Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Tatyana Yu. Sokolova [a], Vera A. Nalimova [a], Oleg V. Fateev [b], Victor V. Avdeev [a], Kirill N. Semenenko [a] & Daniel Guerard [c]

[a] Department of Chemistry, Moscow State University, Leninskie Gory, Moscow, 119899, RUSSIA

[b] Topchiev Institute of Petrochemical Synthesis of Russian Academy of Sciences, Leninsky pr. 29, Moscow, RUSSIA

[c] Laboratoire de Chimie du Solide Minéral, Université de Nancy 1, CNRS n° 158, BP 239, 54506, Vandoeuvre-lès-Nancy, Cedex, FRANCE

Version of record first published: 23 Oct 2006.

To cite this article: Tatyana Yu. Sokolova , Vera A. Nalimova , Oleg V. Fateev , Victor V. Avdeev , Kirill N. Semenenko & Daniel Guerard (1994): Alkali Metal Reaction with $CuCl_2$ Intercalated Graphite, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 35-40

To link to this article: http://dx.doi.org/10.1080/10587259408050079

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 35–40
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Printed in the United States of America

ALKALI METAL REACTION WITH $CuCl_2$ INTERCALATED GRAPHITE

TATYANA Yu. SOKOLOVA*, VERA A. NALIMOVA*, OLEG V. FATEEV**, VICTOR V. AVDEEV*, KIRILL N. SEMENENKO*, DANIEL GUERARD***
* Department of Chemistry, Moscow State University, Leninskie Gory, Moscow, 119899, RUSSIA
** Topchiev Institute of Petrochemical Synthesis of Russian Academy of Sciences, Leninsky pr.,29, Moscow, RUSSIA
*** Laboratoire de Chimie du Solide Minéral, Université de Nancy 1, CNRS n° 158, BP 239, 54506 Vandoeuvre-lès-Nancy, Cedex FRANCE

Abstract Two new phases with I_c= 14.70 Å and 12.55 Å were obtained by interaction of potassium with stage 1 and 2 $CuCl_2$-GICs at 200°C. The following sequences of layers are respectively: K\$CuCl_2$\K\$CuCl_2$ and K\CuCl\K\CuCl.

INTRODUCTION

Many attempts were done to get biintercalation compounds containing subsequence of "donor" and "acceptor" - type layers in graphite matrix[1-6].

Intercalation of acceptor - type GICs by alkali metal is the only way to synthesize donor-acceptor biintercalation GICs. The attempts to realize reaction between donor type GICs and transition metal chloride resulted in reduction of chloride without intercalation [6-9].

$CuCl_2$ - GICs were not investigated in this type of reactions, and we were mainly interested in the way of the reaction of potassium with $CuCl_2$ in quasi-two dimentional state.

SYNTHESIS

For the $CuCl_2$ - GIC synthesis we used disks (D = 6 mm, thickness 0.3 - 0.4 mm) of highly oriented pyrolitic graphite (HOPG). $CuCl_2$ - GICs were synthesized in two-bulb quartz ampoules in chlorine atmosphere and characterized by X-ray diffraction (reflexion, Cu K_α radiation)(I_c = 9.40 Å for stage 1 and 12.75 Å for stage 2). Composition was determined by mass increase, being $C_{4.9\text{-}5.1}CuCl_2$ and $C_{9.8\text{-}10.3}CuCl_2$ respectively.

The interaction of $CuCl_2$ - GICs with potassium was carried out into the two-bulb pyrex tube under vacuum at 200° C with a temperature gradient not more than 10° C.

Different products of the reaction of potassium with stage 1 and stage 2 $CuCl_2$ - GICs at 200° C are listed in Table 1. The reaction was stopped at definite time for the X-ray diffraction study of the sample. The sample was examined from the surface (in Table 1 - outside), after that splitted and examined inside (in Table 1 - inside).

TABLE 1 Interaction of potassium with stage n $CuCl_2$ - GICs

n	Compound	I_c Å	Quantity inside (%) * Time, hours 1	3	5	16	48	Quantity outside (%) * Time, hours 1	3	5	16	48
2	$C_{10.1}CuCl_2$	12.75	100	60	30	20	-	90	tr.	-	-	-
	phase-1	14.70	-	40	70	40	-	10	10	10	-	-
	phase-2	12.55	-	-	tr.	40	55	-	90	90	80	70
	KCl, Cu		-	traces				-	traces			
	KC_8	5.35	-	-	-	tr.	45	-	tr.	tr.	20	30
			Time, hours 1	3	5	18	51	1	3	5	18	51
1	$C_{5.1}CuCl_2$	9.40	100	100	10	-	-	80	80	5	-	-
	phase-2	12.55	-	-	90	100	85	20	20	95	90	85
	KCl, Cu		-	-	traces			traces				
	KC_8	5.35	-	-	-	-	15	-	-	tr	10	15

* The percentages concern only the GICs phases

It is easy to see from Table 1 and Figure 1a that potassium intercalates into stage 2 $CuCl_2$-GIC, forming the compound with I_c=14.70 Å. This value of I_c is a little less than the sum: 9.40 Å (I_c of stage 1 $CuCl_2$ - GIC) + 5.35 Å (I_c of stage 1 K-GIC) = 14.75 Å. So our supposition was that this phase corresponded to the biintercalation compound $CuCl_2$\K\$CuCl_2$\K... (\-graphite layers). To establish the positions of atomic planes along the $\bar{c}$-axis we have done quantitative analysis of the intensities of 00l reflections (see Table 2). Structural factors obtained and used for the Fourier transform give the profile of electronic density $\rho(z)$ shown in Figure 1b. It is in relatively good accordance with the

profile calculated on the basis of the centrosymmetric model, where $Z_{Cu}=0$; $Z_{Cl}=\pm 0.097$; $Z_C=\pm 0.3177$; $Z_K=\pm 0.5$ for the theoretical composition $C_{9.8}CuCl_2K_{0.6}$.

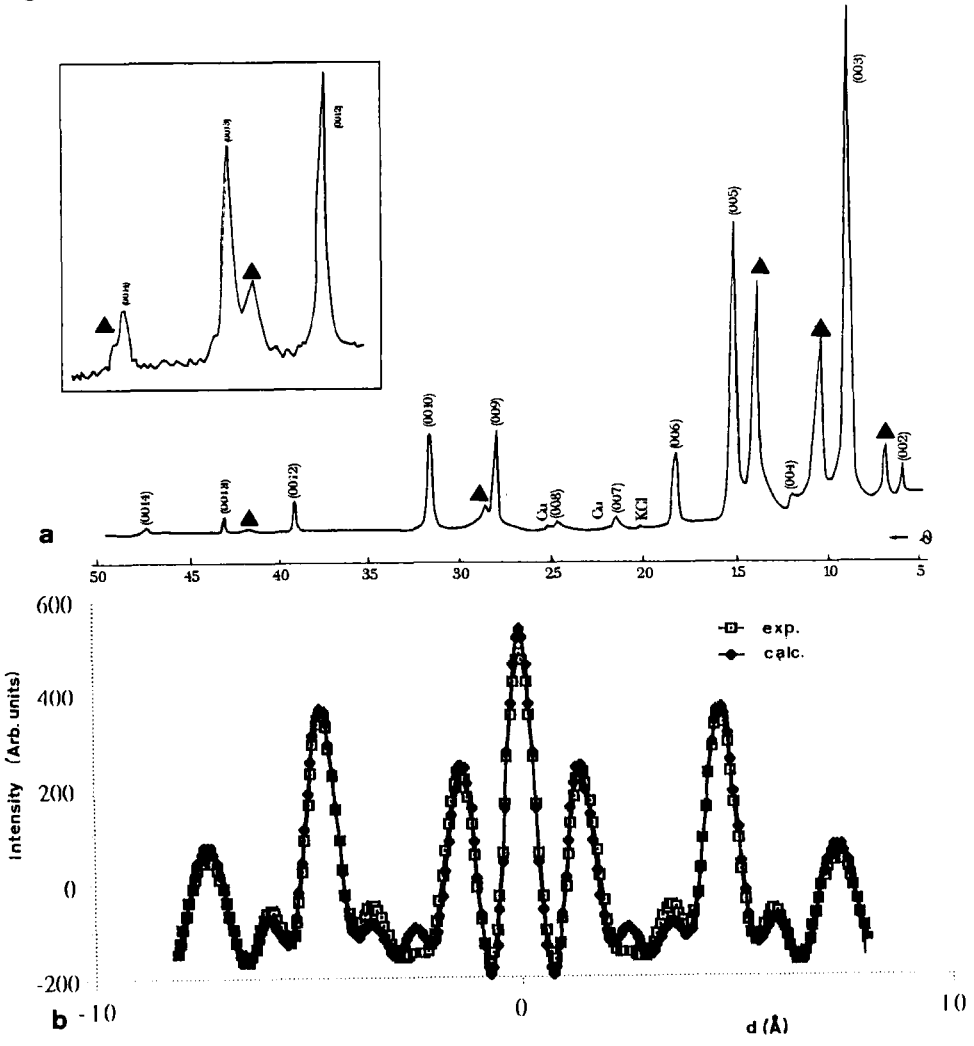

FIGURE 1 a) Stage 2 $CuCl_2$-GIC diffractogram after 5 hours interaction with K at 200°C (inside): ▲ - stage 2 $CuCl_2$-GIC; (00l) - phase with I_c = 14.70 Å. The inset represents an enlargment of 37-47°; b) electronic profile of the phase with I_c = 14.70 Å.

The structure of the $CuCl_2$ layer is close to that, proposed by A.Perignon et al[10] for the stage 2 $CuCl_2$ GIC. The stoichiometry of the potassium layer is close to KC_8.

This biintercalation compound is not stable at further contact with potassium and after 3 hours of reaction there are, close to the surface of the sample, traces of the products of reduction of $CuCl_2$ and also KC_8. At the same time we observe a new phase

TABLE 2 Calculated and experimental intensities of (00l) reflections of the biintercalation compounds in the $CuCl_2$-K-graphite system .

HETEROSTRUCTURE WITH I_c = 14.70 Å				
00l	θ	d_{00l} (Å)	I_{exp}	I_{calc}
001	3.004	14.700	*)	44.7
002	6.015	7.350	6.2	8.4
003	9.044	4.900	100.0	100.00
004	12.099	3.675	1.7	1.1
005	15.188	2.940	34.9	35.2
006	18.324	2.450	13.9	23
007	21.518	2.100	1.2	1.1
008	24.783	1.837	1.2	0.3
009	28.137	1.633	16.0	14.6
0010	31.600	1.470	17.2	18.9
0011	35.196	1.336	0.0	0.3
0012	38.960	1.225	4.9	8
0013	42.936	1.131	1.8	2.3
0014	47.187	1.050	0.5	0.2

R=9.5%

HETEROSTRUCTURE WITH I_c = 12.55 Å				
00l	θ	d_{00l} (Å)	I_{exp}	I_{calc}
001	3.519	12.550	*)	25.5
002	7.051	6.275	0.0	1.3
003	10.610	4.183	8.0	19.2
004	14.211	3.138	100.0	100.00
005	17.871	2.510	0.0	0.01
006	21.608	2.092	*)	0.03
007	25.444	1.793	3.5	3.3
008	29.406	1.569	10.7	10.8
009	33.530	1.394	0.5	0.5
0010	37.861	1.255	0.6	0.00
0011	42.464	1.141	0.6	0.5
0012	47.434	1.046	1.6	1.7

R = 9.8%

*) experimental values substituted by calculated

with I_c = 12.55 Å (Fig.2a). The same phase is observed by the reaction of the stage 1 $CuCl_2$-GIC with potassium after 5 hours. The contents of this phase grows up to 100% after 18 hours of reaction, then KC_8 formation starts (Table 1). This phase corresponds

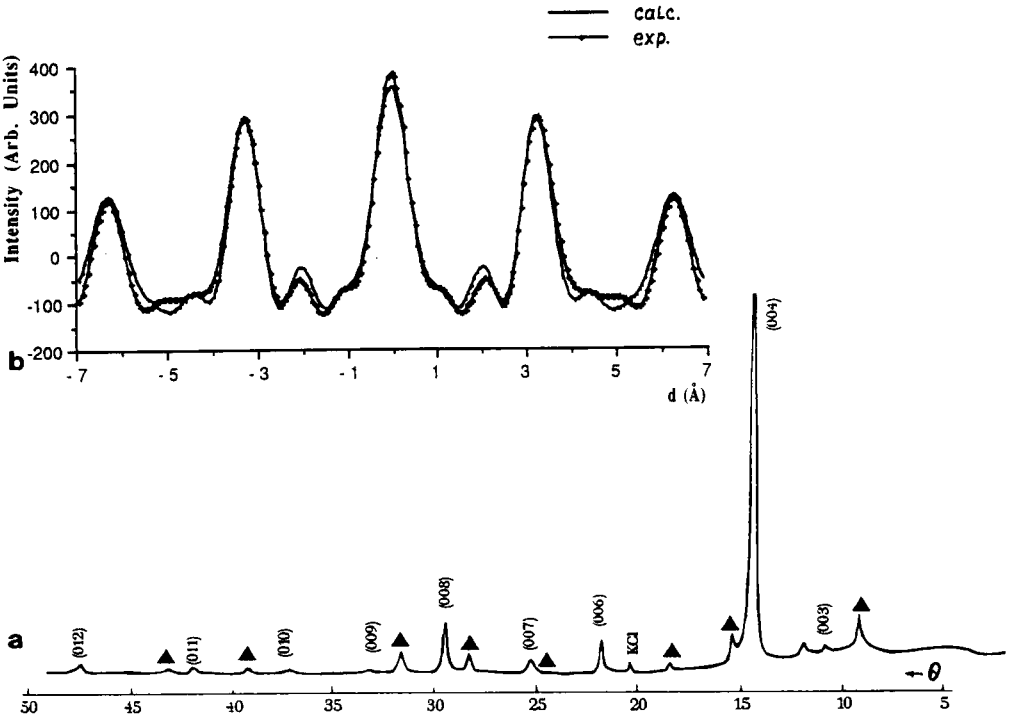

FIGURE 2 a) Stage 2 $CuCl_2$-GIC diffractogram after 5 hours interaction with K at 200° (outside): (001) - phase with I_c = 12.55 Å, ▲ - phase with I_c = 14.70 Å; b) electronic profile for the phase with I_c = 12.55 Å.

probably to the biintercalation compound where $CuCl_2$ is partly reduced, so the stacking of the layers could be as follows : K\CuCl\K\CuCl... Profile of the electronic density ρ(z) obtained by the Fourier transform of the structural factors calculated from the experimental intensities is compared to that calculated on the basis of the proposed model (Figure 2b).The 006 reflection corresponds also to the main line (111) of metallic Cu (d = 2.088 Å), this coincidence explains why we have used theoretical value instead of experimental one (10%) for 006 reflection in our calculations. It should be noted that C-K-C stacking thickness in this compound is larger (5.9 Å) than in KC_8 (5.34 Å). The calculation has shown that this increase of the thickness is probabely due to the splitting of potassium layer along the c-axis, and the concentration of potassium in the layer is higher than in KC_8. Then, the layer containing the copper chloride is quite thin : about

6.7 Å, which is close to the normal thikness of chlorine GIC[11] or compounds presenting single intercalated layers of some transition metal chlorides like, for instance, $AuCl_3$[12].

The reaction of stage 2 $CuCl_2$-GIC with cesium under pressure (in solid state) leads to a golden colored compound with I_c = 6.82 Å. The reaction was accompanied by a substential volume decrease of the system $CuCl_2$-GIC + Cs metal: up to 50%. It seems that even under very mild conditions we have an exchange between $CuCl_2$ and the alkali metal in the layer, which is accompanied by the formation of Cs-GIC and $CuCl_2$ reduction.

Li interaction with $CuCl_2$-GICs proceeds under much harder conditions: 350°C in liquid phase and always is accompanied by $CuCl_2$ reduction. At the same time, there is formation of phase with I_c = 11.35 Å. This one seems to be biintercalation compound with a partly reduced copper chloride layer as in the case of the biintercalation phase with potassium whose I_c = 12.55 Å.

CONCLUSION

This data shows the possibility of Cu(+1) chloride layers formation and conservation in graphite matrix in the reaction with potassium and lithium. This is also an example of the intercalation of a low oxidation state of a transition metal chloride.

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