Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Hiroshi Shioyama (2002): Preparation of stage 3 alcl 3 -gic, Molecular Crystals and Liquid Crystals, 387:1, 179-183

To link to this article: http://dx.doi.org/10.1080/10587250215250

Mol. Cryst. Liq. Cryst., Vol. 387, pp. [403]/179–[407]/183

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113754

PREPARATION OF STAGE 3 $AlCl_3$-GIC

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The preparation of stage 1, 2, 4 and 8 $AlCl_3$-GICs was described in the literature, stage 3 and 5 $AlCl_3$-GICs, however, have never been reported. It has been tried to prepare stage 3 $AlCl_3$-GIC by controlling the pressure of coexisting chlorine gas (Method I), or by adding a chlorinating agent N-chlorosuccinimide (Method II). Although it was not possible to obtain stage 3 $AlCl_3$-GIC by Method I, it was successfully prepared by Method II. The success does not depend upon the precise adjustment of the chlorine pressure, but upon the presence of the degradation products from N-chlorosuccinimide.

Keywords: intercalation; aluminum trichloride; vapour phase; chlorinating agent

1. INTRODUCTION

Many studies have been published in recent years on the preparation of metal chloride-graphite intercalation compounds (GICs) [1]. A peculiarity of GICs is their tendency to form stage structure, and attempts to control the stage number of the products were successful through adjustment of the heat treatment temperature [2], the amount of starting metal chloride [3] or reaction time [4]. With respect to $AlCl_3$ intercalation, although the preparation of stage 1, 2, 4 and 8 GICs was described in the literatures [3,5], stage 3 and 5 GICs have never been reported. We have also tried to prepare stage 3 $AlCl_3$-GIC many times with conventional two-bulb method, but it could not be obtained.

Recently we found a new method to control precisely the stage number of metal chloride-GICs through adjustment of the pressure of coexisting chlorine gas [6]. The present paper reports the attempts to prepare stage 3 $AlCl_3$-GIC by controlling the chlorine pressure. An effect by the coexistence of a chlorinating agent N-chlorosuccinimide is also discussed.

2. EXPERIMENTAL

Slabs ($5 \times 1 \times 0.25$ mm, *ca.* 2.5 mg) of monochromator-grade highly oriented pyrolytic graphite (HOPG) from Advanced Ceramics Corp. were used as the starting materials. For preparation of $AlCl_3$-GIC, two methods were employed. With regard to the first method, a slab of HOPG was sealed in a glass ampoule with *ca.* 300 mg of $AlCl_3$ powder and chlorine gas at a prescribed pressure and heat treated at 150°C for 3 days (Method I). In the other method N-chlorosuccinimide was used in the place of chlorine gas. A slab of HOPG, *ca.* 300 mg of $AlCl_3$ and a prescribed amount of N-chlorosuccinimide were placed in a glass ampoule, sealed under vacuum and heat treated for 3 days (Method II).

After washing alternately with water and acetone to remove unreacted chemical reagents, the products were characterized by X-ray powder diffractometry (Rigaku, LINT-1500).

3. RESULTS

Method I

For the preparation of GICs with the majority of metal chlorides by the vapour phase method, the presence of chlorine is essential. Based on this, we succeeded in preparing pure stage 3, 4, 5 and 6 $EuCl_3$-GICs through adjustment of the pressure of chlorine gas [6]. In general to control the stage number is not easy especially when the stage number is high. We applied this method (Method I) to obtain stage 3 $AlCl_3$-GIC and the results are shown in Table 1. If the chlorine pressure is lower than 2 Torr, no

TABLE 1 Chlorine Pressure Dependence of the $AlCl_3$ Intercalation

Sample	Chlorine pressure (Torr)	Observed stages
1	1	G
2	1.5	G
3	2	G
4	2.5	4
5	4	4
6	5	4
7	6.5	2
8	10	2
9	22	2, 1
10	48	1

G: graphite, no intercalation.

intercalation was observed. Stage 4 GIC was obtained at a chlorine pressure of 2.5 Torr and the stage number decreases with increasing the chlorine pressure. However, neither stage 3 nor stage 5 was not obtained with the Method I, through adjustment of the chlorine gas pressure to a precision of 1 Torr.

Method II

N-chlorosuccinimide is known as a chlorinating agent. Instead of using chlorine gas, N-chlorosuccinimide was added in a reactor for the preparation of $AlCl_3$-GIC, and at elevated temperatures it was pyrolyzed to evolve chlorine gas and hence $AlCl_3$ became feasible to be intercalated into graphite. A brief calculation shows that 50 mg of N-chlorosuccinimide may have an ability to supply *ca.* 100 Torr of chlorine gas in the reactor with *ca.* 30 ml of inner volume. The products obtained by this Method II is listed in Table 2. Stage 1 $AlCl_3$-GIC was obtained when the reactor was heat treated at 115°C with 50 mg of N-chlorosuccinimide. Under this condition, enough amount of chlorine was thought to be liberated to prepare stage 1 GIC. When the reaction temperature was raised, however, the stage number increases; N-chlorosuccinimide turned black with the heat treatment at 135°C or above, and the degradation products might prevent the intercalation of $AlCl_3$. The amount of intercalation is determined by chlorine pressure, amount of inhibitor and vapour pressure of $AlCl_3$. At 200°C the vapour pressure of $AlCl_3$ exceeds 760 Torr and hence stage 1 was observed in Sample G. In the case of Sample H and I, pure stage 1 GIC was not obtained because the chlorine pressure was insufficient and because the amount of inhibitor was too much, respectively. In any event, we succeeded

TABLE 2 Results of $AlCl_3$ Intercalation in the Presence of N-chlorosuccinimide

Sample	Temperature (°C)	Amount of N-chlorosuccinimide(mg)	Observed stages
A	115	50	1
B	135	50	2
C	135	50	2,3
D	135	50	3
E	150	50	2,3
F	150	50	3
G	200	50	1,2
H	115	20	1,2,3
I	115	300	3

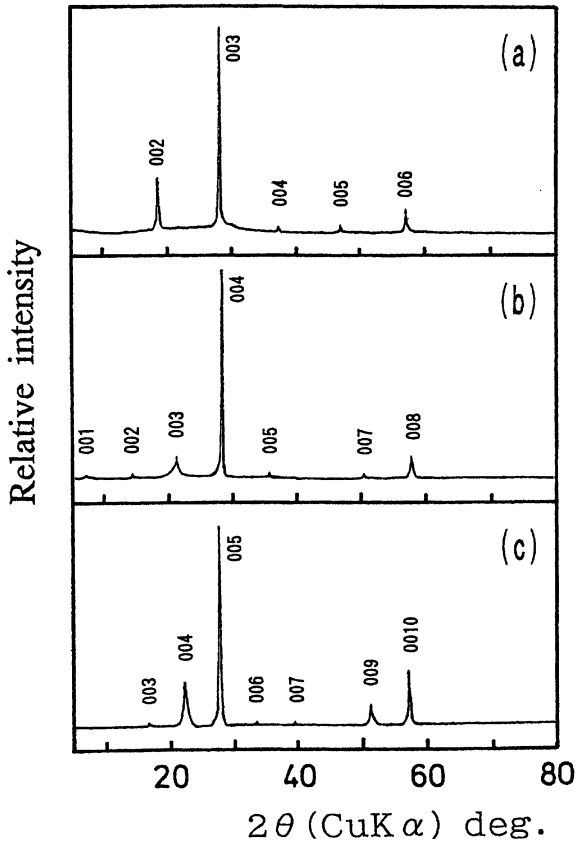

FIGURE 1 X-ray powder patterns of a) stage 1, b) stage 2 and c) stage 3 $AlCl_3$-GICs obtained by Method II.

in preparing stage 3 $AlCl_3$-GIC for the first time. The X-ray powder patterns of stage 1, 2 and 3 $AlCl_3$-GIC are shown in Figure 1.

4. DISCUSSION

Although it was not possible to obtain stage 3 $AlCl_3$-GIC by Method I, it was successfully prepared by Method II. The success does not depend upon the precise adjustment of the chlorine pressure, but upon the presence of the degradation products from N-chlorosuccinimide.

At elevated temperatures during the preparation of $AlCl_3$-GIC by the conventional method or Method I, stage 3 GIC is considered to be thermo-

dynamically unstable in the reaction system of graphite, $AlCl_3$ and chlorine gas, and hence it could not be obtained. Thus far stage n GICs (n: integer) are reported to be obtained with many kinds of intercalate, but stage 3/2 GIC [7] with a stacking sequence of $\cdots$G-I-G-I-G-G$\cdots$ (G:graphite basal plane; I:intercalate layer) or stage 4/3 GIC [8] with a stacking sequence of $\cdots$-G-I-G-I-G-I-G-G$\cdots$ is quite rare. This is due to the thermodynamic unstability of GICs with such a stage number in a similar manner as the case of stage 3 $AlCl_3$-GIC. In contrast stage 3 GIC might be thermodynamically stable in the reaction system containing the degradation products of N-chlorosuccinimide. This leads to a successful preparation of stage 3 $AlCl_3$-GIC.

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