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# Nickel(II) complexes with Schiff-base ligands derived from epimeric pyranose backbones as 2,3-chelators: modeling the coordination chemistry of chitosan

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Abstract—Two mononuclear nickel(II) complexes with Schiff-base ligands derived from the epimeric sugars glucosamine and mannosamine have been synthesized. The X-ray crystal structure reveals a distorted octahedral geometry at the nickel(II) ions with an N<sub>4</sub>O<sub>2</sub> donor set and the rare 2,3-chelation of the donor atoms of the carbohydrate backbone. Upon complexation only the glucopyranose ring maintains the  ${}^{4}C_{1}$  chair conformation, whereas the mannopyranose ring adopts the  ${}^{O}S_{5}$  screw-boat conformation. Dimeric units of complex cations are formed by intermolecular hydrogen bonding which are further assembled by  $\pi$ -stacking affording one-dimensional chains with a twofold screw symmetry.

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## 1. Introduction

Chitosan is the partially deacetylated derivative of chitin, representing the second-most naturally abundant polysaccharide after cellulose. The coordination chemistry of the  $\beta$ -(1 $\rightarrow$ 4)-linked compound is of current interest concerning its application as a supramolecular ligand for heterogeneous catalysis.<sup>1–7</sup> Chitosan has been known for its adsorption properties toward metal ions for several years.<sup>8</sup> Besides its non-toxicity and biocompatibility, this biopolymer meets plenty of demands made on potential heterogeneous catalysts like insolubility, low chemical reactivity, and a large surface area because of its swelling properties in protic solvents. In general, carbohydrates represent enantiomerically pure compounds isolated from the chiral pool and are therefore suitable supports for enantioselective reactions. Furthermore, chitosan is chemically versatile concerning its polyfunctionality facilitating the introduction of additional donor atoms (see Scheme 1). The Schiff-base modified derivatives show good catalytic activities concerning cyclopropanation, alkane oxidation, and C–C coupling reactions.<sup>9–12</sup>

From the coordination chemistry point of view, carbohydrates are suitable chelate ligands functionalized with a set of weakly coordinating donor groups.<sup>13</sup> For complexes of paramagnetic metal centers X-ray diffraction methods are the appropriate method of choice to gain structural information. Unfortunately, carbohydrate–metal complexes show a rather low tendency to crystallize. In the past two decades intense studies



**Scheme 1.** 2-Amino-2-deoxy-**D**-glucose backbone as found in chitosan (left). Schematic structure of the Schiff-base ligands (right).

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were performed on the functionalization of the sugar backbone with amides, amines, imines, and carboxylic groups to accomplish a stronger metal-ion complexation.<sup>14–20</sup> The Schiff-base formation is especially explored concerning their common availability via condensation of amino sugars with aldehyde moieties.<sup>21–29</sup>

Herein the syntheses and crystal structures of the mononuclear nickel(II) complexes with Schiff-base ligands derived from the epimeric sugars glucosamine  $(H_2 sal^{NO_2}Glc)$  and mannosamine  $(H_2 sal^H Man)$  are reported. In the course of our investigations on the binding properties of chitosan toward transition metal ions, the complex [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)(tptz)]ClO<sub>4</sub> was prepared from the Schiff-base ligand derived from 2-amino-2deoxy-D-glucose representing the anhydro glucose unit of this polysaccharide together with 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (tptz) as accompanying co-ligand. The corresponding 2-amino-2-deoxy-D-mannose-based compound [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub> was synthesized to clarify the influence of the configuration at the chelating groups on the coordination behavior, in order to allow for a design of metal-specific coordination pockets on chitosan derivatives.

### 2. Results and discussion

#### 2.1. Synthesis

The Schiff-base ligands benzyl 2-deoxy-2-(5-nitrosalicvlideneamino)- $\alpha$ -D-glucopyranoside (H<sub>2</sub>sal<sup>NO<sub>2</sub></sup>Glc) and benzyl 2-deoxy-2-salicylideneamino-α-p-mannopyranoside (H<sub>2</sub>sal<sup>H</sup>Man) derived from the epimeric sugars glucosamine and mannosamine, respectively, were prepared by a three-step synthesis starting from the corresponding N-acetyl derivatives as represented in Scheme 2. The protection of the glycosidic hydroxy groups via a benzyl ether function leads to additional advantages for the resulting ligands, as this increases their solubility and facilitates the formation of suitable crystals. The latter is of particular interest with respect to potential  $\pi$ -stacking of the resulting complexes in the crystal packing. The protection of the glycosidic hydroxy groups was followed by an alkaline hydrolysis of the amide function at C-2 and subsequently by condensation of the generated primary amino-functionalized sugar with the appropriate 2-hydroxy-benzaldehyde fragment leading to the corresponding Schiff-base ligands. The proton H-1 linked to the anomeric carbon atom C-1 of H<sub>2</sub>sal<sup>NO<sub>2</sub></sup>Glc leads to a doublet in the <sup>1</sup>H NMR spectrum with  ${}^{3}J_{1,2} = 3.7$  Hz. This is indicative for the exclusive presence of the  $\alpha$ -anomer of the saccharide unit associated with the cis configuration of the protons attached to C-1 and C-2. On the other hand, the H-1 of the epimeric ligand H<sub>2</sub>sal<sup>H</sup>Man leads to a Scheme 2. Reaction scheme for the synthesis of the Schiff-base ligands  $H_2sal^{NO_2}Glc$  and  $H_2sal^HMan$ .

doublet with  ${}^{3}J_{1,2} = 1.1$  Hz consistent with the trans ee-configuration of the protons H-1 and H-2.

The mononuclear nickel(II) complexes [Ni(Hsal<sup>NO2</sup>-Glc)(tptz) ClO<sub>4</sub> and [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub> were synthesized by addition of an equimolar amount of nickel(II) perchlorate hexahydrate to a 1:1 mixture of the appropriate Schiff-base ligand and triethylamine in methanol. In the presence of 1 equiv of base, the phenolic hydroxy group was deprotonated upon complexation, and the ligand moiety therefore coordinates as a monoanionic species. Subsequently a methanolic solution of 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (tptz) was added to prevent the coordinative saturation of the metal center via oxo-bridging as it is commonly known from the formation of relevant polynuclear copper(II) complexes with related sugar-modified Schiff-base li-gands.<sup>27-29</sup> Moreover, tptz is well known as co-ligand for octahedral metal centers like nickel(II) and for its ability to support crystallization by an appropriate crystal packing via  $\pi$ -stacking interactions.<sup>30–32</sup> Upon addition of tptz the color of the reaction mixture turned from green to brown accompanied by precipitation of a pale-brown solid which was immediately redissolved by addition of chloroform and/or acetonitrile. From these solutions crystals suitable for X-ray diffraction could be isolated by slow evaporation of the solvent over a period of several weeks.

### 2.2. Electronic spectroscopy

The electronic spectra of the synthesized nickel(II) complexes recorded for solutions in acetonitrile are depicted in Figure 1. The UV-vis spectrum of the mannosamine





**Figure 1.** Electronic spectra of  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4$  (solid line) and  $[Ni(Hsal^HMan)(tptz)]ClO_4$  (dotted line); the spectra are given for solutions in acetonitrile at 20 °C.

containing complex [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub> shows a weak band at 954 nm and a shoulder at about 530 nm consistent with the spin-allowed d–d transitions  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$  and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$  typical for a nickel(II) center placed in an octahedral coordination environment. Whereas the third d–d transition  $({}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P))$  is expected at higher energy and is masked by intense ligand based transitions and charge-transfer bands appearing below 390 nm. ${}^{33-35}$ 

For the glucosamine-based nickel(II) complex  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4$ , the d-d transition bands are slightly blue-shifted as exemplified by the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$  transition occurring at 897 nm. This can be attributed to the presence of the electron-withdrawing nitro group, which on the other hand also leads to an increase in intensity for the charge-transfer band at 378 nm.

#### 2.3. Structure description

**2.3.1.** [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)(tptz)]ClO<sub>4</sub>. The mononuclear complex [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)(tptz)]ClO<sub>4</sub> was obtained as crystals together with co-crystallized acetonitrile and water solvent molecules, which are located at partially occupied crystallographic positions (see Section 4). The complex crystallizes as two crystallographically independent molecules in the monoclinic space group  $P2_1$  consistent with the exclusive presence of solely one enantiomeric form. In Figure 2 the molecular structure of one of the two rather similar complex cations [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)(tptz)]<sup>+</sup> is depicted. The corresponding bond lengths and angles are summarized in Table 1.

The nickel(II) ion is embedded in a distorted octahedral coordination environment with an N<sub>4</sub>O<sub>2</sub> donor set as indicated by the observed cis angles in the range from 76° to 105° and the trans angles varying from 153° to 175°. The tridentate ligands tptz and Hsal<sup>NO<sub>2</sub></sup>Glc<sup>-</sup> are coordinated in a meridional fashion forming three five- and one six-membered chelate rings at the metal center with bite angles of 76° to 81° (N*j*2– N*ij*–N*j*5, N*j*2–N*ij*–N*j*6, and O*j*3–N*ij*–N*j*1; *j* denotes the running number of the molecule) and about 92° (O*j*6– N*ij*–N*j*1), respectively. One of the five-membered chelate rings contains the glucosamine-based Schiff-base ligand Hsal<sup>NO<sub>2</sub></sup>Glc<sup>-</sup> that possesses a <sup>4</sup>C<sub>1</sub> chair conformation of the glucopyranose ring.

The coordinative bonds at the nickel(II) ions fall into two meridional groups which are with values of about 200 and 217 pm found at the lower and upper end of the respective range. The short distance group consists of the imino nitrogen atom N*j*1 and the phenolic oxygen atom O*j*6 of the Schiff-base ligand and the triazine nitrogen atom N*j*2 of the tptz co-ligand, whereas the donor



Figure 2. Molecular structure of one of the two independent complex cations  $[Ni(Hsal^{NO_2}Glc)(tptz)]^+$  in crystals of  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4 \cdot 0.375CH_3CN \cdot 0.75H_2O$ . Thermal ellipsoids are drawn at the 30% probability level. Counterions, solvent molecules and hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (pm) and angles (°) for  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4$ 

Molecule 1		Molecule 2	
Ni1-O13	214.0(6)	Ni2-O23	215.8(6)
Nil-O16	198.7(6)	Ni2-O26	199.5(6)
Nil-N11	201.3(6)	Ni2-N21	198.5(6)
Nil-N12	199.4(6)	Ni2-N22	198.5(6)
Nil-N15	212.6(6)	Ni2-N25	215.2(6)
Nil-N16	223.5(6)	Ni2-N26	217.2(7)
O13-Ni1-O16	172.9(2)	O23-Ni2-O26	173.6(2)
O13-Ni1-N11	81.2(3)	O23-Ni2-N21	81.0(3)
O13-Ni1-N12	93.9(2)	O23-Ni2-N22	92.8(3)
O13-Ni1-N15	91.1(2)	O23-Ni2-N25	91.7(2)
O13-Ni1-N16	91.0(3)	O23-Ni2-N26	90.2(3)
O16-Ni1-N11	91.8(2)	O26-Ni2-N21	92.7(3)
O16-Ni1-N12	93.1(2)	O26-Ni2-N22	93.5(3)
O16-Ni1-N15	91.4(3)	O26-Ni2-N25	90.7(2)
O16-Ni1-N16	89.8(3)	O26-Ni2-N26	90.3(3)
N11-Ni1-N12	174.8(3)	N21-Ni2-N22	173.8(3)
N11-Ni1-N15	101.1(2)	N21-Ni2-N25	101.8(2)
N11-Ni1-N16	105.6(2)	N21-Ni2-N26	104.5(2)
N12-Ni1-N15	77.0(2)	N22-Ni2-N25	77.4(2)
N12-Ni1-N16	76.2(2)	N22-Ni2-N26	76.1(2)
N15-Ni1-N16	153.3(2)	N25-Ni2-N26	153.6(2)

atoms with elongated bond lengths are given by the alcoholic sugar hydroxy group (Oj3) and the pyridyl nitrogen atoms Nj5 and Nj6.

Intermolecular hydrogen-bonding interactions between the C-3 hydroxy group of the sugar backbone of the Schiff-base ligand and the nitrogen atom Nj7 of the dangling pyridyl group of an adjacent complex cation  $[Ni(Hsal^{NO_2}Glc)(tptz)]^+$  leads to the formation of

a hydrogen-bonded dimer as represented in Figure 3. The observed hydrogen-bonding distances are with 280 pm in the expected range for O-H...N interactions.<sup>36,37</sup> As a consequence of the hydrogen-bonding interaction, the dangling pyridyl ring shows a significant out-of-plane torsion with respect to the aromatic plane of the coordinated tptz ligand that results in torsion angles N*j*4–C*j*27–C*j*28–N*j*7 of 10.9° and 14.0° (j = 1, 2). Moreover, within the dimeric unit additional  $\pi$ - $\pi$  interactions at a distance of about 340 pm between the tptz ligands of the two [Ni(Hsal<sup>NO2</sup>Glc)(tptz)]<sup>+</sup> cations are present, enforcing the aggregation of the dimeric units. This is in the range expected for such interactions.<sup>36–38</sup> The angle of  $7^{\circ}$  between the corresponding mean planes of the triazine rings is consistent with their near coplanarity. Additional hydrogen bonding of the free hydroxy groups of the carbohydrate backbone is observed with the perchlorate counterions and the water molecules present in the crystal structure.

Additional  $\pi-\pi$  interactions between the tptz coligands of adjacent hydrogen-bonded dimeric units  $\{[Ni(Hsal^{NO_2}Glc)(tptz)]^+\}_2$  lead to a supramolecular assembly as depicted in Figure 4. This  $\pi$ -stacking affords one-dimensional chains with a twofold screw symmetry along the crystallographic [010] direction. Whereas within the dimeric units the whole tptz co-ligand is involved in the  $\pi-\pi$  interaction, the inter-dimer  $\pi$ -stacking is essentially established by the central triazine ring (N22, N23, and N24) of the complex cations containing Ni2 and the coordinated pyridyl ring (N16) of the Ni1 fragment, at distances ranging between 340 and



Figure 3. Hydrogen-bonded dimer { $[Ni(Hsal^{NO_2}Glc)(tptz)]^+$ }<sub>2</sub>. Perchlorate ions, solvent molecules and hydrogen atoms are omitted for clarity. Pertinent distances: O13···N27 278.9 and O23···N17 280.8 pm.



Figure 4. Supramolecular assembly of the hydrogen-bonded dimers in crystals of complex  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4$ . Perchlorate ions, solvent molecules and hydrogen atoms are omitted for clarity. Symmetry operations: A = -x + 2, y + 0.5, -z and B = x, y + 1, z.

370 pm with an angle of about 8° between the corresponding mean planes. Additional weaker inter-dimer  $\pi$ - $\pi$  interactions are observed between the central triazine ring (N12, N13, and N14) of the complex fragment Ni1 and the dangling pyridyl ring (N27) of the Ni2 fragment of the adjacent dimeric unit, with relevant distances ranging from 350 to 390 pm and an angle of 24° between the mean planes.

**2.3.2.** [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub>. Slow evaporation of the solvent from the mother liquor afforded crystals of [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub> suitable for X-ray diffraction. These crystals contain additional molecules of methanol and water located at partially occupied crystallographic positions (see Section 4). The complex crystallizes enantiomerically pure in the orthorhombic space group  $P2_12_12_1$ . The molecular structure of one of the two crystallographically independent complex cations is represented in Figure 5, and selected bond lengths and angles for both very similar complex cations are compared in Table 2.

The coordination geometry of the nickel(II) ions in [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub> closely resembles that observed for complex [Ni(Hsal<sup>NO2</sup>Glc)(tptz)]ClO<sub>4</sub> (see Table 1). In particular the distances toward the donor atoms of the first coordination sphere also fall into two meridional groups, a short distance group given by the imino nitrogen atom N/1 and the phenolic oxygen atom Oj6 of the Schiff-base ligand and the triazine nitrogen atom N/2 of the tptz co-ligand, as well as the longdistance group composed of the alcoholic sugar hydroxy group  $(O_{i3})$  and the pyridyl nitrogen atoms N<sub>i</sub>5 and N<sub>i</sub>6 (*j* denotes the running number of the molecule). In contrast to the glucosamine-based complex, for the carbohydrate backbone of [Ni(Hsal<sup>H</sup>Man)(tptz)]<sup>+</sup> a strong distortion from the usually observed chair conformation is observed for the monodeprotonated mannosaminederived Schiff-base ligand, leading to a <sup>O</sup>S<sub>5</sub> screw-boat conformation of the sugar backbone.



**Figure 5.** Molecular structure of one of the two independent complex cations  $[Ni(Hsal^{H}Man)(tptz)]^{+}$  in crystals of  $[Ni(Hsal^{H}Man)(tptz)]$ -ClO<sub>4</sub>·3.75CH<sub>3</sub>OH·2.375H<sub>2</sub>O. Thermal ellipsoids are drawn at the 30% probability level. Counterions, solvent molecules and hydrogen atoms are omitted for clarity.

As in the case of the glucosamine-based complex  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4$ , the formation of a hydrogen-bonded dimeric structure is observed with Oj3···Nj7 donor-acceptor distances of about 285 pm as depicted in Figure 6. The  $\pi$ - $\pi$  interaction between the tptz co-ligands of the two adjacent cations within the dimer is observed at distances of 330-350 pm and at an angle between the mean planes of the two triazine rings of 3.5°. In contrast to the glucosamine-based complex system the dangling pyridyl rings are almost coplanar with the central triazine rings with torsion angles Nj4–Cj27–Cj28–Nj7 of  $1.9^{\circ}$  and  $5.5^{\circ}$  (j = 1,2). Additional hydrogen bonding is observed between two methanol molecules and the phenolate oxygen atoms Oj6 of the dimer (see Fig. 6). For the free hydroxy groups of the carbohydrate backbone (at C-4 and C-6) of the

Table 2. Selected bond lengths (pm) and angles (°) for  $[Ni(Hsal^HMan)(tptz)]ClO_4$ 

Molecule 1		Molecule 2	
Ni1-O13	214.6(3)	Ni2023	216.6(3)
Nil-O16	198.9(3)	Ni2-O26	198.1(3)
Nil-N11	197.6(4)	Ni2-N21	198.5(4)
Ni1-N12	198.5(4)	Ni2-N22	200.2(4)
Nil-N15	217.4(4)	Ni2-N25	220.2(4)
Nil-N16	216.9(4)	Ni2-N26	219.5(4)
O13-Ni1-O16	171.42(13)	O23-Ni2-O26	170.37(13)
O13-Ni1-N11	79.59(15)	O23-Ni2-N21	79.12(13)
O13-Ni1-N12	90.63(14)	O23-Ni2-N22	91.07(13)
O13-Ni1-N15	95.51(13)	O23-Ni2-N25	95.73(13)
O13-Ni1-N16	87.75(13)	O23-Ni2-N26	88.16(13)
O16-Ni1-N11	92.82(16)	O26-Ni2-N21	91.86(15)
O16-Ni1-N12	97.18(15)	O26-Ni2-N22	98.00(14)
O16-Ni1-N15	89.72(15)	O26-Ni2-N25	89.66(15)
O16-Ni1-N16	90.71(15)	O26-Ni2-N26	90.88(16)
N11-Ni1-N12	169.55(17)	N21-Ni2-N22	170.12(15)
N11-Ni1-N15	100.10(15)	N21-Ni2-N25	103.79(15)
N11-Ni1-N16	107.10(16)	N21-Ni2-N26	104.58(15)
N12-Ni1-N15	77.01(14)	N22-Ni2-N25	75.88(14)
N12-Ni1-N16	75.90(14)	N22-Ni2-N26	75.93(14)
N15-Ni1-N16	152.75(15)	N25-Ni2-N26	151.59(14)

Schiff-base ligand additional hydrogen bonding is observed with the perchlorate counterions and disordered water molecules located at partially occupied crystallographic positions.

Between the adjacent hydrogen-bonded dimeric units  $\{[Ni(Hsal^{H}Man)(tptz)]^{+}\}_{2}$  additional  $\pi$ - $\pi$  interactions of the tptz co-ligands are observed. As depicted in Fig-

ure 7 this  $\pi$ -stacking leads to one-dimensional chains with a twofold screw symmetry along the crystallographic [100] direction. Unlike the  $\pi$ -stacking within the dimeric units, only part of the tptz co-ligand is involved in inter-dimer  $\pi$ - $\pi$  interactions. In contrast to the glucosamine-based compound [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)-(tptz)]ClO<sub>4</sub> only two of the peripheral pyridyl rings are involved, leading to pairwise interactions between the dangling pyridyl rings (N*j*7 and N*k*7) and one of the coordinated pyridyl rings (N*j*6 and N*k*6) of adjacent dimers at distances of 350–370 and 320–350 pm, respectively, and with deviations from coplanarity of less than 8°.

## 2.4. Pyranose ring conformation

In general, carbohydrates exhibiting a trans ee or a cis configuration of the vicinal donor atoms are ligands suitable for chelation of transition metal ions.<sup>39</sup> Most of the mononuclear sugar-based nickel(II) complexes are obtained from either aldohexose moieties with a 1,2-coordination mode and participation of the glycosidic group as additional donor function<sup>39–42</sup> or from ketohexoses<sup>43,44</sup> exhibiting a 1,2,3-coordination. Consequently, the carbohydrate derivatives of both of these groups are not suitable ligand systems for chitosan-like model complexes. In this context, we recently reported a copper(II) complex as the first example of a transition metal complex with the 2,3-coordination mode of a



**Figure 6.** Hydrogen-bonded dimer  $\{[Ni(Hsal^HMan)(tptz)]^+\}_2$  and hydrogen-bonded methanol molecules. Perchlorate ions, additional solvent molecules and hydrogen atoms are omitted for clarity. Pertinent distances: O13···N27 285.3, O23···N17 284.2, O16···O1M 277.3, O26···O2M 266.8 pm.



**Figure 7.** Supramolecular assembly of the hydrogen-bonded dimers in crystals of complex [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub>. Perchlorate ions, solvent molecules and hydrogen atoms are omitted for clarity. Symmetry operations: A = x + 0.5, -y + 1.5, -z + 2 and B = x + 1, *y*, *z*.

glucosamine required for such chitosan-like model compounds.<sup>28</sup> Subsequently, recent NMR studies of platinum(II) group metal complexes with mono- or disaccharides containing the 2-amino-2-deoxy-D-glucose unit suggested a trans-2,3-coordination with no evidence for the participation of the C-6 hydroxy group in the chelation of the metal ion.<sup>45</sup> We recently communicated the extension of this concept toward nickel(II) as the coordinated metal ion for which we reported the first structurally characterized nickel(II) complex with the rare trans-2,3-chelation of a glucosamine moiety.<sup>35</sup> A similar coordination mode has previously only been observed for glucosamine-containing disaccharides.<sup>46</sup>

The tptz co-ligand utilized for the coordinative saturation of the nickel(II) moieties based on the sugar-derived Schiff-base ligands  $H_2$ sal<sup>NO<sub>2</sub></sup>Glc and  $H_2$ sal<sup>H</sup>Man requires a meridional coordination at the metal center. As a consequence, also the Schiff-base ligands need to adopt meridional configuration at the nickel(II) ion. The resultant different pyranose ring conformations of the nickel(II) complexes with the Schiff-base ligands of the epimeric sugars glucosamine and mannosamine are depicted in Figure 8. For uncoordinated 2-amino-2deoxy-D-glucose usually a  ${}^{4}C_{1}$  chair conformation is observed for the glucopyranose ring.<sup>19,20</sup> In case of the glucosamine-based ligand  $H_2$ sal<sup>NO<sub>2</sub></sup>Glc this  ${}^{4}C_{1}$  chair conformation is retained upon complexation of the nickel(II) ions affording a five-membered chelate ring ( $\tau$ [N*j*2– Cj2–Cj3–Oj3] = 55.1 (j = 1), 51.8° (j = 2)) with  $\delta$ -conformation for complex [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)(tptz)]ClO<sub>4</sub>.

Although also uncoordinated 2-amino-2-deoxy-Dmannose prefers a  ${}^{4}C_{1}$  chair conformation for the pyranose ring,<sup>47</sup> the situation is different for the mannosamine-based complex [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub>. In this case the required meridional coordination of the Schiff-base ligand leads to a distortion of the pyranose ring to a  ${}^{O}S_{5}$  screw-boat conformation. Moreover, the five-membered chelate ring adopts a  $\delta$ -gauche conformation  $(\tau [N_{j2}-C_{j2}-C_{j3}-O_{j3}] = 47.7 \ (j = 1), 52.1^{\circ} \ (j = 1)$ 2)), which is similar to what is observed for the glucosamine analog [Ni(Hsal<sup>NO2</sup>Glc)(tptz)]ClO<sub>4</sub>. Nevertheless, this is in contrast to the  $\lambda$ -conformation of the chelate sequence Nj2-Cj2-Cj3-Oj3 as it is observed for the  ${}^{4}C_{1}$  chair conformation of 2-amino-2-deoxy-D-mannose with a relevant torsion angle of  $-54.8^{\circ}$ .<sup>47</sup> The observed distortion from the chair conformation for the mannosamine-based complex [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub> can be related to a formal flip of the C-2 group interchanging their equatorial and axial positions, which leads to nearly eclipsed conformations for the neighboring Cj1-Ci2 and Ci3-Ci4 bonds with torsion angles of about  $-24^{\circ}$  and  $-14^{\circ}$ , respectively. Consequently, it is tempting to attribute the observed distortion to the steric requirements of the rigid tptz co-ligand, forcing the coordinated metal moiety in an equatorial-like position at the mannosamine backbone.



Figure 8. Comparison of the pyranose ring conformation of the complex cations  $[Ni(Hsal^{NO_2}Glc)(tptz)]^+$  and  $[Ni(Hsal^HMan)(tptz)]^+$ , together with the first coordination sphere of the chelated nickel(II) ions.

To the best of our knowledge complex [Ni(Hsal<sup>H</sup>-Man)(tptz)]ClO<sub>4</sub> is the first transition metal complex exhibiting a non-chair conformation of a mannopyranose ring. In transition metal complexes derived from mannose or the related L-rhamnose, containing more flexible co-ligand moieties like (aminoalkyl)amines<sup>48-53</sup> instead of the rigid tptz molecule or obtained from less donor-functionalized sugar moieties,<sup>54-57</sup> the pyranose ring generally adopts the expected chair conformation. The rare examples of pyranose rings with a screw-boat conformation have been found for Pt-capped  $\alpha$ -cyclodextrins<sup>58</sup> and ferrocenyl-4,5-(D-glucopyrano)-[2,1-d]oxazolines.<sup>59</sup> Moreover, the pyranose rings in 1,2-O-ethvlidene- or 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose derivatives have been generally found to feature conformations between screw-boat  ${}^{O}S_{5}$  and twist-boat  $^{\rm O}T_2$ , even if not coordinated to any metal ion.<sup>60–66</sup> The distortion from the chair conformation found for these compounds is generally attributed for the rigid acetal or ketal protecting groups.

#### 3. Conclusion

We have synthesized the two nickel(II) complexes  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4$  and  $[Ni(Hsal^HMan)(tptz)]-ClO_4$  with Schiff-base ligands modeling the rare 2,3-chelation of monosaccharides that is assumed to be characteristic for chitosan. The employed epimeric monosaccharides 2-amino-2-deoxy-D-glucose and 2amino-2-deoxy-D-mannose represent two different basic conformations of the relevant chelation mode of the carbohydrate backbone. The X-ray structures of both complexes reveals a distorted octahedral geometry at the nickel(II) centers with an N<sub>4</sub>O<sub>2</sub> donor set given by a sugar-modified Schiff-base ligand and a tptz moiety, both coordinated in a meridional fashion. The complex cations of both compounds are involved in hydrogen-bonding interactions leading to the formation of dimeric units. In addition, the tptz co-ligand utilized for coordinative saturation of the metal centers gives rise to supramolecular aggregation due to its  $\pi$ -stacking ability. In case of Schiff-base ligand H<sub>2</sub>sal<sup>H</sup>Man derived from 2amino-2-deoxy-D-mannose the meridional coordination affords a distortion from the stable  ${}^{4}C_{1}$  chair conformation to the  ${}^{O}S_{5}$  screw-boat conformation of the pyranose ring. This distortion can be attributed to the steric bulk of the employed tptz co-ligand and the C-1 benzyl protecting group.

#### 4. Experimental

#### 4.1. Materials

The starting materials benzyl 2-acetamido-2-deoxy- $\alpha$ -D-glucopyranoside<sup>67</sup> and benzyl 2-acetamido-2-deoxy-D-mannopyranoside<sup>68</sup> were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and used without further purification. Abbreviations used throughout the text: H<sub>2</sub>sal<sup>NO<sub>2</sub></sup>Glc = benzyl 2-deoxy-2-(5-nitrosalicylideneamino)- $\alpha$ -D-glucopyranoside, H<sub>2</sub>sal<sup>H</sup>Man =

benzyl 2-deoxy-2-salicylideneamino- $\alpha$ -D-mannopyranoside, tptz = 2,4,6-tri-(2-pyridyl)-1,3,5-triazine.

*Caution*! Perchlorate salts of metal complexes with organic ligands are potentially explosive.

#### 4.2. Instrumentation

Melting points are given uncorrected and were determined with a Büchi Melting Point B-540 apparatus. Thermogravimetric analyses (TGA) for powdered samples were performed on a Netzsch STA409PC Luxx apparatus under constant flow of nitrogen ranging from room temperature up to 1000 °C with a heating rate of 1 °C/min. Infrared spectra were recorded on a Bruker IFS 55 Equinox spectrometer. <sup>1</sup>H NMR, <sup>13</sup>C NMR,  ${}^{1}H{}^{1}H{}COSY$ , and  ${}^{1}H{}^{13}C{}$  heteronuclear correlation (HMBC and HMOC) NMR experiments were carried out on a Bruker Avance DRX 400 spectrometer. UVvis spectra were recorded with a Varian Cary 5000 UV-vis-NIR-spectrometer. Mass spectra were measured on a Bruker MAT SSQ 710 spectrometer. Elemental analyses were determined on a Leco CHNS/932 Analysator and a Vario EL III.

# 4.3. Benzyl 2-deoxy-2-amino- $\alpha$ -D-glucopyranoside (H<sub>2</sub>amGlc)

A solution of benzyl 2-acetamido-2-deoxy-a-D-glucopyranoside (1.00 g, 3.2 mmol) and KOH (7.01 g, 124.9 mmol) in 25 mL of EtOH (96%) was heated under reflux overnight. After cooling to room temperature, the orange mixture was diluted with 50 mL of EtOH and neutralized with concd HCl. The precipitated KCl was separated via centrifugation. The volume of the filtrate was reduced to about 4 mL. The raw product was purified by size-exclusion chromatography (SEC) with Sephadex LH-20 (MeOH, flow rate: 15 mL/min). After complete removal of the solvent and drying in vacuo, H<sub>2</sub>amGlc was obtained as a pale-brown oil, still containing some solvent. Yield: 748 mg (80%). Selected IR data (KBr, cm<sup>-1</sup>):  $\tilde{v} = 3378$  and 3273 (vO–H, vN–H); 2926  $(v_{as}CH_2)$ ; 1646 ( $\delta$ N–H); 1559 ( $\nu$ C=C); 1456 and 1413 (δCH<sub>2</sub>); 1128, 1114, 1086, 1051 and 1021 (all vC–O). <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz, 25 °C, ppm):  $\delta$  2.45 (dd, 1H,  ${}^{3}J_{2,1} = 3.7$  Hz,  ${}^{3}J_{2,3} = 9.8$  Hz, H-2), 3.08 (dd, 1H,  ${}^{3}J_{4,3} = {}^{3}J_{4,5} = 9.1$  Hz, H-4), 3.26 (dd, 1H,  ${}^{3}J_{3,2} = {}^{3}J_{3,4} = 9.1$  Hz, H-3), 3.42–3.50 (m, 2H, H-5 and H-6a), 3.64 (d, 1H,  ${}^{3}J_{6b,5} = {}^{2}J_{6b,6a} = 10.4$  Hz, H-6b), 4.42 and 4.68 (2d, each 1H,  ${}^{2}J_{7a,7b} = 12.1$  Hz, H-7a and H-7b), 4.76 (d, 1H,  ${}^{3}J_{1,2} = 3.7$  Hz, H-1), 7.26–7.38 (m, 5H, Ph). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz, 25 °C, ppm): δ 56.2 (C-2); 61.0 (C-6); 67.9 (C-7); 70.4 (C-4); 73.5 (C-5); 74.9 (C-3); 98.2 (C-1); 127.4, 127.6, 128.2, and 138.0 (all Ph). ESIMS (MeOH): m/z 270  $[(H_2 amGlc) + H]^+$  (26%), 292  $[(H_2 amGlc) + Na]^+$  (58%),  $324 [(H_2 amGlc) + Na + MeOH]^+ (10\%).$ 

# 4.4. Benzyl 2-deoxy-2-(5-nitrosalicylideneamino)- $\alpha$ -D-glucopyranoside (H<sub>2</sub>sal<sup>NO<sub>2</sub></sup>Glc)

A solution of *p*-nitrosalicylaldehyde (464 mg, 2.8 mmol) in 15 mL of MeOH was added to a solution of H<sub>2</sub>amGlc (748 mg, 2.8 mmol) in 15 mL of MeOH. The reaction mixture was stirred for 3 h at room temperature. After complete removal of the solvent, a yellow solid was obtained. The raw product was purified by size-exclusion chromatography (SEC) with Sephadex LH-20 (MeOH, flow rate: 10 mL/min). After complete removal of the solvent and drying in vacuo, H<sub>2</sub>sal<sup>NO<sub>2</sub></sup>Glc was obtained as a yellow powder. Yield: 940 mg (81%). Selected IR data (KBr, cm<sup>-1</sup>):  $\tilde{v} = 3412$  (vO-H); 3063 and 3032 (vC-H arom.); 2922 (vasCH<sub>2</sub>); 2880 (vsCH<sub>2</sub>); 1646 (vCH=N); 1614, 1547, 1519, and 1496 (vC=C, v<sub>as</sub>NO<sub>2</sub>); 1453 ( $\delta$ CH<sub>2</sub>); 1327 ( $v_s$ NO<sub>2</sub>); 1135, 1096, 1023, and 943 (all vC–O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, 25 °C, ppm): δ 3.26-3.29 (m, 1H, H-3), 3.55-3.57 (m, 3H, H-2, H-4 and H-6a), 3.62-3.65 (m, 1H, H-5), 3.67-3.71 (m, 1H, H-6b), 4.53 and 4.75 (2d, each 1H,  ${}^{2}J_{7a,7b} =$ 12.1 Hz, H-7a and H-7b), 4.65 (s, 1H, OH-6), 5.09 (d, 1H,  ${}^{3}J_{1,2} = 3.7$  Hz, H-1), 5.23 (s, 1H, OH-4), 5.60 (s, 1H, OH-3), 6.68 (d, 1H,  $J_d = 9.5$  Hz, Ph), 7.26–7.35 (m, 3H, Ph), 7.41-7.43 (m, 2H, Ph), 8.05 (dd, 1H,  $J_{\rm d} = 2.9$  Hz, Ph), 8.48 (d, 1H,  $J_{\rm d} = 2.9$  Hz, Ph), 8.72 (s, 1H, H-14), 14.66 (s, 1H, OH-20). <sup>13</sup>C NMR (DMSOd<sub>6</sub>, 60 MHz, 25 °C, ppm): δ 60.5 (C-6); 66.4 (C-4); 68.2 (C-7); 69.8 (C-3); 71.0 (C-5); 73.5 (C-2); 95.5 (C-1); 113.7, 122.6, 127.6, 128.3, 129.3, 132.3, 134.3, and 137.3 (all Ph); 167.8 (C-14); 177.5 (C-20). ESIMS (MeOH): m/z 441 [(H<sub>2</sub>sal<sup>NO<sub>2</sub></sup>Glc)+Na]<sup>+</sup> (100%). Anal. Calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>8</sub> (418.40): C, 57.41; H, 5.30; N, 6.70; Found: C, 55.81; H, 5.06; N, 6.48.

# 4.5. Benzyl 2-deoxy-2-salicylideneamino- $\alpha$ -D-mannopy-ranoside (H<sub>2</sub>sal<sup>H</sup>Man)

Benzyl 2-acetamido-2-deoxy-D-mannopyranoside (1.00 g, 3.2 mmol) and KOH (7.01 g, 124.9 mmol) in 25 mL of EtOH (96%) were heated under reflux overnight. After cooling to room temperature, the orange mixture was diluted with 50 mL of EtOH and neutralized with concd HCl. The precipitated KCl was separated through centrifugation, and the filtrate was reduced to a volume of 20 mL. After addition of NaHCO<sub>3</sub> (350 mg, 4.2 mmol) and salicylaldehyde (450  $\mu$ L, 4.3 mmol), the mixture was stirred for 2.5 h at room temperature. The solvent was completely removed under reduced pressure, and the brownish residue was taken up in a mixture of 25 mL of CHCl<sub>3</sub> and 15 mL of water. The water layer was extracted once with 5 mL of CHCl<sub>3</sub>. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo to a volume of 10 mL. The viscous solution was dropped into 300 mL of *n*-hexane yielding a yellow precipitate. The product was collected

by filtration, washed with a small amount of n-hexane, and finally dried in vacuo affording compound H<sub>2</sub>sal<sup>H</sup>Man as a yellow solid. Yield: 683 mg (57%); mp 75-77 °C. Selected IR data (KBr, cm<sup>-1</sup>):  $\tilde{v} = 3421 (vO-H); 2923 (v_{as}CH_2); 1633 (vCH=N); 1581$ and 1497 (vC=C); 1456 ( $\delta$ CH<sub>2</sub>); 1130, 1059, 1026, and 931 (all vC-O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, 25 °C, ppm):  $\delta$  3.36 (dt, 1H,  ${}^{3}J_{4,OH} = 5.9$  Hz,  ${}^{3}J_{4,3} = {}^{3}J_{4,5} = 9.5$  Hz, H-4), 3.50 (q, 1H,  ${}^{3}J_{6,OH} = {}^{3}J_{6,5} =$ 5.8 Hz, H-6a), 3.56-3.63 (m, 1H, H-5), 3.63 (dd, 1H,  ${}^{3}J_{2,1} = 1.1$  Hz,  ${}^{3}J_{2,3} = 4.0$  Hz, H-2), 3.74–3.78 (m, 1H, H-6b), 3.87 (q, 1H,  ${}^{3}J_{3,OH} = {}^{3}J_{3,2} = 4.6$  Hz, H-3), 4.49 and 4.74 (2d, each 1H,  ${}^{2}J_{7a,7b} = 11.7$  Hz, H-7a and H-7b), 4.63 (t, 1H,  ${}^{3}J_{6,OH} = 5.8$  Hz, OH-6), 4.82 (d, 1H,  ${}^{3}J_{1,2} = 1.1$  Hz, H-1), 4.97 (d, 1H,  ${}^{3}J_{4,OH} = 5.8$  Hz, OH-4), 5.06 (d, 1H,  ${}^{3}J_{3,OH} = 4.8$  Hz, OH-3), 6.84–6.90 (m, 2H, Ph), 7.28–7.38 (m, 6H, Ph), 7.43 (dd, 1H, J<sub>d</sub> = 1.5 Hz, Ph), 8.48 (s, 1H, H-14), 13.54 (s, 1H, OH-20). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz, 25 °C, ppm):  $\delta$  61.4 (C-6); 67.7 and 67.8 (C-4 and C-7); 69.8 (C-3); 71.2 (C-2); 74.7 (C-5); 98.6 (C-1); 116.4, 118.4, 118.6, 127.6, 127.8, 128.3, 131.8, 132.3, and 137.7 (all Ph); 160.8 (C-20); 167.2 (C-14). ESIMS (CHCl<sub>3</sub>/MeOH): m/z 374  $[(H_{2}sal^{H}Man)+H]^{+}$  (8%), 396  $[(H_{2}sal^{H}Man)+Na]^{+}$ (100%). Anal. Calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>6</sub> (373.39): C, 64.33; H, 6.21; N, 3.75; Found: C, 63.11; H, 6.16; N, 3.61.

# 4.6. [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)(tptz)]ClO<sub>4</sub>

Under vigorous stirring a solution of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (95 mg, 0.26 mmol) in 1 mL MeOH was added to a solution of H<sub>2</sub>sal<sup>NO<sub>2</sub></sup>Glc (108 mg, 0.26 mmol) and triethylamine (36 µL, 0.26 mmol) in 3 mL of MeOH. Subsequently, a solution of tptz (81 mg, 0.26 mmol) in 1 mL MeOH was added, during which a color change from pale-green to brown was observed. Within 1 min a pale-brown solid precipitated that was redissolved immediately by addition of 4 mL CHCl<sub>3</sub> and 3 mL CH<sub>3</sub>CN. Slow evaporation of the solvent leads to brown prismatic crystals suitable for X-ray measurements. The crystals were collected by filtration, washed with a small amount of MeOH, and dried in air affording  $[Ni(Hsal^{NO_2}Glc)(tptz)]ClO_4 \cdot 0.375CH_3CN \cdot 0.75H_2O.$  The given content of CH<sub>3</sub>CN and water molecules of crystallization corresponds to the values derived from the crystal structure. Yield: 196 mg (83%). Decomposition interval 287-300 °C. Selected IR data (KBr, cm<sup>-1</sup>):  $\tilde{v} = 3435$  (vO–H); 3064 and 3030 (vC–H arom.); 2924 (v<sub>as</sub>CH<sub>2</sub>); 2886 (v<sub>s</sub>CH<sub>2</sub>); 1636 (vCH=N); 1603, 1576, 1560, 1539, and 1487 (vC=C, vasNO<sub>2</sub>); 1473 and 1456 ( $\delta$ CH<sub>2</sub>); 1314 ( $\nu$ <sub>s</sub>NO<sub>2</sub>); 1145, 1101, 1054, 1030, 1011, 1000, and 949 (vC-O, vClO<sub>4</sub><sup>-</sup>). UV-vis (CH<sub>3</sub>CN solution,  $\lambda_{max}$  in nm ( $\epsilon$  in L mol<sup>-1</sup> cm<sup>-1</sup>)): 240 (36,000), 251 (36,000), 290 (41,000), 378 (24,000), (36). ESIMS (CHCl<sub>3</sub>/MeOH): m/z897 787  $[{Ni(Hsal^{NO_2}Glc)(tptz)}]^+$  (100%). Anal. Calcd for C<sub>38.75</sub>H<sub>35.63</sub>ClN<sub>8.38</sub>NiO<sub>12.75</sub> (916.79): C, 50.77; H, 3.92; N, 12.80; Found: C, 49.32; H, 3.94; N, 12.17.

# 4.7. [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub>

To a solution of H<sub>2</sub>sal<sup>H</sup>Man (80 mg, 0.21 mmol) and Et<sub>3</sub>N (30 µL, 0.22 mmol) in 3 mL of MeOH was added under vigorous stirring a solution of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (79 mg, 0.22 mmol) in 1.5 mL of MeOH. Thereafter a solution of tptz (67 mg, 0.22 mmol) in 1 mL of MeOH was added leading to an immediate color change from pale-green to brown. Within 1 min a pale-brown solid precipitated that was redissolved immediately by addition of 1.5 mL of CH<sub>3</sub>CN. Slow evaporation of the solvent affords brown prismatic crystals suitable for X-ray measurements. After filtration the collected crystals were washed with a small amount of MeOH and dried in air affording [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub>. 1.875CH<sub>3</sub>OH·1.1875H<sub>2</sub>O. The given content of CH<sub>3</sub>CN and water molecules of crystallization corresponds to the values derived from the crystal structure. Yield: 28 mg (15%). Decomposition interval 222–252 °C. Selected IR data (KBr, cm<sup>-1</sup>):  $\tilde{v} = 3400$  (vO–H); 3066 (vC-H arom.); 2927 (v<sub>as</sub>CH<sub>2</sub>); 1624 (vCH=N); 1576, 1560, and 1537 (vC=C); 1467 and 1447 (δCH<sub>2</sub>); 1152, 1122, 1109, 1089, 1046, 1027, and 1010 (vC-O, vClO<sub>4</sub><sup>-</sup>). UV-vis (CH<sub>3</sub>CN solution,  $\lambda_{max}$  in nm ( $\epsilon$  in  $L \mod^{-1} \operatorname{cm}^{-1}$ ): 228 (40,000), 247 (43,000), 289 (45,000), 384 (7600), 530 (130), 954 (36). ESIMS (CHCl<sub>3</sub>/MeOH): m/z 742 [{Ni(Hsal<sup>H</sup>Man)(tptz)}]<sup>+</sup> (100%). Anal. Calcd for C<sub>39.88</sub>H<sub>43.88</sub>ClN<sub>7</sub>NiO<sub>13.06</sub> (924.35): C, 51.82; H, 4.79; N, 10.61; Found: C, 50.47; H, 4.39; N, 10.96.

## 4.8. X-ray structure determinations

For the compounds [Ni(Hsal<sup>NO2</sup>Glc)(tptz)]ClO4 and [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub>, single crystals were selected while still covered with mother liquor under a polarizing microscope and fixed on fine glass fibers. Single-crystal X-ray measurements were carried out on a Nonius Kappa CCD diffractometer using graphite monochromated Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 71.073$  pm). The crystallographic and structure refinement data for both complexes are summarized in Table 3. The structures were solved by direct methods with sHELXS-97 and full-matrix leastsquares refined against  $F^2$  using SHELXL-97.<sup>69</sup> Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were calculated and treated as riding atoms with fixed thermal parameters. For both compounds additional molecules of crystallization were found in the crystal structures, some of which are located on partially occupied crystallographic positions. For [Ni(Hsal<sup>NO<sub>2</sub></sup>Glc)(tptz)]ClO<sub>4</sub> two positions fractionally occupied with CH<sub>3</sub>CN (0.375 CH<sub>3</sub>CN per Ni) and five positions fractionally occupied with water

Table 3. Summary of the crystal and structure refinement data

	[Ni(Hsal <sup>NO2</sup> Glc)(tptz)]ClO <sub>4</sub>	[Ni(Hsal <sup>H</sup> Man)(tptz)]ClO <sub>4</sub>
Empirical formula	C <sub>38,75</sub> H <sub>35,63</sub> ClN <sub>8,38</sub> NiO <sub>12,75</sub>	C <sub>39.88</sub> H <sub>43.88</sub> ClN <sub>7</sub> NiO <sub>13.06</sub>
Formula weight [g/mol]	916.79	924.35
Crystal size [mm]	0.9 imes 0.9 imes 0.9	0.6 imes 0.6 imes 0.5
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_{1}2_{1}2_{1}$
<i>a</i> [pm]	1569.47(7)	1381.86(2)
<i>b</i> [pm]	1518.99(8)	2565.16(5)
<i>c</i> [pm]	1966.79(8)	2646.19(5)
β [°]	101.121(3)	90.00
$V [10^6 \text{ pm}^3]$	4600.8(4)	9379.9(3)
$T[\mathbf{K}]$	183(2)	183(2)
Ζ	4	8
$\rho [\text{g/cm}^3]$	1.324	1.309
$\mu(Mo K_{\alpha}) [mm^{-1}]$	0.547	0.537
$\theta$ Range [°]	2.03–27.47	2.74-27.50
Collected data	34,002	40,550
Unique data $(R_{int})$	18,423 (0.1198)	20,433 (0.0500)
Observed data $[I \ge 2\sigma(I)]$	13,031	15,949
Parameters	1259	1263
Flack parameter	-0.04(2)	0.003(13)
Goodness-of-fit on $F_{o}^{2}$	1.049	1.068
$R_1 \left[ I > 2\sigma(I) \right]$	0.0961	0.0691
$wR_2$ (all data)	0.2739	0.1892

(0.75 H<sub>2</sub>O per Ni) were located. In addition also one of the perchlorate counterions is found to be disordered. For [Ni(Hsal<sup>H</sup>Man)(tptz)]ClO<sub>4</sub> methanol (1.875 MeOH per Ni) and water molecules (1.1875 H<sub>2</sub>O per Ni) of crystallization were found in the crystal structure. The hydrogen-bonded MeOH molecules depicted in Figure 6 are located at fully occupied positions, whereas the remaining MeOH molecules are disordered over four additional positions. The water molecules are disordered over four stallographically observed content of solvent molecules nicely resembles the weight loss determined by TGA measurements. Moreover, for both complexes an additional disorder of the phenyl ring of the benzyl protecting group at the Ni1 fragment could be resolved.

#### 5. Supplementary data

CCDC 667961 and 667962 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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