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NEW DATA CONCERNING THE GRAPHITE-$CuAl_2Cl_8$ COMPOUND (STAGE 1)

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Abstract The intercalation of $CuAl_2Cl_8$ into graphite by action of the gaseous heterocomplex begins with the preintercalation of $AlCl_3$ to form a first stage $AlCl_3$-GIC. Subsequently, the copper dichloride is cointercalated by chemical transport via a gaseous complex in a iso-stage process to give the saturated $C_{22}CuAl_2Cl_{8.5}$ compound. Thermal analyses (TGA and DTA) show a high stability decrease of the intercalated heteromolecule $CuAl_2Cl_8$ as compared to that in the free state. Studies of the in-plane structure of the intercalant (Laue technique and electron diffraction on single crystals) indicate an oblique cell with the lattice constants a=2.566nm, b=0.658nm and γ=112°.

INTRODUCTION

As we have shown in an earlier work[1], vapor copper (II) chloroaluminate reacts with graphite (natural powders or pyrolytic graphite HOPG). The saturated compound $C_{22}CuAl_2Cl_{8.5}$ (stage 1) exhibits an interplanar distance of 0.947nm and the triple sequence Cl/M/Cl with the central metallic layer containing copper and aluminum in the molar ratio of Cu : Al = 0.5.

INTERCALATION PROCESS

Starting from a graphite to complex mass ratio of 2/3, the intercalation was visually followed in a glass furnace and a sealed pyrex reactor using the two temperature method. Under an excess of chlorine (750mm Hg at 25°C), we observed that at 300°C all the starting complex has disappeared after 48 hours in two steps. The first very rapid step (one hour) consists in the quasi-selective preintercalation of $AlCl_3$ and leads to a blue saturated $AlCl_3$-GIC. The second one is the cointercalation of copper dichloride by chemical transport via the gaseous complex $CuAl_2Cl_8$. The quantities involved are usually 310mg of $CuAl_2Cl_8$ for 200mg HOPG.
(00l) and (hk0) diffractograms taken as a function of reaction time (1, 6, 18 hours; 2, 3 days) permit us to confirm the intercalation process. From the beginning (1hour) to the end of the reaction (3days), the (00l) positions are consistent with a first stage compound characterized by a small increasing of the interplanar distance 0.945nm to 0.947nm (Fig.1). During this iso-stage process, (hko) patterns (Fig.2) are in agreement (positions and large

diffusion) with the disorganised α phase $AlCl_3$-GIC which appears immediatly. After several hours, two organised compounds appear on the hko diffractograms: the first with the weakest reflections corresponds to the $CuAl_2Cl_8$-GIC and the other one with the most prononced reflections can be attributed to a ternary (AlC_3,y$CuCl_2$)-GIC. By increasing the reaction time, this last compound, whose struture has not been determined disappears totally leaving a pure $CuAl_2Cl_8$ intercalated compound which gives strong (hko) reflections.

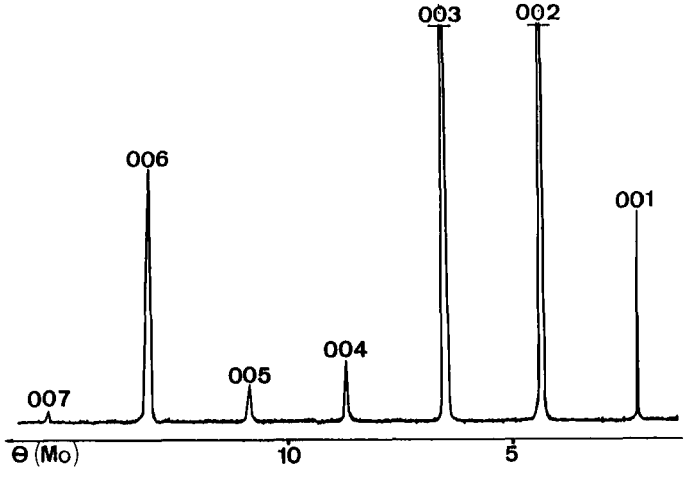

FIGURE 1 Example of 00l diffractogram taken after 1 hour of reaction.

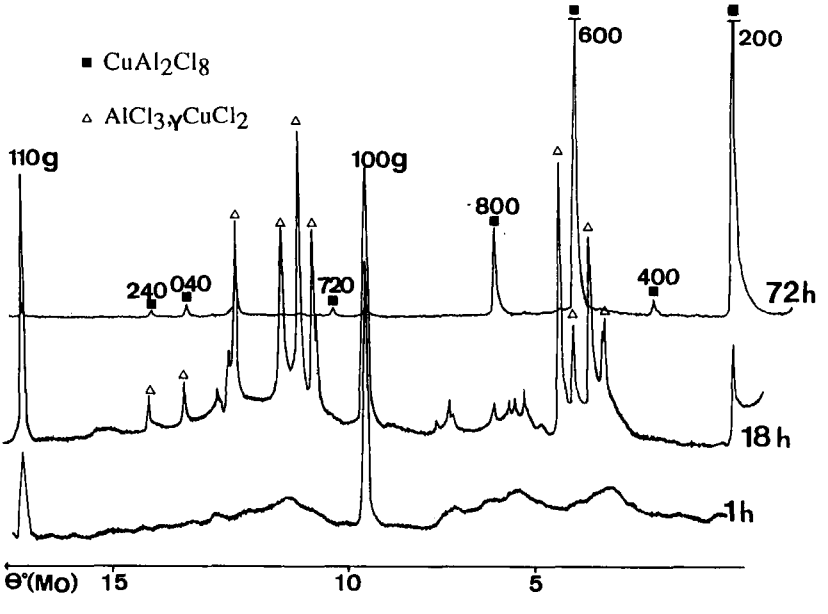

FIGURE 2 Diffractograms of hk0 reflections taken as a function of the reaction time.

According to our experimental study, we can describe the iso-stage process and the 2D structural changes by the following reactions:

$22C_{(s)} + CuAl_2Cl_{8(g)} + xCl_{2(g)} \rightarrow 2C_{11}AlCl_{3+\varepsilon(s)} + CuCl_{2(s)} + (x-\varepsilon)Cl_{2(g)}$

$2C_{11}AlCl_{3+\varepsilon(s)} + CuCl_{2(s)} + (x-\varepsilon)Cl_{2(g)} \rightarrow 2C_{11}AlCl_{3+\varepsilon},yCuCl_{2(s)} + (1-y)CuCl_{2(s)} + (x-\varepsilon)Cl_{2(g)}$

$2C_{11}AlCl_{3+\varepsilon},yCuCl_{2(s)} + (1-y)CuCl_{2(s)} + (x-\varepsilon)Cl_{2(g)} \rightarrow C_{22}CuAl_2Cl_{8.5(s)} + (x-0.25)Cl_{2(g)}$

THERMAL ANALYSIS

The study was carried out using dynamic thermogravimetry (TG) and quantitative differential thermal analysis (DTA). The powder samples(Ø=200µ, 100mg to 150mg for the TG experiments in argon and 100mg to 120mg for the DTA experiments in welded steel crucibles) were conditioned in a dry box after chemical and X-ray characterization.

The aim was to compare the thermal behaviour (range 25°C to 500°C) of the heterocomplex $CuAl_2Cl_8$ in the free state with that of the heterocomplex in the intercalated state (stage1). When the chloroaluminate was heated ($10K.min^{-1}$), a mass loss occurred at 150°C and reached 66% at ca. 210°C, which can be related to the thermal heterocomplex decomposition giving $CuCl_{2(s)}$ and $AlCl_{3(g)}$. The DTA curve shows the effect caused by fusion (at 169°C) and confirms decomposition of the crystal near 216°C (Fig.3). Such thermal transformations of the compound were noticed for the first time and they are very similar to that previously observed on isotype heterocomplex $PdAl_2Cl_8$[2].

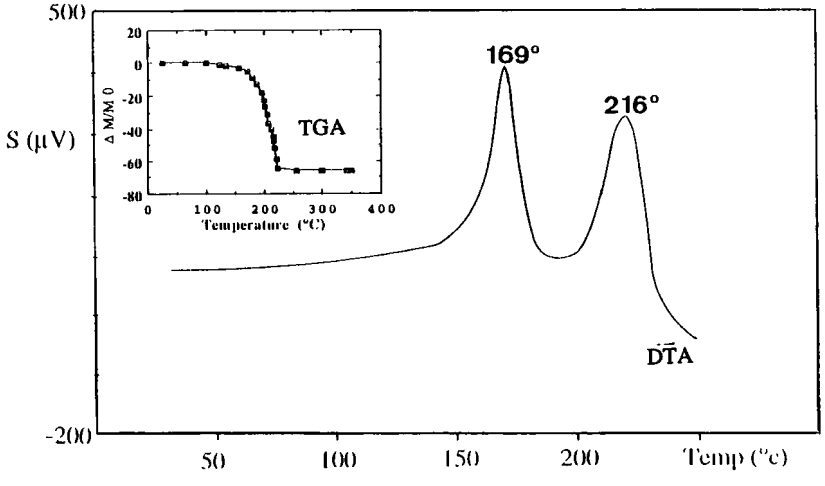

FIGURE 3 TG (inset) and DTA curves for $CuAl_2Cl_8$.

When the TG measurement was carried out on the $CuAl_2Cl_8$-GIC, the mass loss began about 100°C (Fig.4) and it increased continuously up to 35% at 500°C. This mass loss corresponds approximately to the initial content of $AlCl_3$

(40%). Based on the corresponding DTA thermogram, the melting-point of the intercalated heterocomplex appears at 100°C. Such a decrease of the melting-point can be easily explained by the reduced intermolecular interactions in the intercalated heterocomplex. The decomposition of the graphite intercalation compound is exothermic and takes place in the temperature range between 200°C and 300°C.

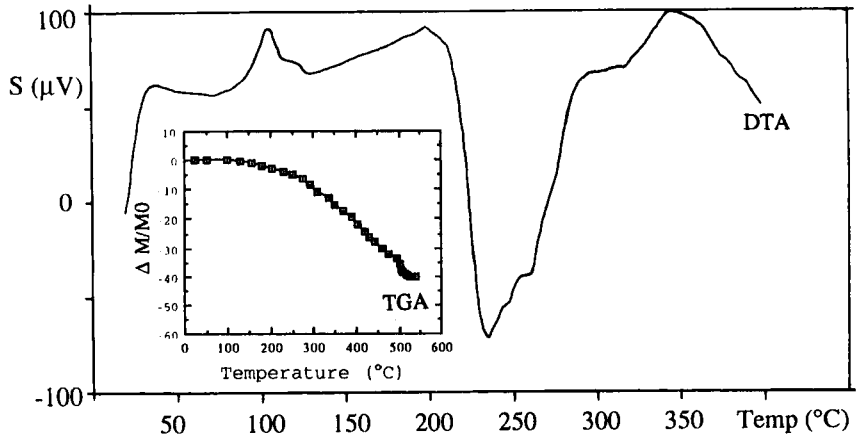

FIGURE 4 TG (inset) and DTA curves for $CuAl_2Cl_8$-GIC.

STUCTURAL ANALYSIS

The crystal structure[3] of copper(II) chloroaluminate is triclinic (a=0.6582nm, b=0.7362nm, c=1.2265nm; a=89°99, b=85°97, γ=89°77; space group P1). Each unit cell contains two (noted A and B) independent $CuAl_2Cl_8$ species: molecule A is at the origin while molecule B is at (0,1/2,1/2). Each copper atom is square-planar coordinated by chlorine atoms with a mean Cu-Cl distance of 0.2295nm. The next nearest neighboring chlorine atoms are located above and below the plane formed by the ($CuCl_4$) group at a distance of 0.2951nm and lead to a $CuCl_6$ distorted octahedra. Each aluminum atom is tetrahedrally coordinated by chlorine atoms. In fact, the crystal stucture can be described by stacking of layers parallel to the (001) plane with the repeat sequence Cu-Cl-Al-Al-Cl. Furthermore the atomic projection on the (a,b) plane leads to placing the chlorine atoms to a approximately hexagonal close-packed array with copper and aluminum atoms occupying a part of the avaible octahedral and tetrahedral interstices, respectively.

A single crystal (stage1) has been investigated by X-ray diffraction and electron diffraction which permits us to select a large single intercalate domain($\varnothing$=1000Å^2). The photographs of the reciprocal equatorial strata can be interpreted by an oblique in-plane cell with lattice parameters: a=2.566nm, b=0.658nm and γ=112°. The reciprocal a* vector of the in-plane intercalate lattice is rotated with respect to the a* vector of the graphite by an angle of 19° (Fig.5). This in-plane organisation is nearly identical to that observed in the (a,b) lattice plane of pristine chloroaluminate. As shown in Figure 6, we find a 2D oblique in-plane cell with lattices parameters a=2.566nm, b=0.658nm and γ=120° and containing three independent $CuAl_2Cl_8$ molecules. But in the free state, the layers are repeated in the sequence

Cu-Cl-Al-Al-Cl which is not consistent with the triple layer sequence Cl-(Cu,Al)-Cl identified in the corresponding GIC. So we have to admit a deformation of the $CuAl_2Cl_8$ units (Fig.7) which permits generating the triple sequence Cl-M-Cl and moreover makes a perfect hexagonal array of chlorine atoms to appear. Assuming that 2 units belong to each graphite cell and 3 units to each intercalate cell, we obtained the theoretical stoichiometry $C_{19.9}CuAl_2Cl_8$. This result is in good agreement with the average formula $C_{22}CuAl_2Cl_{8.5}$ and gives a filling factor of about 90%. In previous work[1] stuctural investigations on a first stage HOPG-based GIC showed that the intercalated layer was organised in a hexagonal lattice (a=1.380nm). In fact this lattice is a substructure of the oblique one described in this paper and involved by the six fold symmetry of the graphene layers.

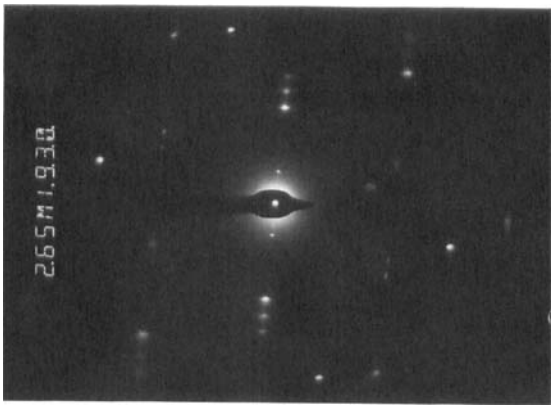

FIGURE 5 Electron diffraction photograph showing the reciprocal equatorial strata.

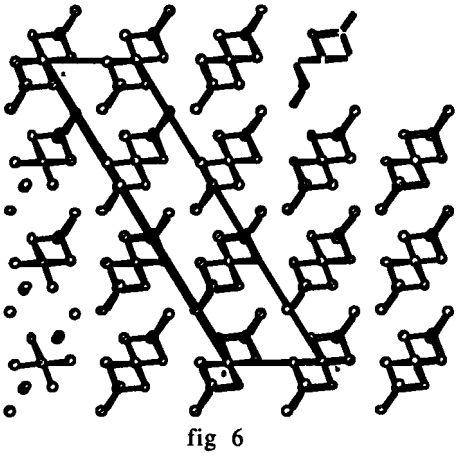

fig 6

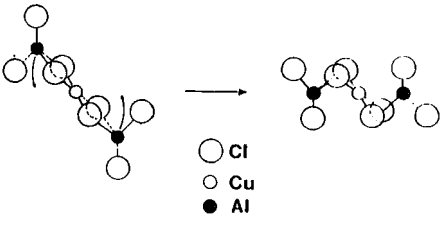

fig 7

FIGURE 6 View of the (a,b) lattice plane of pristine copper chloroaluminate.

FIGURE 7 Deformation sustained by the $CuAl_2Cl_8$ units.

On the base of the magnetic properties of the $CuAl_2Cl_8$-GIC[4] which are consistent with a model of finite chain distribution of spin 1/2 Cu^{2+} ions, it appears that copper and aluminum atoms probably fill holes in the close-packed chlorine lattice in such a way as to form chains parallel to the graphite plane. Such an infinite-chains structure exists in the isotype heterocomplex $CoAl_2Cl_8$[5] and is maintained in the intercalated $CuAl_2Cl_8$.

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