Gas Phase Complexes MX$_3$·4,4′Bpy·M′X$_3$ (M,M′ = Al, Ga; X = Cl, Br): Experiment and Theory

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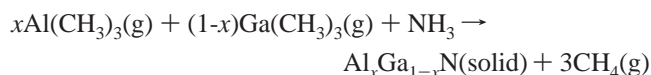
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Donor−acceptor (DA) complexes MX$_3$·LL·M′X$_3$ (M, M′ = Al, Ga; X = Cl, Br; LL = 4,4′-bipyridyl) have been theoretically investigated at the B3LYP/pVDZ level of theory. Addition of the first molecule of MX$_3$ to 4,4′-bipyridyl has a similar exothermicity compared to complexes with the monodentate donor pyridine. Addition of the second molecule of MX$_3$ is significantly (by about 15 kJ mol^{-1}) less exothermic. Nevertheless all 2:1 complexes (including heteroacceptor) are predicted to be stable in the vapor phase up to 660, 760, 830 and 920 K for GaBr$_3$, GaCl$_3$, AlBr$_3$, and AlCl$_3$, respectively. Four homoacceptor MX$_3$·4,4′bpy·MX$_3$ complexes have been synthesized for the first time, and their existence in the vapor phase has been proven by mass spectrometry. The theoretically predicted order of the complex stability AlCl$_3$ > AlBr$_3$ > GaCl$_3$ > GaBr$_3$ correlates well with the experimental observations of M$_2$X$_5$bpy$^+$ ion abundances in the mass spectra. The results obtained show for the first time that the synthesis of the *gas-phase stable* heteroacceptor complexes is feasible, which opens the prospect for their future use as single-source precursors to the stoichiometry-controlled synthesis of 13−15 alloys.

Introduction

Group 13−15 semiconductors play an important role in microelectronics. GaN related alloys are particularly interesting due to their ability to cover a wide spectral range that is not possible with other 13−15 semiconductors.[1] The band gap in the (Al,Ga,In)N-based materials range from 1.9 eV (InN) to 3.4 eV (GaN) to 6.2 eV (AlN). The band structure is thought currently to be a direct band gap across the entire alloy range. Therefore, almost the entire visible range is spanned in the group 13 nitride alloys. In addition, nitrides are resistant to chemical etching, allowing GaN-based devices to operate under harsh environments.[2] The heterometallic nitride alloys such as Al$_x$Ga$_{1-x}$N can be obtained by MOCVD (metal organic chemical vapor deposition) from trimethylaluminum, trimethylgallium, and ammonia:[3]

$$x\text{Al}(\text{CH}_3)_3(\text{g}) + (1\text{-}x)\text{Ga}(\text{CH}_3)_3(\text{g}) + \text{NH}_3 \rightarrow$$
$$\text{Al}_x\text{Ga}_{1-x}\text{N}(\text{solid}) + 3\text{CH}_4(\text{g})$$

However, stoichiometric control of such processes is still a challenge for chemists.[4] The composition of the deposited nitride depends on the process conditions (temperature, total pressure, partial pressures of reagents, type and geometry of the reactor) and generally is not reproducible in different laboratories; that is, the same compositions of initial components result in different Al:Ga ratios in the alloy. An alternative method of alloy

synthesis is to use single-source precursors−volatile compounds, which contain all the necessary elements in an initially specified stoichiometric ratio. Prospective precursors are the molecular donor−acceptor complexes (or adducts), consisting of group 13 metal halides MX$_3$ and polydentate N-containing organic ligands, such as the bidentate donor 4,4′-bipyridyl. Two different acceptors may be coordinated to the two nitrogen atoms in such ligands, for example: MX$_3$·4,4′bpy·M′X$_3$.

Complexes of the organometallic derivatives of the group 13 metals with nitrogen-containing bidentate donors are weakly bound and dissociate into components upon heating.[5] It is expected that substitution of the organometallic acceptor by a metal halide will greatly increase the stability of the complexes. Numerous gas phase complexes between group 13 halides and the monodentate N-containing ligand pyridine are known experimentally.[6−9] Nevertheless, there are apparently no reports of the existence of MX$_3$·LL·MX$_3$ (M = Al, Ga; X = Cl, Br) 2:1 complexes *in the gas phase*. In this communication we report results of theoretical investigations of the stability of the donor−acceptor complexes of 4,4′-bpy with group 13 metal halides and an experimental study of their volatility.

Computational Details

All computations were performed using the Gaussian 94 program package.[10] All geometries were fully optimized using density functional theory (DFT). The hybrid three-parameter exchange functional of Becke[11] with the gradient-corrected correlation functional of Lee, Yang, and Parr[12] (B3LYP) was chosen for this research. As was shown before, it provides accurate results for the thermodynamics of the MX$_3$−NH$_3$[13] and

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TABLE 1: Thermodynamic Parameters for the Dissociation of the Gas Phase Complexes of Al and Ga Trihalides with Pyridine (Py) and 4,4′-Bipyridyl (bpy), and Values of the Temperature $T_{K=1}^{diss}$ at Which the Equilibrium Constant for the Dissociation Process Equals One (B3LYP/pVDZ Level of Theory)

process		$\Delta H_{298}^{\circ\ diss}$, kJ mol^{-1}		$\Delta S_{298}^{\circ\ diss}$, J mol^{-1} K^{-1}		$T_{K=1}^{diss} = (\Delta H_{298}^{\circ\ diss}/\Delta S_{298}^{\circ\ diss})$, K	
		Al	Ga	Al	Ga	Al	Ga
1	MCl$_3$Py = MCl$_3$ + Py	160.8	133.8	147.5	141.2	1091	947
2	MCl$_3$·bpy = MCl$_3$ + bpy	159.1	131.9	138.1	136.4	1152	967
3	MCl$_3$·bpy·MCl$_3$ = MCl$_3$ + MCl$_3$·bpy	144.3	118.1	156.3	154.4	923	765
4	MCl$_3$·bpy·MCl$_3$ = 2MCl$_3$ + bpy	303.4	250.0	294.4	290.8	1031	860
5	MCl$_3$·bpy·M′Cl$_3$ = MCl$_3$ + M′Cl$_3$·bpy	144.8^a	117.6^b	150.4^a	148.7^b	963^a	791^b
6	MBr$_3$Py = MBr$_3$ + Py	147.4	118.4	148.0	118.4	996	816
7	MBr$_3$·bpy = MBr$_3$ + bpy	145.8	116.6	140.5	139.3	1038	837
8	MBr$_3$·bpy·MBr$_3$ = MBr$_3$ + MBr$_3$·bpy	130.5	103.0	156.5	155.6	834	662
9	MBr$_3$·bpy·MBr$_3$ = 2MBr$_3$ + bpy	276.3	219.5	296.9	295.0	930	744
10	MBr$_3$·bpy·M′Br$_3$ = MBr$_3$ + M′Br$_3$·bpy	131.4^a	102.1^b	150.9^a	149.8^b	871^a	682^b

^{a} M = Al, M′ = Ga. ^{b} M = Ga, M′ = Al.
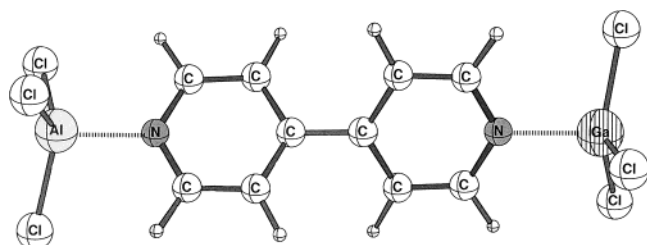
Figure 1. Structure of the Cl$_3$Al-4,4′bpy-GaCl$_3$ complex.

GaX$_3$−Py[14] complexes. The polarized valence double-ζ (pVDZ) basis set of Ahlrichs and co-workers[15] was used throughout. All stationary points on the potential energy surfaces (PES) were characterized by the evaluation of analytic second derivatives and correspond to minima on the PES. As an example, the structure of the AlCl$_3$-bpy-GaCl$_3$ complex is given in Figure 1. Structural features will not be discussed in the present communication. Standard enthalpies were calculated using standard GAUSSIAN procedure, taking into account zero point vibrational energy and thermal corrections, using computed vibrational frequencies (unscaled). Values of the temperature, at which the equilibrium constant equals 1, were estimated from the standard enthalpy and entropy of the complex dissociation according to

$$T_{K=1}^{diss} = \frac{\Delta H_{298}^{\circ\ diss}}{\Delta S_{298}^{\circ\ diss}}$$

The mean difference between values of the temperature calculated using this approximation and experimental values for the MX$_3$ complexes with ammonia was 30 K.[13]

Experimental Details

Due to the high air and moisture sensitivity of the group 13 metal halides and their complexes, all operations have been performed in a glass apparatus in a vacuum ($\sim 10^{-5}$ Torr). Metal halides MX$_3$ have been synthesized by direct interaction of metal and halogen. All components have been purified by multiple (no less than four times) resublimations in a vacuum. Purity control of the samples was performed by means of mass spectrometry and vapor pressure measurements. The complexes MX$_3$·4,4′bpy·MX$_3$ have been synthesized in the vacuum by heating the mixture of the excess of the corresponding metal halide and 4,4′bpy. After mixing, the system was kept at ~ 250 °C for 12−24 h, and the excess of the metal halide was removed by sublimation.

The complexes obtained are low volatility white solids, which have been purified by resublimation in a vacuum at ~ 340 °C. Above 370 °C irreversible destruction processes have been evidenced (change of color to red and black). Mass spectrometry (MS) studies have been carried out using a standard MX1321 mass spectrometer with direct probe introduction. The temperature of the ionization chamber was 200 °C, electron energy 70 and 19 eV. The temperature of the vaporization chamber was varied from 120 to 380 °C.

Results and Discussion

1. Theoretical Studies. A series of donor−acceptor (DA) complexes with 4,4′-bipyridyl (MX$_3$·bpy, MX$_3$·bpy·M′X$_3$) and pyridine (MX$_3$·Py) (M, M′ = Al, Ga; X, X′ = Cl, Br) have been theoretically investigated. Predicted thermodynamic parameters for the dissociation reactions are given in Table 1. As may be seen, the stability of complexes with 4,4′bpy is only about 2 kJ mol^{-1} weaker with respect to pyridine. Note also that gallium adducts are by 30 kJ mol^{-1} less stable, compared to the analogous Al species. This conclusion dovetails with available experimental data on the stability of group 13 metal halide complexes with the monodentate donor pyridine.[6−9] Coordination of the first acceptor molecule to the first nitrogen atom reduces (by about 15 kJ mol^{-1}) the stability of the DA bond formed between second acceptor molecule and the second nitrogen atom. The dissociation enthalpy of the DA bond decreases in two series:

•for acceptors, AlCl$_3$ > AlBr$_3$ > GaCl$_3$ > GaBr$_3$ (difference between each halide is about 15 kJ mol^{-1})

•for donors, py ≥ bpy > GaBr$_3$·bpy ≥ GaCl$_3$·bpy ≥ AlBr$_3$·bpy ≥ AlCl$_3$·bpy

The obtained order of acceptor ability is in good agreement with previous theoretical studies on Lewis acidity of Al and Ga halides.[13,14,16] The difference in donor properties of MX$_3$·bpy (for different metal halides) is small, but the following trend is observed: the stronger the first DA bond, the weaker the second. The temperature at which the equilibrium constant for the dissociation process equals 1 is an important criterion of complex stability. According to the theoretical predictions (Table 1), even the least stable Br-containing complexes should exist in the vapor at temperatures below 660 K (standard pressure). Heteroacceptor complexes (consisting of two different metal halides) are stable with respect to the dissociation of the DA bond up to 400 °C (Table 1). Thus, they appear to be promising subjects for experimental studies. Volatility, one of the crucial parameters of the successful single-source precursor, can only be derived from experiment. Therefore, experimental gas-phase

TABLE 2: Results of Mass Spectrometric Studies of MX$_3$·4,4′bpy·MX$_3$ Adducts (Vaporization Chamber Temperature 603 K, Ionization Chamber Temperature 473 K, Electron Energy 70 eV) and Relative Intensities of Ions (percent), Normalized to the Most Abundant Ion (100%) (Fragment Ions from bpy$^+$ Not Given)

ion	Al$_2$Cl$_6$bpy	Al$_2$Br$_6$bpy	Ga$_2$Cl$_6$bpy	Ga$_2$Br$_6$bpy	AlBr$_3$GaBr$_3$bpy
M$_2$X$_6$bpy$^+$	0.3				
M$_2$X$_5$bpy$^+$	13	6.8	0.9		3.9[a] (0.7[c])
MX$_3$bpy$^+$	8.6	1.1	1.7		1.2[a] (−[b])
MX$_2$bpy$^+$	38	100	19	100	100[a] (9.5[b])
MXbpy$^+$		1.5			3.0[a] (−[b])
MX$_3^+$	14	3.0	14	31	1.1[a] (15[b])
MX$_2^+$	21	24	61	40	20[a] (40[b])
MX$^+$		1.5	7	9.3	−[a] (6.2[b])
bpy$^+$	100	24	100	43	35

[a] M = Al. [b] M = Ga. [c] Refers to the ion AlGaBr$_5$bpy$^+$.

studies of the volatility and stability of the MX$_3$ complexes with bidentate ligand 4,4′bpy have been performed.

2. Experimental Studies. The representative mass spectra of the M$_2$X$_6$bpy complexes are summarized in Table 2. The parent M$_2$X$_6$bpy$^+$ ion was observed only for the strongest Al$_2$Cl$_6$bpy complex. If one assumes that the fragment M$_2$X$_5$bpy$^+$ ions are formed in the gas phase from the parent M$_2$X$_6$bpy molecules, trends in intensities of the M$_2$X$_5$bpy$^+$ ion (AlCl$_3$ > AlBr$_3$ > GaCl$_3$ > GaBr$_3$) confirm the theoretically predicted order of complex stability. Note that the weakest complex, GaBr$_3$·4,4′bpy·GaBr$_3$ was not observed at MS conditions (low pressure will favor dissociation of the complex). The presence of the MX$_3$bpy$^+$ ions evidences the stability of the MX$_3$bpy complexes. The observed order of relative intensities of the MX$_3$bpy$^+$ and MX$_2$bpy$^+$ ions is different from theoretical predictions, probably due to secondary fragmentation processes.

When the mixture of AlBr$_3$ and GaBr$_3$ (Al:Ga ratio 1.61) was reacted with a shortage of 4,4′bpy and the excess of the volatile halides was removed, the mass spectrum of the resulting product exhibits the Al$_2$Br$_5$bpy$^+$ and AlGaBr$_5$bpy$^+$ ions with intensities 3.9% and 0.7%, respectively. This indicates formation of the homoacceptor AlBr$_3$·bpy·AlBr$_3$ and heteroacceptor AlBr$_3$·bpy·GaBr$_3$ complexes. Attempts of their separation by vacuum sublimation failed. Thus, the existence of the 2:1 donor−acceptor complexes, *stable in the gas phase,* has been predicted theoretically and confirmed experimentally. However, the low volatility of complexes with LL = 4,4′bpy prevents their practical use as SSP. It is quite possible that shorter bridging groups LL will be necessary to achieve suitable volatility of the complexes, and such experimental and theoretical studies are now in progress.

Conclusions

The structural and thermodynamic properties of the homo and heteroacceptor complexes of group 13 metal halides with the bidentate donor 4,4′bpy have been theoretically predicted. Complexes of aluminum and gallium trihalides with 4,4′bpy are stable in the vapor phase with respect to dissociation of the donor−acceptor bond. The existence of these new gas phase complexes has been experimentally confirmed by mass spectrometry. This opens exciting possibilities for the use of 2:1 MX$_3$·LL·M′X$_3$ complexes as single-source precursors to the stoichiometry-controlled synthesis of 13−15 alloys.

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