

Review

Amino acid-containing reduced Schiff bases as the building blocks for metallasupramolecular structures

Rakesh Ganguly, Bellam Sreenivasulu, Jagadese J. Vittal*

Department of Chemistry, Science Drive 3, National University of Singapore, Singapore 117543, Singapore

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Abstract

Metal coordination compounds derived from several closely related yet different multidentate reduced Schiff base ligands (obtained by reducing the C=N bond in the Schiff bases formed by the condensation of aldehyde and various natural/unnatural amino acids) are discussed in terms of their mode of binding and coordination to supramolecular network structures. These multidentate ligands have flexible backbone with hydrogen bond donors and acceptors, and readily form metal complexes and coordination polymers with metal ions such as Cu(II), Zn(II), and Ni(II). Various solid-state metallasupramolecular network structures are delineated ranging from hydrogen-bonded linear polymers and helical coordination polymers, 2D sheets to 3D network architectures constructed *via* N–H···O, C=O···H–O_{solvent}, O–H···O, N–H···O=C hydrogen bonds and C=O···π, C–H···π, and π···π stacking interactions. This review gives an account of the observed structural diversity in relation to the role of different donors and acceptors, aqua ligand and solvents, nature of the ligands and metal ions, coordination geometry around the metal ions and counter

* Corresponding author. Tel.: +65 6516 2975; fax: +65 6779 1691.
E-mail address: chmjv@nus.edu.sg (J.J. Vittal).

ions besides the experimental conditions such as temperature, pH, etc. in directing the formation of supramolecular structures in the solid state. Some other related and interesting examples from the literature are also mentioned.

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1. Introduction

In the past decades, significant progress has been achieved in understanding the chemistry of transition metal complexes with Schiff base ligands composed of salicylaldehyde or analogues and α -amino acids [1]. Most of the model studies of such metal complexes have focused upon various binding modes of these ligands and the X-ray crystal structures of complexes revealed that the Schiff base ligands mainly act as tridentate moiety, coordinating through the phenolato oxygen, imine nitrogen, and carboxylate oxygen. The metal complexes containing Schiff bases are the most fundamental chelating systems in coordination chemistry [2]. Casella and Gullotti have shown that Schiff bases formed by amino acids with non-polar side chains and 2-formylpyridine were unstable with Zn(II) and Cu(II), and only imines of histidine or its methyl ester could be isolated in reasonable purity [3]. The problems with ligand instability can be overcome by reducing the C=N bond of the Schiff base to give an amine, also known as *Mannich base*, and the reduced Schiff bases are expected to generate much more interesting coordination chemistry due to the conformationally flexible backbone. In this connection, several copper complexes with reduced Schiff base ligands between salicylaldehyde and amino acids were explored to serve as models for the intermediate species in biological racemization and transamination reactions [4].

The reduced Schiff base ligands, *N*-(2-hydroxybenzyl)-amino acids and *N*-(2-pyridylmethyl)-amino acids derived from various substituted salicylaldehydes and 2-pyridinealdehyde respectively, form a class of multidentate ligands with flexible backbone useful in constructing interesting supramolecular structures. The successful construction of a variety of coordination polymeric structures mainly depends on the lability of metal–ligand bonds in solution which allows for the breaking and making of new bonds in solution. On the other hand, the role of different donors and acceptors, aqua ligand and solvents, nature of the ligands and metal ions, etc., besides the experimental and crystallization conditions determines the type of the complexes formed in the solid state particularly when there are many species in equilibrium in solution. The direction of alignment of these oligomeric species in a particular fashion can be controlled to form interesting supramolecular structures by incorporating hydrogen bond donors and acceptors at the backbone of the ligands apart from the hydrogen bonding possibilities from the lattice water, solvents and aqua ligands. In this context, this review summarizes metal coordination chemistry of natural/unnatural amino-acid based reduced Schiff base ligands and, the structural diversity and the phenomena associated with several solid-state metallasupramolecular network structures of the corresponding metal complexes. The role of various weaker interactions ($N-H \cdots O$, $C=O \cdots H-O_{\text{solvent}}$, $O-H \cdots O$,

$N-H \cdots O=C$, hydrogen bonds and $C=O \cdots \pi$, $C-H \cdots \pi$, and $\pi \cdots \pi$ stacking interactions) is also discussed.

2. Reduced Schiff base ligands

The reduced Schiff base ligands discussed in this review broadly fall into two groups *viz.* *N*-(2-hydroxybenzyl)-amino acids (Fig. 1A) and *N*-(2-pyridylmethyl)-amino acids (Fig. 1B). These ligands are obtained by reducing the C=N bond in the Schiff base formed by the simple condensation of aldehydes with amino acids. Compared to the Schiff bases, the corresponding reduced Schiff bases are expected to be more stable and adaptable to form conformationally flexible 5- or 6-membered rings upon complexation as they are not constrained to be planar. The hydrogen atom on the secondary amine produced after the reduction of the azomethine ($-CH=N-$) fragment of the Schiff base is expected to be significantly acidic due to metal ion coordination to the amine N-atom. Hence this N–H proton can participate in intermolecular hydrogen-bonding interactions ($N-H \cdots O$), with the carboxylate oxygen ($C=O \cdots H-N$) in the amino acid side arm, required for the supramolecular self-assembly of the building blocks. Also, the presence of chiral amino acid side arm in the ligands helps to induce the chirality in the supramolecular connectivity. Another major advantage of these ligands is the effective involvement of carbonyl oxygen donor from the simple amino acid side arm in connecting the neighboring metal centers *via* intermolecular coordination bonds to generate interesting 2D and 3D coordination network structures. Further, these ligands can also afford the choice of coordination environments that determine the nature of metal ions that can be bound within the closest proximity resulting in the dinuclear complexes.

Various supramolecular structures of transition metal complexes obtained from these ligands are discussed in the following sections.

3. Metallasupramolecular structures derived from *N*-(2-hydroxybenzyl)-amino acid ligands

During the self-assembly process resulting in the formation of hydrogen-bonded metal complexes or coordination polymers, there is an advantage that both coordination bonds and, perhaps, more predictable hydrogen bonds can be utilized in constructing supramolecular structures. Furthermore, incorporation of hydrogen bond donors and acceptors at the backbone of the ligands will assist in directing the alignment of coordination polymers in a desired fashion to form interesting multidimensional network structures. In this context, a variety of multidentate reduced Schiff base ligands, *N*-(2-hydroxybenzyl)-amino acids have been employed in the construction of various hydrogen-bonded metal coordination polymeric struc-

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