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Intercalation of mercuric chloride in pyrolytic graphite

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Abstract. The intercalation of HgCl_2 in highly oriented pyrolytic graphite is described. The (00 l) x-ray diffraction up to $l = 13$ is presented and indicates a c axis repeat distance of 16.40 Å. Mass spectroscopy shows that the linear HgCl_2 molecule is intercalated. There is no evidence of Cl_2 in the intercalated compound although Cl_2 gas is required to prepare it.

1. Introduction

Mercuric chloride in graphite is a stage-3 acceptor graphite intercalation compound (GIC) with an intercalant repeat distance along the c axis of 16.45 Å (Stumpf 1977). In stage 3, there are three graphite layers between the intercalant layers. Recent monochromatic Laue photographs show that the intercalant is in an oblique lattice with six equivalent orientations due to domain twinning (Behrens *et al* 1988). However, very few physical, structural and electrical properties of the HgCl_2 GIC have been investigated.

Mercuric chloride is a textbook example of a linear molecule with sp hybridisation. It crystallises in an orthorhombic cell with dimensions $a = 12.765$ Å, $b = 5.472$ Å and $c = 4.330$ Å. The molecule is almost straight with a Cl–Hg–Cl angle of 178.9°. The two Hg–Cl distances in the molecule are 2.284 Å and 2.301 Å with a mean of 2.291 Å. There are four molecules per unit cell. The smallest non-bonded distances are Hg–Cl = 3.37 Å and Cl–Cl = 3.33 Å (Subramanian and Geff 1980).

The intercalation of HgCl_2 only takes place in the presence of chlorine. The previous intercalation was done with finely divided flocculent natural graphite (Rüdorff *et al* 1963) and natural graphite flakes (Hooley 1973, Behrens *et al* 1988). Hooley determined the isotherm of the HgCl_2 vapour on graphite. In a chlorine atmosphere of 600 mbar, the threshold vapour pressure of HgCl_2 was 0.6 atm to form the GIC with a saturation composition of $\text{C}_{22}\text{HgCl}_2$. The composition, by weight, of the sample prepared by Behrens and co-workers was $\text{C}_{17.5}\text{HgCl}_2$. Hooley also suggested from the loss of Cl_2 in the growth tube that 0.34 Cl_2 molecules are intercalated and added to the above formula. This brings up the question of the role of the Cl_2 that is necessary for the intercalation of HgCl_2 .

The first purpose of this work is to report the conditions for intercalating large pieces of highly oriented pyrolytic graphite (HOPG) with HgCl_2 . It is a stage-3 compound, so attempts to make other stages are also given. Three sources of HgCl_2 are used since the purity of the starting material is important for making good GICs. The second purpose is to report the mass spectra of HgCl_2 and the GIC. The mass spectra give information about the intercalated HgCl_2 molecule in a positive and direct way—as was done recently

with the mass spectra of GICs with SbCl_5 , mixed chloride-fluorides of antimony and fluorides (Datars *et al* 1988a, b, Ummat *et al* 1987). The information comes from the detected ions that are dissociated from molecules in the intercalated compound. A third purpose is to show the (00 l) x-ray analysis of the stage-3 pyrolytic GIC.

There are two stable isotopes of Cl and seven of Hg. Their natural abundances are 75.4% (^{35}Cl), 24.6% (^{37}Cl), 0.146% (^{196}Hg), 10.10% (^{198}Hg), 17.0% (^{199}Hg), 23.10% (^{200}Hg), 13.20% (^{201}Hg), 29.65% (^{202}Hg) and 6.80% (^{204}Hg). This gives a characteristic isotopic distribution for each ion.

2. Experimental procedure

The reaction was carried out with cleaved pieces of HOPG that had been cleaned by heating in vacuum. The area of the pieces was approximately 1 cm^2 . The HOPG and HgCl_2 were heated in a sealed reaction tube to the temperature of $250\text{ }^\circ\text{C}$, at which HgCl_2 was a clear, molten liquid. The pressure of Cl_2 in the tube was 800 mbar. An intercalation time of 432 h was required to form a fully developed, stage-3 GIC with a composition, determined by the change in weight, of $\text{C}_{17.4}\text{HgCl}_2$. This is in excellent agreement with the formula $\text{C}_{17.5}\text{HgCl}_2$ reported by Behrens *et al* (1988) for small flakes. It was found that for a time of 240 h intercalation was not complete. Thus, a long period of time is necessary for the intercalation of HOPG pieces with HgCl_2 .

Three sources of HgCl_2 were used. The first was reagent grade, which contained numerous impurities, especially Br compounds. The second was prepared by a double sublimation of the commercial grade to reduce the impurity content. The third was made by reacting high-purity Cl_2 with Hg of purity 99.9999% in a sealed tube. A slight excess of Cl_2 over that required for the stoichiometric reaction was condensed into the reaction tube at liquid nitrogen temperature. The temperature was kept low to prevent the build up of a high pressure of Cl_2 from the exothermic reaction. From liquid nitrogen it was put in dry ice for several hours and then in an ice bath until the reaction was complete. White, crystalline HgCl_2 was produced.

Attempts were made to prepare different stages of the GIC. The reaction was carried out at $500\text{ }^\circ\text{C}$ for 384 h. An x-ray examination of the reaction product showed that it did not contain any unreacted HOPG. However, the sample was a poorly defined mixture of stages. Other attempts were made by using three different solvents: SOCl_2 , CH_3NO_2 and absolute ethanol. In all cases, x-ray diffraction measurements indicated that there was unreacted HOPG in the samples although there was an unidentified diffraction peak at a diffraction angle 2θ of 25.6° . Thus, the conditions for preparing different stages were not found although the stage-3 GIC is prepared in a straightforward manner.

A double-focusing mass spectrometer (model VG ZAB-E) with a mass resolution, $m/\Delta m$, of 1000 at the McMaster Regional Centre for Mass Spectroscopy was used for the mass analysis. Mass spectra were taken while the samples were heated in the source chamber of the spectrometer from 20 to $500\text{ }^\circ\text{C}$ for a period of several minutes. An electron beam with an energy of 70 eV ionised the vapour from the sample, and positive ions that were fragments of the molecules in the source were detected. A second spectrometer (model VG7070-F) that is smaller and more versatile was used to test for Cl and Cl_2 content in the samples.

The (00 l) x-ray diffractogram was made using Cu $K\alpha$ radiation which was set parallel to the (00 l) plane at $\theta = 0$. All x-ray measurements were carried out at room temperature.

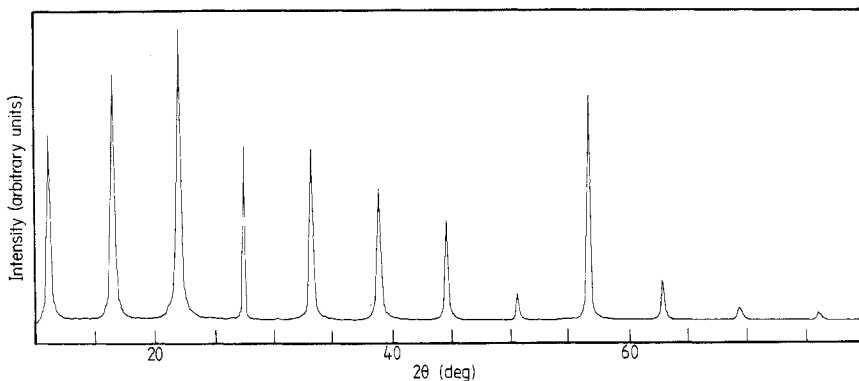


Figure 1. The $(00l)$ x-ray diffraction of stage-3 HgCl_2 graphite measured with $\text{Cu K}\alpha$ radiation as a function of 2θ .

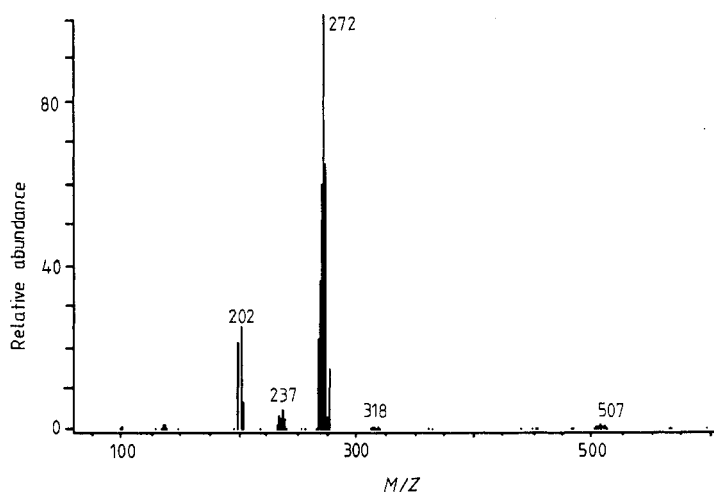


Figure 2. The relative abundance as a function of M/Z of the ions from crystalline, doubly sublimed HgCl_2 .

3. Experimental results

The $(00l)$ diffractogram is shown in figure 1. The diffraction peaks are indexed from (002) to (0013) with increasing 2θ . The (004) peak from the stage-3 sample is the most intense. There is no evidence of diffraction from other stages and from graphite. The c -axis repeat distance, I_c , is 16.40 \AA for the intercalated pyrolytic graphite and is similar to that found previously for the third-stage GIC made from small, natural flakes of carbon (Behrens *et al* 1988).

Figure 2 shows the mass spectrum from doubly sublimed HgCl_2 which serves as a reference for this work. The isotopic distributions as derived from HgCl_2 are assigned to the ions Hg^+ at a mass number of 202, HgCl^+ at 237 and HgCl_2^+ at 271. These assignments are confirmed in figure 3 with the comparison of the distributions with the calculated relative abundances of the isotopes in each of Hg , HgCl and HgCl_2 . The values of M/Z for the observed and calculated distributions do not agree exactly because the observed distributions are at the measured mass values and the calculated ones are at the mass numbers of the isotopes. The expected Hg isotopes are shown in figure 3(a). There is also excellent agreement between the observed and calculated distributions for

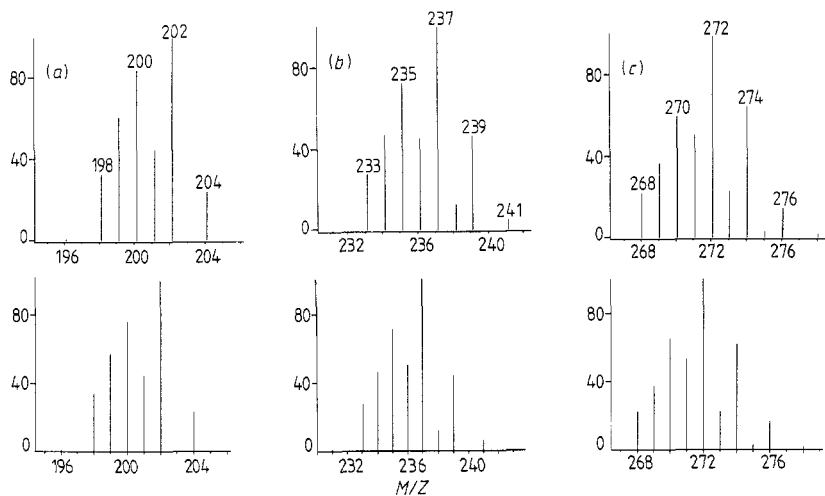


Figure 3. The observed isotopic abundance patterns (upper panel) compared with the calculated isotopic distribution (lower panel) of (a) Hg, (b) HgCl, (c) HgCl₂.

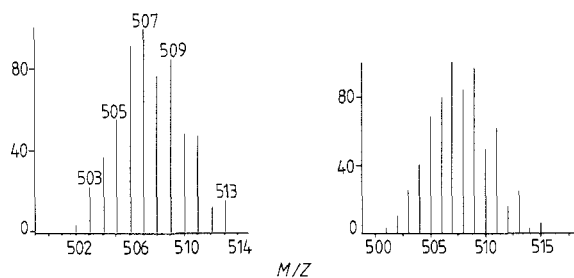


Figure 4. The observed isotopic abundance pattern (left panel) in the region of $M/Z = 507$ compared with the calculated isotopic distribution (right panel) of Hg₂Cl₃⁺.

HgCl and HgCl₂ in figures 3(b) and 3(c), respectively. The distribution at a mass number of 318 is from HgClBr⁺ and that at 507 is identified in figure 4 with Hg₂Cl₃⁺.

The mass spectrum of ions from the GIC made from doubly sublimed HgCl₂ is shown in figure 5. It is very similar to figure 2 for HgCl₂ with the ions Hg⁺, HgCl⁺, HgCl₂⁺, HgClBr⁺ and Hg₂Cl₃⁺.

The data for figures 2 and 5 were taken at a similar time in the middle of the heating cycle of each material. This is important for a meaningful comparison because the detected amounts of Hg⁺ and HgCl⁺ relative to that of HgCl₂⁺ change during the heating cycles and decrease by a factor of two from the beginning to the end. This means that small amplitude differences between figures 2 and 5 are not significant.

The ion Hg₂Cl₃⁺ is not detected during the first part of the heating cycles of HgCl₂ and the GIC. It appears during the last part of the cycle when the ion concentration of HgCl₂⁺ is large.

The mass spectra of ions from the home-made HgCl₂ and the GIC made from it are very similar to those shown in figures 2 and 5, respectively. There is a trace amount of HgClBr⁺, indicating that the use of high-purity starting material does not eliminate Br from the compound. However, the commercial grade of HgCl₂ is very different to the other two samples; the detected amount of HgClBr⁺ is 50 times greater and there are many other impurities. The GIC made from it yields a similar amount of HgClBr⁺ but

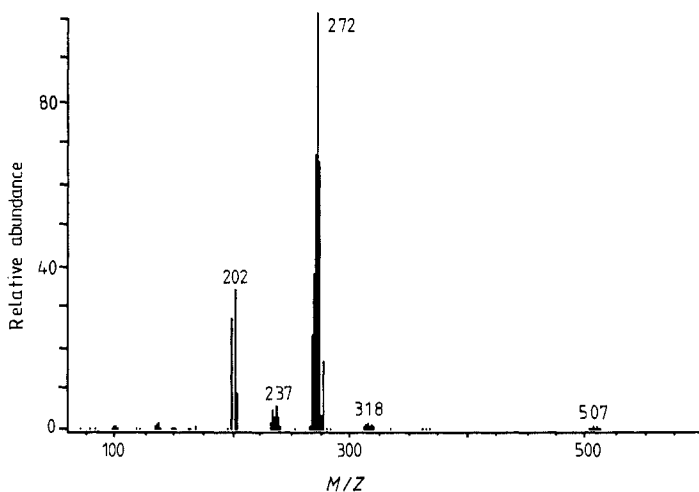


Figure 5. The relative abundance as a function of M/Z of the ions from a stage-3 HgCl_2 GIC.

fewer impurity ions. The relative abundances of Hg^+ , HgCl^+ and HgCl_2^+ from the commercial grade and the GIC are similar.

There is no Cl_2^+ in figures 2 and 5 with the mass scans starting at $M/Z = 50$. Thus additional experiments were done to search for Cl^+ and Cl_2^+ from crystalline HgCl_2 and the GIC. They were put in sample tubes and frozen using liquid nitrogen before the air was pumped from the tubes to make sure that Cl and Cl_2 were not pumped from the samples. The tubes were heated with hot air and in scans of M/Z from 10 to 100, no Cl^+ and Cl_2^+ ions were detected. Then, with the direct ionisation probe Hg^+ , HgCl^+ and HgCl_2^+ were detected but no Cl^+ and Cl_2^+ ions. Finally samples were heated to 500°C . Ions corresponding to Cl^+ were detected then from both HgCl_2 and the GIC with similar abundances and there was only a trace amount of Cl_2^+ .

4. Discussion

The same ions with similar relative abundances are detected from HgCl_2 and the HgCl_2 GIC. This means that the HgCl_2 molecule is intercalated in graphite with a bonding to other molecules similar to that in the crystalline material. This is in contrast with the SbCl_5 GIC in which fractionation into several molecular species takes place during intercalation (see Datars *et al* (1988a) and references therein). The next question is that of the orientation of the molecule in the GIC. The space d_s between the graphite layers separated by the intercalant is 9.7 \AA since $I_c = (n - 1)3.35 \text{ \AA} + d_s$ for stage n . This is sufficient space to allow the linear molecule to be perpendicular to the graphite layers. The Hg ion is probably at the midpoint between the carbon planes while the chloride ions are next to the carbons. The $\text{Cl}-\text{Cl}$ distances of the linear molecule is 5.58 \AA which leaves 2.05 \AA between each Cl atom and a carbon plane. This is greater than the usual $\text{C}-\text{Cl}$ distance of 1.77 \AA in, for example, CCl_4 . Thus, there is weak bonding between Cl and the carbon planes.

The HgCl_2 molecule is ionised without the loss of a Cl atom. This is different from the situation for SbCl_5 and SbCl_4F GICs from which the ionised intercalant molecule is not detected and for which at least one atom is taken from the molecule during the ionisation process.

The Cl^+ ion was only observed with the source at a high temperature and therefore probably resulted from fragmentation of HgCl_2 . About the same amount of ions were observed from HgCl_2 and the GIC and so there is no evidence of additional Cl or Cl_2 in the GIC. Thus, the suggestion by Hooley (1973) that Cl_2 is incorporated in the graphite is not supported by the mass spectroscopy measurements. However, a pressure of 600–800 mbar of Cl_2 is necessary for the intercalation of HgCl_2 , although the role that it plays is not known at present.

The Hg_2Cl_3^+ ions that were detected could result from one of two causes. One possibility is that there is bonding between molecules through the Hg–Cl distance of 3.37 Å. It would have to be similar in crystalline HgCl_2 and the GIC ion because of the similar number of Hg_2Cl_3^+ ions detected relative to HgCl_2^+ in the two cases. However, fragment ions of it were not detected and therefore it is not a dimer, as was observed for the SbCl_3 – SbCl_3 dimer in the SbCl_5 GIC (Datars *et al* 1988a). A second explanation for the Hg_2Cl_3^+ ion is that it results from the collision of HgCl_2^+ ions in the source. This is a possibility because the Hg_2Cl_3^+ is detected only during the last part of the heating cycle when there are the greater number of HgCl_2^+ ions.

5. Conclusions

The stage-3 HgCl_2 GIC is made with large pieces of pyrolytic graphite when intercalation takes place for an extended period of time (432 h) with the sample in chlorine gas with a pressure of 800 mbar at a temperature of a 250 °C. The (00 l) x-ray diffraction indicates that the c -axis repeat distance is 16.40 Å. Mass spectroscopy of crystalline HgCl_2 and the GIC indicates that the linear molecule is intercalated. There is no evidence of Cl_2 in the GIC.

Acknowledgments

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