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手性 N_2O_2 型席夫碱金属络合物的结构
及其集成手性光谱初探

Structures and Preliminary Methodology
on the Integrated Chiroptical Spectroscopy of Chiral
 N_2O_2 -Type Schiff Base Metal Complexes

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Master Dissertation

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Schiff Base Metal Complexes

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摘 要

手性席夫碱金属络合物不仅在不对称催化和手性功能材料等领域有着广泛的应用,而且基于其生色团及手性配位立体化学结构的多样性,使之作为模型化合物,在电子圆二色(ECD)和振动圆二色(VCD)等集成手性光谱的基础研究中具有极高的探究价值。本论文以系列手性席夫碱Ni(II)络合物和Cu(II)络合物为研究对象,结合晶体结构分析,对其手性配位立体化学结构、ECD和VCD光谱以及绝对构型关联进行了深入研究,探讨了它们在固态和溶液中的绝对构型和优势构象;并对具有超分子螺旋手性的Cu(II)络合物进行了初步探究。本论文的构成为以下六章:

第一章为绪论,介绍了席夫碱及salen配体的起源、四配位手性席夫碱金属络合物绝对构型的两种命名法、手性席夫碱络合物的五个手性层次,其中着重关注了超分子螺旋手性。综述了手性席夫碱络合物的集成手性光谱(ECD和VCD)研究及绝对构型关联法。最后,提出本论文的选题依据和研究目标。

第二章采用手性1,2-丙二胺(1,2-pn)、1,2-二苯基乙二胺(1,2-dpen)和*trans*-1,2-环己二胺(*trans*-1,2-chxn)、1,2-联萘二胺(1,2-binam)分别与水杨醛(sal)、3,5-双叔丁基水杨醛(bsal)、脱氢乙酸(dha)缩合,共获得三个系列的手性席夫碱配体及其手性Ni(II)和Cu(II)络合物,并进行了质谱、元素分析、手性光谱(ECD和VCD)和部分络合物的单晶X射线衍射表征。

第三章对脱氢乙酸衍生的手性席夫碱Cu(II)络合物[Cu(dha-*R,R*-chxn)]、[Cu(dha-*S,S*-chxn)]、[Cu(dha-*R,R*-dpen)]、[Cu(dha-*S,S*-dpen)]、[Cu(dha-*R,R*-binam)]、[Cu(dha-*S,S*-binam)]的晶体结构进行了表征。并初步探讨了手性[Cu(dha-*R,R/S,S*-en)](en = chxn、dpen)形成一维手性超分子螺旋链的自组装及其集成手性光谱。

第四章基于上述研究,对所得络合物进行了溶液和固体ECD以及溶液VCD光谱表征。通过单晶结构、ECD以及VCD光谱的比对发现,对于含四齿席夫碱配体的手性Cu(II)络合物,可采用集成手性光谱的激子现象进行绝对构型关联。而对于相应的手性席夫碱Ni(II)络合物,则可应用我们已经建立的ECD关联规则。

第五章根据文献方法对手性铜(II)络合物[Cu^{II}(bsal-*R,R/S,S*-chxn)]进行了氧化,首次获得了其氧化产物[Cu^{III}(bsal-*R,R/S,S*-chxn)]⁺的溶液ECD光谱,并与相应的镍(II)络合物[Ni^{II}(bsal-*R,R/S,S*-chxn)]的ECD光谱进行了比较。

第六章为全文工作总结。

关键词: 手性金属络合物; N₂O₂型四齿席夫碱配体; 电子圆二色(ECD)光谱; 振动圆二色(VCD)光谱; 绝对构型关联

Abstract

Chiral Schiff base metal complexes have been widely applied in the asymmetric catalysis and chiral functional materials areas. They can be used as model compounds in the fundamental research of electronic circular dichroism (ECD) and vibrational circular dichroism (VCD) spectroscopy due to the diversity of their chiral chromophores and coordination stereo-structures. This thesis mainly focuses on the chiral Schiff base Ni(II) and Cu(II) complexes, deeply study their chiral coordination spatial structures, dominating conformations as well as the correlation between their absolute configurations and comprehensive solid or solution state ECD/VCD spectroscopy. The chiral Schiff base Cu(II) complexes which possess helical supramolecular structures were preliminarily discussed. Main contents containing six sections are as follows:

Chapter 1 introduces the origin of Schiff-base, salen ligands and summarizes the different definition rules of the absolute configurations of four-coordinate metal complexes with N_2O_2 -type Schiff base ligands; introduces five levels of chirality in the chiral Schiff base metal complexes and focus on the helical supramolecular structures; then reviews the correlation rules between their absolute configurations and integrated chiroptical (ECD/VCD) spectroscopy. Finally, the selected topics basis and research target of this dissertation is briefly presented.

In chapter 2, chiral Schiff-base ligands and their metal Ni(II) and Cu(II) complexes were synthesized. They were characterized by element analysis, mass spectra, multiple ECD/VCD spectra, and X-ray single crystal diffraction.

In chapter 3, the crystal structures of [Cu(dha-*R,R*-chxn)], [Cu(dha-*S,S*-chxn)], [Cu(dha-*R,R*-dpen)], [Cu(dha-*S,S*-dpen)], [Cu(dha-*R,R*-binam)] and [Cu(dha-*S,S*-binam)] were characterized. The chiral supramolecular self-assemblies in the formation of chiral coordination polymers with one-dimensional helical chains for chiral [Cu(dha-*R,R/S,S*-en)] (en = chxn and dpen) and their integrated chiroptical spectroscopy were preliminarily studied as well.

In chapter 4, the correlation between the multiple chiroptical spectroscopy and absolute configurations of four-coordinate chiral Schiff base Cu(II) complexes were discussed. However, the different ECD correlation rule we have proposed was applied to the related chiral Schiff base Ni(II) complexes.

In chapter 5, based on the above study, the solution ECD spectra of [Cu^{III}(bsal-*R,R/S,S*-chxn)]⁺ was characterized for the first time and compared with those of [Ni^{II}(bsal-*R,R/S,S*-chxn)].

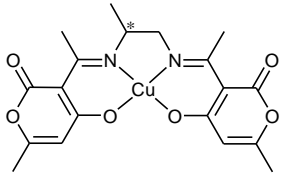
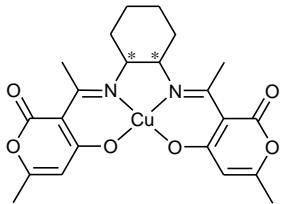
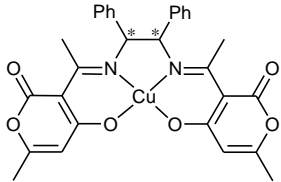
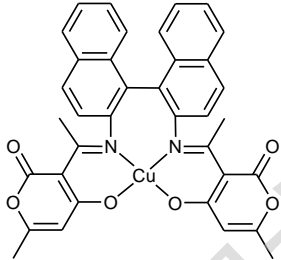
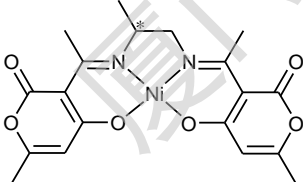
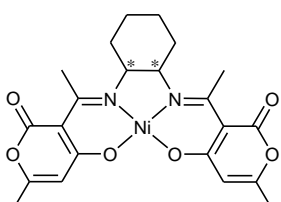
In chapter 6, the thesis is concluded with a brief summary.

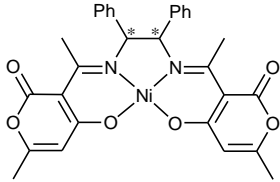
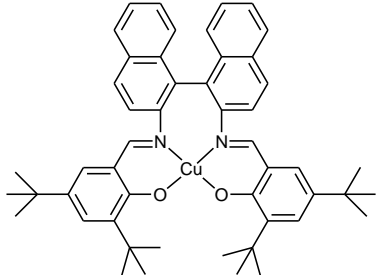
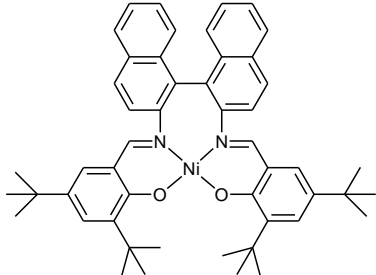
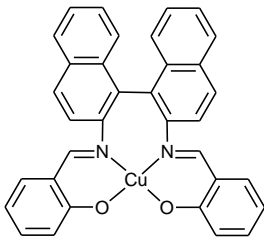
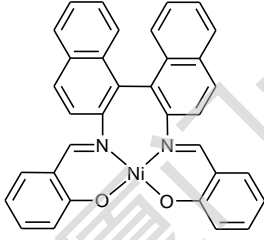
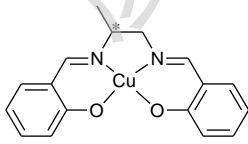
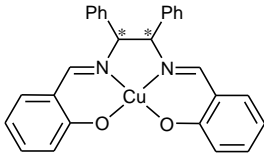
Key Words: Chiral metal complex; N_2O_2 -type quadridentate Schiff base ligand; Electronic circular dichroism (ECD) spectroscopy; vibrational circular dichroism (VCD) spectroscopy; Absolute configuration correlation

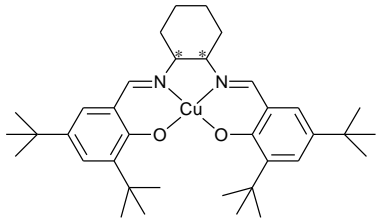
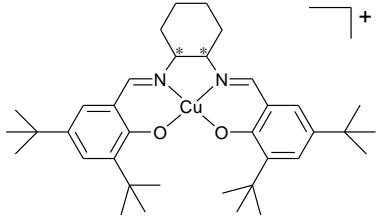
论文中有关化合物的简称与结构式

简称	英文名称	结构式
1,2-pn	1,2-diaminopropane	
1,2-chxn	<i>trans</i> -cyclohexane-1,2-diamine	
1,2-dpen	1,2-diphenylethylenediamine	
1,2-binam	1,1'-Binaphthyl-2,2'-diamine	
sal	salicylaldehyde	
bsal	3,5-di-tert-butyl-2-hydroxybenzaldehyde	
dha	dehydroacetic acid	

论文中金属络合物的简称与结构式

No.	简称	结构式
1	[Cu(dha- <i>S(R)</i> -pn)]	 <p>The structure shows a central copper atom (Cu) coordinated to two dha ligands and two pn ligands. The dha ligands are 2,4,6-trimethyl-3,5-dihydroxyacetophenone, and the pn ligands are 1,2-pyridinediamine. The stereochemistry at the chiral center of the pn ligand is <i>S(R)</i>.</p>
2	[Cu(dha- <i>S,S(R,R)</i> -chxn)]	 <p>The structure shows a central copper atom (Cu) coordinated to two dha ligands and two chxn ligands. The chxn ligands are 1,2-bis(2-phenylethyl)pyridine. The stereochemistry at the chiral center of the chxn ligand is <i>S,S(R,R)</i>.</p>
3	[Cu(dha- <i>S,S(R,R)</i> -dpen)]	 <p>The structure shows a central copper atom (Cu) coordinated to two dha ligands and two dpen ligands. The dpen ligands are 1,2-bis(2-phenylethyl)pyridine. The stereochemistry at the chiral center of the dpen ligand is <i>S,S(R,R)</i>.</p>
4	[Cu(dha- <i>S,S(R,R)</i> -binam)]	 <p>The structure shows a central copper atom (Cu) coordinated to two dha ligands and two binam ligands. The binam ligands are 1,1'-binaphthalene-2,2'-diyl. The stereochemistry at the chiral center of the binam ligand is <i>S,S(R,R)</i>.</p>
5	[Ni(dha- <i>S(R)</i> -pn)]	 <p>The structure shows a central nickel atom (Ni) coordinated to two dha ligands and two pn ligands. The dha ligands are 2,4,6-trimethyl-3,5-dihydroxyacetophenone, and the pn ligands are 1,2-pyridinediamine. The stereochemistry at the chiral center of the pn ligand is <i>S(R)</i>.</p>
6	[Ni(dha- <i>S,S(R,R)</i> -chxn)]	 <p>The structure shows a central nickel atom (Ni) coordinated to two dha ligands and two chxn ligands. The chxn ligands are 1,2-bis(2-phenylethyl)pyridine. The stereochemistry at the chiral center of the chxn ligand is <i>S,S(R,R)</i>.</p>

7	[Ni(dha- <i>S,S(R,R)</i> -dpen)]	 <p>The structure shows a central Nickel (Ni) atom coordinated to two dha ligands. Each dha ligand consists of a 2,6-dimethylphenolate group and a 1-phenylethylamino group. The two phenyl groups on the ethylamino moieties are marked with asterisks to indicate their stereochemistry.</p>
8	[Cu(bsal- <i>S,S(R,R)</i> -binam)]	 <p>The structure shows a central Copper (Cu) atom coordinated to two bsal ligands and two binam ligands. The bsal ligand is a 2,6-bis(salicyl)phenolate, and the binam ligand is a 1,1'-binaphthalene-2,2'-diylidenebis(2,6-di-<i>t</i>-butylphenolate).</p>
9	[Ni(bsal- <i>S,S(R,R)</i> -binam)]	 <p>The structure shows a central Nickel (Ni) atom coordinated to two bsal ligands and two binam ligands, similar to the copper complex above.</p>
10	[Cu(sal- <i>S,S(R,R)</i> -binam)]	 <p>The structure shows a central Copper (Cu) atom coordinated to two salicylate (sal) ligands and two binam ligands.</p>
11	[Ni(sal- <i>S,S(R,R)</i> -binam)]	 <p>The structure shows a central Nickel (Ni) atom coordinated to two salicylate (sal) ligands and two binam ligands.</p>
12	[Cu(sal- <i>S,S(R,R)</i> -pn)]	 <p>The structure shows a central Copper (Cu) atom coordinated to two salicylate (sal) ligands and one pn ligand. The pn ligand is a 1-phenylethyl-2-phenylaminoethane derivative with a chiral center marked with an asterisk.</p>
13	[Cu(sal- <i>S,S(R,R)</i> -dpen)]	 <p>The structure shows a central Copper (Cu) atom coordinated to two salicylate (sal) ligands and one dpen ligand. The dpen ligand is a 1,2-diphenylethane-1,2-diamine derivative with chiral centers marked with asterisks.</p>

<p>14</p>	<p>$[\text{Cu}^{\text{II}}(\text{bsal-}S,S(R,R)\text{-chxn})]$</p>	
<p>15</p>	<p>$[\text{Cu}^{\text{III}}(\text{bsal-}S,S(R,R)\text{-chxn})]^+$</p>	

厦门大学博硕

第一章 绪论

1.1 手性的基本概念

在立体化学中,分子的手性(Chirality)是指互为镜像关系的化合物分子在三维空间上的非重叠性。作为自然界的本质属性之一,天然氨基酸和单糖类物质都存在固有的手性^[1]。在生命活动中,分子的手性识别起着非常重要的作用,例如在药理上,当手性药物的外消旋体进入生物体内并且与酶或细胞表面的受体部位进行相互作用时,由于手性识别和匹配的精密要求,两个对映体分别以不同的过程被吸收、活化或降解,即外消旋药物对映体的生物活性、毒性、代谢途径存在很大差异,造成了不同的对映体在生物体内的活性差别^[2]。因此,有人提出,尤其是在生物体中,不同的对映体应作为不同的化合物来对待,才能达到精准的手性识别和最有效地发挥其生物功能的目的。

1.2 席夫碱及其衍生物简介

1864年^[3],意大利化学家 Hugo Schiff(图 1.1)将伯胺与另一化合物的羰基缩合,首次得到了具有 $R^1R^2C=NR^3$ (亚胺)基团的化合物。之后将这一大类含有特征 $-CH=N-$ 或 $>C=N-$ 基团的有机化合物命名为席夫碱(Schiff base),并沿用至今。由于可以对含 $R^1R^2C=NR^3$ 基团的席夫碱化合物上的 R^1 、 R^2 和 R^3 等取代基进行各种修饰,特别是通过引入手性基团可使其作为重要的有机合成中间体,因此,席夫碱及其衍生物在手性配位立体化学、磁学、光谱学、催化、光电显示、药物等领域的研究中都具有重要的不可替代的作用^[4,5]。



图 1.1 意大利化学家 Hugo Schiff (1834-1915)

迄今为止，化学家们依然引入不同的基团来设计被视为“privileged ligands”的各种席夫碱及其衍生物。其中，最具代表性的是缩写为“salen”的席夫碱，最初是指由乙二胺和水杨醛按 1:2 缩合而成的具有对称结构的化合物，但后来，salen 也被用来表示非对称四齿席夫碱配体^[6]。salen 衍生物通常具有四个配位点，当与中心金属配位形成(准)平面四方或准四面体型单核络合物后，还能通过轴向配位点形成五或六配位络合物^[7]、寡聚络合物或配位聚合物。手性 salen 配体及其金属络合物具有如下特点：(1) 制备简单；(2) 易于对配体进行修饰、配位立体结构具有多样性；(3) 可根据配体和中心金属种类设计高度不对称的配位环境，并且每一种过渡金属络合物都有其独特的电子态；(4) 在不对称催化和功能材料等方面都有潜在应用价值。例如，由取代水杨醛和手性环己二胺(chxn)衍生的“Jacobsen”型席夫碱金属络合物(图 1.2)因其在非官能化烯烃的不对称环氧化中具有重要应用而备受关注^[8-11]，Pasini 等曾将水杨醛与多种手性二胺缩合，并对所得手性 salen 金属络合物的配位立体环境及其 ECD 光谱性质进行了详细的表征与讨论^[7]，为后人提供了极其重要和翔实的实验数据，堪称经典。

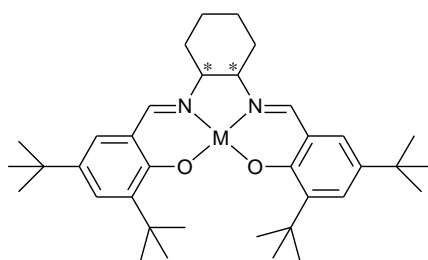


图 1.2 由取代的水杨醛与手性环己二胺衍生的 Jacobsen 型金属络合物
M = Ni^{II}、Cu^{II}、Zn^{II}、Ru^{II}、Co^{II}、Co^{III}、Mn^{III}、Al^{III}、Fe^{III}、V^{IV}、Ti^{IV} 等

1.3 席夫碱及其金属络合物的研究现状

1.3.1 手性席夫碱金属络合物在催化方面的应用

如前所述，将手性席夫碱金属络合物应用于不对称催化反应，具有结构多样、合成简单、原料易得、适用范围广、易于回收可反复利用等优点。自从 Jacobsen 等发明手性 salen-Mn(III)络合物以来，手性 salen 金属络合物作为催化剂的价值逐渐被科学家认识，因此它们在不对称催化反应研究中愈发受到重视^[12,13]。

2003年Shi等报道了一系列由手性1,1'-联萘-2,2'-二胺(binam)衍生的salen金属络合物(M = Zn、Cu、Co等，图1.3)^[14]，发现它们在三乙胺以及二氧化碳存在下能够催化不对称环氧化反应，将三元含氧杂环催化为五元杂环化合物，并采用

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