We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Introductory Chapter: Chirality from Molecular Electronic States

Takashiro Akitsu

1. Chiral assembly of proteins and metal complexes

Needless to say, chirality is an important concept along the fields of biology, chemistry, and physics. Not only steric fitness (stereochemical aspects) but also electronic properties (or electronic states as origin) may be important in such cases, which is a motivation to emphasize the concept of this book.

PIFKIY^① [1] GOLDScore: 49.8676	MAGSOD^② [2] GOLDScore: 53.5195	PAYDEY^③ [3] GOLDScore: 23.2850

DAHBT^④ [4] GOLDScore: 64.4628	EJED [5] GOLDScore: 72.7725	FAGLOP [6] GOLDScore: 77.1745

ENPCUA [7] GOLDScore: 48.2661	DEMTAR [8] GOLDScore: 64.4997	ENOKUO [9] GOLDScore: 40.3257

MOGSOS [10] GOLDScore: 51.4381	FOWCUQ [11] GOLDScore: 48.2838	ANEMAJ [12] GOLDScore: 48.2661

NEXFOM [13] GOLDScore: 53.7217	VUYHUT [14] GOLDScore: 51.2235	CASUAT [15] GOLDScore: 47.3524
BEJSIS [16] GOLDScore: 55.2314	KOQYOG [17] GOLDScore: 54.3256	DUNPIL [18] GOLDScore: 55.4040
QEKDUF [19] GOLDScore: 34.3787	XAXWAU01 [20] GOLDScore: 47.0893	AJIKOU [21] GOLDScore: 58.3212
MIGJUI [22] GOLDScore: 49.0211	ANEMOX [23] GOLDScore: 52.4909	WICBIU03 [24] GOLDScore: 49.7661

Table 1.

GOLD scores of docking copper(II) complexes into lysozyme. Detailed study of the best four complexes will be reported elsewhere.

In recent years, in order to prepare “artificial metalloproteins” composed of natural proteins (typically egg white lysozyme) including synthesized metal complexes (salen-type Cu(II) complexes), we searched and investigated candidate metal complexes using crystal structure databases (CSD [1–24] and PDB). In this context, we used a GOLD program to search well docking features between proteins and ligand of small molecules structurally and obtained docking scores (**Table 1**). As for molecular structures, DFT calculations from a Gaussian 09 program may be useful to obtain not only optimized structures but also detailed electronic states of metal complexes in principle.

At least proteins must be a hard target to discuss. Once I asked to my collaborator of computational chemical physics, “I will ask you DFT calculations of

simulated IR spectra of them. Moreover, I also want to know simulated IR spectra of amide I, II, and some other bands for typical proteins such as lysozyme.” Then he replied, “When you’ll send me the data, I’ll continue with the assignment. I don’t know how long do you like the discussion of the vibrational bands, and what are the most interested bands for you. Additionally, strong bands corresponding to inter-molecular H-bonds appear in the exp. spectrum. If you have the X-ray data of these molecules, I can simulate it and improve the assignments.”

Even employing achiral metal complexes, such hybrid assembly must be a chiral material, which can be experimentally elucidated by means of chiroptical spectroscopy (CD or VCD) [25] as well as quenching of fluorescence intensity (obeying Stern-Volmer plot) [26]. However, calculations of electronic state for such hybrid assembly must be difficult only by means of these conventional or commercially available programs at present [27]. In this way, supramolecular chirality may be one of the challenging targets in near future.

2. Chiral metal complexes by spectroscopy, magnetism, and computational interpretation

In the case of chiral salen-type metal complexes, it is not easy to investigate their electronic properties using both experimental and theoretical methods. Previously, we have systematically studied on preparations, crystal structures, and electronic states for mononuclear (3d) [25–27] and binuclear (3d-4f) [28–32] complexes. Besides X-ray crystallography and IR spectra, CD and UV-vis spectra, XAS spectra, fluorescence spectra, and magnetic measurements were used. However, not all

Figure 1.
Simulated UV-vis and CD spectra for La(III)-Cu(II) complex [27].

methods are valid at the same time for one complex of a certain combination of 3d and 4f metal ions, for example, some complexes were diamagnetic, and some complexes did not exhibit emission. Hence, we also carried out DFT or semiempirical molecular orbital calculations as well as these experiments. However, 4f metal ions having many electrons usually took a long time to calculate with DFT accurately and the results often deviated from the corresponding experimental data largely (for example, simulated CD spectrum shown in **Figure 1**).

In conclusion, beyond stereochemical aspects, chirality may be important, though there are limited methods to elucidate their electronic states in particular theoretically such as chiroptical spectra and expanding supramolecular functions at present.

Author details

Takashiro Akitsu

Department of Chemistry, Faculty of Science, Tokyo University of Science, Tokyo, Japan

*Address all correspondence to: akitsu2@rs.tus.ac.jp

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

- [1] Bhadbhade MM, Srinivas D. Effects on molecular association, chelate conformation, and reactivity toward substitution in copper Cu(5-X-salen) complexes, salen²⁻ = N,N'-ethylenebis(salicylidenediaminato), X = H, CH₃O, and Cl: Synthesis, X-ray structures, and EPR investigations. *Inorganic Chemistry*. 1993;**32**:6122-6130. DOI: 10.1021/ic00078a037
- [2] Thomas F, Jarjayes O, Duboc C, Philouze C, Saint-Aman E, Pierre JL. Intramolecularly hydrogen-bonded versus copper(II) coordinated mono- and bis-phenoxy radicals. *Dalton Transactions*. 2004:2662-2669. DOI: 10.1039/B406009A
- [3] Yao HH, Huang WT, Lo JM, Liao FL, Wang SL. *European Journal of Solid State Inorganic Chemistry*. 1997;**34**:355-366
- [4] Bunce S, Cross RJ, Farrugia LJ, Kunchandy, S, Meason LL, Muir KW, Odonnell M, Peacock RD, Stirling D, Teat SJ. Chiral Schiff base complexes of copper (II), vanadium (IV) and nickel (II) as oxidation catalysts. X-ray crystal structures of [Cu (R-salpn) (OH₂)] and [Cu (±-busalcx)]. *Polyhedron*. 1998;**17**:4179-4187
- [5] Raisanen MT, Kinga M, Nieger M, Repo T. Structural and spectroscopic characterization of Cu(salen) complexes bearing long alkoxy chains. *Journal of Coordination Chemistry*. 2010;**63**:4280-4289. <https://doi.org/10.1080/00958972.2010.533762>
- [6] Paschke R, Balkow D, Sinn E. Lowering Melting Points in Asymmetrically Substituted Salen-Copper(II) Complexes Exhibiting Mesomorphic Behavior. Structure of the Mesogen Cu(5-hexyloxySalen). *Inorganic Chemistry*. 2002;**41**:1949-1953. DOI: 10.1021/ic010875u
- [7] Freiburg C, Reichert W, Melchers M, Engelen B. N,N'-Ethylenbis(1-iminomethyl-2-naphtholato)kupfer(II) und N,N'-Ethylenbis(1-iminomethyl-2-naphtholato)nickel(II) *Acta Crystallographica B*. 1980;**36**:1209-1211. DOI: 10.1107/S056774088000564X
- [8] Karakas A, Elmali A, Unver H, Kara H, Yahsi Y. Synthesis, Structure, Spectroscopic Studies and ab-initio Calculations on First Hyperpolarizabilities of N,N'-Bis(2-hydroxy-1-naphthylmethylidene)-1-methyl-1,2-diaminoethane-N,N',O,O'-copper(II). *Zeitschrift für Naturforschung B*. 2006;**61**:968-974
- [9] Li F, Mei C, Tao R. *Henan Daxue Xuebao. Ziran Kexueban*. 2006;**36**:32
- [10] Biswas S, Dutta A, Dolai M, Debnath M, Jana AD, Ali M. Copper(II) induced oxidative modification and complexation of a schiff base ligand: synthesis, crystal structure, catalytic oxidation of aromatic hydrocarbons and DFT calculation. *RSC Advances*. 2014;**4**:34248-34256. DOI: 10.1039/C4RA06078D
- [11] Xie QF, Chen YM, Huang ML. {4, 4'-Dibromo-2, 2'-[ethane-1, 2-diylbis(nitrilomethylidyne)] diphenolato} copper (II). *Acta Crystallographica E*. 2009;**65**:m903-m903. <https://doi.org/10.1107/S1600536809024015>
- [12] Clegg W, Harrington RW. CCDC ANEMAJ (Private Communication)
- [13] Rigamonti L, Demartin F, Forni A, Righetto S, Pasini A. Copper(II) complexes of salen analogues with two differently substituted (push-pull) salicylaldehyde moieties. A study on the modulation of electronic asymmetry and nonlinear optical properties. *Inorganic Chemistry*. 2006;**45**:10976-10989. DOI: 10.1021/ic0613513

- [14] Assey G, Butcher RJ, Gultneh Y. Acta Crystallographica E. {3,3',5,5'-Tetramethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}copper(II)2010;**66**:m653-m653. <https://doi.org/10.1107/S1600536810017137>
- [15] Arici C, Ercan F, Atakol O, Cakirer O. Aqua[N,N'-bis(salicylidene)-1,3-propanediaminato]copper(II) Acta Crystallographica C. 1999;**55**:1654-1655. DOI: 10.1107/S010827019900894X
- [16] Akhtar F, Drew MGB. Structures of N,N'-propylenebis[(2-hydroxy-1-naphthyl)methaniminato]nickel(II) and N,N'-propylenebis[(2-hydroxy-1-naphthyl)methaniminato]copper(II)-0.5-dimethyl sulphoxide. Acta Crystallographica B. 1982;**38**:1149-1154. <https://doi.org/10.1107/S0567740882005184>
- [17] Li XW, Xue LW, Zhang CX. Synthesis, X-Ray Structures, and Antimicrobial Activities of Nickel(II) and Copper(II) Complexes With Tetradentate Schiff Bases. Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry. 2015;**45**:512-515. <https://doi.org/10.1080/15533174.2013.841217>
- [18] Kitajima N, Whang K, Moro-oka K, Uchida A, Sasada Y. Oxidations of primary alcohols with a copper(II) complex as a possible galactose oxidase model. Journal of the Chemical Society, Chemical Communications. 1986: 1504-1505. DOI: 10.1039/C39860001504
- [19] Chen BH, Yao HH, Huang WT, Chattopadhyay P, Lo JM, Lu TH. Syntheses and molecular structures of three Cu(II) complexes with tetradentate imine-phenols. Solid State Sciences. 1999;**1**:119-131. [https://doi.org/10.1016/S1293-2558\(00\)80069-2](https://doi.org/10.1016/S1293-2558(00)80069-2)
- [20] Elmali A, Zeyrek CT, Elerman Y, Svoboda I. [N,N'-Bis(5-bromosalicylidene)-1,3-diaminopropane]nickel(II) and [N,N'-bis(5-chlorosalicylidene)-1,3-diaminopropane]copper(II). Acta Crystallographica C. 2000;**56**:1302-1304. <https://doi.org/10.1107/S0108270100010428>
- [21] Wang X. Aqua{6,6-dimethoxy-2,2'-[propane-1,3-diylbis(nitrilomethylidyne)]diphenolato-κ4O,N,N',O'}copper(II) acetonitrilesolvate. Acta Crystallographica E. 2009;**65**:m1658-m1658. DOI: 10.1107/S1600536809049137
- [22] Habibi MH, Mokhtari R, Harrington RW, Clegg W. [N,N'-Bis(6-methoxy-salicylidene)-1,3-diaminopropane]copper(II). Acta Crystallographica E. 2007;**63**:m1998-m1998. <https://doi.org/10.1107/S1600536807030723>
- [23] Habibi MH, Harrington RW. CCDC ANEMOX (Private Communication)
- [24] Odabasoglu M, Arslan F, Olmez H, Buyukgungor O. Synthesis, crystal structures and spectral characterization of trans-bisaquabis(o-vanillinato)copper(II), cis-aquabis(o-vanillinato)copper(II) and aqua[bis(o-vanillinato)-1,2-ethylenediimin]copper(II). Dyes and Pigments. 2007;**75**:507-515. <https://doi.org/10.1016/j.dyepig.2006.06.033>
- [25] Tsuda E, Mitsumoto Y, Takakura K, Sunaga N, Akitsu T, Konomi T, et al. Electrochemical tuning by polarized UV light induced molecular orientation of chiral salen-type Mn(II) and Co(II) complexes in an albumin matrix. Journal of Chemistry and Chemical Engineering. 2016;**2**:53-59. DOI: 10.17265/1934-7375/2016.02.001
- [26] Hayashi T, Akitsu T. Fluorescence, UV-vis, and CD Spectroscopic Study on Docking of Chiral Salen-Type Zn(II) Complexes and Lysozyme and HSA Proteins. Threonine: Food Sources, Functions and Health Benefits. NY, USA: Nova Science Publishers Inc.; 2015. ISBN:978-1634825542

[27] Akitsu T, Yamazaki A.
Semiempirical molecular orbital
calculations for 3d-4f complexes
towards artificial metalloproteins.
International Journal of
Pharma Sciences and Scientific
Research. 2017;3:53-54. DOI:
10.25141/2471-6782-2017-2.0049

[28] Akitsu T, Hiratsuka T, Shibata H.
Chiroptical Properties of 3d-4f Chiral
Schiff Base Magnetic Complexes.
Magnets: Types, Uses and Safety. NY,
USA: Nova Science Publishers, Inc.;
2012. ISBN: 978-1614702511

[29] Hiratsuka T, Shibata H, Akitsu T.
Structures and Properties of 3d-4f
and 3d Chiral Schiff base Complexes.
Crystallography: Research, Technology
and Applications. NY, USA: Nova
Science Publishers, Inc.; 2012. ISBN:
978-1620815748

[30] Shibata H, Hiratsuka T, Hayashi T,
Akitsu T. Structures and Electronic
Properties of Photophysical
Chiral Schiff Base 3d-4f Binuclear
Complexes. Integrating Approach to
Photofunctional Hybrid Materials for
Energy and the Environment. NY, USA:
Nova Science Publishers, Inc.; 2013.
ISBN: 978-1624176388

[31] Hayashi T, Shibata H, Orita S,
Akitsu T. Variety of structures of
binuclear chiral Schiff base Ce(III)/
Pr(III)/Lu(III)-Ni(II)/Cu(II)/Zn(II)
complexes. European Chemical
Bulletin. 2013;2:49-57. DOI: 10.17628/
ECB.2013.2.49

[32] Orita S, Akitsu A. Variety of
crystal structures of chiral Schiff
base Lu(III)-Ni(II)/Cu(II)/Zn(II)
and their related complexes. Open
Chemistry Journal. 2014;1:1-14. DOI:
10.2174/1874842201401010001