Journal of Organometallic Chemistry, 394 (1990) C6–C8
Elsevier Sequoia S.A., Lausanne
JOM 21013PC

Preliminary communication

X-ray crystal structure of the dimethylgallium azide polymer and its use as a gallium nitride precursor *

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(Received February 13th, 1990)

Abstract

An X-ray diffraction study reveals that dimethylgallium azide (**1**) exists as a polymer in the solid state. The basic repeating unit, Me_2GaN_3, forms a spiral along the *a*-axis of an orthohombic unit cell. Compound **1** serves as a gallium nitride precursor.

Although several Group 13 dialkyl azides have been known for some time, relatively little structural information in the solid state is available for these compounds [1,2]. Dimethylgallium azide, for example, was prepared via the reaction of Me_3Ga with HN_3, ClN_3, or Me_3GeN_3. The trimeric formulation, $[Me_2GaN_3]_3$, involving a six-membered Ga_3N_3 ring, was based on cryoscopic molecular weight data as well as vibrational spectroscopic data. We have prepared dimethylgallium azide by treatment of Me_2GaCl with NaN_3 **. Interestingly, this compound is polymeric in the solid state.

Crystal data: $[C_2H_6GaN_3]_\infty$, $M = 141.83$ (monomer), orthohombic, space group $P2_12_12_1$, a 5.217(8), b 8.452(2), c 12.690(2) Å, U 559.6 Å^3, D_c 1.690 g cm^{-3}, $Z = 4$,

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* This manuscript is dedicated to Professor F.G.A. Stone, F.R.S., on the occasion of his 65th birthday and in recognition of his many seminal contributions to organometallic chemistry.

** Dimethylgallium chloride was prepared in situ by the slow addition of two equivalents of MeLi to one equivalent of $GaCl_3$ in toluene solution at −78 °C. The Me_2GaCl solution was then added to one equivalent of NaN_3 in toluene at −78 °C. The stirred reaction mixture was allowed to warm to room temperature, following which it was heated under reflux for eighteen hours. After removal of the solvent under vacuum the white residue was purified by sublimation (58 °C at 10^{-3} Torr). The yield of colorless crystalline $[Me_2GaN_3]_\infty$ was > 95%. M.P. 58–59 °C (lit. 64° [1]); I.R. 2175 s br (ν(N≡N)) cm^{-1}; ^1H NMR (PhMe-d_8, 300 MHz, 25 °C, rel. Me_4Si (δ 0.0)), δ 0.720 s Ga–CH_3; mass spec. (E.I. 70 eV), highest peak observed at $m/e = 412$ ($[Me_2GaN_3]_3 - CH_3$).

0022-328X/90/$03.50

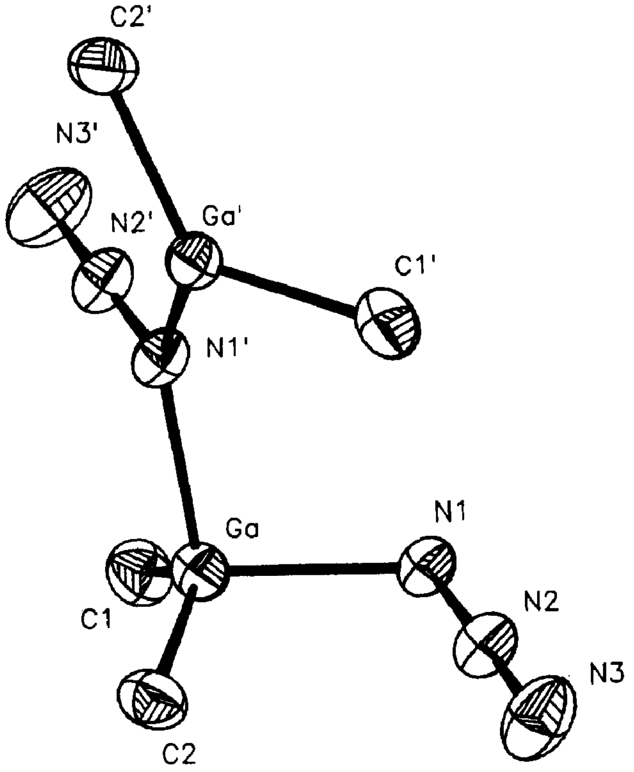

Fig. 1. Structure of polymeric dimethylgallium azide (1). Important bond lengths and angles: Ga–N(1) 2.039(6), Ga–N(1)′ 2.051(6), N(1)–N(2), 1.201(9), N(2)–N(3) 1.121(9), Ga–C(1) 1.924(8), Ga–C92) 1.947(8) Å, Ga–N(1)–N(2) 115.2(5), N(1)–N(2)–N(3) 179.3(9), N(1)–Ga–N(1)′ 98.6(2), Ga–N(1)–Ga′ 131.5 (1)°, N(1)–Ga–C(1) 106.3(3), N(1)–Ga–C(2) 103.4(3), C(1)–Ga–C(2) 132.5(4)°.

$\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu(\text{Mo-}K_\alpha)$ 47.85 cm^{-1}. A total of 1987 reflections was collected on an Enraf-Nonius CAD 4 diffractometer at 23 ± 2° using the $\theta/2\theta$ scan mode. The data were corrected for Lorentz, polarization, decay, and absorption. The structure was solved by Patterson methods and refined (full-matrix least-squares) using 906 reflections with $I > 6.0\sigma(I)$. The final R and R_w values were 0.0394 and 0.0428, respectively.

The basic repeating unit, Me_2GaN_3 (Fig. 1), forms a spiral along the a-axis of the orthorhombic unit cell. The gallium atoms in the chain (Ga, Ga′) are bridged by a single nitrogen (N(1)) of the azide group. Within experimental error, the distances are equal along the Ga–N chain (2.039(6) and 2.051(6) Å) and the bond angles at Ga and N are 98.6(2)° and 131.5(1)°, respectively. Within each azide group there are two distinct N–N bond distances: 1.201(9) and 1.121(9) Å for N(1)–N(2) and N(2)–N(3), respectively. As in the case of the dialuminum azide anion $[\text{Al}_2(\text{CH}_3)_6\text{N}_3]^-$ [3], the longer distance corresponds to the bond between the middle nitrogen and the nitrogen bonded to the metal. The geometries at nitrogen and gallium are trigonal planar and tetrahedral, respectively. However, there is a wide variation of angles at gallium and the C–Ga–C angle is surprisingly large (132.5(4)°).

We have found that 1 is an excellent precursor for the growth of GaN under relatively mild conditions [4]. Film growth was achieved in a cold-wall reactor at a substrate temperature of 400 ° C and a helium carrier gas pressure of 10 Torr. The substrate was Si(100). The deposited film was identified as GaN by the presence of N(2*s*) and Ga(3*d*) XPS peaks at 397.2 and 19.7 eV, respectively. However, it was difficult to establish the stoichiometry exactly because of preferential elimination of nitrogen during sputtering. The GaN was shown to be polycrystalline by X-ray powder diffraction.

Acknowledgements. We thank the National Science Foundation, the Robert A. Welch Foundation and the ARO Grant No. DAAL03-89-K-0164 for financial support.

References

1 J. Müller and K. Dehnicke, J. Organomet. Chem., 7 (1967) P1; J. Müller and K. Dehnicke, J. Organomet. Chem., 12 (1968) 37; N. Roder and K. Dehnicke, Chimia, 28 (1974) 349.
2 J. Müller, Z. Naturforsch., 34B (1979) 531.
3 J.L. Atwood and W.R. Newberry III, J. Organomet. Chem., 65 (1974) 145.
4 While the present work was in progress a publication appeared describing the preparation of gallium nitride from diethylgallium azide. J. Kouvetakis and D.B. Beach, Chem. Mater., 1 (1989) 476. For the deposition of aluminium nitride using dialkylaluminum azides see, D.C. Boyd, R.T. Haasch, D.R. Mantell, R.K. Schulze, J.F. Evans and W.L. Gladfelter, Chem. Mater., 1 (1989) 119.