Al
17	384	83AlCl,6O...Al	380	86AlCl
18	300	52AlO,16CNO,15AlCl	294	54AlO,16CNO,12AlCl,13*Xal*
19	203	44*b*,25*Xal*,24*T*(NO)	202	58*b*,28*T*(NO)
20	182	29*b*,24*Xal*,20NO...Al	181	30*b*,19*a*,20NO...Al
21	156	43*b*,26*a*,16*Xal*,10O...Al	155	48*Xal*,20*a*,14*b*,11O...Al
22	131	50*a*,26*Xal*,15*b*	131	80*a*,10*T*(NO)
23	126	31NOAl,31*a*,18*b*,15*Xal*	125	48*a*,29NOAl,9*Xal*
24	96	89*T*(CN)	85	73*T*(CN),23*T*(O...Al)
25	71	45*b*,34NO...Al	70	53*b*,40NO...Al
26	69	86*T*(O...Al)	67	83*T*(Al...O),17*T*(CN)
27	39	52*T*(NO),27*b*	38	59*T*(NO),31*b*

Note. Notations of internal coordinates are as follows. Bond stretch coordinates: CN, NO_i (i = 1, 2), CH_j (j = 1—3), O...Al, and $AlCl_j$ (j = 1—3). Bond-angle change coordinates: CNO_k (k = 1, 2), ONO, NO...Al, *bi* (i = 1—3) for the O...Al—Cl bond angles, *ai* (i = 1—3) for the ClAlCl bond angles, B_i (i = 1—3) for the NCH bond angles, and A_{ij} (i, j = 1—3) for the HCH bond angles. Out-of-plane deviation coordinates: *X* for the NO bond deviation with respect to the CNO_2 plane and *Xal* for a Cl atom deviation with respect to the plane passing through the ClAlCl atoms. Torsional coordinates: *T*(CN), *T*(O...Al), and *T*(NO) for torsional motions about the C—N, O...Al, and N—O bonds, respectively. Figures in the PED column denote the total contributions of internal coordinates. For instance, 90*A* means that all angles of the HCH type make a 90% contribution and 15*b* means that all angles of the O...Al—Cl type make a 15% contribution, *etc.*

former being more stable. This suggests a rather low probability of experimental detection of complexes **2b**. After optimization at the B3LYP/6-31G* level, structure **2a** was found to be similar to that of the $Al_2Cl_7^-$ anion[27] provided that one Cl atom is replaced by the organic donor molecule.

Interpretation of IR absorption spectra of the complexes using the results of quantum-chemical calculations. Tables 2 and 3 list the calculated vibrational frequencies of complexes **1**, **2a**, and **2b** and the potential energy distribution (PED) over vibrations[28—30] in the system of internal coordinates described in the notes

Table 3. Vibrational frequencies (ω) and potential energy distribution (PED) in complexes $Al_2Cl_6 \cdot MeNO_2$ (**2a**) and $(AlCl_3)_2 \cdot MeNO_2$ (**2b**) obtained from B3LYP/6-31G* calculations

Vibration number	$Al_2Cl_6 \cdot MeNO_2$ (**2a**)		$(AlCl_3)_2 \cdot MeNO_2$ (**2b**)	
	ω/cm^{-1}	PED (%)	ω/cm^{-1}	PED (%)
1	3239	100CH	3243	100CH
2	3197	100CH	3155	100CH
3	3106	100CH	3075	100CH
4	1692	89NO	1607	81NO
5	1491	89*A*,10*B*	1480	76*A*,16NO
6	1486	88*A*,10*B*	1476	85*A*,13*B*
7	1436	47*B*,45*A*	1458	41*B*,23*A*,27NO
8	1402	64NO,10CN,8ONO	1406	40NO,27*B*,22*A*
9	1150	78*B*,10*A*,12*X*	1154	75*B*,13*A*,11*X*
10	1131	76*B*,11NO,7*A*	1141	72*B*,12NO,8*A*
11	934	43CN,26NO,17ONO	946	37CN,22NO,25ONO
12	672	43CN,32ONO,16CNO	678	49CN,29ONO,11CNO
13	618	79*X*,11*B*,6*T*(NO)	605	77*X*,10*B*
14	594	43AlCl(1),49AlCl(2)	605	94AlCl(1)
15	586	48AlCl(1),47AlCl(2)	584	95AlCl(2)
16	523	81AlCl(2),8CNO	584	88AlCl(2)
17	512	68CNO,10Cl...Al1,10AlCl(2)	559	90AlCl(1),7*a*1
18	468	86AlCl(1),6AlCl(2)	512	76CNO,6*B*
19	385	59AlCl(2),18AlCl(1),10Al...Cl	380	52AlCl(2),42AlCl(1)
20	332	49Al...Cl,32AlCl(2),8AlCl(1)	371	54AlCl(1),44AlCl(2)
21	300	76AlCl(1),18*b*2	277	27O1...Al,23O2...Al,10O2...AlCl
22	242	57O...Al,13*b*1,9*b*2	227	22O2...Al,15O1...Al,20*b*2,17O2...AlCl
23	222	40*b*2,22O...Al	208	23*X*2,22*b*1,24*T*(NO2),19*T*(NO1)
24	220	64*b*1,23*T*(NO)	202	53*b*1,12*a*1
25	200	24*b*1,19*b*2,15*a*2,10NO...Al	193	37*b*1,23*T*(NO1)17*a*11
26	175	34*X*2,23*a*2,16*b*2	168	27*a*1,19*b*1,18*X*2,13*b*2
27	170	52*b*1,22*a*2,17Cl...AlCl	168	76*T*(CN),10*X*2
28	138	34*b*1,18*a*1,15*a*2,16*X*2	163	19*b*2,15O1...Al,14O2...Al,18NO2...Al
29	126	53*T*(AlCl),29*b*2	148	29*a*2,24*X*2
30	124	42NO...Al,20*b*2,14*X*1	135	50*a*2,32*a*1
31	110	22*a*2,18*b*2,18*a*1,18*X*2,17*X*1	134	24NO1...Al,24*a*2,20*a*1
32	98	36*b*2,13*X*2,11*X*1,11Cl...AlCl	133	71*a*1,24*a*2
33	93	42AlCl...Al,18O...Al,10*b*1	88	100*T*(O1...Al)
34	86	50*T*(O...Al),30*T*(CN),15*T*(NO)	81	34*b*2,18*a*2,13NO2...Al,11*b*1
35	70	53*T*(O...Al),12*T*(CN)	69	62*b*1,13*b*2,10NO1...Al
36	54	40*T*(CN),15*T*(AlCl),11*b*2	51	70*T*(O2...Al)
37	51	42*b*1,25NO...Al,10Cl...AlCl,10*X*1	36	39NO1...Al,39*b*2,10NO1...Al
38	34	38*T*(NO),15*T*(CN)	19	28*T*(O2...Al),16*T*(O1...Al),12*T*(NO1)
39	17	57*T*(Cl...Al),35*T*(AlCl)	18	42*T*(O1...Al),24*T*(NO2),11*T*(O2...Al)

Note. A number of internal coordinates were introduced by analogy with those describing the $AlCl_3 \cdot MeNO_2$ (1 : 1) complex (see note to Table 2). The newly introduced coordinates are as follows. Bond stretch coordinate: O2...Al for the $AlCl_j$ (j = 4—6) bonds. Bond-angle change coordinates: *ai* (i = 4—6) for the ClAlCl bond angles and *bi* (i = 4—6) for the O2...AlCl bond angles. Out-of-plane deviation coordinates: *X*1 for the Cl(1) deviation with respect to the plane passing through the Cl(2), Al, and Cl(3) atoms and *X*2 for the Cl(4) deviation with respect to the plane passing through the Cl(5), Al, and Cl(6) atoms. Torsional coordinates: *T*(Cl...Al), *T*(AlCl), *T*(O1...Al), and *T*(O2...Al) for torsional motions about the Cl(1)...Al, Al—Cl(4), O(1)...Al, and O(2)...Al bonds, respectively. In the "PED" column, AlCl(i) (i = 1, 2) denotes the total contribution of bond stretch coordinates for the AlCl bonds in the $AlCl_3$ fragment coordinated to the O(1) or O(2) atoms or linked to the Cl(1) atom. Analogously, *a*1 and *b*1 respectively denote the total contributions of the ClAlCl and O...Al—Cl angles in the first $AlCl_3$ group, *etc.*

to the corresponding Tables. Based on the PED, we suggested the assignment of the main vibrational frequencies in the IR spectra (see Table 1).

Complex 1. As can be seen from the data listed in Table 1, the vibrational frequencies of complex **1** obtained from DFT calculations are in reasonable agreement with the experimental IR spectrum of the 1 : 1 complex (for detailed assignment of vibrational frequencies, see Table 2). In particular, we succeeded to correctly reproduce the directions of the $\nu^{as}(NO_2)$ and $\nu^{s}(NO_2)$ frequency shifts in the IR spectrum of this complex (see Table 1). Calculations of complex **1** predict a shift of the deformation vibration frequency of nitro group, $\rho(NO_2)$, toward larger wavenumbers (an increase to 529 cm^{-1}, *cf.* 480 cm^{-1} for NM) and a decrease in the frequency of the doubly degenerate ν(Al—Cl) vibration of the $AlCl_3$ group. According to calculations, the band corresponding to the latter vibration should be split into two components, at 565 and 563 cm^{-1}, due to removal of degeneracy caused by complex formation. Close-lying bands corresponding to the $\rho(NO_2)$ and ν(Al—Cl) vibrations have substantially different intensities (see Table 1). The former (low-intensity) band can be overlapped with the latter (intense) one. Therefore, the very broad absorption band in the IR spectrum of **1**, with a maximum near 535 cm^{-1} and a shoulder at 546 cm^{-1}, can be interpreted as superposition of three vibrations. These are two ν(Al—Cl) vibrations, *viz.*, a symmetrical vibration and asymmetrical one, and the $\rho(NO_2)$ vibration. According to calculations, a weak band at 408 cm^{-1} should be assigned to the third ν(Al—Cl) vibration.

Complexes 2a and 2b. The calculated vibrational frequencies of structure **2a** are in better agreement with the experimental spectrum of complex **2**. Frequency shifts of the NO_2 group stretching vibrations calculated for this structure follow the same pattern as those found for complex **1** and correspond to the frequency shifts observed in this spectral region (see Tables 1 and 3). According to calculations for complex **2b** (see Table 3), the frequency difference between the ν^{as}(N—O) and ν^{s}(N—O) vibrational bands should decrease due to lowering of the frequency ν^{as}(N—O) and an increase in the frequency ν^{s}(N—O). However, this contradicts the experimental data and confirms the assumptions[4,6] of the character of possible frequency shifts of ν(N—O) vibrations in the spectra of more stable 2 : 1 complexes with respect to the corresponding frequencies of free reagents and complex **1**. The position and intensity of a band at 903 cm^{-1} in the spectrum of complex **2a** remain virtually unchanged as compared to those of the corresponding band in the spectrum of complex **1**. This band can be assigned to the ν(CN) vibration, which is also in agreement with the calculated frequency of this vibration in structure **2a**. Calculations of structure **2b** predict a decrease in the intensity and a shift of this frequency toward high-frequency region. Similarly to the spectrum of **1**, a very broad intense band of complex shape in the region 550 cm^{-1} can be interpreted as superposition of bands corresponding to the Al—Cl stretching vibrations and deformation vibration $\rho(NO_2)$.

Thus, a comparison of calculated vibrational frequencies of structures **2a** and **2b** with the experimental spectra of the $2AlCl_3 \cdot MeNO_2$ (2 : 1) complex suggests preferred formation of structures of the type **2a**.

Summing up, density functional (B3LYP/6-31G*) calculations allow the main characteristics of the IR spectra of the complexes under study to be satisfactorily reproduced without scaling provided that the anharmonicity corrections to the experimental vibrational frequencies are included. It is known that the band intensities in the IR spectra are usually calculated worse than frequencies. However, in the case of complexes **1** and **2a** we obtained reasonable agreement between the results of B3LYP calculations and the experimental data.

Thus, a combination of low-temperature IR spectroscopy and quantum-chemical calculations allowed the detection of the $2AlCl_3 \cdot MeNO_2$ (2 : 1) molecular complex and establishment of its structure. In this complex, one $AlCl_3$ molecule is coordinated to one O atom of the nitro group, while the other forms a bridging Al...Cl bond to give a pseudocyclic Al_2Cl_6 fragment.

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