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Reactions of Metal Complexes with Carbohydrates. Synthesis and Structure of (2-[(2-Aminoethyl)amino]-2-deoxy-L-sorbose)(ethylenediamine)-nickel(II) Dichloride Hemi Methanol Solvate: [Ni(en)(L-sor-en)]$Cl_2 \cdot 1/2CH_3OH$ (en=ethylenediamine and sor=sorbose)

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The synthesis and crystal structure of the complex [Ni(en)(L-sor-en)]$Cl_2 \cdot 1/2CH_3OH$ which was derived from the reaction of tris(ethylenediamine)nickel(II) dichloride dihydrate with L-sorbose are described. Crystallographic details for the complex are follows: space group C2 (monoclinic); a=17.862(2) Å, b=8.212(1) Å, c=12.644(2) Å, β=90.89(1)°; Z=4; D_{calcd}=1.53 gcm^{-3}. The structure was solved by heavy atom methods, and the structure parameters including almost all hydrogen atoms were refined by least-squares methods. The final R factor was 0.032 for 2680 independent reflections. The nickel atom is octahedrally coordinated with a bidentate ethylenediamine and a tetradentate glycosylamine ligand of L-sor-en. L-Sorbose moiety adopts the six-membered α-$^2C_5$ chair conformation. In addition to the synthesis and structure of this complex, we report the results of absorption and circular dichroism spectroscopy.

Carbohydrates have long been known to form complexes with metal ions. The interactions between metal and carbohydrates in solution have been much studied; by potentiometric titration,[1] electrophoresis,[2] circular dichroism,[3] NMR spectroscopy,[4] ESR spectroscopy,[5] and chromatography,[6] *etc.* There are many complexes of alkaline earth metals with carbohydrates, some of which were analyzed by X-ray crystallography,[7] however only a few transition metal complexes, which were confirmed to have sugar chelates, have been reported.[8]

Recently the structure of both complexes [Ni(en)(D-fru-en)]$CL_2 \cdot CH_3OH$[9] (**1**) and [Ni(L-rham-tn)$_2$]$Br_2 \cdot 2H_2O \cdot CH_3OH$[10] (en=ethylenediamine, D-fru-en=2-[(2-aminoethyl)amino]-2-deoxy-D-fructose, tn=trimethylenediamine, L-rham=tn=1-[(3-aminopropyl)amino]-1-deoxy-L-rhamnose) was determined by X-ray crystallography. The crystal structure of complex **1** suggested that an N-glycoside derived from a ketose and a diamine coordinates to the nickel atom through the two oxygen atoms of the hydroxyl groups on C-1 and C-3 of the sugar moiety and through the two nitrogen atoms of the diamine. It also indicated that the coordination structure of a ketose will depend on the orientation of the C-3 hydroxyl group and this makes a significant contribution to the circular dichroism.

In the course of our study to clarify the interactions between transition metals and carbohydrates,[9,10] we have prepared and characterized a new nickel(II) complex containing an N-glycoside which was derived from the reaction of tris(ethylenediamine)nickel(II) ion with L-sorbose. Since L-sorbose is C-5 epimer of D-fructose, the absolute configurations around other asymmetric carbon atoms are the same as those of D-fructose in the pyranose form (Fig. 1). Consequently the coordination behaviour of N-glycosides derived from L-sorbose, and the circular dichroism of their complexes are expected to be similar to those for complexes of D-fructose. However, the CD curves of the complexes are different, as is shown later in this report. To clarify the stereochemistry of this complex, we have undertaken a crystal and molecular structure determination. A preliminary account of this work has already appeared.[11]

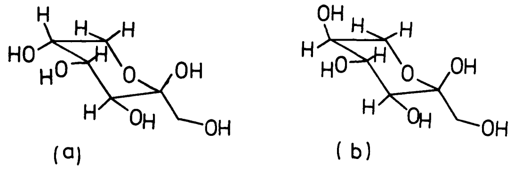

Fig. 1. The structure of ketohexoses in the pyranose form: (a) α-L-sorbose and (b) β-D-fructose.

Experimental

All materials were reagent grade. L-Sorbose was purchased from Tokyo Kasei Co., [Ni(en)$_3$]$Cl_2 \cdot 2H_2O$[12] was prepared by the ordinary method.

Preparation of [Ni(en)(L-sor-en)]$Cl_2 \cdot 1/2CH_3OH$ (2)

This complex was prepared from tris(ethylenediamine)-nickel(II) complex and L-sorbose by a similar method described previously[9] with slight modifications, as follows. To a solution of 8.8 mmol [Ni(en)$_3$]$Cl_2 \cdot H_2O$ in 80 mL of methanol was added 17.6 mmol of L-sorbose and 8.8 mmol of NH_4Cl, and heated to reflux for 1 h. The color of the solution changed from violet to blue. Then it was concentrated to about 30 mL by a rotary evaporator and poured on to a column of Sephadex LH-20 gel (4 cm×90 cm), and the material was eluted with methanol. The colored material was separated into violet, blue, yellow, and orange bands. The blue fractions were collected and concentrated to about 15 mL and kept at 5 °C. Blue crystals (520 mg) were obtained, they were recrystallized from a minimum amount of hot methanol. Found: Ni, 14.3; C, 29.19; H, 6.86; N, 13.36; Cl, 16.56; Calcd. for $C_{10.5}H_{28}N_4O_{5.5}Cl_2Ni$: Ni, 13.7; C, 29.46;

H, 6.61; N, 13.09; Cl, 16.56.

Measurements Visible and near infrared absorption spectra were measured with a Hitachi model 340 recording spectrophotometer. Reflectance spectra were recorded on this instrument equipped with a reflectance attachment. Circular dichroism spectra were recorded on a Jasco J-500 recording spectropolarimeter. Magnetic susceptibility was measured at room temperature using a Shimadzu MB-100 magnetic balance (Faraday method). Diamagnetic corrections were calculated from Pascal's constants.[13]

Crystal Data and Intensity Data Collection of [Ni(en)(L-sor-en)]Cl₂·1/2CH₃OH. A block-shaped blue crystal (0.56×0.50×0.35 mm), which was coated with epoxy cement, was used to collect diffraction data on a Rigaku AFC-5 four-circle automated diffractometer controlled by a Facom U-100 computer and the Rigaku FOS program system, equipped with Mo $K\alpha$ radiation (λ=0.71073 Å). The accurate unit cell dimentions were determined by least-squares methods from θ values for 40 reflections in the range of 25°—31° measured on the diffractometer. Crystal data are as follows.

[Ni(en)(L-sor-en)]Cl_2·1/2CH_3OH, $C_{10.5}H_{28}N_4O_{5.5}Cl_2Ni$, M.W.=428.02, Monoclinic, space group C2, a=17.862(2), b=8.212(1), c=12.644(2) Å, β=90.89(1)°, D(obsd)=1.55 g cm^{-3} (by flotation in 1,2-dichloroethane and 1,2-dibromoethane mixture), D(calcd)=1.53 g cm^{-3}, Z=4.

Intensity data were collected by θ-2θ method ($2\theta \leqq 60°$), scan speed=3°/min, scan width=(1.2+tanθ)°. Backgrounds were measured both at the beginning and the end of the scan, each for half time of the scan. Three standard reflections were monitored for every fifty reflections, and no significant changes were found. Of the 2997 reflections collected, 2680 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used in the structure analysis. The intensity data were corrected for standard Lorentz-polarization effects. An absorption correction with a numerical integration procedure was applied; μ=13.92 cm^{-1} (Mo $K\alpha$).

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 computing program UNICS-III.[14] The initial coordinates of the nickel atom were determined by a three dimensional Patterson synthesis. The positions and isotropic temperature factors of other nonhydrogen atoms were determined by means of mutual cycles of Fourier synthesis and block-diagonal least squares refinement. Atomic scattering factors were taken from Ref. 15. A methanol molecule was found to be located close to a special position on the twofold axis. A weighting scheme $1/w=\sigma_{\text{count}}^2+(0.015|F_o|)^2$ was employed and anomalous scattering factors[16] for non hydrogen atoms were introduced in F_c. Least-squares refinement of the atomic parameters with isotropic temperature factors of the nonhydrogen atoms gave convergence at R=10.16%. ($R=\sum||F_o|-|F_c||/\sum|F_o|$). The absolute configuration of this complex was determined from the known configuration of L-sorbose. When the f'' values of Ni, Cl, O, N, and C atoms were reversed in sign to test the structure, the convergence was reached to R=10.34%. At this stage, anisotropic temperature factors were introduced for all nonhydrogen atoms. Difference Fourier synthesis made clear the locations of all hydrogen atoms of the complex cation except for H(C9)1, the coordinates of this H(C9)1 were calculated by assuming a tetrahedral coordination with C–H bond distance of 1.08 Å. The positional parameters and isotropic temperature factors of all hydrogen atoms are also refined. The final R factor was 0.032, and R_w was 0.042 (R_w=$[\sum w(|F_o|-|F_c|)^2/\sum w\cdot|F_o|^2]^{1/2}$). The final difference Fourier synthesis revealed no unusual features with the highest peak being 0.71 Å^{-3}. The anisotropic thermal parameters and complete list of the $|F_o|$ and $|F_c|$ values have been preserved by the Chemical Society of Japan (Document No. 8425).

Results and Discussion

Synthesis. The reaction of L-sorbose with [Ni(en)$_3$]Cl_2·H_2O was studied and the new complex containing glycosylamine ligand (L-sor-en) was isolated. The method of preparation was almost the same as described previously to prepare the glycosylamine complex containing another monosaccharides.[9] When tris diamine nickel(II) complex and L-sorbose are refluxed in methanol, the solution becomes blue. This solution is separated into four bands by gel permeation chromatography. The first violet band consists of the starting nickel-diamine complex, the second blue band contains glycosylamine complex, and the contents of the third and the fourth fractions (yellow and orange) are not clear. Blue crystals are obtained from blue fractions. When NH_4Cl is not added to the reactant, more reaction time is necessary and about half of the yield of glycosylamine complex is obtained. Consequently NH_4Cl appears to act as a general acid base catalyst similar to the formation of glycosylamine without metal.[17] Analytical data indicated that this complex has a glycosylamine and a diamine similar to [Ni(en)(D-fru-en)]Cl_2·CH_3OH.[9] This complex is soluble in methanol and water, but it decomposes in a few days in water.

Magnetic Moments and Absorption Spectra. Magnetic moments and absorption spectra were measured to investigate the coordination geometry of the nickel complex. The effective magnetic moment at room temperature of this complex **2** is 3.17 μ_B, which is normal for octahedral nickel(II) complexes.[18] Near-infrared and visible absorption spectra and CD spectra of this complex together with complex **1** in methanolic solution are given in Fig. 2. Table 1 lists their spectral data. Both of these absorption spectra possess three peaks in the near-infrared and visible region

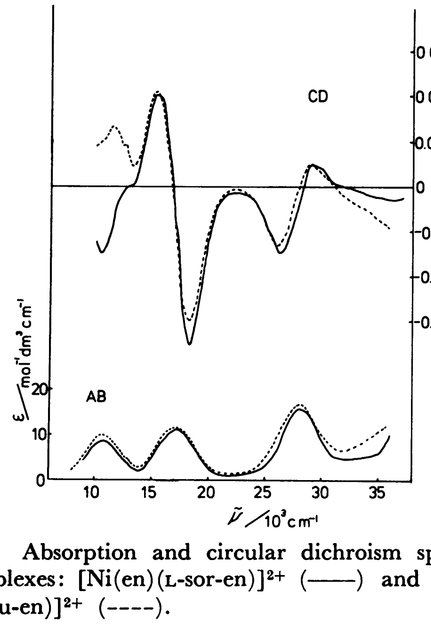

Fig. 2. Absorption and circular dichroism spectra of complexes: [Ni(en)(L-sor-en)]$^{2+}$ (——) and [Ni(en)(D-fru-en)]$^{2+}$ (----).

Table 1. Absorption, circular dichroism, and reflectance spectral data of complex [Ni(en)(L-sor-en)]$Cl_2 \cdot 1/2CH_3OH$

Abs. max.[a)] 10^3 cm^{-1}	ε dm^3 mol^{-1} cm^{-1}	CD. max.[a)] 10^3 cm^{-1}	Δε 10^{-2} dm^3 mol^{-1} cm^{-1}	Ref. max. 10^3 cm^{-1}
10.7	8.7	10.4	−3.14	10.6
12.8^{sh}	3.8			
17.2	11.1	15.3	+4.16	17.5
		18.3	−7.02	
28.0	15.8	26.2	−2.89	27.7
		29.2	+1.02	

a) Absorption and circular dichroism spectra were recorded in methanol solution.

Table 2. Atomic parameters and estimated standard deviations for non-hydrogen atoms

Atom	x[a)]	y[a)]	z[a)]	B_{eq}[b)]
Ni	8012(1)	5000(0)	2232(1)	2.6
Cl(1)	6958(1)	4822(2)	−985(1)	4.6
Cl(2)	6191(1)	1661(2)	3697(1)	6.0
O(1)	9037(1)	5970(3)	2857(2)	3.7
O(2)	9708(1)	1939(3)	3364(2)	3.7
O(3)	7895(1)	3880(3)	3729(2)	2.8
O(4)	7666(1)	851(4)	4793(2)	3.7
O(5)	8686(2)	−1706(3)	4203(2)	4.2
N(1)	8772(1)	3041(4)	2131(2)	2.7
N(2)	8362(2)	5545(4)	722(2)	4.0
N(3)	7395(2)	7023(4)	2626(2)	3.7
N(4)	6980(2)	4059(5)	1761(2)	3.9
C(1)	9491(2)	4740(5)	3368(3)	3.8
C(2)	9121(2)	3077(4)	3187(3)	2.9
C(3)	8491(2)	2799(4)	4001(2)	2.5
C(4)	8225(2)	1050(4)	3999(2)	2.7
C(5)	8895(2)	−35(6)	4235(2)	3.2
C(6)	9474(2)	264(5)	3383(3)	3.5
C(7)	9262(2)	3364(6)	1216(3)	4.2
C(8)	8788(3)	4097(7)	342(3)	4.9
C(9)	6596(3)	6603(9)	2590(5)	6.7
C(10)	6425(3)	5349(10)	1838(6)	7.9
C(M)	5000(0)	3234(23)	0(0)	14.7
O(M)	5190(15)	4076(53)	−366(19)	28.7

a) Positional parameters are multiplied by 10^4. b) Thermal parameters are given by the equivalent temperature factors.

Table 3. Bond distances and their estimated standard deviations for non-hydrogen atoms

Atom A	Atom B	Distances l/Å	Atom A	Atom B	Distances l/Å
Ni	-O(1)	2.137(3)	Ni	-O(3)	2.118(2)
Ni	-N(1)	2.109(3)	Ni	-N(2)	2.068(3)
Ni	-N(3)	2.059(3)	Ni	-N(4)	2.078(3)
O(1)	-C(1)	1.441(5)	O(3)	-C(3)	1.425(4)
O(4)	-C(4)	1.436(4)	O(5)	-C(5)	1.422(5)
O(2)	-C(2)	1.419(4)	O(2)	-C(6)	1.438(5)
N(1)	-C(2)	1.466(4)	N(1)	-C(7)	1.485(5)
N(2)	-C(8)	1.496(6)	N(3)	-C(9)	1.470(6)
N(4)	-C(10)	1.456(8)	C(1)	-C(2)	1.532(5)
C(2)	-C(3)	1.553(4)	C(3)	-C(4)	1.513(5)
C(4)	-C(5)	1.519(5)	C(5)	-C(6)	1.524(5)
C(7)	-C(8)	1.507(6)	C(9)	-C(10)	1.431(10)
O(M)	-C(M)	0.902(40)			

and the molar absorption coefficient of these peaks are comparatively small. These spectral features are typical for octahedral nickel(II) complexes.[19)] The $10D_q$ value of complex **2**, which is equal to the energy of the first absorption peak in the case of d^8 octahedral complex, is 10.7 kcm^{-1}, that is normal for N_4O_2 nickel(II) octahedral complex.[19)] The absorption spectra of the complexes **1** and **2** are almost identical, so it is deduced that these complexes have similar ligand fields around the nickel atoms.

Crystal and Molecular Structure of [Ni(en)(L-sor-en)]-$Cl_2 \cdot 1/2CH_3OH$. Since this structure analysis yielded a high degree of convergence of parameters for a sugar-containing complex (R=0.032), the coordinates of all atoms including hydrogen atoms of the complex cation were determined. The final atomic coordinates, bond distances, and bond angles are listed in Tables 2, 3, and 4, respectively.

Fig. 3 shows an ORTEP drawing[20)] of the complex cation [Ni(en)(L-sor-en)]$^{2+}$. The nickel atom is coordinated with four nitrogen atoms and two oxygen atoms. The coordination geometry of this complex resembles that of the D-fructose complex **1**. The nickel atom is coordinated with a tetradentate glycosylamine (L-sor-en) and a bidentate diamine (en).

The glycosylamine coordinates to the nickel atom at four points through the two hydroxyl groups on carbon 1, and carbon 3 of the sugar moiety, and the two nitrogen atoms of the ethylenediamine residue. In the glycosylamine, L-sorbose moiety has the usual α-$^2C_5$ pyranose form. This form is the most stable in the solution of L-sorbose alone,[21)] and it is known that crystalline α-L-sorbose also takes this form.[22)] This anomeric structure is equivalent to the case of the D-fru-en complex **1**, although the nomenclature of the anomeric form in the complex **1** is β because the nomenclature of the anomeric form is reversed whether the absolute configuration of the ketose is D or L. In the tetradentate glycosylamine ligand, five membered chelate ring of the ethylenediamine moiety adopts a symmetrical gauche conformation, but other five membered chelates (Ni-N(1)-C(2)-C(3)-O(3)) and

Table 4. Bond angles and their estimated standard deviations for non-hydrogen atoms

Atom B	Atom A	Atom C	Angle $\phi/°$	Atom B	Atom A	Atom C	Angle $\phi/°$
O(1)	-Ni	-O(3)	85.9(1)	O(1)	-Ni	-N(1)	76.1(1)
O(1)	-Ni	-N(2)	89.5(1)	O(1)	-Ni	-N(3)	93.9(1)
O(1)	-Ni	-N(4)	174.9(1)	O(3)	-Ni	-N(1)	78.2(1)
O(3)	-Ni	-N(2)	162.8(1)	O(3)	-Ni	-N(3)	94.2(1)
O(3)	-Ni	-N(4)	89.7(1)	N(1)	-Ni	-N(2)	84.6(1)
N(1)	-Ni	-N(3)	167.7(1)	N(1)	-Ni	-N(4)	105.5(1)
N(2)	-Ni	-N(3)	102.7(1)	N(2)	-Ni	-N(4)	95.5(1)
N(3)	-Ni	-N(4)	83.9(1)	Ni	-O(1)	-C(1)	112.1(2)
Ni	-O(3)	-C(3)	113.7(2)	C(2)	-O(2)	-C(6)	114.8(2)
Ni	-N(1)	-C(2)	101.2(2)	Ni	-N(1)	-C(7)	107.4(2)
C(2)	-N(1)	-C(7)	117.3(3)	Ni	-N(2)	-C(8)	106.7(3)
Ni	-N(3)	-C(9)	109.1(3)	Ni	-N(4)	-C(10)	108.2(3)
O(1)	-C(1)	-C(2)	108.7(3)	O(2)	-C(2)	-N(1)	115.7(3)
O(2)	-C(2)	-C(1)	104.4(2)	O(2)	-C(2)	-C(3)	109.9(3)
N(1)	-C(2)	-C(1)	109.3(3)	N(1)	-C(2)	-C(3)	107.3(2)
C(1)	-C(2)	-C(3)	110.3(3)	O(3)	-C(3)	-C(2)	107.2(2)
O(3)	-C(3)	-C(4)	110.9(2)	C(2)	-C(3)	-C(4)	111.7(3)
O(4)	-C(4)	-C(3)	109.2(3)	O(4)	-C(4)	-C(5)	110.5(3)
C(3)	-C(4)	-C(5)	108.1(3)	O(5)	-C(5)	-C(4)	110.8(3)
O(5)	-C(5)	-C(6)	108.4(3)	C(4)	-C(5)	-C(6)	108.0(3)
O(2)	-C(6)	-C(5)	111.5(3)	N(1)	-C(7)	-C(8)	108.2(3)
N(2)	-C(8)	-C(7)	111.4(3)	N(3)	-C(9)	-C(10)	112.8(5)
N(4)	-C(10)	-C(9)	115.5(4)				

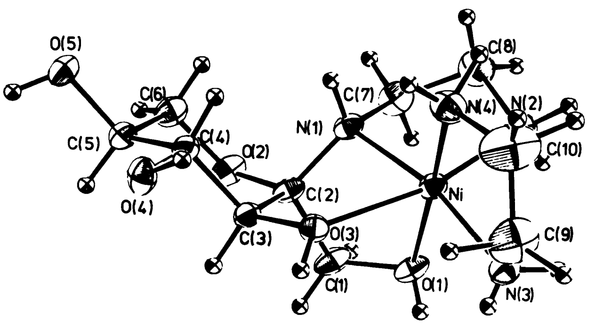

Fig. 3. A perspective drawing of the complex cation $[Ni(en)(L\text{-}sor\text{-}en)]^{2+}$.

(Ni-N(1)-C(2)-C(1)-O(1)) are in the asymmetrical ones. The absolute configuration of the secondary nitrogen atom is *S*. These structural features around the nickel atom are common to complex **1** and **2**. The bidentate ethylenediamine chelate has the δ-gauche conformation (Fig. 4), although the corresponding ethylenediamine chelate ring of the complex **1** has the λ-gauche conformation. This is the most conspicuous difference of the structure around the nickel atom between complex **1** and **2**.

The coordination geometry around the nickel atom of the complex **2** is distorted octahedral symmetry. The least cis angle around the nickel atom is 76.1° (O(1)-Ni-N(1)), and the largest cis angle is 105.5° (N(1)-Ni-N(4)). Furthermore, the least trans angle around the nickel atom is 162.8° (Table 4). This tendency for distortion from an octahedron is similar to the case of complex **1**. The bite angle of the five membered chelate rings are smaller than ninety degrees, and they are normal.[24] The conformation of L-sorbose moiety is the typical chair form. The angles of C–C–C and C–O–C in the pyranose ring are within 110°±2.1° similar to α-L-sorbose crystals.[22]

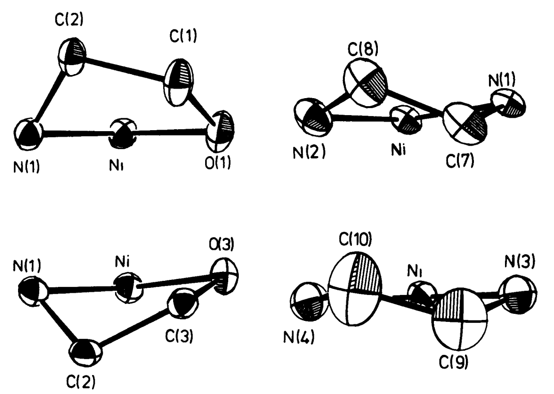

Fig. 4. Perspective drawings of the chelate rings.

The average nickel-nitrogen bond distance of 2.08 Å is very close to that in the complex **1** (2.07 Å), and they are normal values in comparison with the reported nickel-nitrogen bond distances. The average nickel-oxygen bond distance of 2.13 Å is slightly shorter than that in the complex **1** (2.17 Å), however these values are considerably longer compared with the reported nickel-oxygen distances of carboxylate complexes.[23] These results show that the coordinate bond between the nickel and the hydroxyl groups is comparatively weak. In this structure analysis the coordinates of all hydrogen atoms of the complex cation were refined by least squares methods. The average oxygen-hydrogen bond distance of the coordinated hydroxyl groups is 0.76(4) Å, which is shorter than that of free hydroxyl groups (0.88(4) Å). The average angle around the coordinated oxygen atoms is 114(2)°. As mentioned above, the coordination structure of the hydroxyl groups to the nickel ion is revealed. This is one of the important results of this structure analysis, since the orientation of hydroxyl groups can not be estimated by geometric considerations. This is a rare sample to clarify the coordination geometry of hydroxyl groups to the nickel ion.

The unit cell contains four complex cations, eight Cl^- anions and two methanol molecules of solvation. The carbon atom of this methanol molecule is located at a special position on the twofold axis, so that the oxygen atom of this methanol is disordered to two positions, each of which has a population of 0.5. The stereoview of the unit cell is shown in Fig. 5. Hydrogen bonds of the type O-H···Cl and N-H···Cl probably exist between O(4)···Cl(2), O(5)···Cl(2), N(1)···Cl(1), and N(3)···Cl(1). Since the interatomic distance of O(3)···O(4) between two molecules is short (2.68 Å), they are probably linked by hydrogen bonding. The hydrogen bonding distances are listed in Table 5.

Circular Dichroism. In the octahedral ligand field, only the lowest energy transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$ is magnetic dipole allowed in the case of nickel(II) com-

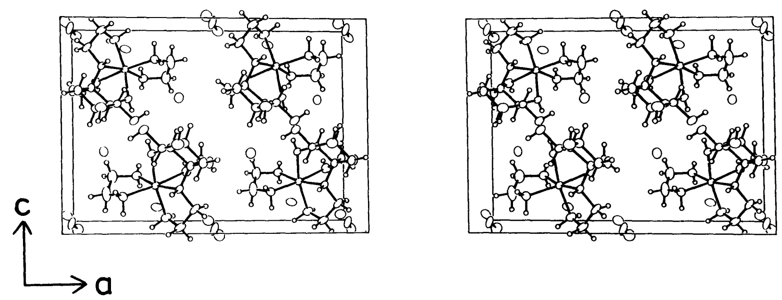

Fig. 5. A stereo view of the unit cell.

TABLE 5. INTERATOMIC DISTANCES<3.5 Å OUTSIDE THE COMPLEX CATION AND ESTIMATED STANDARD DEVIATIONS: A-H···B

Atom A	Atom B	A-H Distance l/Å	A···B Distance l/Å	Symmetry of Atom B
O(4)	Cl(2)	0.90(5)	3.032(2)	x, y, z
O(5)	Cl(2)	0.86(3)	2.980(3)	$1.5-x$, $-0.5+y$, $1-z$
O(3)	O(4)	0.90(5)	2.678(4)	$1.5-x$, $0.5+y$, $1-z$
N(3)	Cl(1)	0.88(4)	3.275(3)	$1.5-x$, $-0.5+y$, $1-z$
N(3)	Cl(1)	0.93(5)	3.316(3)	$1.5-x$, $-0.5+y$, $1-z$

plex. The two higher energy spin allowed transitions are magnetic dipole forbidden and are expected for CD bands significantly weaker than the allowed transitions. It is often observed that the CD pattern of the first transition band is too much influenced by stereochemical features of dissymmetric nickel(II) complexes.[25] The CD spectra of $[Ni(en)(D\text{-fru-en})]^{2+}$ and $[Ni(en)(L\text{-sor-en})]^{2+}$ in methanol are shown in Fig. 2. They have CD curves of opposite sign in the first absorption region. The X-ray crystal structure analysis for both the complexes revealed that the structure of the two complex cations are similar except for the orientation of each C-5 atom and the conformation of each bidentate ethylenediamine. In this case the contributions of these stereochemical differences mentioned above can be ruled out, since each C-5 atom is far from the central metal atom to effect the circular dichroism in the d-d bands, and an ethylenediamine chelate makes a rapid interconversion between δ and λ in solution. Therefore it is an unusual fact that the CD curves of the complexes are dissimilar. On the other hand it is interesting to note that their CD spectra are nearly identical in the second and third absorption region. These results indicate that detailed stereochemical examinations using many kinds of diamines and ketoses are necessary to establish the relationships between the structure of the complexes and their CD spectra.

The results obtained in this study revealed that L-sorbose reacts with $[Ni(en)_3]^{2+}$ to yield the octahedral nickel(II) complex which is surrounded with a bidentate ethylenediamine and a tetradentate *N*-glycoside. The X-ray crystallographic study of this complex revealed the coordination structures of hydroxyl groups to the nickel atom. The results of the crystal structure of $[Ni(en)(D\text{-fru-en})]Cl_2\cdot CH_3OH$[9] and $[Ni(en)(L\text{-sor-en})]Cl_2\cdot 1/2CH_3OH$ confirmed that the coordination geometry of these complexes is almost the same, and that the coordination pattern of an *N*-glycoside ligand derived from a ketose and a diamine depends on the orientation of the C-3 hydroxyl groups of the sugar. Unusual features were observed in the CD spectra of these complexes.

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