

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION
COMMISSION ON HIGH TEMPERATURE
AND SOLID STATE CHEMISTRY*

NOMENCLATURE AND TERMINOLOGY OF GRAPHITE INTERCALATION COMPOUNDS

(IUPAC Recommendations 1994)

Prepared for publication by

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Nomenclature and terminology of graphite intercalation compounds (IUPAC Recommendations 1994)

Abstract

Recommendations are presented for the nomenclature and terminology of graphite intercalation compounds, i.e. compounds that retain the planarity of the layers in the graphite structure. Not included are compounds with covalent bonding of heteroatoms to the carbon atoms which leads to a sp^3 hybridization of the carbon atoms and a corresponding loss of planarity of the layers. Rules for a structural notation are described in addition to those for the naming and the formulation of graphite intercalation compounds.

1. PREFACE

The present recommendations have been formulated by a subgroup appointed by the International Committee for Characterization and Terminology of Carbon and Graphite, after discussions with numerous colleagues in the field of intercalation into graphite, and after close consultation with Prof. R. Metselaar, Department of Chemical Engineering, Technische Universiteit, Eindhoven, Netherlands, at the time of the preparation of these recommendations chairman of the IUPAC Commission on High Temperatures and Solid State Chemistry and of a Working Party that was preparing Chapter I-6 on solids for the "Red Book" (Nomenclature of Inorganic Compounds (1)). Other members of this Working Party were also consulted during the preparation of the present paper. During these discussions, it became clear that a vocabulary of structural characterization should be included in the rules for nomenclature and terminology of the graphite intercalation compounds.

In drafting the present report, the subgroup was led by the following considerations:

- the rules for nomenclature and terminology should agree, as much as possible, with other IUPAC rules for naming chemical compounds, e.g. general nomenclature, description of non-stoichiometric solid phases, etc.;
- the terms should be easy to translate into other languages;
- the terms should be derived following the principles used in related areas;
- the terms chosen should not give rise to incorrect conclusions and should not lead to confusion with terms already used in chemistry for other defined classes of compounds;
- the fact that a term has been used in the literature for a long time is no reason for not replacing it by a more systematic term.

2. GENERAL CONSIDERATIONS

In view of the complexity and number of structures met in the graphite intercalation compounds, some specific cases may not have been - or will not be - covered by the present rules. Each author should decide whether the names and descriptions which follow cover the case considered. If this were not so, it is up to the author to define as precisely as possible a particular (and perhaps temporary) nomenclature.

Several types of compounds are derived from graphite. One may distinguish compounds which have species bound by covalent two-electron bonds to the carbon atoms, and compounds in which there is a charge transfer to or from the "graphene layers" (cf. par. 3.3) of the graphite structure. The species (atoms, ions, or molecules) is, in both cases, inserted between

the carbon sheets. This results in a more or less pronounced expansion which may be detected by X-ray diffraction and which occurs in a direction perpendicular to the carbon sheets.

Necessarily, the carbon layers lose their planarity in the case of covalent bonding and convert to a puckered-layer structure. Covalent bonds are formed by reactions of graphite with elements or groups of high electronegativity, e.g. fluorine (which yields graphite fluorides), oxygen or hydroxyl groups (which give graphite oxide, also called graphitic acid), etc. The disruption of the π -electron system generally leads to a drastic decrease of electrical conductivity.

In the case of charge transfer interaction, the carbon sheets retain their planar structure (apart from the possible presence of local defects) even though the guest material is found in the expanded interlayer intervals of the host structure. The compounds thus formed are called *graphite intercalation compounds*. Electronic interaction with the carbon sheets of the graphite host structure leads, in general, to a remarkable increase of in-plane electrical conductivity, although this may be offset by the presence of defects originally present or formed during the intercalation process. One should keep in mind that, in general, and even though this is not sufficiently recognized in the literature, these graphite intercalation compounds have a more or less broad range of compositions and are *non-stoichiometric compounds*.

The term "graphite intercalation compound(s)" may be abbreviated to GIC. In order to avoid confusion in computer-aided searches, it is however recommended that this abbreviation be avoided in titles since IC generally stands for "integrated circuit".

3. VOCABULARY

3.1 The reaction

The term *intercalation* is used to describe the overall process whereby a compound is formed without loss of planarity for the layers of carbon atoms, with heteroatoms or molecules residing between the original layers of carbon etc., as described in par. 2 above. The reverse process, i.e. the loss of some or all of the intercalated species, by whatever means, is *deintercalation* or *disintercalation*.

3.2 The intercalated layer

In connexion with the graphite intercalation compounds, "intercalated" must be used to qualify the guest (e.g. potassium or bromine) and not the host species (graphite). Consequently, the description "intercalated potassium (or bromine) in graphite" is correct, but not "intercalated graphite". The present participle "intercalating" should not be used to describe a state but rather a process, hence "intercalating potassium" describes those atoms which are reacting with graphite to become finally "intercalated potassium". To prevent possible ambiguities, the substantive "intercalant" should be avoided. However, by analogy with an IUPAC rule (2), "intercalate" can be used to describe the guest intercalated in the host lattice.

3.3. The carbon layers

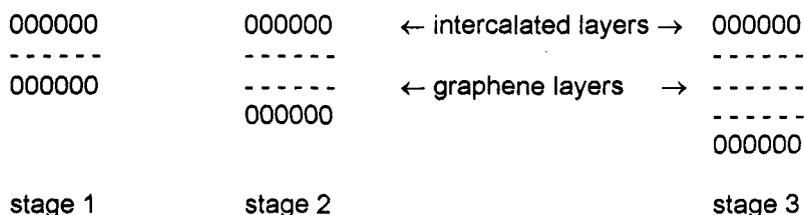
The term "graphite" designates a mineral as well as an allotropic form of elemental carbon and its crystal structure. In graphite, planar sheets of carbon atoms, with each atom bound to three neighbors in a non-compact, honeycomb structure, are stacked regularly, with three-dimensional order (3). "Graphitic carbon" is only applicable to materials which give rise at least to a modulation of the *hk* reflexions in X-ray diffraction. It is therefore not correct to speak of "graphite layers" when meaning single, two-dimensional carbon sheets. Even the terms "carbon layer" or "carbon sheet" are inappropriate.

The suffix *-ene* is used for fused polycyclic aromatic hydrocarbons, even when the root of the name is of trivial origin, e.g. naphthalene, anthracene, coronene, etc. A single carbon layer of the graphitic structure can be considered as the final member of this series and the term *graphene* should therefore be used to designate the individual carbon layers in graphite intercalation compounds (see "Note a").

Note a: Use of the term "graphene layer" is also considered for the general terminology of carbons (in preparation).

3.4 Stages

A peculiarity of graphite intercalation compounds is their tendency to form regularly stacked structures in which the intercalate is only found in a fraction of the interlayer spaces between the graphene layers. In a first-stage (or stage 1) compound, single layers of graphene alternate regularly with single layers of intercalated species (the latter may be more than one atom thick). In a second-, third-, ... stage compound, two, three, ... graphene layers separate two successive layers of intercalate:



According to accepted rules (4), the unit forming a polymer by continuous succession is called a "constitutional repeating unit" (CRU). By analogy, the layer sequence of a stage, as shown above, would be the CRU of a graphite intercalation compound.

In another structural model, second- third-, ... stage compounds are characterized by the fact that the area over which the layer of intercalated species is found between each pair of successive graphene layers is one half, one third, ... of the interlayer area (5).

In contrast with intercalation compounds given by other species such as TaS₂, high-number stages (10, 11, etc.) have been observed with graphite intercalation compounds, as well as compounds with *fractional* stage numbers (in which, for instance and with reference to the first structural model described above, two out of three interlayer spaces contain the intercalate) or with *average* stage numbers. In such cases, a full description and explanation should be given in the text. A clear distinction should be made between these cases and occasional stacking faults.

4. CLASSIFICATION OF GRAPHITE INTERCALATION COMPOUNDS

4.1 Donor and acceptor compounds

In graphite intercalation compounds, the graphene layers either accept electrons from or donate electrons to the intercalated species. It has now been generally accepted, however, that the description of the electronic exchange in these compounds be specified from the standpoint of the acceptor or donor properties of the intercalated species rather than from that of the graphene layers, as customary with doped semiconductors. Potassium-graphite is therefore a *donor graphite intercalation compound*, whereas bromine-graphite, or arsenic pentafluoride-graphite, or graphite hydrogensulfate are *acceptor compounds*.

For the graphite intercalation compounds in which different intercalated species located in specific regions of the interlayer space bear charges of opposite sign, the description *mixed donor-acceptor intercalation compound* can be used.

The extent of charge transfer has frequently been defined by the fraction of intercalated species carrying a charge. This practice is discouraged in view of the non-stoichiometric nature of the graphite intercalation compounds. Also, in many cases, the layers of intercalate are known to differ in order and density. It is therefore recommended that the charge transfer be defined by the average charge accepted or donated per carbon atom of the graphene layer. It must however be borne in mind that in stages higher than the second, most of the charge may be concentrated on the graphene layers immediately adjacent to the intercalated layers. Each author should therefore specify how the value of the charge transfer is defined.

4.2 Graphite salts

Following a long-established usage, the name *graphite salt* can be given to a subclass of acceptor compounds formulated $C_m^+X^- \cdot n \text{HX}$, in which HX represents a molecule of a Brønsted acid. This name reflects the fact that these compounds are known to contain discrete ions, such as HSO_4^- , or NO_3^- , as witnessed, among other proofs, by the method of preparation which involves oxidation of the graphene layers by chemical or electrochemical means in the presence of the acid. The space between the anions in the intercalated layers is filled by molecules of the acid.

Similarly, compounds containing intercalated cationic layers, with the graphene layers negatively charged, have been called *graphitides*, in accordance with the rules applicable to names of salts of non-complex anions. In view of the arguments developed in par. 3.3, the name *graphenide* seems more appropriate.

4.3 Binary, ternary, quaternary, ... compounds

The order of a graphite intercalation compound indicates the number of components in it: *binary compounds* are those which contain a single chemical species besides the carbon in the original graphite, i.e. in which the total number of species is two. In this connexion, ions cognate to an intercalated neutral atom or molecule and co-intercalated with it (as in the graphite salts of par. 4.2) will not be considered to be a different chemical species. *Ternary, quaternary, ... graphite intercalation compounds*, respectively, contain two, three, ... different chemical species besides the original carbon in the graphite.

4.4 Multi-intercalation compounds

The term *bi-intercalation compound* describes a ternary graphite intercalation compound in which two different *guests* occupy separate interlamellar spaces of the host structure:

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stage 1 bi-intercalation compound

This nomenclature applies, with appropriate modifications, to compounds in which three, four, ... different guests occupy separate and successive interlayer spaces of the host structure, forming *tri-intercalation, quadri-intercalation, ... compounds*. These terms do not apply to solid solutions of one guest species in the intercalated layers of another guest species.

4.5 Heterostructures

Some attempts at preparing ternary compounds result in the formation of two phases, visible by the presence of both diffraction patterns in the X-ray diffractogram. Since the individual domains are of such microscopic size that the mechanical separation of the two phases is excluded, these mixtures can be described as *heterostructures*.

5. NON-FORMULATIVE DESCRIPTION OF GRAPHITE INTERCALATION COMPOUNDS

The *name* of a graphite intercalation compound is formed by combining the noun "graphite" with the name of the intercalated substance, separated by a hyphen. If necessary, the composition and the stage may be added, between brackets. The oxidation number of an element may

be specified according to the current accepted rules. In a non-formulative description, the custom is to put the intercalated guest species first, whether it be donor or acceptor. In some cases (especially with graphite salts), it may be found more convenient to put the noun "graphite" first (*vide infra*), with no hyphen between it and the name of the anion.

Examples:

1. lithium-graphite (1/6, st.1)
2. potassium-graphite (1/24, st.2)
3. iodine monochloride - graphite (~1/8, st.2)
4. iron(III) chloride - graphite (~1/18)
5. graphite tetrachloroaurate(III)

Experience has shown that compounds may exhibit a considerable range of compositions and the exact constitution should only be given when the sample under discussion has been analysed. Similarly, doubts as to the exact value of the stage number preclude it being given.

In ternary compounds containing co-intercalated molecules which solvate the anion or cation between the layers of graphene, the name of the molecules is always placed after that of the solvated species.

Examples:

6. potassium-benzene-graphite (1/2,2/24, st.1)
7. graphite tetrafluoroborate-tetrahydrofuran

6. FORMULATION OF GRAPHITE INTERCALATION COMPOUNDS

Formulae should be specified only if accurately known, otherwise it is preferable to use a non-formulative description such as potassium-graphite (st.2), or K-GIC (st.2). No stage number should be given if it is undefined.

In agreement with the recommendations of IUPAC Red Book (1) rule I-4.6.1.2, the electro-positive constituent must be placed first in the formula.

Examples:

1. strontium-graphite (1/6, st.1) = SrC_6 (st.1)
2. iron(III) chloride - graphite (1/14, st.2) = $\text{C}_{14}\text{FeCl}_3$ (st.2)

In ternary or higher order compounds, similar constituents appear in the formula in alphabetical order of the chemical symbol.

Example:

3. caesium-potassium-graphite (st.1) = $\text{Cs}_{1-x}\text{K}_x\text{C}_8$ (st.1)

With solvated ions, the symbol of the solvating molecules follows that of the ion.

Examples:

4. barium-ammonia-graphite (1/2.5/10.9, st.1) = $\text{Ba}(\text{NH}_3)_{2.5}\text{C}_{10.9}$ (st.1)
5. graphite hexafluorophosphate-tetrahydrofuran = $\text{C}_{24}^+\text{PF}_6^-(\text{THF})_n$

It is also possible to specify the cointercalated molecules after a dot at mid-line level.

Example:

6. $\text{C}_m^+\text{PF}_6^- \cdot n \text{ THF}$

Bi-intercalation (i.e. different species intercalated in different interlayer spaces) should be made apparent in the formula.

Examples:

7. thallium bromide-thallium chloride-graphite (st.1) = $C_{12.5}TlBr_{3.2} \cdot C_{12.5}TlCl_{3.6}$ (st.1)
8. caesium-hydrogen-potassium-graphite (st.1) = $CsC_8 \cdot K_2H_{4/3}C_8$ (st.1)

It is desirable that any non-stoichiometry of the intercalation compounds be also expressed in the formulation. Thus, $K_{1-x}C_8$ implies that some potassium atoms are missing in the two-dimensional intercalated layers of KC_8 . A commensurate structure necessarily implies an integral number of carbon atoms and if, for example, $x = 0.1$ in $K_{1-x}C_8$, it would be wrong to give the formula as $KC_{8.9}$. Similarly, the formula $C_{13.2}NiCl_{2+x}$ implies that there is an excess of chlorine with respect to the integral stoichiometry $Cl/Ni = 2$, and that no simple integral ratio exists for the number of C atoms to each Ni atom in nickel(II) chloride - graphite, hence that the intercalated $NiCl_2$ layers are non-commensurate with respect to the graphene layers.

It should however be recognized that it is not always possible to indicate unambiguously by a chemical formula whether a given structure is commensurate or non-commensurate with the graphene layers. Moreover, an ambiguity arises from the use of non-integral indices in the formulae: whereas the index 0.8 in $Li_{0.8}C_8$ is meant to indicate that only 80 % of the Li sites in the first-stage lithium graphite derivative are occupied, the same index in $K(\text{furan})_{0.8}C_8$ gives the actual maximum content of furan molecules since these occupy *all* the available space, and not just 80 % of it. If the appropriate information is available, the type of defect responsible for the non-integral stoichiometry can be indicated using standard notation, i.e. V for vacancies and i for interstitials. (Rule I-6.4.2, Red Book (1)).

7. STRUCTURAL NOTATION

7.1 Description of the stacking sequence

In the hexagonal form of graphite, the graphene layers are stacked so that all even-numbered layers are shifted with respect to the odd-numbered layers by one-third of the crystallographic parameter, as reflected in the notation ABAB... Similarly, graphene layers in different relative positions can be indicated by capital Roman letters (A, B, C, ...). For the intercalated layers, a distinction should be made between the following two cases:

- for commensurate layers in epitaxy on the graphene layers, lower-case Greek letters ($\alpha, \beta, \gamma, \dots$) can be used to distinguish between individual layers;
- non-commensurate or disordered layers can be identified by χ (chi) or ξ (xi).

Thus, the structure of LiC_8 (st.1) is described by $A\alpha A\alpha A\alpha\dots$, while KC_8 (st.1), more correctly formulated as $(KC_8)_4$ (st.1), is described by $A\alpha A\beta A\gamma A\delta\dots$

7.2 Description of the crystal lattice

The symmetry of the crystal lattice of a given stage may be indicated by the modified Gard system (6) (already used for other polytypes), with an Arabic numeral and a capital Roman letter preceding the chemical formula. The numerical symbol indicates the number of constitutional repeating units (CRU) in the identity period, and the letter indicates the symmetry (H = hexagonal, T = trigonal with hexagonal Bravais lattice, R = trigonal with rhombohedral Bravais lattice, O = orthorhombic).

Examples:

1. $1H-LiC_8$ (st.1); stacking sequence: $A\alpha A\alpha A\alpha\dots$
2. $2H-KC_{24}$ (st.2); stacking sequence: $AB\chi BA\chi\dots$

3. 3R-CsC₈ (st.1); stacking sequence: A α A β A γ ...
4. 4O-KC₈ (st.1); stacking sequence: A α A β A γ A δ ...

7.3 Description of the epitaxial layers

The ordered relation between graphene layers and intercalated layers in the (*a*,*b*) plane is indicated by the notation for epitaxial overlayers (7). The size of the new unit cell, normalized with respect to the *a* and *b* parameters of the graphene layers, is given in parentheses, and rotation with respect to the graphite unit cell is indicated by R θ .

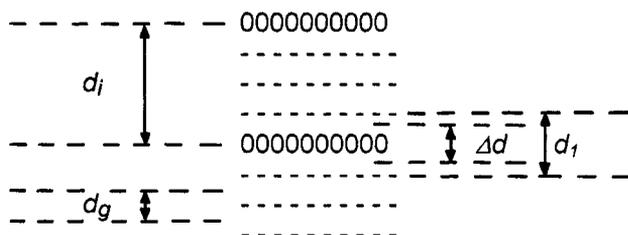
Examples:

1. LiC₆ (st.1); ($\sqrt{3} \times \sqrt{3}$) R 30°
2. KC₈ (st.1); (2 \times 2)
3. CsC₂₈ (st.2); ($\sqrt{7} \times \sqrt{7}$) R 19.1°

7.4 Symbols for various distances

The symbol l_c , often used in the literature to indicate the thickness of the CRU (i.e. the distance between two successive intercalated layers) can be confused with *l*, which stands for the body-centered unit cell. To conform with the accepted crystallographic symbolism, the following symbols should be used:

- d_G is the distance between two successive carbon layers in graphite, hence $d_G \approx 335$ pm;
- d_i is the distance between two successive layers of intercalate; this is not necessarily the crystallographic identity period *c*, which will be a multiple of d_i if screw axes or translation vectors are present; thus, in the case of (KC₈)₄, $c \approx 2160$ pm = 4 \cdot d_i ;
- d_g is the distance between two adjacent layers of graphene, if this has been found to be different from 335 pm;
- d_1 is the repeat distance of the first stage compound with the same layer of intercalate as the one in the intercalation compound considered, irrespective of whether this first-stage compound can exist or not;
- Δd is the apparent thickness of the intercalated layer, given by $\Delta d = d_1 - d_G$ or $\Delta d = d_1 - d_g$



- d_{CC} is the in-plane C-C distance in a layer of graphene; it is not necessarily the same distance as in graphite (≈ 142.1 pm) owing to the charge transfer caused by intercalation;
- $\Delta d_{CC} = u = d_{CC} - 142.1$ pm is the variation of in-plane C-C distance due to the charge transfer.

Acknowledgements

We have particularly appreciated helpful criticism and suggestions from: Groupe Français d'Etude des Carbones; F.J. DiSalvo, Cornell University, Ithaca, NY, USA; M.S. Dresselhaus, Massachusetts Institute of Technology, Cambridge, MA, USA; J.M. Honig, Purdue University, West Lafayette, IN, USA; M. Inagaki, Hokkaido University, Sapporo, Japan; A. Marchand, University of Bordeaux, Talence, France; J. Rouxel, University of Nantes, France; S. Tanuma, Gunma University, Japan; P.A. Thrower, Pennsylvania State University, University Park, PA, USA; A.R. Ubbelohde (deceased), Imperial College, London, UK.

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