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Structural study and crystal chemistry of the first stage calcium graphite intercalation compound

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Abstract

A novel and efficient synthesis method concerning the preparation of the first stage calcium graphite intercalation compound is provided. It makes use of a reaction between liquid metallic alloy and pyrolytic graphite. From now on it is especially easy to obtain bulk CaC_6 samples. Thanks to such samples, it was possible to study in detail the crystal structure of this binary intercalation compound. It has been entirely specified, so that we know that CaC_6 crystal is rhombohedral and belongs to the $R\bar{3}m$ space group with the following parameters: $a = 517$ pm and $\alpha = 49.55°$. The elemental unit cell contains one calcium atom and six carbon atoms. In this paper, we show also how the various MC_6 structures evolve according to the size of the intercalated element and to the bond nature that appears in the final compound. CaC_6 is unique, since all the other MC_6 compounds exhibit a hexagonal symmetry.

Keywords: Graphite; Intercalation; Calcium; X-ray diffraction; Crystal structure; Charge transfer

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1. Introduction and synthesis

It is an obvious fact that the intercalation into graphite of the alkaline earth metals is much more difficult than the one of the alkali metals. Moreover, in these both columns of the periodic table, it is clear that the heavier elements exhibit a better ease to intercalate into graphite. Among the alkaline earth metals [1], barium and strontium intercalate rather easily, but, for calcium, the intercalation is largely more difficult. Indeed, the reaction between calcium vapour and a platelet of pyrolytic graphite leads only to a very slight intercalation, which is extremely superficial, and moreover the reaction temperature has to remain not very high, in order to avoid the formation of calcium carbide. For this reason, the study of the structure of the first stage graphite–calcium compound was not carried out up till now. The only known elements for this binary compound are its colour, which is very pale yellow with the characteristic metallic brightness, and the interlayer distance between graphene planes after intercalation that reaches 450 pm, instead of 335 pm in pristine graphite. The nature of the *c*-axis stacking of the metallic and graphene layers is unknown; therefore, it has been impossible to determine neither the symmetry and space group of the compound nor the atomic positions in the unit cell.

Recently, we have succeeded [2] in synthesising this compound in bulk and is almost pure. The reaction is carried out for ten days under argon atmosphere between a pyrolytic graphite platelet and a molten lithium–calcium alloy at around 350 °C. The reactive alloy is very rich in lithium and poor in calcium, since its composition corresponds to a Li/Ca ratio included between 3 and 4. Nevertheless, only the calcium is intercalated into graphite, so that, for this reaction, the main role of lithium is of course allowing the calcium

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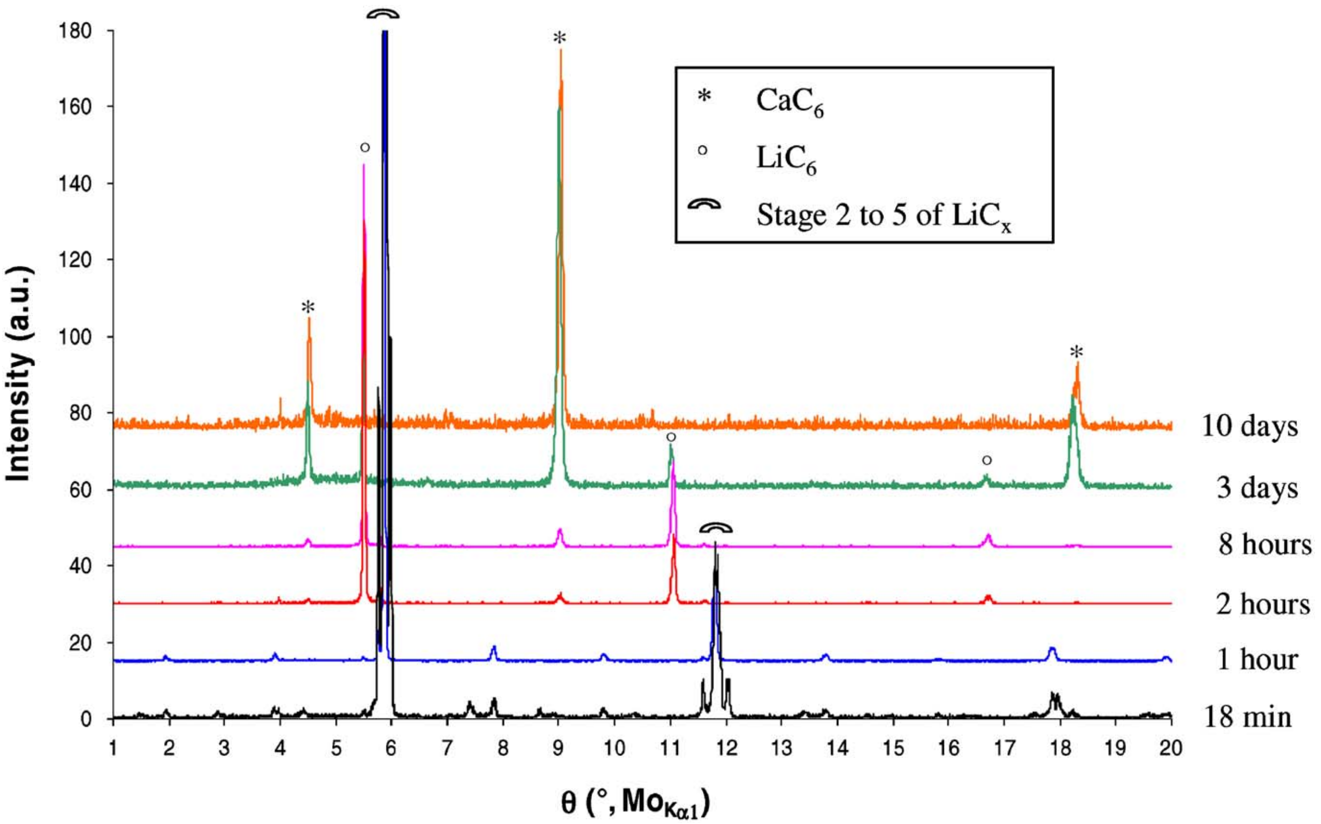

Fig. 1. The 0 0 *l* X-ray patterns (Mo*K*α1) registered at successive steps of the intercalation of Li–Ca alloy (Li/Ca = 3/1).

melting. In spite of its dilution, the liquid calcium retains a sufficiently high thermodynamical activity in order to intercalate into graphite. But it is likely that, concerning the kinetics, lithium plays also another role. Indeed, in the first time, only lithium intercalates leading to high stage binary compounds, and in the second time, the intercalated lithium is progressively replaced by calcium atoms until all graphitic intervals are occupied by calcium layers. The kinetic process is followed by X-ray diffraction (Fig. 1). In spite of the weak calcium concentration of the reactive alloy and the speed of lithium intercalation, it is clear that the thermodynamics strongly favours the calcium intercalation to the detriment of lithium. It is not allowed to entirely eliminate the possible presence of very weak lithium amount in calcium intercalated layers, but no experiment has shown this lithium existence.

Thanks to this novel synthesis process, it becomes possible to study and to determine the crystal structure of the first stage graphite–calcium intercalation compound, using a bulk sample obtained from a pyrolytic graphite platelet.

It is well established that the first stage binary graphite–metal intercalation compounds possess a very well specific stoichiometry corresponding to MC_8 for the biggest metals [3–5] and to MC_6 for the smallest ones [1,6,7]. Indeed, when the repeat distance is higher than 530 pm, the first stoichiometry is observed (K, Rb, Cs) and the second one, when this distance is smaller than 530 pm (Li, Sr, Ba, Eu, Yb). Consequently, for calcium, the expected chemical formula is then CaC_6. This stoichiometry [8] corresponds to an $AAA\ldots$ stacking for the successive graphene planes, so that all metal atoms are located in prismatic hexagonal sites: the adjacent graphene and metal planes are of course epitaxial. In each graphitic interval, one out of three prismatic sites is occupied by a metal atom, so that it appears in three different manners able to receive a metal plane in a graphitic interval (denoted α, β and γ). Three different *c*-axes stacking can be thus considered [6]:

$A\alpha A\alpha A\alpha A\alpha A\alpha\ldots$

$A\alpha A\beta A\alpha A\beta A\alpha\ldots$

$A\alpha A\beta A\gamma A\alpha A\beta\ldots$

In the first case, the c parameter of the unit cell is obviously identical to the repeat distance ($c = d_i$). For the second stacking, $c = 2d_i$; and for the third one, $c = 3d_i$. The first and the second stackings lead to a hexagonal crystal symmetry, since the third one, on the contrary, corresponds to a rhombohedral symmetry (Fig. 2).

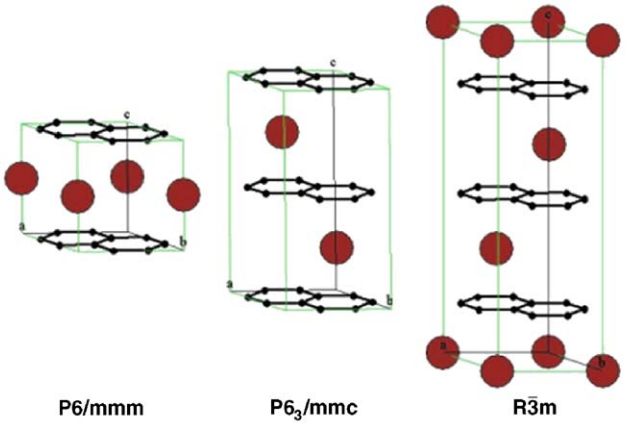

Fig. 2. Possible structures for binary MC_6 graphite intercalation compounds.

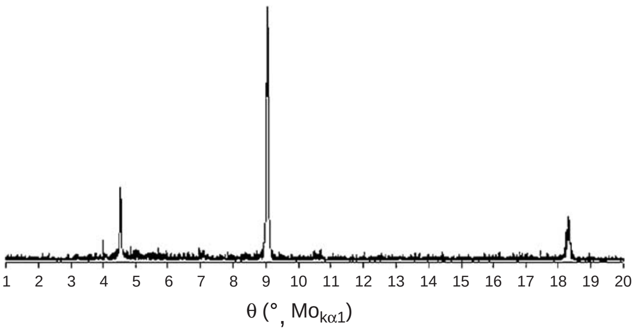

Fig. 3. The 0 0 l X-ray diagram (Mo$K\alpha$1) of CaC_6.

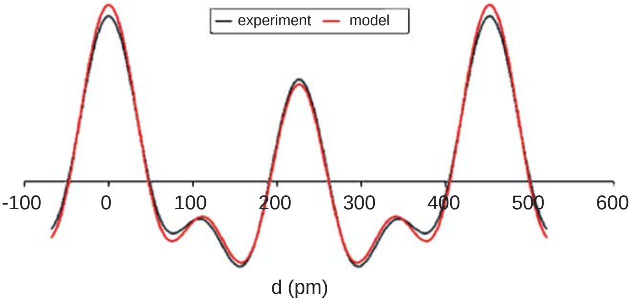

Fig. 4. The 1D electronic density profiles (calculated and experimental) along the c-axis of CaC_6 (residual factor 6.7% calculated from structure factors).

The first stacking has been observed only for LiC_6 [7]. And the other known MC_6 compounds (SrC_6, BaC_6, EuC_6, SmC_6 and YbC_6) select all the second stacking [1,6,9]. Consequently, all these binary compounds exhibit systematically a hexagonal crystal structure.

In the following report, we show that CaC_6 is different, since its symmetry is rhombohedral according to the third stacking.

2. Experiments and results

Thanks to the characteristic texture of the pyrolytic graphite, the graphite–calcium compound obtained from such a sample is able to reveal the diagram of the 0 0 l reflections alone by X-ray diffraction (Fig. 3). The position of these reflections gives directly the value of the repeat distance of the compound. In order to obtain a very accurate value, the bulk sample is plunged in diamond powder, which constitutes an internal standard, before the adjustment of its orientation compared with the X-rays beam. This repeat distance is equal to 452.4 pm, so that the binary graphite–calcium compound belongs in principle to the category of the MC_6 phases, since it is less than 530 pm.

Using their structure factors, the intensities of the 0 0 l reflections allow besides to draw the c-axis electronic density profile of the compound (Fig. 4). This experimental profile is compared with another that is obtained from a one-dimensional model: along the c-axis, the calcium and carbon atoms are arranged according to successive alternated layers. The carbon ones contain n carbon atoms, whereas the metallic ones consist of one calcium atom. On the other hand, the distance between two atoms layers is chosen of course as half the repeat distance. Consequently, the unique adjustable parameter of the model is n (number of carbon atoms for one calcium atom), so that it is possible to determine the n value, which leads to an optimal agreement between both profiles. After several testings, we observe that the best agreement is reached for $n = 6$ (Fig. 4). The value of the residual factor is 6.7% using the structure factors, and only 3% using the intensities. This result shows that the chemical formula of the compound has to be written CaC_6, according to the previous forecast. At last, this latter stoichiometry has been confirmed with precision by means of nuclear microprobe [2].

The study of the $hk0$ and hkl reflections of the compound has to confirm its particular stoichiometry. Indeed, if we consider the projection of the calcium atoms plane on the adjacent graphene plane, the MC_6 formula leads to a characteristic 2D hexagonal unit cell, whose a parameter is close to $a_G\sqrt{3}$ (with $a_G = 246$ pm), if we ignore the dilation of the graphene plane caused by the electron transfer from the calcium atoms to the carbon sheets. Another and frequently used notation for this 2D cell is the following: $\sqrt{3}.\sqrt{3}\ R\ 30°$, which reveals the shift of 30° between the 2D graphene cell and the MC_6 one. In order to know the value of this a parameter, a particularly interesting way consists in carrying out a diffraction pattern by the rotating crystal method (Fig. 5). The horizontal strata are easily identified and numbered. And we observe, in the perpendicular direction, the [hk] rows, whose first one corresponds to [10] with the reticular distance of $a\sqrt{3}/2$. The calculation of a gives the value of approximately 433 pm, which is very close to $a_G\sqrt{3}$. Consequently, this

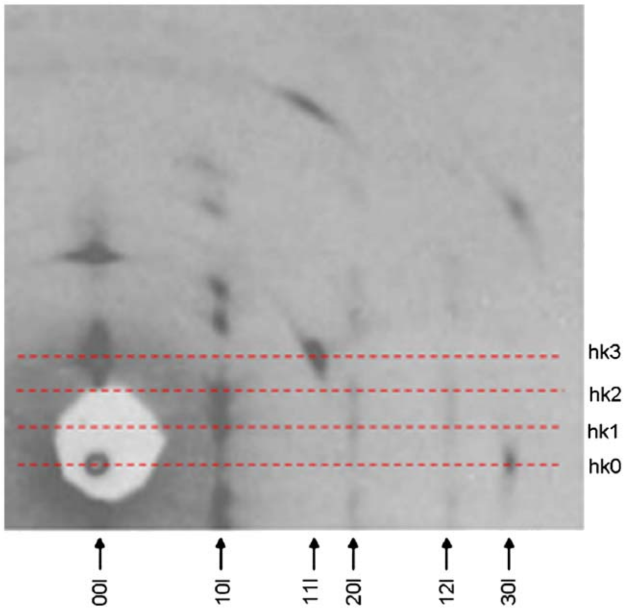

Fig. 5. “Rotating crystal” pattern obtained by X-ray diffraction (Mo anticathod) of the CaC_6 compound.

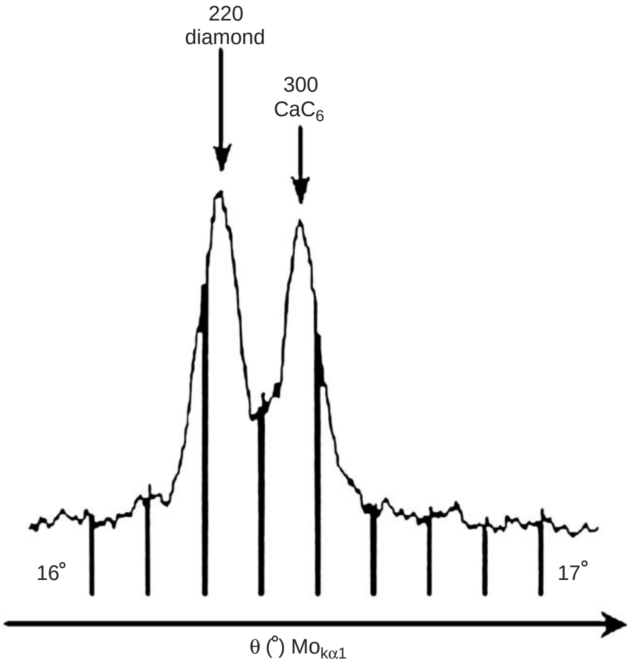

Fig. 6. The $hk0$ X-ray diagram of the CaC_6 compound showing its 300 reflection and the 220 reflection of diamond powder used as internal standard.

result appears as an additional confirmation of the CaC_6 stoichiometry.

The positions of the following [*hk*] rows are in good agreement with this previous 2D hexagonal unit cell. For instance, the [11] row, which corresponds to a reticular distance of 216 pm, corresponds also to the [10] row of the 2D graphene unit cell ($a_G = 246$ pm).

If we analyse in detail the [10] row of the diffraction pattern, it appears clearly that the reticular distance corresponding to the space between two successive strata reaches the value of 1357.2 pm. It is obviously the value of the *c* parameter of the 3D hexagonal unit cell of the compound. Consequently, this parameter is three times as much as the repeat distance ($1357.2 = 3 \times 452.4$). This phenomenon can obviously be attributed to the $A\alpha A\beta A\gamma A\alpha A\beta\ldots$ specific stacking. But other observations have to confirm this interpretation.

Along the same [10] row, there is no reflection on the zero stratum, and, similarly, the reflections are lacking on the 3 and 6 strata. These specific lacks are very characteristic of the previous stacking, since they appear as systematic extinctions in this system. On the whole, the hkl reflections of the diffraction pattern obey the general diffraction condition: $-h+k+l = 3n$. This result is a good confirmation of the proposed model for the *c*-axis calcium planes stacking.

We know that, with this stacking, the symmetry of the crystal is not hexagonal but rhombohedral. The specific symmetries of the stacking lead to the $R\bar{3}m$ space group for the CaC_6 crystal. But in order to simplify their representation, the rhombohedral crystals are generally described by a hexagonal unit cell that is three times as large as the rhombohedral one. In the case of CaC_6, the very accurate value of the *a* parameter of this hexagonal unit cell is obtained from the 300 reflection registered using diamond as internal standard too (Fig. 6). In this unit cell, the parameters are then: $a = 433.3 \pm 0.2$ and $c = 1357.2 \pm 0.2$ pm, with the following Wyckoff’s atomic positions (Fig. 2):

Carbon:	18 atoms	18*g*	$(\frac{1}{3}0\frac{1}{2})$
Calcium:	3 atoms	3*a*	(000)

Thanks to the knowledge of this unit cell and its contents, it is possible to calculate the structure factors and the intensities of the various Bragg’s reflections of CaC_6. All these values are gathered in Table 1. It is interesting to underline that several reflections possess extremely weak intensities, as 110 or 009 for instance. It is a matter of fortuitous extinctions, and they are indeed lacking as planned in the diffraction pattern (Fig. 5).

The value of the *a* parameter is three times as high as the carbon–carbon distance in the graphene planes of the compound. This distance is equal to 144.4 pm, so that its dilation after intercalation reaches 2.4 pm, that is to say 1.69%. Using the Pietronero–Strässler formula [10], it is possible to calculate the charge transfer resulting from the intercalation of calcium into graphite. Reduced to one carbon atom, this electron transfer reaches 0.103. We have to point out that, among all the

Table 1
Structure factors of CaC_6

h k l	Structure factors	f_{hkl}	I_{calc}
0 0 1	0	0	0
0 0 2	0	0	0
0 0 3	$3f_{Ca}-18f_C$	−38.03	29.66
1 0 0	0	0	0
1 0 1	$3f_{Ca}$	48.22	38.02
0 0 4	0	0	0
0 1 2	$3f_{Ca}$	46.95	32.61
1 0 3	0	0	0
0 0 5	0	0	0
1 1 0	$3f_{Ca}-9f_C$	10.37	1.28
1 1 1	0	0	0
1 0 4	$3f_{Ca}$	42.99	20.69
1 1 2	0	0	0
1 1 3	$3f_{Ca}+9f_C$	71.19	51.33
0 0 6	$3f_{Ca}+18f_C$	100.09	100.00
0 1 5	$3f_{Ca}$	40.65	16.01
1 1 4	0	0	0
1 0 6	0	0	0
0 0 7	0	0	0
1 1 5	0	0	0
2 0 0	0	0	0
0 2 1	$3f_{Ca}$	37.40	11.31
2 0 2	$3f_{Ca}$	36.83	10.64
2 0 3	0	0	0
1 1 6	$3f_{Ca}-9f_C$	12.69	1.19
1 0 7	$3f_{Ca}$	35.77	9.49
0 0 8	0	0	0
1 2 0	0	0	0
2 1 1	$3f_{Ca}$	35.09	8.81
2 0 4	$3f_{Ca}$	34.77	8.51
1 2 2	$3f_{Ca}$	34.61	8.36
1 2 3	0	0	0
1 1 7	0	0	0
0 1 8	$3f_{Ca}$	33.43	7.33
2 0 5	$3f_{Ca}$	33.42	7.32
0 0 9	$3f_{Ca}-18f_C$	−7.98	0.41
2 1 4	$3f_{Ca}$	32.87	6.87
2 0 6	0	0	0
1 1 8	0	0	0
1 2 5	$3f_{Ca}$	31.72	6.02
0 0 10	0	0	0
1 0 9	0	0	0
0 2 7	$3f_{Ca}$	30.48	5.20
1 2 6	0	0	0
1 1 9	$3f_{Ca}+9f_C$	48.03	12.46
1 0 10	$3f_{Ca}$	29.31	4.49
2 1 7	$3f_{Ca}$	29.21	4.43
2 0 8	$3f_{Ca}$	29.03	4.34
3 0 0	$3f_{Ca}+18f_C$	63.99	20.95
3 0 1	0	0	0
0 0 11	0	0	0
3 0 2	0	0	0
1 1 10	0	0	0
3 0 3	$3f_{Ca}-18f_C$	−5.93	0.17
1 2 8	0	0	0
3 1 0	0	0	0
1 3 1	$3f_{Ca}$	27.80	3.69
2 0 9	0	0	0
3 0 4	0	0	0
0 1 11	$3f_{Ca}$	27.59	3.58
3 1 2	$3f_{Ca}$	27.58	3.58
3 1 3	0	0	0
3 0 5	0	0	0
0 0 12	$3f_{Ca}+18f_C$	59.52	15.94
1 2 9	0	0	0
1 3 4	$3f_{Ca}$	26.77	3.19

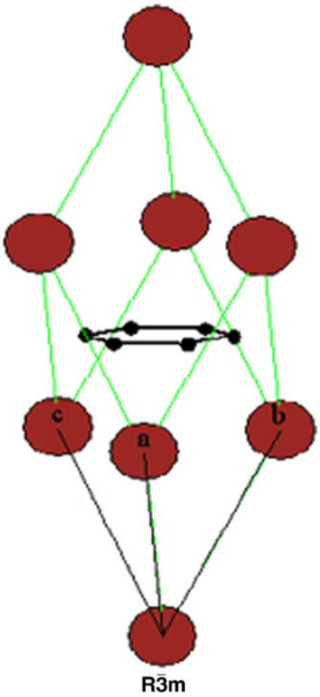

Fig. 7. Rhombohedral unit cell of CaC_6 compound.

MC_6 compounds, the previous carbon–carbon distance dilation and charge transfer are the highest ones.

Fig. 7 exhibits the elemental rhombohedral corresponding unit cell whose characteristic parameters are $a = 517\,\text{pm}$ and $\alpha = 49.55^\circ$, and the Wyckoff's atomic positions are the following ones:

Carbon:	6 atoms	6*g*	$(\frac{151}{662})$
Calcium:	1 atom	1*a*	(000)

The six carbon atoms draw a graphitic hexagon in the median plane of the 3D unit cell. It is primitive, centrosymmetrical and belongs to the holohedry of the rhombohedral system.

3. Discussion

Among the known first stage MC_6 graphite intercalation compounds, CaC_6 is only to possess this $R\bar{3}m$ rhombohedral structure. Each of them [1,6,9] exhibits the $P6_3/mmc$ hexagonal structure except LiC_6 [7], whose crystal symmetry is hexagonal too, but with the $P6/mmm$ space group.

In the case of KC_8 and RbC_8 compounds [3,4], it is well established that the interactions between the successive intercalated cations planes lead to the $A\alpha A\beta A\gamma A\delta A\alpha\ldots$ stacking, because the interaction is exerted on a great distance (as far as the fourth intercalated plane, that is to say 2140 and 2248 pm for KC_8 and RbC_8, respectively). For CsC_8, the equivalent distance would be 2368 pm, so that it is too high in order the interactive effects remain appreciable. The interaction is thus limited to the third intercalated plane, according to the $A\alpha A\beta A\gamma A\alpha\ldots$ stacking [5], and corresponding to 1776 pm only.

A comparable phenomenon appears with the MC_6 compounds. Indeed, in the case of CaC_6, the interaction can be exerted as far as the third intercalated plane (1357 pm), because the repeat distance is relatively short. On the other hand, if the repeat distance is higher, the interaction is limited to the second intercalated plane only, as it is observed for EuC_6, YbC_6, SrC_6 and BaC_6.

This general rule includes an exception with LiC_6. Indeed, its strongly short repeat distance (370 pm) due to the very small size of lithium would be of course favourable to the same rhombohedral stacking as for CaC_6. But we observe exactly the opposite, since the lithium atoms are strictly superimposed along the *c*-axis, according to the $P6/mmm$ space group [7]. In order to explain this unexpected result, we have to consider another interaction phenomenon that can appear only when the repeat distance is very short. In this case, the metal–metal distance can become extremely short through one graphene sheet (370 pm), if the successive metal planes are exactly superimposed. Indeed, this distance is a little higher than the Li–Li one observed in the classic centred cubic lithium metal (304 pm) [11]. Thanks to this especially weak distance, a covalent attractive interaction between lithium atoms [12] thus appears, which strongly weakens the cationic repulsive interaction, so that the ionic character of intercalated metal has to simultaneously decrease considerably. In LiC_6, the electron transfer reaches 0.07 only, while its value is 0.103 in CaC_6 (approximately 0.5 time higher).

4. Conclusion

The binary compounds, for which crystal structure is unknown, are currently very few. Among the first stage binary graphite intercalation compounds with electron donors, CaC_6 was the last one that did not reveal its structure. Thanks to our novel synthesis method, this gap is filled now. Besides its originality due to its rhombohedral symmetry, this structure can be compared to the other MC_6 ones that are all hexagonal, so that, concerning the crystal chemistry of these various phases, it is very interesting to connect each structure to the size of the intercalated atom and to the bond nature in the compound.

Moreover, thanks to the opportunity created by this synthesis method, it is from now on possible to study successfully the electronic and physical properties of CaC_6, since we have the use of bulk samples.

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