

Isolation and Structure of $[\text{Ph}_3\text{P}(\text{OH})]^+[\text{N}_3]^-$

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$[\text{Ph}_3\text{P}(\text{OH})]^+[\text{N}_3]^-$ 의 분리 및 구조

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Abstract

From the reaction of $\text{Na}[\text{Ga}(\text{N}_3)_4]$ with PPh_3 , an ionic compound $[\text{Ph}_3\text{P}(\text{OH})]^+[\text{N}_3]^-$ (**1**) was isolated. Compound **1** was characterized by spectroscopy (^1H -NMR, $^{13}\text{C}\{^1\text{H}\}$ -NMR, and IR) and X-ray diffraction. Crystallographic data for **1**: orthorhombic space group $P2_12_12_1$, $a = 10.491(4)$ Å, $b = 11.603(5)$ Å, $c = 13.149(5)$ Å, $Z = 4$, $R(wR_2) = 0.0547(0.0978)$.

요 약

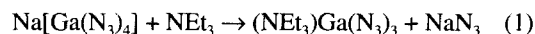
$\text{Na}[\text{Ga}(\text{N}_3)_4]$ 와 PPh_3 의 반응으로부터 이온성 화합물 $[\text{Ph}_3\text{P}(\text{OH})]^+[\text{N}_3]^-$ (**1**)이 분리되었다. 화합물 **1**의 구조가 분광학적 방법 (^1H -NMR, $^{13}\text{C}\{^1\text{H}\}$ -NMR, IR) 및 X-ray 회절법으로 규명되었다. 화합물 **1**의 결정학 자료: 사방정계 공간군 $P2_12_12_1$, $a = 10.491(4)$ Å, $b = 11.603(5)$ Å, $c = 13.149(5)$ Å, $Z = 4$, $R(wR_2) = 0.0547(0.0978)$.

1. Introduction

Recently, the group 3 nitrides (MN; M = Al, Ga, and In) have been the focus of intense study and device developments. They are ideal for high-power applications due to their chemical inertness, and they are utilized in high-temperature and high-power micro-electronic and optoelectronic devices¹. In particular, gallium nitride (GaN) has got considerable attractions because of the recent development of commercial blue-light emitters based on this species².

An ideal GaN single-source precursor would be a non-pyrophoric, air-stable liquid with a high vapor pressure, because it can enable us to avoid hazardous and pyrophoric gaseous precursors (for example, GaH_3 or NH_3) and very harsh conditions to deposit GaN. Recently, organometallic gallium azides of several types, $(\text{R}_3\text{N})_2\text{Ga}(\text{N}_3)$, $(\text{N}_3)_2\text{Ga}\{\text{N}[\text{CH}_2\text{CH}_2(\text{NEt}_2)]_2\}$, and $(\text{R}_3\text{N})\text{Ga}(\text{N}_3)_3$, have been reported to act as sin-

gle-source precursors for the GaN growth, in which the azide group behaves as a major nitrogen source²⁻⁶. For example, Fischer and co-workers reported a route to hexagonal GaN nano-crystals by the detonations of gallium azides, $[\text{Ga}(\text{N}_3)_3]_n$ ². In their studies, $[\text{Ga}(\text{N}_3)_3]_n$ was prepared by the detonation of molten $(\text{NEt}_3)\text{Ga}(\text{N}_3)_3$, which was formed by the addition of the Lewis base (NEt_3) to $\text{Na}[\text{Ga}(\text{N}_3)_4]$ (eq. 1). These results prompted us to prepare other Lewis-base adduct $(\text{L})\text{Ga}(\text{N}_3)_3$ ($\text{L} = \text{PR}_3$), which might also act as a single precursor for the GaN source. Therefore, we treated $\text{Na}[\text{Ga}(\text{N}_3)_4]$ with triphenylphosphine to prepare $[(\text{PPh}_3)\text{Ga}(\text{N}_3)_3]$. However, we isolated an ionic compound, $[\text{Ph}_3\text{P}(\text{OH})]^+[\text{N}_3]^-$ (**1**), from the recrystallization of the reaction product. We report here the isolation and structure of **1**.



2. Experimental Section

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for about 24 h and washed with distilled water and acetone before use. Glassware was either flame- or oven-dried. Hydrocarbon solvents were stirred over concentrated H₂SO₄ for about 48 h, neutralized with K₂CO₃, stirred over sodium metal, and distilled by vacuum transfer. Tetrahydrofuran (THF) was stirred over sodium metal and distilled by vacuum transfer. NMR solvent (CDCl₃) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. GaCl₃, PPh₃, and NaN₃ were purchased from Aldrich company. Na[Ga(N₃)₄] was prepared by the literature method²⁾.

¹H- and ¹³C{¹H}-NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane (TMS). IR spectra were recorded with a Nicolet 205 FT-IR spectrophotometer. Melting points were measured with a Thomas Hoover capillary-melting-point apparatus without calibration.

Isolation of [Ph₃P(OH)]⁺[N₃]⁻ (1). Na[Ga(N₃)₄] (0.10 g, 0.56 mmol) and excess triphenylphosphine (0.40 g, 1.68 mmol) in THF (30 ml) were stirred for 24 h at room temperature. The resulting white solution was filtered, and the solvent was removed under vacuum to give white solids. These solids were washed with diethyl ether (30 ml×2) and recrystallized from THF-hexane to give colorless crystals of **1** (0.02 g, 0.062 mmol, 11%).

¹H-NMR (CDCl₃): δ 7.587.79 (Ph). ¹³C{¹H}-NMR (CDCl₃): 129.31~133.23 (Ph). mp: 180°C. IR (KBr): 3215 (O-H), 2025 (N₃), 1520, 1480, 1180, 1054, 756 cm⁻¹.

X-ray Structure Determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 22 reflec-

tions in the range 10.0 < 2θ < 25.0°. Three check-reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. No absorption corrections were made. All calculations were carried out with use of the SHELXTL programs⁷⁾.

A colorless crystal of **1**, shaped as a block of approximate dimensions 0.14×0.12×0.10 mm³, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences, *h*00 (*h* = 2*n* + 1), 0*k*0 (*k* = 2*n* + 1) and 00*l* (*l* = 2*n* + 1), unambiguously indicated *P*2₁2₁2₁ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The O-H hydrogen atom was located in the difference-Fourier maps and refined isotropically. The remaining hydrogen atoms were generated in ideal positions and refined in a riding mode.

Table 1. X-ray data collection and structure refinement

empirical formula	C ₁₈ H ₁₆ N ₃ OP
fw	321.31
temperature, K	296(2)
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	10.491(4)
<i>b</i> , Å	11.603(5)
<i>c</i> , Å	13.149(5)
<i>V</i> , Å ³	1601(1)
<i>Z</i>	4
<i>d</i> _{cal} , g cm ⁻³	1.333
μ, mm ⁻¹	0.180
<i>F</i> (000)	672
2θ range (°)	3.5~50
scan type	ω
scan speed	variable
No. of reflns measured	1617
No. of reflns unique	1617
No. of reflns with <i>I</i> > 2σ(<i>I</i>)	898
No. of params refined	212
Max. in Δρ (e Å ⁻³)	0.220
Min. in Δρ (e Å ⁻³)	-0.268
<i>GOF</i> on <i>F</i> ²	1.063
<i>R</i>	0.0547
<i>wR</i> ₂ ^a	0.0978

$$^a wR_2 = [w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]^{1/2}$$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	$U(\text{eq})^a$
P(1)	-1976(2)	-5223(1)	-1341(2)	46(1)
O(1)	-1491(6)	-4115(5)	-744(5)	87(2)
C(1)	-900(6)	-5465(6)	-2323(5)	42(2)
C(2)	-97(8)	-6380(6)	-2360(6)	57(2)
C(3)	780(8)	-6476(7)	-3134(7)	72(2)
C(4)	866(7)	-5687(7)	-3855(7)	69(2)
C(5)	48(7)	-4772(7)	-3861(6)	69(2)
C(6)	-829(7)	-4673(7)	-3092(6)	60(2)
C(7)	-2077(6)	-6451(5)	-562(5)	46(2)
C(8)	-2831(7)	-7380(6)	-788(5)	63(2)
C(9)	-2913(8)	-8289(6)	-158(7)	71(2)
C(10)	-2239(8)	-8319(7)	713(7)	65(2)
C(11)	-1497(8)	-7414(7)	961(6)	75(2)
C(12)	-1407(7)	-6501(7)	318(6)	63(2)
C(13)	-3493(6)	-4948(5)	-1827(5)	42(2)
C(14)	-4271(6)	-4148(6)	-1376(6)	58(2)
C(15)	-5502(8)	-3993(8)	-1727(8)	75(3)
C(16)	-5954(8)	-4646(8)	-2494(8)	73(2)
C(17)	-5204(7)	-5435(7)	-2947(6)	62(2)
C(18)	-3957(7)	-5600(6)	-2614(6)	55(2)
N(1)	-8814(7)	-3929(6)	-449(7)	96(3)
N(2)	-8293(5)	-3078(6)	-596(5)	52(2)
N(3)	-7749(6)	-2224(6)	-740(5)	76(2)

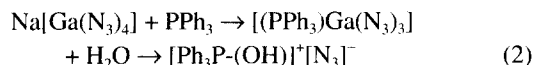
^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Details on crystal data and intensity data are given in Table 1. Final atomic coordinates and some selected bond distances and bond angles are shown in Tables 2 and 3, respectively.

3. Results and Discussion

Isolation of [Ph₃P(OH)]⁺[N₃]⁻ (1). Na[Ga(N₃)₄] reacted with triphenylphosphine (PPh₃) in THF. During the reaction, an initially white slurry slowly turned to a colorless solution. The solid product was recrystallized from THF-hexane to give color-

less crystals, whose structure has turned out to be [Ph₃P(OH)]⁺[N₃]⁻ (1), but not our target compound [(PPh₃)Ga(N₃)₃]. We speculate that the compound 1 was formed by the hydrolysis of the reaction product [(PPh₃)Ga(N₃)₃] because of the water present in the reaction mixture (eq. 2). However, we cannot rule out the possibility that the trace amount of water in solvents might have caused the product to undergo hydrolysis during recrystallization.



Compound 1 appears to be air- and moisture-stable both in solution and in the solid state. The phenyl protons resonate at 7.58~7.79 ppm in the ¹H-NMR spectrum. ¹³C{¹H}-NMR spectra of compound 1 exhibit peaks at 129.3~133.2 ppm for phenyl carbons. In the IR spectrum, the N₃ stretching mode appears at 2025 cm⁻¹ and the O-H stretching mode at 3215 cm⁻¹.

Structure. The structure of an ionic compound 1 with the atom-numbering scheme is shown in Fig. 1. The geometry of phosphorus can be described as tetrahedral, with three phenyl (Ph) and one hydroxyl (OH) groups.

All bond distances and bond angles are normal within experimental errors. For example, the N-N bond distances (1.145(8) and 1.159(7) Å) in the counterion N₃⁻ are almost equal, just as in the free N₃⁻ in NaN₃ in which the bond distance of N-N is 1.167(13) Å⁸⁾. The O-H hydrogen atom is involved in the intermolecular hydrogen bond of the type O-H...N: O1-HO1 = 1.047 Å, O1...N1 = 2.844 Å, HO1...N1 = 1.822 Å, and O1-HO1...N1 = 167.71°. The bonding parameters of this hydrogen bond indicates a relatively strong hydrogen bonding.

In summary, we have structurally characterized an ionic compound, [Ph₃P(OH)]⁺[N₃]⁻, which was iso-

Table 3. Selected bond distances (Å) and bond angles (°)

P1-O1	1.590(6)	P1-C1	1.739(7)	P1-C13	1.745(6)
P1-C7	1.758(6)	N1-N2	1.145(8)	N2-N3	1.159(7)
O1-P1-C1	106.8(3)	O1-P1-C13	109.0(3)	C1-P1-C13	110.4(3)
O1-P1-C7	112.8(3)	C1-P1-C7	110.0(3)	C13-P1-C7	107.9(3)
N1-N2-N3	178.9(8)				

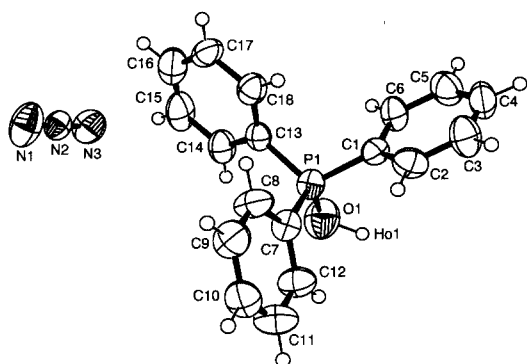


Fig. 1. An ORTEP drawing of 1 with the atom-labeling scheme and 50% probability thermal ellipsoids.

lated from the reaction of $\text{Na}[\text{Ga}(\text{N}_3)_4]$ with triphenylphosphine (PPh_3).

4. Supplementary Material

Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

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