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Review

Metal-organic molecular architectures with 2,2′-bipyridyl-like and carboxylate ligands

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Contents

Abstract

This review provides an overview on the crystal structures and properties of metal carboxylate coordination compounds with 2,2′-bipyridyl-like ligands reported in the past 4 years, which exhibit interesting structural features. This covers coordination polymers in one, two and three dimensions, as well as molecular architectures assembled by hydrogen-bonding and/or π–π stacking interactions from low-dimensional entities to higher-dimensional supramolecular architectures.

Keywords: Molecular architecture; Supramolecular interactions; Coordination bond; Hydrogen bond; π–π; Interactions; 2,2′-Bipyridine; 1,10-Phenanthroline; Carboxylate

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Abbreviations: bpy, 2,2′-bipyridine; dmbpy, 4,4′-dimethyl-2,2′-bipyridine; dmphen, 2,9-dimethyl-1,10-phenanthroline; Hglyo, glycolic acid; Hobpy, 6-hydroxy-2,2′-bipyridine; Hophen, 2-hydroxy-1,10-phenanthroline; 3-Hpya, *trans*-3-(3-pyridyl)acrylic acid; 4-Hpya, 4-pyridylacrilic acid; Hsba, 4-sulfobenzoic acid; Hsbal, *N*-(2-hydroxybenzyl)-β-Alanine; Hsgly, (*N*-(2-hydroxybenzyl)-α-glycine; Hsval, (*N*-(2-hydroxybenzyl)-α-valine; H_2aa, adipic acid; 1,2-H_2bdc, 1,2-benzenedicarboxylic acid; 1,3-H_2bdc, 1,3-benzenedicarboxylic acid; 1,4-H_2bdc, 1,4-benzenedicarboxylic acid; H_2bpa, 4,4′-biphenyldicarboxylic acid; 3,3′-H_2bpyda, 2,2′-bipyridyl-3,3′-dicarboxylic acid; 4,4′-H_2bpyda, 2,2′-bipyridyl-4,4′-dicarboxylic acid; H_2chdc, 1,4-cyclohexanedicarboxylic acid; H_2eob, ethylenedi(4-oxybenzenecarboxylic acid); H_2fum, fumaric acid; H_2glu, glutaric acid; H_2ma, maleic acid; H_2oba, 4,4′-oxybis(benzenecarboxylic acid); H_2pa, pimelic acid; H_2sal, salicylic acid; H_2sala, (*N*-(2-hydroxybenzyl)-α-alanine; H_2su, succinic acid; H_2sub, suberic acid; H_2tda, thiodiglycolic acid; H_3bta, 1,2,4-benzenetricarboxylic acid; H_3btc, 1,3,5-benzenetricarboxylic acid; H_3nat, nitrilotriacetic acid; H_3oa, orotic acid; 4-H_3oip, 4-hydroxyisophthalic acid; 5-H_3oip, 5-hydroxyisophthalic acid; H_3sip, 5-sulfoisophthalic acid; H_4btac, 1,2,4,5-benzenetetracarboxylic acid; mal, malonate dianion; ox, oxalate dianion; phen, 1,10-phenanthroline

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1. Introduction

Crystal engineering of metal complexes, especially coordination polymers has been greatly developed in the past decade [1–8]. Coordination molecular architectures consist of metal ions (and metal clusters) functioning as nodes and organic ligands as bridges. These exhibit a wide range of infinite zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) frameworks with different interesting structural features, resulting from coordination bonding, hydrogen bonding, aromatic π–π stacking interactions as well as van der Waals forces [1–8]. Aside from coordination bonding interactions, relatively strong hydrogen bonding and $\pi-\pi$ stacking interactions, the solvent molecules, counterions and templates also influence the formation of the ultimate architectures. As such, non-coordinating ions or molecules may sometimes be used to control the crystallization processes and solid-state architectures. On the other hand, many supramolecular architectures based on metal–ligand interactions have, in fact, been designed for purely symmetry and esthetics grounds. The intense interest in this field, given impetus by synthetic and theoretical chemists, crystallographers and materials scientists, has resulted not only in beautiful and diversified structures, but in potential applications as electronic, magnetic, optical, absorbent and catalytic materials [7,9].

Coordination molecular architectures can be directly constructed by coordination bonds using metal ions existing in varied coordination geometries (for example, tetrahedron, square, trigonal bipyramid or octahedron) to combine with multifunctional (linear or angular bidentate, planar or pyramidal tridentate, planar or tetrahedral quadridentate) ligands into multi-dimensional frameworks. Another synthetic approach utilizes supramolecular synthons since π–π stacking interactions and hydrogen bonds have directionality and recognition compared with weak electrostatic interactions and van der Waals forces [10]. The strengths of these interactions are moderate, falling between the extremes of strong covalent bonds and weak van der Waals forces. Compared with inorganic compounds, however, coordination polymers built upon molecular building-blocks hold great promise for processability, flexibility, structural diversity, and geometrical (size, shape, and symmetry) control. As such, supramolecular architectures assembled by coordination bonds and/or supramolecular interactions allow for more predictable control over directional assemblies and packing arrangements in the solid state.

The exo-bidentate dipyridyl heterocyclic compounds as bridging ligands, include, for example, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane and *trans*-bis(4-pyridyl)ethene; the chemistry of coordination polymers of these ligands has recently been reviewed [11,12]. In contrast to the exo-bidentate dipyridyl compounds, 2,2′-bipyridyl-like (designated as bpy-like hereafter) ligands are bidentate chelating ligands, which can only act as terminal ligands and may provide supramolecular interaction sites for molecular recognition. Meanwhile, as bridging ligands, carboxylates, especially multi-carboxylates are of immense interest in the construction of polymeric coordination architectures owing to the fact that these polymers have a wide range of structural diversities and potential applications as porous materials and magnetic materials [7,9].

We have been interested in this aspect of coordination polymers, but we have not found any recent critical review of this subject, particularly from the crystallographic view. In this review, we summarize the recent progress in design and crystal structural investigations of coordination supramolecular networks based on bpy-like (such as bpy, phen and their derivatives) and carboxylate ligands, which are assembled by coordination bonds, hydrogen bonds as well as π–π stacking interactions. The literature covers the years 2000–2003, along with some reports which appeared in January 2004. The coordination-bonded frameworks are categorized into 1D, 2D and 3D polymeric architectures in Section 2, in which the supramolecular hydrogen bonding and $\pi-\pi$ interactions do not play a critical role; the supramolecular architectures assembled via hydrogen bonds and $\pi-\pi$ interactions based on the low-dimensional metal complexes are presented in Sections 3 and 4, respectively.

2. Molecular architectures assembled via coordination bonds

One of the most challenging research fields in modern chemistry is the design and synthesis of multifunctional compounds and materials with predictable structures and properties. In the 1970s, A.F. Wells focused on the overall structures of inorganic compounds and abstracted crystal structures in terms of their topology by reducing them to a series of points of a certain geometry that are linked to a fixed number of other points [13]. The final structures can thus be described either as polyhedra or as infinite networks. In the early 1990s, R. Robson developed and extrapolated Wells' work into the realm of metal-organic compounds and coordination supramolecular chemistry [14].

In order to design the targets with the different structural features and potential functions, an important step is selection and synthesis of the nodes including mono-, bi- and poly-nuclear structural units. Different metal ions may exhibit different coordination geometries. For example, two- or three-coordinate motifs with linear or T-shaped fashions found in Ag(I) and Cu(I) complexes can be employed to assemble a large number of supramolecular architectures [15] (Scheme 1). Square-planar and tetrahedral coordination motifs, are usually found in four-coordinate metal complexes, and have been well documented in supramolecular architectures [3,16]. Octahedral coordination spheres are ubiquitously adopted to construct coordination polymers. Metal ions in different coordination geometries as