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Ternary Metal Chloride Graphite Intercalation Compounds Synthesized from Chlorometallate Salts

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Ternary metal chloride graphite intercalation compounds synthesized from chlorometallate salts.

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The action of MCl_2-$AlCl_3$ molten salt systems (M=Cu, Cd, Pd, Co) does not permit the intercalation into graphite the heteromolecules MAl_2Cl_8 which exist in the liquid. All these molten chloroaluminate reagents give intercalated species which correspond to an $AlCl_3$ layer with low divalent ionic content the basal plane structure of which appears to be dependent on the divalent metal. In the case of copper, palladium and cobalt, this 2D order corresponds to a hexagonal cell (a=600pm) whose study based on the experimental and calculated (hko) intensities suggests a substitutional process between the Al^{3+} and M^{2+} ions in the intercalated layers.

Keywords: graphite; intercalation; chloroaluminate; $AlCl_3$

INTRODUCTION

Molten salt systems have been used successfully to synthesize graphite intercalation compounds[1,2]. By using mixtures of two different metal chlorides, ternary graphite intercalation compounds are obtained in which the two chlorides are randomly mixed in the same gallery (GMICs)[3]. The stage of the compounds (single stage or mixtures of different stages) and chemical stoichiometry appear to be dependent on several factors: reaction temperature and time, starting graphite/chloride ratio, starting chloride1/chloride2 ratio.

It is known that MAl_2Cl_8 heteromolecules obtained by the association of gaseous metal chlorides (MCl_2= $CuCl_2$, $CoCl_2$, $CdCl_2$, $PdCl_2$)[4] and dimeric Al_2Cl_6 also exist in liquid or in crystalline condensed phases which are distinguished by their very low melting temperature[5-8]. Previous work has shown, by vapor two-zone synthesis, the direct intercalation of the $CuAl_2Cl_8$ and $PdAl_2Cl_8$ heteromolecules[9]. In the same conditions, the Cd and Co-based heteromolecules lead to a stage 1 ternary compound with a low transition metal content[10] which appears to be very different from previous products obtained by chemical transport[11].

In this work, we present the results of a detailed study concerning whether it might be possible by the action of the liquid, to obtain GICs in which the intercalate layer corresponds to a crystalline condensed phase related to the starting reagent.

EXPERIMENTAL PROCEDURE

GICs were synthesized in the presence of an excess of dry chlorine gas in a sealed two-compartment reactor (length=10cm and diameter=0.9cm) using HOPG samples (15mm x 1mm x 0.1mm) and presynthesized chlometallate reagents placed at either end. To form the stage 1 compound, the reactor is placed in a vertical furnace without a temperature gradient and then undergoes the following three-step procedure:

1- melting of the reagent in the bottom compartment.

2- reversing the furnace and heating the molten salts and the HOPG. The reaction with liquid MAl_2Cl_8 was carried out at low temperature depending on the melting and dissociation temperatures of the chloroaluminates for a reaction time of 24hours.

3- returning the furnace to the initial position to isolate the GIC.

After synthesis, the intercalated compounds were transferred under inert atmosphere and their stage determined by 00l X-ray diffraction measurements using MoK_α radiation. The in-plane unit cell parameters of the intercalate were investigated either by hk0 X-ray diffractograms or by selected area electron diffraction patterns (PHILIPS CM20 TWIN STEM 200KV). Chemical

analyses are determined in parallel by the "Centre de Microanalyse du CNRS" (Vernaison - France) and the analysis service of "Centre de Recherches Pétrographiques et Géologiques" (Nancy - France).

RESULTS AND DISCUSSION

We summarize in Table 1 the details of the reaction conditions, the stage identification and the chemical compositions.

T_R	$P(Cl_2)$	00l X-ray analysis	Chemical analysis
200°C	0,5 atm	stage 1 Ic=950 pm	$C_{8.5}AlPd_{0.12}Cl_{3.5}$
250°C	0,5 atm	stage 1 Ic=955pm	$C_{10}AlCd_{0.20}Cl_{3.3}$
210°C	0,5 atm	stage 1 Ic=948pm	$C_{10}AlCu_{0.23}Cl_4$
210°C	0,5 atm	stage 1 Ic=945pm	$C_{8.9}AlCo_{0.02}Cl_{3.3}$

TABLE 1 Reaction conditions, stage identification and chemical compositions for the GICs.

The experimental and calculated c-axis charge densities (Fourier transform using integrated 00l X-ray intensities) are in good agreement and confirm the chlorine-metal(Al+M)-chlorine stacking sequence, as classically observed in the compounds of graphite with the metallic chlorides (Fig.1). In all cases, the central metallic plane contains aluminum and the divalent metal but contrary to what is observed in the related GMCIs[11] there is a single outer layer of chlorine atoms. The crystallo-chemical model used in this pattern-fitting structure refinement leads to the stoichiometry $C_{9.05}Co_{0.02}AlCl_{3.3}$ very close to the chemical analysis.

The comparison of the carbon interlayer distances (d_i) and the interlayer M-Cl distances ($d_{M\text{-}Cl}$) with those observed in the related binaries (GICs) or ternaries (GMICs) suggests the influence of the divalent metal on the resulting thickness of the intercalated sandwich (Tab.2).

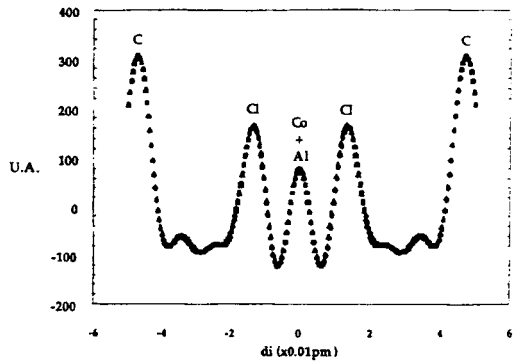

FIGURE 1 Charge density distribution along c-axis in the stage 1 $C_{8.9}Co_{0.02}AlCl_{3.3}$ (o experimental, Δ calculated, Debye-Waller parameter B=2, reliability factor r=5.8%)

d_i(pm)	GICs	d_i(pm)	GMICs	this work
$CdCl_2$	958	M = (Cd,Al)	958	955
$CoCl_2$	939	M = (Co,Al)	942	945
$AlCl_3$	949			

$d_{M\text{-}Cl}$(pm)	GICs	$d_{M\text{-}Cl}$(pm)	GMICs	this work
M = Cd	151	M = (Cd,Al)	135-152	151
M = Co	138	M = (Co,Al)	132-139	141
M = Al	147			

TABLE 2 Values for the interlayer separation d observed in related stage 1 graphite intercalated compounds[11-13].

Analysis of the two-dimensional (2D) structures shows that the organization of the intercalated layers depends on the nature of the divalent metal: disordered for $C_{8.5}AlPd_{0.12}Cl_{3.5}$, ordered (orthorombic cell: a=1276pm and b=1228pm) and commensurate with that of graphite for $C_{10}AlCd_{0.23}Cl_{3.3}$ (Fig.2) and ordered (hexagonal cell: a=600pm and $\delta(a_g,a_i)=30°$) but incommensurate for $C_{10}AlCu_{0.23}Cl_4$ and $C_{8,9}AlCo_{0.02}Cl_{3.3}$ (Fig.3).

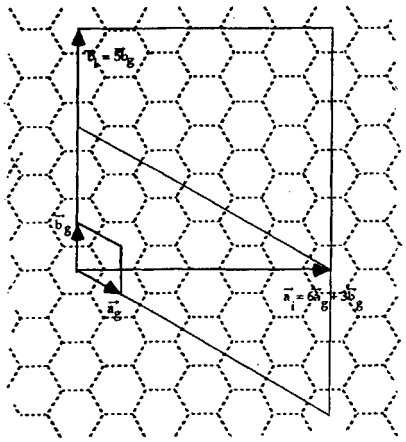

FIGURE 2 Real space commensurate structure for $C_{10}AlCd_{0.20}Cl_{3.3}$.

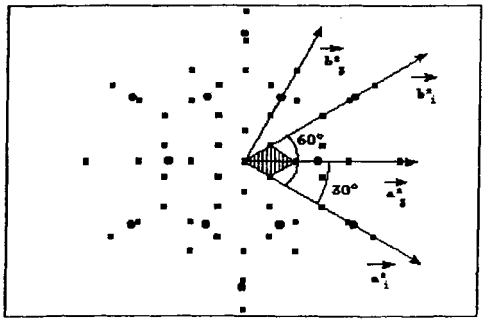

FIGURE 3 Schematic representation of diffraction pattern for $C_{8.9}AlCo_{0.02}Cl_{3.3}$.

As it is possible to determine a hexagonal unit cell with the same parameter (a=600pm) in the (a,b) plane of pristine $AlCl_3$, we have compared the experimental hk0 reflexion intensities to those calculated from a pure intercalated $AlCl_3$ layer or containing a low proportion of Co^{2+} ions substituted for the Al^{3+} ions. The best concordance is obtained for the composition $C_9Co_{0.02}AlCl_{3.06}$ which is in good agreement with the elementary analysis (Table 3).

hk0	100	110	200	210	300	220	310	400
d_{hklk}(pm)	519,4	299,8	259,77	196,3	173,1	149,9	144	129,8
I_{exp}(%)	33,1	24,3	4,4	5	100		3	1,25
I_{theor}(%)*	93,9	10,7	16,1	14,44	100	1,7	5,3	1,822
I_{theor}(%)**	33	24,9	5	4,28	100	0,9	1,42	0,47

TABLE 3 Comparison of the hk0 intensities:
I_{exp}(%): experimental values for $C_{8.9}AlCo_{0.02}Cl_{3.3}$; I_{theor}(%)*: calculated values for a pure intercalated $AlCl_3$ layer ; I_{theor}(%)**: calculated values for an intercalated $AlCl_3$ layer containing the atomic ratio Co/Al=2%.

In conclusion, the direct intercalation of the heteromolecule MAl_2Cl_8 has never been observed via molten reagents contrary to previous results via gaseous reagents. In addition to the results described above, it can be pointed out that the two synthesis methods (via liquid or gaseous chloroaluminates) lead in the case of Cd and Co to GICs of low divalent metal content.

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