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Structure and Circular Dichroism of Nickel(II) Complexes Containing a Glycosylamine Derived from Ketoses

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The reactions of ketoses (D-fructose, L-sorbose, D-tagatose, and D-psicose) with some tris(diamine)nickel(II) complexes were studied. Six new complexes containing a glycosylamine derived from D-fructose (D-fru) or L-sorbose (L-sor) were isolated and characterized by elemental analysis, magnetic moments, and absorption and CD spectra. The structure of one of the complexes, $[Ni(S\text{-ampr})(L\text{-sor-}S\text{-ampr})]Cl_2{\cdot}CH_3OH{\cdot}H_2O$, was determined by X-ray crystallography, where *S*-ampr is 2(*S*)-(aminomethyl)pyrrolidine and L-sor-*S*-ampr is 2-[(2(*S*)-pyrrolidinylmethyl)amino]-2-deoxy-L-sorbose. Crystallographic details for the complex are as follows: formula $NiC_{17}H_{40}N_4O_7Cl_2$, space group $P2_12_12_1$ (orthorhombic), $a = 9.954$ (1) Å, $b = 30.823$ (2) Å, $c = 8.534$ (1) Å, $V = 2618.4$ (4) Å^3, $Z = 4$, $d_{calcd} = 1.38$ g cm^{-3}, $R = 0.049$. This complex has one tetradentate glycosylamine ligand (L-sor-*S*-ampr), which was made from L-sorbose and *S*-ampr, and one diamine ligand (*S*-ampr). The coordination geometry of the glycosylamine complex is similar to that in $[Ni(en)(D\text{-fru-en})]Cl_2{\cdot}CH_3OH$[2] and in $[Ni(en)(L\text{-sor-en})]Cl_2{\cdot}{}^1/_2CH_3OH$,[5] where en is ethylenediamine. The glycosylamine ligand connects to the nickel atom through the two nitrogen atoms of the diamine residue and through the two oxygen atoms of the sugar residue. The absolute configuration around the nickel atom is Δ. The relationship between the structures and the related metal complexes has been examined. The configuration at C(3) is important for the overall shape of the complexes and for the CD signs of the second and third d-d transition regions. The pattern of CD curves of the first absorption regions is affected by the configuration of diamines (*R*-pn and *S*-pn) or by the configuration of the coordinated nitrogen atom of the diamine (*S*-ampr), where pn is propylenediamine.

Introduction

In recent years, we have extensively studied the synthesis and characterization of the novel type nickel(II) complexes containing glycosylamine(s) derived from the reaction of a diamine and a monosaccharide.[2-5] In these studies, it has been shown that the patterns of CD spectra of the complexes derived from aldoses correspond closely to the structure of the aldoses.[2-4]

For ketose-containing complexes, however, the relationships between the CD spectra of the complexes and their structures have not been established. Recently, X-ray crystal structure determinations of both $[Ni(en)(D\text{-fru-en})]Cl_2{\cdot}CH_3OH$ (**1**)[2] and $[Ni(en)(L\text{-sor-en})]Cl_2{\cdot}{}^1/_2CH_3OH$ (**2**)[5] were performed. (en = ethylenediamine, D-fru-en = 2-[(aminoethyl)amino]-2-deoxy-D-fructose, L-sor-en = 2-[(aminoethyl)amino]-2-deoxy-L-sorbose.) The results of these studies showed that (1) each complex has one tetradentate glycosylamine ligand, which coordinates to a nickel atom through the hydroxyl groups on C(1) and C(3) of the ketose residue, and the two nitrogen atoms of the diamine residue, and one bidentate ethylenediamine ligand, and (2) that the two complex cations have similar structures except for the orientation of each hydroxyl group on C(5) atom of the sugar moiety and the conformation of each bidentate ethylenediamine (Figure 1a,b). It is often observed that the CD signs of d-d transition bands are influenced by stereochemical features of dissymmetric nickel(II) complexes.[6] **1** and **2** exhibit CD curves of opposite sign in the first absorption region, but their CD spectra of the second and third absorption regions are nearly identical. These results indicate that more detailed investigations are desirable to clarify the stereochemistry and the circular dichroism of this system.

We have chosen D-fructose, L-sorbose, D-tagatose (D-tag), and D-psicose (D-psi) as the starting sugars. The former three sugars have the same *S* configuration around the C(3) atom of the ketoses, and the last one has the opposite *R* configuration. Consequently, the coordination behavior of the glycosylamines derived from the first three ketoses are expected to be similar, and that derived from D-psi would be different. In order to establish the general coordination behavior of the glycosylamine derived from ketoses and to confirm the correlation between these coordination structures and their CD spectra, we have carried out detailed stereochemical investigations using nickel(II) complexes of some diamines (including optically active forms) and four ketohexoses, including the crystal structure determination of a newly isolated diamine-ketose complex $[Ni(S\text{-ampr})(L\text{-sor-}S\text{-ampr})]Cl_2{\cdot}CH_3OH{\cdot}H_2O$ (Figure 1c), where *S*-ampr is 2(*S*)-(aminomethyl)pyrrolidine and L-sor-*S*-ampr is 2-[(2(*S*)-pyrrolidinylmethyl)amino]-2-deoxy-L-sorbose.

Experimental Section

All materials were obtained commercially and used without further purification. (*R*)- and (*S*)-propylenediamine (*R*- and *S*-pn) were resolved from racemic propylenediamine according to the method of Dwyer et al.,[7] and 2(*S*)-(aminomethyl)pyrrolidine (*S*-ampr) was prepared from L-proline in a manner similar to the method of Schnell and Karrer.[8] D-Psicose was prepared from D-fructose by the method of ref 9 and was used as a syrup.

Preparation of Tris(diamine)nickel(II) Complexes. $[Ni(S\text{-pn})_3]Cl_2{\cdot}2H_2O$,[10] $[Ni(R\text{-pn})_3]Cl_2{\cdot}2H_2O$, and $[Ni(tn)_3]Cl_2{\cdot}2H_2O$[11] (tn = trimethylenediamine) were prepared from nickel chloride hexahydrate and the corresponding diamine by a known method, and they were recrystallized from a minimum amount of hot water.

$\mathbf{[Ni(S\text{-}ampr)_3]Cl_2{\cdot}C_2H_5OH}$ was newly prepared as follows. A 4.3-g sample of $NiCl_2{\cdot}6H_2O$ and 5.5 g of *S*-ampr were dissolved in a small amount of water and evaporated to dryness at room temperature under a reduced pressure. This crude product was recrystallized from a minimum amount of hot ethanol. The yield was 5.7 g (65%). This complex was very soluble in water. Anal. Calcd. for $NiC_{17}H_{42}N_6OCl_2$: C, 42.88; H, 8.89; N, 17.65; Cl, 14.89. Found: C, 42.88; H, 8.69; N, 17.38; Cl, 14.79.

$\mathbf{[Ni(S\text{-}ampr)_3]Br_2{\cdot}{}^1/_2C_2H_5OH}$. A 2.18-g sample of $NiBr_2$ was added to 20 mL of an aqueous solution containing 3.00 g of *S*-ampr, and this mixture was stirred for 1 h at room temperature. This suspension was filtered, and the filtrate was evaporated to dryness under reduced pressure

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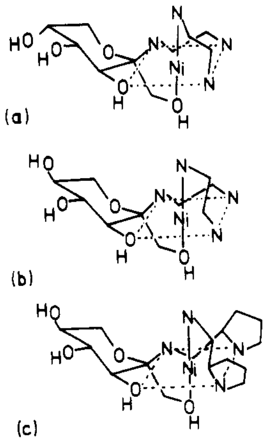

Figure 1. Structures of (a) $[Ni(en)(D\text{-fru-en})]^{2+}$,[2] (b) $[Ni(en)(L\text{-sor-en})]^{2+}$,[5] and (c) $[Ni(S\text{-ampr})(L\text{-sor-}S\text{-ampr})]^{2+}$.

at room temperature. This crystalline product was recrystallized from a minimum amount of hot ethanol. The yield was 3.6 g (66%). Anal. Calcd for $NiC_{16}H_{39}N_6O_{0.5}Br_2$: C, 35.46; H, 7.25; N, 15.50; Br, 29.48. Found: C, 35.36; H, 7.72; N, 15.82; Br, 28.60.

Reaction of Ketoses with Nickel(II) Diamine Complexes. The reactions of ketoses (D-fructose, L-sorbose, D-tagatose, and D-psicose) with nickel diamine complexes were studied in methanol. The following complexes were used as the starting nickel complexes: $[Ni(en)_3]Cl_2\cdot 2H_2O$, $[Ni(tn)_3]Cl_2\cdot 2H_2O$, $[Ni(S\text{-pn})_3]Cl_2\cdot 2H_2O$, $[Ni(R\text{-pn})_3]Cl_2\cdot 2H_2O$, $[Ni(S\text{-ampr})_3]Cl_2\cdot C_2H_5OH$, $[Ni(S\text{-ampr})_3]Br_2\cdot {}^1/_2C_2H_5OH$. But for D-tagatose and D-psicose, only $[Ni(en)]Cl_2\cdot 2H_2O$ and $[Ni(tn)_3]Cl_2\cdot 2H_2O$ were examined. In these studies we isolated several new complexes as crystals.

General Preparation Method of Ketose Complexes. To a solution of 3 mmol of $[Ni(diamine)_3]^{2+}$ in 40 mL of methanol were added 6 mmol of ketose and 3 mmol of NH_4Cl,[12] and the mixture was heated to reflux for 1 h. The color of the solution changed from violet to blue. Then it was concentrated to about 20 mL by a rotary evaporator and poured on to a column of Sephadex LH-20 gel (d = 4 cm, h = 90 cm), and the material was eluted with methanol. The colored materials were separated into violet, blue, and yellow bands. The blue fractions were collected and concentrated to about 15 mL and kept at 5 °C. When blue crystals were obtained, they were recystallized from a minimum amount of hot methanol. Only in the case of the tn complex did the blue complex crystallize in the middle of reflux. Since these crystals were somewhat hygroscopic, treatment in the atmosphere must be done quickly.

Measurements. Visible and near-infrared absorption spectra were measured with a Hitachi Model 340 recording spectrophotometer. Diffusion reflectance spectra were recorded on this instrument equiped with a reflectance attachment. Circular dichroism spectra were recorded on a JASCO J-500 recording spectropolarimeter. Magnetic susceptibility was measured at room temperature by using a Shimadzu MB-100 magnetic balance (Faraday method). Diamagnetic corrections were calculated from Pascal's constants.[13] Microanalyses were performed by Shonan Bunseki Center Co., Ltd.

Crystal Data and Intensity Data Collection for $[Ni(S\text{-ampr})(L\text{-sor-}S\text{-ampr})]Cl_2\cdot CH_3OH\cdot H_2O$. A block-shaped blue crystal, which was coated with epoxy cement, was used in the structure analysis. Diffraction data were collected at room temperature on a Rigaku Denki AFC-5 four-circle automated diffractometer controlled by a FACOM U-100 computer and RIGAKU FOS program system. The crystal parameters and measurement method are listed in Table I. Three standard reflections were monitored and showed intensity change within 5%, for which no correction was made. The intensity was corrected for Lorentz–polarization factors, and an absorption correction with a numerical integration procedure with a Gaussian grid (6 × 6 × 6) was applied.

Structure Solution and Refinement. All calculations were carried out on a HITAC M-200H system of the computer center of the Institute for Molecular Science with a universal program UNICSIII.[14] The coordinate of the Ni atom was determined from the three-dimensional Patterson synthesis. The positions of the other non-hydrogen atoms were determined by means of mutual cycles of Fourier synthesis and block-diagonal least-squares refinement. Anisotropic temperature factors for non-hydrogen atoms were used in the refinement of parameters. Atomic scattering factors were taken from ref 15. A weighting scheme $1/w = \sigma_{count}^2 + (0.015|F_o|)^2$ was employed. $\sum w(|F_o| - |F_c|)^2$ was minimized in the least-squares procedure. The absolute configuration of this complex was determined from the known absolute configurations of L-sorbose and S-ampr. The effects of anomalous dispersion were corrected in structure factor calculation, and the values $\Delta f'$ and $\Delta f''$ for non-hydrogen atoms were taken from ref 16. Least-squares refinement of the positional and individual anisotropic thermal parameters of the non-hydrogen atoms gave convergence at R = 7.26%.[17] When the $\Delta f''$ values were reversed in sign in order to test the structure, the convergence was reached with R = 7.92%, which is significantly larger than the former value. This result agreed with the earlier determination made by using the internal reference of asymmetric centers. Difference Fourier syntheses clarified the existence of a water molecule, which was disordered to three positions. The hydrogen atoms that are connected with carbon atoms were assumed to be tetrahedrally coordinated, with a C–H bond distance of 1.08 Å, but the positions of H(O3) and H(O4) were determined from a difference Fourier map. The positional and isotropic thermal parameters of these hydrogen atoms were also refined. The final R and R_w factors, were 4.9% and 5.5%, respectively. The final difference Fourier synthesis revealed no unusual features with the highest peak being 0.88 e Å^{-3}.

Table I. Crystal Data and Conditions of Intensity Data Collection

formula	$NiC_{17}H_{40}N_4O_7Cl_2$
fw	542.09
cryst system	orthorhombic
space group	$P2_12_12_1$
a, Å	9.954 (1)
b, Å	30.823 (2)
c, Å	8.534 (1)
V, Å	2618.4 (4)
cryst size, mm	0.5 × 0.3 × 0.5
d_{obsd}, g cm^{-3}	1.41
d_{calcd}, g cm^{-3}	1.38
Z	4
abs coeff μ, cm^{-1}	10.34 (Mo Kα)
wavelength, Å	0.71073 (Mo Kα, graphite monochromatized)
scan method	$\omega(2\theta \le 15°)$, ω–2θ $(2\theta > 15°)$
scan width, deg	1.1 + tan θ
scan speed, deg min^{-1}	3
data collcn range	$2\theta < 55°$ $(+h,-k,+l)$
no. of data measd	3634
no. of indep data with $\|F_o\| \le 3\sigma(\|F_o\|)$	2457

Results and Discussion

Synthesis of Ketose-Containing Complexes. The reactions of ketoses with tris(diamine)nickel(II) complexes in methanol were examined, and six new complexes containing a ketose residue were isolated. The reaction time necessary was about 1 h. Yellow-orange and violet fractions were separated from the objective blue fractions by gel chromatography. The starting nickel diamine complexes were obtained from the violet fractions. The yields of ketose-diamine complexes were relatively low. However, in the case of the trimethylenediamine complex, almost no yellow components were detected, the reaction was found to complete more rapidly, and the objective blue complexes ($[Ni(tn)(D\text{-fru-tn})]Cl_2\cdot CH_3OH$[2b] (**9**) and $[Ni(tn)(L\text{-sor-tn})]Cl_2$ (**8**)) could be obtained in comparatively good yield (see Table II). It has been already shown in this laboratory that aldose–tn complexes are obtained with comparatively good yield rather than aldose–en complexes. When the reaction time was prolonged, the more yellow fractions separated by gel chromatography. Since these blue complexes are hydrolyzed gradually in water, the CD intensity of a water solution of these complexes was purged in 1 or a few days.

Formula and Electronic Spectra of Isolated Complexes. The analytical data of the isolated complexes shown in Table II indicate

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(12) Less yield was obtained in the absence of NH_4Cl. See ref 5b.

(13) "Landolt-Bornstein Tabellen", Neue Serie; Springer-Verlag: West Berlin, 1966; Vol. II, Part 2.

(14) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69–77.

(15) (a) For Ni, Cl, O, N, and C atoms: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, pp 270–276. (b) For H atoms: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

(16) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17–23.

(17) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Analytical, Yield, and Magnetic Moment Data of Ketose Complexes

compd	analytical data,[a] % C	H	N	Cl (Br*)	yield,[b] %	magnetic moment, μ_B
$[Ni(S\text{-pn})(\text{L-sor-}S\text{-pn})]Cl_2$ (**3**)	32.52	7.19	12.42	16.13	7	3.14
	(32.76)	(6.87)	(12.73)	(16.12)		
$[Ni(S\text{-pn})(\text{D-fru-}S\text{-pn})]Cl_2 \cdot CH_3OH$ (**4**)	32.66	7.26	11.75	14.87	12	3.11
	(33.07)	(7.26)	(11.87)	(15.02)		
$[Ni(R\text{-pn})(\text{L-sor-}R\text{-pn})]Cl_2 \cdot {}^1/_2CH_3OH \cdot {}^1/_2H_2O$ (**5**)	32.27	7.29	11.82	15.61	5	3.14
	(32.22)	(7.15)	(12.05)	(15.25)		
$[Ni(S\text{-ampr})(\text{L-sor-}S\text{-ampr})]Cl_2 \cdot CH_3OH \cdot H_2O$ (**6**)	37.16	7.52	10.21	13.45	15	3.17
	(37.66)	(7.45)	(10.34)	(13.08)		
$[Ni(S\text{-ampr})(\text{D-fru-}S\text{-ampr})]Br_2 \cdot CH_3OH \cdot {}^1/_2H_2O$ (**7**)	32.53	6.25	9.43	25.62*	13	3.27
	(32.22)	(6.22)	(9.11)	(25.98)*		
$[Ni(tn)(\text{L-sor-tn})]Cl_2$ (**8**)	32.26	7.10	12.59	16.48	50	3.19
	(32.76)	(6.87)	(12.73)	(16.12)		

[a] Calculated values are given in parentheses. [b] These values are calculated on the basis of starting nickel complexes.

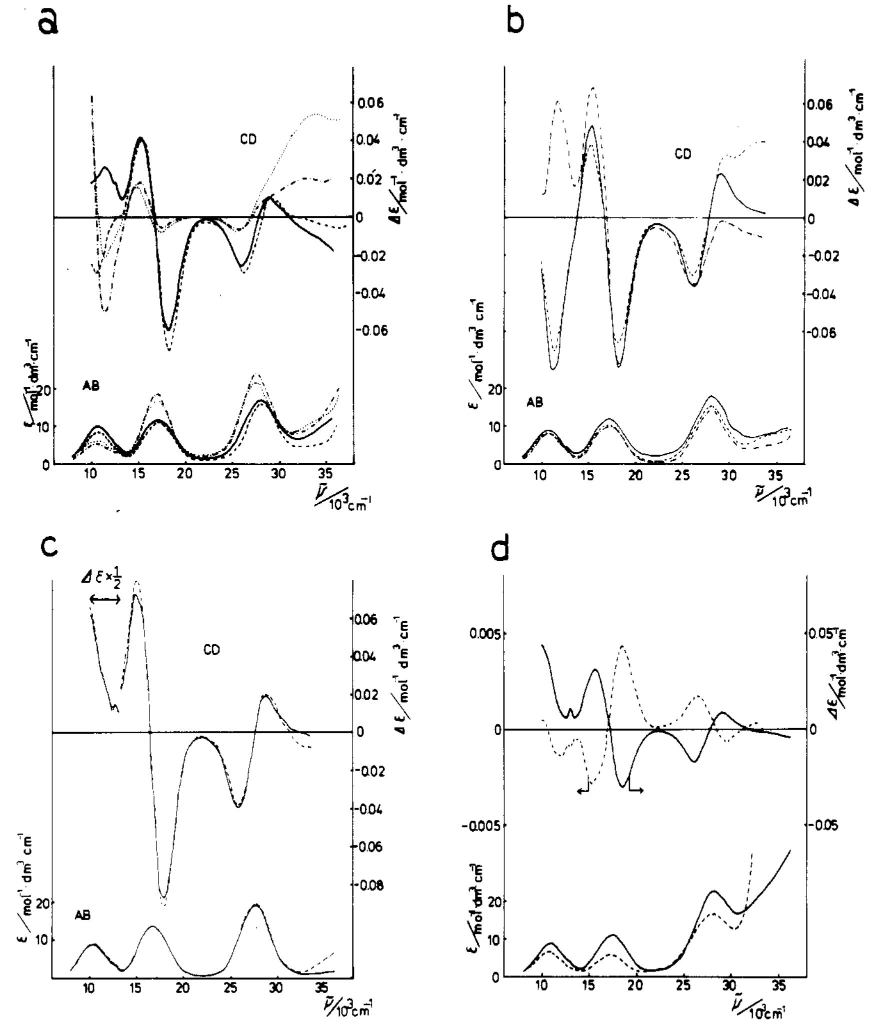

Figure 2. Electronic absorption and CD spectra of the complexes in methanol: (a) $[Ni(en)(\text{D-fru-en})]^{2+}$ (—), $[Ni(en)(\text{L-sor-en})]^{2+}$ (- -), $[Ni(tn)(\text{D-fru-tn})]^{2+}$ (···), $[Ni(tn)(\text{L-sor-tn})]^{2+}$ (-·-); (b) $[Ni(S\text{-pn})(\text{L-sor-}S\text{-pn})]^{2+}$ (—), $[Ni(S\text{-pn})(\text{D-fru-}S\text{-pn})]^{2+}$ (- -), $[Ni(R\text{-pn})(\text{L-sor-}R\text{-pn})]^{2+}$ (-·-); (c) $[Ni(S\text{-ampr})(\text{L-sor-}S\text{-ampr})]^{2+}$ (—), $[Ni(S\text{-ampr})(\text{D-fru-}S\text{-ampr})]^{2+}$ (- -); (d) $[Ni(en)(\text{D-tag-en})]^{2+}$ (—), $[Ni(en)(\text{D-psi-en})]^{2+}$ (- -).

that each nickel(II) complex has one diamine ligand and one ketosylamine ligand (L-sor-*S*-pn = *N*-L-sorbosyl-(*S*)-propylenediamine,[18] L-sor-*R*-pn = *N*-L-sorbosyl-(*R*)-propylenediamine, D-fru-*S*-pn = *N*-D-fructosyl-(*S*)-propylenediamine, D-fru-*S*-ampr = 2-[(2(*S*)-pyrrolidinylmethyl)amino]-2-deoxy-D-fructose, L-sor-tn = 2-[(3-aminopropyl)amino]-2-deoxy-L-sorbose, D-fru-tn = 2-[(3-aminopropyl)amino]-2-deoxy-D-fructose). This result is similar to the previously reported cases of $[Ni(en)(\text{D-fru-en})]Cl_2 \cdot CH_3OH$ (**1**) and $[Ni(en)(\text{L-sor-en})]Cl_2 \cdot {}^1/_2CH_3OH$ (**2**). The effective magnetic moments of these complexes are also listed in Table II. These values fall in the range reported for octahedral nickel(II) complexes.[19]

The absorption spectra of these complexes in methanol are shown in Figure 2,[20] and their band locations and intensities together with the data of their diffusion reflectance spectra in the

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[18] It is uncertain which nitrogen atoms connect to the sugar molecule, so that the correct name of L-sor-*S*-pn may be *N*-(1-amino-2-propyl)-L-sorbopyranosylamine or *N*-(2-aminopropyl)-L-sorbopyranosylamine. In the cases of L-sor-*R*-pn and D-fru-*S*-pn the situations are similar.

[19] Sacconi, L. *Transition Met. Chem. (N.Y.)* **1968**, *4*, 199–296.

[20] In the cases of D-psicose and D-tagatose, the complexes were not isolated, so that the blue solution refined three times by gel chromatography was used to obtain spectroscopic data. The concentrations of nickel were determined by atomic absorption analysis.

Table III. Electronic Absorption, Reflectance, and Circular Dichroism Spectral Data

complex	abs max, 10^3 cm^{-1} (ϵ, M^{-1} cm^{-1})	ref max, 10^3 cm^{-1}	CD max, 10^3 cm^{-1} ($\Delta\epsilon$, M^{-1} cm^{-1})
[Ni(en)(D-fru-en)]Cl$_2$·CH$_3$OH[a] (**1**)	10.8 (10.0), 12.8 sh (4.7)	11.4	11.5 (+0.026), 12.6 (+0.019)
	17.1 (11.7)	17.1	15.3 (+0.042), 18.2 (−0.060)
	28.2 (17.0)	27.8	26.1 (−0.026), 29.0 (+0.010)
[Ni(en)(L-sor-en)]Cl$_2$·$^1/_2$CH$_3$OH[b] (**2**)	10.7 (8.7), 12.8 sh (3.8)	10.6, 12.9 sh	10.4 (−0.031)
	17.2 (11.1)	17.5	15.3 (+0.042), 18.3 (−0.070)
	28.0 (15.8)	27.7	26.2 (−0.029), 29.2 (+0.010)
[Ni(*S*-pn)(L-sor-*S*-pn)]Cl$_2$ (**3**)	10.8 (9.0), 12.7 sh (4.4)	10.8, 12.7 sh	11.1 (−0.081)
	17.2 (11.8)	17.2	15.4 (+0.048), 18.2 (−0.079)
	28.2 (18.0)	28.3	26.1 (−0.036), 29.1 (+0.023)
[Ni(*S*-pn)(D-fru-*S*-pn)]Cl$_2$·CH$_3$OH (**4**)	10.6 (8.4), 12.8 sh (3.5)	11.2, 12.8 sh	11.3 (−0.071)
	17.2 (10.4)	17.6	15.2 (+0.038), 18.2 (−0.066)
	28.1 (15.2)	28.2	26.2 (−0.031), 29.9 (+0.033)
[Ni(*R*-pn)(L-sor-*R*-pn)]Cl$_2$·$^1/_2$CH$_3$OH·$^1/_2$H$_2$O (**5**)	10.6 (8.0), 12.6 sh (3.6)	11.2, 12.8 sh	11.6 (+0.062)
	17.1 (10.0)	17.4	15.4 (+0.067), 18.3 (−0.077)
	28.0 (14.2)	28.3	26.0 (−0.038)
[Ni(*S*-ampr)(L-sor-*S*-ampr)]Cl$_2$·CH$_3$OH·H$_2$O (**6**)	10.3 (8.1), 12.6 sh (3.4)	10.3, 12.7 sh	[10.0 (+0.12)],[c] 12.6 (+0.030)
	16.8 (12.4)	16.6	15.0 (+0.073), 17.9 (−0.087)
	27.7 (17.5)	27.7	25.8 (−0.040), 28.7 (+0.019)
[Ni(*S*-ampr)(D-fru-*S*-ampr)]Br$_2$·CH$_3$OH·$^1/_2$H$_2$O (**7**)	10.5 (8.6), 12.6 sh (3.7)	10.7, 12.6 sh	[10.0 (+0.13)],[c] 12.6 (+0.029)
	16.8 (13.0)	16.6	15.1 (+0.080), 18.0 (−0.092)
	27.7 (18.8)	27.7	25.8 (−0.039), 28.8 (+0.020)
[Ni(tn)(L-sor-tn)]Cl$_2$ (**8**)	10.5 (5.2), 12.7 sh (3.1)	10.6, 12.7 sh	10.4 (−0.051)
	17.1 (18.1)	17.0	15.1 (+0.020), 17.4 (−0.0064)
	27.5 (23.6)	27.2	25.7 (−0.0065), 33.0 (+0.020)
[Ni(tn)(D-fru-tn)]Cl$_2$·CH$_3$OH[a] (**9**)	10.4 (4.1), 12.6 sh (3.7)	10.7, 12.7 sh	10.4 (−0.022)
	17.0 (16.6)	17.2	14.8 (+0.015), 17.3 (−0.0086)
	27.4 (21.4)	27.4	25.3 (−0.0084), 33.7 (+0.054)

[a] Data from ref 2b. [b] Data from ref 5b. [c] These are the values at the limit of wavenumber on this instrument.

Table IV. Fractional Coordinates and Equivalent Thermal Factors for [Ni(*S*-ampr)(L-sor-*S*-ampr)]Cl$_2$·CH$_3$OH·H$_2$O[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Ni	493.5 (7)	−1055.7 (2)	4414.0 (9)	2.3
Cl(1)	5005 (2)	−547 (1)	4261 (2)	4.5
Cl(2)	1522 (2)	−1632 (1)	−287 (2)	5.1
O(1)	−1125 (4)	−887 (1)	5935 (5)	3.3
O(2)	−810 (4)	220 (1)	4690 (5)	3.1
O(3)	1542 (4)	−610 (1)	5936 (5)	2.8
O(4)	3238 (4)	151 (2)	5852 (5)	3.6
O(5)	2255 (5)	803 (2)	3630 (5)	4.3
N(1)	−56 (5)	−453 (2)	3506 (6)	2.3
N(2)	−644 (5)	−1294 (2)	2513 (6)	3.1
N(3)	2307 (5)	−1167 (2)	3284 (6)	3.0
N(4)	1021 (5)	−1597 (2)	5693 (6)	3.1
C(1)	−1358 (6)	−427 (2)	5945 (7)	3.0
C(2)	−309 (6)	−200 (2)	4942 (7)	2.6
C(3)	1043 (6)	−179 (2)	5811 (6)	2.5
C(4)	2044 (6)	111 (2)	4948 (7)	2.8
C(5)	1427 (7)	551 (2)	4651 (7)	3.1
C(6)	68 (7)	502 (2)	3843 (7)	3.2
C(7)	−1205 (6)	−526 (2)	2414 (8)	3.1
C(8)	−870 (7)	−920 (2)	1442 (8)	3.6
C(9)	−2041 (8)	−1051 (3)	398 (9)	5.3
C(10)	−2873 (9)	−1349 (3)	1470 (14)	7.3
C(11)	−1969 (8)	−1515 (3)	2732 (10)	5.0
C(12)	2794 (7)	−1599 (2)	3740 (9)	3.8
C(13)	2457 (6)	−1681 (2)	5422 (8)	3.5
C(14)	2635 (11)	−2175 (3)	5842 (12)	6.6
C(15)	1302 (11)	−2367 (3)	5942 (14)	7.5
C(16)	338 (8)	−2020 (2)	5426 (10)	5.1
O(M)	6506 (5)	−1211 (2)	6271 (9)	7.2
C(M)	5950 (16)	−1561 (6)	6868 (28)	18.9

[a] Estimated standard deviations are given in parentheses.

Table V. Bond Distances (Å) for Non-Hydrogen Atoms of [Ni(*S*-ampr)(L-sor-*S*-ampr)]Cl$_2$·CH$_3$OH·H$_2$O[a]

Ni–O(1)	2.133 (4)	Ni–O(3)	2.159 (4)
Ni–N(1)	2.085 (5)	Ni–N(2)	2.111 (5)
Ni–N(3)	2.075 (5)	Ni–N(4)	2.062 (5)
O(1)–C(1)	1.438 (8)	O(2)–C(2)	1.403 (7)
O(2)–C(6)	1.429 (8)	O(3)–C(3)	1.425 (7)
O(4)–C(4)	1.422 (7)	O(5)–C(5)	1.427 (8)
N(1)–C(2)	1.475 (8)	N(1)–C(7)	1.492 (8)
N(2)–C(8)	1.488 (9)	N(2)–C(11)	1.496 (10)
N(3)–C(12)	1.469 (9)	N(4)–C(13)	1.471 (8)
N(4)–C(16)	1.487 (9)	C(1)–C(2)	1.520 (9)
C(2)–C(3)	1.537 (8)	C(3)–C(4)	1.528 (9)
C(4)–C(5)	1.510 (9)	C(5)–C(6)	1.527 (9)
C(7)–C(8)	1.509 (10)	C(8)–C(9)	1.522 (10)
C(9)–C(10)	1.539 (13)	C(10)–C(11)	1.495 (13)
C(12)–C(13)	1.496 (10)	C(13)–C(14)	1.574 (12)
C(14)–C(15)	1.455 (15)	C(15)–C(16)	1.504 (13)

[a] Estimated standard deviations are given in parentheses.

solid state are listed in Table III. The absorption spectra of these complexes all show three peaks over the near-infrared and visible regions with comparatively low intensity ($\epsilon < 25$). The absorption maxima are in the range of (10.5 ± 0.3), (17.0 ± 0.2), and (27.9 ± 0.4) × 10^3 cm^{-1} for all complexes, and the peaks are not split apparently in the first absorption region. These facts agree with the reported pseudooctahedral *cis*-(*O*-*O*)-[NiN$_4$O$_2$] complexes,[21] although a small shoulder at ca. 12.7 × 10^3 cm^{-1} is shown in every case. The reflectance spectra of these complexes also have three peaks. Although some differences of wavenumber of peaks between absorption spectra and reflectance spectra (within 600 cm^{-1}) are observed, both spectra in the two states can be regarded as a similar pattern for all complexes. Accordingly these complexes seem to have basically similar structure both in the solid state and in solution.

Crystal and Molecular Structure of [Ni(*S*-ampr)(L-sor-*S*-ampr)]Cl$_2$·CH$_3$OH·H$_2$O. The unit cell consists of four complex cations, eight Cl$^-$ anions, and four methanol and four water molecules of solvation. The locations of the water molecules are found to be disordered to three positions and each of their populations was arbitrarily set at 0.33. In the crystal lattice, complex cations, counterions, and solvated molecules are linked together by hydrogen bond. Intermolecular hydrogen bonds of the type O–H···O probably exist between O(1)···O(M) and O(3)···O(5),

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(21) Martin, J. W. L.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1975**, 87–91.

Table VI. Bond Angles (deg) for Non-Hydrogen Atoms of [Ni(*S*-ampr)(L-sor-*S*-ampr)]$Cl_2 \cdot CH_3OH \cdot H_2O$[a]

O(1)–Ni–O(3)	81.0 (2)	O(1)–Ni–N(1)	79.1 (2)
O(1)–Ni–N(2)	98.5 (2)	O(1)–Ni–N(3)	168.5 (2)
O(1)–Ni–N(4)	93.9 (2)	O(3)–Ni–N(1)	77.6 (2)
O(3)–Ni–N(2)	160.6 (2)	O(3)–Ni–N(3)	88.0 (2)
O(3)–Ni–N(4)	94.2 (2)	N(1)–Ni–N(2)	83.3 (2)
N(1)–Ni–N(3)	101.7 (2)	N(1)–Ni–N(4)	169.8 (2)
N(2)–Ni–N(3)	93.0 (2)	N(2)–Ni–N(4)	105.2 (2)
N(3)–Ni–N(4)	83.7 (2)	Ni–O(1)–C(1)	111.5 (4)
C(2)–O(2)–C(6)	114.9 (5)	Ni–O(3)–C(3)	112.3 (3)
Ni–N(1)–C(2)	102.0 (3)	Ni–N(1)–C(7)	107.4 (4)
C(2)–N(1)–C(7)	117.9 (5)	Ni–N(2)–C(8)	106.4 (4)
Ni–N(2)–C(11)	122.4 (4)	C(8)–N(2)–C(11)	107.3 (5)
Ni–N(3)–C(12)	108.3 (4)	Ni–N(4)–C(13)	107.9 (4)
Ni–N(4)–C(16)	120.7 (5)	C(13)–N(4)–C(16)	105.5 (5)
O(1)–C(1)–C(2)	109.9 (5)	O(2)–C(2)–N(1)	114.9 (5)
O(2)–C(2)–C(1)	105.4 (5)	O(2)–C(2)–C(3)	110.2 (5)
N(1)–C(2)–C(1)	110.0 (5)	N(1)–C(2)–C(3)	105.9 (5)
C(1)–C(2)–C(3)	110.4 (5)	O(3)–C(3)–C(2)	107.5 (5)
O(3)–C(3)–C(4)	110.8 (5)	C(2)–C(3)–C(4)	111.3 (5)
O(4)–C(4)–C(3)	109.5 (5)	O(4)–C(4)–C(5)	110.7 (5)
C(3)–C(4)–C(5)	110.0 (5)	O(5)–C(5)–C(4)	110.8 (5)
O(5)–C(5)–C(6)	106.9 (5)	C(4)–C(5)–C(6)	110.2 (5)
O(2)–C(6)–C(5)	112.0 (5)	N(1)–C(7)–C(8)	107.1 (5)
N(2)–C(8)–C(7)	108.7 (5)	N(2)–C(8)–C(9)	105.7 (6)
C(7)–C(8)–C(9)	111.4 (6)	C(8)–C(9)–C(10)	102.9 (7)
C(9)–C(10)–C(11)	108.0 (7)	N(2)–C(11)–C(10)	106.5 (7)
N(3)–C(12)–C(13)	109.5 (6)	N(4)–C(13)–C(12)	109.8 (6)
N(4)–C(13)–C(14)	104.1 (6)	C(12)–C(13)–C(14)	110.9 (6)
C(13)–C(14)–C(15)	107.7 (8)	C(14)–C(15)–C(16)	106.0 (7)
N(4)–C(16)–C(15)	106.7 (7)		

[a] Estimated standard deviations are given in parentheses.

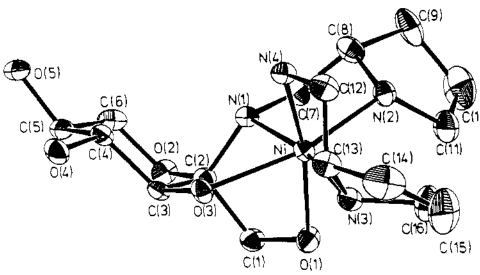

Figure 3. Perspective drawing of the complex cation [Ni(*S*-ampr)(L-sor-*S*-ampr)]$^{2+}$.

at a distance of 2.577 (7) and 2.658 (6) Å, respectively. Hydrogen bonds of the type O-H⋯Cl and N-H⋯O are also possible for Cl(1)⋯O(4) (3.093 (5) Å), Cl(2)⋯O(5) (2.979 (5) Å), and N(1)⋯O(4) (3.045 (6) Å).

The fractional coordinates, bond distances, and bond angles of non-hydrogen atoms are listed in Tables IV–VI, respectively. The ORTEP drawing of the complex cation is given in Figure 3. The nickel atom is coordinated with a bidentate *S*-ampr ligand and a tetradentate L-sor-*S*-ampr ligand. The coordination structure of this complex is found to be essentially equivalent to those of complexes **1** and **2**. The glycosylamine ligand (L-sor-*S*-ampr) attaches to the nickel atom through the two hydroxyl groups on C(1) and C(3) of the L-sorbose moiety and through the two nitrogen atoms of the diamine residue. The anomer carbon atom connects to the primary nitrogen atom of the 2(*S*)-(aminomethyl)pyrrolidine. The absolute configuration of this glycosidic nitrogen atom is *S*. The L-sorbose moiety forms the usual α-$^2C_5$ pyranose ring, which is known to be the most stable form in the solution,[22] and this anomeric form is equivalent to the case of complexes **1** and **2**. In all three crystal structures, the absolute configuration of each complex is Δ, which is defined by the two diamine chelates. The five-membered chelate rings of both diamine residues (in the bidentate and tetradentate ligands) adopt the symmetrical δ gauche conformation. On the other hand, the conformations of the other five-membered chelate rings in the sugar moiety (Ni–O(1)–C(1)–C(2)–N(1) and Ni–O(3)–C(3)–C(2)–N(1)) are fairly distorted, as shown in Figure 4. These conformations are very close to those of complex **2** (see ref 5b, Figure 4). The absolute configuration of the chiral nitrogen atoms in the pyrrolidine ring is *S*. The carbon atoms C(9), C(10), C(14), and C(15) in the pyrrolidine ring have large anisotropic thermal parameters. This fact suggests that pseudorotation of rings occurs. These coordination phenomena of pyrrolidine ligand are similar to those of the previously reported case.[23] The average value of the nickel–nitrogen bond length is 2.08 Å, they are normal values similar to those of complexes **1** and **2**. The coordination geometry around the nickel atom is fairly distorted from octahedral symmetry with cis A–Ni–B angles ranging from 77.6 to 94.2°. The least trans angle is 160.6°. This tendency of distortion from octahedron is also similar to that in complexes **1** and **2**.

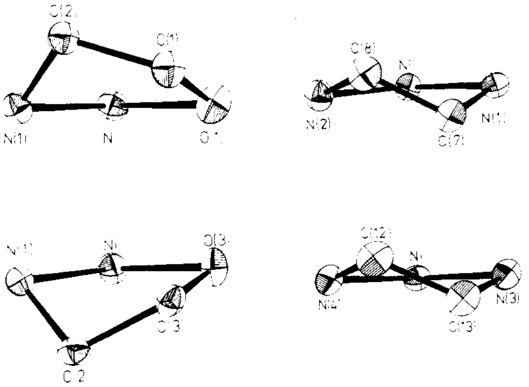

Figure 4. Perspective drawings of chelate rings.

Coordination Structure and CD Pattern of Ketose Complexes. The three crystal structures of the nickel(II) complexes of D-fru-en, L-sor-en, and L-sor-*S*-ampr showed that the coordination geometries are very similar; they have the same (*S*) anomeric configuration, (*S*) of the glycosidic nitrogen atoms, and (Δ) configuration around the nickel atom. From these results some important conclusions could be drawn. The conformation of the chelate ring involving the sugar pyranose ring will depend on the orientation of the hydroxyl group on the C(3) atom of the sugar residue, and this will force the absolute configuration around the glycosidic nitrogen atom and the orientation of the hydroxymethyl group on the anomeric carbon atom (this decides the overall configuration of the complexes) and will influence the chelate conformation of the diamine part of the glycosylamine. Thus, the absolute configuration around the C(3) atom of ketoses would be very important to govern the coordination geometry of the glycosylamine derived from ketoses. Consequently the coordination structures of the glycosylamines derived from D-fru, L-sor, and D-tag, which have the same *S* C(3) configuration, are expected to be similar each other (Figure 5a–c), and a glycosylamine from D-psi, which is the C(3) epimer of D-fructose, would form the enantiomeric Λ structure as shown in Figure 5d. These structural features are evident in the CD curves of the complexes.

The CD spectra of the ketosylamine complexes are shown in Figure 2. In the octahedral approximation, only the lowest energy d–d transition $^3A_{2g} \rightarrow {}^3T_{2g}$ is magnetic dipole allowed for d^8 metal complexes. Therefore, it is ordinarily seen in the pseudooctahedral nickel(II) complexes that the CD intensity in the higher energy d–d transition region ((15–30) × 10^3 cm^{-1}) is significantly weaker than that of the lowest transition region ((10–15) × 10^3 cm^{-1}).[24] However in the case of the present ketose–diamine complexes, where the diamine part is en, pn, or tn, the CD intensity over the three d–d transition regions is comparable. Since these complexes

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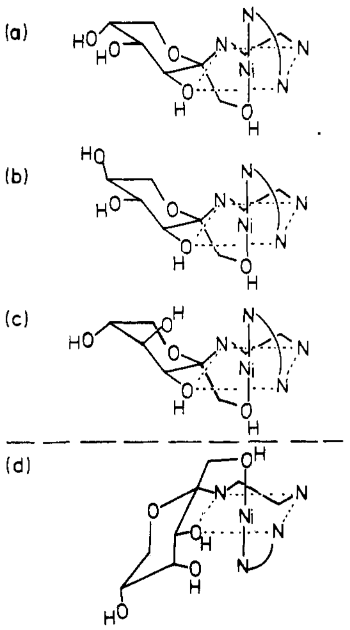

Figure 5. Structures of ketose-diamine complexes derived from (a) D-fructose, (b) L-sorbose, (c) D-tagatose, and (d) D-psicose.

are fairly distorted from the octahedron, as shown by X-ray crystallography, it seemed that the two higher energy transitions would be magnetic dipole allowed due to the reduction in symmetry from O_h.[25]

It is often observed that the CD signs of the d–d absorption bands are influenced too much by stereochemical features of dissymmetric nickel(II) complexes. The complexes containing D-fru, L-sor, or D-tag moieties, in which each C(3) atom has the same *S* configuration, show the different CD spectra in the first absorption region, but their CD spectra are nearly identical with each other over the second and third absorption regions (Figure 2). For the complex containing a D-psi residue, whose absolute configuration around the C(3) atom is *R*, the CD pattern in the second and third absorption regions is opposite in sign from those observed for the D-fru, L-sor, or D-tag complexes. This reversal of sign can be attributed to the configurational effect of the glycosylamine complexes as was discussed above on the basis of the three crystal structures. Therefore, the results obtained indicate that the coordination structure of the glycosylamine ligands derived from a ketose and a diamine significantly contributes to the CD signs over the second and third absorption regions.

It is generally accepted that *S*- and *R*-pn chelate rings will take the δ and λ gauche conformation with an equatorially oriented methyl group, respectively, in solution.[26] However these complexes containing *R*-pn and those having *S*-pn showed similar CD curves in the second absorption region and slightly different patterns in the third absorption region. These observations suggest that the *R*-pn chelate ring of the glycosylamine ligands takes the unpreferred δ gauche conformation with an axial *C*-methyl group. This is consistent with the above structural arguments where the steric requirements of the D-fru or L-sor residues would force the δ gauche conformation on the diamine moiety of the glycosylamine.

In these ketose–diamine complexes, it is noteworthy that when the diamine is *S*-pn the CD sign in the first absorption region is (+), when the diamine is *R*-pn the CD sign is (−), and when the diamine is *S*-ampr CD the intensity is large (+) in that region, although they have the similar Δ absolute configuration. These observations indicate that some structural differences, except the overall configuration of the complexes, significantly contribute to the CD curves in the lowest absorption region in these ketose–diamine complex systems.

Conclusion. The Structure of Ketose–Diamine Complexes and Their CD Spectra. The coordination structures of these glycosylamine complexes derived from nickel(II) diamine complexes and ketoses are dependent on the configuration of the C(3) atom of the ketoses. When the configuration is *S* (D-fructose, L-sorbose, D-tagatose), the absolute configuration of these complex is Δ, which is defined by the two diamine residues. Inversely, when the configuration of C(3) is *R* (D-psicose), the coordination geometry is supposed to be a mirror image of the former complexes, and the absolute configuration is Λ. In these ketose–diamine nickel complex system, it was found that the overall configuration of these complexes affect the CD spectra in the second and third absorption regions. The pattern of the CD curves in the first absorption region is swayed by the seemingly small chiral effects except in the overall configurational effect.

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Registry No. **1**, 76243-66-8; **2**, 85954-73-0; **3**, 97749-36-5; **4**, 97806-13-8; **6**, 97749-38-7; **7**, 97806-14-9; **8**, 97858-55-4; **9**, 88658-43-9; en, 107-15-3; tn, 109-76-2; *S*-pn, 15967-72-3; *R*-pn, 6852-78-4; *S*-ampr, 69500-64-7; $[\mathrm{Ni(en)(D\text{-}tag\text{-}en)}]^{2+}$, 97858-56-5; $[\mathrm{Ni(en)(D\text{-}psi\text{-}en)}]^{2+}$, 97858-37-2; $[\mathrm{Ni}(S\text{-ampr})_3]\mathrm{Cl}_2$, 97732-31-5; $[\mathrm{Ni}(S\text{-ampr})_3]\mathrm{Br}_2$, 97732-32-6; $[\mathrm{Ni(en)}_3]\mathrm{Cl}_2$, 13408-70-3; $[\mathrm{Ni(tn)}_3]\mathrm{Cl}_2$, 20577-76-8; $[\mathrm{Ni(pn)}_3]\mathrm{Cl}_2$, 39494-22-9.

Supplementary Material Available: Lists of atomic parameters of hydrogen and water atoms, anisotropic thermal parameters, and observed and calculated structure factors and a stereoview of the crystal lattice (15 pages). Ordering information is given on any current masthead page.

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(25) Since these complexes actually have C_1 symmetry, all electronic states belong to the "A" representation. In this condition, all transitions are magnetically allowed.

(26) (a) Yano, S.; Ito, H.; Koike, Y.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3184–89. (b) Yano, S.; Tukada, T.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1978**, *17*, 2520–26.