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Unprecedented preparation of dinuclear nickel(II) and zinc(II) complexes with Schiff base ligands transformation under solvolthermal conditions

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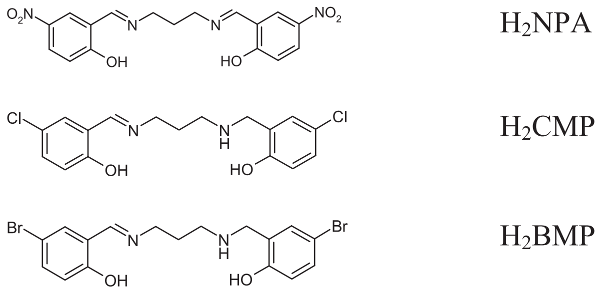
ABSTRACT

Two novel centrosymmetric dinuclear nickel(II) and zinc(II) complexes were unprecedented prepared from mono-Schiff bases with salicylaldehyde derivatives and metal acetate under solvolthermal conditions. The mono-Schiff bases bearing 2-[(3-cyclohexylaminopropylimino)methyl]phenol backbones used to prepare nickel and zinc complexes can be transformed to other ligands in the reactions, which never occur under mild synthetic procedures.

Schiff bases are a kind of versatile ligands in coordination chemistry which are readily synthesized from the reaction of primary amines with carbonyl-containing compounds. In recent years, much work has been carried out on the syntheses and properties of Schiff bases and their complexes [1–5]. Solvolthermal syntheses have been proven to be an efficient way to construct novel structures of complexes especially for those hardly soluble in common conditions. Considering the excellent solubility in common organic solvents, syntheses of Schiff base complexes under solvolthermal conditions have seldom been reported. In recent years, we have tried to prepare Schiff base complexes with solvolthermal method, and a series of trinuclear acetato-bridged cobalt(II), nickel(II), and manganese(II) complexes with bis-Schiff bases have been reported [6–8]. It was found that the mono-Schiff base ligand 4-chloro-2-[(3-cyclohexylaminopropylimino)methyl]phenol can be transformed to bis-Schiff base ligand *N,N′*-bis(5-chlorosalicylidene)-1,3-propanediamine under solvolthermal condition [8]. Recently, our research group has reported two interesting dinuclear zinc(II) complexes derived from 4-chloro-2-{[3-(5-chloro-2-hydroxybenzyl)aminopropylimino]methyl}phenol and 4-bromo-2-{[3-(5-bromo-2-hydroxybenzyl)aminopropylimino]methyl}phenol under solvolthermal condition [9]. It is interesting that the mono-Schiff bases underwent structural transformation during the reaction. As further investigation on the novel reactions of Schiff base complexes under solvolthermal conditions, in the present work, two new centrosymmetric dinuclear nickel(II) and zinc(II) complexes, $[Ni_2(NPA)_2(H_2O)(MeOH)]$ (**1**) and $[Zn_2(CMP)(BMP)]$, where NPA is the dianionic form of *N,N′*-bis(5-nitrosalicylidene)-1,3-propanediamine (H_2NPA), CMP is the dianionic form of 4-chloro-2-{[3-(5-chloro-2-hydroxybenzyl)aminopropylimino]methyl}phenol (H_2CMP), and BMP is the dianionic form of 4-bromo-2-{[3-(5-bromo-2-hydroxybenzyl)aminopropylimino]methyl}phenol (H_2BMP), have been unprecedented prepared and structurally characterized. The Schiff bases are summarized in Scheme 1.

The mono-Schiff bases 2-methoxy-6-[(3-cyclohexylaminopropylimino)methyl]phenol (HMP) and 4-chloro-2-[(3-cyclohexylaminopropylimino)methyl]phenol (HCP) were prepared according to the literature method [10]. The nickel(II) complex **1** was prepared by reaction of HMP with 5-nitrosalicylaldehyde and nickel acetate in methanol under solvolthermal conditions [11]. The zinc complex **2** was prepared by reaction of HCP with 5-bromosalicylaldehyde and zinc acetate in methanol under solvolthermal conditions [12]. It is notable that the same structure of the zinc complex 2 can also be obtained by reaction



Scheme 1. The Schiff bases.

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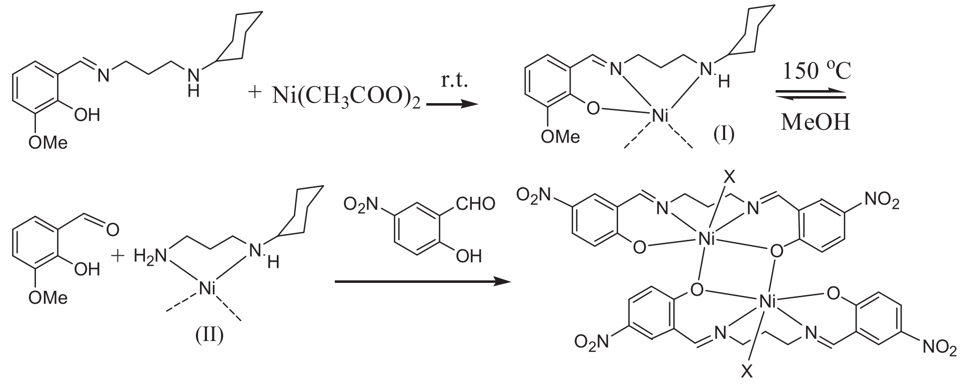

Chart 1. A proposed possible synthesis mechanism for **1**. X = 0.5 H_2O + 0.5 MeOH.

of 4-bromo-2-[(3-cyclohexylaminopropylimino)methyl]phenol (HBP) with 5-chlorosalicylaldehyde and zinc acetate in methanol under solvolthermal conditions (CCDC: 889061).

The possible mechanism for the reaction of complex **1** is shown in Chart 1. Under solvolthermal condition, the mono-Schiff base ligand MP of the nickel complex (I) may underwent a reversible

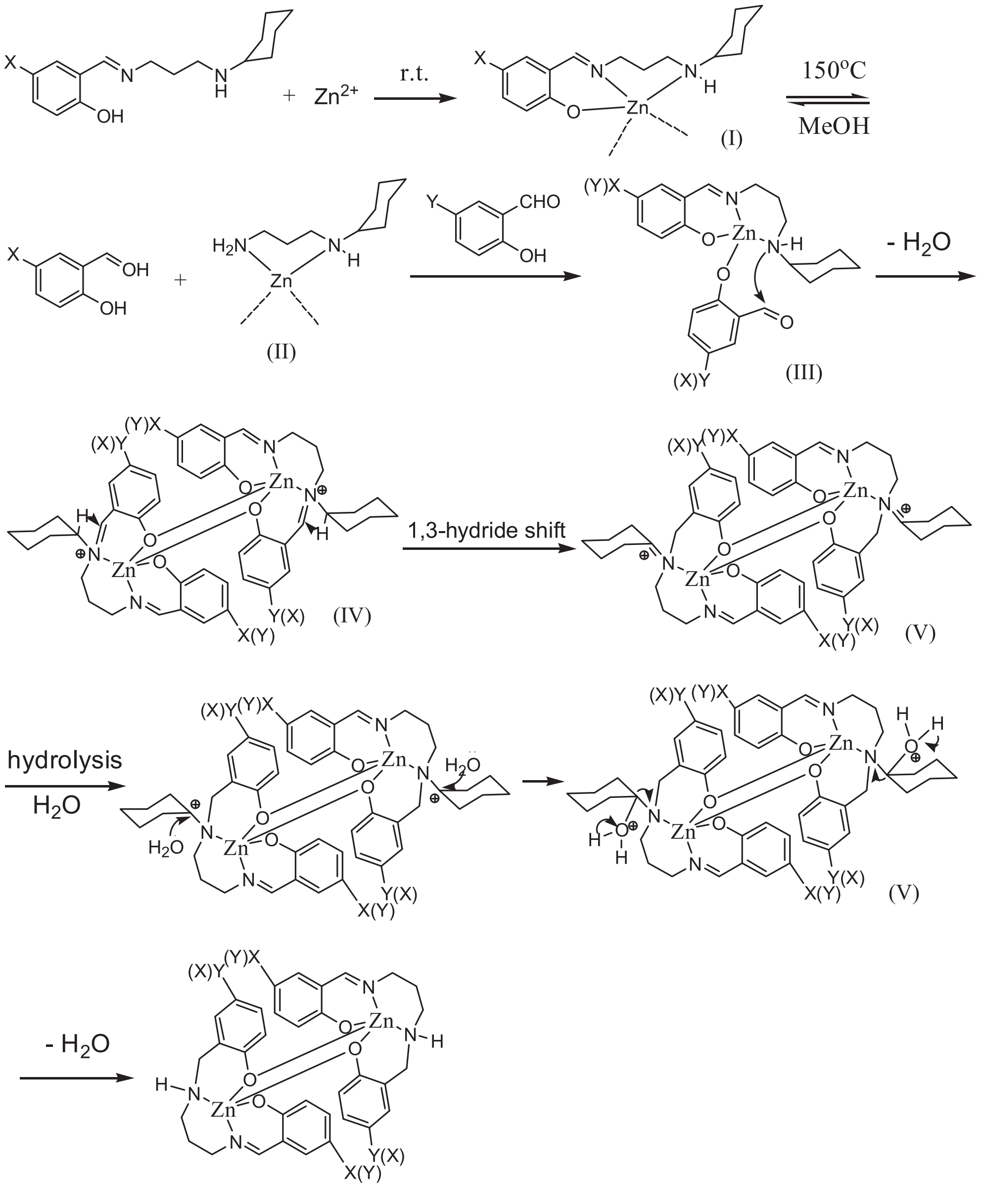

Chart 2. A proposed possible synthesis mechanism for **2**. X = Cl, Y = Br; or X = Br, Y = Cl.