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Mini-review

Coordination compounds of benzidine: A versatile family in coordination chemistry and crystal engineering

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ABSTRACT

Synthetic methods, structural features, and exciting properties of some novel mono-, di- and polynuclear compounds with benzidine as ligands are described in this short review.

Contents

1. Introduction

An aromatic amine means a compound in which a hydrogen atom(s) of ammonia is/are replaced by an aromatic group(s). Specific examples of the aromatic amines include aniline, toluidine, xylidine, anisidine, naphthylamine, diphenylamine, triphenylamine, benzidine etc. [1]. Among them, the symmetric aromatic diamine, benzidine [2–18] (trivial name, molecular weight is 184.2 g/mol), also called 4,4'-diaminobiphenyl (systematic name), is the slightly reddish crystalline solid with the formula $(C_6H_4NH_2)_2$. It is a component of a test for cyanide [2]. Related derivatives are used in the production of dyes [3]. In the past, benzidine was used to test for blood [4]. A variety of derivatives of benzidine [5] are commercially produced mainly as precursors to dyes and pigments. These derivatives show electroluminescent properties [6]. On the other hand, benzidine chain extended polyurethane-urea [7] leads to high tensile strength, high elongation, increased thermal stability and superior dielectric properties. Some benzidine-derivatives reveal multielectrochromic characteristics [8]. The benzidine derivative poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT) is used on the synthesis of hydrogel materials having macroscopic-scale liquid crystal structures with specific functions [9]. Sometimes antibody was detected by applying 100 μL of tetramethyl benzidine (TMB) substrate [10]. Very recently a new class of potent inhibitors based upon a benzidine prolinamide skeleton is reported [11] which is nontoxic and is anticipated to be an effective hepatitis C virus (HCV) drug candidate with highly potent anti-HCV activity.

However, the coordination chemistry of benzidine (Scheme 1) is relatively less explored [12–18]. It may be used as a monodentate [16] or bridging ligand [14, 16–18] to afford different coordination complexes.

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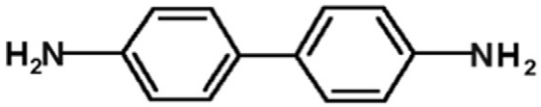


Scheme 1. Framework of benzidine.

The formation of mono-, di- and polynuclear compounds with this organic blocker is disproportionately sparse when compared with those of other aliphatic amines considering its ability to create not only hydrogen bonds [19] through active amine (–NH_2) hydrogens but also several weak and lateral non-covalent interactions like π···π [20] and C–H···π [21] interactions. This novel interaction now has become a common tool in supramolecular chemistry, especially in crystal engineering [22]. The compounds containing this amine may show luminescence through intraligand π–π* transition [23]. Recently different Schiff bases are prepared [15, 24, 25] using benzidine/benzidine-derivatives and appropriate carbonyl compounds. These Schiff bases are of great interest because of their structural variety, varied denticities and subtle steric and/or electronic effects leading to complexes of different dimensionalities. More over their ability to form different non-covalent interactions like hydrogen bonding, π···π and C–H···π interactions is very much important in crystal engineering to understand the intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties. In addition, the free Schiff bases and their compounds show antifungal, antibacterial, antitumor, anti-inflammatory and antipyretic properties [24, 25].

In spite of having such versatile usefulness, production of benzidine and its derivatives is banned in many countries due to their toxic effect that may cause bladder and pancreatic cancer [26]. So, the benzidine and benzidine-based chemical substances should be used only in very small amounts and volumes and handled with proper care.

The aim of the present review is to give an overview of syntheses, structures and exciting properties of some novel coordination compounds containing benzidine as ligand.

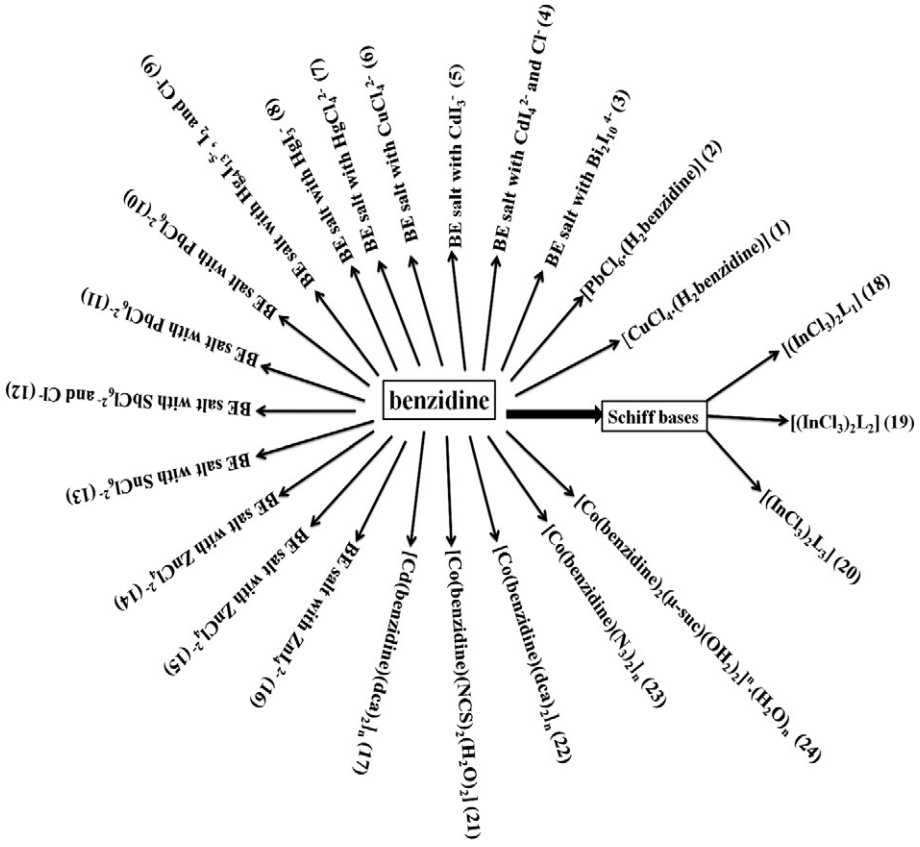
2. Synthetic studies

Syntheses of a number of novel coordination complexes containing benzidine [12–18] will be discussed now one by one. A common scheme (Scheme 2) is used to show the syntheses of these compounds at a glance.

[Here BE salts = salts of benzidine cation; dca = dicyanamide anion; L_1 = *N*,*N*′-bis(3-methoxy-salicylidene)benzidine; L_2 = *N*,*N*′-bis(3-methoxysalicylidene)-2,2′-dimethyl-benzidine; L_3 = *N*,*N*′-bis(3-methoxysalicylidene)-*o*-dianisidine; suc = succinate ion]

Two novel hybrid inorganic–organic compounds (**1** and **2**) are prepared [12] using the simple phenylamine derivative benzidine with copper(II) chloride or lead(II) chloride as the metal atom source. For the preparation of compounds **1** and **2** [12], $CuCl_2$ (0.19 mmol) (for **1**)/$PbCl_2$ (0.20 mmol) (for **2**) was dissolved in 8 mL concentrated hydrochloric acid. A 5 mL ethyl ether solution of benzidine (0.11 mmol) was added as a top layer in each case. Solvent diffusion over several days afforded pale yellow plates of **1** and colorless needles of **2**.

A series of novel inorganic–organic hybrid salts (**3**–**16**) of benzidine dication containing complex inorganic anions such as metal halides [13] have been synthesized. All the crystals were prepared by a slow evaporation process from an acidified water solution of a mixture of suitable metal halides with benzidine. Crystals **4** and **9** were grown from a mixture of a metal iodide and benzidine dichloride water solution acidified by HCl, while the rest of the crystals were prepared simply from benzidine and metal halides dissolved in the appropriate diluted hydrohalogen acid.



Scheme 2. Syntheses of different coordination complexes containing benzidine.