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Ni(II) complexes with Schiff bases derived from amino sugars

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Abstract

It was found by ^{1}H and ^{13}C NMR spectroscopy that the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose exhibits enol-imine–keto-amine and anomeric equilibria in methanolic, and in dimethyl sulfoxide solutions. The reaction of the Schiff base with nickel acetate gave the bidentate, mononuclear Ni(II) complex that was characterized by spectroscopic methods and by cyclic voltammetry. The coordination of the Schiff base to the metal is through the enol–imine tautomeric form, and the anomeric equilibrium remains in dimethyl sulfoxide solutions. This complex was also obtained by reaction of D-glucosamine with Ni(II) salicylaldehydate. The same reaction was employed for the synthesis of bis-*N*-[2-deoxy-D-galactopyranosyl-2-(2-hydroxybenzaldiminate)]Ni(II). The small paramagnetic shifts of the ^{1}H NMR resonances of the complexes suggest that paramagnetic species are present in low proportions.

Keywords: D-Galactosamine; D-Glucosamine; Schiff bases; Ni(II) complexes

1. Introduction

It is well known that carbohydrates form complexes with metal ions. They are usually studied in solution, and some have been isolated as stable solids.[1–4] The synthesis and characterization of Ni(II), Co(III), and Cu(II) complexes with N-glycosides formed from aldoses and diamines were reported.[5,6] Yano and coworkers have studied the synthesis and have characterized the nickel(II) complexes containing N-glycosides derived from the reaction of amino sugars with diamines.[7] Epimerization and stereoselective uptake of epimeric sugars by Ni(II) complexes have been reported by Yano.[8] Recently, Gyurcsik and Nagy reviewed the studies conducted in the last two decades on the metal-ion complexes with simple sugars and their derivatives.[9]

The use of Schiff bases as ligands in the formation of transition-metal complexes have been extensively studied.[10] Amino sugars readily form Schiff bases with aromatic aldehydes, which have been shown to give stable complexes with transition-metal ions suchs as Cu(II), Fe(III), and Co(II).[11–13] Adam and Hall could not obtain Ni(II) complexes with salicylaldimines derived from amino sugars, probably due to the low stability constant of the complexes.[11] Complexes with chiral Schiff base ligands might be useful as asymmetric catalysts. Holland and coworkers reported that Cu(II) Schiff base complexes derived from amino sugars catalysed the asymmetric cyclopropanation of olefins.[14]

In this work the characterization in solution of the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose, and the synthesis and characterization of Ni(II) complexes with the Schiff bases derived from 2-amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-galactose with *o*-salicyladehyde are presented.

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2. Results and discussion

2.1. The Schiff base of 2-amino-2-deoxy-D-glucose with *o*-salicylaldehyde

Although the Schiff base of *o*-salicylaldehyde with D-glucosamine has been known for many years, its properties in solution have not been described. In MeOH and DMSO solutions, the Schiff base presents the anomeric and the enol–imine versus keto–imine equilibria (Fig. 1). Tautomerization in the condensation products of methylamine and benzylamine with 2-hydroxy-1-naphtaldehyde has been reported. In deuterochloroform, the keto-amine form was detected by ^{1}H NMR spectroscopy.[15] Korobov and coworkers found by spectroscopic methods that the Schiff base of alkyl amines with 5-nitrothiosalicylaldehyde exist predominantly in the keto-amine form in nonpolar solvents.[16] On the other hand, the 2-hydroxynaphthaldimines of D-galactosamine, D-glucosamine and D-mannosamine exhibit the enol-imine–keto-amine and the anomeric equilibria in DMSO solutions.[17]

The ^{1}H NMR spectrum of the Schiff base obtained by reaction of D-glucosamine with *o*-salicylaldehyde showed the presence of two tautomeric equilibria in MeOH. At low field, the signal assigned to the imino proton appeared as two singlets at 8.401 and 8.384 ppm, due to the sugar residue in the $\alpha \rightarrow \beta$ equilibrium.[17] Also, two signals assigned for the vinyl proton of the keto-amine tautomer appeared at 6.843 and 6.823 ppm due to the anomeric equilibrium. Integration values for the imino protons (0.942 and 1.362) and for the vinyl protons (0.722 and 0.699) indicate that the enol-imino form predominates. The anomeric proton of the α sugar residue appeared as two pairs of doublets at 5.264 ppm (*J* 3.56 Hz) and 5.165 (*J* 3.49 Hz). The doublet at 4.820 ppm (*J* 7.81 Hz) was assigned to the anomeric proton of the β sugar residue. Integration values of the α anomeric proton (1.714) and of the β anomeric proton (2.015) indicates a slight predominance of the β anomer.

The spectrum of the Schiff base in DMSO-d_6 showed, moreover, two singlets at 14.143 and 13.412 ppm assigned to the aromatic hydroxyl proton (Fig. 2). The resonances of the O–H and =CN–H protons (8.441 and 8.369 ppm) were confirmed by measuring the spectrum after adding D_2O and are in accordance with data previously found for 2-hydroxynaphthaldimines of amino sugars.[17] The doublets at 7.432, 7.376, and 7.299, 7.254 ppm were assigned, according to the literature to H-4 and H-5 of the aromatic ring.[18] The signals at 7.134 and 7.125 ppm were attributed to the vinyl proton of the keto-amine tautomeric form. At higher field, the signals of H-6 and H-3 appeared at 6.854 and 6.793 ppm, respectively. The two doublets at 5.265 ppm (*J* 4.8 Hz) and 5.143 (*J* 4.8 Hz) were assigned to the anomeric protons of the α anomer in the enol-imine and keto-amine equilibrium, while the doublet at 4.9885 (*J* 7.60 Hz) was attributed to H-1 of the β form. It was found that the α/β ratio for the anomeric proton signals was 2.0:1.0, which is in good agreement with the ratio of the

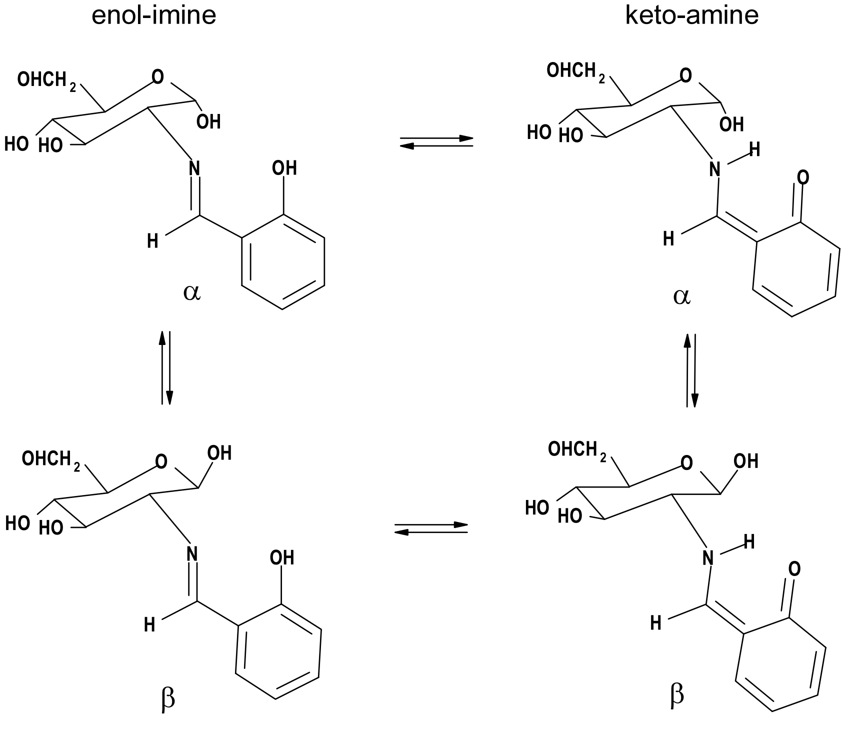

Fig. 1. Enol-imine versus keto-amine and anomeric equilibria of the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose, in MeOH or DMSO solution.

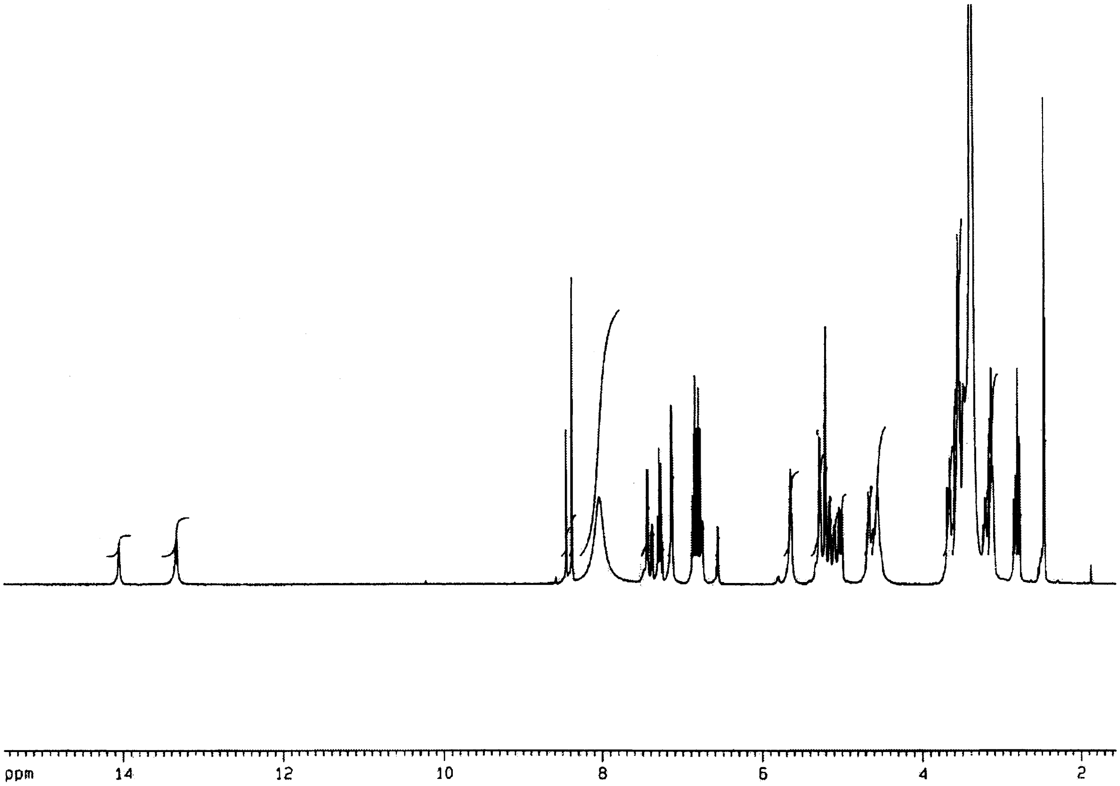

Fig. 2. ^{1}H NMR spectrum (400 MHz, 30 °C, DMSO-d_6) of the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose.

phenolic protons (1.84:1.00). Although the signals of the proton of the O–H group were present in the spectrum taken in DMSO-d_6, integration ratio of the imino proton and the vinyl proton (1.00:1.06) indicates a slight predominance of the keto-amine tautomeric form.

Fig. 3 shows the ^{13}C NMR spectrum of the Schiff base in DMSO. The spectrum does not present resonances assigned to the carbonyl carbon, but the signal at 116.88 ppm could be assigned in the HMQC spectrum (Fig. 4) to the olefinic carbon linked to nitrogen of the HC=C–N group, which indicates the existence of the keto-amine versus enol-imine equilibrium. Two signals for each of the anomeric carbons support this assumption.

2.2. Synthesis of bis-*N*-[2-deoxy-D-glucopyranosyl-2-(2-hydroxybenzaldiminate)]nickel(II) (1) and bis-*N*-[2-deoxy-D-galactopyranosyl-2-(2-hydroxybenzaldiminate)]nickel(II) (2)

Synthesis of the Ni(II) complex of 2-deoxy-2-(2-hydroxybenzalaldimino)-D-glucose was accomplished by two methods. In the first method the Schiff base was reacted in a 2:1 molar ratio with $Ni(OAc)_2$ to result in the formation of the complex. The microanalysis results are consistent with a bidentate, mononuclear Ni(II) complex. The FTIR spectrum showed a shift (25 cm^{-1}) to lower wavenumbers in the C=N absorption relative to the free ligand spectrum, indicating the coordination of the nitrogen atom to the Ni ion. Two new bands, in relation to the free ligand, in the second-derivative spectrum assigned to Ni–O (397.8 cm^{-1}) and to Ni–N (276.7 cm^{-1}) stretching vibrations corroborates the formation of the Ni(II) complex.[19]

An alternative method involved the reaction of D-glucosamine with Ni(II) salicylaldehydate, which afforded the same compound as a brown solid.

The reaction of D-galactosamine with salicylaldehyde did not result in the formation of the Schiff base. The yellow syrup obtained in the reaction decomposed when purification was attempted on silica gel column chromatography. Therefore, the complex was prepared by reaction of the free sugar with Ni(II) salicylaldehydate. The FTIR spectrum showed the C=N stretching absorption at lower values compared with free imines, and at the same position of the C=N absorption in the Ni(II) complex **1** (Fig. 5).[9] The bands at 399.9 and 295.1 cm^{-1} in the second-derivative spectrum are indicative of complex formation.[19]

2.3. NMR studies

The ^{1}H NMR spectra of the Ni(II) complexes **1** and **2** derived from D-glucosamine and D-galactosamine, re-

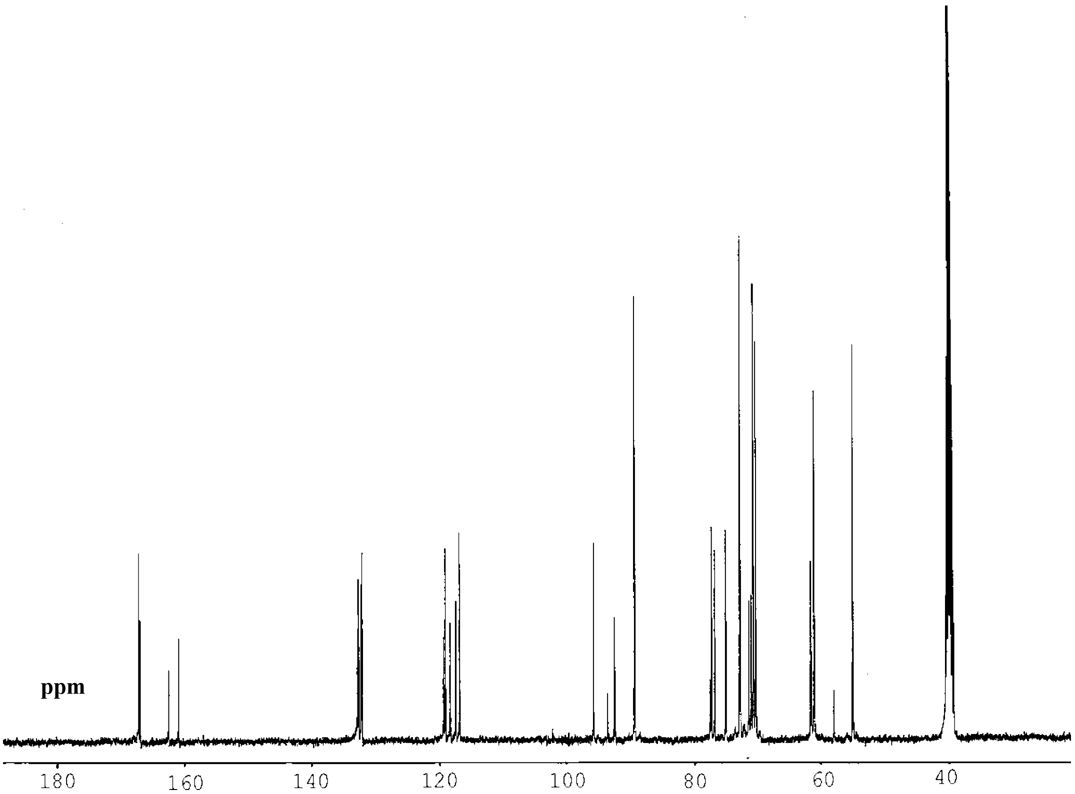

Fig. 3. ^{13}C NMR spectrum (100 MHz, 30 °C, DMSO-d_6) of the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose.

spectively are very similar. They present small upfield shifts ($\Delta\delta$) of the imine proton when compared to the same proton in the Schiff base of D-glucosamine ($\Delta\delta \sim$ 0.6 ppm) (Fig. 6). These results were corroborated by the upfield shift values ($\Delta\delta \sim 6$ ppm) observed for the imine carbon in the ^{13}C NMR spectrum of the same complexes. No signals of the amine proton (=C–NH) or the vinyl proton (=CH–N) of the keto-amine tautomer were found in the ^{1}H NMR spectra of the Ni(II) complexes **1** and **2**. All the aromatic protons of both complexes show upfield shifts of ~0.2 ppm. Comparison of the anomeric proton chemical shift values in the ^{1}H NMR spectrum of the Ni(II) complexes with those of the Schiff base of D-glucosamine revealed higher upfield shifts for the α anomers ($\Delta\delta \sim 0.4$ ppm) than for the β anomers ($\Delta\delta \sim 0.2$ ppm). From integration of the anomeric proton signals, the ratio of α/β anomers were 1.0:1.1 and 1.0:1.6 in complex **1** and complex **2**, respectively. The ^{1}H NMR spectra of many nickel(II) complexes with Schiff bases derived from aliphatic amines have shown great variations in the chemical shifts of the protons compared to the free imine due to the planar diamagnetic-tetrahedral paramagnetic equilibria.[10] The small paramagnetic shifts in the NMR spectra of the Ni(II) complexes **1** and **2** are indicative of a small proportion of non-planar species in DMSO solutions.

2.4. Cyclic voltammetry

Fig. 7 shows the voltammograms in DMF of the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose and of the Ni(II) complexes. They were scanned to the cathodic region, the potentials being referred to $Cp_2Fe^{+/0}$. The ligand shows two reduction irreversible peaks at −1.26 and −2.39 V. The behaviour of Ni(II) complex **1** is very similar to that of Ni(II) complex **2**. They both present a prewave at −1.85 V, which may be related to the coordinated ligand, and a reduction peak located at −2.11 V associated with the quasi-reversible reduction of Ni(II) to Ni(I). Coulometric measurements on the peak at −2.11 V indicated that 1 mol of electrons is involved in the process. The values observed for these systems are similar to those reported for bidentate mononuclear nickel(II) complexes with 2-hydroxynaphthaldimines derived from low-molecular-weight aliphatic amines.[10]

2.5. Absorption studies

The band at 420 nm in the UV–vis spectrum of the Schiff base may be assigned to the π→π* transitions originating in the enol-imine and keto-amine tautomeric chromophores. This band shifted to lower wavelength by 10 nm in the Ni(II) complex **1**, and by 20 nm in

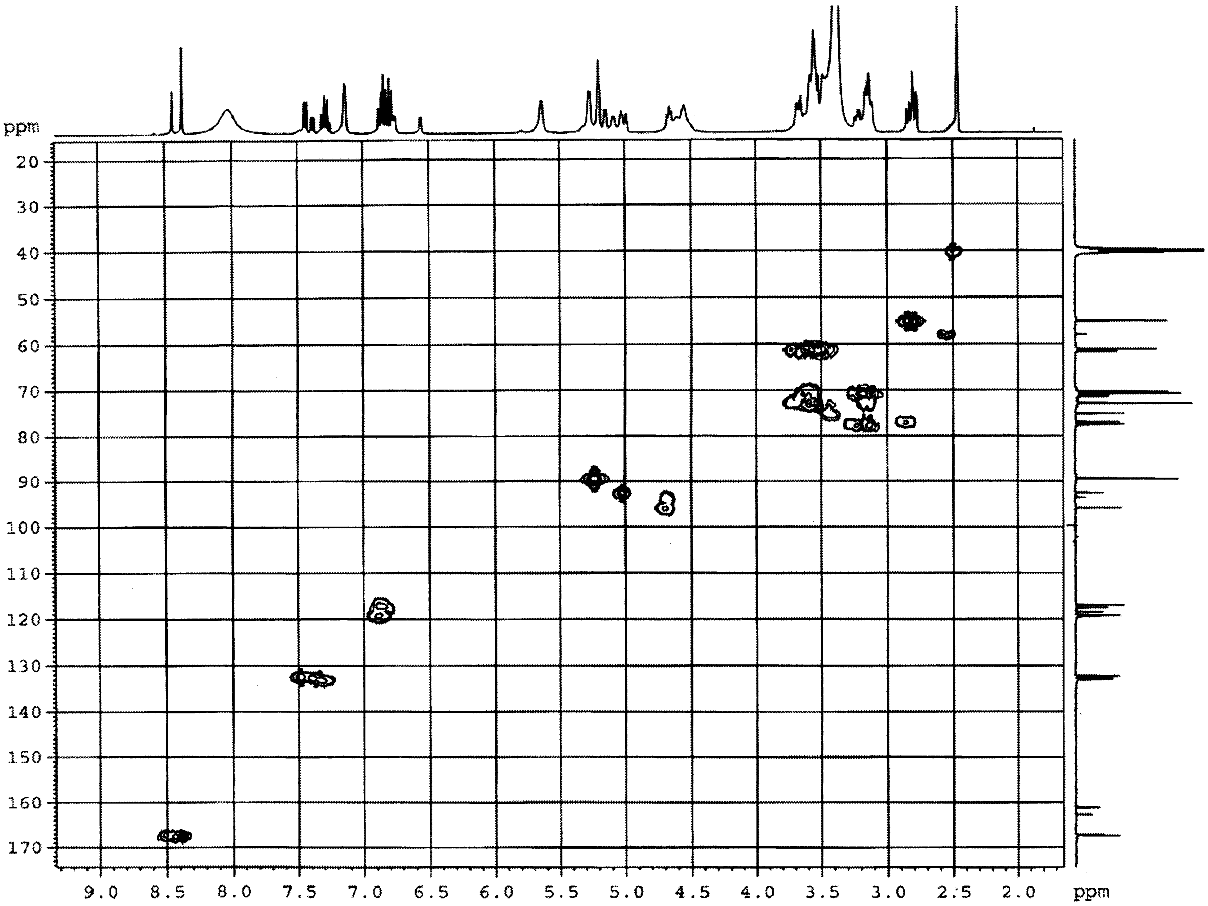

Fig. 4. HMQC spectrum (400 MHz, 30 °C, DMSO-d_6 of the Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose.

complex **2**. The Ni(II) complexes **1** and **2** present two intense bands associated to the $\pi \rightarrow \pi^*$ transitions of the aromatic ring in the region 260–270 nm, which are also shifted to lower wavelength in comparison of those of the Schiff base of D-glucosamine. The weak band near 600 nm due to d–d transition for a square-planar complex, probably is under the intense band at around 400 nm in the complexes. Moreover, in DMSO solution, no absorption was observed in the region expected for a penta-coordinated or hexa-coordinated complexes.[20]

Previously, it was found by circular dichroism studies that the coordination of 2-hydroxynaphthaldimines of D-glucosamine and methyl 2-amino-2-deoxy-β-D-glucopyranoside to Cu(II) ion is through the enol-imine tautomeric form. Furthermore, the formation of the complex, bis-*N*-[methyl-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-2-(2-hydroxynaphthaldiminate)]copper(II), was indicative of the fact that the imino group participates in the complexation.[13] Results found in this work indicate that the salicylaldimines of D-glucosamine and D-galactosamine give bidentate mononuclear Ni(II) complexes with *quasi* spin-paired planar stereochemistry through the enol-imino tautomer form (Fig. 8). The participation of the hydroxyl groups of the sugar residues might be excluded.

3. Experimental

3.1. General methods

Melting points were determined in an Electrothermal apparatus and are uncorrected. Microanalysis were performed at Facultad de Química, Universidad Católica de Chile. The nickel content was determined by atomic absorption using a Perkin–Elmer 2380 equipment. FTIR spectra were recorded as KBr disks using a Bruker 66*v* spectrophotometer in the region of 4000–200 cm^{-1}. Derivation, including the Savitzky–Golay algorithm was performed using the OPUS/I:R: version 1.4 sofware incorporated into the hardware of the instrument.[21–23] Optical rotations were measured with a Perkin–Elmer 241 spectropolarimeter. UV–vis spectra were registered using a Varian Cary 1E spectrophotometer in the 900–190 nm region, and using a Carl Zeiss model DMR 22 instrument in the 2000–350 nm region. ^1H and ^{13}C NMR spectra were registered on a Bruker Avance DRX 400 spectrometer operating at 400.13 (^1H) and 100.62 MHz (^{13}C), respectively using MeOH-d_4 or Me_2SO-d_6 as a solvent at 30 °C with MeOH as internal standard. DEPT and two-dimensional spectra (COSY

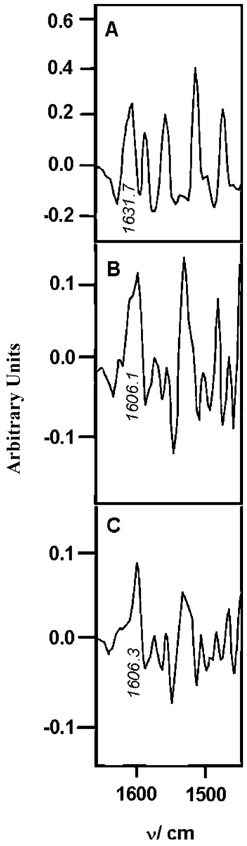

Fig. 5. Second-derivative FTIR spectra in the region ~1700–1400 cm^{-1} of: (A) 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose; (B) bis-*N*-[2-deoxy-D-glucopyranosyl-2-(2-hydroxybenzaldiminate)]Ni(II) (**1**); (C) bis-*N*-[2-deoxy-D-galactopyranosyl-2-(2-hydroxybenzaldiminate)]Ni(II) (**2**).

and HMQC) were measured using standard Bruker software.

3.2. Electrochemical measurements

Cyclic voltammetry was measured using Princeton Applied Research PAR 173 Potentiostat–Galvanostat and PAR 179 Coulometer coupled to a PAR 175 Universal programmer. A two-compartment, three-electrode, locally built cell was used. The compartment of the working electrode (vitreous carbon disk) was separated from that of the counter electrode (Pt wire) by fine porosity fritted glass. The vitreous carbon electrode was prepared by polishing with 0.3 μm alumina (Buehler Co.) to obtain a mirror-like surface. After the polishing procedure, the electrode was sonicated in distilled water for several minutes. Measurements were conducted in DMF. The solutions were 1×10^{-4} M in electroactive species and contained 0.01 M $(C_2H_5)_4NClO_4$ as the supporting electrolyte. All measurements were carried out under nitrogen at 20 °C. The $E_{1/2}$ of the reversible couple ferrocenium–ferrocene ($Cp_2Fe^{+/0}$) measured in the same solution was used as internal standard. All potentials are reported versus $Cp_2Fe^{+/0}$ couple.

3.3. Preparation of bis-*N*-[2-deoxy-D-glucopyranosyl-2-(2-hydroxybenzaldiminate)]nickel(II) (1)

3.3.1. By reaction of the Schiff base with Ni(II) acetate. The Schiff base, 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranoside was synthesized according to Adam and Hall: mp 178–179 °C, $[\alpha]_D^{23}$ +352.0 → +364.4° (*c* 0.22, MeOH), $[\alpha]_D^{23}$ +124.4° (*c* 0.22, DMSO).[11] Lit. mp 183–184 °C, $[\alpha]_D$ +11.0° (MeOH).[24] IR (KBr) cm^{-1}: 3357 (O–H), 1632.1 (–C=N) and 1582.3 (aromatic C=C), and 768.9 (C–H, Ar. 1,2 sust.). ^1H NMR (Me_2SO-d_6): δ 14.143 (s, 0.35 H, C-2–OH), 13.412 (s, 0.65 H, C-2–OH), 8.441 (s, 0.40 H, HC=N), 8.369 (s, 0.60 H, HC=N), 8.025 (s, =CNH), 7.432 (d, *J* 7.60 Hz, H-4), 7.376 (d, *J* 7.87 Hz, H-4), 7.294 (d, *J* 8.0 Hz, H-5), 7.254 (d, *J* 8.8 Hz, H-5), 7.134 (s, 0.53 H, C=CHN), 7.125 (s, 0.47 H, C=CHN), 6.854 (s, 1 H, H-6), 6.793 (t, *J* 7.80 Hz, H-3), 5.265 (d, *J* 4.8, 0.47 Hz, H-1′α), 5.143 d, *J* 4.8 Hz, 0.21 H, H-1′α), 4.985 (d, *J* 7.6 Hz, 0.32 H, H-1′β), 3.680 (m, H-2′α), 3.650 (m, H-2′β), 3.576 (m, H-6′), 3.132 (m, H-4′). ^{13}C NMR (CH_3OH-d_4): δ 169.10 and 168.43 (C=N), 162.34 (C-2), 134.88 (C-4), 133.63 (C-5), 120.36 (C-6), 119.43 (C-3), 117.65 (=C–N), 97.04 (C-1′β), 94.95 (C-1′β), 93.87 (C-1′α), 90.87 (C-1′α), 78.37 (C-4′), 76.47 (C-5′), 73.37 (C-3′), 71.53 (C-2′), 62.89 (C-6′). ^{13}C NMR (Me_2SO-d_6): δ 167.26 and 161.01 (C=N), 162.58 (C-2), 132.76 (C-4), 132.22 (C-5), 119.13 (C-1), 118.37 (C-6), 117.47 (C-3), 116.88 (=C–N), 95.80 and 93.60 (C-1′β), 92.54 and 89.42 (C-1′α), 77.52 (C-4′), 76.89 (C-5′), 72.89 (C-3′), 71.09 (C-2′), 61.58 and 61.62 (C-6′). UV–vis (Me_2SO); λ_{max} nm ($\varepsilon = M^{-1}\ cm^{-1}$): 280 (7000), 275 (6500), 420 (4500).

The Schiff base (0.050 g, 0.17 mmol) was refluxed for 16 h with $Ni(OAc)_2 \cdot 4\ H_2O$ (0.022 g, 0.08 mmol) in 5.0 mL of 1-BuOH. Upon cooling to 60 °C, the mixture was filtered off, and the filtrate was concentrated in vacuo. The resulting solid was washed with distilled water (5 × 2 mL) and recrystallized from MeOH to give brown crystals (88.2% yield): mp 250–251 °C. IR (KBr) cm^{-1}: 3.416.4 (O–H), 1606.1 (–C=N), 755.5 (C–H, Ar.1,2 sust.), 397.8 (Ni–O), 276.7 (Ni–N). ^1H NMR (Me_2SO-d_6): δ 7.866 (s, 0.41 H, HC=N), 7.835 (s, 0.59 H, HC=N), 7.308 (m, H-4), 7.116 and 7.112 (m, H-5), 6.693 (s, H-6), 6.499 and 6.490 (m, H-3), 4.837 (s, 0.48 H, H-1′α), 4.590 (d, *J* 10.0 Hz, 0.0.52 H-1′β). ^{13}C NMR (Me_2SO-d_6): δ 162.70 and 160.52 (C=N), 133.63 (C-4), 133.27 (C-5), 119.64 (C-6), 119.48 (C-3), 87.36 (C-1′β), 63.10 (C-6′). UV–vis (Me_2SO); λ_{max} nm ($\varepsilon = mol^{-1}\ cm^{-1}$): 266 (8000), 270 (6000), 410 (4000). Anal. Calcd for $(C_{13}H_{16}NO_6)_2$: Ni; C, 50.10; H, 5.13; N, 4.49; Ni, 9.42. Found: C, 50.35; H, 5.21; N, 4.45; Ni, 9.22.

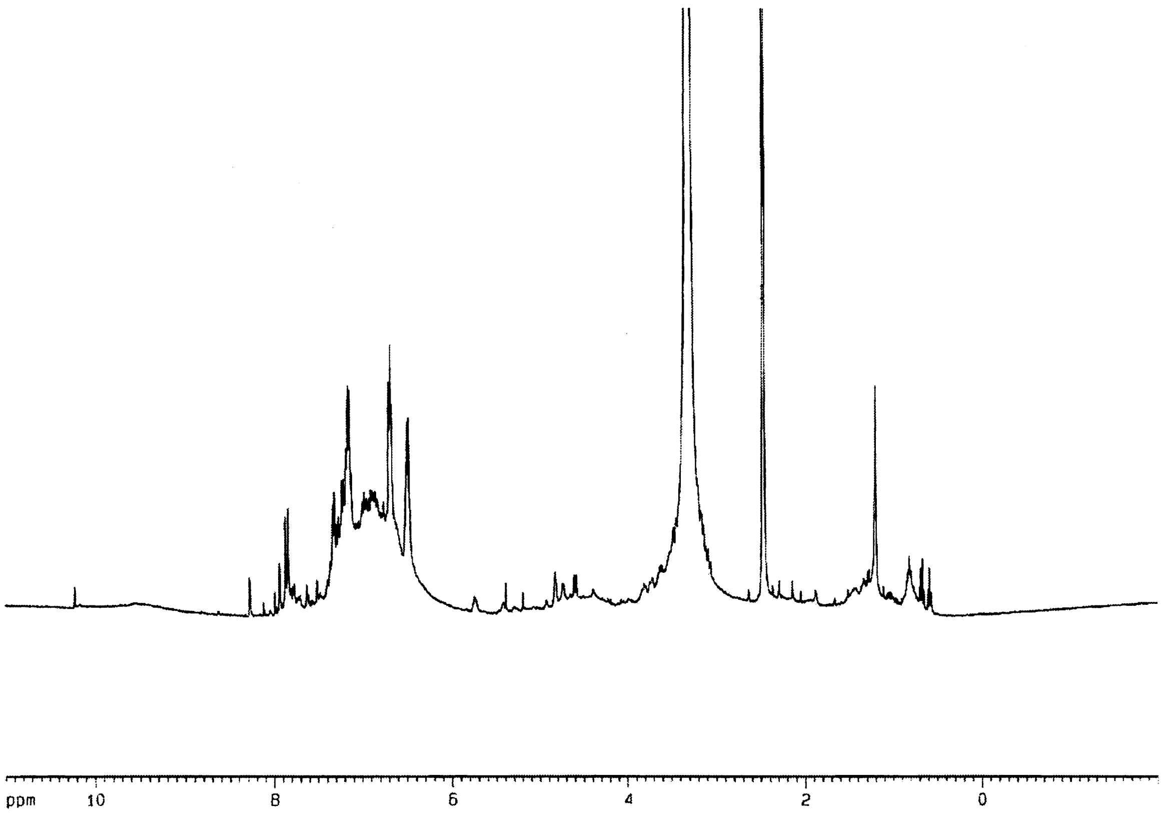

Fig. 6. ^{1}H NMR spectrum (400 MHz, 25 °C, DMSO-d_6) of bis-*N*-[2-deoxy-D-glucopyranosyl-2-(2-hydroxybenzaldiminate)]Ni(II) (**1**).

3.3.2. By reaction of D-glucosamine with the Ni(II) 2-hydroxybenzaldehyde complex. 2-Hydroxybenzaldehyde (0.200 g, 1.6 mmol) and $Ni(CH_3COO)_2 \cdot 4\ H_2O$ (0.204 g, 0.8 mmol) in 5 mL of EtOH were refluxed for 10 min and then cooled to rt. Aq 1 M NaOH was added until the pH of the solution was 6.0, resulting in a green solid product. The solid was separated by filtration, washed with distilled water (5 × 2 mL) and dried.

To the 2-hydroxybenzaldehyde nickel(II) complex (0.084 g, 0.46 mmol) in 3.0 mL of 1-butanol a solution of D-glucosamine hydrochloride (0.100 g, 0.46 mmol) and 0.045 g of NaOAc in 1 mL of water was added. The resulting solution was refluxed for 16 h. The hot solution was filtered through a fritted glass funnel, and the filtrate was concentrated in vacuo. The syrup was washed with cold distilled water (5 × 2 mL), and the resulting solid was recrystallized from MeOH to give a brown solid (79.7% yield): mp 250–251 °C; IR (KBr) cm^{-1}: 3416.4 (O–H), 1606.1 (–C=N), 755.5 (C–H, Ar.1,2 sust.), 397.8 (Ni–O), 276.7 (Ni–N).

3.4. Bis-*N*-[2-deoxy-D-galactopyranosyl-2-(2-hydroxybenzaldiminate)]nickel(II) (2)

This compound was prepared using the Ni(II) salicylaldehydate and D-galactosamine by adopting the procedure described for D-glucosamine. After 16 h, the hot reaction mixture was filtered through a fritted glass funnel, and the filtratae was concentrated in vacuo until crystallization was observed. On cooling, a brown solid separated and was washed with distilled water (5 × 2 mL), followed by diethyl ether. Yield 87.9%: mp 262–263 °C. IR (KBr) cm^{-1}: 3423.1 (O–H), 1606.3 (C=N), 758.1 (C–H Ar. 1,2 sust.), 399.9 (Ni–O), 295.1 (Ni–N) cm^{-1}. ^{1}H NMR (Me_2SO-d_6): δ 7.884 (s, 0.47 H, HC=N), 7.874 (s, 0.53 H, HC=N), 7.312 (s, 1 H, H-4), 7.217 (d, *J* 6.80 Hz, 0.5 H, H-5), 7.145 (d, *J* 7.52 Hz, 0.5 H, H-5), 6.677 (m, H-6), 6.677 (d, H-3), 6.482 (s, H-3), 4.827 (s, 0.40 H, H-1′α), 4.538 (d, 0.60 H, H-1′β), 2.198 (m, 2 H, H-6′). ^{13}C NMR (Me_2SO-d_6): δ 163.03 and 161.05 (C=N), 134.82 (C-4), 121.0 (C-6), 119.0 (C-3), 89.0 (C-1′β), 57.02 (C-6′). UV–vis (Me_2SO); λ_{max} nm (ε = mol^{-1} cm^{-1}): 261 (8000), 271 (6000), 400 (4000). Anal. Calcd for $(C_{13}H_{16}NO_6)_2Ni \cdot 0.5\ C_4H_{10}O$: C, 50.93; H, 5.60; N, 4.24; Ni, 8.89. Found: C, 50.73; H, 5.54; N, 4.31; Ni, 9.22.

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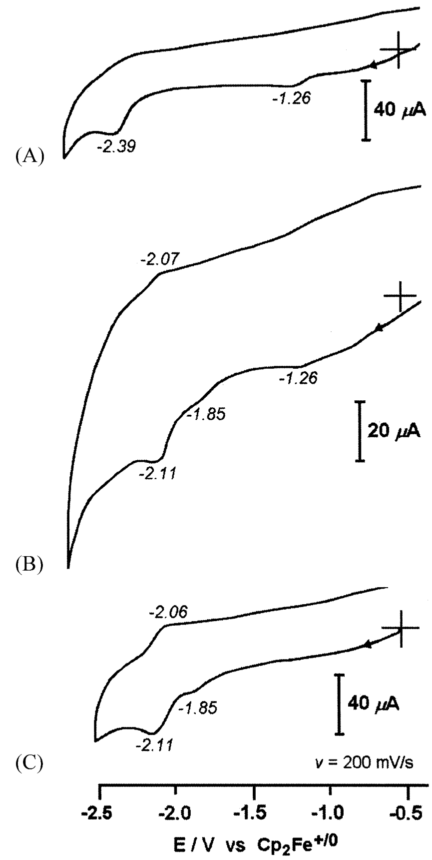

Fig. 7. Cyclic voltammograms of: (A) 2-deoxy-2-(2-hydroxybenzaldimino)-D-glucopyranose; (B) bis-*N*-[2-deoxy-D-glucopyranosyl-2-(2-hydroxybenzaldiminate)]Ni(II) (**1**); (C) bis-*N*-[2-deoxy-D-galactopyranosyl-2-(2-hydroxybenzaldiminate)]Ni(II) (**2**).

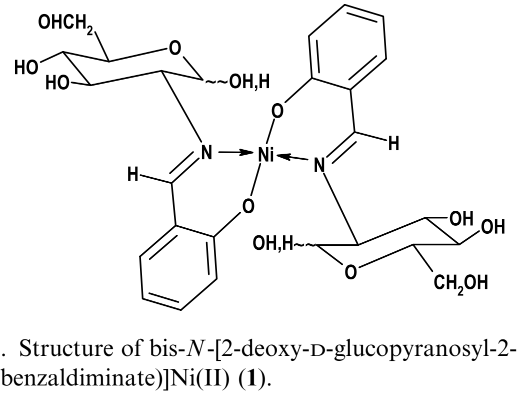

Fig. 8. Structure of bis-*N*-[2-deoxy-D-glucopyranosyl-2-(2-hydroxybenzaldiminate)]Ni(II) (**1**).

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