

SYNTHESIS AND CHARACTERIZATION OF BIS(5-DIISOPROPYLAMINO-1,2,3,4-TETRAZOLATO)-TRIS(DIMETHYLAMIDO)GALLIUM: THE FIRST EXAMPLE OF A GALLIUM TETRAZOLATE COMPLEX

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ABSTRACT

GaN continues to be an important material for thin films and can be deposited by CVD or ALD using single source precursors that preferentially avoid Ga–C bonds. In this report, the complex bis(5-diisopropylamino-1,2,3,4-tetrazolato)tris(dimethylamido)digallium (**1**) was synthesized to potentially serve as a precursor to GaN. **1** is the first example of a Ga-tetrazolate complex, and was prepared by protonolysis of tris(dimethylamido)gallium using an equimolar amount of 5-diisopropylamino-1*H*-1,2,3,4-tetrazole. The complex was characterized spectroscopically and structurally. It exhibits a Ga₂N₂ 4-membered ring, with a very close Ga–Ga distance of 2.8917(5) Å. The coordination to the tetrazolate ligand occurs at N², which is unusual due to N¹ being more basic. This unusual coordination is due to the steric hindrance provided by the very bulky substituent, the diisopropylamino group.

Keywords: Gallium, nitride, tetrazolate, tetrazole, bulky.

INTRODUCTION

There is continued interest in the development of gallium nitride thin films (Quah and Cheong, 2013). One of the many uses of gallium nitride and related III–V semiconductor alloys include blue and white light emitting diodes and laser diodes, electronic devices such as field effect transistors, and high-power, high-efficiency optoelectronic devices (Luo *et al.*, 2004; Puchingera *et al.*, 2002). The thin film deposition processing has focused on chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) (Puchingera *et al.*, 2002; Uhlet *et al.*, 2011). Approaches to GaN based on single-source precursors offer the potential for significant improvement in the growth process and film quality (Luo *et al.*, 2005; Kouvetakis *et al.*, 2000). For the CVD of gallium-containing films, there is interest in developing non-pyrophoric, alternative precursors to trimethyl or triethyl gallium. It is also desirable for these precursors to minimize carbon contamination. This can be achieved by the use of complexes that do not contain direct gallium–carbon bonds (Luo *et al.*, 2005; Kouvetakis *et al.*, 2000). Complexes can be stabilized with bulky ligands to eliminate the formation of oligomers (Luo *et al.*, 2005). Tetrazoles are a group of compounds that can serve as ligands for several metal centers. They have the potential to reduce the possibility of carbon contamination when used in CVD due to the potential to form N–Ga bonds and also due to the relatively low percentage of carbon atoms in the molecule. For this reason I was interested in exploring the synthesis of gallium tetrazolate complexes.

MATERIALS AND METHODS

General Considerations

All reactions other than ligand syntheses were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Toluene was distilled from sodium. Tris(dimethylamido)gallium was purchased from Sigma-Aldrich and used as received.

¹H and ¹³C NMR were obtained at 500 MHz and 125 MHz, respectively, in benzene-*d*₆. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed in-house. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and were uncorrected.

Preparation of bis(5-diisopropylamino-1,2,3,4-tetrazolato)tris(dimethylamido)digallium (1)

A 100 mL Schlenk flask equipped with a stir bar and a rubber septum was charged with 5-diisopropylamino-1*H*-1,2,3,4-tetrazole (tetzH) (0.516g, 3.05 mmol) and tris(dimethylamido)gallium (0.614 g, 3.04 mmol). Toluene (50 mL) was added and the resulting mixture was refluxed for 18 hours. The solvent was removed by vacuum and the identity of the crude product was verified by NMR. The product was then extracted with toluene (30 mL), filtered through a pad of Celite, and recrystallized by storing at –20°C. Complex **1** (0.687g, 69.2%) was isolated as air sensitive pale yellow crystals. Mp 132°C dec.; ¹H NMR (C₆D₆, 18°C, δ) 4.06 (septet, 4 H, (CH₃)₂CH), 2.44 (s, 24 H, (CH₃)₂N), 1.27 (d, 24H, (CH₃)₂CH); ¹³C NMR (C₆D₆, 18°C, δ) 166.81 (s, CN₄), 47.41 (s, (CH₃)₂CH), 32.20 (s, (CH₃)₂N), 21.32 (s,

(CH₃)₂CH). Anal. calcd for C₂₂H₅₂Ga₂N₁₄: C, 40.51; H, 8.04; N, 30.07. Found: C, 41.51; H, 7.88; N, 30.67.

RESULTS AND DISCUSSION

Synthetic Aspects

I hereby report the reaction of tris(dimethylamido)gallium with 5-diisopropylamino-1*H*-1,2,3,4-tetrazole (tetzH) to produce bis(5-diisopropylamino-1,2,3,4-tetrazolato)tris(dimethylamido)digallium (**1**). TetzH was prepared from diisopropylcyanamide and sodium azide following a modified literature procedure (Fig. 1) (Koguro *et al.*, 1998). **1** was synthesized by reacting 1 equivalent of tetzH with Ga[N(CH₃)₂]₃ in toluene under an atmosphere of argon (Fig. 2). **1** has been characterized by spectral analysis and X-ray measurements.

X-ray Crystal Structures

The X-ray crystal structure of **1** was obtained to establish the solid state configuration. Experimental crystallographic data are summarized in table 1 and selected bond lengths and angles are presented in tables 2 and 3. Representative perspective views of **1** are shown in figure 3 and figure 4. The molecular structure of **1** displays two Ga centers bridged by two dimethylamido ligands forming a Ga₂N₂ ring. The Ga–N bond distances are 1.993(2) Å and 2.012(2) Å. The N–Ga–N and Ga–N–Ga bond angles are 87.58(10)° and 92.42(10)° respectively making it almost a perfect square. Each gallium center also bears a terminal dimethylamido ligand and a terminal η¹-tetz ligand bonded through N².

Table 1. Experimental crystallographic data for **1**.

	1
Empirical formula	C ₂₂ H ₅₂ Ga ₂ N ₁₄
Fw	652.22
Space group	P-1
a (Å)	7.2450(7)
b (Å)	8.1574(8)
c (Å)	13.7304(14)
α (deg)	94.658(2)
β (deg)	93.198(2)
γ (deg)	101.082(2)
V (Å ³)	791.59(14)
Z	1
λ	0.71073
Calcd (g cm ⁻³)	1.368
μ (mm ⁻¹)	1.738
R	0.0448
Rw	0.1335

Complex **1** exhibits several interesting features. Firstly it is the first structurally characterized tetrazolato complex of gallium. The chemistry of pyrazolato and triazolato ligands with main group metallic elements is very well established (Kobrsi *et al.*, 2006; Saly and Winter, 2010; Sirimanne *et al.*, 2005; El-Kaderi *et al.*, 2005a; El-Kaderi *et al.*, 2005b; Zheng *et al.*, 2004) and for no gallium tetrazolato complexes to be present in the literature

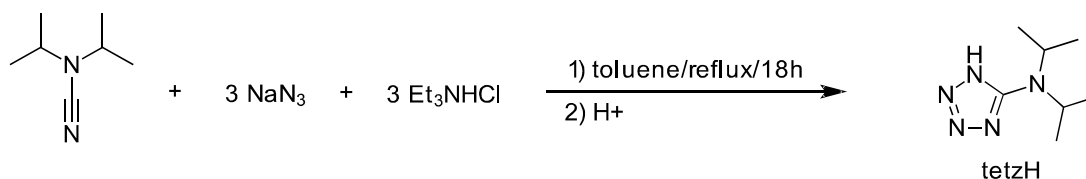


Fig. 1. Synthesis of tetzH from diisopropylcyanamide.

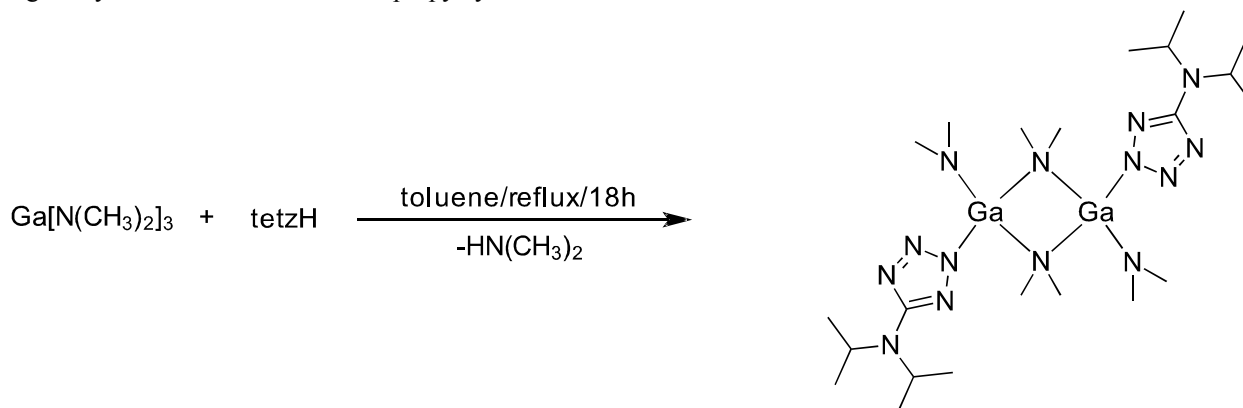


Fig. 2. Synthesis of **1**.

indicates that their synthesis is very difficult. Secondly, the Ga–Ga bond distance is 2.8917(5) Å, which puts it at the borderline of Ga–Ga covalent bond distances, generally ranging from about 2.3598(3) Å to about 2.5298(10) Å (Sanden *et al.*, 2012). Thirdly, the tetrazolato ligand is coordinated through N² and not the more basic N¹. This is rarely observed since if sterically undemanding, the tetrazolato core would generally coordinate through N¹ or N⁴ due to their higher basicity (Kobrsi *et al.*, 2006; Kobrsi *et al.*, 2005). When these two more basic N's are difficult to bond to due to steric hindrance such as that provided by the diisopropylamino group, the tetrazolato core will coordinate through the less basic but more accessible N² and N³ (Kobrsi *et al.*, 2005; Kobrsi and Bassioni, 2011). This complex has been synthesized at a scale of tens of grams, and can be purified easily by recrystallization, making it a favorable candidate for assays as a molecular precursor for CVD and/or ALD.

Table 2. Selected bond lengths (Å) for **1**.

Ga(1)–N(2)	1.814(2)	N(3)–N(4)	1.324(3)
Ga(1)–N(3)	1.948(2)	N(3)–N(6)	1.348(3)
Ga(1)–N(1)	1.993(2)	N(4)–N(5)	1.325(4)
Ga(1)–N(1)	2.012(2)	N(5)–C(5)	1.357(4)
Ga(1)–Ga(1)	2.8917(5)	C(5)–N(6)	1.339(4)
N(1)–C(1)	1.483(4)	C(5)–N(7)	1.376(4)
N(1)–C(2)	1.495(4)	N(7)–C(6)	1.473(4)
N(2)–C(3)	1.440(4)	C(6)–C(7)	1.520(5)

CONCLUSION

A gallium tetrazolato complex can be synthesized by protonolysis of tris(dimethylamido)gallium by tetzH. The complex is molecular and does not form oligomers or polymers as is common with azole-type ligands. This is due in part to the bulkiness of the diisopropylamino group, which makes the ligand sterically demanding and

blocks further coordination. This steric bulk also provides for coordination at the N² site and not the expected N¹ site. This complex will be further studied to determine its thermal behavior, volatility, and suitability as GaN precursor.

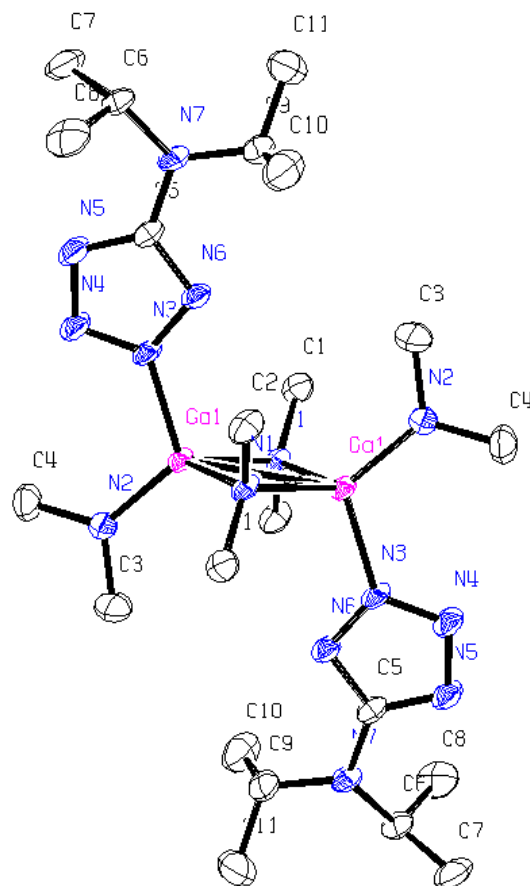


Fig. 3. Molecular structure of **1** (50% probability thermal ellipsoids).

Table 3. Selected bond angles (deg) for **1**.

N(2)–Ga(1)–N(3)	113.66(11)	C(3)–N(2)–C(4)	110.7(3)
N(2)–Ga(1)–N(1)	121.13(12)	N(4)–N(3)–N(6)	112.1(2)
N(3)–Ga(1)–N(1)	108.24(10)	N(4)–N(3)–Ga(1)	126.3(2)
N(1)–Ga(1)–N(1)	87.58(10)	N(3)–N(4)–N(5)	107.8(2)
Ga(1)–N(1)–Ga(1)	92.42(10)	N(4)–N(5)–C(5)	105.5(2)
C(1)–N(1)–Ga(1)	115.22(18)	N(6)–C(5)–N(5)	112.2(3)
C(3)–N(2)–Ga(1)	123.9(2)	N(6)–C(5)–N(7)	123.8(3)
C(1)–N(1)–C(2)	106.8(2)	C(5)–N(7)–C(6)	119.1(3)

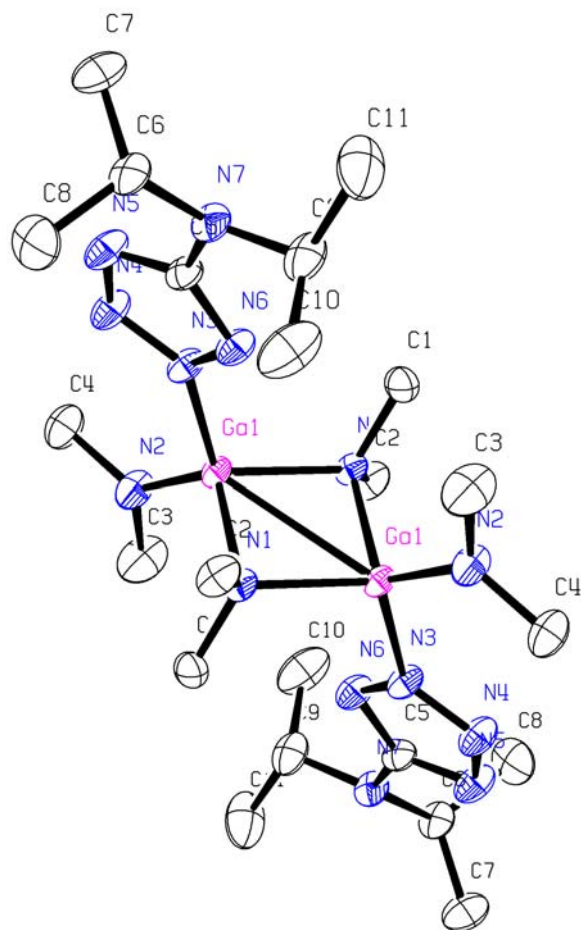


Fig. 4. Molecular structure of **1** with a clear view of the Ga₂N₂ diazametallacyclobutane (50% probability thermal ellipsoids).

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