Coordination Chemistry Reviews 284 (2015) 1–18

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Applications of chiroptical spectroscopy to coordination compounds

Tao Wu[a,b,*], Xiao-Zeng You[a], Petr Bouř[b]

[a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, 210093 Nanjing, PR China

[b] Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo nám. 2, 16610 Prague, Czech Republic

Contents

1. Introduction 1
2. Chiroptical spectroscopic methods in coordination chemistry 3
   2.1. Electronic circular dichroism (ECD) and optical rotatory dispersion (ORD) 3
   2.2. Circularly polarized luminescence (CPL) 5
   2.3. Vibrational circular dichroism (VCD) 6
   2.4. Vibrational Raman optical activity (ROA) 10
3. Applications of chiral coordination compounds 11
   3.1. Second-order nonlinear optic (NLO) materials 11
   3.2. Ferroelectric materials 12
   3.3. Chiral molecular conductors 12
   3.4. Chiral molecule-based magnets 13
   3.5. Multi-functional materials 13
4. Conclusions and perspectives 16
   Acknowledgements 16
   References 16

ARTICLE INFO

Article history:
Received 16 June 2014
Accepted 19 September 2014
Available online 28 September 2014

Keywords:
Chirality
Coordination compounds
Chiroptical spectroscopy
New materials

ABSTRACT

Chiroptical methods represent indispensable tools for structural studies of chiral coordination compounds. Numerous applications in asymmetric catalysis, chiral recognition, chiral materials, and supramolecules stabilized by metals have fuelled their ongoing development. Materials derived from chiral coordination compounds have attracted considerable interest due to the possibility to fine-tune their physical properties through versatile chemical synthesis. This review provides an overview of the applicability range of chiroptical methods as a principle tool for chirality investigation, and typical applications of chiral coordination chemistry. The potential of electronic and vibrational chiroptical methods in the design and characterization of coordination compounds is discussed. The electronic optical activity in the form of circular dichroism (CD) continues to be the most frequent tool in stereo-chemical analysis. The potential of vibrational optical activity (VOA) for chiral coordination compounds is still poorly explored, especially when compared with VOA's role in organic chemistry and biochemistry. However, the vibrational region can often provide unique and more detailed information than the electronic methods, because of higher spectroscopic resolution, reduced dependence on characteristic chromophores, and better reproducibility of the spectra by theoretical methods.

1. Introduction

Chirality, the so called left- and right-hand symmetry, is defined in chemistry by IUPAC as: The geometric property of a rigid object (or spatial arrangement of points or atoms) of being nonsuperimposable on its mirror image; such an object has no symmetry elements of the second kind (a mirror plane, $\sigma = S_1$, a centre of inversion, $i = S_2$, a rotation reflection axis, S_{2n}). If the object is

* Corresponding author. Tel.: +420 220183 445.
E-mail addresses: njutwu@gmail.com (T. Wu), youxz@nju.edu.cn (X.-Z. You), bour@uochb.cas.cz (P. Bouř).

http://dx.doi.org/10.1016/j.ccr.2014.09.012
0010-8545/

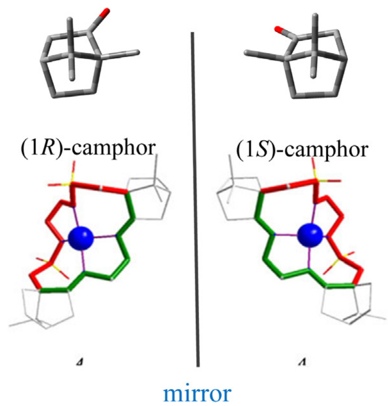

Fig. 1. Examples of chirality of an organic compound, camphor (top), and a copper(II) coordination compound (containing the camphor residue, too, bottom).

superimposable on its mirror image the object is described as being achiral [1]. Molecular chirality is essential for the functioning of living organisms. For coordination compounds, the issue of chirality emerged almost as early as the coordination chemistry was founded by Alfred Werner [2]. Chirally resolved (enantiomeric) coordination compounds could be utilized in many domains of chemistry including asymmetric catalysis, chiral recognition, chiral materials, and supramolecular chemistry [3].

In spite of that, chirality is not so frequently explored in coordination chemistry as it is in organic chemistry and biochemistry [4]. One of the reasons may be the complicated relation between the geometry and electronic configuration of coordination compounds. Heavy metals contain d and higher angular-momentum orbitals, sometimes spin-polarized, and the theoretical description is more complicated than for the majority of organic compounds, often containing s and p orbitals only. Additionally, for elements of higher atomic number, relativistic effects cannot be neglected [5].

In metal complexes, chirality is often realized by an asymmetric ligand arrangement around one or several coordination centres of high coordination number [2,6]. To some extent, the metal plays the role of the asymmetric carbon in organic molecules, often with a similar chiral scaffold (Fig. 1). The chiral arrangement is variable in crystals in which optically active compounds (both organic and inorganic) may belong to one of 15 symmetry point groups, C_1, C_s, C_2, C_{2v}, D_{2v}, C_3, D_3, C_4, S_4, D_{2d}, D_4, C_6, D_6, T, and O.

The most common coordination compounds that are chiral at molecular level possess elements of octahedral (OC-6), tetrahedral (T-4), distorted square planar (SP-4), and helical symmetries. According to the milestone work of Zelewsky, the transfer of chirality from ligand to the metal ion centre is the most efficient way of asymmetric synthesis of coordination compounds [7].

A remarkably large variety of coordination compounds has been prepared via a self-assembly of metal ions and optically active ligands. Their properties are relatively well-predictable from geometry and cooperative effects [3,8].

Materials made from coordination compounds have thus been attracting attention as their physical properties may be fine-tuned through versatile chemical synthesis [9]. Materials exhibiting multiple optical, electrical, and magnetic properties are sometimes referred to as multi-functional [10].

Optical spectroscopic methods can be conveniently utilized to study the synergetic effects between the geometry and physical properties due to manipulated chirality. Chiroptical spectroscopies are based on the interaction of chiral matter with left- and right-circularly polarized light [11].

Historically, optical rotation and the optical rotation dispersion (ORD) were the easiest methods to apply. However, the spectra were difficult to interpret in terms of the structure, as the rotation at each wavelength comprises contributions of many electronic transitions. Currently, the most widely applied technique is thus *circular dichroism* (CD) detecting the absorption difference between left- and right-circularly polarized light for individual transitions (Fig. 2). It includes the traditional electronic CD (ECD) sensing electronic transitions and sometimes referred to as ultra-violet CD (UVCD), although commercially available spectrometers cover a broad range of wavelengths (~180–800 nm). This range may be severely restricted by the solvent transmission, material of the sample cell, etc. Below 180 nm, special vacuum techniques and synchrotron radiation can be used as the source of light. Low-lying electronic transitions, for example in lanthanide complexes, can be seen by extending the wavelength range to the near-infrared region (800–1100 nm).

Theoretically, a technique akin to ECD is circularly polarized luminescence (CPL). It detects transitions from the excited states, i.e. it measures the differences in emission of the left- and right-circularly polarized light [12].

In 1970s, molecular vibrational optical activity (VOA) was developed [13], which brought about the possibility to study the vibrational transitions, usually more numerous and better resolved than the electronic ones. Additionally, the calculation of VOA spectra is easier than for the electronic ones since one only needs to model the electronic ground state.

The instrumentation for vibrational analogue of ECD, vibrational circular dichroism (VCD), has been commercially available since about 1997. The technique operates with infrared radiation.

Somewhat less common is the other form of VOA, Raman optical activity (ROA) which detects the differences in scattering intensities of right- and left-circularly polarized light. ROA instrumentation has been commercially available since about 2003.

Table 1 summarizes some basic properties of various chiroptical techniques. However, any categorical division is only approximate. For example, VOA spectroscopies can also include contributions from low-lying electronic states; VCD has also been extended to the near-infrared region (NIR-VCD), although applications in coordination chemistry have not been reported so far [14].

Unlike for simple infrared absorption, VCD optical elements limit the wavenumber range and sometimes the choice of solvent. Also, samples suitable for VCD measurement should exhibit absorbance in a relatively narrow range of 0.1–1.0; the most desirable value is ca. 0.5. The absorbance can be optimized by a combination of sample concentration, optical pathlength, and the choice of solvent. Deuterated organic solvents are frequently employed in order to reduce the absorbance and broaden the spectroscopic window. For insoluble compounds, solid state VCD may be helpful while employing dispersion in mineral oil, or KBr pellet.

Compared with VCD, ROA measurement requires even slightly higher sample concentration on average. Note that for many compounds the recommended concentrations in Table 1 are not possible due to the limited solubility. Unlike for VCD, water is a very good solvent for the Raman techniques, whereas scattering from organic solvents often masks the signal from the sample. Although theoretically possible [15], ROA above ~2400 cm^{-1} is rarely measured due to the limits of the coupled-charge detector. Both of the VOA methods (VCD and ROA) are more reliable than the electronic ones to determine the conformation or absolute configuration.

ORD and ECD are probably the most flexible and most sensitive techniques. Many organic solvents enabling ECD measurement in a large part of the 180–800 nm intervals are available, and the concentration can be lower than for VOA. The electronic spectra, however, provide a limited number of features, not necessarily associated with local geometry. ECD interpretation requires rather extensive computations of excited electronic states, for which available methods provide a limited precision only.