YCl_3–Y_2O_3 mixture in the reactants provides *only* the 3R-M_xY-ClO phase,[5,17] clearly via a simple interconversion along the lines suggested by Beck.

The present experiments also show that the polymorphism can be backed off significantly to lighter rare-earth elements by synthesis at lower temperatures, giving HoOCl in both the YOF and SmSI forms and YOCl as the YOF type. The last is not surprising when it is noted that the Y^{3+} and Ho^{3+} crystal radii are virtually identical for a variety of coordination numbers.[18] The cell volume of YOCl is slightly greater than that of HoOCl in the PbFCl form and smaller in the YOF version (Table IV).

The expanded list of polymorphs now known for the heavier lanthanides and yttrium is as follows, where bold-faced type represents the stable forms obtained by more traditional high-temperature methods, and italics, those found in the present work.

Dy	Y	Ho	Er	Tm	Yb	Lu
PbFCl	PbFCl	PbFCl	PbFCl	PbFCl	PbFCl	PbFCl
	YOF	*YOF*	*YOF*	*YOF*		
		SmSI	SmSI	SmSI	SmSI	SmSI

The structure of ScOCl was established to be of the FeOCl type (Table IV).

The pyrohydrolysis of the useful $(NH_4)_3RCl_6$ salts provides a convenient quantitative route to crystalline ROCl phases although these are clearly at the lower limit of coherent crystallinity (to X-rays) for the rhombedral structures of some systems when the pyrohydrolysis is carried out at 400 °C or below. This procedure does prevent the formation of any PbFCl type for YOCl, but a mixture is always obtained of HoOCl. It appears that this route must exercise some kinetic control over the product since the preparation of disordered ErOCl in this way and its conversion to the SmSI form in LiCl–KCl both take place in the same temperature region where the low-temperature PbFCl modification has been obtained by decomposition of $ErCl_3 \cdot 6H_2O$ in air.[3] We have confirmed the latter result for both YOCl and ErOCl at the same temperature used for the formation of the disordered $R\bar{3}m$ material. It is difficult to imagine a topotactic route for the decomposition of either $(NH_4)_3RCl_6$ or $RCl_3 \cdot 6H_2O$; some nucleation control is likely to be involved. In another contrast, YOCl gives the YOF form (along with Y_3O_4Cl and Y_2O_3) from KCl at 850 °C but the PbFCl type on cooling its solution in YCl_3 from 910 to 620 °C. The decompositions observed in KCl at 800–900 °C and to a lesser degree in LiCl–KCl at ~600 °C doubtlessly are furthered by formation of $M^I_3RCl_6$ and other ternary compounds and could be diminished by the use of relatively less alkali-metal chloride or of a MCl–RCl_3 eutectic solvent. The latter has been briefly explored only for yttrium and thulium. Clearly, these flux processes deserve more attention.

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Registry No. $(NH_4)_3YCl_6$, 59230-45-4; $(NH_4)_3DyCl_6$, 73520-18-0; $(NH_4)_3HoCl_6$, 73520-19-1; $(NH_4)_3ErCl_6$, 94499-15-7; $(NH_4)_3TmCl_6$, 73520-05-5; $(NH_4)_3YbCl_6$, 94499-16-8; HoOCl, 14973-85-4; TmOCl, 15605-37-5; ErOCl, 13759-19-8; YOCl, 13759-29-0; Y_3O_4Cl, 12394-40-0; Yb_3O_4Cl, 64616-02-0; Dy_3O_4Cl, 72673-50-8; Ho_3O_4Cl, 72673-53-1; Na_xYOCl, 86993-42-2; YbOCl, 13759-96-1; DyOCl, 14986-29-9.

Supplementary Material Available: Tables of observed and calculated powder pattern data for HoOCl, ErOCl, TmOCl, and YbOCl in YOF and SmSI forms (4 pages). Ordering information is given on any current masthead page.

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Reactions of Metal Complexes with Carbohydrates: Isolation and Characterization of Novel Nickel(II) Complexes Containing *N*-Glycoside Ligands Derived from Amino Sugars

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Tris(ethylenediamine)nickel(II) ions react with the hydrochloride salts of D-glucosamine, D-galactosamine, or D-mannosamine to give blue-violet, paramagnetic bis(tridentate)nickel(II) complexes in which the tridentate ligand is the *N*-glycoside formed from an amino sugar and a diamine. The nickel(II) complexes have been characterized by elemental analysis, magnetic susceptibility, and electronic, infrared, and circular dichroism spectroscopy. To elucidate the detailed stereochemistry of this system, we have undertaken a crystal and molecular structure determination on the one of the complexes, $[Ni(D\text{-}N\text{-gl-en})_2]Br_2 \cdot 4H_2O$, where D-*N*-gl-en is the tetradentate *N*-glycoside ligand 1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-glucose. The structure of the complex was determined from the three-dimensional X-ray counter data. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 16.461$ (2) Å, $b = 23.371$ (3) Å, $c = 15.956$ (3) Å, and $Z = 8$ (two independent molecules per asymmetric unit). The structure was solved by direct methods followed by least-squares and Fourier techniques. Refinement using 4102 reflections with $F_o > 3[\sigma(F_o)]$ gave $R = 0.052$ and $R' = 0.064$. Both structures of the two independent complexes in the asymmetric unit are chemically identical. The two *N*-glycoside ligands complete a distorted-octahedral coordination around the nickel atom in the meridional mode; the complex has approximately C_2 symmetry. Each sugar moiety forms a five-membered chelate ring with the nickel atom in the λ-gauche conformation. The pyranose ring of the sugar is in the usual β-$^4C_1$ form. The relationship between the X-ray crystal structure and the CD spectra of the related metal complexes has been examined.

Amino acids and sugars are important compounds in the building of complex biochemical and biological molecules. These compounds are very interesting in coordination chemistry as ligands and in bioinorganic chemistry in connection with metal-containing enzymes. A great number of transition-metal complexes containing amino acids or their derivatives have been synthesized, isolated, and characterized. In spite of the fact that it has been well-known that sugars can form complexes with transition metals, the field of sugar–metal complexes is still largely unexplored.

As a significant part of a program of study to elucidate sugar–transition-metal interactions, we have now examined amino sugars. Amino sugars (2-amino-2-deoxyaldoses) are of widespread occurrence in nature. They are combined in many polysaccharides and mucosaccharides of microbiological and animal origin, where they play an important role in physiological processes, and in a number of antibiotics. In spite of the importance of amino sugars

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and their derivatives, investigations using amino sugars as ligands are relatively rare in the literature.[2] There is very limited information concerning the coordination behavior of amino sugars since no X-ray crystal structure determination has been undertaken.

Recently we have reported the successful uptake of some natural hexoses by nickel(II) complexes of diamines, where a monosaccharide reacted with one of the amine centers of tris(diamine)nickel(II) salts to give an *N*-glycoside.[3] We concluded that an *N*-glycoside from an aldose and a diamine coordinates to the nickel atom through the oxygen atom of the hydroxyl group on C-2 of the sugar moiety and through the two N atoms of the diamine. Since amino sugars have a donor NH_2 group on the C-2 atom instead of the hydroxyl group of aldoses, the coordination behavior of *N*-glycosides derived from amino sugars is expected to be similar to that of *N*-glycosides formed from aldoses.

In this paper we wish to report the successful isolation and characterization of novel mononuclear nickel(II) complexes containing *N*-glycosides derived from the reaction of ethylenediamine and amino sugars, including an X-ray crystal structure determination on one of the complexes, and to present a potentially useful tool in assigning coordination behavior of amino sugars by means of circular dichroism spectroscopy.

Experimental Section

Materials. All reagents were of the best commercial grade and were used without further purification. The following abbreviations are used: en, ethylenediamine; D-*N*-gl-en, 1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-glucose; D-*N*-gal-en, 1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-galactose; D-*N*-man-en, 1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-mannose.

Bis[1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-glucose]nickel(II) Dichloride–Water, $[Ni(D\text{-}N\text{-}gl\text{-}en)_2]Cl_2{\cdot}H_2O$. Tris(ethylenediamine)nickel(II) dichloride dihydrate (2.25 g, 6.5 mmol), prepared by the known method,[4] is dissolved in 200 mL of methanol. The hydrochloride salt of D-glucosamine (4.20 g, 19.5 mmol) is added, and the mixture is refluxed for 1.5 h. The color of the solution changes from lavender to blue-violet. Some undissolved materials are removed by filtering, and the solution is left at room temperature. Blue-violet crystals form. The crude product is filtered, washed with methanol and ether, and dried in vacuo. This compound is insoluble in methanol. Recrystallization of the compound from a minimum amount of warm water containing methanol gives blue-violet crystals that are stable in water; the yield is 3.7 g (96.6%).

Bis[1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-galactose]nickel(II) Dichloride–3.5-Water, $[Ni(D\text{-}N\text{-}gal\text{-}en)_2]Cl_2{\cdot}3.5H_2O$. To a stirred solution of $[Ni(en)_3]Cl_2{\cdot}2H_2O$ (1.15 g, 3.33 mmol) in 200 mL of methanol is added 2.14 g (9.91 mmol) of the hydrochloride salt of D-galactosamine. The solution is warmed to about 60 °C with stirring and becomes blue-violet after about 10 min. The solution is left to reflux for 40 min more and concentrated. The solution is loaded on a LH-20 gel permeation column and eluted with methanol. The colored materials separate into a blue-violet band and pale yellow one. The blue-violet fractions are collected and purified three times on the column. Final blue-violet fractions thus obtained are concentrated. The solution is set in a refrigerator to cool. A blue-violet product separates from the solution. Owing to hygroscopicity of the product, all following operations are carried out under a dry nitrogen atmosphere, with use of standard Schlenk techniques unless otherwise specified. The compound is collected at the pump, washed with ether, and dried under a reduced pressure at 50 °C. It may be recrystallized from methanol; the yield is 0.108 g (9%).

Bis[1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-mannose]nickel(II) Dichloride–2-Water–Methanol, $[Ni(D\text{-}N\text{-}man\text{-}en)_2]Cl_2{\cdot}2H_2O{\cdot}CH_3OH$. The method described immediately above is followed precisely but with 0.98 g of $[Ni(en)_3]Cl_2{\cdot}2H_2O$ and 2.14 g of D-galactosamine hydrochloride, respectively. The product is isolated and purified in the same way; the yield is 0.212 g (12%).

Table I. Crystal Data for $[Ni(D\text{-}N\text{-}gl\text{-}en)_2]Br_2{\cdot}4H_2O$

formula	$NiC_{16}H_{46}N_6O_{12}Br_2$
mol wt	773.09
cryst size, mm	0.35 × 0.48 × 0.40
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	16.461 (2)
b, Å	23.371 (3)
c, Å	15.965 (3)
V, Å^3	6142 (2)
d(obsd), g cm^{-3}	1.61
d(calcd), g cm^{-3}	1.60
Z	8
λ, Å	0.7107 (Mo Kα)
abs coeff, cm^{-1}	40.9
monochromator	graphite
take off angle, deg	5
method	ω–2θ ($2\theta < 20°$), θ–2θ ($2\theta > 20°$)
scan speed, deg min^{-1}	3
bkgd counts, s	8
stds	3 every 50 reflcns
2θ limits, deg	50
no. of data	6285
no. of obsd data	4102 ($F_o > 3\sigma(F_o)$)
R	0.052

Physical Measurements. Infrared spectra were obtained as KBr pellets or Nujol mulls on a Shimazu IR-400 recording spectrometer. Spectra of finely ground solid samples were obtained with a Hitachi 340 spectrophotometer equipped with a reflectance attachment using USP $MgCO_3$ as a blank. Solution spectra of the complexes were obtained with a Jasco J-500C recording spectropolarimeter (circular dichroism spectra) and a Hitachi 340 spectrophotometer (electronic absorption spectra). Magnetic moments were determined by the Faraday method at room temperature with a Shimazu Model MB-100 magnetic balance. The molar susceptibility in each case was corrected for the diamagnetism of the ligand.[5] Microanalyses were performed by Shonan Bunseki Center Co., Ltd.

Crystal Data and Intensity Measurements for $[Ni(D\text{-}N\text{-}gl\text{-}en)_2]Br_2{\cdot}4H_2O$. Since the chloride obtained above was unsuitable for X-ray crystallography, we have newly prepared the bromide as follows. The perchlorate was obtained from the reaction between $[Ni(en)_3](ClO_4)_2$[6] and the hydrochloride salt of D-glucosamine and purified by column chromatography on the LH-20 gel permeation column. The perchlorate obtained was dissolved in water and converted to the bromide form by allowing it to pass through a Dowex 2-X8 anion-exchange-resin column (100–200 mesh, Br^- form). The pure bromide salt was obtained upon evaporation of the resultant solution to near-dryness. A blue-violet powder was obtained, which yielded fine blue-violet crystals upon recrystallization from a minimum amount of a methanol–water solution. The crystals were collected, washed with methanol and ether, and dried in vacuo at 50 °C. In this process the bromide lost 3 mol of water. Anal. Calcd. for $[Ni(D\text{-}N\text{-}gl\text{-}en)_2]Br_2{\cdot}4H_2O$: $C_{16}H_{38}N_6O_8NiBr_2{\cdot}4H_2O$: C, 26.22; H, 6.32; N, 11.46; Br, 21.70. Found:[6] C, 28.29; H, 5.77; N, 12.03; Br, 22.63. AB and CD spectra of the bromide are almost identical with those of the chloride.

The crystallographic and experimental data are summarized in Table I. A blue-violet crystal coated with epoxy cement on a glass fiber was mounted on the goniometer head of a Rigakudenki AFC-5 four-circle diffractometer. Three standard reflections were monitored every 50 reflections and showed only a 1–2% random variation in intensity, for which no correction was made. The standard Lorentz, polarization, and absorption corrections were applied.

Structure Solution and Refinement. The structure was solved by direct methods; the locations of Br and Ni atoms were determined from the *E* map with the highest figure of merit. The coordinates of the remaining atoms were deduced by means of alternate cycles of difference Fourier synthesis and block-diagonal least-squares refinement. Atomic scattering factors were taken from ref 7. The weighting scheme

$$1/w = \sigma c^2 + (0.015|F_o|)^2$$

was employed, where σc defined as $\sigma c = (\bar{N})^{1/2}$ is a counting statistics error with Gaussian distribution function $P(N) = (1/2\bar{N})^{1/2} \exp[-(N - \bar{N})^2/2\bar{N}]$. Since the complex was derived from D-glucosamine, the known

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(6) Analysis of this complex was performed after the structure determination was undertaken. The crystals were ground to powder and kept in a dry environment. Anal. Calcd for $[Ni(D\text{-}N\text{-}gl\text{-}en)_2]Br_2{\cdot}H_2O$, $C_{16}H_{38}N_6O_8NiBr_2{\cdot}H_2O$: C, 28.30; H, 5.94; N, 12.38; Br, 23.53.

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Table IIa. Fractional Coordinates and Equivalent Thermal Parameters for Non-Hydrogen Atoms[a]

atom	x	y	z	B_{eq}, Å^2	atom	x	y	z	B_{eq}, Å^2
Ni(1)	203 (1)	−2269 (1)	4970 (1)	2.5	Ni(2)	2058 (1)	−2251 (1)	−8 (1)	2.4
N(1)	684 (7)	−2485 (5)	3756 (7)	3.7	N(7)	1573 (7)	−2372 (5)	1215 (7)	3.5
N(2)	−350 (6)	−3067 (4)	4793 (6)	2.4	N(8)	2520 (6)	−3065 (4)	263 (6)	2.3
N(3)	−365 (6)	−2379 (4)	6201 (7)	2.5	N(9)	2619 (6)	−2459 (4)	−1214 (7)	2.6
N(4)	−810 (6)	−1781 (5)	4519 (7)	3.8	N(10)	3114 (6)	−1803 (5)	400 (7)	3.1
N(5)	650 (6)	−1427 (5)	5162 (6)	2.8	N(11)	1682 (6)	−1419 (4)	−283 (7)	2.7
N(6)	1377 (6)	−2494 (5)	5531 (6)	2.5	N(12)	847 (6)	−2451 (4)	−544 (7)	2.3
O(1)	−1067 (5)	−3789 (4)	5470 (5)	3.0	O(9)	3154 (6)	−3869 (4)	−321 (6)	3.4
O(2)	−1665 (5)	−2682 (4)	7420 (6)	3.4	O(10)	3871 (5)	−2888 (4)	−2402 (5)	3.3
O(3)	−1984 (6)	−3892 (4)	7550 (6)	4.2	O(11)	4116 (6)	−4121 (4)	−2357 (6)	4.2
O(4)	−2523 (6)	−4450 (4)	5578 (6)	4.6	O(12)	4572 (6)	−4555 (6)	−343 (8)	5.8
O(5)	1589 (5)	−940 (4)	5987 (6)	3.0	O(13)	759 (5)	−915 (4)	−1144 (5)	3.0
O(6)	3048 (5)	−2387 (4)	6229 (6)	3.7	O(14)	−830 (5)	−2291 (4)	−1189 (5)	2.6
O(7)	3201 (6)	−1461 (4)	7406 (6)	4.4	O(15)	−963 (5)	−1402 (4)	−2418 (6)	4.0
O(8)	2920 (7)	−221 (5)	6008 (6)	5.5	O(16)	−452 (7)	−86 (5)	−1279 (7)	5.6
C(1)	323 (9)	−3029 (8)	3463 (8)	4.5	C(17)	1848 (8)	−2917 (7)	1564 (9)	3.7
C(2)	158 (9)	−3412 (7)	4212 (9)	4.0	C(18)	1977 (8)	−3350 (6)	872 (9)	3.0
C(3)	−529 (7)	−3310 (6)	5599 (7)	2.1	C(19)	2678 (8)	−3368 (6)	−498 (8)	2.6
C(4)	−928 (7)	−2853 (6)	6118 (8)	2.7	C(20)	3127 (7)	−2979 (6)	−1069 (8)	2.5
C(5)	−1225 (7)	−3105 (6)	6948 (8)	2.8	C(21)	3409 (8)	−3284 (6)	−1868 (8)	3.1
C(6)	−1764 (9)	−3633 (6)	6784 (8)	3.4	C(22)	3888 (8)	−3816 (6)	−1631 (9)	3.5
C(7)	−1278 (9)	−4056 (6)	6235 (8)	3.2	C(23)	3389 (8)	−4182 (5)	−1053 (9)	2.6
C(8)	−1772 (10)	−4576 (6)	6010 (10)	4.6	C(24)	3812 (9)	−4711 (7)	−748 (11)	4.6
C(9)	−657 (9)	−1154 (6)	4592 (10)	3.8	C(25)	3000 (9)	−1191 (6)	285 (10)	4.0
C(10)	−67 (8)	−1051 (6)	5299 (10)	3.6	C(26)	2419 (8)	−1080 (6)	−454 (10)	3.6
C(11)	1213 (7)	−1473 (5)	5863 (8)	2.4	C(27)	1090 (8)	−1469 (6)	−973 (8)	2.9
C(12)	1843 (7)	−1950 (6)	5683 (8)	2.4	C(28)	445 (7)	−1888 (5)	−737 (8)	2.2
C(13)	2425 (7)	−1989 (6)	6411 (8)	2.5	C(29)	−177 (7)	−1933 (6)	−1426 (8)	2.2
C(14)	2791 (8)	−1406 (6)	6620 (8)	3.0	C(30)	−502 (7)	−1334 (6)	−1653 (8)	2.4
C(15)	2129 (9)	−946 (7)	6697 (9)	3.4	C(31)	191 (8)	−925 (6)	−1843 (8)	2.9
C(16)	2479 (9)	−335 (6)	6750 (9)	3.8	C(32)	−88 (9)	−309 (7)	−1981 (10)	4.2
Br(1)	1094 (1)	−3115 (1)	7509 (1)	3.8	Br(3)	2527 (1)	−3210 (1)	3993 (1)	4.7
Br(2)	4705 (1)	−1946 (1)	8916 (1)	4.4	Br(4)	1003 (1)	−1251 (1)	2765 (1)	5.4
					Br(4)′	1070 (12)	−1187 (8)	2171 (12)	5.8
O(17)	1030 (7)	−662 (5)	1032 (9)	7.4	O(21)	1638 (13)	−4354 (7)	6639 (18)	20.0
O(18)	−2781 (9)	629 (7)	2232 (14)	13.5	O(22)	1988 (19)	−5142 (16)	1688 (27)	14.9
					O(22)′	1397 (23)	−4790 (13)	1971 (19)	13.4
O(19)	−3998 (9)	−4940 (7)	6075 (12)	11.4	O(23)	623 (24)	5456 (12)	407 (27)	44.8
O(20)	421 (9)	757 (7)	2696 (13)	13.1	O(24)	3559 (19)	4759 (16)	4063 (28)	40.7

[a] Positional parameters are multiplied by 10^4; their estimated standard deviations are in parentheses.

Table III. Analytical and Magnetic Data of the Nickel(II) Complexes

compd		% C	% H	% N	% Cl	μ_{eff}, μ_B
[Ni(D-*N*-gl-en)$_2$]Cl$_2$·H$_2$O	found	32.42	6.73	13.97	12.40	3.03
	calcd	32.56	6.83	14.24	12.01	
[Ni(D-*N*-gal-en)$_2$]Cl$_2$·3.5H$_2$O	found	29.86	7.52	13.31	12.04	3.12
	calcd	30.26	7.14	13.23	11.16	
[Ni(D-*N*-man-en)$_2$]Cl$_2$·2H$_2$O·CH$_3$OH	found	31.54	7.50	13.09	11.46	3.03
	calcd	31.90	7.24	13.13	11.08	

absolute configurations of the asymmetric carbon atoms were used as internal reference asymmetric centers to determine the absolute configuration of the complex ion. The effects of anomalous dispersion included in F_c values of f' and f'' for Br, Ni, O, N, and C were taken from ref 8. Least-squares refinement, allowing all the atoms except for hydrogen atoms to vibrate anisotropically, converged to R and R' values of 0.0578 and 0.0674, respectively, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R' = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. When the f'' values of Br, Ni, O, N, and C atoms were reversed in sign in order to test the final structure, convergence was reached with $R = 0.0718$ and $R' = 0.0839$, which are significantly larger than the values of 0.0578 and 0.0674 for the final structure. This result agreed with the earlier determination using internal reference asymmetric centers. The difference synthesis suggested disorder for one Br atom and one water molecule. One of the four Br atoms, Br(4), was located at two positions, Br(4) and Br(4)′, with the populations of 0.9 and 0.1, respectively. One of the eight water molecules of crystallization was also located at two positions, O(22) and O(22)′, with each having a population of 0.5. At this stage, idealized positions of hydrogen atoms except for the hydroxyl groups and water molecules of crystallization were calculated by assuming a tetrahedral coordination about carbon atoms and nitrogen atoms, with C–H and N–H bond distances of 1.08 Å. Hydrogen atom scattering factors were taken from the compilation[9] of Stewart et al. On inclusion of fixed contributions from hydrogen atoms with isotropic thermal parameters $B = 3.0$ Å^2, further refinement of the non-hydrogen parameters converged to $R = 0.052$ and $R' = 0.064$. A final difference Fourier map still showed peaks at heights up to 2 e Å^{-3} around the bromide and nickel atoms, although the electron density did not rise above 1.5 e Å^{-3} elsewhere. The final positional parameters along with their standard deviations are listed in Table II. Compilations of the anisotropic thermal parameters and observed and calculated structure factors are available.[10] The calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computing Program System UNICS III.[11]

Results and Discussion

A series of novel nickel(II) complexes with *N*-glycoside ligands, viz., D-*N*-gl-en, D-*N*-gal-en, and D-*N*-man-en,[12] were prepared and isolated by a method similar to that described for previous nickel(II) complexes containing *N*-glycosides using the hydro-

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(12) See Experimental Section for ligand abbreviations.

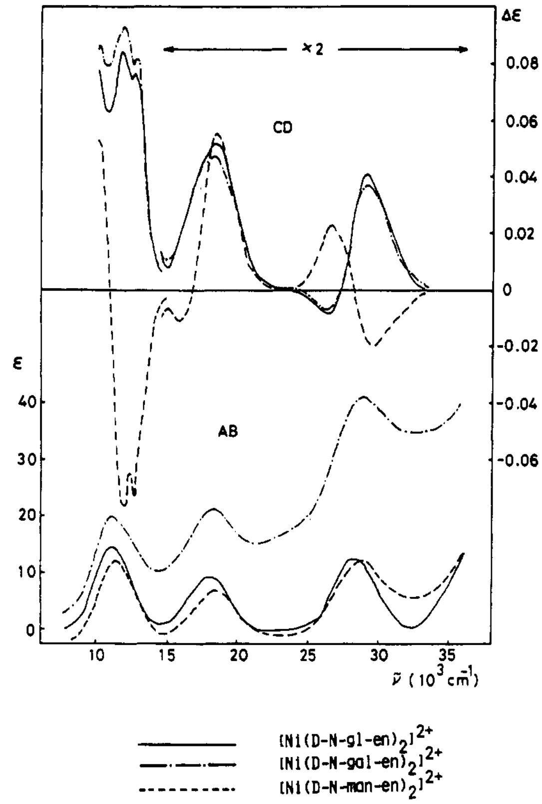

Figure 1. Absorption and circular dichroism spectra of the nickel(II) complexes in water.

Table IV. Absorption, Circular Dichroism, and Reflectance Spectra of the Ni(II) Complexes

	AB[a] $\nu_{\max}$[b] (ϵ)	CD[a] $\nu_{\max}$[b] ($10^2\Delta\epsilon$)	reflectance $\nu_{\max}$[b]
$[Ni(D\text{-}N\text{-gl-en})_2]^{2+}$	11.2 (14.7)	11.8 (+8.5)	11.5
		12.6 (+7.7)	
	18.2 (9.6)	18.4 (+2.6)	18.2
	28.5 (13.1)	26.3 (−0.4)	28.3
		29.0 (+2.1)	
$[Ni(D\text{-}N\text{-gal-en})_2]^{2+}$	11.2 (20.2)	11.8 (+9.3)	11.2
		12.7 (+8.1)	
	18.3 (21.6)	18.4 (+2.4)	18.3
	29.0 (41.2)	26.3 (−0.4)	28.5
		29.0 (+1.9)	
$[Ni(D\text{-}N\text{-man-en})_2]^{2+}$	11.3 (13.7)	11.9 (−7.7)	11.5
		12.7 (−7.4)	
	18.5 (9.3)	18.4 (+2.7)	18.3
	28.7 (14.9)	26.5 (+1.1)	28.7
		29.4 (−0.9)	

[a] In aqueous solution. [b] 10^3 cm^{-1}.

chloride salts of amino sugars instead of monosaccharides.[3] Since amino sugars are unstable in aqueous solutions and readily dimerize, particularly in the presence of base,[13] we have used the HCl salts of amino sugars. The analytical data reveal a 2:1 ratio of *N*-glycoside ligand to metal for all of the complexes (Table III).

No significant differences were observed among the spectra of the complexes in water, methanol, and ethylene glycol. Especially, $[Ni(D\text{-}N\text{-gl-en})_2]Cl_2{\cdot}H_2O$ and $[Ni(D\text{-}N\text{-gl-en})_2]Br_2{\cdot}4H_2O$ can be recrystallized from water containing methanol without any evidence of decomposition. Thus, these complexes exhibit a high degree of hydrolytic stability in contrast to the instability of the analogous complexes derived from monosaccharides.[3] It can be attributed to the strength of the Ni–N bonds as compared with that of the Ni–O bonds.

Table V. Spectral Data of the Nickel(II) Complexes

compd	ν_2/ν_1	*Dq*, cm^{-1}	*B*, cm^{-1}	β
$[Ni(D\text{-}N\text{-gl-en})_2]^{2+}$	1.63	1120	873	0.84
$[Ni(D\text{-}N\text{-gal-en})_2]^{2+}$	1.63	1120	913	0.88
$[Ni(D\text{-}N\text{-man-en})_2]^{2+}$	1.64	1120	920	0.88

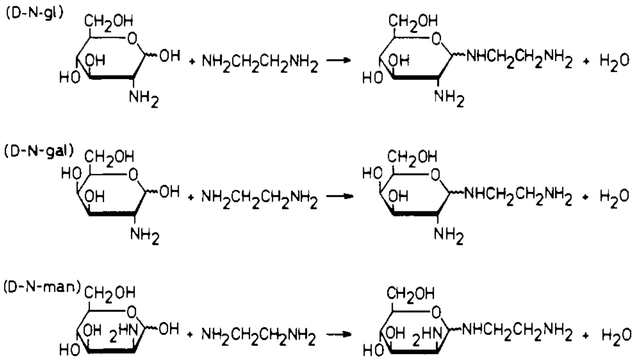

Figure 2. Reaction scheme.

The magnetic data demonstrate that nickel ions in these compounds have two unpaired electrons, and the magnetic moments (Table III) fall within the range of 2.9–3.4 μ_B reported for octahedral complexes of Ni(II).[14] Absorption (AB) and circular dichroism (CD) spectra of the complexes are presented in Figure 1. The spectral data together with the reflectance spectral results are summarized in Table IV. The positions of the absorption maxima of the complexes in aqueous solution are almost identical with the corresponding bands in the reflectance spectra (Table IV). This indicates that geometric structures are essentially equivalent in the two environments. The solution spectra of the nickel(II) complexes in the near-infrared and visible regions consist of the principal bands ν_1, ν_2, and ν_3 with comparatively low intensities (10–20) as shown in Figure 1, which are characteristic of octahedral nickel(II) complexes. The three principal bands in the spectra obtained are assigned to the three spin-allowed octahedral nickel(II) transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. Crystal field theory provides a simple interpretation of the spectra of nickel(II) in the fields of O_h symmetry as follows.[15] Generally, the ratio ν_2/ν_1 of the frequencies of the first and second band maxima lies in most octahedral nickel(II) complexes between 1.5 and 1.7. The values of *Dq* found in octahedral complexes of nickel(II) vary between 640 and 1270 cm^{-1}, depending on the position of the ligand in the spectrochemical series. The values of the Racah parameter *B* found in complexes are always less than the value of 1041 cm^{-1} found in the free ion. The usual values of β, which is the ratio *B*(found)/*B*(free ion), fall in the interval 0.7–0.9. In Table V are shown values of *Dq*, β, and ν_2/ν_1 for the three complexes. The values obtained here fall within the ranges expected for octahedral complexes of nickel(II) having six identical donor nitrogen atoms.

The absence of a C=N stretching band (~1600 cm^{-1}) in the infrared spectra of the three complexes ruled out the Schiff base nature of the coordinated ligands. The results obtained suggest the cyclic amino acetal nature of the sugar residues of the ligand.

It is well-known that sugars react with amines to yield *N*-glycosides under mild conditions.[16] Consequently, it can be predicted that each amino sugar will react with one of the amine centers of $[Ni(en)_3]^{2+}$ to form the corresponding *N*-glycoside (Figure 2).

The elemental analyses, coupled with the magnetic susceptibility and spectral data, suggest that all of the compounds are octahedral bis(tridentate)nickel(II) complexes in which the ligand is the *N*-glycoside formed from amino sugars and ethylenediamine.

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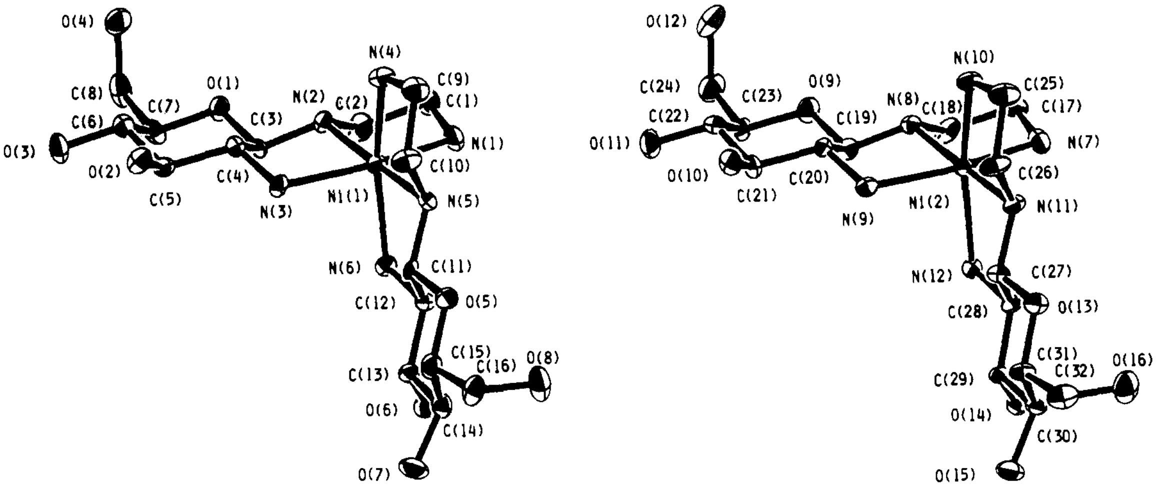

Figure 3. ORTEP view of [Ni(D-*N*-gl-en)$_2$]$^{2+}$ ions with the atomic numbering scheme in an asymmetric unit.

Some geometrical isomers, including the *mer* and *fac* modes, are possible for octahedral bis(tridentate)nickel(II) complexes. It is difficult to assign the geometry of these compounds by AB, CD, and magnetic data. The following section deals with the detailed structural results from X-ray diffraction on one of the products.

X-ray Structural Analysis of [Ni(D-*N*-gl-en)$_2$]Br$_2$·4H$_2$O. A perspective drawing of the complex cations showing ellipsoids of thermal motion is given in Figure 3. There are two complexes in the asymmetric unit. Since the structures of both the complex cations are nearly identical, the following description of the molecular structure applies equally to both the complex ions. The nickel atom is surrounded by six nitrogen atoms at the apices of a distorted octahedron. One nitrogen atom of ethylenediamine expectedly binds to carbon 1 of D-glucosamine. Two *N*-glycoside ligands coordinate to the nickel atom meridionally with the Δ configuration as the similar tridentate ligands; the complex has approximately C_2 symmetry. Each ligand coordinates to the metal at three points through the sugar amino group on carbon 2 and through the two nitrogen atoms of the ethylenediamine residue. The pyranose ring of the sugar moiety is in the usual β-$^4C_1$ chair conformation. The two chelate conformations involving sugar moieties are both λ. Both the diamine parts form the five-membered chelate ring with the nickel atom in the δ-gauche conformation. The arrangement of the group around the secondary nitrogen atom is an *S* configuration in the notation of Cahn, Ingold, and Prelog.[17] The two nitrogen atoms on carbon 1 and carbon 2, coordinating to the nickel atom, occupy equatorial positions with respect to the pyranose ring. A selection of intramolecular bond distances and bond angles is given in Tables VI and VII. There are no significant differences between analogous bond distance angles in the two independent complex ions. The Ni–N distances range from 2.09 (1) to 2.22 (1) Å. The values are normal for Ni(II) complexes of ethylenediamine.[18] The large deviations from the ideal angle (90°) occur for the ring angles at the nickel atoms for the five-membered chelate rings; N(1)–Ni–N(2), N(2)–Ni–N(3), N(4)–Ni–N(5), N(5)–Ni–N(6), N(7)–Ni–N(8), N(8)–Ni–N(9), N(10)–Ni–N(11), and N(11)–Ni–N(12) are 80.2 (4), 80.2 (4), 79.9 (4), 81.9 (4), 80.0 (4), 80.1 (4), 81.3 (4), and 81.3 (4)°, respectively. The average angle between the terminal coordinated atoms of the *N*-glycoside ligands at the nickel atom, i.e. N(1)–Ni–N(3), N(4)–Ni–N(6), N(7)–Ni–N(9), and N(10)–Ni–N(11), is 160.7°. Thus the complex cations are found to be highly distorted from ideal O_h symmetry.

Table VI. Bond Distances (Å) for Non-Hydrogen Atoms[a]

Ni(1)–N(1)	2.16 (1)	Ni(1)–N(2)	2.10 (1)
Ni(1)–N(3)	2.19 (1)	Ni(1)–N(4)	2.15 (1)
Ni(1)–N(5)	2.12 (1)	Ni(1)–N(6)	2.19 (1)
Ni(2)–N(7)	2.13 (1)	Ni(2)–N(8)	2.09 (1)
Ni(2)–N(9)	2.19 (1)	Ni(2)–N(10)	2.13 (1)
Ni(2)–N(11)	2.09 (1)	Ni(2)–N(12)	2.22 (1)
N(1)–C(1)	1.48 (2)	N(2)–C(2)	1.49 (2)
N(2)–C(3)	1.44 (2)	N(3)–C(4)	1.45 (2)
N(4)–C(9)	1.49 (2)	N(5)–C(10)	1.49 (2)
N(5)–C(11)	1.46 (2)	N(6)–C(12)	1.51 (2)
N(7)–C(17)	1.46 (2)	N(8)–C(18)	1.48 (2)
N(8)–C(19)	1.43 (2)	N(9)–C(20)	1.49 (2)
N(10)–C(25)	1.45 (2)	N(11)–C(26)	1.48 (2)
N(11)–C(27)	1.47 (2)	N(12)–C(28)	1.50 (2)
O(1)–C(3)	1.44 (2)	O(1)–C(7)	1.41 (2)
O(2)–C(5)	1.44 (2)	O(3)–C(6)	1.41 (2)
O(4)–C(8)	1.45 (2)	O(5)–C(11)	1.41 (2)
O(5)–C(15)	1.44 (2)	O(6)–C(13)	1.42 (2)
O(7)–C(14)	1.43 (2)	O(8)–C(16)	1.42 (2)
O(9)–C(19)	1.44 (2)	O(9)–C(23)	1.43 (2)
O(10)–C(21)	1.47 (2)	O(11)–C(22)	1.41 (2)
O(12)–C(24)	1.45 (2)	O(13)–C(27)	1.43 (2)
O(13)–C(31)	1.46 (2)	O(14)–C(29)	1.41 (1)
O(15)–C(30)	1.45 (2)	O(16)–C(32)	1.37 (2)
C(1)–C(2)	1.52 (2)	C(3)–C(4)	1.50 (2)
C(4)–C(5)	1.53 (2)	C(5)–C(6)	1.54 (2)
C(6)–C(7)	1.54 (2)	C(7)–C(8)	1.51 (2)
C(9)–C(10)	1.51 (2)	C(11)–C(12)	1.55 (2)
C(12)–C(13)	1.51 (2)	C(13)–C(14)	1.53 (2)
C(14)–C(15)	1.54 (2)	C(15)–C(16)	1.54 (2)
C(17)–C(18)	1.51 (2)	C(19)–C(20)	1.48 (2)
C(20)–C(21)	1.53 (2)	C(21)–C(22)	1.52 (2)
C(22)–C(23)	1.50 (2)	C(23)–C(24)	1.50 (2)
C(25)–C(26)	1.54 (2)	C(27)–C(28)	1.49 (2)
C(28)–C(29)	1.51 (2)	C(29)–C(30)	1.54 (2)
C(30)–C(31)	1.52 (2)	C(31)–C(32)	1.53 (2)

[a] Estimated standard deviations are given in parentheses.

The bond distances (N–C, C–C, and C–O) and angles (N–C–C, N–C–O, C–C–C, C–O–C, and C–C–O) for each sugar moiety are similar to the reported values for *N*-acetyl-D-glucosamine[19] and the hydrochloride of D-glucosamine.[20] Thus, in the glucopyranose rings, there seems to be no significant strain upon coordination.

A stereoview of the contents of one unit cell is available.[10] The unit cell consists of the 8 complex cations, 16 Br counteranions, and 32 waters of crystallization, in which disorder for a part of Br and H$_2$O has been observed. Hydrogen bonds of the type N–H···O, O–H···O, and O–H···Br probably exist.

Circular Dichroism and Structure. Δ and Λ structures are theoretically possible for a *mer*-bis(unsymmetrical linear tridentate ligand)nickel(II) complex. We recently determined the crystal

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Table VII. Bond Angles (deg) for Non-Hydrogen Atoms[a]

N(1)-Ni(1)-N(2)	80.2 (0.4)	N(1)-Ni(1)-N(3)	159.4 (0.4)
N(1)-Ni(1)-N(4)	96.2 (0.4)	N(1)-Ni(1)-N(5)	102.8 (0.4)
N(1)-Ni(1)-N(6)	89.3 (0.4)	N(2)-Ni(1)-N(3)	80.2 (0.4)
N(2)-Ni(1)-N(4)	95.2 (0.4)	N(2)-Ni(1)-N(5)	174.5 (0.4)
N(2)-Ni(1)-N(6)	102.9 (0.4)	N(3)-Ni(1)-N(4)	91.8 (0.4)
N(3)-Ni(1)-N(5)	97.3 (0.4)	N(3)-Ni(1)-N(6)	88.9 (0.4)
N(4)-Ni(1)-N(5)	79.9 (0.4)	N(4)-Ni(1)-N(6)	161.7 (0.4)
N(5)-Ni(1)-N(6)	81.9 (0.4)	N(7)-Ni(2)-N(8)	80.0 (0.4)
N(7)-Ni(2)-N(9)	159.3 (0.4)	N(7)-Ni(2)-N(10)	95.2 (0.4)
N(7)-Ni(2)-N(11)	101.8 (0.4)	N(7)-Ni(2)-N(12)	89.4 (0.4)
N(8)-Ni(2)-N(9)	80.1 (0.4)	N(8)-Ni(2)-N(10)	95.0 (0.4)
N(8)-Ni(2)-N(11)	176.0 (0.4)	N(8)-Ni(2)-N(12)	102.4 (0.4)
N(9)-Ni(2)-N(10)	91.9 (0.4)	N(9)-Ni(2)-N(11)	98.4 (0.4)
N(9)-Ni(2)-N(12)	89.6 (0.4)	N(10)-Ni(2)-N(11)	81.3 (0.4)
N(10)-Ni(2)-N(12)	162.5 (0.4)	N(11)-Ni(2)-N(12)	81.3 (0.4)
Ni(1)-N(1)-C(1)	109.8 (0.8)	Ni(1)-N(2)-C(2)	108.8 (0.8)
Ni(1)-N(2)-C(3)	108.7 (0.8)	C(2)-N(2)-C(3)	117.4 (1.0)
Ni(1)-N(3)-C(4)	106.3 (0.8)	Ni(1)-N(4)-C(9)	111.4 (0.8)
Ni(1)-N(5)-C(10)	107.1 (0.8)	Ni(1)-N(5)-C(11)	105.1 (0.8)
C(10)-N(5)-C(11)	115.9 (1.0)	Ni(1)-N(6)-C(12)	108.1 (0.7)
Ni(2)-N(7)-C(17)	110.4 (0.8)	Ni(2)-N(8)-C(18)	109.0 (0.7)
Ni(2)-N(8)-C(19)	109.9 (0.8)	C(18)-N(8)-C(19)	116.4 (1.0)
Ni(2)-N(9)-C(20)	106.3 (0.8)	Ni(2)-N(10)-C(25)	109.9 (0.8)
Ni(2)-N(11)-C(26)	107.2 (0.8)	Ni(2)-N(11)-C(27)	106.3 (0.8)
C(26)-N(11)-C(27)	116.6 (1.1)	Ni(2)-N(12)-C(28)	106.9 (0.7)
C(3)-O(1)-C(7)	111.7 (0.9)	C(11)-O(5)-C(15)	112.1 (1.0)
C(19)-O(9)-C(23)	113.7 (1.0)	C(27)-O(13)-C(31)	112.1 (1.0)
N(1)-C(1)-C(2)	109.3 (1.1)	N(2)-C(2)-C(1)	105.8 (1.2)
N(2)-C(3)-O(1)	107.7 (0.9)	N(2)-C(3)-C(4)	107.6 (1.0)
O(1)-C(3)-C(4)	111.2 (1.0)	N(3)-C(4)-C(3)	108.3 (1.0)
N(3)-C(4)-C(5)	114.7 (1.1)	C(3)-C(4)-C(5)	110.2 (1.1)
O(2)-C(5)-C(4)	110.6 (1.1)	O(2)-C(5)-C(6)	110.4 (1.0)
C(4)-C(5)-C(6)	110.2 (1.0)	O(3)-C(6)-C(5)	110.2 (1.1)
O(3)-C(6)-C(7)	110.6 (1.1)	C(5)-C(6)-C(7)	108.1 (1.1)
O(1)-C(7)-C(6)	109.6 (1.1)	O(1)-C(7)-C(8)	106.4 (1.1)
C(6)-C(7)-C(8)	111.8 (1.2)	O(4)-C(8)-C(7)	114.3 (1.2)
N(4)-C(9)-C(10)	108.9 (1.2)	N(5)-C(10)-C(9)	107.9 (1.1)
N(5)-C(11)-O(5)	108.8 (1.0)	N(5)-C(11)-C(12)	109.7 (1.0)
O(5)-C(11)-C(12)	111.6 (1.0)	N(6)-C(12)-C(11)	107.3 (0.9)
N(6)-C(12)-C(13)	113.4 (1.0)	C(11)-C(12)-C(13)	109.0 (1.0)
O(6)-C(13)-C(12)	110.0 (1.0)	O(6)-C(13)-C(14)	110.2 (1.0)
C(12)-C(13)-C(14)	111.5 (1.1)	O(7)-C(14)-C(13)	107.5 (1.1)
O(7)-C(14)-C(15)	109.1 (1.1)	C(13)-C(14)-C(15)	111.2 (1.1)
O(5)-C(15)-C(14)	112.5 (1.1)	O(5)-C(15)-C(16)	105.4 (1.1)
C(14)-C(15)-C(16)	112.8 (1.2)	O(8)-C(16)-C(15)	108.7 (1.2)
N(7)-C(17)-C(18)	110.4 (1.1)	N(8)-C(18)-C(17)	105.3 (1.1)
N(8)-C(19)-O(9)	109.6 (1.0)	N(8)-C(19)-C(20)	108.0 (1.1)
O(9)-C(19)-C(20)	110.4 (1.0)	N(9)-C(20)-C(19)	108.4 (1.0)
N(9)-C(20)-C(21)	114.8 (1.1)	C(19)-C(20)-C(21)	112.1 (1.1)
O(10)-C(21)-C(20)	110.3 (1.1)	O(10)-C(21)-C(22)	113.0 (1.1)
C(20)-C(21)-C(22)	109.3 (1.1)	O(11)-C(22)-C(21)	110.3 (1.1)
O(11)-C(22)-C(23)	111.2 (1.2)	C(21)-C(22)-C(23)	109.6 (1.1)
O(9)-C(23)-C(22)	111.0 (1.0)	O(9)-C(23)-C(24)	106.3 (1.1)
C(22)-C(23)-C(24)	114.5 (1.2)	O(12)-C(24)-C(23)	109.7 (1.2)
N(10)-C(25)-C(26)	110.0 (1.2)	N(11)-C(26)-C(25)	106.2 (1.1)
N(11)-C(27)-O(13)	108.9 (1.0)	N(11)-C(27)-C(28)	109.5 (1.0)
O(13)-C(27)-C(28)	111.9 (1.0)	N(12)-C(28)-C(27)	108.2 (0.9)
N(12)-C(28)-C(29)	112.9 (1.0)	C(27)-C(28)-C(29)	110.2 (1.0)
O(14)-C(29)-C(28)	111.2 (1.0)	O(14)-C(29)-C(30)	109.7 (0.9)
C(28)-C(29)-C(30)	110.2 (1.0)	O(15)-C(30)-C(29)	106.2 (1.0)
O(15)-C(30)-C(31)	107.1 (1.0)	C(29)-C(30)-C(31)	111.0 (1.0)
O(13)-C(31)-C(30)	109.8 (1.0)	O(13)-C(31)-C(32)	106.8 (1.1)
C(30)-C(31)-C(32)	113.4 (1.1)	O(16)-C(32)-C(31)	111.8 (1.3)

[a] Estimated standard deviations are given in parentheses.

structure of [Ni(L-rham-tn)$_2$]Br$_2$·2H$_2$O·CH$_3$OH (L-rham = 6-deoxy-L-mannose and tn = trimethylenediamine),[21] the result of which suggests that a nickel(II) complex containing two *N*-glycosides derived from the reaction of D-mannose or its derivatives and a diamine will adopt the Δ configuration. From the two crystal structures of the D-*N*-gl-en and L-rham-tn complexes, the three complexes obtained should have the Δ configuration. The present crystal structure indicates that the gauche conformation of the chelate ring formed by the sugar moiety will depend on the orientation of the amino group on carbon 2 of the sugar moiety and the chelate conformation involving a sugar residue will influence the absolute configuration around the secondary glycosidic nitrogen atom. Accordingly, each amino group of D-glucosamine or D-galactosamine, which are the C_4 epimers of each other, is in the equatorial position with respect to each pyranose ring, producing a λ-gauche conformation involving the sugar moiety and yielding an *S* configuration for the secondary nitrogen atom. In contrast, the five-membered chelate ring involving the D-mannosamine moiety, which is the C_2 epimer of D-glucosamine, will adopt the σ-gauche form and the configuration of the secondary nitrogen atom will be expected to be *R*. Thus, the present crystal structure suggests that the coordination patterns of the other two *N*-glycosides (D-*N*-gal-en and D-*N*-man-en) are predictable (Figure 4).

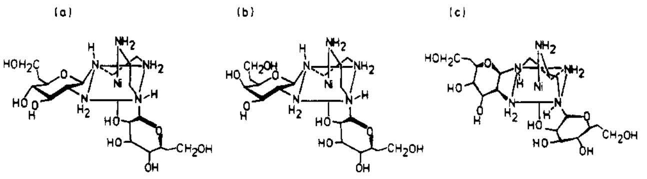

Figure 4. Structures of the complex ions: (a) [Ni(D-*N*-gl-en)$_2$]$^{2+}$; (b) [Ni(D-*N*-gal-en)$_2$]$^{2+}$; (c) [Ni(D-*N*-man-en)$_2$]$^{2+}$.

The CD spectra of the complexes in aqueous solution are presented in Figure 1. The spectral data are summarized in Table IV.

The use of magnetic dipole selection rules in assigning CD bands for dissymmetric metal complexes has been discussed by Gillard.[22] Only the lowest energy transition for octahedral nickel(II) complexes, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, is magnetic dipole allowed. The higher energy spin-allowed transitions are magnetic dipole forbidden and are expected to give rise to CD bands significantly weaker than the allowed transition.

The CD spectra of the complexes show dominant CD bands in the vicinity of ν_1 and comparatively weak CD bands in the region of ν_2 and ν_3 as expected above.

It is generally accepted that stereochemical features that can contribute to the circular dichroism of a dissymmetric metal complex can be classified as follows: (1) the distribution of ligands around the metal ion (configurational effect), (2) the puckered dissymmetric conformation of individual chelate rings (conformational effect), and (3) the presence of asymmetric groups on the ligand (vicinal effect). When the configurational effect is a major one, the same sign of the CD spectra would appear for the three complexes in the first d–d transition since all of the complexes have the similar Δ configuration (Figure 4). However, the CD curves of [Ni(D-*N*-gl-en)$_2$]$^{2+}$ and [Ni(D-*N*-gal-en)$_2$]$^{2+}$ are quite similar to each other and that of [Ni(D-*N*-man-en)$_2$]$^{2+}$ has the opposite sign in the first absorption region, where the first two complexes and the last complex are nearly mirror images. It indicates that the first contribution is not likely to be particularly large. This observation could be attributed to (i) a significantly small configurational contribution due to the *mer* form or (ii) configurational exchange between Δ and Λ structures.[23] Anyhow, the configurational contribution seems to be negligible.

The stereochemical features that may have influence on the conformational and vicinal effects are in the same sense for the D-*N*-gl-en and D-*N*-gal-en complexes, and these are in the opposite sense for the D-*N*-man-en complex. Accordingly, the CD sign in the first absorption region can be attributed to the coordination geometry of each *N*-glycoside ligand.

Thus, the present crystal structure serves as a reference by which the coordination in complexes containing amino sugars can be assigned by correlation of their CD spectra.

Summary

As observed in the case of aldohexoses,[3] amino sugars react with

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(22) Gillard, R. D. "Physical Methods in Advanced Inorganic Chemistry"; Hill, H. A. O., Day, P. Eds.; Interscience: New York, 1968; Chapter 5.

(23) It is well-known that nickel(II) complexes that are dissymmetrical in their structures, such as tris(ethylenediamine)nickel(II), are normally unresolvable for kinetic reasons.[22] Even in the case of so-called inert cobalt(III) complexes, such as an (L-histidinato)(iminodiacidato)cobalt(III) complex, configurational exchange occurred in water without any catalysis.[24]

tris(ethylenediamine)nickel(II) salts in methanol to give the novel type of nickel(II) complexes containing two *N*-glycosides derived from the reaction of an amino sugar and a diamine.

Previously we predicted that an *N*-glycoside from an aldose and a diamine coordinates to the nickel ion through the oxygen atom of he hydroxyl group on C-2 of the sugar moiety and through the two N atoms of the diamine.[3] Though the sugars are amino sugars and they have an amino group on C-2 instead of a hydroxyl group, the coordination behavior of *N*-glycosides derived from amino sugars is expected to be similar to that of glycosylamines from aldohexoses. Thus, the present work could confirm our previous structural prediction for nickel(II) complexes of aldoses.[3]

The present crystal structure and circular dichroism studies of the related complexes indicate that the gauche conformation of the sugar chelate ring and the absolute configuration around the secondary nitrogen atom will depend on the orientation of the amino group on C-2 of the sugar moiety and they make significant contributions to the circular dichroism. Thus the results obtained in this work suggest that the CD pattern of the first d–d transition offers a potentially useful tool in assigning the coordination geometry of amino sugars.

The complexes obtained exhibit a high degree of hydrolytic stability in contrast to the instability of the analogous complexes derived from monosaccharides.[3] This fact is noteworthy in connection with the medical usefulness of amino sugars.

Recently much attention has been attracted to nickel-containing hydrogenases.[25] Accordingly, elucidation of the fundamental coordination behavior of sugars or amino sugars to nickel should provide useful information to aid in the interpretation of reaction mechanisms of metal-containing enzymes.

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Registry No. en, 107-15-3; [Ni(D-*N*-gl-en)$_2$]Cl$_2$, 94595-50-3; [Ni(D-*N*-gal-en)$_2$]Cl$_2$, 94499-89-5; [Ni(D-*N*-man-en)$_2$]Cl$_2$, 94595-99-0; [Ni(D-*N*-gl-en)$_2$]Br$_2$·4H$_2$O, 94595-51-4; tris(ethylenediamine)nickel(II) dichloride, 13408-70-3; D-glucosamine, 3416-24-8; D-galactosamine, 7535-00-4; D-galactosamine hydrochloride, 1772-03-8.

Supplementary Material Available: A listing of the anisotropic thermal parameters (Table IIb), a stereoscopic view of the unit cell, and a table of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Facile CO$_2$ Uptake by Zinc(II)–Tetraazacycloalkane Complexes. 1. Syntheses, Characterizations, and Chemical Properties of (Monoalkyl carbonato)(tetraazacycloalkane)zinc(II) Complexes

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Zn(II)–tetraazacycloalkane complexes take up CO$_2$ in alcohol very easily and reversibly at room temperature to fix it into resulting complexes as monoalkyl carbonate. A series of Zn(II)–monoalkyl carbonato complexes, Zn(L)(O$_2$COR)(ClO$_4$) (L = [14]aneN$_4$, [15]aneN$_4$, Me$_2$[14]aneN$_4$, Me$_4$[14]aneN$_4$; R = CH$_3$, Et) and [Zn(L)]$_3$(O$_2$COR)$_2$(ClO$_4$)$_4$ (L = [15]aneN$_4$; R = *n*-Bu), have been obtained from the reactions with CO$_2$ and characterized by IR and NMR spectroscopies. Generally, addition of a base such as NaOR or NEt$_3$ facilitates the uptake reaction of CO$_2$. In systems of methanol solution of the [14]aneN$_4$ or [15]aneN$_4$ complex, the reaction proceeds spontaneously in a neutral solution below ca. 10 °C, CO$_2$ being taken up from the air. The monoalkyl carbonato complex (Zn–O$_2$COR) exists in organic solvents such as chloroform and dichloromethane in equilibrium with its decarboxylated Zn–OR complex. The equilibrium involves reversible desorption and absorption of CO$_2$. A decrease in temperature makes the equilibrium shift toward the increase in the amount of the Zn–O$_2$COR complex. For the [15]aneN$_4$ system, the equilibrium constant (K = [Zn([15]aneN$_4$)–O$_2$COCH$_3$]/[Zn([15]aneN$_4$)–OCH$_3$][CO$_2$]) is found to be $K_{20.2\,°\mathrm{C}}$ = 5.8 M^{-1}. The monoalkyl carbonato ligand has been converted into dialkyl carbonate by treatment with FSO$_3$R (R = CH$_3$, Et). Various factors influencing the efficient CO$_2$ uptake have been discussed.

Introduction

Coordination of CO$_2$ to a transition-metal complex and reactions of the resulting complex have been of interest in connection with the utilization of CO$_2$.[1] Besides direct coordination of CO$_2$ to transition metals with its intact form,[2] many insertion reactions of CO$_2$ into an M–X bond (X = H, C, O, N) have been reported.[3] Most cases of X = O are various metal alkoxides. Chisholm et al. proposed an alcohol-catalyzed chain mechanism for apparent CO$_2$ insertion into a Mo–O bond of Mo$_2$(OR)$_6$ in solution.[3d]

$$\mathrm{ROH + CO_2 \rightleftharpoons ROCOOH}$$

$$\mathrm{M{-}OR + ROCOOH \rightarrow M{-}O_2COR + ROH} \qquad (1)$$

They also reported that reaction of dialkylamide complexes of

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