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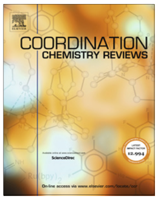

Review

Structural diversity of coordination compounds derived from double-chelating and planar diazinedicarboxylate ligands

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ABSTRACT

The use of diazinedicarboxylate ligands in the construction of preconceived molecular entities and crystal structures deserves a good understanding of their coordination capacity in order to employ them for their rational design of functional materials. Therefore, the scope of the present review is to provide a comprehensive account of the architectures built up from these ligands rationalizing them through a conscientious analysis of their coordination modes in which the preponderance for establishing double chelating five-member rings holds a central role. The study covers the coordination features offered by transition, representative and lanthanide metal ions, with special emphasis on the coordination mode prevalence for each ligand. The structural rationalization is assessed during the examples along with their more relevant properties.

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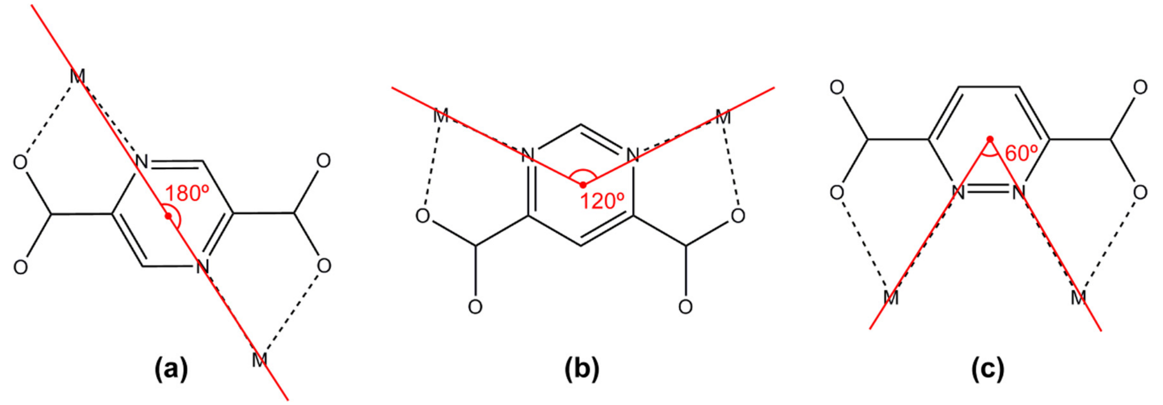
1. Introduction

Coordination polymers (CPs) and in particular, metal–organic frameworks (MOFs), constitute a very well-known but still emerging class of functional materials that need no introduction in most areas related to chemistry and materials science owing to the vast contribution they are bringing in many applications [1]. The large interest they are attracting lies mainly on the unlimited diversity of framework topologies acquired as well as the broad set of properties afforded by their metal–organic nature [2]. On the one hand, the increasing number of fascinating structures origins at well established rational design that obeys the principles dictated by "reticular chemistry", which considers the crystal structures as a result of the self-assembling among the nodes (metal ions or clusters) and linkers (organic ligands) [3]. Among the broad set of functional properties exhibited by these materials, permanent porosity constitutes a cornerstone since it provides them with excellent performances in gas storage and separation [4], although very promising performances in the fields of luminescence, magnetism and catalysis have also been observed [5]. Therefore, the selection of organic ligands and metal ions is a crucial point since, in addition to reaction conditions, are responsible for directing the self-assembling process towards the desired architectures, and subsequently, the properties chased [1b,6].

Diazines encompass a largely employed family of aromatic heterocycles of $C_4H_4N_2$ formula. They may be classified into three isomers according to the relative position of the nitrogen atoms in the ring: pyridazine (1,2-diazine), pyrimidine (1,3-diazine) and pyrazine (1,4-diazine). A perusal of the CSD database [7] of metal (including representative, transition, lanthanide, and actinide ions) complexes, in which these molecules are at least coordinated to one nitrogen atom, gives 1246, 239 and 164 hits for pyrazine, pyrimidine and pyridazine, respectively. This number decreases subtly when the ligands act as bridges: 1098, 177 and 100, respectively. This fact may be related to their coordinative capacity, in such a way that the observed pyrazine > pyrimidine > pyridazine trend derives from the proximity of the heteroatoms in the aromatic ring, which hinders progressively a simultaneous coordination. It is worth noticing the abrupt drop in the number of hits for lanthanides (11, 2 and 2, respectively), in good agreement with their oxophilic character. An effective way of enhancing the coordination capacity of diazine ligands is achieved by introducing carboxylate groups, which afford a hard character according to the Hard Soft Acid Base (HSAB) theory in addition to negative charge [8]. The disposition of the carboxylate groups imposes the coordination mode to a large extent, thus affording a certain degree of predictability that allows one to perform a design of the complexes. In particular, the occurrence of carboxylate groups adjacent to nitrogen atoms of the aromatic ring (α position) permits establishing five member chelating rings upon coordination, which provides a preferred rigid coordination mode and improves the structural predictability. When comparing the coordination modes of these diazinedicarboxylate ligands with other usual ligands such as pyridinedicarboxylate ones it seems obvious that the rigid coordination mode involving a five member chelating ring, can be only achieved when the heteroatom in the ring occupies an α position with regard to the carboxylic group. As it will be later discussed, in diazinedicarboxylate ligands, the presence of two heteroatoms adjacent to the carboxylic groups provides a preferred coordination mode involving the occurrence of two five member chelating rings. In the case of the largely employed terephthalate ligand, which contains no heteroatoms in the aromatic ring, there is a great diversity of coordination modes among which the tetradentate $\kappa O:\kappa O':\kappa O'':\kappa O'''$ prevails.

Among all possible isomers, this review focuses on three diazinedicarboxylate ligands that comply with the aforementioned feature: pyrazine-2,5-dicarboxylate (pzdc), pyrimidine-4,6-dicarboxylate (pmdc), pyridazine-3,6-dicarboxylate (pddc). These ligands tend to acquire planar structures owing to the establishment of two simultaneous chelating rings with metal centres, which ensures certain connectivity in the metal–organic network as to achieve high-dimensional systems. In fact, as it will be detailed in the following sections, bis-chelating (bis-bidentate N/O) coordination mode is the predominant pattern for the three ligands. From a topological point of view, the different relative disposition of the N/O sites in the three isomers modifies the connectivity of these ditopic connectors, such that different predominant motifs may be expected. At this point, a clear distinction may be made between pzdc and pmdc/pddc linkers. On the one hand, pzdc acts as a linear connector by placing metal ions in front of each other with regard to the ring centre ($\mathrm{M}\cdots\mathrm{ring}_{\mathrm{cent}}\cdots\mathrm{M}$ of 180°). Instead, pmdc and pddc are regarded as angular connectors given that wide ($\mathrm{M}\cdots\mathrm{ring}_{\mathrm{cent}}\cdots\mathrm{M}$ of *ca.* 120°) and acute ($\mathrm{M}\cdots\mathrm{ring}_{\mathrm{cent}}\cdots\mathrm{M}$ of *ca.* 60°) angles, respectively, are established (Scheme 1). In any case, the definite shape acquired by these ligands is also determined by the features of coordinated metal atom (charge, size, and subsequent coordination number and geometry) as well as the employed solvent (coordinative capacity, size and so on) and/or the presence of additional co-ligands. All these factors introduce many variables in the reaction scenario and promote rich structural diversity on the systems involving coordination modes with higher denticity.

All in all, this review gives an overview of all possibilities offered by diazinedicarboxylate ligands in the design of multifunctional CPs. Organized on the basis of the three explored isomeric ligands, all reported materials are listed according to their metal



Scheme 1. Bis-chelating coordination modes and connector shapes of: (a) pzdc, (b) pmdc, and (c) pddc ligands.