Synthesis and Characterization of Nickel(II) Complexes containing Ligands derived from Disaccharides and 1,3-Diaminopropane†

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The reaction of [Ni(tn)₃]²⁺ ions (tn = 1,3-diaminopropane) with disaccharides having a glucose reducing terminal, i.e. maltose, lactose, cellobiose, and melibiose, in the presence of a catalytic amount of ammonium chloride gave blue, paramagnetic bis(N-D-aldosylpropane-1,3-diamine)nickel(II) complexes. The complexes were characterized by elemental analysis, magnetic susceptibilities, electronic absorption and circular dichroism spectroscopies, X-ray absorption and crystallographic analyses. The complex bis[N-(4-O-α-D-glucopyranosylglucosyl)propane-1,3-diamine]nickel(II) bromide dihydrate crystallizes in the hexagonal space group P6₄22, with a = 22.125(8), c = 21.464(9) Å, and Z = 6. The structure was solved by Patterson methods and refined by full-matrix least-squares techniques to R = 0.080 and R' = 0.094. The complex cation has C₂ symmetry and the central nickel atom is octahedrally co-ordinated by two tridentate glycosylamine ligands formed from maltose and tn. Each ligand is bonded through the oxygen atom of the hydroxyl group at C² of maltose and through the two nitrogen atoms of the diamine in a meridional mode. The co-ordination behaviour of the glucose unit in the octahedral nickel(II) complexes has been established. In the crystal packing, the complex cation exists in a novel dimeric form supported by intermolecular hydrogen bonds, which might provide some fundamental information concerning sugar–sugar interactions in biological systems.

Amino acids and sugars are indispensable units of biological molecules, and also play a very significant role in co-ordination chemistry as ligands, in connection with metal-containing enzymes. In contrast with the wide variety of transition-metal complexes containing amino acids and their derivatives, the chemistry of sugar–metal complexes is still largely unexplored and has been very slow to develop due to a lack of crystallographic studies owing to the highly hygroscopic properties of these compounds.[1,2]

We have reported the synthesis and characterization of nickel(II) complexes containing glycosylamines derived from the reaction of sugars and diamines,[2–9] and some cobalt(III) complexes.[10] The reactions of [Ni(diamine)₃]²⁺ [diamine = 1,2-diaminoethane (en) or 1,3-diaminopropane (tn)] with a ketose gave octahedral (D-ketosyldiamine)(diamine)nickel-(II)]²⁺, where glycosylamine acts as a tetradentate ligand through the two oxygen atoms of the hydroxyl groups on C¹ and C³ of the sugar moiety and the two nitrogen atoms of the diamine.[3–6] The similar reaction with an aldose afforded bis-(aldosyldiamine)nickel(II)]²⁺ complexes in which the glycosylamine co-ordinates to the nickel atom in a tridentate manner via the oxygen atom of the hydroxyl group on C² of the sugar moiety and the two nitrogen atoms of the diamine.[3,7] These reactions were strongly influenced by the substituents at the N atoms of the diamines. By using 1,2-bis(methylamino)ethane (dmen) a binuclear nickel(II) complex with a multidentate glycosylamine bridging between the two nickel atoms was

obtained in the reaction of [Ni(H₂O)₂(dmen)₂]²⁺ with D-mannose.[8,9] Moreover, nickel(II) complexes of further N-methylated diamines, 1-dimethylamino-2-(methylamino)-ethane and 1,2-bis(dimethylamino)ethane, promote a novel stereospecific rearrangement of the carbon skeleton resulting in C² epimerization of aldoses.[11–13]

In our studies the carbohydrate source was limited to monosaccharides and their amino derivatives.[14] Oligosaccharides including disaccharides have attracted increasing attention, because they are involved in the biological activity of many glycoproteins, glycolipids, and antibiotics. Their metal complexes are assumed to be one of the most suitable models for interpretation of interactions between metal ions and living organisms. However, reports on the structurally characterized metal complexes of disaccharides are extremely limited thus far.[15,16] In this paper we report the successful isolation and characterization of mononuclear nickel(II) complexes containing glycosylamines derived from 1,3-diaminopropane and disaccharides having glucose as reducing terminal, the structures of which were determined by extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES) and X-ray crystallography.

Experimental

All reagents were of the best commercial grade used without further purification. The complexes [Ni(tn)₃]Cl₂·2H₂O and [Ni(tn)₃]Br₂·2H₂O were prepared by the known method.[17] The following abbreviations are used: Glcα4Glc (maltose, 4-O-D-glucopyranosyl-D-glucose); Galβ4Glc (lactose, 4-O-β-D-galactopyranosyl-D-glucose); Glcβ4Glc (cellobiose 4-O-β-D-glucopyranosyl-D-glucose); Galα6Glc (melibiose, 6-O-α-D-

galactopyranosyl-D-glucose); L-Rha (L-rhamnose, 6-deoxy-L-mannose); D-GlcN (2-amino-2-deoxy-D-glucose); Glcα4Glc-tn [N-(4-O-α-D-glucopyranosyl-D-glucosyl)propane-1,3-diamine]; Galβ4Glc-tn [N-(4-O-β-D-galactopyranosyl-D-glucosyl)propane-1,3-diamine]; Glcβ4Glc-tn [N-(4-O-β-D-glucopyranosyl-D-glucosyl)propane-1,3-diamine]; Galα6Glc-tn [N-(6-O-α-D-galactopyranosyl-D-glucosyl)propane-1,3-diamine]; L-Rha-tn [N-(L-rhamnosyl)propane-1,3-diamine]; D-GlcN-en [N-(2-amino-1,2-deoxy-D-glucosyl)ethane-1,2-diamine].

Measurements.—Infrared spectra were measured as KBr pellets or Nujol mulls on a Perkin Elmer 1740 recording spectrometer, electronic absorption spectra on a Shimazu UV-3100 spectrophotometer and circular dichroism spectra on a JASCO J-20 spectropolarimeter. Magnetic moments were determined by the Faraday method at room temperature with a Shimazu Model MB-2 magnetic balance. The molar susceptibilities were corrected for the diamagnetism of the ligand.[18]

Preparations of Nickel(II) Complexes containing Amines of Disaccharides.—[Ni(Glcα4Glc-tn)₂]X₂·nH₂O (X = Br, n = 2 1a; X = Cl, n = 2.5 1b). Maltose monohydrate (3.24 g, 9.0 mmol), [Ni(tn)₃]Br₂·2H₂O (1.43 g, 3.0 mmol), and a catalytic amount of NH₄Cl (150 mg) were dissolved in methanol (50 cm³) and the mixture was refluxed for 20 min. The resultant solution was concentrated to ca. 30 cm³ on a rotary evaporator and was loaded onto a Sephadex LH-20 gel permeation column (diameter 4.5 cm, height 70 cm) and eluted with methanol. The coloured materials separated into a major blue band, a minor green one, and the starting tris(diamine) complex. The blue fraction was collected, purified on a small-size LH-20 gel permeation column, and concentrated to ca. 10 cm³. After addition of ethanol, the solution was kept at 5 °C in a refrigerator to give blue microcrystals, which were collected, washed with diethyl ether, and dried *in vacuo* (yield 7%) (Found: C, 34.65; H, 6.65; N, 5.35. Calc. for C₃₀H₆₄Br₂N₄NiO₂₂ 1a: C, 34.25; H, 6.15; N, 5.35%).

Complex 1b was prepared by similarly using [Ni(tn)₃]Cl₂·2H₂O as the starting complex. Yield 7% (Found: C, 37.10; H, 6.75; N, 5.77. Calc. for C₃₀H₆₅Cl₂NiO₂₂.₅: C, 36.80; H, 7.20; N, 5.35%).

[Ni(Galβ4Glc-tn)₂]X₂·nH₂O (X = Br, n = 1.5 2a; X = Cl, n = 4 2b). To a solution of lactose monohydrate (9.0 mmol, 3.24 g) in dimethylformamide (70 cm³) were added [Ni(tn)₃]Br₂·2H₂O (3.0 mmol, 1.43 g) dissolved in methanol (30 cm³) and NH₄Cl (160 mg). The mixture was incubated at 65 °C for 50 min. The coloured materials were chromatographed on a LH-20 gel permeation column, the main blue band was collected and further purified on a small-size LH-20 column three times. The blue solution was concentrated to ca. 10 cm³ and addition of propan-2-ol gave blue microcrystals of [Ni(Galβ4Glc-tn)₂]Br₂·1.5H₂O 2a in 33% yield (Found: C, 34.80; H, 6.85; N, 5.10. Calc. for C₃₀H₆₃Br₂N₄NiO₂₁.₅: C, 34.55; H, 6.10; N, 5.40%).

Complex 2b was prepared similarly using [Ni(tn)₃]Cl₂·2H₂O, in 22% yield (Found: C, 36.25; H, 7.30; N, 5.60. Calc. for C₃₀H₆₈Cl₂N₄NiO₂₄: C, 36.10; H, 6.85; N, 5.60%).

[Ni(Glcβ4Glc-tn)₂]X₂·nH₂O (X = Br, n = 2 3a; X = Cl, n = 4.5 3b). To a solution of cellobiose (9.0 mmol, 3.08 g) in dimethylformamide (120 cm³) was added [Ni(tn)₃]Br₂·2H₂O (3 mmol, 1.43 g) dissolved in methanol (30 cm³) and NH₄Cl (160 mg). The mixture was refluxed for 2–3 h. The resultant solution was chromatographed on a LH-20 gel permeation column. The purified blue solution was concentrated to ca. 10 cm³ and addition of ethanol gave blue microcrystals of [Ni(Glcβ4Glc-tn)₂]Br₂·2H₂O 3a in 16% yield (Found: C, 34.60; H, 6.85; N, 5.15. Calc. for C₃₀H₆₄Br₂N₄NiO₂₂: C, 34.45; H, 6.80; N, 5.30%).

Complex 3b was prepared from [Ni(tn)₃]Cl₂·2H₂O in 19% yield (Found: C, 35.50; H, 7.05; N, 5.45. Calc. for C₃₀H₆₉Cl₂N₄NiO₂₄.₅: C, 35.55; H, 6.85; N, 5.55%).

[Ni(Galα6Glc-tn)₂]X₂·nH₂O (X = Br, n = 1.5 4a; X = Cl,

n = 2.5 4b). These complexes were prepared by a similar method to that described for 2, using melibiose as disaccharide source: 4a, yield 4% (Found: C, 34.90; H, 6.75; N, 5.05. Calc. for C₃₀H₆₃Br₂N₄NiO₂₁.₅: C, 34.55; H, 6.10; N, 5.40%); 4b, yield 4% (Found: C, 37.05; H, 7.05; N, 5.30. Calc. for C₃₀H₆₅Cl₂N₄NiO₂₂.₅: C, 37.10; H, 6.75; N, 5.75%).

X-Ray Crystallography of Complex 1a.—Microcrystals of complex 1a were recrystallized from a minimum amount of hot methanol to yield large prismatic blue crystals apparently suitable for X-ray crystallography. However, the crystals were extremely delicate in air and lost clarity immediately after removal from the mother-liquors. So a crystal sealed into a glass capillary tube (diameter 0.7 mm) with the mother-liquor was used to collect diffraction data at room temperature on a Rigaku AFC5 four-circle automated diffractometer, ω–2θ mode with ω scan width = 1.30 + 0.30 tanθ and ω scanning speed = 8° min⁻¹. Even under such conditions only a low-grade intensity data set could be obtained, in particular very weak and poor reflection data in the high-angle range of 2θ > 30°. The unit-cell dimensions were determined by a least-squares method with 20 reflections in the range 10 < 2θ < 20°. Three standard reflections were monitored every 150 and showed only a ≈2% random variation in intensity for which no correction was made. Reflections in the one-eighth reciprocal space (h ⩾ 0, k ⩾ 0, l ⩾ 0) were measured (2θ < 45°) and Bijovoet pairs were not averaged. Intensities were corrected for Lorentz and polarization effects, and an absorption correction by the ψ-scan method was applied.

Crystal data. C₃₀H₆₄Br₂N₄NiO₂₂, M = 1051.36, hexagonal, space group P6₄22, a = 22.125(8), c = 21.464(9) Å, U = 9099(7) Å³, λ = 0.7107 Å, Z = 6, D_c = 1.151 g cm⁻³, crystal dimensions 0.70 × 0.65 × 0.40 mm, μ(Mo-Kα) = 1.68 mm⁻¹, F(000) = 3276.

Structure solution and refinement. The position of the nickel atom was determined by Patterson methods and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The structure was refined by full-matrix least-squares techniques. The hydrogen atoms bound to carbon were located by assuming a tetrahedral co-ordination with a C–H bond distance of 0.95 Å, and were not refined. The final refinement was carried out with anisotropic thermal parameters for the Ni and Br atoms and isotropic ones for other non-hydrogen atoms {127 parameters and 971 [I > 4σ(I)] of 2092 reflections}, and converged to R = Σ||F_o| − |F_c||/Σ|F_o| = 0.080 and R' = [Σw(|F_o| − |F_c|)²/Σw|F_o|²]^½ = 0.094 [w = 1/σ²(F_o)]. The atomic scattering factors and values of f' and f'' for Br, Ni, O, N and C atoms were taken from refs. 19 and 20. The known absolute configurations of the asymmetric carbon atoms of maltose were used as internal references for asymmetric centres to determine the absolute configuration of the complex. The final Fourier difference synthesis still showed peaks at heights up to 0.39 e Å⁻³ around the Br atoms. The final atomic co-ordinates for non-H atoms are listed in Table 1. All calculations were performed on a Digital Vax station 3100 M38 computer with the TEXSAN-TEXRAY package.[21] The perspective views were drawn by using the program ORTEP.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Measurement of X-Ray Absorption Spectra.—Beam line 10B at the Photon Factory of the National Laboratory for High Energy Physics[23] (2.5 GeV, 300–340 mA) was used with a Si(311) channel-cut monochromator. The experiments were done in the transmission mode on boron nitride pellets. The monochromated X-ray beam (1 × 6 mm) passed through the first ionization chamber (17 cm, detecting gas N₂), which measured incident-beam intensity I₀, then through the sample, and finally through another ionization chamber (31 cm, detecting gas 85% N₂ + 15% Ar), which measured the

Table 1 Atomic coordinates of non-hydrogen atoms with estimated standard deviations (e.s.d.s) for complex **1a**

Atom	x	y	z
Br	0.599 3(3)	0.187 3(2)	0.203 74(17)
Ni*	0.613 07(10)	1.226 1	1.000 0
O(1)	0.583 3(7)	1.140 4(6)	1.066 9(7)
O(2)	0.556 0(7)	0.994 0(8)	1.099 5(6)
O(3)	0.678 3(7)	1.001 3(8)	1.140 5(6)
O(4)	0.751 2(7)	1.151 7(8)	1.037 4(7)
O(5)	0.797 6(17)	1.057 9(16)	1.033 2(15)
O(6)	0.560 8(11)	0.875 2(10)	1.123 5(9)
O(7)	0.548 7(13)	0.813 0(12)	1.238 8(13)
O(8)	0.672 0(18)	0.900 3(17)	1.302 8(16)
O(9)	0.739 6(10)	0.945 4(10)	1.148 0(10)
O(10)	0.862(2)	1.001(2)	1.218 0(18)
O(111)	0.461(2)	0.344(2)	0.260 1(19)
N(1)	0.702 8(9)	1.210 6(9)	0.994 9(10)
N(2)	0.651 3(9)	1.295 4(8)	1.075 3(8)
C(1)	0.771 7(11)	1.280 4(11)	0.981 9(10)
C(2)	0.767 8(11)	1.316 9(11)	0.922 3(11)
C(3)	0.625 9(11)	1.344 8(11)	1.072 4(11)
C(11)	0.703 0(11)	1.175 6(11)	1.045 1(10)
C(12)	0.630 8(12)	1.116 5(12)	1.050 7(11)
C(13)	0.619 1(13)	1.059 8(13)	1.099 2(12)
C(14)	0.683 9(10)	1.042 7(10)	1.087 7(10)
C(15)	0.749 8(12)	1.112 1(12)	1.087 2(13)
C(16)	0.815 2(14)	1.101 8(14)	1.080 0(14)
C(21)	0.680 6(12)	0.942 1(12)	1.122 4(11)
C(22)	0.619 7(12)	0.880 7(12)	1.153 6(13)
C(23)	0.617 9(13)	0.880 7(12)	1.221 1(11)
C(24)	0.691 6(18)	0.900 3(17)	1.245 1(18)
C(25)	0.738 6(13)	0.944 6(12)	1.205 6(13)
C(26)	0.788(3)	0.937(3)	1.261(3)

* Multiplicity is 0.5 in the special position (C_2).

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transmitted intensity I. In order to avoid contamination from higher harmonics, the maximum absorbance measured by this system was kept less than 4. Under such conditions, the amount of higher harmonics X-rays detected by a solid-state detector (SSD) is less than 0.2% of the fundamental X-rays.[24] The absorption spectra, $\mu x = \ln(I_0/I)$, where x is the sample thickness and μx is the total absorption, were recorded as a function of the X-ray photon energy E, with an integration time of 1 s per point at room temperature, 700 steps covering the K edge for Ni (7630–9840 eV), 260 steps for XANES (8280–8420 eV) and 250 steps for EXAFS (8420–9130 eV). Samples of complexes **1a**, **2a**, **3a**, **4a** and [Ni(L-Rha-tn)$_2$]Br$_2$·2H$_2$O·MeOH **5** were measured.

The EXAFS spectrum is derived from the absorption spectrum above the Ni K edge where $\mu(k)$ is the absorption coefficient as a function of k, the photoelectron wave vector defined as $[(2m/\hbar^2)(E - E_0)]^{\frac{1}{2}}$ ($E_0 = 8332\,\text{eV}$). After conversion of E into the photoelectron wave vector k, the data were multiplied by k^3 and the modulation of the absorption coefficient, $\chi(k) = (\mu - \mu_0)/\mu_0$, was obtained by removing a cubic spline background fit to the data with four sections each of $\Delta k = 4.0\,\text{Å}^{-1}$, normalized with the edge jump, and corrected for the μ_0 drop-off via Victoreen's true absorption. The theoretical expression (1) is obtained for the case of single scattering[25]

$$k^3\chi(k) = \Sigma_i(k^2N_i/r_i^2)S_iF_i(k)\exp(-2\sigma_i^2k^2)\sin[2kr_i + \varphi_i(k)] \quad (1)$$

where r_i, N_i, S_i, $F_i(k)$, $\varphi_i(k)$ and σ_i represent the interatomic distance, the co-ordination number, the reducing factor, the backscattering amplitude, the phase shift, and the Debye–Waller factor, respectively. The backscattering amplitude $F_i(k)$ and the phase shift $\varphi_i(k)$ functions employed were the theoretical curves tabulated by Teo and Lee.[26,27] Four parameters, N_i, r_i, E_{0i}^{p} (empirical E_0 value) and σ_i, were varied

in the non-linear least-squares refined curve fitting, and the fixed reducing factors S_i obtained from the analysis of complex **5** were used. All calculations were performed on a HITAC S-800 computer at the Computer Center of the University of Tokyo with the systematic programs EXAFS1.[28]

Results and Discussion

Synthesis of Nickel(II) *Complexes containing Disaccharides.*— From the reaction of disaccharides with [Ni(tn)$_3$]X$_2$·2H$_2$O (X = Br or Cl), in methanol or methanol–dimethylformamide, bis(N-D-aldosylpropane-1,3-diamine)nickel(II) complexes **1–4** were isolated. The yields varied (4–33%) according to the starting disaccharide used and the refluxing time. In the case of maltose, a prolonged refluxing time decreased the yield of **1** due to degradations of the carbohydrate resulting in brown compounds (so-called 'browning reaction').[29] All the compounds isolated were very hygroscopic and should be treated under a nitrogen atmosphere.

Analytical data showed that complexes **1–4** consisted of two diamines and two disaccharide residues per nickel atom, together with some solvated water molecules. In the IR spectra, besides a broad band for hydroxyl groups, a moderate peak corresponding to $\delta(N-H)$ was observed around 1600 cm^{-1}, shifted to higher energy compared with that of the starting complex [Ni(tn)$_3$]$^{2+}$, suggesting glysoylamine formation just as observed in the reactions of [Ni(diamine)$_3$]$^{2+}$ (diamine = en or tn) with monosaccharides (D-glucose, -galactose, -mannose and L-rhamnose).[2,3,7]

The magnetic data demonstrated that the nickel ions have two unpaired electrons, and the magnetic moments fall within the range of 3.04–3.56 expected for octahedral complexes of nickel(II) (Table 2).[30]

maltose (Glcα4Glc)   lactose (Galβ4Glc)

cellobiose (Glcβ4Glc)   melibiose (Galα6Glc)
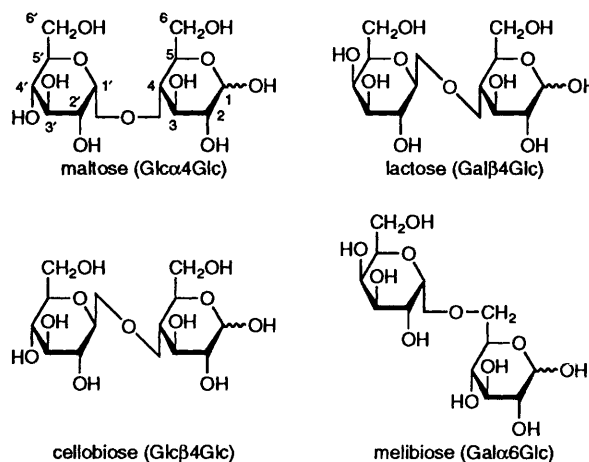
Absorption and circular dichroism spectra of the complexes are presented in Fig. 1, and summarized in Table 2. The positions of the absorption maxima in methanol are almost identical for **1–4**, indicating that these complexes have essentially the same structure around the metal centre. Further, no conspicuous difference between the bromide and the chloride salts ruled out the co-ordination of halide anions to the nickel. The absorption spectra in the near-infrared and visible regions consist of three principal bands, v_1, v_2 and v_3, with comparatively low intensities ($\varepsilon < 30$ dm^3 mol^{-1} cm^{-1}), which are characteristic of octahedral nickel(II) complexes and assigned to the three spin-allowed transitions $^3A_{2g}(F) \longrightarrow ^3T_{2g}(F)$, $^3A_{2g}(F) \longrightarrow ^3T_{1g}(F)$ and $^3A_{2g}(F) \longrightarrow ^3T_{1g}(P)$, respectively.[31] The energies of these maxima (10^3 cm^{-1}) are 10.5 ± 0.2, 17.0 ± 0.1, and 27.4 ± 0.4 respectively for all compounds, and are almost identical to those found for [Ni(L-Rha-tn)$_2$]Br$_2$·2H$_2$O·MeOH **5**.[7]

In the CD spectra of complexes **1–4** large Cotton effects

Table 2 Absorption and circular dichroism spectral (in methanol)* and magnetic data for the nickel(II) complexes of disaccharides

Compound	Absorption $v_{max}(\varepsilon)$	CD v_{max} ($10^2 \times \Delta\varepsilon$)		μ_{eff}
1a [Ni(Glcα4Glc-tn)₂]Br₂	10.54 (7.72)	14.29 (−2.0)		3.50
	17.12 (16.39)	17.64 (+3.0)		
	27.55 (29.22)	27.93 (+0.9)		
1b [Ni(Glcα4Glc-tn)₂]Cl₂	10.57 (7.45)	11.98 (−3.9)		3.04
	17.02 (18.70)	17.01 (+8.7)		
	27.25 (23.28)	27.78 (+3.1)		
2a [Ni(Galβ4Glc-tn)₂]Br₂	10.59 (5.81)	12.80 (+0.2)	28.33 (+0.5)	3.56
	17.09 (15.09)	17.27 (+3.8)		
	27.35 (22.44)	24.94 (+0.9)		
2b [Ni(Galβ4Glc-tn)₂]Cl₂	10.32 (4.23)	12.72 (−1.0)	17.15 (+1.6)	3.35
	17.01 (13.88)	14.25 (+3.8)	28.33 (+0.7)	
	27.25 (23.31)	25.16 (+1.0)		
3a [Ni(Glcβ4Glc-tn)₂]Br₂	10.45 (6.82)	12.69 (−2.2)	25.25 (+1.0)	3.48
	17.01 (16.31)	14.08 (+4.5)	27.93 (+16.3)	
	27.32 (26.03)	17.27 (+0.8)		
3b [Ni(Glcβ4Glc-tn)₂]Cl₂	10.47 (6.77)	12.80 (+1.0)	28.41 (+1.2)	3.39
	17.01 (15.54)	17.27 (+4.9)		
	27.40 (29.60)	25.13 (+1.3)		
4a [Ni(Galα6Glc-tn)₂]Br₂	10.66 (6.82)	14.29 (−1.6)		3.31
	16.98 (14.91)	17.24 (+2.4)		
	27.25 (26.80)	28.57 (+0.7)		
4b [Ni(Galα6Glc-tn)₂]Cl₂	10.53 (7.29)	12.20 (−3.2)		3.32
	17.12 (16.39)	17.24 (+4.0)		
	27.74 (30.26)	25.00 (+1.2)		

* v_{max} in 10^3 cm⁻¹, ε or $\Delta\varepsilon$ in dm³ mol⁻¹ cm⁻¹.

Table 3 Selected bond distances (Å) and angles (°) of complex 1a with e.s.d.s in parentheses

Ni–O(1)	2.20(1)	Ni–N(1)	2.18(2)
Ni–N(2)	2.09(2)	O(1)–C(12)	1.43(3)
N(1)–C(1)	1.56(2)	N(1)–C(11)	1.33(3)
N(2)–C(3)	1.46(3)	C(1)–C(2)	1.54(3)
C(2)–C(3')	1.50(3)	C(11)–C(12)	1.48(3)
O(1)–Ni–O(1')	83.4(7)	O(1)–Ni–N(1)	78.5(6)
O(1)–Ni–N(1')	89.7(6)	O(1)–Ni–N(2)	88.0(6)
O(1)–Ni–N(2')	169.1(6)	N(1)–Ni–N(1')	164.3(9)
N(1)–Ni–N(2)	95.0(8)	N(1)–Ni–N(2')	94.9(8)
Ni–O(1)–C(12)	102(1)	Ni–N(1)–C(1)	112(1)
Ni–N(1)–C(11)	109(2)	C(1)–N(1)–C(11)	116(2)
Ni–N(2)–C(3)	110(1)	N(1)–C(1)–C(2)	113(2)
C(1)–C(2)–C(3')	113(2)	N(2)–C(3)–C(2')	118(2)
N(1)–C(11)–C(12)	105(2)	O(1)–C(12)–C(11)	111(2)

were observed in the region of 9000–20 000 cm⁻¹ (around v_1 and v_2), and the spectral patterns were similar to each other. It is well known that the co-ordination of an optically active ligand to a metal ion induces optical activity in the d–d electronic transitions of the metal ion.[2] Thus, the CD spectral data strongly suggested the co-ordination of sugar residues to the nickel atom. Furthermore, it was implied that the co-ordinative interaction between the metal ion and the dissaccharide residue was exlusively comprised of the reducing terminal unit (D-glucose), and not of the non-reducing terminal one which was presumably away from the metal centre.

From these analytical, magnetic, and spectral data the nickel(II) complexes 1–4 were assumed to have a pseudo-octahedral cis-(O,O)-[NiN₄O₂] structure where two glycosyl-amine ligands from a diamine and a disaccharide, n-(4- or 6-D-aldopyranosylglucosyl)propane-1,3-diamine, co-ordinate to the nickel atom in a tridentate manner. Assuming this structure, some isomers, including the Δ and Λ configuration around the metal centre and the *mer* and *fac* geometrical modes, are possible, but they could not be determined by spectroscopic analyses. In order to clarify the detailed structure, an X-ray diffraction analysis of complex 1a was undertaken.
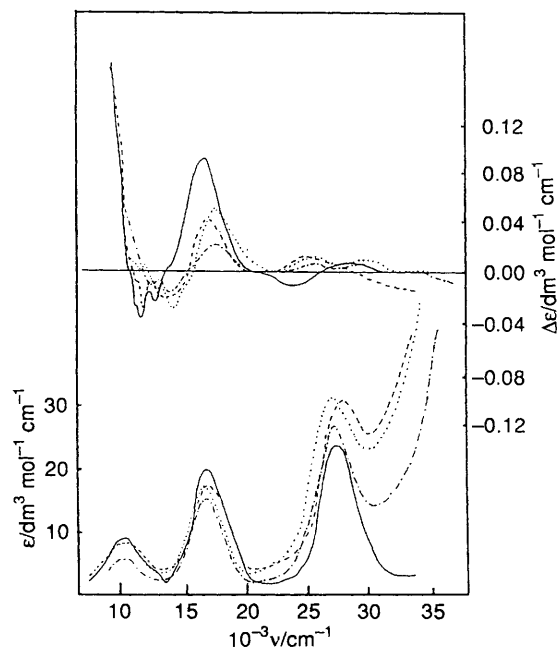
Fig. 1 Electronic absorption (lower) and circular dichroism spectra of nickel(II) complexes of disaccharides in methanol: ——, 1a; — · —, 2b; — — — —, 3b; and — — — — —, 4b

Molecular Structure of [Ni(Glcα4Glc-tn)₂]Br₂·2H₂O 1a.—A perspective drawing of the complex cation is given in Fig. 2, and selected bond distances and angles are in Table 3. Although the present X-ray analysis is a low-grade one owing to the extremely delicate nature of the single crystals as mentioned in the Experimental section, the whole steric structure of 1a could be discernible. The compound consists of one complex cation, two bromide anions, and two water molecules of crystallization. The nickel atom is located on a crystallographic C_2 symmetry axis and is octahedrally co-ordinated by two glycosylamine ligands (Scheme 1), through four nitrogen atoms and two oxygen atoms. The two oxygen atoms lie in a *cis* arrangement. The
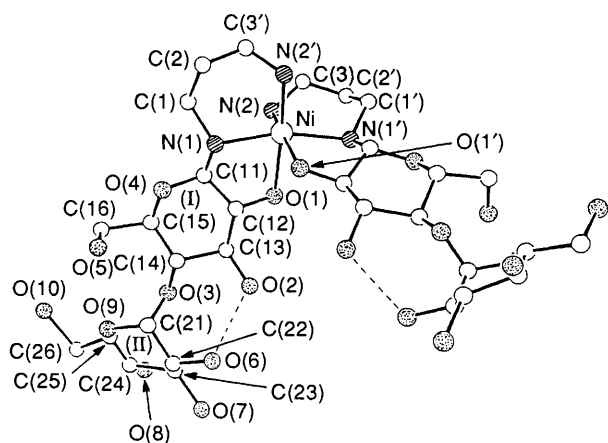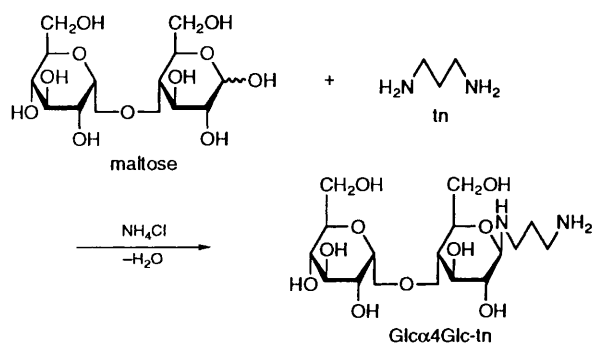
Fig. 2 Perspective drawing of the complex cation of 1a

Scheme 1

Fig. 3 Perspective view showing the dimeric structure of complex 1a

complex cation is fairly distorted from ideal O_h symmetry with the minimum trans angle of 164.3(9)° [N(1)–Ni–N(1')]. The two glycosylamine ligands co-ordinate to the nickel atom in a meridional mode with Λ configuration around the metal centre, as found in [Ni(L-Rha-tn)₂]²⁺ 5 which has also the Λ configuration around the metal.[7] Each ligand attaches to the metal at three points through the oxygen atom of the hydroxyl group on C² of the maltose moiety and the two nitrogen atoms of the 1,3-diaminopropane residue. The pyranoid ring (I) of the reducing terminal unit in maltose adopts the usual β-⁴C₁ chair conformation and the ring (II) of the non-reducing terminal unit takes the α-⁴C₁ chair form. The dihedral angle between the two least-squares planes for the pyranoid rings is 50.5°; this folded structure of the disaccharide part is attributable to the hydrogen-bonding interaction between the hydroxyl group on C³ and that on C²' [O(2)···O(6) 2.73(3) Å], which was also observed in the crystal structure of maltose.[32] In our series of nickel(II)–sugar complexes also including the present complex, the anomeric form of the N-glycosidic linkage is exclusively β, and no complex with α-glycosylamine has been isolated thus far. The five-membered chelate ring involving the sugar moiety [NiN(1)C(11)C(12)O(1)] adopts a λ-gauche conformation and the six-membered chelate ring of the diamine part [NiN(1)-C(1)C(2)C(3')N(2')] adopts a stable chair form. The absolute configuration around the secondary nitrogen atom [N(1)] is S in the notation of Cahn et al.[33] and the primary nitrogen atom [N(2')] occupies the equatorial position with respect to the pyranose ring. Consequently, the gauche conformation of the chelate ring formed by the sugar moiety and the absolute configuration around the secondary glycosidic nitrogen atom depend on the orientation of the hydroxyl group on the C² carbon atom of the carbohydrate as predicted from the crystal structures of [Ni(L-Rha-tn)₂]²⁺ 5 and [Ni(D-GlcN-en)₂]²⁺ 6. This is the first structurally characterized nickel(II) complex involving a glycosylamine from D-glucose, and is also the first example of transition-metal complexes containing maltose.
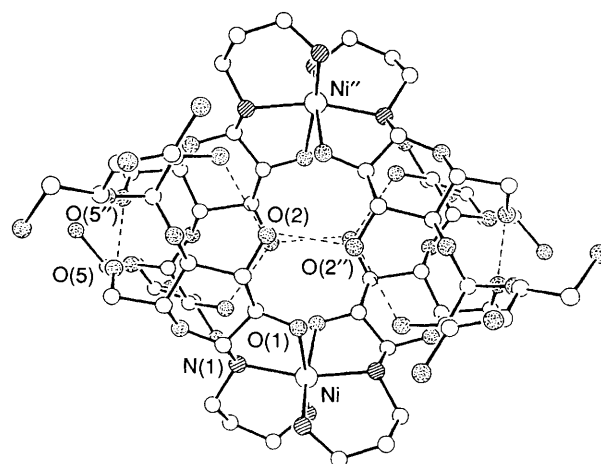
Unlike complex 5, in which the pyranose ring of L-rhamnose (6-deoxy-L-mannose) rises out of the equatorial plane defined by the nickel atom and the two co-ordinated nitrogen and one oxygen atom of the L-Rha-tn moiety, the pyranoid ring (I) (the reducing terminal unit) in complex 1a is almost coplanar with the equatorial plane defined by the Ni, N(1), N(2') and O(1) atoms, the dihedral angle between them being 17.6°.

The bite angle of the six-membered chelate ring including the diamine part [N(1)–Ni–N(2')] is 94.9(8)°, and that of the five-membered one involving the sugar moiety [N(1)–Ni–O(1)] is 78.5(6)°, which are normal values for six- and five-membered diamine rings, respectively. The trans angle between the terminally co-ordinating atoms of the glycosylamine ligand [N(2')–Ni–O(1)] is 169.1(6)° which is similar to those in complex 5 (168.4°) but larger than that observed in 6 (160.7°). From these, the strain existing in the multiple chelation of the glycosylamine ligands is presumed to be significantly relieved by the effect of the six- compared with that of the five-membered diamine ring.

In the crystal packing the complex cation of 1a exists in a novel dimeric form as shown in Fig. 3. The two complex cations interact along the C_2 symmetry axis and are supported by four intermolecular hydrogen bonds between the hydroxyl groups on the C³ carbons and between those on the C⁶ carbons of the reducing terminal unit in maltose, based on the interatomic distances O(2)···O(2") (1 − x, 2 − y, z) 2.62(3) and O(5)···O(5") (x − y + 1, 2 − y, 2 − z) 2.64(6) Å. The dimer involves a small cavity in the centre which is surrounded by the four carbohydrate residues. The metal–metal separation Ni···Ni" (1 − x, 2 − y, z) is 8.667(8) Å. The intermolecular sugar–sugar interaction between the transition metal–sugar complexes as observed in 1a is the first of its type as far as we know. Although it is not clear whether the dimeric structure is maintained in solution, the elucidated structure could provide some basic information in connection with interactions between oligosaccharide chains in biological systems, and could be considered to involve a useful inclusion site for chiral organic compounds having polar groups.

X-Ray Absorption Analyses.—In order to obtain direct structural parameters relevant to the nickel centre for the other disaccharide complexes, X-ray absorption spectroscopic analyses were performed on 1a, 2a, 3a and 4a as well as [Ni(L-Rha-tn)₂]²⁺ 5 as a reference. The XANES spectra were derived from the absorption spectra around the Ni K edge (8280–8420 eV) by removing background via Victoreen's pre-edge fits, and were normalized by setting the intensity of the post-edge background absorption at 8390 eV to unity. The spectra of 1a–4a and 5 are closely similar and in every case three peaks A–C are observed (Fig. 4). The feature A could be assigned to a 1s ⟶ 3d transition and B and C have generally

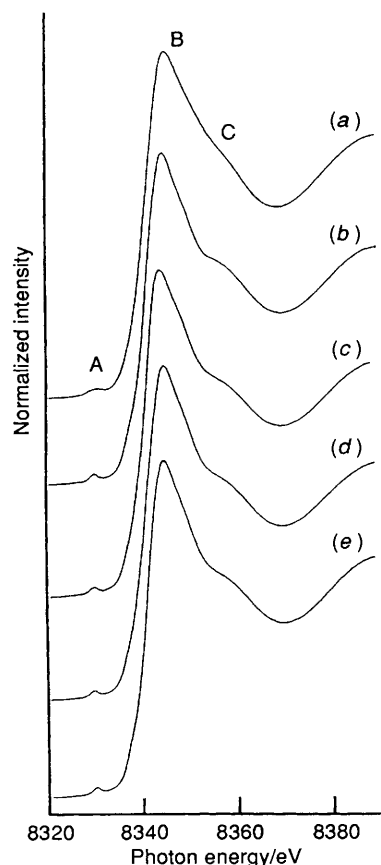Fig. 4 The XANES spectra of the nickel(II) complexes, 5 (a), 1a (b), 2a (c), 3a (d) and 4a (e)

Table 4 XANES spectral data for the nickel(II) complexes

	Peak A		B		C	
Compound	E^a/eV	$10^2 I^b$	E/eV	I	E/eV	I
5	8332.0	4.9	8346.7	1.45	8360.7	0.98
1a	8332.0	5.6	8347.0	1.66	8358.2	1.09
2a	8332.0	4.6	8346.8	1.56	8361.1	1.01
3a	8332.0	4.9	8346.9	1.56	8361.3	1.01
4a	8332.0	4.7	8347.5	1.56	8361.6	0.99

^{a} The energy for A is fixed. ^{b} Normalized intensity.

been understood as arising from continuum resonances involving multiple-scattering effects, or a 1s ⟶ 4p transition and 1s ⟶ continuum resonance.[34] The normalized peak intensities and their positions are summarized in Table 4. The peak energies and intensities of 1a–4a are distributed in a narrow range, and are quite similar to those of 5.

The Fourier transforms of the raw EXAFS oscillation $[k^3\chi(k)]$ are shown in Fig. 5. Those of 1a and 5 showed an intense peak at about 1.7 Å and a moderate peak around 2.7 Å (before phase-shift correction), which were back-Fourier transformed by the use of an appropriate window (1.1–3.2 Å) to produce abstracted EXAFS oscillation subject to curve-fitting analysis (Fig. 6). The structural parameters from the two-term curve-fitting techniques, $k^3\chi_{calc}(k) = k^3\chi_{O/N}(k) + k^3\chi_C(k)$, are in good agreement with those from X-ray crystallography, and indicated that the first large peak is attributable to the nitrogen and oxygen atoms directly co-ordinated to the nickel and the second peaks to the contribution of the carbon atoms in the chelation rings. The nitrogen and the oxygen atoms in the first shell could not be distinguished in the present analyses. The
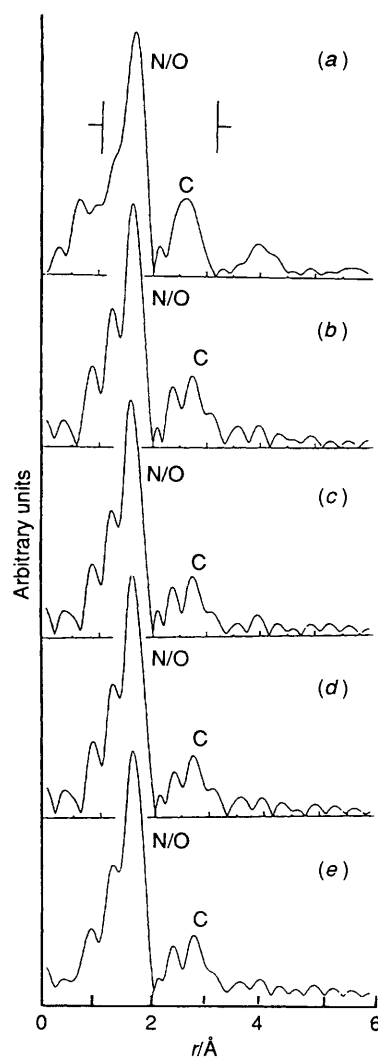

Fig. 5 The EXAFS Fourier transforms of the complexes in Fig. 4

Table 5 Atomic parameters for the first shell determined by EXAFS analysis

	EXAFS					Crystallography	
Compd.	A–B^a	r^b/Å	N^c	σ	R (%)^d	r/Å	N
5	Ni–N/O	2.10	6.0	0.063	4.0	2.12	6.0
1a	Ni–N/O	2.09	5.4	0.057	5.7	2.16	6.0
2a	Ni–N/O	2.09	5.6	0.053	5.6		
3a	Ni–N/O	2.09	5.5	0.054	5.3		
4a	Ni–N/O	2.09	5.9	0.059	5.7		

^{a} A is the absorber (Ni) and B the backscattering atom. All backscattering atoms in the first sphere are calculated as nitrogen. Fourier-filtered $k^3\chi_{obs}(k)$ was fitted with $k^3\chi_{N/O}(k) + k^3\chi_C(k)$. ^{b} Estimated errors are ±0.03 Å. ^{c} The number of neighbouring atoms (Ni–N/O, Ni–C) referenced to $[Ni(L-Rha-tn)_2]^{2+}$ 5. Estimated errors are ±0.6. ^{d} $R = \{\Sigma[k^3\chi_{obs}(k) - k^3\chi_{calc}(k)]^2/\Sigma[k^3\chi_{obs}(k)]^2\}^{\frac{1}{2}}$, where $\chi_{obs}(k)$ and $\chi_{calc}(k)$ are Fourier-filtered and calculated data.

other three Fourier transforms for 2a, 3a and 4a exhibited closely similar patterns to that of 1a, and the structural parameters also indicated an octahedral mononuclear nickel(II) structure (Table 5).

From the X-ray absorption analyses as well as the other spectroscopic data it was concluded that the disaccharide complexes 1–4 have almost identical geometrical, configur-
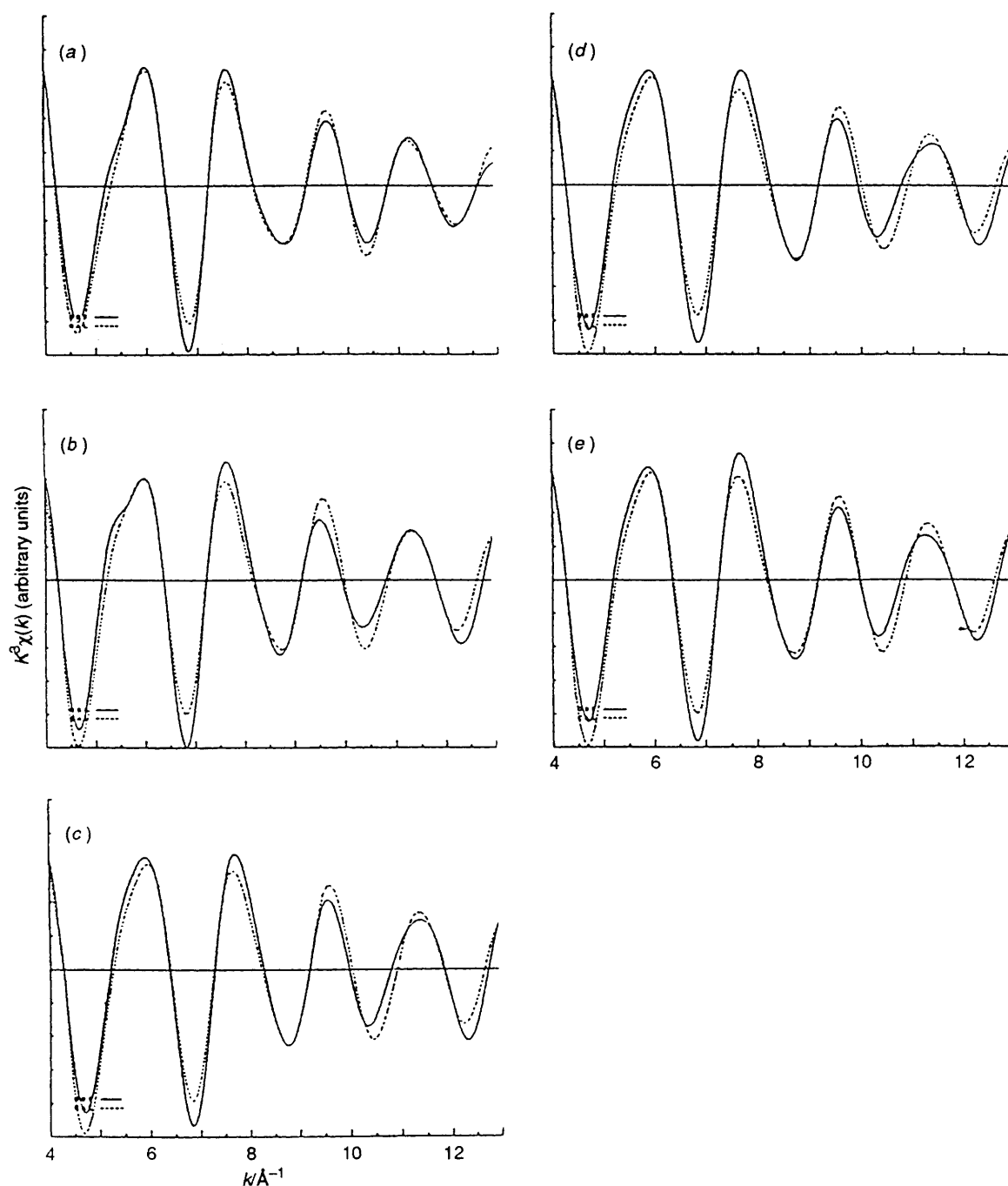
Fig. 6 k^3-Weighted Fourier-filtered experimental EXAFS oscillation [$k^3\chi_{obs}(k)$, solid line] and simulated EXAFS oscillation [$k^3\chi_{calc}(k)$, dotted line] of the complexes in Fig. 4

ational, and conformational modes around the nickel atom as depicted in Fig. 7. The central nickel atom is octahedrally co-ordinated by two tridentate glycosylamine ligands, N-(β-D-aldosyl)propane-1,3-diamine, in a *meridional* mode with Λ configuration around the metal. The *gauche* conformation of the chelate ring formed by the D-glucose moiety is λ and the absolute configuration around the secondary glycosidic nitrogen atom is S. The non-reducing terminal unit of the disaccharides had no influence on the metal centre at all.

The present study clearly revealed the structure of the nickel(II) complexes containing disaccharides. It should be noted that this is the first example of (1) a novel intermolecular sugar–sugar interaction and (2) where the co-ordination behaviour of the glucose unit in an octahedral nickel(II) complex is crystallographically established. Further, the

spectral data presented will be useful fundamental information to explore the chemistry of transition metal–sugar complexes.

Acknowledgements

(a)

(b)

(c)
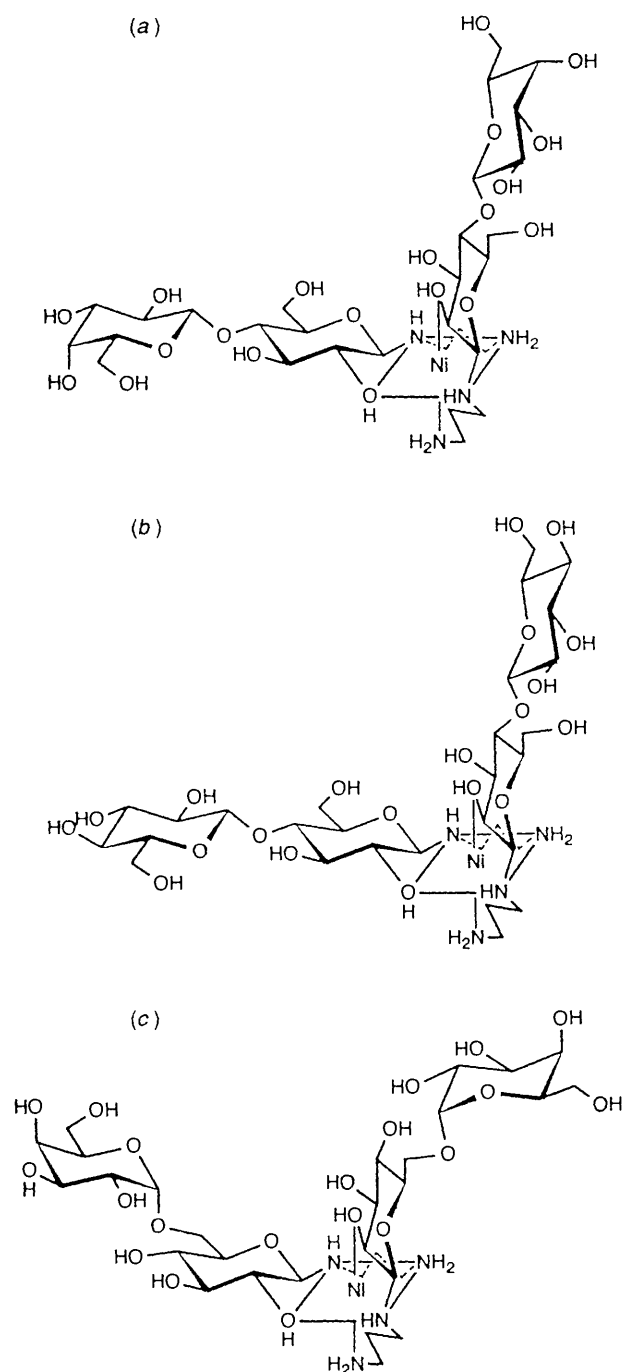
Fig. 7 Proposed structures for (a) [Ni(Galβ4Glc-tn)₂]²⁺ **2**, (b) [Ni(Glcβ4Glc-tn)₂]²⁺ **3** and (c) [Ni(Galα6Glc-tn)₂]²⁺ **4**

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