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Review

Coordination motifs in modern supramolecular chemistry

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Self-assembling
Templating

ABSTRACT

In this paper we describe the contribution of coordination chemistry to the creation and development of supramolecular chemistry. Both discrete- and infinite buildups are examined. The first group comprises metal-containing host molecules and organic acceptors for metal cations; the second includes coordination polymers, ionic -and liquid crystals. Their potential- and practical applications are briefly explained.

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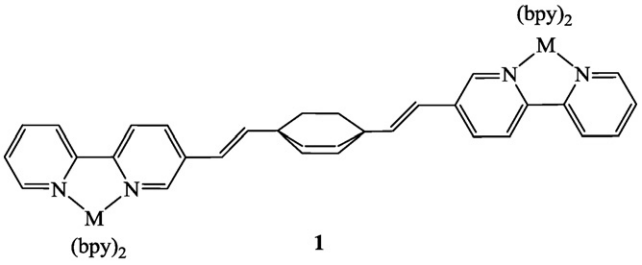

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Fig. 1.

$[Ru\{(2,3\text{-dpp})[Ru(2,3\text{-dpp})Ru\{(2,3\text{-dpp})Ru(bpy)_2\}_2]_2\}_3]^{44+}$

2,3-dpp =

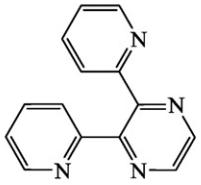

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Fig. 2.

1. Introduction

Supramolecular chemistry owes its nascence, more than 40 years ago, to the coordination motifs of Pedersen and Frensdorff's crown-ethers (coronands) [1] and Lehn's cryptands [2]. This amazing variety of organic molecular structures is based on tetravalent carbon with the diversifying power of structural multiplicity in supramolecular chemistry being considerably enlarged by the inclusion of its sixty metal ions with their valences, coordination numbers, and geometries.

The property of metallosupramolecular structures to self-assemble is frequently coupled with the template effect [3,4,10,11] and is the most common method of preparing these structures [3–9], liberating the chemist from tedious multi-step synthetic procedures. Moreover, thermodynamic aspects [5] too are involved here, since self-assembly occurs by the formation of unstable structures in thermodynamic equilibrium with one another. Since erroneous structures are eliminated, the self-assembled products so formed are thermodynamically maximally stable, generally with high (frequently quantitative) yields.

A wide spectrum of coordination bond energies (10–30 kcal/mol) provides the process route required. Practical applications of the products obtained call for circumventing their thermodynamic character, which is achieved by altering their structures using certain methods [12].

Studies available in the literature referred above focus on only some coordination motifs in the supramolecular chemistry and do not present an overall view of the problem. The present review, we hope, resolves this issue concisely, avoids superfluous details, and achieves the balance required of a review article. The morphological principle, based on dimensionalities of the structures, permits a logical discussion of this important area of the supramolecular chemistry, and was thus chosen as the framework for presentation.

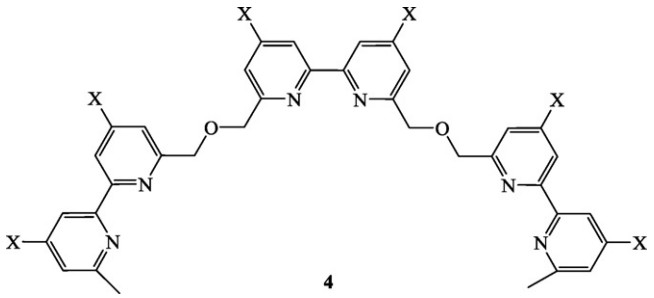

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Fig. 4.

2. Monodimensional (1D) structures

1D structures are extended polynuclear buildups possessing a large principal axis. Even though they exhibit the least multiplicity, it is possible to derive all the other varieties of coordination supramolecular structures from them.

2.1. Linear polynuclear metal complexes

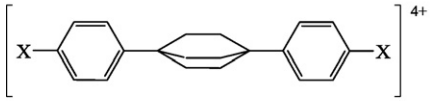
A comprehensive list of linear polynuclear molecules of the type **1** (Fig. 1) is given in Balzani et al. review [13], where M represents various metals or metals of distinct oxidation numbers.

Superficially, this appears to be simply a large molecule (supermolecule), which does not appear to correspond to the definition of the supramolecule as comprising a complex system of molecular components with distinct individual properties [4,13]. The type **1** structure (Fig. 1) is represented here as A∼B, where "∼" signifies any type of bonding between the components A and B with weak interaction between them, when they behave almost as individual buildups; so a structure of the type **1** (Fig. 1) is a supramolecule. Since this interaction is performed through a spacer "∼", its precise nature determines whether this structure is a supermolecule or supramolecule. Linear supramolecules can be very lengthy, for example, a record-holder — the compound **2** (Fig. 2), which includes 44 ruthenium atoms [13].

Certain less common types are hard linear structures and molecular rods [5,6,14] of the type **3** (Fig. 3), where the coordination sites are connected by a hard spacer.

2.2. Helicates

An unusual capacity of definite linear metal complexes with regular structure is to form spiral supramolecules – known as helicates [15,16] – that result from the tetrahedral coordination of Cu^{I}, Ag^{I} cations. This becomes clear from the example of typical ligands **4** (Fig. 4), whose hard bipyridine fragments are connected by flexible spacers, and inter-chain coordination tetrahedrons form as self-assembled double helicates **5** (Fig. 5).



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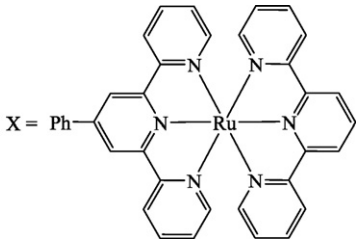

Fig. 3.

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