

PMMA Matrix Viscosity Dependence of CD Bands of Flexible Chiral Schiff Base Ni(II), Cu(II), and Zn(II) Complexes

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Abstract

Three chiral Schiff base (bis(*N-R*-2-phenylpropyl-3,5-dichlorosalicydenaminato)) nickel(II), copper(II), and zinc(II) complexes have been investigated by means of electronic and CD (circular dichroism) spectra in the solid state as well as PMMA solutions of various concentration. Because these complexes possess long and flexible pendant groups, they are sensitive to viscosity of matrix environment. Indeed so-called solid state (artifact) CD peaks could be observed as characteristic to oriented molecules without free molecular rotation and they indicated changes of intensity depending on matrix environment (not concentration but viscosity). For the first time, we have employed chiral metal complexes indicating conformational changes and found that solid state CD peaks can be affected by not only environmental viscosity of a softmatter matrix but also structural and spectral features of chiral materials.

Keywords: Circular Dichroism, Chirality, Softmatter PMMA, Viscosity

Introduction

Recently, organic/inorganic hybrid materials composed in a polymer matrix have been developed not only achiral compounds but also chiral ones [1]. When chiral molecules take anisotropic orientation with restricted degree of freedom about molecular motion, it has been stated that so-called artifact peaks sometimes may be serious problem for solid state CD spectra [2-17]. However this issue has been mainly dealt with in view of improvement to reduce noise of CD spectra in the solid state. Positive applications of it may provide useful methodology for researches of softmaters or organic/inorganic hybrid materials.

Previously, we reported on some chiral Schiff base complexes exhibited intensity changes of solid state CD peaks in PMMA cast films or in a pure acetone, as acetone solutions of PMMA (different concentrations), and in the solid state (KBr pellets) [18, 19]. Although clear correlation between intensity of solid state CD peaks and concentration of matrix were observed, actual viscosity of the solutions and effect of original CD spectra (reflecting environmental effect of conformation of chiral compounds) could not be elucidated in the study on relatively rigid chiral complexes.

Herein, we have investigated on intensity of solid state CD peaks of chiral Schiff base (bis(*N-R*-2-phenylpropyl-3,5-dichlorosalicydenaminato)) nickel(II) (**Ni**), copper(II) (**Cu**), and zinc(II) (**Zn**) complexes (Fig. 1) [20], which potentially exhibit flexible conformational changes by long pendant groups and discussed its correlation based on viscosity of PMMA acetone solutions (with solid state KBr pellets and acetone solutions).

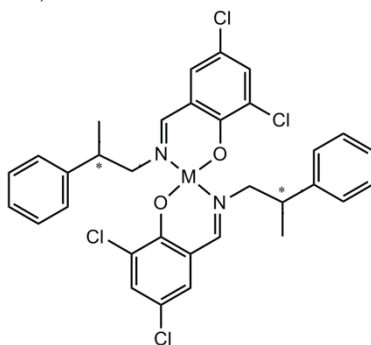


Fig. 1. Molecular structures of bis(*N-R*-2-phenylpropyl-3,5-dichlorosalicydenaminato) nickel(II) [**Ni**], copper(II) [**Cu**], and zinc(II) [**Zn**] (M = Ni, Cu, and Zn, respectively).

Experimental Sections

Procedures. Chiral complexes (**Ni**, **Cu**, and **Zn**) were prepared according to the literature [20]. KBr pellets, PMMA cast films and PMMA acetone solutions of 0 (pure acetone), 2.5, 5.0, 10, 15, 25 % concentrations (w/w) were prepared and

measured electronic and CD spectra. The corresponding viscosity of the solutions was measured independently.

Physical Measurements. Absorption electronic spectra were measured on a JASCO V-570 spectrophotometer in the range of 900–200 nm at 298 K. Circular dichroism (CD) spectra were measured on a JASCO J-725 spectropolarimeter in the range of 800–200 nm at 298 K. Viscosity was measured on an A&D SV-10A type SV (30 Hz frequency) at 298 K.

Results and Discussion

Characterization of solid state CD peaks. Fig. 2 depicts CD spectra (measured as KBr pellets) and the corresponding diffuse reflectance spectra and for **Ni**, **Cu**, and **Zn**. Complexes **Ni** and **Cu** in the conformation of solid states indicated characteristic CD peaks of d-d bands at about 660 nm and 640 nm, while **Zn** did not indicated d-d bands due to d^{10} electronic configurations. These features resulted from coordination environment. The region below about 450 nm is assigned to be interligand transitions, which result from conformation of ligands. Solid state CD peaks could be assigned to be about 660 nm (negative) for **Ni**, 640 nm (positive) for **Cu**, and 600 nm (negative) for **Zn** by comparing with CD spectra of solutions (Fig. 3). Although the identical organic ligand is employed, the spectral features of interligand transitions are different among **Ni**, **Cu**, and **Zn**. Not only charge transfer bands of different metal ions, preferred coordination environment of different metal ions also resulted in spectral differences of **Ni**, **Cu**, and **Zn**.

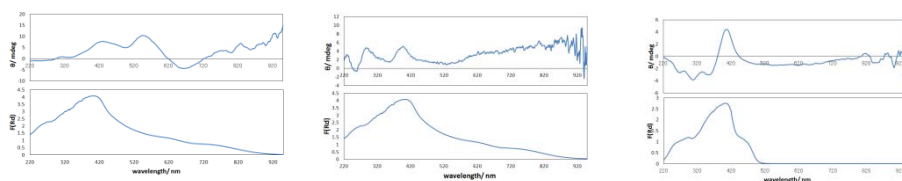


Fig. 2. Solid state CD spectra [up] and diffuse reflectance electronic spectra [down] for **Ni** [left], **Cu** [middle], and **Zn** [right].

Concentration dependence of solution CD spectra and conformation of complexes.

Fig. 3 depicts CD spectra and absorption (measured as KBr pellets) for **Ni**, **Cu**, and **Zn**. In pure acetone solutions, the complexes did not appear the solid state CD peaks mentioned above. However, spectral differences of solid states and solutions are predominantly attributed to conformational changes of the complexes. In this context, optimized structures for **Ni**, **Cu**, and **Zn** are also shown in Fig. 4 as a model of stereochemical features in the solutions. Concentration dependence of CD peaks could be extracted clearly by comparing CD spectra.

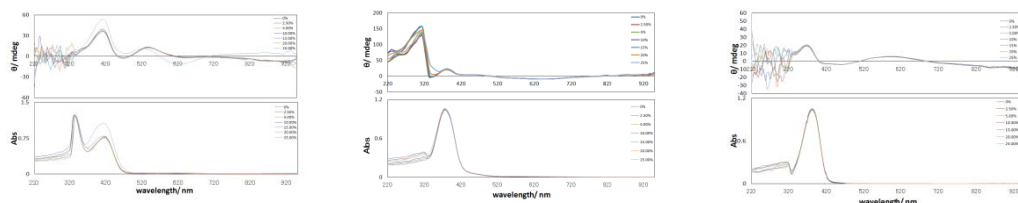


Fig. 3. Concentration dependence of CD and electronic spectra for PMMA acetone solutions of **Ni** [left], **Cu** [middle], and **Zn** [right].

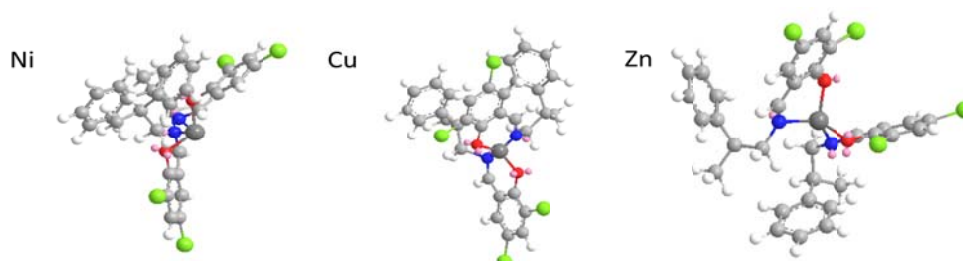


Fig. 4. MM2 optimized structures for **Ni**, **Cu**, and **Zn**.

Correlation between intensity of solid state CD peaks and viscosity. Fig. 5 depicts plots the intensity of solid state CD peaks and viscosity of PMMA acetone solutions converted from concentration (also considering cast films). It is important that effective matrix environment for chiral complexes is not concentration of PMMA but viscosity actually. Additionally the viscosity of polymer solutions is not proportional to their concentration simply. Although the intensity of solid state CD peaks is approximately good correlation to the viscosity of polymer solutions, each **Ni**, **Cu**, and **Zn** sample exhibited differently characteristic feature in detail.

As for **Ni**, only the most concentrate (25 % PMMA acetone) solution deviates from other diluted solutions. The reason may be that generally Schiff base Ni(II) complexes can easily received from various factors of solutions such as solvatochromism (namely permittivity of solvents) and coordination of solvent molecules (to yield paramagnetic species) [21]. Therefore, 25 % PMMA acetone and PMMA cast films may be ideal condition to measure these properties. As for **Cu**, which potentially shows the most drastic changes of coordination environment from square planar to tetrahedral among three complexes, CD spectra are affected not only environment of solutions but also conformational changes of Cu(II) complex in itself under the diluted concentration region. As for **Zn**, which possess a rigid distorted tetrahedral coordination environment more than the analogous Ni(II) or Cu(II) complexes, the effect of conformational changes of ligands is obviously detected as well as the effect of matrix environment.

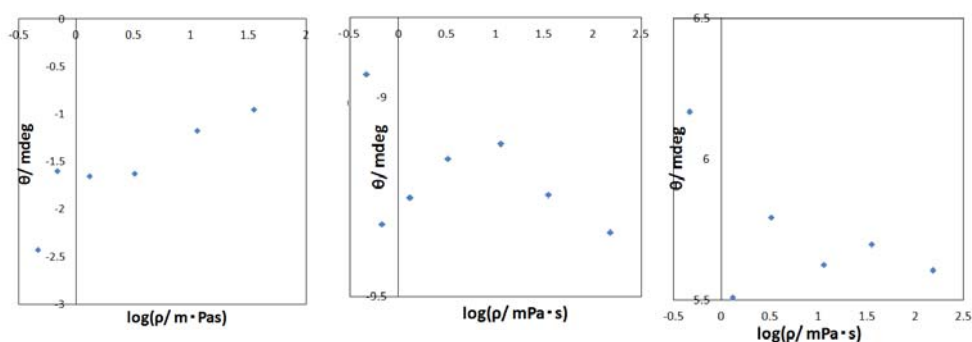


Fig. 5. The correlation between the intensity of CD peaks vs viscosity for [left] Ni, [middle] Cu, and [right] Zn.

Conclusions

In summary, the correlation between the intensity of solid state CD peaks and viscosity (converted from concentration) of PMMA acetone solutions have been investigated for three trans-type chiral Schiff base complexes, Ni, Cu, and Zn for the first time. The solid state CD peaks appeared at about 660 nm (negative), 640 nm (positive), and 600 nm (negative) for Ni, Cu, and Zn, respectively. In contrast to previous trans-type chiral Schiff base complexes cis-type chiral Schiff base complexes, flexible trans-type ones indicated drastic conformational changes of ligands and coordination geometries of complexes by changing environment of solutions. It is necessary to consider properties of a chiral metal complex of itself to employ these tests.

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