

EDITORIAL SECTION

NOMENCLATURE AND TERMINOLOGY OF GRAPHITE INTERCALATION COMPOUNDS

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(Received 12 August 1985)

Report by a subgroup of the International Committee for Characterization and Terminology of Carbon and Graphite on suggestions for rules for the nomenclature and terminology of graphite intercalation compounds.

1. PREFACE

The International Committee for Characterization and Terminology of Carbon and Graphite has appointed a subgroup to deal with the nomenclature and terminology of graphite intercalation compounds. Members of this subgroup are H. P. Boehm, R. Setton and E. Stumpp. The suggestions formulated shall, after eventual adoption by the International Committee, become the basis of IUPAC nomenclature rules for this class of compounds.

The present suggestions have been formulated by the subgroup after discussions with numerous researchers in the field of graphite intercalation, as well as in close contact with Prof. R. Metselaar, Department of Chemical Engineering, Technische Hogeschool, Eindhoven, The Netherlands, who is Chairman of a subgroup of the IUPAC Commission on High Temperatures and Solid State Chemistry. This subgroup is preparing chapter I-6 on solids for the "Red Book" (nomenclature of inorganic compounds). Other members of this subgroup have been consulted, too, in the preparation of the present draft. In all these discussions it became clear that rules for the structural characterization should be included in the rules for the nomenclature and terminology of the graphite intercalation compounds.

In drafting the present report the subgroup "graphite intercalation compounds" was led by the following considerations:

- The rules for the nomenclature and terminology of graphite intercalation compounds should agree as far as possible with other IUPAC rules for naming of chemical compounds, e.g. general nomenclature, description of non-stoichiometric solid phases etc.

- The terms should be easy to translate into other languages.

- Terms should be derived following the principles used in related areas.

- The term chosen should not give rise to false conclusions and it 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 literature for a long time is no reason for not replacing it by a more systematic term.

All researchers interested in intercalation compounds of layered materials are asked to help in the final formulation of the rules for the nomenclature and terminology of graphite intercalation compounds. Please send comments and suggestions to Prof. Dr. H. P. Boehm, Institut für Anorganische Chemie der Universität München, Meiserstraße 1, D-8000 München 2, F.R.G.

2. GENERALITIES

Several types of compounds are derived from graphite. One may distinguish such compounds, which have heteroatoms 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. Section 4) of the graphite structure. The bound material (atoms, ions or molecules) is in both cases inserted between the carbon sheets leading to a more or less pronounced expansion (in the direction perpendicular to the carbon sheets) which may be detected by X-ray diffraction.

Necessarily, the carbon sheets lose their planarity in the case of covalent bonding and convert to a puckered-layer structure. Such compounds are known with elements of very high electronegativity, i.e. fluorine [graphite fluoride], oxygen (also hydroxyl groups) [graphite oxide, also called graphitic acid], etc. These compounds should be called *graphite compounds*. The disruption of the π -electron system leads generally to a drastic decrease of electric conductivity.

In the case of charge-transfer interaction, the carbon sheets keep their planar structure (apart from defects), and the reacting material is found in the expanded intervals of the host structure. Such compounds are called *graphite intercalation compounds*. The electronic interaction with the carbon sheets of the host graphite leads, in general, to a remarkable increase in electric conductivity parallel to the orientation of the carbon sheets.

The term "graphite intercalation compound(s)" may be abbreviated *GIC*. However, in order to avoid confusion in computer-aided searches it is recommended not to use this abbreviation in the titles of communications (IC is the general abbreviation for integrated circuits).

Too frequently, in the literature the fact is not recognized that these graphite intercalation compounds usually have a more or less broad range of composition, that is that they are *non-stoichiometric* compounds.

3. ORIGIN OF THE TERM INTERCALATION AND TERMS DERIVED FROM IT

Intercalation is the noun derived from the Latin verb *intercalare*. This was the term used by the Romans for inserting an extra day into the calendar (intercalary day). Accordingly the verb describing the process of inserting a substance in between the carbon sheets of the graphite lattice is called *to intercalate*. Analogously formed terms are hydration/to hydrate or hydrogenation/to hydrogenate.

The verb "to intercalate" should describe the process of intercalation, e.g. potassium is intercalated in graphite. Consequently, the formulation "intercalated potassium" (in graphite) is permissible when speaking of potassium in the intercalated state. It is misleading, however, to speak of "intercalated graphite" when a graphite intercalation compound is meant. The process of reversing intercalation may be described as *de-intercalation* (verb: *to de-intercalate*).

In contrast to frequent usage it is not correct to call the intercalated substance an "intercalant." (Webster's New World Dictionary: *-ant*: a noun-forming suffix meaning a person or thing that . . . occupant, accountant. Accordingly, an intercalant would be a person who intercalates substances into graphite.)

In analogy to an IUPAC recommendation[1] to use the term "adsorbate" for an adsorptive in the adsorbed state, the noun *intercalate* would designate the substance intercalated in a host lattice, e.g. graphite. The suffix *-ate* is generally used for an electronegative, heteropolyatomic constituent (IUPAC rule 2.23), but this should not be a source of confusion.

4. DESIGNATION OF THE CARBON SHEETS DERIVED FROM THE GRAPHITE LATTICE

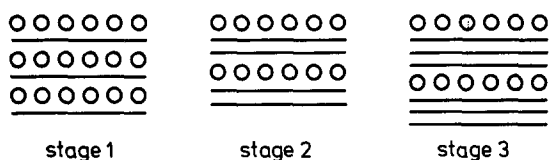
The term "graphite" designates a mineral as well as the crystal structure of a modification of the chemical element carbon. In graphite, coplanar sheets of carbon atoms, with each atom bound to three neighbors in a honeycomb-like structure, are stacked in a regular way with three-dimensional order.[†] The term "graphitic carbon" is applicable only to materials which give rise to at least a modulation of the (hk) bands in X-ray diffraction. It is not correct, therefore, to speak of "graphite layers" when meaning single two-dimensional carbon sheets. Even the terms "carbon layer" or "carbon sheet" are not unambiguous.

The ending *-ene* is used for fused polycyclic aromatic hydrocarbons, even when the root of the name is of trivial origin, e.g. naphthalene, anthracene, tetracene, coronene, ovalene. A single carbon layer of the graphitic structure would be the final member of infinite size of this series. The term *graphene* layer should be used for such a single carbon layer.[‡]

5. DESIGNATION OF STAGES IN (GRAPHITE) INTERCALATION COMPOUNDS

A peculiarity of graphite intercalation compounds is their tendency to form regularly stacked compounds in which only a fraction of the interlayer spacings between the graphene layers are filled with intercalated substance.

Such compounds are designated *stages* of a given GIC. In a first stage (or stage 1), graphene layers and intercalated layers are stacked successively; in a second stage, two graphene layers follow an intercalated layer; in a third stage, three graphene layers etc.:



According to accepted rules[2], the unit forming a polymer by continuous succession is called a "constitutional repeating unit" (CRU). In analogy, the layer sequence of a stage, as shown above, would be the CRU of a graphite intercalation compound.

In contrast to other intercalation compounds, e.g. with TaS₂, regularly stacked stages of high stage numbers (10, 11 etc.) have been observed with graphite intercalation compounds.

When the sequence of filled and empty intervals between graphene layers is not regular, this should be in-

[†]See: International Committee for Characterization and Terminology of Carbon: "First publication of 30 tentative definitions" Terms No. 3 and No. 6, *Carbon* **20**, 445 (1982).

[‡]The use of the term "graphene layers" is also considered for the general terminology of carbons (Term No. 104, in preparation). It should be adopted for graphite intercalation compounds when (and only if) it is finally accepted for the terminology of carbon.

licated; if necessary the stage of such a GIC may be indicated by an *approximate value*. A clear distinction should be made from occasional stacking faults.

6. CLASSIFICATION OF GRAPHITE INTERCALATION COMPOUNDS

6.1 Donor- and Acceptor-Compounds

In graphite intercalation compounds, the graphene layers either accept electrons from the intercalated substance, e.g. potassium, or they donate electrons to the intercalate, e.g. bromine, arsenic pentafluoride etc. It is general usage, however, to *define the donating/accepting property from the standpoint of the intercalated substance*. Potassium graphite is a *donor compound*, therefore; bromine-graphite, arsenic pentafluoride-graphite and graphite hydrogensulfate are *acceptor compounds*.

Since the sense of electron donation is not obvious, the terms "donor/acceptor compound" should not be used in the titles of communications.

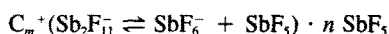
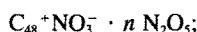
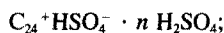
In some ternary or higher-order graphite intercalation compounds, the different intercalated species bear charges of opposite sign, e.g. in $(\text{KHg})_2\text{C}_8$ or in $\text{KH}_{2/3}\text{C}_8$. In this case, one should look at the charge of the graphene layers for the definition as donor or acceptor compound (both cases mentioned above are donor compounds).

The extent of charge transfer has frequently been defined by the fraction of intercalated molecules carrying a charge. This practice is to be disapproved in view of the non-stoichiometric nature of the graphite intercalation compounds. The intercalate layers are known to differ in order and in density. Therefore, it is recommended to define the charge transfer by the average charge accepted or donated per carbon atom of the graphene layers. However in stages higher than second, the charge is concentrated on the graphene layers adjacent to the intercalated layers. It is recommended that each author specifies how the value for the charge transfer is defined.

6.2 Order of Graphite Intercalation Compounds

Graphite intercalation compounds should be called *binary* when they contain one chemical species besides graphite, *ternary*, when they contain two distinct chemical species besides graphite, etc. In this connection, the ions derived from the intercalated compound, or species which are in chemical equilibrium, will not be considered different chemical species. (In thermodynamics, the components of a system are defined as the least number of independently variable chemical constituents necessary and sufficient to express the composition of each phase present in any state of equilibrium.)

Examples for binary compounds:



The term *bi-intercalation compound* describes a ternary GIC in which two different guests occupy separate,

successive interspaces of the host structure, e.g. $\text{A}\xi_1 \text{A}\xi_2 \text{A}\xi_1 \dots$ in the notation of Section 9, e.g. TiCl_3 and TlBr_3 . This term does not apply to solid solutions of one guest species in the intercalated layers of another guest species.

7. VERBAL DESIGNATION 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 is added in parentheses (see examples). The oxidation number of an element may be specified according to the current accepted rules. The stage number is added in parentheses, e.g. -(st.1), -(st.2).

Examples: LiC_6 = lithium-graphite(1/6, st.1)
 KC_{24} = potassium-graphite(1/24, st.2)
 C_7FeCl_3 = iron(III)-chloride-graphite(1/7, st.1)
 C_8ICl = iodine monochloride-graphite (1/8, st.1).

The stage number is not stated when unknown or undefined.

It is desirable that it be made clear that the formula given is an idealized formula for a phase with a considerable range of composition. It is possible to state an exact composition only when the sample under discussion has been analyzed.

potassium-graphite ($\approx 1/24$, st.2)
 iron(III)-chloride-graphite ($\approx 1/6$, st.1).

In intercalation from solution, solvent is often co-intercalated, usually solvating the intercalated ions. In the case of donor compounds, the solvent molecules should be mentioned after the electropositive constituent. With graphite salts, the solvent is named after the anion.

Examples: lithium-dimethylsulfoxide-graphite
 potassium-benzene-graphite
 graphite-tetrafluoroborate-tetrahydrofuran

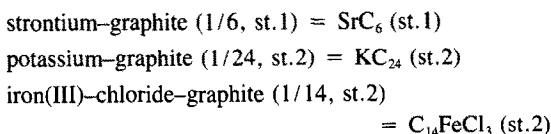
Names such as "graphite bisulfate" or "graphite hydrogensulfate" are retained for the *graphite salts* with well-defined anions, without excluding the names formed by the above rules.

Examples: graphite nitrate = nitric acid-graphite
 graphite tetrachloroaurate (III)
 = tetrachloroauric acid (III)-graphite

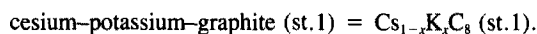
8. FORMULATION OF GRAPHITE INTERCALATION COMPOUNDS

IUPAC rule 2.15[3] states that in chemical formulae the electropositive constituent is placed first. This leads

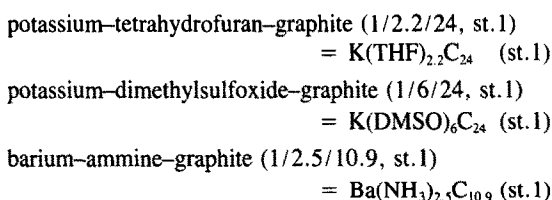
to the following formulations:



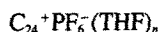
In the case of ternary or higher order compounds, similar constituents should appear in the formula in alphabetical order (see IUPAC rule 2.15), e.g.



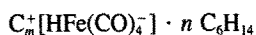
When the ions of the electropositive element are solvated, the symbol for the solvate molecules follows the symbol of the electropositive constituent, e.g.



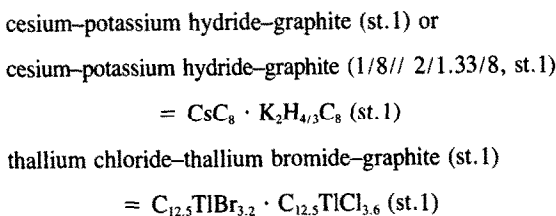
With graphite salts, the analogous symbolism is used, e.g.



When solvent or other neutral molecules fill the space between intercalated anions, it is also possible to add the spacer molecules after a point at mid-line level, e.g.



If two different species are intercalated in different interlayer spaces (bi-intercalation), this should be made clear in the formulae, e.g.

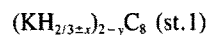


A formula should be given only if accurately known, otherwise it is preferable to write K-GIC (st.2), FeCl₃-GIC (st.10) etc. No stage number is given if it is unknown or undefined.

It is desirable that the non-stoichiometric nature of the graphite intercalation compounds be also expressed in the formulation; e.g. the formula $\text{Eu}_{0.8}\text{C}_6$ indicates that 20% of the metal sites in the compound EuC_6 are unoccupied. K_{1+x}C_8 implies that interstitial potassium atoms are present in the two-dimensional potassium layers of KC_8 . $\text{C}_{13.2}\text{NiCl}_{2+x}$ implies that there is a stoichiometric excess of chlorine above the ratio $\text{Cl/Ni} = 2$, and that no simple integer ratio exists for the number of carbon

atoms per intercalated Ni atom in nickel(II)-chloride-graphite (the intercalated NiCl_2 -layers are non-commensurate with respect to the graphene layers). Analogously, the formula $\text{KC}_{8.3}$ implies a non-commensurate structure.

Other examples: $(\text{KHg}_{1-x})_{2-y}\text{C}_8$ (st.1)



However, it is not possible to indicate by a chemical formula whether a partial structure is commensurate or non-commensurate with the graphene layers. Furthermore, an ambiguity arises from the use of fractional indices in the formulae: The formula $\text{Li}_{0.8}\text{C}_{12}$ implies that only 80% of the Li sites in second stage lithium graphite are occupied. However, in $\text{K(Furan)}_{0.8}\text{C}_8$, the furan molecules occupy *all* the available space, and not only 80%.

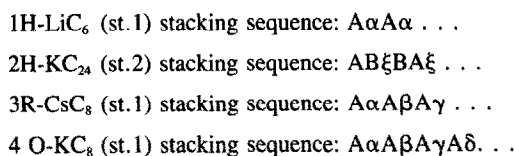
If the information is available the kind of non-stoichiometry can be indicated using the defect notation, i.e. *V* (italics) for vacancies and subscript *i* (italics) for interstitials, e.g. $\text{K}_{1+x_i}\text{C}_8$.†

9. STRUCTURAL NOTATION

The graphene layers are stacked in hexagonal graphite in such a way that every odd layer is shifted in relation to the even layers by one third of a unit cell dimension. In other words, the stacking sequence is ABAB. . It is ABCABC in rhombohedral graphite. In graphite intercalation compounds the relative positions of the graphene layers are indicated in the same way by capital Roman letters. The relative positions of the intercalated layers are designated by small greek letters, $\alpha, \beta, \gamma, \delta$, if known, and by ξ (ξ) if non-commensurate, disordered or unknown, e.g. for KC_8 (st.1): $\text{A}\alpha\text{A}\beta\text{A}\gamma\text{A}\delta$. . .

The symmetry of the structure of a given stage may be indicated by the modified Gard system[4] as with polytypes, e.g. of metal dichalcogenides, by an Arabic numeral and a capital Roman letter preceding the chemical formula. The numerical symbol indicates the number of CRUs 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, ψH = pseudo-hexagonal).

Examples:

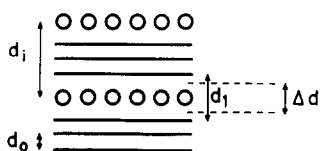


There is some confusion in the literature with regard to a symbol for the thickness of the CRU, i.e. the distance

†This notation is contained in the draft for IUPAC rules on nomenclature of inorganic compounds ('Red book', Chapter I-6: Solids). The symbol for vanadium, V, is set in upright type, it may be written *V*_a in cases of doubt (Chapter I-3.3.3).

between intercalated layers. Often, the symbol I_c is used in contrast to crystallographic usage where I_c is equivalent to c_0 , the dimension of the unit cell in c -direction. In the case of KC_8 , I_c is stated as 540 pm, whereas c_0 is $4 \times 540 \text{ pm} = 2160 \text{ pm}$. In order to avoid this confusion the use of I_c is not recommended. It is suggested to use d_i instead.

The spacing of two neighboring graphene layers should be indicated by d_0 ($\approx 335 \text{ pm}$), and the thickness of the intercalated layer, including one graphene layer, as d_i (= the repeat distance in a stage 1 compound). The thickness of the intercalated layer alone would then be $\Delta d = d_i - d_0$.



The variation of the in-plane C–C distance due to intercalation can be designated by Δd_{cc} ($= d_{cc} - 142.1 \text{ pm}$).

The ordered relation between graphene layers and intercalated layers in the a,b -plane is indicated by the notation for epitaxial overlayers[5]. The size of the new unit cell in relation to the graphite unit cell is given in parentheses, an eventual rotation with respect to the graphite

unit cell is indicated by $R.^\circ$.

Examples: $\text{LiC}_6 (\sqrt{3} \times \sqrt{3})R30^\circ$

$\text{KC}_8 (2 \times 2)$

$\text{Rb}_{1\pm x}\text{C}_{28} (\text{st.2}) (\sqrt{7} \times \sqrt{7}) R19.1^\circ$

Acknowledgement—In particular, helpful criticism and suggestions are appreciated from: the Groupe Français d'Etudes des Carbones; F. J. DiSalvo, Bell Laboratories, Murray Hill, NJ, U.S.A.; M. S. Dresselhaus, MIT, Cambridge, MA, U.S.A.; M. Inagaki, Toyohashi University of Technology, Japan; A. Marchand, University of Bordeaux, Talence, France; J. Rouxel, Univ. Nantes, France; S. Tanuma, Gumma University, Japan; A. R. Ubbelohde, Imperial College, London, U.K.

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EDITORIAL ANNOUNCEMENT

Seventh Series of George D. Graffin Lectures in Carbon Science and Engineering

The seventh series of lectures to honor the late George D. Graffin, one of the pioneers of the graphite industry [see *Carbon* **20**, 163 (1982) and *Carbon* **19**, 241 (1981)] was presented by Dr. J. L. White of the Aerospace Corporation, Los Angeles, CA, U.S.A. With primary support from Asbury Carbons, Inc., Dr. White presented lectures under the general title "High-Modulus Mesophase Carbon Fibers: Their Relationship to Liquid Crystal Technology" at eleven universities: California (Berkeley, Los Angeles, and San Diego), Carnegie-Mellon, Case Western Reserve, Illinois, Lehigh, Marquette, North Texas State, Pennsylvania State, and Stanford. In this series, the lectures were extended to industrial laboratories, Lockheed—Palo Alto and Mobil—Princeton, and we thank these organizations for supplementary support that enabled significant extensions to the lecture tours. Following the lead of the previous lecturer, Dr. L. S. Singer, the

diversity and future promise of carbon materials were illustrated by a traveling exhibit of articles ranging from rocket nozzles to heart valves, and Dr. White wishes to thank the following organizations for the provision of specimens in which students found considerable interest:

Acurex Corporation	Dr. J. E. Zimmer
Airco Carbon	Dr. E. A. Heintz
Asbury Carbons, Inc.	Mr. W. M. Kenan
Carbomedics, Inc.	Dr. J. C. Bokros
Poco Graphite, Inc.	Mr. R. K. Carlson
The Aerospace Corporation	Dr. R. A. Meyer
Union Carbide Corporation	Dr. L. S. Singer

The lecturer selected for the eighth series of lectures is Dr. R. T. K. Baker of Exxon Research and Engineering Company, Annandale, NJ, U.S.A.