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Sébastien Cahen, Lucie Speyer, Philippe Lagrange, Claire Hérold. Topotactic Mechanisms Related to the Graphene Planes: Chemical Intercalation of Electron Donors into Graphite. *European Journal of Inorganic Chemistry*, 2019, 2019 (45), pp.4798-4806. <10.1002/ejic.201900758>. <hal-02393705>

HAL Id: hal-02393705

<https://hal.univ-lorraine.fr/hal-02393705v1>

Submitted on 31 Jan 2022

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Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201900758

Link to VoR: <http://dx.doi.org/10.1002/ejic.201900758>

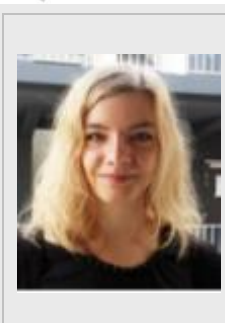
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Topotactic Mechanisms Related to the Graphene Planes: Chemical Intercalation into Graphite of Electron Donors

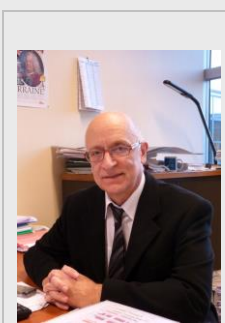
Cahen Sébastien ^[a], Speyer Lucie ^[a], Lagrange Philippe ^[a], and Hérold Claire*^[a]

Abstract: The intercalation into graphite of electron donor species belongs to the class of the two-dimensional topotactic reactions. During the intercalation, which requires an oxido-reduction between the reagents, the graphene planes, which form the skeleton of the host material, remain indeed quasi unaltered while their spacing is strongly expanded allowing the setting up of the guest reagent layers. Intercalation into graphite is so the prototype of the topotactic reaction. The intercalation mechanisms of these electron donors such as metals, metallic alloys and metal-(molecule, electronegative element) combinations have been significantly studied at length. They are especially numerous and greatly diversified. In this paper, we do not aim to depict all the known graphite intercalation compounds but to draw up an inventory of the whole of these mechanisms. The latter are systematically illustrated by means of several characteristic examples for each one. This significant diversity appears as a remarkable distinctive feature of graphite as host lamellar material.

Lucie Speyer is an assistant professor at the European School of materials science and engineering (University of Lorraine). Her research activity is realized at the Jean Lamour Institute of Nancy.



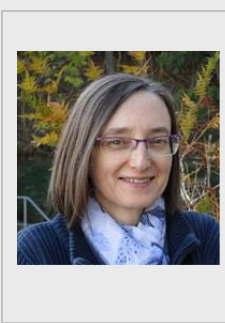
Philippe Lagrange is a senior researcher at the Jean Lamour Institute in Nancy. He taught chemistry during thirty six years and is now emeritus Professor at the University of Lorraine.



Sébastien Cahen is an assistant professor at the department of chemistry (University of Lorraine). His research activity is realized at the Jean Lamour Institute in Nancy (FR). He is member of the advisory board of the International Symposium on Intercalation Compounds.



Claire Hérold is a senior researcher in solid state chemistry at the Jean Lamour Institute in Nancy. She received a chemistry prize from the French Academy of Sciences in 2005 and the Japan Carbon Award for Innovative Research in 2008. She belongs to the board of the French Carbon Group.



Their work is focused on low dimensional carbon-based materials and especially intercalation chemistry. They investigate new synthesis routes of graphite intercalation compounds. They study elaboration, characterization and design of novel carbon materials.

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1. Introduction

Topotactic reactions are typically used in order to synthesize novel materials using solid-state chemistry routes. Among the possible hosts used for topotactic reactions by intercalation, graphite is a noteworthy host material, especially in the case of the insertion of metals and metallic alloys. Indeed, graphite appears easily as a very good electron acceptor towards the electron donors such as strongly electropositive elements, which abandon their outlying electron(s) without many difficulties.

The topic of this mini-review deals with the processes of homogeneous intercalation into graphite of the numerous electron donor species able to react with this carbon layered material: metals, metallic alloys and metals in association with electronegative elements or covalent molecules. Only the chemical intercalation reactions are taken into account, while the electrochemical ones are excluded of this focus. The understanding of intercalation mechanisms leading to homogeneous compounds is discussed in order to support future chemical or physical characterizations of such Graphite Intercalation Compounds (GIC).

Graphite is a stacking of mono-atomic hexagonal graphene layers whose carbon atoms are sp^2 hybridized.^[1] These graphene planes are solidly built by means of strong covalent bonds, whereas very weak van der Waals's bonds allow their cohesion as an ordered stacking. During the intercalation reaction, two simultaneous phenomena occur:^[2]

- a translation of the graphene planes leading to a AAA stacking occurs simultaneously with an opening of the graphitic intervals (also called interlayer/van der Waal's galleries or gaps), allowing the putting up of the reagent between the graphene layers, which remain almost unaltered;

- an electron transfer appears between graphene and reagent, generating an oxido-reduction process: in the case of the metallic reagents, the graphene planes are reduced by intercalated metals or metallic alloys.

Such reactions that preserve the structural skeleton of the pristine material are called topotactic reactions. They imply no break of strong chemical bonds, so that they occur with a weak consumption of energy and a modification of the repeat distance l_c (Figure 1).

As it is largely explained in the following paragraphs, several methods can be used in order to synthesize these electron donor GIC. According to the selected preparation route and the nature of the species to intercalate, we observe that the intercalation mechanisms are particularly varied. So, it is important to describe all the reaction mechanisms that have been identified through the numerous syntheses of GIC obtained with electron donor species. It is precisely the purpose of this paper in which reactions can be classified in several families. In each case, we systematically provide an illustration through one or two examples only, so that our goal does not aim exhaustiveness of all these GIC but rather to draw up an inventory of all reaction mechanisms. Alkali metals, alkaline earth metals and several lanthanides are various elements able to intercalate into graphite by themselves. Intercalation reactions occur together with an electron transfer from metal to graphite, what is easily explained considering the

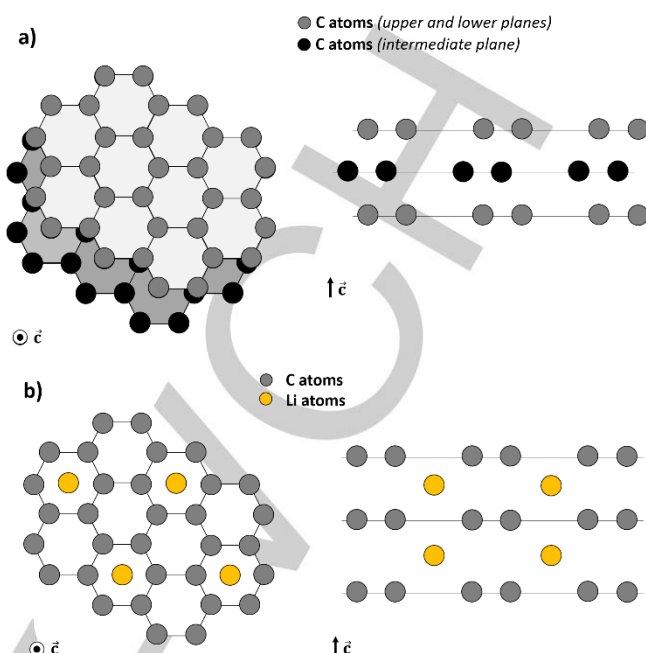


Figure 1. Topotactic intercalation of lithium into graphite (the graphene planes remain undamaged):

a) pristine hexagonal graphite ($l_c = 335$ pm). The c -axis stacking of the graphene planes is ABAB...

b) first stage LiC_6 binary compound ($l_c = 370$ pm). The host structure is expanded along the c -axis and the graphene planes are henceforth exactly superimposed according to the AAA... stacking.

high electropositivity of these metals. The product of such a reaction is of course a binary compound.

Other metals whose electronegativity is higher can also intercalate but only if a second metal very strongly electropositive assists them (i. e. an alkali metal). In these systems, the reaction product is sometimes a binary compound but most often a ternary one.

Very small amounts of an electronegative element (such as oxygen or sulphur) dissolved in alkali metals can also be intercalated, leading to donor-type compounds. The intercalation reaction leads once again to ternary donor-type GIC and it significantly resembles to the previous ones.

In another scenario, different metals intercalate as soon as they are dissolved in a suitable molten salts medium, graphite sample being plunged in this mixture. The reaction product is henceforth a binary phase.

Many other even more complex phases can be synthesized by the mean of several successive interventions of the experimenter. These practical works (called ternarization and even quaternarization) lead indeed to ternary or quaternary particularly sophisticated compounds.

A specific family of ternarized compounds can be highlighted and presented separately, i.e. the alkali metal binary compounds able to physisorb different gas as dihydrogen for instance. The so-obtained ternary phases are stable only at low temperature.

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In the similar manner, some much more complex molecules as ammonia, hydrocarbons or dimethylsulfoxide for instance are able to solvate intercalated alkali metal cations inside the van der Waals's galleries even at ambient temperature.

The guest species that sets up between the graphene planes can saturate all the graphitic intervals, but can equally occupy only a part of these van der Waals's gaps. For this reason, it is necessary to specify the "stage" n of the GIC. It is an integer that indicates the number of superimposed graphene planes included between two successive intercalated sheets (for instance, a stage 1 compound is saturated, while in the case of a stage 2 compound, only the half of the intervals is occupied, etc...). This "staging" phenomenon is a distinctive feature of graphite, especially concerning very high stage GIC ($n > 3$), and it is very little common in the case of other layered structures able to lead to intercalation reactions even if it is however mentioned for instance in borocarbonitrides, layered double hydroxydes or transition metal dichalcogenides.^[3-5]

The intercalation reactions into graphite take place generally between solid graphite and gaseous or liquid reagent (metal vapour, liquid metal, liquid alloy or dissolved metal into liquid medium). We underline below how much the corresponding intercalation mechanisms are especially diversified.

2. Direct intercalation by staging

Intercalation by Chemical Vapor Transport (CVT) of metal is the simplest and the first of all the procedures. Indeed a volatile metal is heated with graphite in a closed tube sealed under secondary vacuum. Excellent results are obtained with potassium, rubidium and caesium.^[6-8] The reaction is more difficult in the cases of lithium^[9] or sodium,^[10-12] and alkaline earth metals,^[13] and even more with a few lanthanides^[14] as samarium, europium, thulium and ytterbium. Depending on the metal-graphite system, three situations are known: 1st stage-GIC can be prepared, mixtures of graphite and 1st stage compounds can be observed, or in the specific case of Na only high stage GIC are reported.

In the ideal case of potassium for instance, a well-known mechanism takes place by successive stages. The potassium atoms attack graphite by the edges of the graphene planes; they spread apart the van der Waals's gaps and occupy the so open intervals. At first, one interval in n only is occupied by mono-atomic potassium layer (stage n compound) then one interval in $(n-1)$ etc...^[15] Finally, all the intervals are occupied (stage 1 compound) leading to a binary phase whose chemical formula is KC_8 with the c -axis stacking sequence written C-K-C-K-C...

In the less favorable cases (Sr, Ba, lanthanides), only superficial intercalation is observed, so that the corresponding bulk GIC cannot be obtained by this way.

It is interesting to return to the concept of stage. Indeed, during such an intercalation, it is observed that the stage n GIC transforms into $(n - 1)$ one. This modification is particularly significant since it concerns a large de-intercalation / re-intercalation atomic movement, that seems however little credible. For this reason, the Daumas-Hérold model^[16-18] suggests a transformation more plausible. It considers that in a stage n GIC, all the van der Waals's galleries are intercalated, but only partly. Indeed in each gallery, the filling factor reaches exclusively the value of $1/n$. Along the c -axis, these intercalated zones get into position in such a way that they reappear every n gaps. Moreover, thanks to this model, the passage from stage n to stage $(n - 1)$ requires only a much weaker atomic transfer (Fig. 2). In order to try to displace the intercalation equilibrium, it is also possible to put the liquid metal in contact with graphite. In that case, the intercalation reaction becomes extremely fast, but the staging process remains the same one. K, Rb and Cs for instance intercalate with a large ease by this way.^[19]

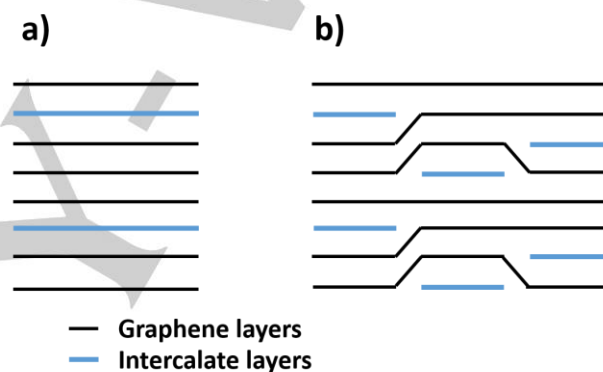


Figure 2. Schematic representation of a stage 3 GIC:

- a) Rüdorff's model
b) Daumas-Hérold's model (folded graphene sheets).

A molten alloy of two alkali metals, Rb-Cs for instance, can intercalate also without difficulty into graphite. As previously, the mechanism takes place once again by successive stages. In this case, the reaction product is a first stage ternary phase also called co-intercalation compound, for which the intercalated sheets are mono-atomic layers constituted by a 2D disordered alloy.^[20] It is, in this example, a solid solution of both RbC_8 and CsC_8 binary compounds, whose chemical formula has to be written $Rb_xCs_{1-x}C_8$ with $0 \leq x \leq 1$. It has been shown that this solid solution can be obtained in any proportion. In addition, the spacing of the graphitic galleries varies according to its composition.

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3. Mechanism of intercalation by successive steps

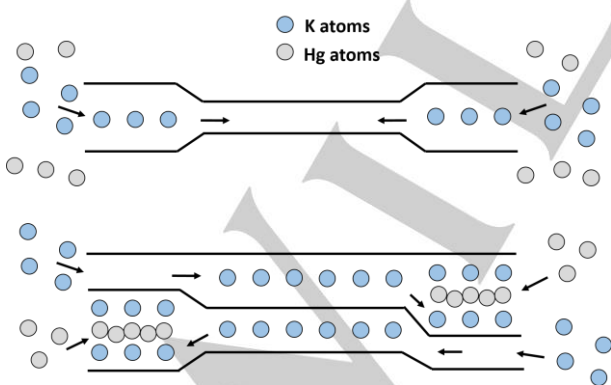
3.1. Reaction between graphite and a liquid alloy

Synthesis of ternary compounds

Associated with K, Rb or Cs, several metals (Hg, Tl, Au)^[21-25] and semi-metals (As, Sb, Bi)^[26-29] totally unable to intercalate by themselves into graphite become able to intercalate since the alkali metal and the second one remain combined inside the intercalated sheets. In this case, the reaction product is of course a ternary compound, but not constituted of mono-atomic intercalated sheets.

For these reactions, platelets of pyrolytic graphite are preferably used. A bulk graphite sample is plunged in a homogeneous binary liquid alloy,^[30] so that the reaction takes place between a solid and a liquid. The well-known case of the KHg amalgam is chosen here to illustrate this kind of intercalation.

The liquid KHg alloy easily intercalates into graphite by means of two successive steps.^[31] Firstly, potassium penetrates alone in the van der Waals's intervals, while mercury remains in the reactive liquid. The end of this step is characterized by the formation of the previously described first stage KC_8 binary phase: it is a selective intercalation of potassium. It is very easy for the alkali metal to spread apart the graphene layers and to intercalate. Consecutively to the spacing of the C planes, a second step occurs that completes the reaction. In this step, potassium and mercury intercalate simultaneously, increasing again the distance between the graphene planes: it is a simultaneous cooperative intercalation of both metals. During this second step, no change of stage occurs, but the nature of the intercalated sheets is completely transformed. Thick three-layered K-Hg-K intercalated sheets replace the previous potassium monolayers. The chemical formula of this ternary compound writes $KHgC_4$. This phase is obviously particularly rich in metal and contains twice as many potassium as KC_8 compound (Scheme 1).



Scheme 1. Schematic representation of the intercalation into graphite of the KHg amalgam. First step: selective intercalation of potassium by staging mechanism (1st stage KC_8 with $l_c = 535$ pm); second step: simultaneous cooperative intercalation of both potassium and mercury (1st stage $KHgC_4$ with $l_c = 1016$ pm). Arrows represent the migration path of atoms.

Another comparable mechanism has been pointed out during the reaction of liquid lithium-europium alloys with graphite. At first, lithium spreads apart the graphene planes and intercalates alone, and finally both lithium and europium intercalate simultaneously. At the end of the intercalation, the obtained ternary phase is a first stage compound of formula $Li_{0.2}Eu_2C_6$, for which the intercalated sheets are also three-layered, according to the Li-Eu-Li *c*-axis sequence.^[32,33]

Similar reactions occur with suitable alloys in the (K, Rb, Cs)-(As, Sb, Bi),^[19-22] (K,Rb)-(Hg,Tl),^[21-22] K-Au^[23] and also Li-Ca^[34] systems leading every time to ternary compounds for which the poly-layered intercalated sheets can be even more complex.

A representative example of a poly-layered sheet can be observed in the case of the intercalation of a potassium-thallium alloy. At the end of the reaction (after both first and second steps), the synthesized GIC is a ternary phase of formula $KTl_{1.5}C_4$. Its intercalated sheets are five-layered and consequently extremely thick ($l_c = 1210$ pm) and correspond to the K-Tl-Tl-Tl-K *c*-axis stacking sequence (Fig. 3).^[35]

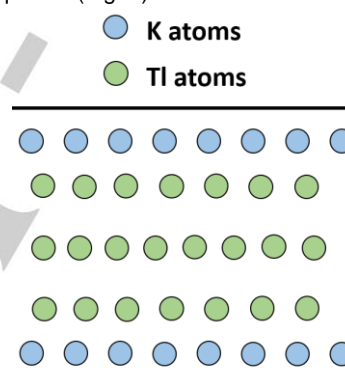


Figure 3. Five-layered potassium-thallium intercalated sheets into graphite (1st stage $KTl_{1.5}C_4$ with $l_c = 1210$ pm).

On one hand, all the ternary phases obtained in the abovementioned systems systematically contain poly-layered intercalated sheets. It should be highlighted that the chemical composition of the intercalated alloy is usually different from that of the reactive one. On the other hand, according to an unexpected process, such synthesis routes also allow to prepare binary GIC as detailed in the next section.

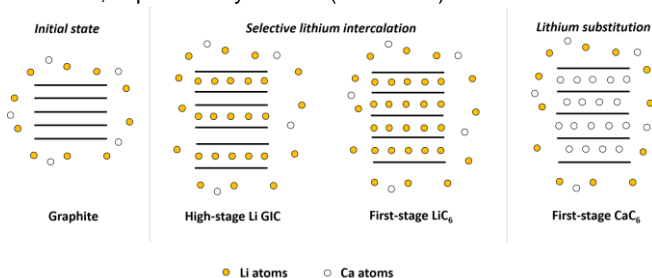
Synthesis of binary compounds

Lithium and calcium intercalate by themselves into graphite. By vapour phase method, the reactions are quite difficult, especially because these metals are insufficiently electropositive (case of calcium for instance). As a consequence, it is almost impossible to prepare a bulk first stage CaC_6 compound using CVT process.

Nevertheless, liquid calcium-lithium alloys rapidly react with graphite leading to this binary compound.^[36] As previously, two successive steps occur during synthesis. At first, lithium intercalates alone between the graphene planes leading to the

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first stage saturated LiC_6 binary compound (all the intervals are of course occupied by mono-atomic lithium layers). It is a selective intercalation of lithium. Then, calcium enters the van der Waals's galleries, substituting the lithium atoms with this last metal: that is how LiC_6 turns into CaC_6 . The mono-atomic lithium layers are replaced by mono-atomic calcium ones. It is a mechanism of intercalation-substitution which is due to the fact that, in these experimental conditions, CaC_6 is the thermodynamically stable phase. By this way, it is possible to successfully synthesize a bulk CaC_6 first stage GIC, whose direct synthesis, as previously indicated, is particularly difficult (Scheme 2).



Scheme 2. Schematic representation of the intercalation into graphite of calcium starting from a liquid Li-Ca binary alloy.

First step: selective intercalation of lithium by staging mechanism (1st stage LiC_6); second step: evacuation of lithium, which is replaced by calcium (1st stage CaC_6 with $l_c = 453$ pm).

In the same manner and by using Li-based molten alloys, the bulk binary BaC_6 and EuC_6 GIC have been prepared, whereas their direct synthesis remains largely not easy.^[37,38]

3.2. Reaction between graphite and a liquid metal doped with an electronegative element

Liquid alkali metals (as potassium for instance) are able to dissolve very small amounts (a few at. %) of an electronegative element such as some halogens, oxygen, sulphur, selenium, phosphorus...^[39-43] It is possible to observe fast reactions between graphite and such liquids. The reaction products are first stage ternary compounds that greatly resemble the ternary GIC obtained in the case of the reactions between graphite and liquid alloys. The intercalated sheets are three-layered too, according to the *c*-axis K-third element-K sequence.

The real difference lies in the fact that the central layer contains an especially small amount of the electronegative element. Indeed its electronegativity is high enough in order to build a three-layered sheet with much less atoms (Fig. 4). For instance, the GIC chemical composition is $\text{KC}_{3.7}\text{O}_{0.08}$ for the poorer in electronegative element, and $\text{KC}_{3.3}\text{S}_{0.24}$ for the richer.

The reaction mechanisms have to be the same in both cases (metallic alloy and metal doped with an electronegative element): at first, selective intercalation of potassium leading to binary GIC with mono-layered intercalated sheets, then simultaneous cooperative intercalation of potassium and the third element leading to a rearrangement as three-layered intercalated sheets.

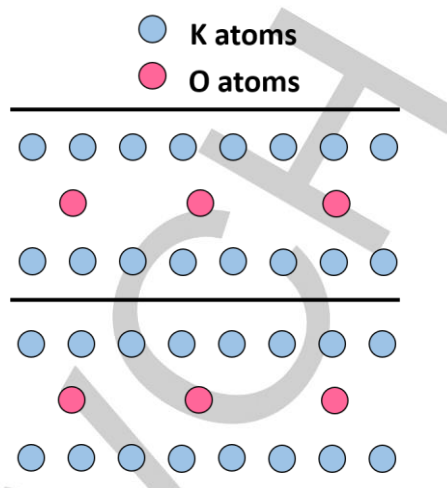
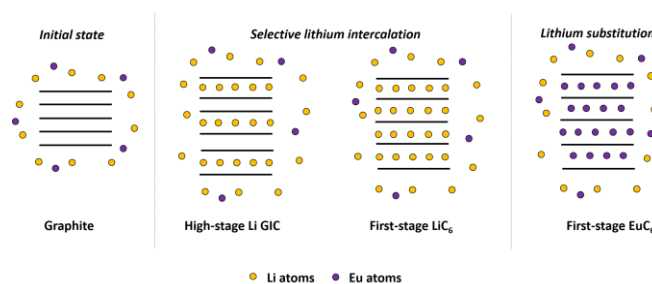


Figure 4. Three-layered potassium-oxygen intercalated sheets between graphene planes ($\text{KC}_{3.7}\text{O}_{0.08}$ with $l_c = 850$ pm).

3.3. Mechanism of intercalation into graphite by reaction with a metal introduced in a molten salts medium

Using the LiCl-KCl liquid eutectic in which is dissolved a metal quite struggled to intercalate by itself into graphite, it can be possible to make greatly easier the topotactic reaction.^[44-45] The case of europium is a typical example for this intercalation method. A graphite platelet is plunged in the molten eutectic containing dissolved europium. The final reaction product is the first stage EuC_6 compound for which all the graphitic intervals are occupied by mono-atomic europium layers.^[46] The intercalation of europium occurs by a three steps mechanism. Firstly, the Eu metal reduces Li^+ cations into Li metal. The latter is then intercalated by staging into graphite giving rise to the first stage LiC_6 GIC. After that, europium get rid of Li intercalated species. These latter are finally totally substituted with europium ones in the 2D galleries until the formation of pure first stage EuC_6 . It is once again an intercalation-substitution process (Scheme 3).



Scheme 3. Schematic representation of the intercalation into graphite of europium starting from europium dissolved in the LiCl-KCl molten eutectic.

First step: Eu metal reduces Li^+ cations into Li metal within the liquid (not shown); second step: selective intercalation of lithium by staging mechanism (1st stage LiC_6); third step: evacuation of lithium, which is replaced by europium (1st stage EuC_6 with $l_c = 490$ pm).

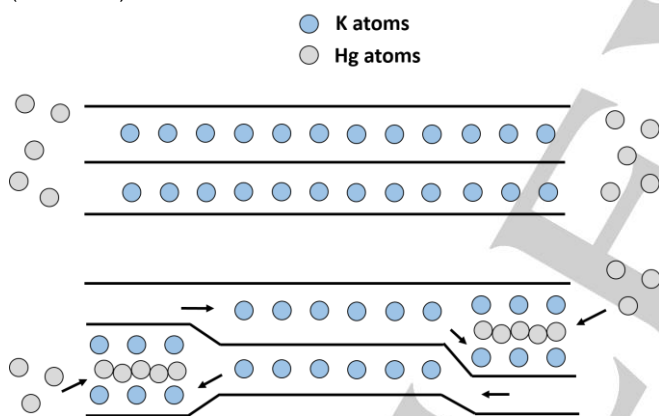
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Both SrC_6 and BaC_6 bulk first stage GIC^[47] are also synthesized using this method that appears as a particularly efficient route to prepare these bulk compounds. Moreover, currently, no other method is able to lead to bulk SrC_6 samples.

4. Synthesis of a ternary compound from a binary one (ternarization phenomenon)

The formation of a ternary GIC can be obtained from a binary one using a method requiring a double intervention of the experimenter. A typical example is given in the case of the graphite-potassium-mercury system. In the latter, the preparation of the second stage KHgC_8 GIC previously needs the obtaining of the first stage KC_8 binary one.^[31]

KC_8 is easily obtained by CVT method. The sample is then heated under vacuum in a closed tube containing also liquid mercury. The latter vaporizes under the effect of the temperature, and its vapour can thus react with the intercalated potassium monolayers. In each gallery, the potassium plane splits and translates creating two superimposed layers stabilized by an intermediate mercury plane. Henceforth the intercalated potassium monolayers evolve towards their replacement by K-Hg-K three-layered sheets. The half of the van der Waals's gaps is consequently released, so that the reaction product is a second stage GIC of formula KHgC_8 (Scheme 4).



Scheme 4. Schematic representation of the ternarization by mercury of the 1st stage KC_8 GIC leading to 2nd stage KHgC_8 with $l_c = 1016 + 335 = 1351$ pm. Arrows represent the migration path of atoms.

The same phenomenon is observed when hydrogen reacts with the first stage KC_8 GIC.^[48] Indeed, the reaction product is again a second stage compound, whose chemical formula writes $\text{KH}_{2/3}\text{C}_8$. Its intercalated sheets are three-layered according to the K-H-K c-axis stacking.

This kind of reaction appears as a double intercalation with stage increase.

5. Bi-intercalation

This mechanism mainly consists in transforming a second stage ternary GIC into a quaternary one, and it requires also several interventions of the experimenter. The most representative example will be described above and needs at first the synthesis of a second stage $\text{KH}_{2/3}\text{C}_8$ GIC.

This $\text{KH}_{2/3}\text{C}_8$ ternary is subjected to a vapour of a heavy alkali metal M (M = K, Rb or Cs). If the reaction temperature is weak enough, the alkali metal vapour does not attack the three-layered intercalated sheets, but selects only to intercalate into the empty galleries.^[49] Henceforth all the graphitic intervals are occupied as in a first stage compound, but the half of them contains K-H-K three-layered sheets and the other half M mono-layered ones, according to the c-axis alternate sequence C-K-H-K-C-M-C... The formula of this metastable bi-intercalation compound writes $\text{MK}_2\text{H}_{4/3}\text{C}_{16}$ or more explicitly $[\text{K}_2\text{H}_{4/3}\text{C}_8, \text{MC}_8]$ (Fig. 5).

In opposition with the aforementioned ternarization mechanism, this bi-intercalation reaction mechanism turns out to be a double intercalation with stage decrease.

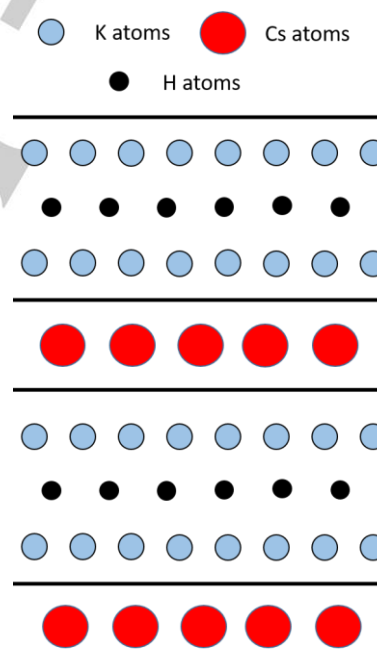


Figure 5. Representation of the quaternary bi-intercalation $[\text{K}_2\text{H}_{4/3}\text{C}_8, \text{CsC}_8]$ GIC ($l_c = 853 + 592 = 1445$ pm).

6. Physintercalation of molecules into a binary alkali metal GIC

Due to the electron transfer that occurs during the intercalation reaction, the binary alkali metal GIC include some cationic species between their graphene planes. These positive species are able to interact with various molecules by means of van der Waals's bonds. Consequently, these molecules do not undergo any dissociation since they are fixed by physisorption. This

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phenomenon occurs inside the intercalated sheets, so that it is called "physintercalation".

According to the nature of the physisorbed molecule, the final compound is only stable at low temperatures (greatly volatile species – i. e. dihydrogen) or contrarily is also stable at room temperature (liquid species – i. e. NH_3 , benzene, THF).

6.1. Physintercalation of dihydrogen into a second stage alkali metal GIC

The density of the monolayers present in the second stage alkali metal (K for instance) GIC is noticeably less large than the one of the metal layers contained in the corresponding first stage compounds. The C/K atomic ratios reach respectively 24 for the second stage and 8 for the first one. If these ratios are related to an unique adjacent graphene plane in both cases, they become 12 (second stage) and 8 (first stage). Considering the transformation from first stage to second stage GIC, this difference in the chemical composition is due to K dilution along the *c*-axis and in the *ab* plane too. Thus, the density of the potassium layers is 1.5 time higher in the first stage. Consequently, the second stage compound has to include some empty spaces inside the intercalated layers. This difference is well illustrated by the ability of KC_{24} to physisorb dihydrogen at low temperature (liquid nitrogen: 77.4 K), while KC_8 appears entirely ineffective.^[50-52]

At H_2 saturation, KC_{24} physisorbs two dihydrogen molecules per potassium atom (formula KC_{24} , 2 H_2). The mechanism of this physintercalation needs to put in order the voids in the potassium layers. Indeed, at room temperature, these potassium monolayers are in liquid state. Nevertheless, a structural organization of the intercalated atoms appears in these planes when the cooling occurs.^[53] This reorganization is particularly complex, but it allows however the H_2 molecules to accommodate in the heart of these loose intercalated potassium layers. Dihydrogen and potassium are thus co-intercalated in the van der Waals's galleries, henceforth filled with mixed monolayers. After reaction, the stage of the GIC is of course unmodified. Moreover, the spacing of the galleries remains perfectly unaltered.

Furthermore, it has been shown that this phenomenon is purely physisorption, since the H_2 molecules are not split up during their sorption thanks to the setting-up of van der Waals's bonds with metallic cations. This molecular condensation at low temperature has been envisaged for molecular sieve application.

Finally, a rise of temperature releases the H_2 molecules out of the solid and the KC_{24} phase is perfectly regenerated.

Some other diatomic molecules (N_2 , CO) are able to physisorb into KC_{24} too. However, these molecules are very much sizeable than H_2 , so that the amount of fixed gas at the saturation is noticeably lower.

6.2. Case of the graphite-metal-molecule ternary compounds

Very numerous graphite intercalation compounds belonging to this category have been synthesized during several decades.^[54-55] In these ternary compounds, the intercalated metal is essentially an alkali metal (Li, Na, K, Rb, Cs), and an emblematic associated

molecule is NH_3 . However, many other molecules, mostly organic, were used for these syntheses (HMPT, benzene, toluene, ethane, ethylene, acetylene, hexane, DMSO, furan, THF, dioxan, DMF, crown-ethers, diamines, etc...).

The first method, which is largely used in the case of ammonia, consists in dissolving an alkali metal or an alkaline earth one into pure liquid ammonia at low temperature (solid carbon dioxide: 194.5 K). A graphite sample is immersed in the so-obtained dark blue solution, so that the intercalation reaction occurs. Metal and ammonia penetrate simultaneously in the graphitic galleries leading to mixed intercalated sheets. However, the specific mechanism of this intercalation is not well known due to lack of peculiar studies. A well able example illustrating this kind of topotactic reaction consists in the first stage graphite-potassium-ammonia whose chemical formula is written $\text{K}(\text{NH}_3)_{4.3}\text{C}_{24}$ (Fig. 6).^[56]

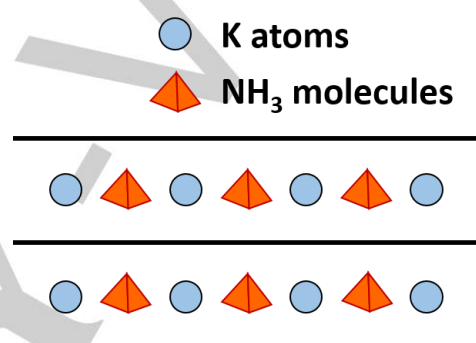


Figure 6. Schematic representation of the 1st stage $\text{K}(\text{NH}_3)_{4.3}\text{C}_{24}$ GIC showing mixed intercalated sheets

A second method was systematically used in the case of all the previously cited organic molecules. It is exactly identical to the ternarization, which is described in part 4. A binary graphite-alkali metal compound (stage 1 or higher) is subjected to the vapour of ammonia or of the organic species. The mechanism is the following: the molecules penetrate into the occupied galleries in order to solvate the already intercalated metallic cations. Ultimately, as previously, the intercalated sheets appear as mixed. Once again, a rearrangement of the metal atoms in the van der Waals's gaps occurs in order to allow the molecular solvation. The intercalated sheets remain quite often mono-layered (sometimes however they become poly-layered) with an increase of the repeat distance. Among a huge collection of compounds, here are four examples of first or second stage compounds obtained by means of this mechanism:

$\text{K}(\text{C}_6\text{H}_6)_{2.2}\text{C}_{24}$	stage 1 graphite-potassium-benzene ^[57]
$\text{Cs}_x(\text{C}_6\text{H}_{14})_{0.59}\text{C}_{30}$	stage 2 graphite-caesium-(n-hexane) ^[58]
$\text{K}(\text{C}_4\text{H}_4\text{O})_{0.76}\text{C}_8$	stage 1 graphite-potassium-furan ^[59]
$\text{K}(\text{C}_{10}\text{H}_{20}\text{O}_5)\text{C}_x$	stage 1 graphite-potassium-(15-crown-5 ether) ^[60]

In the case of these ternary physintercalated compounds, the structural organization of the intercalated sheets is especially diversified. For instance, starting from a 2nd stage KC_{24} compound, ternarization leads to the obtaining of either second or first stage GIC, depending on the nature of the intercalated molecule.

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7. Conclusion

The whole of all these examples clearly illustrates the significant diversity of the reactivity of graphite towards several media. This paper highlights that numerous methods are able to lead to the topotactic intercalation of metals (pure or combined with other species) and metallic alloys into graphite, which is a particularly welcoming host material for the electron donor guest species. These methods make use of many intercalation mechanisms particularly specific to this lamellar solid: staging, co-intercalation, selective intercalation, simultaneous cooperative intercalation, intercalation-substitution, ternarization, bi-intercalation, physintercalation, etc... This very large variety of mechanisms is probably a unique case in the field of the 2D topotactic intercalation reactions.

The liquid metallic alloys method has allowed to greatly open the possibilities to carry out numerous new syntheses during the past decades. The much more recent route using a molten salts medium is today very promising. Indeed, the novel results already obtained by this means are quite encouraging, concerning the synthesis of future new intercalation compounds.

Thanks to the variety of intercalation reactions, it is possible to prepare numerous GIC. Their chemical and physical properties are particularly interesting and largely studied around the world for their effective and potential applications.^[54-55]

Exfoliation is a huge and active field of research concerning the preparation of graphene, and intercalation into graphite plays a key role for solving this issue.^[61]

The understanding of the intercalation mechanisms in GIC is useful for both experimental and theoretical studies concerning alkali metal-ion battery future technologies with lithium, sodium and potassium.^[62-64]

The study of physical properties is a large field of research including magnetism, superconductivity or electrical conductivity. In order to increase the knowledge in the different models dealing with superconductivity, GIC are ideal two-dimensional compounds for establishing structure-physical properties relationships. For instance, several works have been carried out in order to study the influence of the intercalated layer on superconductivity in K-based and Ca-based GIC.^[65-68] The intercalation of various species will also drastically modify the electrical conductivity and anisotropy compared to pristine graphite.^[69-70]

Finally, the knowledge of the formation mechanisms of GIC can also be useful for the calculation of various physical properties concerning this class of materials.^[71]

Keywords: intercalations • graphene • topochemistry • reaction mechanisms • layered compounds

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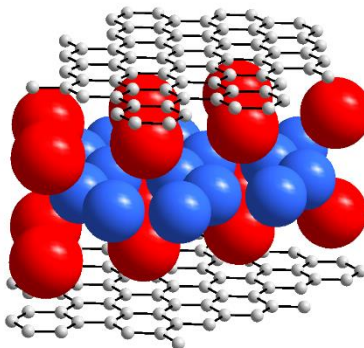
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All the mechanisms of intercalation of electron donors into graphite by a lot of methods are systematically listed. These topotactic reactions lead to layered compounds showing unexpected chemical and physical properties and appearing often as quantum materials (superconductivity, magnetic order). They lead also to interesting applications (electrodes of Li-ion batteries).



**intercalations • graphene •
topochemistry • reaction mechanisms
• layered compounds**

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C**

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**Ternary KHgC_4 GIC synthesized after
topotactic intercalation**