Synthesis and thermal properties of the pyrazolato germanium complexes

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Pyrazolato ligand is a good choice for the synthesis of germanous complexes that can be used in chemical vapor deposition (CVD)/atomic layer deposition (ALD) precursors for its special properties, such as the stability of the complexes based on the conjugated structure and the excellent volatility based on the low melting point. Here, several pyrazolato germanium(II) precursors were prepared and characterized. The correlation between the volatility and the amount of the substitute group was investigated. The thermal behavior was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments in order to demonstrate the enhancement of their thermal stability. The experiments indicated thermostability, and the volatilization of samples made them suitable as potential membrane materials.

1. Introduction

Thermal stability has always been desired in the development of chemical vapor deposition (CVD)/atomic layer deposition (ALD) precursors. Cyclopentadienyl and β-diketiminate ligands have been the most widely employed, because these ligands can provide monomeric structures with sufficient thermal stability to allow vapor transport [1-3]. However, such precursors have many problems in terms of film growth, including low vapor pressure, erratic vapor transport, unacceptably high carbon incorporation in the thin-film materials and premature precursor decomposition by loss of neutral ligands. In order to resolve these problems, polydentate donor ligands have been used to saturate the coordination spheres of the metal ions. The pyrazolato ligand has been employed with many metals across the periodic table as a versatile nitrogen donor ligand [4-8].
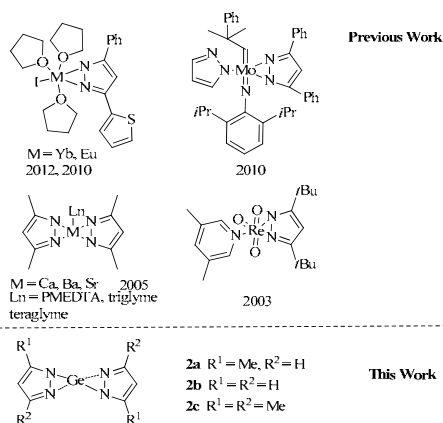
Scheme1. Three member ring pyrazole metal complexes

Researchers have explored the coordination chemistry of pyrazolato ligands with metals (Scheme 1) [9]. Different metals have been coordinated to the pyrazol ligands to form the ternary ring and other auxiliary ligands to saturate the coordination sphere. Among these complexes, Ca complexes draw our attention. Ca and Ge are in the same period. The atomic radius of Ge (Å: 1.52) is shorter than Ca (Å: 2.23), and consequently less ring tension hinders the formation of

an N-Ge-N ternary ring. Additionally, the Ge atom has more empty orbitals in the 4p and 4d electron sub-shell than Ca does in order to accept the electron pairs from ligands. Thus it is very possible to form the Ge ternary ring structure, which is similar to the Ca complexes.

Germanium complexes play an important role in the Ge-Sb-Te (GST) ternary films. Very few germanium(II) precursors have been explored with regard to their applications in the CVD/ALD of Ge/GST films [10-18]. Among these complexes, some with similar structures, having a maximum of ten electrons, have already been applied as CVD/ALD precursors, while others are in the research phase [19]. As part of our research related to the further exploration of germanium(II) precursors, we set out to explore germanium pyrazolato complexes. Herein we report the synthesis, structure and properties of a series of germanium complexes that contain various pyrazolato ligands. We also describe the thermal stability and volatility of these complexes.

2. Experimental

All manipulations were carried out using standard Schlenk techniques or in a glove box under a nitrogen atmosphere. Diethyl ether was freshly distilled from Na prior to use. The compounds $GeCl_2$.(dioxane) were prepared by literature procedures [20]. Other chemicals were purchased from Aldrich and used as received.

A solution of lithium salt of pyrazol ligands (2 mmol) was added drop wise to a stirred solution of $GeCl_2$.dioxane (1 mmol) in diethyl ether (40 mL) at -78 °C. The reaction mixture was warmed to room temperature and was stirred for 3 h. After removal of all volatiles, the residue was extracted with toluene (30 mL). Storage of the extract in a -29 °C freezer for 3 days afforded orange-red crystals.

3. Results and discussion

3.1 Synthesis of Ge Complexes 2

First, 3-methylpyrazole was chosen as the model substrate for reaction optimization. We started with the reaction using LiMe as a base in THF, and fortunately the desired product was obtained, albeit with a low yield. Furthermore, the screening of reaction conditions was carried out so as to obtain higher yields. When LiMe was used as a base in ether, the desired product was obtained at a higher yield. The results were summarized in Table 1.

It was found that the base was very important to the reaction, given that the reaction did not take place with inorganic bases or in the absence of any base. The results showed that lithium alkylide was the best choice. Toluene is better than ether as the solvent due to its convenience in the processes of separating the mixture of the reaction, although it yields essentially the same result that ether does.

Table 1. Screening of reaction conditions [a]
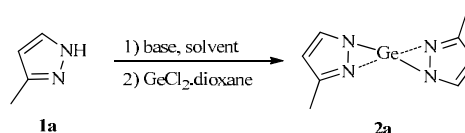
Entry	Base	Solvent	Time (h)	Yield[%][b]
1	K_2CO_3	ether	24	-
2	KH	ether	24	-
3	LiMe	ether	24	63
4	*n*-BuLi	ether	24	62
5	LiMe	THF	24	<5
6	LiMe	hexane	24	15
7	LiMe	toluene	24	65
8	LiMe	ether	12	62
9	LiMe	ether	36	63
10	none	ether	24	-

a: Conditions: 1) **1a** (1 mmol), LiMe (1 mmol), toluene, -78 °C~RT, 3 h, in N_2, 2) $GeCl_2$.dioxane (0.5 mmol), toluene, 24 h, -78 °C~RT, in N_2.[b] Isolated yields, separated by recrystallization.

Having delineated the optimal conditions for the reactions of pyrazole ligand salts with $GeCl_2$.dioxane (Scheme 2), we applied them to a variety of substrates in order to determine the scope and limitations of the method used to obtain the corresponding product. The amount of methyl substituent has almost no influence upon the reaction. There was no difference among the ligands in terms of conditions or yields.

Scheme 2. The synthesis of the pyrazolato germanium complexes. [a]
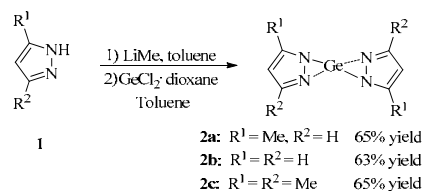
a: Conditions: 1) **1** (1 mmol), LiMe (1 mol), toluene, -78 °C~RT, 3 h, in N_2, 2) $GeCl_2$.dioxane (0.5 mmol), toluene, 24 h, -78 °C~RT, in N_2.

Regarding the ^{1}H NMR spectrum, N-H peak disappeared and other H had some subtle chemical shift compared to the ligand before coordination (see the SI file). This indicated that two N atoms were participants in coordination because, if just the N atom with H had coordinated to the Ge atom, some difference between the chemical environments of two N atoms would have been apparent. Moreover, the difference would be reflected in the ^{1}H and ^{13}C NMR spectra. In the case of **2b** (Scheme 3), wherein the ^{1}H spectrum of the pyrazol H atom (a) and the H atom (c) were a double peak, while the C atom 1 and C atom 3 were the same peak in the ^{13}C NMR spectra. After two N atoms coordinated to the Ge, they were in the same relationship in this work. If just the N atom with the H atom had coordinated to Ge, the chemical environment of C atom 1 and C atom 3, H atom a and H atom c would have changed, as would have been apparent in the ^{1}H and ^{13}C NMR spectra, but not in the same peak. Thus the phenomenon in the ^{1}H and ^{13}C NMR spectra confirmed the structures of the complexes. In order to further confirm the structures, we are endeavoring to obtain the single crystals of the complexes.
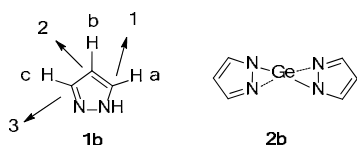
Scheme 3 pyrazole ligand 1b and complexe 2b

3.2 Thermal property

Concurrently, a thermogravimetric analysis (TGA) experiment was conducted in order to check the volatilization for germanium(II) precursors. The thermal curve is shown in Fig 1. The temperatures of 50% mass (T_{50}) loss derived from TGA in simultaneous thermal analysis (STA) experiments for the pyrazole ligand complexes **2a-2c** are given in Table 2. The T_{50} values have been shown to correlate with the volatility of the samples and are therefore used for the comparison of relative volatilities. The TGA plots (Figure 1) show significant differences in each curve, although the ligands used in the three precursors resemble one another in their molecular symmetry and rigidity. The amount of methyl in ligands is believed to be responsible for the change in the onset temperature and T_{50}. The complex **2b** with no methyl ligand has the lowest onset temperature, while **2c** with two methyl ligand has the highest onset temperature and T_{50}. Both onset temperature and T_{50} increase as the molecular mass increases. All the complexes yield multi-step transport TGA curves with corresponding endothermic peaks in the DSC plot that suggests thermal decomposition. Only 90.5% of precursor **2c** is transported up to 300 °C as compared with 95.6% of the

precursor **2a** at 250 °C. However, **2a** and **2c** leave nonvolatile residues during the transport of 1-2% (Table 2). Even the first step of weight loss is far below that calculated for the elemental germanium content. This discrepancy is due to weight loss from intact transportation of the precursors prior to pyrolytic decomposition. **2b** has two weight-loss steps. One of them, 32% of precursor **2b** is transported up to 154 °C. This proportion is the ratio of one pyrazole ligand in the molecular weight. This indicates that chemical bond was broken due to the heat. This phenomenon was not observed in the curves of **2a** and **2c**, thus indicating that methyl may improve the molecular and thermal stability. However, there were secondary but subtle weight-loss steps in the curves of **2a** and **2c** at approximately 430 °C and 520 °C, respectively. This phenomenon may indicate that there was a balance between decomposition and volatilization. In other words, at a given temperature interval decomposition was less than volatilization and in the higher temperature interval volatilizations was less than decomposition. For example, in the curve **2a**, volatilization at less than 300 °C was the main phenomenon, while just 4% **2a** remained. At temperatures above 430 °C, decomposition was highlighted and the second weight-loss step appeared. Volatilization was less than decomposition. For example, in the curve **2a**, volatilization at less than 300 °C was the main phenomenon, while just 4% **2a** remained. At temperatures above 430 °C, decomposition was highlighted and the second weight-loss step appeared.
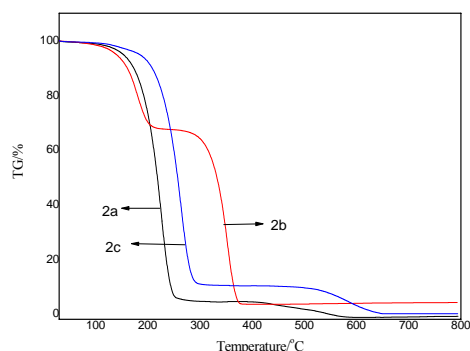

Fig. 1. Thermogravimetric curves of germanium(II) precursors.

To confirm the viewpoint on the balance between decomposition and volatilization, further investigation on the transport properties of the most volatile candidate **2a** isothermal TGA experiments was carried out, in which the temperature of the STA furnace was held at different temperatures for 6 hours and the curves was shown in Fig 2. The weight loss was not complete at 100 °C because the temperature was lower than the onset temperature but some undetectable weight loss was already happened. This was coinciding with the balance

viewpoint because at 100 ^{o}C there was no decomposition in the heating process. The higher the temperature maintained the more rapidly weight loss and less residual. The temperature of 200 ^{o}C is between the onset temperature and T_{50}, so incomplete volatilization took place and the residual increased to 20%, while the step was curvy but not sharp. The temperatures of 300 ^{o}C and 400 ^{o}C are above the onset temperature and T_{50}, so the residuals are close to the first step in the TGA curve of **2a**, while 400 ^{o}C is closer.
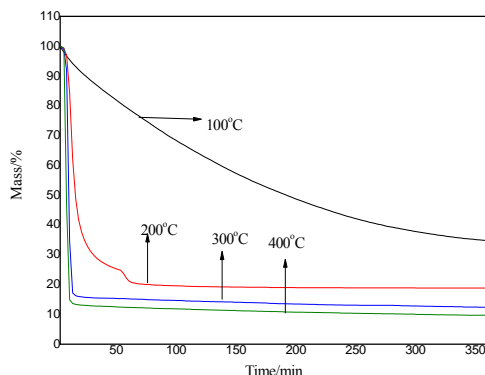

Fig. 2. Constant temperature curves of germanium(II)

*precursors **2a***

All of the foregoing phenomena coincided with T_{50} and onset temperature, thus confirming good volatility. At 200 °C, 300 °C and 400 °C, subsequent to rapid weight loss, the residual was stable for the remaining time. This indicated that the second weight-loss step was dependent on temperature as opposed to time. Compared to the TGA curves, there was no second weight-loss step. This confirmed the balanced viewpoint: Decomposition did not take place below 430 ^{o}C because, at that temperature, volatilization was the main phenomenon so the residual could be stable.

*Table 2. STA Data of Complexes **2a-2d**^{a,b}*

Entry	T_{50} (^{o}C)	Onset temp (^{o}C)	Residual mass (%)
1	218	192	0
2	-	154	4
3	257	229	1

^{a} Gas atmosphere: argon, sample size (mg): 7.57, **1**; 8.03, **2**; 7.57, **3**. ^{b} T_{50} stands for the temperature at which 50% mass of a sample is lost. Mass residuals were measured at 800 °C.

4. Conclusions

We have developed an effective method by which to synthesize pyrazol germanium(II) precursors and obtain good yields. These pyrazol germanium(II) precursors were tested with TG experiments, and the curves showed regular changes. Some of them showed good volatilization, particularly the constant-temperature curves of **2a** showed stability after volatilization. Collectively, the experiments provide some empirical theory on the connection between structure and properties, and the results indicated that the thermostability and volatilization of samples were suitable as a potential membrane material. Further work on the CVD/ALD of Ge metallic films is underway.

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