Journal of Inclusion Phenomena **1**, 79–85. 0167–7861/83/0011–0079$01.05

A Proposal for the Classification and Nomenclature of Host-Guest-Type Compounds

E. WEBER★ and H.-P. JOSEL
Institut für Organische Chemie und Biochemie der Universität, Gerhard-Domagk-Straße 1, D–5300 Bonn 1, F.R.G.

(Received: 27 October 1982)

Abstract. We suggest a system of classification and naming of general application to host-guest-type compounds. The classification is based on several criteria, including the host-guest type and the host-guest interaction, but also on topological and numerical considerations. The application of this concept to the classification of any host-guest situation is illustrated by several examples.

Key words: Host-guest-type compounds (complexes, clathrates, inclusion compounds, addition compounds), classification system, nomenclature.

1. Introduction

There is much confusion in the literature over the terminology used for the description of inclusion compounds [1]. Over the years, a large number of descriptions have been used [2], some examples being: *addition compound, adduct, associate, cage compound, clathrate complex, donor-acceptor complex, clathrate hydrate, hydrocarbon clathrate, inclusion compound, gas hydrate, host-guest complex, intercalate, interlamellar sorbent, lock and key complex, loose addition complex*, and *molecular compound*. Since these terms have not been precisely defined, different authors have used different terms to describe the same compound, e.g., *occlusion* and *inclusion* have been used synonymously and *adduct* has frequently been substituted for *complex*. The term *intercalation* has sometimes been replaced by *insertion* and has even been interchanged with *inclusion* etc. [3]. Newly-coined terms, such as *cascade complex, supermolecular complex, molecular complex associate, speleate* [4] plus other terms mentioned in Section 2.2 of Davies *et al.* [5] add to the present confusion.

An increase in the number of new host molecular structures is expected on a larger scale than in the past [6], because of the growing interest in the chemistry of 'weak interactions' [7]. The definite characterization of these host molecular structures by the present system of naming [8] will become more and more difficult [9]. For these reasons we have drawn up a new system of classification and naming, which should be applicable not only to the presently-known types of host-guest compounds, but also to future possible types.

2. The Classification System

The main classification is based on the criteria of (a) the host-guest *type* and the host-guest *interaction*, (b) the *topology* of the host-guest aggregate, and (c) the dependence on the *number* of the various components forming the aggregate (Table I).

★ Corresponding author.

Table I. Classification/nomenclature of host-guest-type compounds

HOST-GUEST COMPOUNDS

I. COORDINATION-Type Aggregate		II. LATTICE-Type Aggregate
	I (II). Lattice-assisted COMPLEX *"Clathratocomplex"* [a]	*CLATHRATE*
COMPLEX	II (I). Coordination-assisted CLATHRATE *"Coordinatoclathrate"*	

Host-Guest-Type	and	Host-Guest Interaction
1. Ionic (charged)		1'. Ion-ion
2. Polar (di-, tripolar, ..., betaine-like)		2'. Ion-dipole
3. Neutral (uncharged)		3'. Dipole-dipole
		4'. Donor-acceptor
		5'. van der Waals
		6'. Hydrophobic effect
		7'. Steric barrier

A. INCLUSION Compound Intramolecular host-guest aggregate (Host cavity) *"Cavitate"*	B. ADDITION Compound Extramolecular host-guest aggregate (no host cavity) *"Adduct"*

Topology	
	a. Layer, sandwich: *Intercalate*
	b. Ring: *Coronate*, *Podate*
	c. Channel: *"Tubulate"* [b]
	d. Pocket, niche: *"Aediculate"* [c]
	e. Cage: *Cryptate*

Number of Components

Individuals of the Host-Guest Aggregate	Host Particles (assembled in the host-guest unit)	Guest Particles
α) two: *binary*	α') one: *mono-*	α") one: *mono-*
β) three: *ternary*	β') two: *bi-*	β") two: *bi-*
γ) four: *quaternary*	γ') three: *tri-*	γ") three: *tri-*
δ) several: *oligonary*	δ') several: *oligo-*	δ") several: *oligo-*
ε) many: *polynary*	ε') many: *polymolecular*	ε") many: *polynuclear*

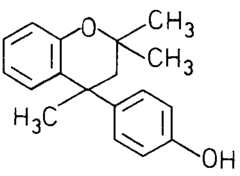
[a] Terms which are marked by inverted commas represent new proposals. [b] Derived from the Latin word 'tubus' meaning tube. [c] Derived from the Latin word 'aedicula' meaning niche, pocket.

2.1. THE HOST-GUEST TYPE AND INTERACTION

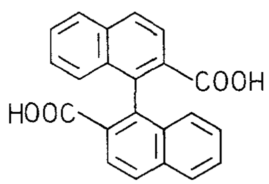
In the first instance, a division is made into the extremes of *complex* and *clathrate*.

Those host-guest aggregates which are derived from a *coordination* between the host and guest components will be defined as *complexes*. The host-guest compounds formed by crown ethers and cryptands are typical examples of *complexes* (Figures 1a - 1c).

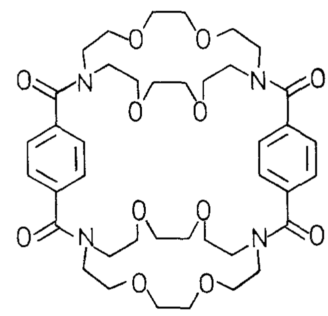
The term *clathrate* [11] will be used for host-guest aggregates where the guest is retained by steric barriers formed by the host lattice (*crystal lattice forces*). Thus, the host-guest compounds formed by Dianin's compound (**1**) [13], by urea [14] and by graphite [15] are typical examples of *clathrates*, (Figures 1d-lf).



(**1**)



(**2**)



(**3**)

Another way of distinguishing between complexes and clathrates is to make use of the fact that complexes retain their identity in solution, whereas clathrates normally decompose on dissolution.

Since all host-guest aggregates cannot be classified as either complexes or clathrates, the borderline cases must be treated as *complex/clathrate hybrids*. We thus introduce two other classes: *Coordinatoclathrates* which demonstrate a certain degree of coordinative participation but have a dominant clathrate character, and *clathratocomplexes* (lattice complexes), where the influence of coordination to binding sites predominates, but the coordination is much weaker than that which is present in *complexes*.

The recently-discovered new class of clathrate compounds formed by 1,1′-binaphthyl-2,2′-dicarboxylic acid (**2**) with different OH-, NH- and CH-acidic guest compounds can be quoted as a typical example of a *coordinatoclathrate* (Figure 1h) [16]. The great majority of the known crown ether complexes with neutral guest molecules [1] are examples of *clathratocomplexes*.

2.2 TOPOLOGICAL CONSIDERATIONS

In the second instance, we apply topological aspects and distinguish between *inclusion compounds* (intramolecular host-guest aggregates) [17] which operate via any sort of host cavity (*cavitate*), and *addition compounds* (*adducts*) [18] which do not contain a host cavity (extramolecular host-guest aggregates) [19]. Typical examples of *adducts* being charge transfer and simple hydrogen-bonded complexes [20].

Thus, we have the following topologies for *cavitates* displaying increasing encapsulation: two-dimensional open layer-, sandwich- and ring structures, belonging to the *intercalate-type* [8], the *coronate-type* [21] or the *podate-type* [21] respectively; one-dimensional open channel structures (we suggest the term *tubulates*); pocket-like host arrangements (*aediculate-type*) [4b] and, finally, totally-enclosed cage structures (*cryptates*) [21].

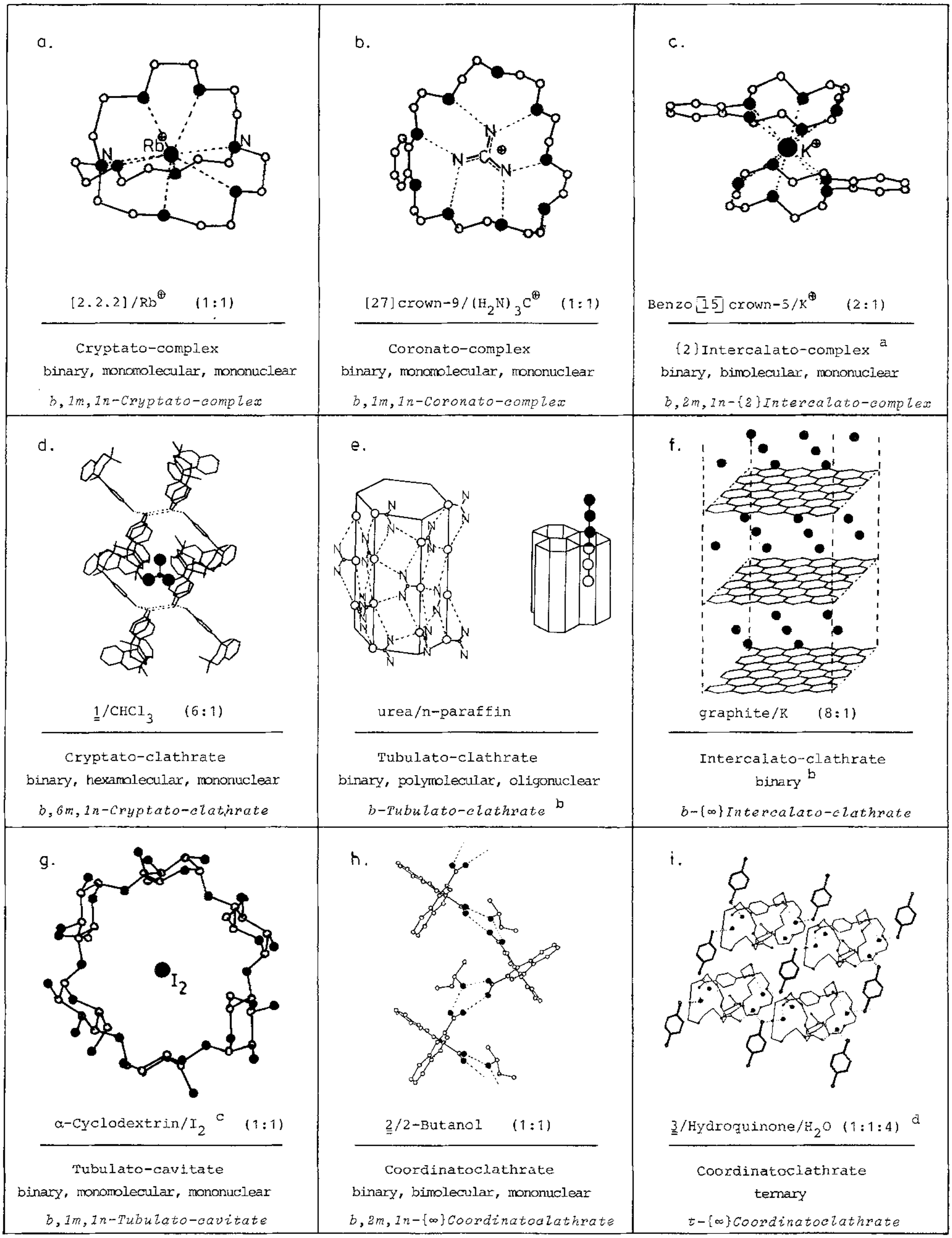


Fig. 1. Graphical representation of different host-guest situations and their nomenclature.

[a] In the case of a 'molecular' intercalate the term 'sandwich' may be used alternatively. [b] No clear decision in regard to the number of the individual particles forming the host-guest unit can be made. [c] Molecules of water of hydration (4 H_2O) have been omitted for clarity. [d] A decision between the host and the guest part of this aggregate cannot be made clearly.

Consequently, the Rb^+-aggregate with the ligand [2.2.2.] [4a] will be classified as a typical *cryptato-complex* (Figure 1a), as in the conventional sense (cryptate). The classical quinol and Dianin (**1**) host-guest compounds [8,15] (Figure 1d) will be classified as *cryptato-clathrates*. Correspondingly, the 27-crown-9-guanidinium ion [22] (Figure 1b) is best described by the term *coronato-complex*, the urea/*n*-paraffin inclusion compound (Figure 1e) by the term *tubulato-clathrate* and the aggregate consisting of graphite and K (Figure 1f) [8,15] by the term *intercalato-clathrate* [23].

For a more complicated host-guest topology and/or host-guest interaction, a further subdivision by means of a special prefix notation (cf. Figures 1c, 1f, 1h and 1i) will help to clarify the situation, e.g., the symbol $\{2\}$ which is placed in front of the term *intercalato-complex* (Figure 1c) denotes the two molecular crown layers forming the sandwich and $\{3\}$ would denote a triple-layer sandwich. The prefix notation $\{\infty\}$ in Figures 1h and 1i denotes the coordinative interaction existing between the host and the guest to be in the form of an infinite propagation (chain, plane, three-dimensional network [24]).

2.3. NUMERICAL CONSIDERATIONS

Another subdivision is possible by using numerical aspects of the host-guest aggregate. In the first instance, use is made of the total *number* of *individual components* (in a chemical sense) involved in the respective host-guest compound. If an aggregate is composed of two individual molecular or ionic components, then it would be classified as a *binary* aggregate. A three component system would be classified as a *ternary* aggregate etc., until the terms *oligo/polynary* would be used.

Thus, the recently-discovered aggregate [25] consisting of the tetraamide cryptand (**3**), hydroquinone and water (Figure 1i), which crystallizes in a layer structure, is to be designated as a *ternary clathrate*. As the three components are in contact with each other via a system of hydrogen-bond interactions, there is a coordination character and a more definitive classification would be a *ternary coordinato-clathrate*. Finally, one could denote the layered structure of the aggregate by adding the term *intercalato*. This systematic naming shows immediately that the cryptand (**3**) does not act as a cryptandoligand (cryptate; cf. Figure 1a), otherwise it would be classified as a *complex* rather than a *clathrate*.

An analogous but more precise classification is obtained by considering the *number* of *particles* (host, guest separately) combined in the host-guest unit (see Table I). Thus, the 1 : 1 α-cyclodextrin/I_2 compound (Figure 1g) can be characterized by the term *monomolecular mononuclear* (contracted to 1*m*,1*n*), and Figure 1h would be completely specified by the classification *b*,2*m*,1*n*-$\{\infty\}$*coordinatoclathrate* (*b* standing for binary).

A more extensive specification is possible by using the host-guest-type (ionic, polarized, neutral) and the nature of the interaction (ion-ion, ion-dipole etc.) (Table I). It can, however, occasionally be difficult to distinguish between these possibilities. This is particularly true of the nature of the interactions, since several types of interaction may be present in the one compound.

3. Conclusions

A pre-requisite for the application of this classification system is a knowledge of the crystal structure of the compound under discussion or to have a structural assignment, e.g., *via* spectroscopy. In principle, the more details which are known of the structure, the more illustrative becomes the proposed nomenclature of the host-guest compound. In an ideal case, an illustrative and realistic picture of the geometry and interaction within the host-guest unit can be obtained using the nomenclature proposed above. For compounds of unknown structure we suggest that the term *host-guest compound* be used.

As a general guideline, a host-guest compound should be specified as completely as possible by using a combination of the above systems. For instance, use of the term *cryptato-cavitate* instead of *cryptato-complex* for the host-guest situation shown in Figure la, would not be a good choice because it does not stress the importance of the coordinative interaction, which is the dominant factor in stabilizing the [2.2.2.]/Rb^+ host-guest aggregate. On the other hand, the alternative term *cavitato-complex* does not clearly describe the topology of the host-guest aggregate. In cases where the host-guest geometry is not known in detail, apart from an indication of the existence of some sort of cavity, then the description *cavitato-complex* would be the correct one.

Figure 1 contains nine examples of different types of host-guest compounds which have been classified according to the above scheme.

As already used for crown ethers [21], it is also possible to distinguish between a free-host molecule and the appropriate host-guest compound by using the specific termination *and* and *ate*. For instance, *clathrand* would be used for a guest-free host lattice molecule and *clathrate* would be used for its host-guest compound. The terms *tubuland* and *tubulate*, *cavitand* and *cavitate* [26] would be similarly used.

The proposed system of classification is still subject to a certain degree of subjectivity with borderline cases, since there are no sharp boundaries between the different classes. We believe, however, that this is rather advantageous since, in cases of doubt there is a certain degree of freedom which enables one to include a borderline host-guest compound in the most appropriate classification system.

The main advantage of this new classification/nomenclature system for host-guest-type compounds comes from the concept itself, which is modular in design and is therefore expected to be easy to use and also capable of development as new types of host-guest compounds are discovered.

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