Into the Next Dimension: Nanometer-Sized, Oligonuclear Coordination Compounds with C_3-Symmetric Ligands

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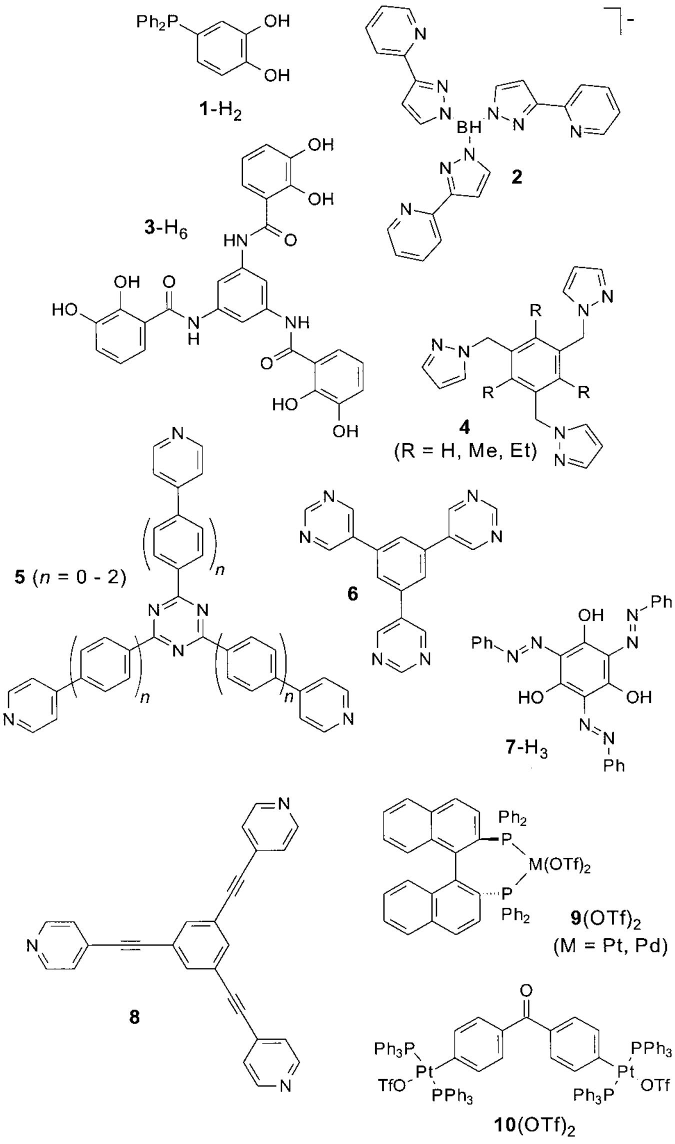
"Nanotechnology" is an interdisciplinary field of research which has recently inspired many researchers to transfer the function of macroscopic objects (e.g. machines) onto microscopic aggregates. Two different approaches can be discussed for this scientific challenge: The size of macroscopic objects can be reduced to a minimum, or microscopic species can be formed on a molecular basis. Examples for the latter are given by nature. For example, enzymes can act as molecular "machines" which are able to perform specific functions.[1]

The stepwise synthesis of nanometer-sized molecules is very troublesome. Therefore, molecular self-assembly processes represent a useful alternative to "classical" strategies. Several components aggregate by noncovalent interactions to form supramolecular species. Large, highly symmetrical molecules can be formed from simple molecular building blocks which possess an appropriate symmetry. Here the assembly process is controlled by the symmetry of the components as well as thermodynamic factors (entropy, enthalpy).[2] It is important that the noncovalent bonds can be formed and cleaved reversibly to enable the correction of errors resulting during the self-assembly process.[3]

Studies of the self-assembly of relatively small oligonuclear units involve the formation of helicates (one-dimensional),[4] molecular squares (two-dimensional),[5] and tetrahedra (three-dimensional)[6] from ligands with two (or more) binding sites for metals. The molecular cylinders described by Lehn et al. represent a class of somewhat larger complexes.[7] However, large—nanometer-sized—coordination compounds were just recently obtained using C_3-symmetric ligand systems with three ($[(\mathbf{1})_3\mathrm{Ti}]^{2-}$, **2**–**6**, **8**) or six binding sites (**7**) for metal ions (Scheme 1). The metal complex units can possess a linear (e.g. *trans*-$\mathrm{Pd^{II}Br_2}$) or bent structure (e.g. *cis*-(en)$\mathrm{Pd^{II}}$).

The diphenylphosphane-substituted catechol ligand **1**-H_2 forms with titanium(IV) ions the homoleptic coordination compound $[(\mathbf{1})_3\mathrm{Ti}]^{2-}$. Subsequent reaction with $\mathrm{PdBr_2}$ leads to the heteronuclear complex $[\{(\mathbf{1})_3\mathrm{Ti}\}_2(\mathrm{PdBr_2})_3]^{4-}$.[8] Here the $[(\mathbf{1})_3\mathrm{Ti}]^{2-}$ unit acts as a C_3-symmetric ligand bearing three phosphorus donor atoms which can bind to the *trans*-$\mathrm{PdBr_2}$ moiety (for a simple representation, see Scheme 2).



Scheme 1. Molecular building blocks discussed here for the self-assembly of nanometer-sized coordination compounds.

The C_3 symmetry of ligands **2**–**6** and **8** enables, upon reaction with metal ions or complex units, the formation of

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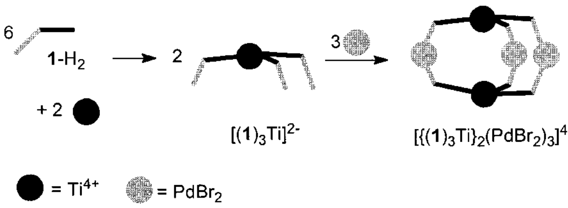

Scheme 2. Formation of $[\{(\mathbf{1})_3Ti\}_2(PdBr_2)_3]^{4-}$.

simple polyhedra which are built up from triangular faces (e.g. tetrahedron, hexahedron, octahedron).[2]

Ligand **2** with manganese(II) ions[9] as well as the deprotonated ligand **3**-H_6 with titanium(IV) ions[10] form tetrahedral tetranuclear complexes $[(\mathbf{2})_4Mn_4]^{4+}$ and $[(\mathbf{3})_4Ti_4]^{8-}$. The metal ions are located at the corners and the ligands on the faces of the tetrahedron. The geometry corresponds to that of structure **A** in Figure 1. Figure 1 a shows the spatial arrangement of the four ligands and the four metal centers. The representation in Figure 1 b is reduced to the basic polyhedron (here the tetrahedron), showing only the position of one ligand and the metals bound to this ligand. Coordination of the ligands **2** and **3** to metal ions that prefer an octahedral coordination geometry occurs through bidentate ligand units, resulting in a structure of type **A**.

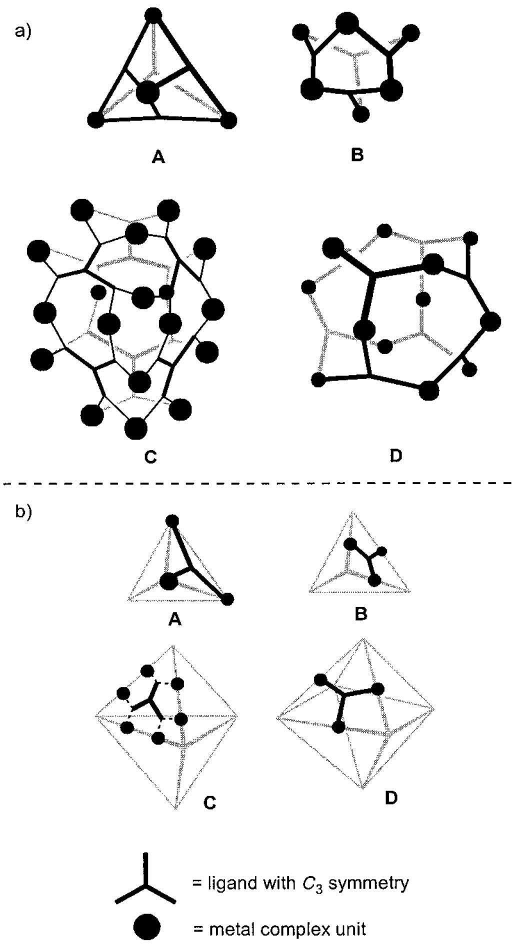

Figure 1. Types of structures of metal complexes which are formed from C_3-symmetric ligands and appropriate metal complex units. a) Schematic representation of different structures of metal complexes; b) reduction of the structures to simple polyhedra: tetrahedron **A**, **B**, hexahedron **C**, and octahedron **D** (only one of the ligands and the metal ions which bind to this ligand are shown).

The structure of the metal complex formed from four ligands **4** and six *trans*-$PdCl_2$ units also can be described as a tetrahedron.[11] The complex $[(\mathbf{4})_4(PdCl_2)_6]$ represents a structure of type **B**. The ligands bridge the faces of the tetrahedron and are rotated by 30°, while the bridging metals are located at the center of the edges. Thus, the metal ions form an octahedron. In the case of $[(\mathbf{4})_4(PdCl_2)_6]$ the angle which connects the "trigonal faces" at the edges of the tetrahedron is given by the specific geometry of the ligands. The complex $[(\mathbf{5})_4\{(en)Pd\}_6]^{12+}$ (en = ethylenediamine), which is formed by the reaction of four ligands **5** with $[(en)Pd(NO_3)_2]$, is also a complex of type **B**.[12] In contrast to $[(\mathbf{4})_4(PdCl_2)_6]$, which is formed from ligand **4**, in this case the *cis*-(en)Pd unit acts as a cornerstone to connect the triangular faces of $[(\mathbf{5})_4\{(en)Pd\}_6]^{12+}$. Introduction of differently sized spacers (direct bond, *p*-phenylene, 4,4′-biphenyl) in ligands **5** influences the size of the self-assembled coordination compounds $[(\mathbf{5})_4\{(en)Pd\}_6]^{12+}$. These possess internal cavities with diameters in the range of 1.9 to 4.6 nm, depending on the spacer. Guest molecules can be encapsulated in the interior of the complexes and under appropriate conditions can be exchanged against others.[12]

Recently, a supramolecular coordination compound which possesses a hexahedral ("trigonal-bipyramidal") structure, $[(\mathbf{6})_6\{(en)Pd\}_{18}]^{36+}$ (Figure 2), was described by Fujita et al. This complex is formed from 24 components (6 ligands and 18 (en)Pd units). The structure corresponds to a type **C** geometry. Here (en)Pd complexes doubly connect the trigonal faces of the hexadentate C_3-symmetric ligand **6** to neighboring ligands. The compound has a molecular mass of 7103 Da and dimensions of 3 × 2.5 × 2.5 nm with an internal volume of 900 Å^3. Stepwise reaction of **6** with $[(en)Pd(NO_3)_2]$ allows the isolation and characterization of the intermediates $[(\mathbf{6})_2\{(en)Pd\}_2]^{4+}$ and $[(\mathbf{6})_3\{(en)Pd\}_4]^{8+}$, which are formed during the assembly of $[(\mathbf{6})_6\{(en)Pd\}_{18}]^{36+}$.[13]

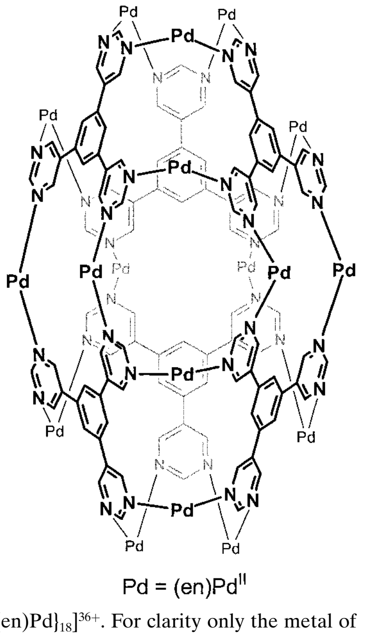

Figure 2. The structure of $[(\mathbf{6})_6\{(en)Pd\}_{18}]^{36+}$. For clarity only the metal of the $(en)Pd^{II}$-units is shown.

Derivative **7**-H_3 is deprotonated by $[Me_4N]OH$ and forms with $Cu(NO_3)_2$ the neutral polynuclear copper(II) complex $[(\mathbf{7})_8Cu_{12}]$. Each copper(II) ion of the complex connects two ligands and shows a distorted square-planar geometry with a *trans*-N_2O_2 arrangement. The six ligands **7** form the faces of an octahedron and are connected by the metal ions which are located at the centers of the edges (see **D**, Figure 1). Here the copper ions do not act as real cornerstones, but the distortion from a square-planar geometry leads to the formation of a nearly spherical cage compound. This complex has a diameter of 1.4 nm with a volume of approximately 816 Å^3. Up to six DMF molecules can be encapsulated as guests. The copper(II) ions of $[(\mathbf{7})_8Cu_{12}]$ are located on the corners of a cube so that the geometry also can be described as cubeoctahedral.[14]

All compounds discussed up to now could be characterized by X-ray structural analysis. In the following two coordination compounds will be described which contain the ligand **8** as organic building block. The structures of those complexes were assigned based on spectroscopic investigations and symmetry considerations.

Ligand **8** forms with the platinum(II) or palladium(II) complexes **9**$(OTf)_2$ ($Tf = F_3CSO_2$) enantiomerically pure cage compounds $[(\mathbf{8})_4(\mathbf{9})_6]^{12+}$, which possess a structure of type **B**. NMR spectroscopy shows the symmetry of the complexes, while the composition is assigned by mass spectrometry (ESI-FTICR).[15] The use of building blocks **10**, which contain two linear *trans*-platinum(II) units connected by a bent spacer, leads to the formation of the complex $[(\mathbf{8})_8(\mathbf{10})_{12}]^{24+}$. This compound possesses a cubeoctahedral geometry (**D**) and has, according to computer models, a cavity with a diameter of approximately 5 nm. A similar complex is obtained upon use of a planar C_3-symmetric trisplatinum(II) complex and bent bispyridine derivatives.[16]

Use of the building block **10**, with a 120° angle (sp^2), instead of **9**, with a 90° angle, leads upon reaction with **8** to the preferred formation of the cubeoctahedron $[(\mathbf{8})_8(\mathbf{10})_{12}]^{24+}$ (**D**) in contrast to the tetrahedral $[(\mathbf{8})_4(\mathbf{9})_6]^{12+}$ (**B**). This shows that slight variations in the geometry of the supramolecular building blocks can have a big influence on the structures of the self-assembled polynuclear metal complexes.

In summary, oligonuclear coordination compounds can be formed from C_3-symmetric ligands and different metal complex fragments. The complexes obtained are nanometer-sized and possess structures which can be reduced to basic geometries (tetrahedron, hexahedron, octahedron). Which structure is obtained is influenced by the geometry of the building blocks used. The described complexes possess cavities that allow guests to intrude. A next step will be to perform chemical reactions in the interior of the cavities and thus to imitate the function of reactive centers in enzyme pockets.

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