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Synthesis and characterization of [Ga(TPP)H] (TPP = tetraphenylporphyrinato)

Yaoyu Feng *, Say-Leong Ong, Jiangyong Hu, Wun-Jern Ng

Department of Civil Engineering, National University of Singapore, Singapore 119260, Singapore

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Abstract

The synthesis, spectroscopic and structural characterization of the stable gallium hydride compound [Ga(TPP)H] (TPP = 5,10,15,20-tetraphenylporphyrinato) have been reported. The hydride compound was synthesized in high yield (85%) by reducing [Ga(TPP)Cl] with sodium borohydride in N,N-dimethylformamide. The title compound was fully characterized by spectroscopic methods (IR, UV–Vis, and ^{1}H NMR spectroscopy) and its molecular structure was established by X-ray crystallography. The Ga–H IR stretch occurs at 1864 cm^{-1}, and the hydride ^{1}H NMR resonance locates at −6.47 ppm. The gallium–hydrogen distance is 1.48(4) Å, whereas the gallium atom lies 0.46(1) Å from the perfect porphyrin plane.

Keywords: Gallium; Porphyrin; Hydride; Crystal structure

1. Introduction

The chemistry of gallium hydrides has attracted extensive interest due to their potential application in areas ranging from organic synthesis (serving as precursors to solid-state materials such as gallium nitride, and as reducing agents etc.) to chemical vapor deposition [1]. Stable gallium hydride compounds are usually obtained in the form of Lewis acid–base adducts, H_3Ga(base) [2–4]. There are also a significant number of other structurally characterized alkyl gallium monohydrides and dihydrides that are most often formed using $LiGaH_4$ or GaH_3 [5–9]. Recent work has shown that it is possible to use bulky aryl groups to synthesize Group 13 hydride species [10–12].

In this paper we used the macrocyclic ligand tetraphenylporphyrin as the coordinating reagent to stabilize the gallium hydride compound. Similarly, rhodium porphyrin hydride compounds have been reported and extensively used in chemical synthesis and catalysis [13–15]. The obtained hydride compound [Ga(TPP)H] (**1**) is considerably stable at ambient environment and thus has the potential to act as the precursor for a series of σ-bonded alkyl and aryl porphyrins, bi- or trimetallic metal–metal-bonded metalloporphyrins due to the weakness and reactivity of the Ga–H bond.

2. Experimental

2.1. Synthesis

To a solution of Ga(TPP)Cl [16] (200 mg, 0.28 mmol) in N,N-dimethylformamide (DMF) (100 ml), sodium borohydride (30 mg, 0.79 mmol) was added. With the addition of sodium borohydride, the color of the solution changed from red to green gradually and green precipitate was formed in the reaction mixture. The reaction system was vigorously stirred at room temperature for 1 h, then the resulting reaction mixture was filtered and the green crystalline **1** was obtained (160 mg, yield: 85%) after thoroughly washed with distilled water and methanol. Elemental analysis found (calcd. based on $C_{44}H_{29}GaN_4$): C 77.04 (77.32); H 4.42 (4.28); N 8.01 (8.20). IR (KBr pellet, cm^{-1}) v: 1864(m), 1596(m), 1513(w), 1487(m), 1440(m), 1342(m), 1206(m), 1175(m), 1071(m), 1003(vs), 803(s), 750(s), 702(s), 662(w), 646(w).

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[*] Corresponding author. Tel.: +65-68745265; fax: +65-68745266.
E-mail address: cvefyy@nus.edu.sg (Y. Feng).

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UV–Vis [λ_{max}(toluene)/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})]: 338(9), 420(28), 437(117), 518(1), 570(4), 611(3). ^{1}H NMR (toluene-d$_8$, −50 °C) δ : 9.08 (s, 8H, pyrrole-H), 8.28 (m, 8H, *o*-H), 7.83 (m, 12H, *m,p*-H), −6.47 (s, 1H, GaH).

Single crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of a solution of the compound in toluene at −20 °C during a few weeks.

2.2. X-ray structural study of 1

The intensity data of the compound was collected on a Nonius Kappa CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms except M–H were assigned to calculated positions.

Crystal structure analysis data for **1**: [GaC$_{44}$H$_{28}$N$_4$)H], $Mr = 683.46$, tetragonal, I4, $a = 13.370(2)$, $b = 13.370(2)$, $c = 9.750(2)$ Å, $V = 1742.9(5)$ Å^3, $Z = 2$, $\mu = 0.827$ mm^{-1}, GOF = 1.155, $F(000) = 704$, $R1 = 0.0645$, $wR2 = 0.1731$, 118 parameters, 1528 reflections [$I > 2\sigma(I)$].

3. Results and discussion

The presence of hydride ligand in the compound was confirmed by the IR spectrum. The Ga–H IR stretch occurs at 1864 cm^{-1}, which locates in the typical region for other terminal gallium hydrides (ca. 1850–1900 cm^{-1}) [17,18]. The high-field hydride signal (δ: −6.47 ppm) in the ^{1}H NMR spectrum gives further support for the existence of hydride. Unlike Ga(TPP)Cl, which shows a “normal” porphyrin electronic spectrum, **1** shows electronic absorption spectrum belonging to the hyperclass [19]. The Soret band is split into two bands (labeled band I and band II), which appear between 338 and 437 nm. The B(1,0) blue-shifted band is observed at 420 nm, and the three Q bands are located at 518, 570 and 611 nm. Band I may be attributed to $4P_z \rightarrow e_g(\pi^*)$ transition, while band II is assigned as a $\pi \rightarrow \pi^*$ electronic transition. For comparison, the electronic absorption spectra of [Ga(TPP)Cl] and **1** are shown in Fig. 1.

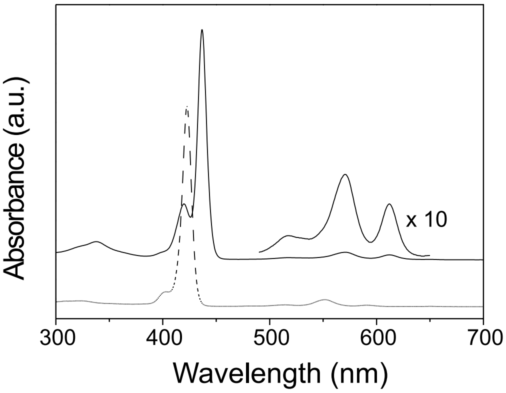

Fig. 1. Electronic absorption spectrum of Ga(TPP)H (solid line) and Ga(TPP)Cl (dashed line) in toluene.

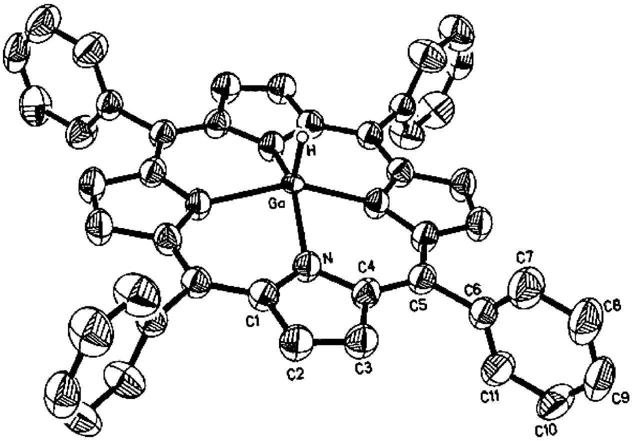

Fig. 2. ORTEP view of the compound **1** showing the 50% probability thermal motion ellipsoid. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ga–N 2.035(4), Ga–H 1.48(4), N–C(1) 1.381(6), N–C(4) 1.378(6), C(1)–C(2) 1.434(7), C(2)–C(3) 1.341(7), C(3)–C(4) 1.446(6), C(4)–C(5) 1.386(7).

The molecular structure of **1** is shown in Fig. 2 with important bond lengths and angles in figure caption. A crystallographic 4-fold axis passes through Ga and is perpendicular to the porphyrin plane relating the four equal parts of the molecule. As observed for Fe(TPP)Cl [20] and Ga(TPP)Cl [16], the gallium and hydrogen atoms are statistically disordered up and down the porphyrin macrocyclic plane. The coordination polyhedron of the metallic atom is a square pyramid and the metal atom lies 0.46(1) Å from the porphyrin plane, which is a little longer than that in Ga(TPP)Cl (0.317(1) Å) [16]. The Ga–H distance is 1.48(4) Å, which is at the medium of previously reported terminal Ga–H bonds (ca. 1.4–1.6 Å) [21,22]. The bond distances and angles in the porphyrinic group are statistically equal to those usually found.

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