606 © 1992 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 65, 606—608 (1992) [Vol. 65, No. 2

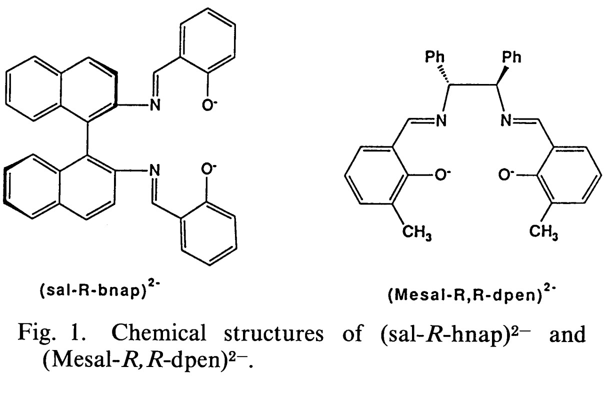
CD Spectral Diagnosis of Absolute Configuration of Tetrahedral or Pseudo-Tetrahedral Metal Complexes of Salicylideneiminates

Hiroshi Sakiyama,* Hisashi Ōkawa,* Nobuki Oguni,†
Tsutomu Katsuki, and Ryo Irie
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki 6-10-1, Higashiku, Fukuoka 812
†Department of Chemistry, Faculty of Science, Yamaguchi University,
Yoshida 1677-1, Yamaguchi 753
(Received October 17, 1991)

Synopsis. Circular dichroism spectra of tetrahedral or pseudo-tetrahedral metal complexes of chiral salicylideneaminates have been examined with respect to the absolute configuration about the metal ion. The CD couplet pattern associated with the azomethine π-π* transition differs from each other between the complexes of bidentate salicylideneaminates (class A) and the complexes of quadridentate salicylideneaminates (class B), but within each class the CD pattern is well correlated with the absolute configuration around the central metal.

The stereoselectivities of diastereomeric tetrahedral or pseudo-tetrahedral metal complexes of chiral salicylideneaminates have been studied by means of ^{1}H NMR[1,2] and circular dichroism (CD) spectra[2,3] and single crystal X-ray method.[3–5] In the previous paper[3] we have pointed out that the CD couplet pattern induced at the azomethine π-π* transition can be correlated with the absolute configuration (*Δ* or *Λ*) about the central metal ion. For the bis-type complexes of bidentate salicylideneaminates the CD pattern of (+, −) sign from lower frequency was referred to the *Δ* configuration about the central metal and vice versa. For the complexes of quadridentate salicylideneaminates, on the other hand, the CD pattern of (+, −) sign from lower frequency was assigned to the *Λ* configuration about the central metal.

In order to confirm further the CD/configuration correlation for tetrahedral or pseudo-tetrahedral salicylideneaminate complexes, CD spectral investigations have been made for a wide range of four-coordinate metal complexes of bidentate and quadridentate salicylideneaminates, including two new complexes [*N,N'*-disalicylidene-(*R*)-1,1'-binaphthyl-2,2'-diaminato] copper(II) [Cu(sal-*R*-bnap)] and [*N,N'*-bis(3-metylsalicylidene)-(1*R*,2*R*)-diphenyl-1,2-ethanediaminato]copper(II) [Cu(Mesal-*R,R*-dpen)]. The chemical structures of (sal-*R*-bnap)$^{2-}$ and (Mesal-*R,R*-dpen)$^{2-}$ are given in Fig. 1.



(sal-R-bnap)$^{2-}$ (Mesal-R,R-dpen)$^{2-}$

Fig. 1. Chemical structures of (sal-*R*-hnap)$^{2-}$ and (Mesal-*R,R*-dpen)$^{2-}$.

Experimental

Preparations. [Cu(sal-*R*-bnap)]. The ligand H_2(sal-*R*-bnap) was obtained by the reaction of (*R*)-1,1'-binaphthyl-2,2'-diamine[6,7] (280 mg, 1.0 mmol) with salicylaldehyde (280 mg, 2.3 mmol) in methanol as a yellow solid, which was crystalslized from acetone to form yellow crystals melting at 248 °C. The yield was 83 %. Found: C, 82.86; H, 4.88; N, 5.71 %. Calcd for $C_{34}H_{24}N_2O_2$: C, 82.86; H, 4.88; N, 5.71%.

To a hot ethanolic solution (3 cm^3) of copper(II) acetate monohydrate (60 mg, 0.30 mmol) was added an ethanolic solution (3 cm^3) of H_2 (sal-*R*-bnap) (150 mg, 0.30 mmol), and the resulting deep green solution was stirred at 55 °C for 5 h. After the removal of the solvent under reduced pressure, water (10 cm^3) was added to the residue and the product was extracted with three 30 cm^3 portions of benzene. A crystalline product was obtained on concentrating the benzene solution, which was recrystallized from acetone as deep green prisms. The yield was 156 mg (94%).

Found: C, 73.60; H, 4.12; N, 5.02; Cu, 11.0%. Calcd for $C_{34}H_{22}CuN_2O_2$: C 73.70; H, 4.00; N, 5.06; Cu, 11.5%.

[Cu(Mesal-*R*,-*R*-dpen)]. The ligand H_2 (Mesal-*R,R*-dpen) was prepared by the reaction of 3-methylsalicylaldehyde (111 mg, 0.815 mmol) with (1*R*,2*R*)-1,2-diphenylethanediamine (Aldrich Chemical Co., 86.5 mg, 0.407 mmol) in absolute ethanol.

A suspension of copper(II) acetate monohydrate (74 mg 0.407 mmol) in 2,2'-dimethoxypropane (6.5 cm^3) was refluxed for one hour and then concentrated to dryness. To the residue was 3 added an ethanolic solution (6.5 cm^3) of H_2 (Mesal-*R,R*-dpen), and the mixture was stirred at 50 °C for 15 h to give deep purple crystals. They were recrystallized from a dichloromethane–hexane (1 : 1 in volume) mixture. The yield was 64%.

Found: C, 70.51; H, 5.14; N, 5.50; Cu, 12.1 %. Calcd for $C_{30}H_{26}CuN_2O_2$: C, 70.64; H, 5.14; N, 5.49; Cu, 12.5%.

Physical Measurements. Elemental analyses of C, H, and N were obtained at the Service Center of Elemental Analysis, Kyushu University. Metal analyses were made on a Shimadzu AA-680 Atomic Absorption/Flame Emission Spectrophotometer. Magnetic susceptibilities were measured at room temperature on a Faraday balance. Electronic spectra were recorded on a Shimadzu MPS-2000 spectrometer in chloroform. Circular dichroism (CD) spectra were recorded on a JASCO J-600 spectropolarimeter in chloroform at room temperature.

Results and Discussion

Electronic and CD spectra of the new complexes in chloroform are given in Fig. 2. [Cu(sal-*R*-bnap)] shows a d-d band maximum at 15500 cm^{-1} and a shoulder near 12000 cm^{-1}. Such a spectral feature is characteristic of tetrahedral copper(II) complexes of salicylideneaminates.[8] The large magnetic moment of this complex (2.09 μ_B at 297 K) is consistent with a nearly tetrahedral surrounding about the metal ion.[9] The absorption band of a significant intensity at 24900 cm^{-1} can be assigned to the π–π^* transition of the azomethine moiety.[10]

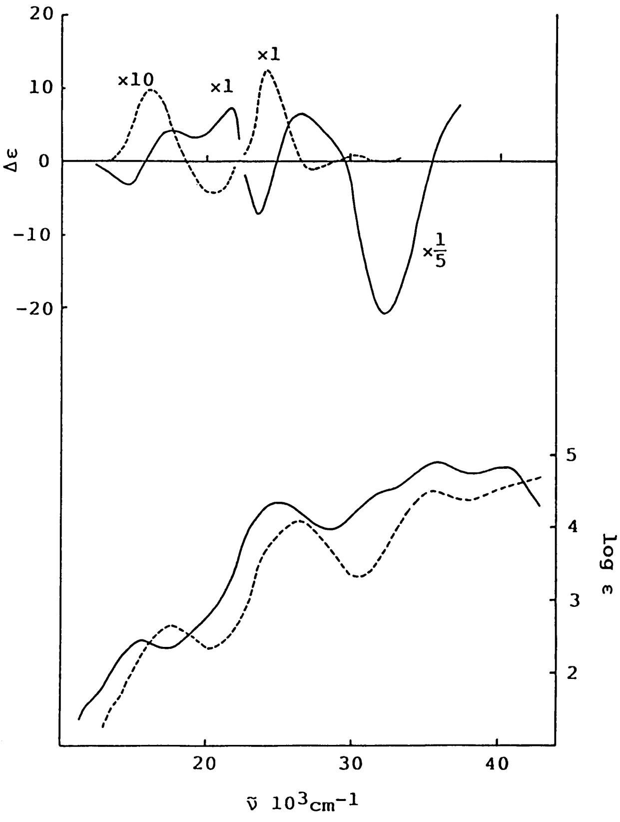


Fig. 2. Electronic spectra (bottom) and CD spectra (top) of (——) [Cu(sal-*R*-hnap)] and (----) [Cu(Mesal-*R*,*R*-dpen)].

[Cu(Mesal-*R*,*R*-dpen)] shows a d–d band maximum at 17500 cm^{-1} and a shoulder near 1400 cm^{-1}, indicating a pseudo-tetrahedral surrounding about the copper ion. The moderately large magnetic moment (1.95 μ_B at 298K) also supports a pseudo-tetrahedral configuration. The azomethine π–π^* transition band of this complex is slightly shifted to higher frequency (26400 cm^{-1}).

Both complexes show circular dichroism (CD) in the visible region according to the d–d and the asomethine π–π^* transition bands. The CD spectral features of the complexes differ from each other in the region 10000—23000 cm^{-1} because the splitting mode of one-electron d-orbitals is sensitive to the degree of distortion around Cu(II) ion. In this study our attention is focussed on the CD band associated with the azomethine π–π^* transition. As seen in Fig. 2 both complexes show a CD couplet at the π–π^* transition. The appearance of a CD couplet of opposite sign is explained in terms of exciton theory.[11] The CD pattern for [Cu(sal-*R*-bnap)] is represented as (−, +) with the couplet signs from lower frequency. Similarly, the CD pattern of [Cu(Mesal-*R*,*R*-dpen)] is represented as (+, −).

The absolute configuration of [Cu(sal-*R*-bnap)] with respect to the disposition of the ligand along C_2 axis of the complex molecule is decided as *Δ* in view of the (R) atropisomerism of 1,1′-binaphthyl. The preferred absolute configuration of [Cu(Mesal-*R*,*R*-dpen)] is *Λ*, as judged from the fact that the phenyl substituents assume an axial orientation with respect to a gauche ethylene backborn.[12–14]

In Table 1 are tabulated the CD pattern at the azomethine π–π^* transition and the configuration assigned to the present complexes and related salicylideneaminate comxes of known absolute configuration.[10,12] The complexes are classified into two classes. To class A belong bis-type tetrahedral or pseudo-tetrahedral complexes of bidentate salicylideneaminates. To class B belong metal complexes of quadridentate salicylidene-

Table 1. Absolute Configuration and CD Pattern at the Azomethine π–π^* Transition of Salicylideneaminate Complexes

	Complex	Configuration	CD pattern	Ref.
Class A	[Co(sal-Rmb)$_2$]	*Λ*	(−, +)	5
	[Zn(sal-Rmb)$_2$]	*Λ*	(−, +)	3
	[Cu(sal-Rmb)$_2$]	*Δ*	(+, −)	4
	[Co(sal-ment)$_2$]	*Δ*	(+, −)	5
	[Cu(sal-ment)$_2$]	*Δ*	(+, −)	5
Class B	[Zn(sal-*R*-pn)]	*Λ*	(+, −)	10
	[Cu(sal-*R*-pn)]	*Λ*	(+, −)	10
	[Cu(sal-*S*-pn)]	*Δ*	(−, +)	12
	[Cu(sal-*SS*-bn)]	*Δ*	(−, +)	12
	[Cu(sal-*RR*-chxn)]	*Δ*	(−, +)	10
	[Cu(sal-*SS*-chxn)]	*Λ*	(+, −)	10
	[Cu(sal-*SS*-dpen)]	*Δ*	(−, +)	12
	[Cu(Mesal-*RR*-dpen)]	*Λ*	(+, −)	This work
	[Cu(sal-*R*-bnap)]	*Δ*	(−, +)	This work

Abbreviations: (sal-Rmb)$^-$=*N*-[(*R*)-1-phenylethyl]salicylideneaminate, (sal-ment)$^{2-}$=*N*-(*l*-(menthyl)-salicylideneaminate, (sal-*R*-pn)$^-$=*N*,*N*′-disalicylidene-(2*R*)-1,2-propanediaminate, (sal-*SS*-bn)$^{2-}$=*N*,*N*′-disalicylidene-(2*S*,3*S*)-2,3-butanediaminate, (sal-*RR*chxn)$^{2-}$=*N*,*N*′-disalicylidene-(1*R*,2*R*)-cyclohexanediaminate, (sal-*SS*-dpen)$^{2-}$=*N*,*N*′-disalicylidene-(1*S*,2*S*)-1,2-diphenylethanediaminate, (Mesal-*RR*-dpen)$^{2-}$=*N*,*N*′-bis(3-methylsalicylidene)-(1*R*,2*R*)-diphenyl-1,2-ethanediaminate, (sal-*R*-bnap)$^{2-}$=*N*,*N*′-disalicylidene-(*R*)-1,1′-binaphthyl-2,2′-diaminate.

aminates. In most class B complexes the chirality is caused by the steric requirement of the chiral ethylene backborn, like (*R*)-propylene, (1*R*,2*R*)-1,2-dimethylethylene, (*R*)-1-phenylethylene, or (1*R*,2*R*)-1,2-diphenylethylene (or their (*S*)-forms). A new type of this class is [Cu(sal-*R*-bnap)] in which the chirality around the metal arises from the atropisomerism of 1,1′-binaphthyl bridge.

As seen in Table 1 a good correlation holds within each class between the sign of the CD couplet at the azomethine π–π^* transition and the absolute configuration about the metal ion. For class A the CD pattern is (+, −) for *Δ* configuration and vice versa, whereas for class B the CD pattern is (+, −) for *Λ* configuration and vice versa. The result indicates that for one absolute conformer, *Δ* for example, the spiral disposition of two C=N electric transition moment vectors along the C_2 axis (dextral or sinistral) is opposed to one another between the class A and class B complexes. The electric transition moment vector of the C=N chromophore may be subject to the conjugation with the aromatic part of the ligand and also to the mixing with metal orbitals. Because of the difficulty in evaluating these effects, futher efforts were not made to rationalize the different Cotton effect at the azomethine π–π^* transition between the two classes.

Chiral quadridentate salicylideneamines derived from chiral ethylenediamine derivatives have been extensively used for CD spectral investigations of various metal ions such as oxovanadium(IV), iron(III), cobalt(III), cobal t(II), nickel(II), and copper(II).[10,12,15] Our empirical rule cannot be applied to oxovanadium(IV), iron(III), and cobalt(III) complexes because they assume a five- or six-coordination around the central metal ion. Our rule may be applied to low-spin cobalt(II) complexes of quadridentate salicylideneaminates, but the CD couplet at the azomethin π–π^* transition is not well-resolved for those complexes because d–d transition bands and CT bands are superposed on the azomethine π–π^* transition band.[12]

From the present study it is proved that the CD pattern at the azomethine π–π^* transition can be used as a diagnosis to determine the absolute configuration (*Δ* or *Λ*) of tetrahedral or pseudo-tetrahedral salicylideneaminate complexes.

References

1) R. H. Holm, A. Chakravorty, and G. O. Durek, *J. Am. Chem. Soc.*, **86**, 379 (1964); R. E. Ernst, M. J. O'conner, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6104 (1967); M. J. O'conner, R. E. Ernst, J. E. Schoenborn, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 1744 (1968); M. J. O'conner, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 5735 (1968).

2) H. Ōkawa, M. Nakamura, and S. Kida, *Inorg. Chim. Acta*, **120**, 185 (1986).

3) H. Sakiyama, H. Ōkawa, N. Matsumoto, and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1990**, 2935.

4) T. Kawamoto, A. Takeuchi, H. Kuma, and Y. Kushi, represented on 39th Symposium on Coordination Chemistry of Japan, Mito (1989).

5) H. Sakiyama, H. Ōkawa, N. Matsumoto, and S. Kida, *Bull. Chem. Soc. Jpn.*, **64**, 2644 (1991).

6) S. Miyano, M. Nawa, A. Mori, and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **57**, 2171 (1984).

7) R. Kuhn and P. Goldfinger, *Liebigs Ann. Chem.*, **470**, 183 (1929).

8) S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Jpn.*, **36**, 755 (1963).

9) B. N. Figgis, *Nature* (*London*), **182**, 1568 (1958); J. H. Griffiths, *Trans. Faraday Soc.*, **54**, 1109 (1958).

10) R. S. Downing and F. L. Urbach, *J. Am. Chem. Soc.*, **91**, 5977 (1969); B. Bosnich, *J. Am. Chem. Soc.*, **90**, 627 (1968).

11) W. Moffit, *J. Chem. Phys.*, **25**, 467 (1956); J. A. Schellman, *Acc. Chem. Res.*, **1**, 144 (1968).

12) A. Pasini, M. Gulloti, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, **1977**, 346.

13) M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, **1973**, 417.

14) F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, **1960**, 2633; D. Hall, T. N. Waters, and P. E. Wright, *J. Chem. Soc., Dalton Trans.*, **1973**, 1508.

15) M. Gullotti, L. Casella, A. Pasini, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, **1977**, 339.