[Chem. Pharm. Bull. 27(11)2688—2694(1979)]

UDC 542.953.4'546.74.04.08 : 543.47.06

Optical Properties and Structures of Metal Complexes of Schiff Bases obtained from Substituted Salicylaldehydes and Amino Sugars

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(Received April 9, 1979)

Nickel(II) and copper(II) complexes of amino sugars (glucosamine, galactosamine, and mannosamine) derived from salicylaldehyde or its derivatives have been newly synthesized and characterized. In these metal complexes, the Schiff bases are tridentate, the nickel(II) complexes are octahedral, and the copper(II) complexes are tetrahedral or pseudotetrahedral except for Cu(II)(N-salicylidene mannosamine)$_2$, which is nearly planar. The nickel(II) and copper(II) complexes of N-salicylidene mannosamine show electronic spectra, magnetic moments, and circular dichroism spectra which are different from those of the complexes of N-salicylidene glucosamine and -galactosamine.

Keywords——amino sugar; glucosamine; galactosamine; mannosamine; N-salicylidene amino sugar; nickel(II) complex; copper(II) complexes; circular dichroism; configuration of complex; magnetic moment

Various amines, including amino sugars, condense with aromatic *o*-hydroxy aldehydes to yield Schiff base-type aldimines. N-Pyridoxylidene derivatives, obtained from amino acids or amino sugars and pyridoxal, form intense blue fluorescent chelates with zinc(II) ions in methanol–pyridine solution and this reaction has been applied to the microdetermination of amino acids and amino sugars.[2,3)] The metal chelates of the aldimines derived from α-amino acids or optically active amines show a Cotton effect, whose sign depends on the configuration of the amino group.[4)] Previously, we reported that metal chelates of aldimines with salicylaldehyde or pyridoxal and various amino sugars exhibit intense Cotton effects. Amino sugars having the L-(*S*)-configuration exhibit a negative Cotton effect, expect in the case of 2-amino-2-deoxy-D-mannose (D-MN).[5)]

Though various metal chelates of aldimines derived from salicylaldehyde and amines were studied by Yamada and Yamanouchi,[6)] there are few reports on the optical properties of the metal chelates derived from optically active N-salicylidene amines. In the present work, we examined the relationship between optical activity and the structure of the chelates of N-salicylidene amino sugars.

Experimental

Preparation of N-Salicylidene-amino Sugar Metal Chelates——M(X-Sal-N-R)$_2$; X=H, 3-CH_3O and 5,6-benzo; R=2-amino-2-deoxy-D-glucose (GN), 2-amino-2-deoxy-D-galactose (GalN) and 2-amino-2-deoxy-D-mannose (MN); M=nickel(II) and copper(II). Bis(N-substituted salicylaldiminato)-nickel(II) or -copper(II) complexes were prepared by the general method described below.

Preparation of Ligand——An aldehyde derivative (1.2 mmol) in MeOH was added dropwise to an amino sugar (1 mmol) dissolved in a small amount of water at pH 9.0. The Schiff base formed was separated and recrystallized from MeOH. A solution of MeONa or Et_3N was added dropwise to a solution of metal acetate (1 mmol) and the ligand (2 mmol) in MeOH (20—30 ml), and the reaction mixture was allowed to stand at

1) Location: *Hatanodai 1-5-8, Shinagawa-ku, Tokyo, 142, Japan.*
2) M. Maeda, T. Kinoshita, and A. Tsuji, *Anal. Biochem.*, **38**, 121 (1970).
3) M. Maeda and A. Tsuji, *Anal. Biochem.*, **52**, 555 (1973).
4) Y. Nishina and S. Kida, *Bull. Chem. Soc. Jpn.*, **43**, 3814 (1970).
5) M. Maeda, T. Kinoshita, and A. Tsuji, *Tetrahedron Lett.*, 1968, 3407.
6) S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, **42**, 2543, 2562 (1969).

room temperature for 6 hr or overnight, depending on the ligand used. After removal of the solvent, the residual crude crystalline powder was recrystallized from a suitable solvent such as MeOH or EtOH.

Materials——Amino sugars were purchased from Sigma Chemical Co., and other reagents used were of reagent grade.

Measurements——The electronic absorption spectra of the complexes in solution and in the solid state were determined with a Hitachi EPS-3T automatic recording spectrophotometer and a Shimadzu MPS-50L spectrophotometer, respectively. The magnetic moments of nickel(II) and copper(II) complexes in the solid state were measured by Gouy's method. The Pascal constants were used for diamagnetic correction. The effective magnetic moments were determined using the equation, $\mu_{eff}=2.828\sqrt{(\chi_A-N)T}$, where the temperature-independent paramagnetisms for nickel(II) and copper(II) ions are estimated to be 198×10^{-6} and 60×10^{-6} e.s.u./mol, respectively. The circular dichroism (CD) spectra were measured with a Jasco ORD CD/UV-5 spectrophotometer.

Results and Discussion

The analytical data for complexes are given in Table I. All of them contained from 2 to 5 molecules of water. The ratio of ligand to metal ion was 2:1. Nickel(II) complexes are green-yellow crystalline powders except for Ni(II)(N–SalMN)$_2$4H$_2$O, and copper(II) complexes are dark-green crystalline powders. All these complexes are soluble in methanol and pyridine, but insoluble in chloroform, benzene, and ether. The color of nickel(II) complexes in pyridine chenges from light green to reddish brown.

It is well known that the electronic absorption spectrum of nickel(II) complexes depends on the configuration. The electronic absorption spectra and data for some nickel(II) complexes (Nos. 1—5) in the solid state, in methanol, and in pyridine are shown in Fig. 1 and Table II.

Table I. Analytical Data for Bis(N-substituted salicylaldiminato)-nickel(II) and -copper(II) Complexes

No.	Complex	Analysis (%) Found C	Found H	Found N	Calcd. C	Calcd. H	Calcd. N	MW	Color
1	(N–SalGN)$_2$Ni 4H$_2$O	43.72	5.62	3.64	44.30	5.66	3.45	695	Yellow-green
2	(NSal–GalN)$_2$Ni 5H$_2$O	43.70	5.87	4.37	43.70	5.89	3.93	713	Yellow-green
3	(N–SalMN)$_2$Ni 4H$_2$O	44.10	5.64	3.49	44.30	5.66	3.45	695	Brown
4	(N–3MeOsalGN)$_2$Ni 4H$_2$O	44.25	5.87	3.76	44.52	5.83	3.71	755	Yellow-green
5	(N-5,6-BenzsalGN)$_2$ Ni 2H$_2$O	54.65	5.85	4.22	53.70	5.27	3.69	795	Yellow-green
6	(N–SalGN)$_2$Cu 2H$_2$O	46.91	5.44	3.87	47.02	5.43	4.22	664	Dark green
7	(N–SalGalN)$_2$Cu 5H$_2$O	42.81	5.84	4.23	43.48	5.85	3.90	718	Dark green
8	(N–SalMN)$_2$Cu 2H$_2$O	46.94	5.40	3.98	47.02	5.43	4.22	664	Dark green
9	(N–3MeOsalGN)$_2$Cu 3H$_2$O	45.37	5.77	3.82	45.31	5.66	3.78	742	Dark green
10	(N-5,6-BenzsalGN)$_2$Cu 2H$_2$O	54.64	5.64	3.55	53.44	5.24	3.66	764	Dark green

Although the absorption maxima of each complex near 11×10^3 and 16×10^3 cm^{-1} are slightly different, the electronic absorption spectra of Ni(II) complexes are almost identical with the absorption spectrum of a typical hexa-coordinated nickel(II) complex. Thus, the nickel(II) complexes take an octahedral configuration in the solid state, as well as in nondonor (methanol) and in donor (pyridine) solvents. Heating these complexes at about 100° in a vacuum for 4 hr resulted in loss of the water molecules. Though the electronic absorption spectra of these anhydrous complexes in the solid state do not clearly indicate their structures, as shown in Fig. 2, they may be of octahedral type.

It seems likely that the alcoholic hydroxyl group in the ligand is linked to the nickel(II) ion in these anhydrous complexes, in which the Schiff bases behave as a tridentate ligand.

Table II. Electronic Absorption Spectral Data for Nickel(II) Complexes ($\nu \times 10^{-3}$cm^{-1})

Complex No.	Solvent	ν (log ε)	ν (log ε)
1	Solid	11.76	15.38
	Methanol	10.00(1.28)	16.60(1.23)
	Pyridine	11.11(1.28)	14.29(1.03)
2	Solid	12.12	16.67
	Methanol	10.00(1.21)	16.60(1.13)
	Pyridine	11.11(1.35)	14.29(1.13)
3	Solid	13.33	16.67
	Methanol	10.00(1.37)	16.67(1.38)
	Pyridine	10.00(1.35)	16.67(1.72)
4	Solid	12.12	13.18
	Methanol	10.00(1.17)	16·67(1.15)
	Pyridine	11.70(1.22)	
5	Solid	12.29	16.67
	Methanol	10.00(1.36)	16.67(1.34)
	Pyridine	12.32(1.37)	

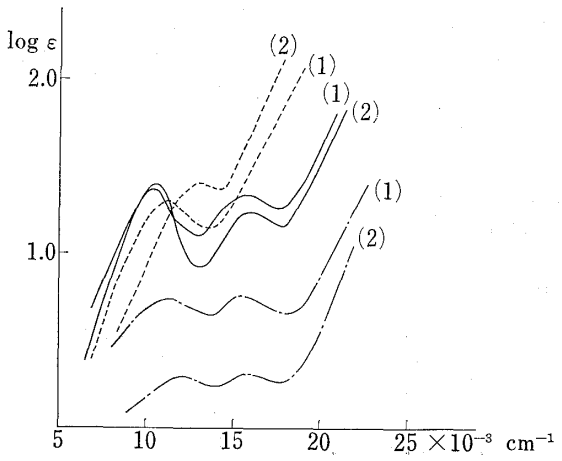


Fig. 1. Electronic Absorption Spectra of Ni(II)(N–SalGN)$_2$ (1) and Ni(II)(N-5,6-BenzosalGN)$_2$ (2) in Solvent and as a Solid
———, solid; ———, in MeOH; ·····, in pyridine.

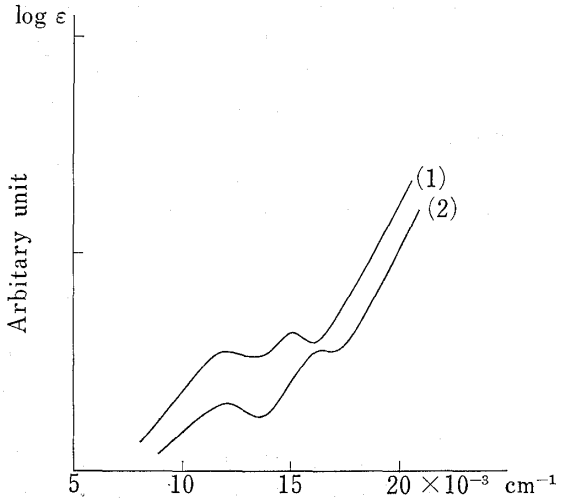


Fig. 2. Electronic Absorption Spectra of Anhydrous Ni(II)(N–SalGN)$_2$ (1) and Ni(II)(N-5, 6-BenzosalGN)$_2$ (2)

The intensity of the absorption band of Ni(II)(N-SalMN)$_2$ at about 16.7×10^3 cm^{-1} in pyridine is slightly stronger than that at 10×10^3 cm^{-1}, and the same band of Ni(II) (5,6-benzosal GN)$_2$ is superposed by a stronger absorption band of 12.32×10^3 cm^{-1} in pyridine. The absorption band of Ni(II)(3-MeOsalGN)$_2$ at 10×10^3 cm^{-1} in methanol shifted slightly to higher frequency and that at 16×10^3 cm^{-1} disappeared due to the overlapping of a stronger absorption band in pyridine. It is considered that the regular octahedral structure of the complexes is distorted by coordination of the complexes with pyridine molecules.

Data on the electronic absorption spectra of copper(II) complexes in the ligand field region are summarized in Table III, and typical spectra are shown in Fig. 3.

Theses complexes are green in the solid state and in methanol. In general, complexes of the type Cu(II)(X–Sal–R)$_2$ (R=n-alkyl and aryl) are known to take essentially a square planar configuration. Yamada *et al.*[7] reported that copper(II) complexes with bulky substitu-

7) S. Yamada and N. Nishikawa, *Bull. Chem. Soc. Jpn.*, **36**, 775 (1963).

Table III. Electronic Absorption Spectral Data for Copper(II) Complexes ($\nu \times 10^{-3}$ cm^{-1})

Complex No.	Solvent	ν (log ε)
6	Solid	15.38
	Methanol	15.87(2.16)
	Pyridine	15.38(2.36)
7	Solid	15.38
	Methanol	15.38(1.04)
	Pyridine	15.38(2.00)
8	Solid	16.13
	Methanol	16.13(2.01)
	Pyridine	15.33(2.33)
9	Solid	14.29
	Methanol	16.00(2.19)
	Pyridine	15.87(2.32)
10	Solid	15.87
	Methanol	16.00(1.96)
	Pyridine	16.00(2.07)

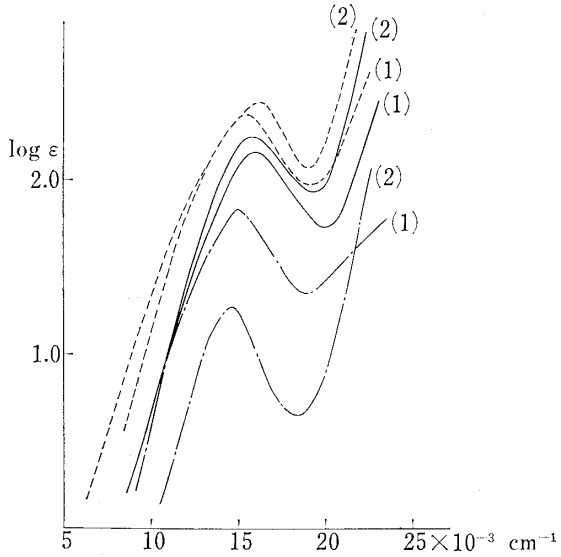


Fig. 3. Electronic Absorption Spectra of Cu(II)(N-SalGN)$_2$ (1) and Cu(II)(N-3-MeOsalGN)$_2$ (2) in Solvent and as a Solid
——, solid; ——, in MeOH; ------, in pyridine.

ents, such as *t*-butyl, isopropyl, or cyclohexyl, show ligand field bands at much lower frequency (about 13—15.3$\times 10^3$ cm^{-1}) than complexes with small alkyl groups and in non-donor solvents (17.6$\times 10^3$ cm^{-1}), indicating that the configuration of these complexes is not planar but tetrahedral or pseudotetrahedral. The absorption bands of the copper(II) complexes in Table III, except for Nos. 8 and 10, are in the range of 14.3—16.0$\times 10^3$ cm^{-1}. These values are at lower frequency than those of typical square planar alkyl-substituted complexes. Glucosamine, galactosamine, and mannosamine are bulky groups, like the *t*-butyl group, *etc.* Therefore, it is concluded that the copper(II) complexes of glucosamine and galactosamine have a tetrahedral or pseudotetrahedral configuration. The complex of D-mannosamine (No. 8) has a d→d* band at about 16.1$\times 10^3$ cm^{-1}, which is higher than those of other complexes mentioned above. In this case, distortion from planarity is considered to be small and the configuration is nearly square planar. Assignment of these structures is supported by the values of magnetic susceptibility.

Yamada *et al.*[8] reported that the nickel(II) complexes of N-hydroxyalkyl salicylideneimines and related compounds in the solid state are hexa-coordinated and show paramagnetism corresponding to two unpaired electrons (μ_{eff} 2.95—3.22 BM). Table IV shows that the salicylideneaminato-Ni(II) complexes, to which octahedral structures have been assigned on the basis of the spectral evidence, have magnetic moments of 2.78—3.25 BM at room temperature, except for the complex No. 3. In order to clarify the relatively small magnetic moment of complex No. 3, the magnetic susceptibility was measured at various temperatures.

The results are shown in Fig. 4. Since this complex obeys the Curie-Weiss law and its Weiss constant is small ($\theta = +36°$ K) and positive, it is evident that the relative low magnetic moment is attributable to the presence of a ferromagnetic spin interaction between nickel(II) ions.

The magnetic moments of copper(II) complexes were also measured and are given in Table IV. Theses values, except for complex No. 8, are relatively high compared with the ordinary range (1.83—1.86 BM), which is quite common for copper(II) in a square planar environment. Pseudotetrahedral complexes of copper(II)-N-alkylsalicylideneamine (alkyl=

8) S. Yamada, Y. Kuge, and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, **40**, 1864 (1967).

Table IV. Magnetic Data for Complexes at Room Temperature (296 °K)

Complex No.	Molar susceptibility ($\chi_p \times 10^6$)	μeff (B.M)
1	4005	3.08
2	4440	3.24
3	2103	2.23
4	4420	3.25
5	3250	2.78
Theoretical		2.83
Found		2.9—3.4
6	2294	2.33
7	1814	2.07
8	1014	1.57
9	1640	1.97
10	1862	2.10
Theoretical		1.73
Found		1.8—2.2

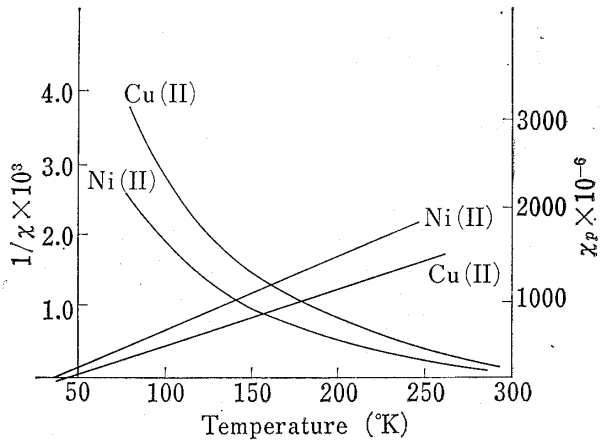


Fig. 4. Magnetic Susceptibilities of Ni(II)(N-SalMN)$_2$ and Cu(II) Complexes at Various Temperatures

t-butyl, *sec*-butyl, isopropyl) show higher magnetic moments (1.91, 1.91, and 1.90 BM) than normal alkylamines.[9] Therefore, the complexes Nos. 6, 7, 9, and 10 have tetrahedral or pseudotetrahedral configurations, as expected from their spectral data.

From the data measured at low temperature, it appears that complex No. 8 obeys the Curie-Weiss law; the Weiss constant (θ) is 42 °K which suggests the presence of a ferromagnetic exchange interaction. Therefore, the small magnetic moment of complex No. 8 might be explained in terms of a binuclear structure with Cu–Cu exchange interaction.[10]

Circular Dichroism Spectra

The CD spectral data for Schiff bases and complexes of Ni(II) and Cu(II) are presented in Table V, and typical spectra are shown in Fig. 5.

Our previous paper reported that the aldimine of D-mannosamine exhibits a negative Cotton effect, corresponding to an L(*R*)-configuration of the amino group, and the Cotton

Table V. Circular Dichroism Spectral Data for Amino Sugar Derivatives

Compound	Schiff base		Ni(II) chelate		Cu(II) chelate	
	Methanol	Pyridine	Methanol	Pyridine	Methanol	Pyridine
N–Sal-D-GN	+2.6(405) +10.8(315)	+2.6(370) +18.3(300)	−8.0(400) +58.9(372)	−10.5(440) +0.3(370) +7.5(325)	+34.2(369)	+31.3(378)
N–Sal-D-MN	−1.9(397) −7.7(315)	−0.2(375) +1.5(312)	−6.4(395) +26.3(370)		+32.0(375)	+21.5(375)
N–Sal-D-GalN	+1.8(400) +4.6(310)	+0.9(380) +9.8(300)	−24.1(379) +63.7(375)	−8.1(430) +14.6(370) +10.7(320)	+29.3(375)	+15.8(378)
N–3-MeO–Sal-D-GN	+2.7(395) 0 (300)	+1.8(350) +2.3(300)	−22.9(415) +33.9(380) −7.6(350)	−7.5(430) +1.2(380) −17.8(320)	+28.3(380)	+39.9(386)
N–5,6-Benz–Sal–D-GN	+2.1(420) −25.6(302)	+1.9(410)	−8.0(425) +65.8(388) +16.1(325)	−20.1(410) +9.7(360)	+37.7(395)	+46.1(398)

Figures in parentheses are wavelengths (nm), $[\theta] \times 10^{-3}$.

9) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, **1964**, 276.
10) M. Kato, Y. Muto, H.B. Jonassen K. Imai, and A. Harano, *Bull. Chem. Soc. Jpn.*, **41**, 1864 (1968).

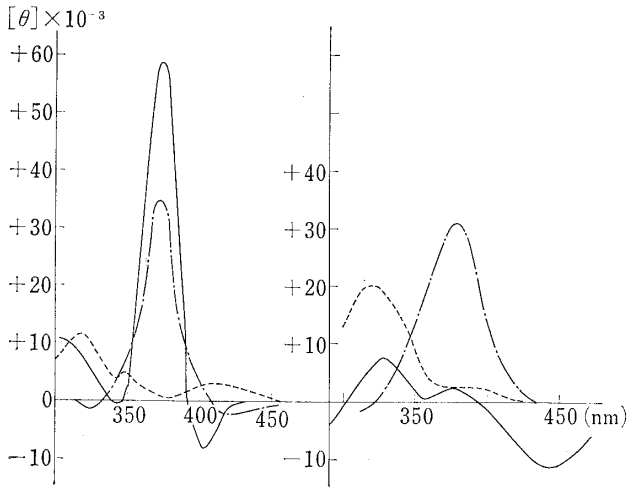


Fig. 5. Circular Dichroism Spectra of (N-SalGN) and Its Chelates in Methanol (Left) and in Pyridine (Right)

-----, Schiff base; ——, Ni(II) chelate; – – –, Cu(II) chelate.

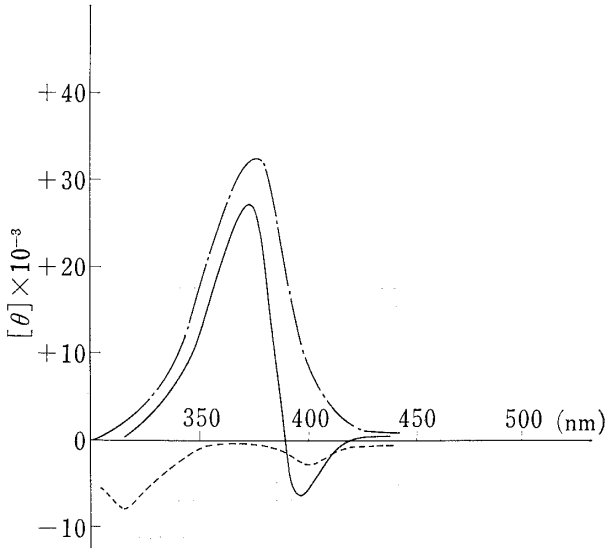
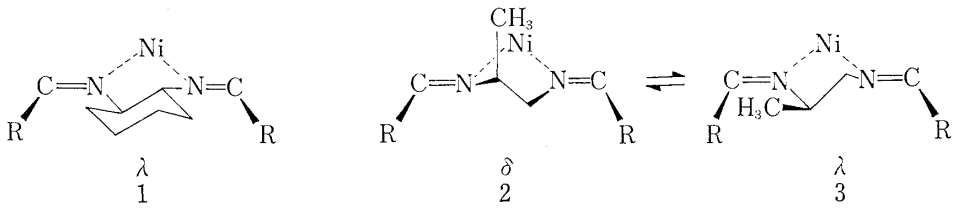


Fig. 6. Circular Dichroism Spectra of (N-SalMN) and Its Chelates in Methanol

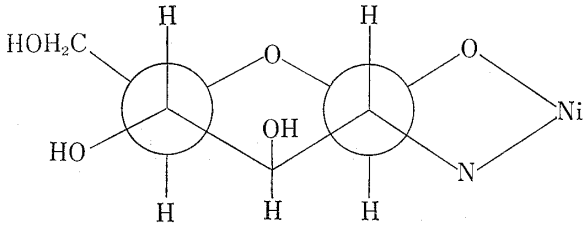
-----, Schiff base; ——, Ni(II) chelate; – – –, Cu(II) chelate.

effect of the chelate with Cu(II) or Ni(II) undergoes sign inversion, resulting in an anomalous positive Cotton effect in contrast to other amino sugars and amino acids. As shown in Figs. 5 and 6, the CD spectra of the Schiff bases derived from D-glucosamine and D-mannosamine bear a mirror image relationship, and the spectra of the Ni(II) and Cu(II) complexes show the same pattern and sign, even though the amino groups in the parent amino sugars have an opposite absolute configuration. The spectra of Ni(II) complexes show two peaks of opposite sign, an intense positive peak and a small negative peak, while the spectra of Cu(II) complexes show only one positive peak. Downing and Ulbach[11] found that the CD spectra of Ni(II) and Cu(II) complexes with Schiff bases derived from (*R*)(−)-propane-1,2-diamine and (*R*,*R*)(−)-cyclohexane-1,2-diamine were observed as mirror images, although the parent diamines have the same absolute configuration. In the (*R*,*R*)(−)-cyclohexane-1,2-diamine-Schiff base chelates, the central ring is locked stereospecifically in the λ conformation (1), while in the (*R*)(−)-propane-1,2-diamine, the preference for the reverse δ conformation (2) can be ascribed to the in-plane 1,3-interaction with the hydrogen or methyl group in the equatorial conformation (λ conformation).[3]



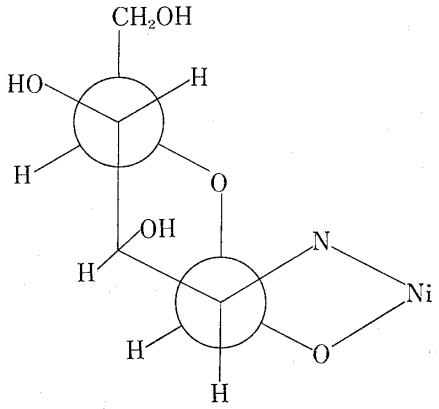
The β-anomeric OH group in D-glucosamine in the Cl conformation can coordinate with the central metal ion and form a λ-conformational chelate ring with the azomethine N atom in the ligand (Fig. 7a). On the other hand, a similar structure involving the pyranose ring of D-mannosamine will be very unstable because the bulky pyranose ring coordinates to the chelate ring perpendicularly (Fig. 7b).

11) R.S. Dowing and F.L. Ulbach, *J. Am. Chem. Soc.*, **92**, 5861 (1970).

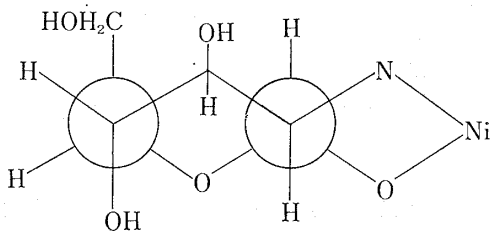


β-D-glucosamine Cl (λ)

Fig. 7a



α-D-mannosamine Cl (δ)



α-D-mannosamine 1C (δ)

Fig. 7b

We consider that if the pyranose ring of D-mannosamine in the complex has a 1C conformation, the whole configuration of the complex may become planar and stable, and the chelate ring formed with azomethine N and OH in complex will be in the δ-conformation. Therefore, in the case of D-mannosamine, the CD spectrum of the Ni(II) or Cu(II) complex can be attributed more to the stronger conformational effect of the chelate ring attached to the metal atom than to the vicinal effect of the α-asymmetric carbon atom.

Acknowledgement The authors wish to thank Dr. Minoru Kinoshita, Faculty of Science, University of Tokyo, for a valuable discussion on magnetic moments.