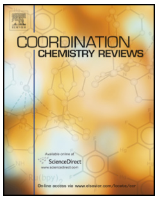
Coordination Chemistry Reviews 276 (2014) 34–58

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

# Coordination polymers with nucleobases: From structural aspects to potential applications

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**Contents**

A R T I C L E  I N F O

*Article history:*
Received 12 February 2014
Accepted 20 May 2014
Available online 28 May 2014

*Keywords:*
Coordination polymers
Metal–nucleobase chemistry
MOFs
Porous materials

A B S T R A C T

This review article focuses on the current state-of-the-art of coordination polymers using nucleobases as ligands. It collects the literature already published in a comprehensive way and attempts to provide perspectives for this research field. The article integrates two important concepts of coordination chemistry, metal–nucleobase chemistry and coordination polymers. It tries to demonstrate novel opportunities for these coordination polymers in terms of architectures and potential applications. The text is presented in three general sections according to the dimensionality of the coordination polymer, and then is subdivided in sections that take into account the structural role of the nucleobase as ligand (either terminal or bridging), and the nature of the nucleobase (pyrimidine *vs* purine). Synthetic, structural aspects and physico-chemical properties are presented for each sample. Valuable potential applications and perspectives for these novel materials are also discussed.

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*Abbreviations:* A, adenine; G, guanine; C, cytosine; Hpur, purine; U, uracil; 1-MeU, 1-methyluracil; 1-MeT, 1-methylthymine; 1-MeC, 1-methylcytosine; 9-MeA, 9-methyladenine; 3-MeA, 3-methyladenine; 9-MeHx, 9-methylhypoxantine; 1,9-MeG, 1,9-dimethylguanine; Hdap, 2,6-diaminopurine; G-Et-en, ethylenediamine-N9-ethylguanine; A-Et-en, ethylenediamine-N9-ethyladenine; 6-MPH, 6-mercaptopurine; 6-ThioGH, 6-thioguanine; 9-AA, 9-allyladenine; TAcOH, thymine-1-acetic acid; UPrOH, uracil-1-propionic acid; 7-atp, 7-amine-1,2,4-triazolo[1,5-a]pyrimidine; HIN, isonicotinic acid.

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http://dx.doi.org/10.1016/j.ccr.2014.05.017
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## 1. Introduction

For many years, metal–nucleobase complexes have attracted great attention due to the fact that these compounds may act as biomimetic models for the understanding of the biological effects of metal ions. They are relatively simple models useful to provide some keys for the role of action of metal ions in biological systems; in particular the studies focused on metal ions with nucleobases can be useful as models to understand the interaction of those metals with DNA. As well as providing valuable insight into the mode of action of numerous metal-containing drugs (*e.g. cis*-platin) understanding these interactions has provided opportunities for exploiting the nucleobases as highly versatile ligands. Moreover, some of metal–nucleobase complexes have proven to be useful as direct drugs for the treatment of several diseases [1–4].

The basic aspects of the coordination chemistry of purine and pyrimidine derivatives have been discussed in several reviews [5]. During the last decades, more than six hundred metal nucleobase complexes have been prepared and crystallographically characterized. The number of crystal structures of metal ions with nucleobases as ligands has dramatically increased in recent years reflecting the great interest in these compounds.

In addition to the "simple" complex formation, the structural characteristics of nucleobases allow extension beyond basic coordination chemistry towards larger and more complex molecular architectures based on the formation of supramolecules. The selective combination of metal ions with just nucleobases or using additional ligand leads to two types of structures: discrete and infinite supramolecules. These structures may be formed exclusively using coordination bonds or/and complementary H-bonding of nucleobases acting as ligands to metal centres [6]. The formation of a particular supramolecular architecture requires the selection of suitable building blocks. Supramolecular systems require their components to have appropriate spacing and configuration relative to each other, and ideally a library of related structural units is required. The structural subunits for the construction of coordination supramolecules are the metal ions, or complexes, and organic ligands. Architectures based on these systems have been the subject of numerous investigations due to their potential for applications based on their useful properties such as molecules and ions host, optical properties, porous materials and catalytic activity [7–10]. Geometrical aspects have a critical role in determining the final architecture of the supramolecular entity. Specifically, in the case of metal ions (or complex fragments) and nucleobases two different types of building blocks are used for constructing finite or infinite molecular assemblies. The most typical syntheses proceed in a single step by self-assembly, however, in a few cases multi-step synthetic approaches have been shown to be more convenient, *i.e.* non-labile metal fragments.

Coordination polymers (CPs) are a class of hybrid materials comprising metal ion-based, vertices, and organic ligands, linkers, that serve to connect the vertices into one, two or three-dimensional periodic structures. This is a field of great current interest in both chemistry and material science. The structures and properties of CPs can be carefully tailored by judicious selection of metal ion and organic linker building blocks. They have shown a broad panel of properties (Fig. 1) ranging from luminescence [11–13], to non-linear optics [14], magnetism [15] and electrical conductivity [16]. In particular polymers with porous structures, named as metal–organic frameworks (MOFs), also named as porous coordination polymers (PCPs), have attracted great attention due to their capabilities. The intrinsic porosity of these materials as well as their large inner surface area, tuneable pore sizes and topologies [17], lead to various architectures [18,19], which renders them potentially useful for gas adsorption and storage [20–23], gas and liquid separation [24–42], drug delivery [43–45], sensor technology [46], heterogeneous catalysis [47–53], as hosts for metal colloids or nanoparticles [54] or polymerization reactions [55], pollutant sequestration [56], and recently water sorption for heat transformation [57–63]. Indeed, most of these applications rely on highly specific host–guest interactions.

Their promising properties, coupled with the ease by which their structures can be modified, make MOFs one of the most exciting, diverse, and rapidly growing areas of modern chemistry research. Very recently some studies have been focused on the potential properties and applications of CPs in nanotechnology. However, this field is still in its infancy. It seems clear that many potential applications of CPs will require them to be constructed from building blocks that are biologically and environmentally compatible. For example, most biological applications, including drug delivery or intracellular imaging, would clearly require non-toxic and biocompatible materials. In addition, some of the suggested applications will require large quantities of CPs. To reduce their environmental impact, bulk CP materials should be either environmentally friendly and/or easily recyclable. From this perspective the new generations of CPs should be designed according to specific composition criteria that address environmental and biological standards.

Therefore, CPs containing biomolecules, and particularly those with nucleobases, have emerged as an attractive area [64]. The use of nucleobases as building blocks offers several advantages, which are highlighted here: (i) they can lead to biologically compatible CPs; (ii) they are structurally diverse; (iii) they can be either structurally rigid or flexible, aspects that impact the functional nature of the resulting CP; (iv) they can present many different metal-binding sites and consequently, they can exhibit multiple possible coordination modes, a feature that increases their architectures as CPs; (v) nucleobases have intrinsic self-assembly properties which can be used to direct the structure and function of CPs; and finally, (vi) natural nucleobases are available in quantities and at prices amenable to preparing bulk quantities of materials.

In summary, metal–nucleobase coordination chemistry has been an active research area of coordination chemistry that currently spreads into new fields of material science and nanoscience. In 2009, we published a general perspective article on supramolecular aspects of metal–nucleobase chemistry, which included discrete and polymeric structures and the supramolecular arrangements that can be formed using H-bonding interactions [65]. The article focused on coordination polymers involving nucleobases as ligands, because this is a current blooming research field. In fact, most of the references provided belong to works published during the last 5–10 years. We have tried to provide a general overview of the current state-of-the-art of this field, dealing with synthetic and structural aspects of these compounds and highlighting their physico-chemical properties and current directions in this new field. The manuscript includes studies published before 2000, which essentially deal with synthetic and structural aspects of nucleobase-CPs, and more recent literature in which a clear evolution towards a search of novel multifunctional materials, including nanomaterials, with interesting physico-chemical properties is being developed. This review is structured in a rational way attending to dimensionality of the different CPs architectures and the structural role of the nucleobase as ligand paying attention to aspects concerning synthesis, structure and properties.

## 2. The building blocks

### 2.1. Nucleobases as building blocks

Nucleobases are key constituents of nucleic acids that are normally involved in base-pairing: adenine binds to thymine or uracil