X-Ray Crystal Structure of a Conducting Polymer Precursor: Bridge-stacked Phthalocyanine Gallium Fluoride

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Summary Phthalocyanine gallium fluoride has a structure in which Ga achieves octahedral co-ordination through bonding to four phthalocyanine (pc) nitrogen atoms and equidistant *trans* fluorine atoms; the latter act to link together the Ga(pc) moieties in a cofacially bridge-stacked arrangement.

WE have previously shown that iodine oxidation of bridged-stacked fluoroaluminium and fluorogallium phthalocyanine (pc) yields highly conducting materials of composition $[M(pc)FI_x]_n$ where $x = 0{\cdot}012$—$3{\cdot}4$ (M = Al) and $x = 0{\cdot}048$—$2{\cdot}1$ (M = Ga).[1,2] In this work a bridged-stacked structure for the M(pc)F starting material was assumed, based on previous studies which suggested ring-ring separations of 3·66 and 3·86 Å for Al(pc)F and Ga(pc)F, respectively.[3,4] In view of the unique structure proposed for M(pc)F and related Cr(pc)F,[5] Si(pc)O,[6] Ge(pc)O,[6] and Sn(pc)O[6] systems, and the high conductivity, thermal stability, and other interesting physical properties of their doped derivatives, and also the paucity of detailed structural data in this area, it is of interest that we have obtained a single crystal *X*-ray structure for Ga(pc)F.

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Single crystals of Ga(pc)F were obtained by slow sublimation (5 h at 480 °C and 0·01 mmHg) on to a collection finger filled with water, which boiled vigorously under these conditions. *Crystal data:* $C_{32}H_{16}FGaN_8$, $M = 601{\cdot}26$, triclinic, space group $P\bar{1}$, $a = 3{\cdot}8711(3)$, $b = 12{\cdot}601(1)$, $c = 12{\cdot}793(1)$ Å, $\alpha = 90{\cdot}271(1)$, $\beta = 96{\cdot}42(1)$, $\gamma = 91{\cdot}28(1)°$, $U = 620{\cdot}0$ Å^3, $Z = 1$, $D = 1{\cdot}61$ g cm^{-3}. X-Ray data with $13° < \theta < 45°$ were collected with an Enraf Nonius CAD4 diffractometer using Cu-K_α radiation. The structure was solved by the heavy atom method and refined to $R_1 = 4{\cdot}1\%$ and $R_2 = 5{\cdot}7\%$ for 2645 unique reflections.‡

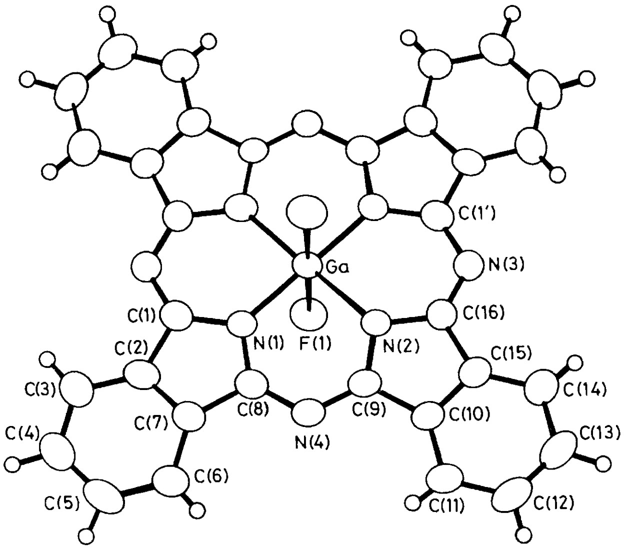

FIGURE 1. The structure of Ga(pc)F. Some important distances: Ga–F(1), 1·936(1); Ga–N(1), 1·969(2); Ga–N(2), 1·970(2); N(1)–C(1), 1·369(3); N(1)–C(8), 1·375(3); N(2)–C(9), 1·375(3); N(2)–C(16), 1·379(3); N(3)–C(1), 1·330(3); N(3)–C(16), 1·329(3); N(4)–C(8), 1·330(3); N(4)–C(9), 1·328(3) Å.

The structure of Ga(pc)F is shown in Figures 1 and 2. Gallium is octahedrally co-ordinated by four nitrogen and two fluorine atoms. The gallium atom is at an inversion centre and thus the *trans* Ga–F and *trans* Ga–N bonds, respectively, have identical bond distances. Another consequence of the inversion centre is the location of the fluorine atoms in a symmetric bridging position (Ga–F = 1·936 Å). This symmetric bridging is similar to that found in $[Mn(pc)(py)]_2O$[7] (py = pyridine) and $[Me(OSiMe_3)_2SiOSi(pc)O]_2Si(pc)$.[8] A comparison of X-ray powder diffraction data with those for Ga(pc)F provides evidence that Al(pc)F, Cr(pc)F, and Si(pc)O also have symmetrically bridged structures.

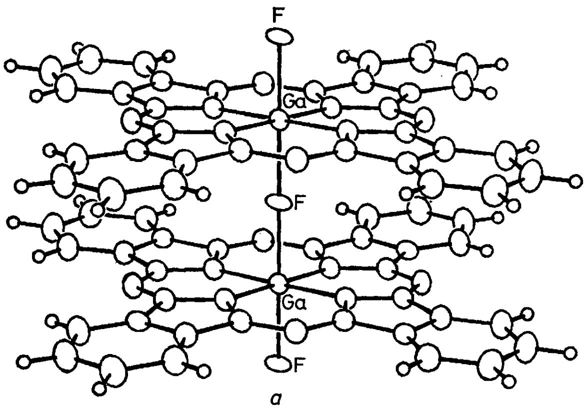

FIGURE 2. A view of the Ga(pc)F structure which shows molecular stacking.

An unusual feature of the present structure is that the (pc) rings are eclipsed (Figure 2). In all prior structures in which (pc) rings are collinearly stacked the rings are staggered. The closest approach to a collinearly stacked eclipsed structure is found for $[Me(OSiMe_3)_2SiOSi(pc)O]_2Si(pc)$, where the central ring is rotated by 15·9° with respect to the terminal rings.[8] Other stacked phthalocyanines are staggered by *ca.* 40° or more.[7,9]

Considering that conductivity occurs through a conduction band formed by the overlap of the (pc) rings, it is surprising that the conductivity of iodine-doped Ga(pc)F is high [$\sigma = 0{\cdot}12$ ohm^{-1} cm^{-1} (compacted pellet) for $Ga(pc)FI_{0\cdot93}$] in view of the relatively large ring separation observed for pristine Ga(pc)F [3·872(2) Å].§ The comparable compaction value for $Ni(pc)I_{1\cdot0}$ is 0·7 ohm^{-1} cm^{-1}, where the ring–ring separation known from a single crystal X-ray structure is 3·244(2) Å. The high conductivity for the bridge-stacked gallium materials could be explained by assuming the eclipsed ring structure for Ga(pc)F persists in the partially oxidized material. Thus the inter-ring overlap lost owing to increased inter-ring-separation may be made up in a large part by the eclipsed ring conformation. In contrast, $Ni(pc)I_{1\cdot0}$ has an inter-ring rotation of 40°, and despite a short inter-ring separation the conductivity is only modestly better than $Ga(pc)FI_{0.93}$ because of the staggered conformation.

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‡ Structure determined at the Molecular Structure Corporation, College Station, Texas. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Doping of Ga(pc)F with iodine leads to loss of X-ray scattering and at the present time we have been unable to grow crystals of doped materials by other methods. Nevertheless, it is unlikely that any major change occurs in the polymeric stacked Ga(pc)F structure on partial oxidation.

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