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Classification and Nomenclature of Coronands, Cryptands, Podands, and of Their Complexes

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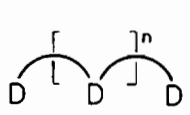
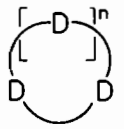
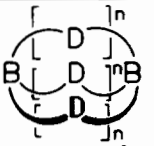
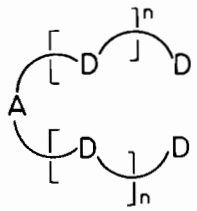
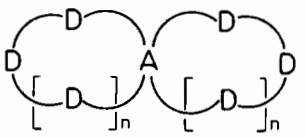
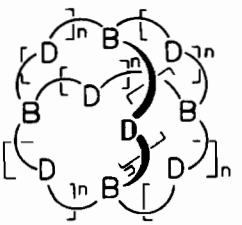
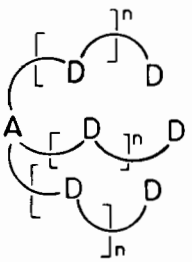
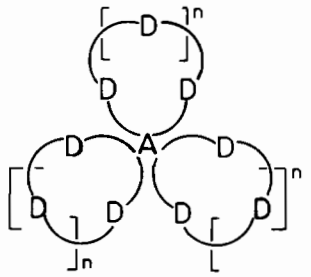
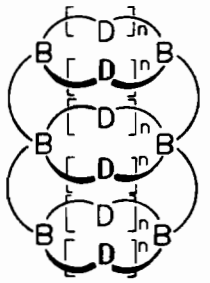
The common notations in use nowadays for crown ethers and cryptands like '[18]crown-6' [1] and '[2.2.2]cryptand' [2] have been extended in various ways during recent years to neutral ligands, which contain heteroatoms other than O and N, aromatic nuclei and chains other than $-CH_2-CH_2-$ [3–7]. For open-chain polyethers various glyme notations independent of the above ones have been employed [8, 9]. Since these notations are often incomplete [3, 5, 6, 10] and difficult to be compared with one another [4, 7, 11], it is desirable to unite them in a common nomenclature, to precisely define them and enlarge their scope without losing their practicability [12].

Table I shows a classification of the various organic neutral ligand systems, which is first of all essential: Multidentate monocyclic ligands with any type of donor atoms are called *coronands* [13] ('crown compounds'), while the term *crown ether* is reserved for cyclic oligoethers containing oxygen only. Moreover, a subdivision of the coronands, *cryptands* [2] and *podands* [14] according to the number of arms or bridges is demonstrated, whilst

TABLE I. Topology and Classification of Organic Neutral Ligands[a] (D = Donor Atom, A = Anchor Group, ⌒ = Chain Segment without Donor Atom, B = Bridgehead Atom).

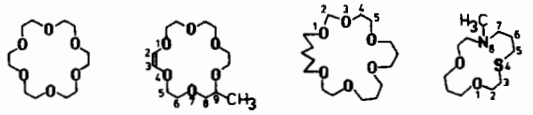
Podands[b] (open-chain)	Coronands[c,d] (cyclic)	Cryptands[e] (spherical)
		
{1} Podand[f] (Monopodand)	{1} Coronand[f] (Monocoronand)	{2} Cryptand[f] (Dicryptand)
		
{2} Podand (Dipodand)	{2} Coronand (Dicoronand)	{3} Cryptand (Tricryptand)[g]
		
{3} Podand (Tripodand)	{3} Coronand (Tricoronand)	{4} Cryptand (Tetracryptand)[g]

[a]For mixed open-chain/cyclic ligand systems lying between these topologies we suggest notations like 'podando-coronand' or 'coronando-cryptand' under consideration of the following order of priority: podand < coronand < cryptand; the class name is derived from the topologically higher ligand unit. [b]$n = 0 - \infty$. [c]$n = 1 - \infty$. [d]D = 0 (crown ether). [e]$n = 1 - \infty$. [f]For simplificity the numbers in the braces may be omitted. [g]Different topologies apart from those shown exist.

the minimum number of donor atoms, chain segments and anchor groups are stated. Names are also derived from these structural elements.

Coronand Nomenclature

A few samples of crown compound names are given below:

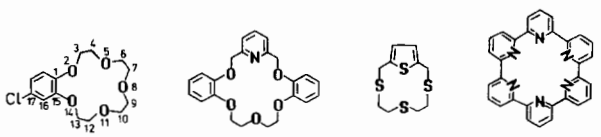


1 2 3 4

1: 18⟨O_6Coronand-6⟩; short name: 18C6
2: 9-Methyl-18⟨O_6coronand-6⟩2-en
3: 22⟨O_6-1.2.3$_2$.2.5-Coronand-6⟩
4: 8-Methyl-14⟨OSNO-2.3.2.3-coronand-4⟩

Punctuation and Symbolism

In the *braces* {} one obtains information about the *topology* of the ligand (comp. Table I), whereby {1} may be omitted. The number following the braces or preceding the angular brackets ⟨⟩ give the *ring size, e.g.* '18' for 1 and 2. In presence of aromatic and heteroaromatic units in the ring the shortest way to the next donor atom is considered (comp. 6–8). The *angular brackets* ⟨⟩ contain in the following order: a) *donor hetero atoms* expressed by the elemental symbols O, S, *etc.*; b) *bridges, i.e.* C–C chains between the donor hetero atom, denoted by numbers which correspond to the bridging C-atoms, bridge units like aromatic nuclei or more complex groups (their positions are marked in *round brackets*). The designation '2' for ethano, the most common bridge, is omitted when only this bridge is present or when such a procedure does not curtail the clarity of the structure (comp. 1 and 2). With heteroaromatics the direct annexation of nuclei is to be regarded as a normal case and as such is not be considered separately (*e.g.* denoted by 'O' in 8). c) Also included in the angular brackets are the *class name* (*e.g.* coronand) and d) the *total number* of donor heteroatoms. Examples for aromatic unit- and heteroaromatic unit-containing coronands are:



5 6 7 8

5: 17-Chloro-15⟨O_5-(1,2)benzeno.2$_4$coronand-5⟩
6: 18⟨O_5(2,6)Pyridino-(1,2)benzeno.2$_2$.(1,2)benzeno.1.1-coronand-6⟩
7: 12⟨(2,6)Thiopheno,S_3-1.2$_2$.1-coronand-4⟩
8: 18⟨(2,6)Pyridino$_6$coronand-6⟩

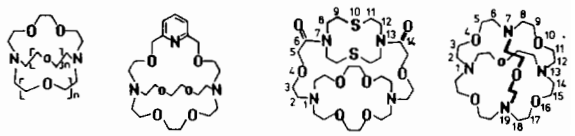
Substituents and *functional groups* in the basic skeleton (class name) are denoted by prefixes and suffixes (comp. 2 and 5).

Heteroatom and Bridge Sequence, Numbering

The sequence of *donor sites* in the ligand skeleton is given by hetero elemental symbols arranged in the order or priority laid down by the IUPAC rules [O precedes S and N (comp. 4), lowest locants for the second heteroatom (comp. 3) or for substituents and functional groups (comp. 2)]. Heterocycles with donor sites are treated as single atoms (comp. 6–8). The sequence for the *chain segments* without donor atoms corresponds to that of the heteroatoms, beginning from the donor atom of highest priority. The *numbering* is principally carried out according to IUPAC rules (this is also valid for the cryptands but does not apply in case of the podands; see below).

Cryptand Nomenclature

It is developed using the same symbolism in principle (see 9–13). In the angular brackets the *bridgehead atom* of highest priority is named, and in the square brackets follows the sequence of the individual *bridges*, starting from the preceding bridgehead. The bridge with the highest number of donor atoms has priority; with equal numbers of donor atoms in the bridges, the priority is determined by that of the heteroatoms and in second instance by that of substitution. Following the notations of the bridges are the symbol of the *second bridgehead atom*, the class name and finally the whole number of donor heteroatoms. Further bridges are specified before the class name by square brackets with superscripts indicating their locations (comp. 12, 13).



9: n = 1, 10: n = 2 11 12 13

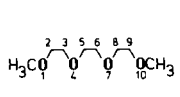
9: ⟨N[O_2][O]$_2$N-Cryptand-6⟩
10: ⟨N[O_2]$_3$N-Cryptand-8⟩
11: ⟨N[O(2,6)Pyridino-O-2.1$_2$.2][O_2]$_2$N-cryptand-8⟩
12: {3}⟨N[ONSNO][O_2]$_2$N⟨[S]^{7,13}Cryptand-12⟩6,14-dion
13: {3}⟨N[ONO]$_2$[O]N⟨[O]^{7,19}Cryptand-10⟩

Podand Nomenclature

The sequence and numbering begin with the donor atom of highest priority at one *end of the chain*; the

numbering thus differs from that of IUPAC, in this case only. Ends without donor aoms (*e.g.* methyl in 14) are treated as substituents which prefix the name; otherwise the rules, which have been develloped for coronands, are also valid for the monopodands. In the case of oligopodands (comp. 16) the chain with the highest number of donor atoms is first named. Additional arms are then denoted in decreasing order of priority and with superscripts to their location, whereby the following sequence applies: number of donor atoms, type (priority) of the donor atoms, priority of end groups (the latter based on IUPAC rules (C-14.1.)).

Examples are:



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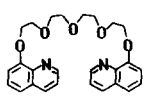

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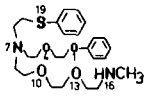

16

14: 1,10-Dimethyl⟨O_4podand-4⟩

15: ⟨(8)Quinolino,O_5(8)quinolinopodand-7⟩

16: 16-Methyl-1,19-diphenyl{3}⟨$O_2NO_2N⟨S^{(7)}$-podand-7⟩

For the designation of *Coronand-, Cryptand-, Podand-Complexes,* we use the common rules for cationic complex units in coordination chemistry, *e.g.* 18⟨O_6-Coronand-6⟩potassium thiocyanate for the 1-potassium thiocyanate complex and ⟨$N[O_2]_3N$-Cryptand-8⟩barium iodide for 10-BaI_2, *etc.*

The nomenclature described here allows an essentially easier recognition of the compound group and other important characteristics such as topology and donor centers. Details and borderline cases will be discussed in a full paper.

Acknowledgement

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