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Thermodynamic Characteristics of Gaseous $GaCl_3$pyz and $GaCl_3$pyz$GaCl_3$ Complexes

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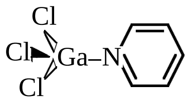
Abstract — Thermodynamic characteristics of vaporization and gas-phase dissociation of the complexes $GaCl_3$pyz and $GaCl_3$pyz$GaCl_3$ (pyz is pyrazine) were determined by static tensimetry with a membrane zero gage. Structural and thermodynamic characteristics of the complexes were calculated by the B3LYP/pVDZ quantum-chemical method.

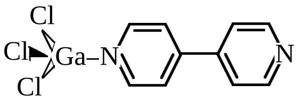
Donor–acceptor complexes of Group IIIa elements with polydentate nitrogen-containing donor ligands are perspective as starting compounds for precipitation of binary nitrides and composites based on them [1]. Potential starting compounds should have strong metal–nitrogen bonds and be sufficiently volatile. Complexes of such polydentate donors as pyrazine (pyz) and triazine with boron-containing acceptors $B(N_3)_3$ and $B(C_6F_5)_3$ [2, 3], as well as 4,4'-bipyridyl (bipy) complexes with aluminium and gallium [4–8] exist in the crystal state but dissociate into components on passing into vapor. The use of aluminum and gallium trihalides as acceptors renders the complexes much more stable. In this connection it becomes topical to study the thermal stability of model complexes formed by Group IIIa halides with bidentate donors. Berezovskaya *et al.* [9–11] synthesized complexes of $AlCl_3$, $GaCl_3$, and $GaBr_3$ with bipy and showed that the adducts pass into vapor but are low-volatile, and their constituent donor undergo irreversible decomposition above 370°C. It was assumed that replacement of bipy by the less bulky ligand pyz would increase the volatility of the complexes.

The purpose of the present work was to study experimentally the gas-phase complex formation in the system $GaCl_3$–pyz. In this system, 1 : 1 ($GaCl_3$pyz) and 2 : 1 ($GaCl_3$pyz$GaCl_3$) complexes can form in principle. In a situation when several processes occur simultaneously in the gas phase, quantum-chemical calculations can be rather helpful.

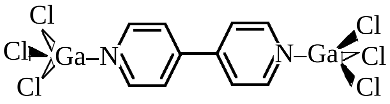
The calculations were carried out with the use of the B3LYP/pVDZ [12–14] hybrid density functional method using the standard GAUSSIAN-94 software package [15]. Geometry optimization followed by vibrational analysis were performed; all the resulting structures correspond to minima on the potential energy surface. The structures of the complexes under study are shown schematically below, and their principal thermodynamic and structural characteristics are summarized in Table 1. The structural parameters of the complex $GaCl_3$ with a monodentate donor, pyridine (py), are given for comparison.



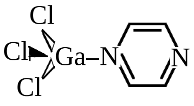
$GaCl_3$–py (C_s)



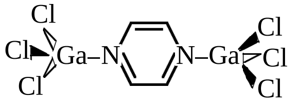
$GaCl_3$–bipy (C_s)



$GaCl_3$–bipy$GaCl_3$ (C_{2h})



$GaCl_3$–pyz (C_s)



$GaCl_3$–pyz$GaCl_3$ (C_{2h})

According to the calculations, the bond of $GaCl_3$ with pyz is weaker than with py and bipy. Moreover, the second $GaCl_3$ molecule is much weaker bound with the donor atom than in the bipy complex. Nevertheless, the calculation shows that the 2 : 1 complex ($GaCl_3$pyz$GaCl_3$) should exist in vapor in noticeable amounts at temperatures of no higher than 300°C.

The quantum-chemical calculations are qualitatively confirmed by the results of a mass-spectral study of the vapor composition. The mass spectrum of the vapor over solid 1 : 1 and 2 : 1 complexes is given in Table 2. It is evident that under conditions of the mass-spectral experiment no species containing two gallium atoms were detected in the vapor over the 1 : 1 complex. The base peak is formed by the pyz$^+$ ion,

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Table 1. Structural and thermodynamic characteristics of donor–acceptor complexes of $GaCl_3$ with mono- and bidentate ligands, as given by B3LYP/pVDZ calculations

Complex	$\Delta H^{0\,dis}_{298}$, kJ mol^{-1}	$\Delta S^{0\,dis}_{298}$, J mol^{-1} K^{-1}	q_{CT}	r(Ga–N), Å	$T(K^{dis} = 1)$, K	μ, D
$GaCl_3$–py	133.8	141.2	0.265	2.078	947	8.7
$GaCl_3$–bipy	131.9	136.4	0.265	2.076	967	7.6
$GaCl_3$–bipy$GaCl_3$	118.1	154.4	0.243	2.092	765	0
$GaCl_3$–pyz	115.9	144.5	0.237	2.102	802	5.9
$GaCl_3$–pyz$GaCl_3$	87.0	154.8	0.190	2.141	562	0

Table 2. Mass-spectral analysis of the vapor over the $GaCl_3$pyz and $GaCl_3$pyz$GaCl_3$ adducts

Ion	*m/z*	$GaCl_2$pyz, *I*, %		$GaCl_2$pyz$GaCl_3$, *I*, %		
		120°C	170°C	120°C		170°C
				Exp. onset	Exp. end	
Cl^+	35–37	0.5	3.9	[a]	10.7	2.7
HCl^+	36–38	1.3	4.1	[a]	8.9	12.6
C_3HN^+	51	1.3	2.4	1.3	13	1.8
$C_3H_2N^+$	52	4.0	5.6	0.9	9.4	4.7
$C_3H_3N^+$	53	16.9	20.7	2.0	29.2	18.4
Ga^+	69–71	4.9	12.0	6.0	20.1	8.0
$C_4H_4N^+(pyz^+)$	80	100.0	100.0	100.0	100.0	100.0
$GaCl^+$	104–108	1.5	9.4	3.3	14.6	6.4
$GaCl_2^+$	139–145	17.7	85.4	23.8	97.6	61.6
$GaCl_3^+$	174–182	2.5	21.0	3.7	18.5	15.4
$GaCl_2pyz^+$	219–225	23.1	23.1	8.2	13.6	27.6
$Ga_2Cl_5^+$	313–327	–	–	<0.1[b]	–	–
$Ga_2Cl_5pyz^+$	393–407	–	–	<0.1[b]	–	–

[a] Were not studied. [b] Content in the vapor from 10^{-3} to 10^{-1}%. The intensity ratio of the $Ga_2Cl_3pyz^+$ and $Ga_2Cl_5{}^+$ ion peaks is 1.79 : 1.

and the peak intensity of the $GaCl_2pyz^+$ ion that contains a gallium–nitrogen bond is 23–28% of the base peak. Note that the mass spectrum lacks $Ga_2Cl_5^+$ ion peaks characteristic of free $GaCl_3$ [16]. This finding suggests that either all observable ions are fragment in nature (and the complex is not dissociated under conditions of the mass-spectral experiment) or the process is not equilibrium under these conditions.

The ions $Ga_2Cl_5pyz^+$ and $Ga_2Cl_5^+$ were detected in the mass spectrum of the 2 : 1 sample at 120°C, which points to vaporization of the $GaCl_3$pyz$GaCl_3$ complex and its simultaneous thermal dissociation; however, the intensity of the detected ion peaks is low. At 170°C, these ions are absent from the vapor, which points to a low stability of the 2 : 1 complex. The noticeable variation in the intensities of ion peaks during mass-spectral measurements implies nonequilibrium character of the processes that occur under conditions of the mass-spectral experiment that, however, allowed us to establish existence of a gaseous 1 : 1 complex and detect the 2 : 1 complex in vapors at low (120°C) temperatures.

The equilibrium dissociation of the complexes was studied by tensimetry.

Tensimetric study. Processes in saturated and unsaturated vapor were studied by a static method with a quartz membrane zero gage [17]. Four composition regions were studied: 1 : 1 complex with excess of pyrazine, 1 : 1 complex, 2 : 1 complex, and 2 : 1 complex with excess $GaCl_3$. The plots of saturated and unsaturated vapor pressure vs. temperature for each composition are given in Fig. 1. As the main

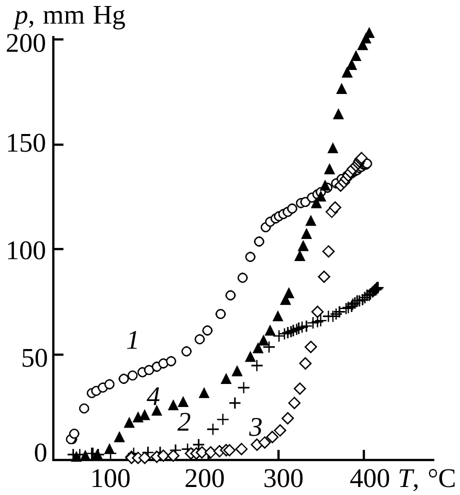

Fig. 1. Plot of vapor pressure (*p*) vs. temperature (*T*) for various experimental series ($GaCl_3$: pyz ratios). (*1*) Excess pyz, (*2*) 1 : 1 complex, (*3*) 2 : 1 complex, and (*4*) excess $GaCl_3$.

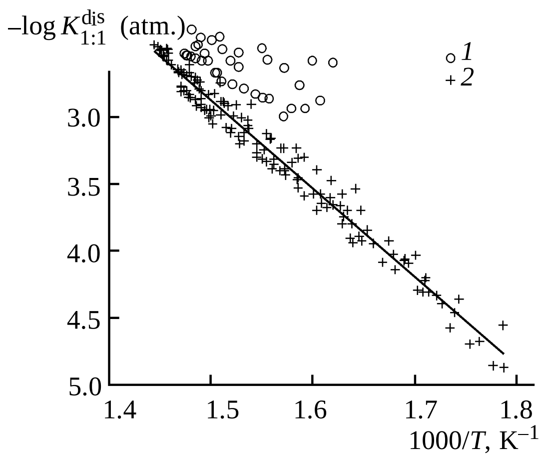

Fig. 2. Plot of the $\log K^{dis}_{1:1}$ of $GaCl_3pyz$ vs. inverse temperature (1000/*T*) (numbers of series are the same as in Table 4). (*1*) Series no. 1 and (*2*) series no. 2.

problem was the study the unsaturated vapor dissociation of the complexes, experiments were carried out with small (~20–100 mg) samples.

Thermodynamic characteristics of the unsaturated vapor dissociation of the 1:1 complex. Two series of experiments were carried out for this composition region: with excess pyz (series no. 1) and with excess 1 : 1 complex (series no. 2). In series no. 1, excess pyz suppresses dissociation of the complex, and, as a result, the pressure of dissociation products is as low as ≤3 mm Hg. The thermodynamic characteristics were calculated from the temperature dependence of the equilibrium constant $\ln K^d = f(1/T)$ (calculation by the second law). In the case of low partial pressures of dissociation products, the calculation by the second law involved a considerable inaccuracy (Fig. 2). Therefore, the results were treated using the dissociation entropy of the complex [134.0 $J\,mol^{-1}\,K^{-1}$ at 600 K], obtained by quantum-chemical calculations (calculation by the third law).

In series no. 2, assuming that the 2 : 1 complex is not formed in vapors, we obtained thermodynamic characteristics of the dissociation of the complex $GaCl_3pyz$ by Eq. (1).

$$GaCl_3pyz(gas) = GaCl_3(gas) + pyz(gas). \quad (1)$$

The calculation was carried out with account for $GaCl_3$ dimerization [18] [Eq. (2)].

$$2GaCl_3(gas) = Ga_2Cl_6(gas)$$
$$\log K_d = 16.14 - 4894/T - 2.013\log T. \quad (2)$$

Here K_d is the equilibrium constant of $GaCl_3$ dimerization and *T*, absolute temperature. The equilibrium constant $K^{dis}_{1:1}$ of the unsaturated vapor dissociation of the 1:1 complex in the entire temperatures range was calculated by Eq. (3).

$$K^{dis}_{1:1} = (\Delta p)^2/(p_0 - 2\Delta p). \quad (3)$$

Here p_0 is the total pressure in the system (mm Hg); $\Delta p = p_0 - p'$, difference between the total pressure p_0 and the hypothetical pressure p' of thermal expansion of the vapor of nondissociated complex. Values of $p'(GaCl_3pyz)$ were determined from the sample weight and refined during treatment of the experimental data. The results of the calculations by the second law are given in Table 3, the dissociation enthalpies are nicely consistent with those calculated by the third law (Table 4).

Thermodynamic characteristics of the unsaturated vapor dissociation of the 2 : 1 complex. As the content of the 2 : 1 complex in the vapor is low, we used the composition with excess $GaCl_3$. The pressure in the system did not increase after 2-h exposure at 372°C (experiment with a considerable excess of $GaCl_3$). Thus, the concentration of the substance in the membrane chamber remains constant at this temperature. The thermal dissociation is reversible up to 420°C, which is proved by reproducible heating and cooling data. The shape of the temperature dependence of the dissociation constant is rather complicated, and we cannot use the whole set of points for thermodynamic calculations. The weights of the

Table 3. Characteristics of the dissociation of the complexes $GaCl_3pyz$ and $GaCl_3pyzGaCl_3$ into components (unsaturated vapor). Calculation by the second law[a]

Complex	Exp. no.	$m(GaXl_3/pyz)$, mg	V,[b] ml	T, K	$\log K^{dis}(atm) = a/T + b$		T_{av}, K	$\Delta H^{dis}(T_{av})$, kJ mol^{-1}	$\Delta S^{dis}(T_{av})$, J mol^{-1} K^{-1}
					a	b			
$GaCl_3pyz$	2	14.9/6.8	55.15	559–692 (148 points)	–6563 ± 86	6.965 ± 0.134	625	125.6 ± 1.6	133.3 ± 2.6
$GaCl_3pyzGaCl_3$	3	43.8, complex	55.29	628–715 (120 points)	–5583 ± 138	8.027 ± 0.207	672	106.2 ± 2.6	152.6 ± 3.9
$GaCl_3pyzGaCl_3$	4	48.8/6.8	53.76	627–736 (128 points)	–5434 ± 168	7.981 ± 0.248	682	103.1 ± 3.2	151.8 ± 4.7
$GaCl_3pyzGaCl_3$	Average by series nos. 3 and 4			627–736 (248 points)	–5865 ± 144	8.536 ± 0.214	682	111.5 ± 2.7	162.3 ± 4.1

[a] For series nos. 1 and 5, calculation by the second law is impossible because of the large errors in the low partial pressures of the dissociation products. [b] V is the device volume.

Table 4. Dissociation enthalpies of the 1 : 1 and 2 : 1 complexes

Complex	Exp no.	$m(GaCl_3/pyz)$, mg	V, ml	T_{av}, K	$\Delta H^{dis}(T_{av})$, kJ mol^{-1}, calculation	
					by the 2nd law	by the 3th law
$GaCl_3pyz$	1	14.9/13.9	56.25	655	–	121.1 ± 2.0
$GaCl_3pyz$	2	14.9/6.8	55.15	625	125.6 ± 1.6	125.9 ± 1.1
$GaCl_3pyzGaCl_3$	3	43.8, complex	55.29	672	106.2 ± 2.6	98.9 ± 1.0
$GaCl_3pyzGaCl_3$	4	48.8/6.8	53.76	682	103.3 ± 3.2	96.5 ± 1.5
$GaCl_3pyzGaCl_3$	5	95.0/10.1	55.57	646	–	99.7 ± 2.8

components (and complexes) are taken as differences of large quantities. The inaccuracy in weighing ~0.2 mg produces an error of about 6–8 kJ mol^{-1} in the calculated thermodynamic characteristics. Therefore, we used the method of successive approximations [19] to calculate the dissociation enthalpy and entropy of the complex. As the first approximation, we found the gross pressures p'_{GaCl_3} and p'_{pyz} of $GaCl_3$ and pyz from the sample weights and the volume of the membrane chamber. Then, using Eq. (4), we calculated the equilibrium dissociation constant of the 2 : 1 complex with account for dimerization of gallium trichloride (K_d) and dissociation of the 1 : 1 complex ($K^{dis}_{1:1}$).

$$K^{dis}_{2:1} = \frac{p_{GaCl_3}(2p_0 - p'_{GaCl_3} - p_{GaCl_3} - 2p_{pyz})}{p'_{GaCl_3} + p'_{pyz} + p_{GaCl_3} - 2p_0 + p_{pyz}}, \qquad (4)$$

$$p_{GaCl_3} = [0.25(K_d)^2 - K_d(p_0 - p'_{pyz})]^{1/2} - 0.5K_d,$$

$$p_{pyz} = \frac{2p_0 - p'_{GaCl_3} - p_{GaCl_3}}{2 + p_{GaCl_3}/K^{dis}_{1:1}}.$$

The resulting dependence of $\log K^{dis}_{2:1}$ on $1000/T$ is nonlinear; the largest deviations are observed in the high-temperature region. For some points in this region, the p' values estimated from sample weight data lead to negative (clearly fallacious) partial pressures. By varying the complex weight at 0.2-mg steps we could plot the regression coefficient R^2 vs. p'. As seen from Fig. 3, first R^2 sharply increases, and then the dependence rapidly converges to a certain limit. As the convergence criterion we selected a point where R^2 differs from the limiting value by 0.01. The resulting $\log K^{dis}_{2:1}$ values (Fig. 4) were treated by the least-squares procedure, and the calculated gas-phase dissociation characteristics are given in Table 3. Independent treatment resulted in a satisfactory agreement of the results of the two experiements. Note that the dissociation entropy and enthalpy of the complex $GaCl_3pyzGaCl_3$, calculated with the whole set of experimental points (Table 3), are overestimated.

Our *ab initio* quantum-chemical calculations allow us to calculate standard dissociation entropy for the complex. With the standard dissociation entropy

[141.7 J mol^{-1} K^{-1} at 700 K], we can calculate the dissociation enthalpy by the third law. The calculated data are given in Table 4. The dissociation enthalpies calculated by the third law are lower than those calculated by the second law. In view of the fact that the error in weighing a sample of about 0.2 mg produces the error in the calculated thermodynamic characteristics of about 6–8 kJ mol^{-1}, we prefer the dissociation enthalpy calculated by the third law: ΔH^{dis}_{667} ($GaCl_3pyzGaCl_3$) 98.4 ± 3.3 kJ mol^{-1}.

Estimation of vapor composition under conditions of mass-spectral experiment. Taking the value of $K^{dis}_{2:1}$ for the 2:1 complex from tensimetric data, we find for the total pressure of 10^{-6} mm Hg that the ratio of the partial pressures of the complex and its dissociation products at 120°C is 0.16%, and at 170°C it is only 3.3×10^{-3}%, which qualitatively agrees with the mass-spectral data (traces of the 2:1 complex were detected at 120°C, and at 1700C the complex was not detected).

Thermodynamic characteristics of vaporization of the complexes. The saturated vapor pressure over a solid 1:1 complex was calculated with the data of series nos. 1 and 2 from the total pressures with account for thermal dissociation of the complex [calculated by Eq. (3)] and $GaCl_3$ dimerization.

The experimental data for series nos. 1 and 2 allowed us to calculate the temperature dependence of vapor pressure over a solid 1:1 complex (up to 470 K) and over its melt. The sublimation and vaporization characteristics are given in Table 5. The standard enthalpy of vaporization was calculated by the following formula [20].

$$\Delta H^{vap}_{298} = \Delta H^{vap}_{T} \left(\frac{1 - 298/T_{cr}}{1 - T/T_{cr}} \right)^{0.38}.$$

Here ΔH^{vap}_{298} is the standard vaporization enthalpy; ΔH^{vap}_{T}, vaporization enthalpy at temperature T; and T_{cr}, critical temperature. The critical temperature T_{cr} was estimated as T_{cr} = 1.41bp + 66 [21]. The normal boiling point was estimated from tensimetric data. The standard vaporization enthalpy of the 1:1 complex, ΔH^{vap}_{298}($GaCl_3pyz$), calculated with the data for series nos. 1 and 2 is 61.9 ± 3.2 kJ mol^{-1}. To find the saturated vapor pressure over the melt of a complex, one should take into account the possibility of interaction of the vapors with the melt. Unfortunately, no data on the solubility of the components in the melt of the complex are available, and, therefore, in view of the superposition of dissociation and vaporization processes, the resulting vaporization enthalpies are more likely to be an estimate. We also estimated the melting enthalpy and entropy of the complex as a difference of the corresponding characteristics for the sublimation and vaporization processes: ΔH^{melt}($GaCl_3pyz$) 12 ± 5 kJ mol^{-1}, ΔS^{melt}($GaCl_3pyz$) 23 ± 13 J mol^{-1} K^{-1}.

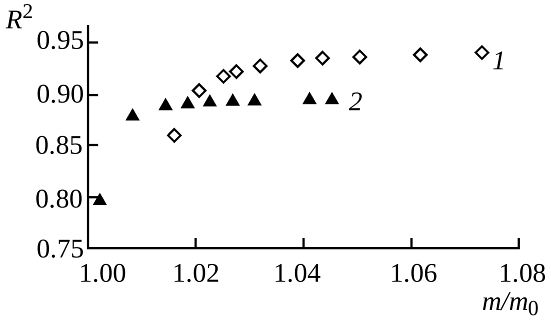

Fig. 3. Plot of correlation coefficient R^2 (for the dependence of $\log K^{dis}_{2:1}$ vs. inverse temperature) vs. m/m_0 (m_0, sample weight and m, weight used for calculation of p'). (*1*) 2:1 complex and (*2*) excess $GaCl_3$.

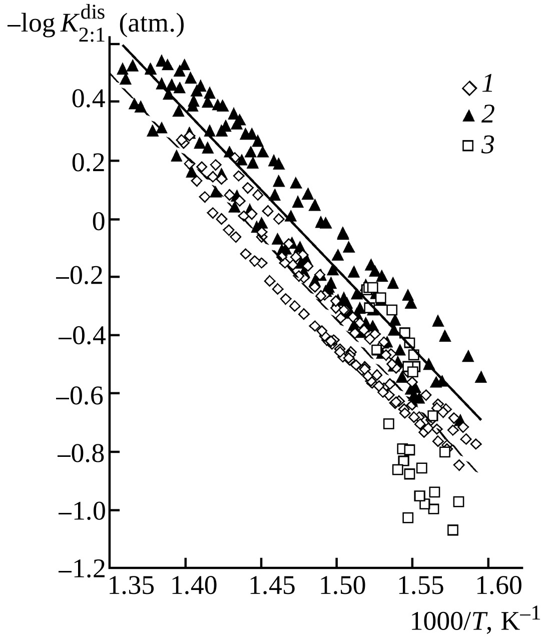

Fig. 4. Plot of the $\log K^{dis}_{2:1}$ of $GaCl_3pyzGaCl_3$ vs. inverse temperature (1000/T) (numbers of experiments correspond to Table 4). (*1*) Series no. 3, (*2*) series no. 4, and (*3*) series no. 5 (large excess of $GaCl_3$).

We have calculated temperature dependence of vapor pressure for the 2:1 complex from the data for series nos. 3–5 (up to the melting point of the complex at 303°C). Because of the low saturated valor pressure of the complex under these conditions (≤ 20 mm Hg), the thermodynamic sublimation characteristics of the complex 2:1 could only be estimated

Table 5. Sublimation and vaporization characteristics of the complex $\mathrm{GaCl_3pyz}$

Process	Exp. no.	Temperature range, K	$\log p(\mathrm{mm\ Hg}) = a/T + b$		T_{av},	$\Delta H(T_{\mathrm{av}})$, kJ mol^{-1}	$\Delta S(T_{\mathrm{av}})$, J mol^{-1} K^{-1}
			a	b			
Sublimation	1	376–472 (13 points)	–3494 ± 382	8.443 ± 0.899	424	66.9 ± 7.3	106.5 ± 17.2
	2	347–470 (25 points)	–3236 ± 292	7.519 ± 0.717	409	61.9 ± 5.6	88.8 ± 13.7
	All points	347–472 (38 points)	–3456 ± 250	8.159 ± 0.606	410	66.2 ± 4.8	101.0 ± 11.6
Vaporization	1	482–535 (13 points)	–2608 ± 114	6.556 ± 0.221	508	49.9 ± 2.2	70.4 ± 4.2
	2	477–543 (22 points)	–2858 ± 104	6.958 ± 0.206	510	54.7 ± 2.0	78.0 ± 3.9
	All points	477–543 (35 points)	–2853 ± 123	6.980 ± 0.241	510	54.6 ± 2.4	78.5 ± 4.6

Table 6. Thermodynamic dissociation characteristics of the complexes at various temperatures, as given by B3LYP/pVDZ calculations

T, K	$\mathrm{GaCl_3pyz = GaCl_3 + pyz}$		$\mathrm{GaCl_3pyzGaCl_3 = GaCl_3pyz + GaCl_3}$	
	$\Delta H^0(T)$, kJ mol^{-1}	$\Delta S^0(T)$, J mol^{-1} K^{-1}	$\Delta H^0(T)$, kJ mol^{-1}	$\Delta S^0(T)$, J mol^{-1} K^{-1}
298	115.9	144.5	87.0	154.8
500	112.9	136.8	83.9	147.0
600	111.3	134.0	82.3	144.1
700	109.7	131.6	80.8	141.7

with a great inaccuracy: $\Delta H^{\mathrm{subl}}_{537}(\mathrm{GaCl_3pyzGaCl_3})$ 92.1 ± 9.4 kJ mol^{-1} and $\Delta S^{\mathrm{subl}}_{537}(\mathrm{GaCl_3pyzGaCl_3})$ 182.7 ± 17.5 J mol^{-1} K^{-1}. Because of the small sample weights of the complex and superposition of the dissociation and vaporization processes, the vaporization enthalpy of the 2 : 1 complex is impossible to estimate quantitatively.

The results of this study establish existence in the GaCl3–pyz system of 1 : 1 and 2 : 1 complexes that pass into vapor. Vaporization processes are complicated by equilibrium thermal dissociation of gaseous $\mathrm{GaCl_3pyz}$ and $\mathrm{GaCl_3pyzGaCl_3}$ complexes. Therewith, the latter complex exists in noticeable amounts only when excess $\mathrm{GaCl_3}$ is present. The resulting data allowed us to determine the following thermodynamic characteristics.

	T, K	ΔH_T, kJ mol^{-1}	ΔD_T, J mol^{-1} K^{-1}
		$\mathrm{GaCl_3pyz}$	
Sublimation	410	66.2 ± 4.8	101.0 ± 11.6
Vaporization	510	54.6 ± 2.4	78.5 ± 4.6
Dissotiation	625	124.2 ± 2.8	133.6 ± 2.6
		$\mathrm{GaCl_3pyzGaCl_3}$	
Sublimation	537	92.1 ± 9.4	182.7 ± 17.5
Dissotiation	667	98.4 ± 3.3	

Our present results reasonably agree with the calculated dissociation characteristics of the complexes (Table 6). The calculated dissociation enthalpies are underestimated compared to experiment. This finding allows us to state that a complex stable by the results of calculations at the B3LYP/pVDZ level of theory should be stable in experiment.

EXPERIMENTAL

In view of high hygroscopicity of the compounds under study, all operations, starting from their synthesis and purification before filling tensimetric devices, were carried out in all-soldered evacuated glass systems completely excluding contact with atmospheric air and moisture. Pyrazine was purified by multiple resublimation in a vacuum. Gallium trichloride was synthesized from elements and additionally purified by multiple resublimation in a vacuum. Adducts were synthesized from components in a vacuum; the 1 : 1 complex was synthesized with excess pyrazine and the 2 : 1 complex, with excess gallium trichloride. The systems were heated for 12 h at 200°C, after which excess components were removed by vacuum sublimation. The 2 : 1 and 1 : 1 adducts were additionally purified by vacuum distillation at 280–300°C. The resulting complexes represent colorless crystalline substances melting at 199°C ($\mathrm{GaCl_3pyz}$) and 303°C ($\mathrm{Ga_2Cl_6PYz}$). Their melts tend to supercool (to 152 and 272°C, respectively). Above 350°C, solid complexes get black, but the reproducible heating thermograms suggest only slight pyrolysis. Note that the complexes are more stable in vapor than in the condense phase. Thermal dissociation in unsaturated vapor is reversible up to 420°C, as evidenced by the reproducible heating and cooling data. At temperatures above 440°C (experiment with the 2 : 1 complex), the pressure in the system irreversibly increases (pyrolysis of the complexed donor).

Processes in saturated and unsaturated vapor were studied by static tensimetry with a membrane zero gage. The pressure was measured to 0.1 mm Hg with an MChR-3 mercury gage. The temperature was controlled with two thermocouples (chromel–alumel), the thermal emf was measured with an Shch-1516 digital voltmeter, the temperature was accurate to ±0.05°C. The volume of the membrane chamber was found from the difference in the weights of water-filled and empty systems. The error in the volume was ±0.02 ml, that is 0.04% at the system volume of 50 ml.

Mass spectrometry was performed on an MKh-1321 instrument, ionization energy 70 eV, batch temperatures 120 and 170°C.

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