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Modeling the coordination chemistry of chitosan: Synthesis and characterization of a nickel(II) complex with a 2-aminoglucose Schiff-base ligand

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Abstract

Based on the sugar-modified Schiff-base ligand derived from salicylaldehyde and benzyl 2-deoxy-2-amino-α-D-glucopyranoside (H_2salagluc) the new mixed-ligand nickel(II) complex [Ni(Hsalagluc)(tptz)]ClO_4 has been synthesized (tptz = 2,4,6-tri-(2-pyridyl)-1,3,5-triazine). The X-ray crystal structure reveals a distorted octahedral geometry at the nickel(II) center with the rare 2,3-chelation of the *trans*-configured donor atoms of the carbohydrate backbone. Intermolecular hydrogen bonding leads to dimeric units of the complex cations. The supramolecular assembly of these units by π-stacking of the tptz coligands affords one-dimensional chains along the two fold screw axis. O–H···π(Ar) hydrogen bonding is observed for a methanol molecule of crystallization. Magnetic susceptibility measurements are consistent with a high-spin nickel(II) ion with a zero-field-splitting of $D = -11.5\ \mathrm{cm}^{-1}$ ($g = 2.311$).

Keywords: Carbohydrates; Schiff-bases; Nickel(II) complexes; Supramolecular chemistry; Self-assembly; π-Stacking

The β-(1–4)-linked polysaccharide chitosan obtained from alkaline deacetylation of chitin is well known for its adsorption properties towards metal ions [1]. Due to its versatility, biocompatibility, insolubility and non-toxicity chitosan is of current interest as support and supramolecular ligand for heterogeneous catalysis [2–9]. Schiff-base modified derivatives of chitosan show good catalytic activities concerning cyclopropanation, alkane oxidation and C–C coupling reactions [10–13]. In previous studies, we investigated the binding properties and structural features of copper(II) complexes with Schiff-base ligands derived from 2-aminoglucose to clarify the coordination chemistry of chitosan [14,15]. These complexes were found to tend to self-assembly affording oxo-bridged oligonuclear compounds with unexpected magnetic properties [15]. In an effort to prepare mononuclear model complexes for the chitosan system (Scheme 1) avoiding the self-aggregation problem we now utilized the preferentially octahedral nickel(II) ion together with a triazine based capping chelate ligand. Herein we report the first nickel(II) complex derived from an aminosugar showing the rare *trans*-2,3-chelation which was previously reported only for glucose-containing disaccharides [16]. Whereas the majority of the mononuclear sugar-based nickel(II) complexes were derived from *N*-glycosilated ligands exhibiting a corresponding 1,2-coordination [17–22].

The reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ with the tridentate Schiff-base ligand benzyl 2-deoxy-2-salicylideneamino-α-D-glucopyranoside (H_2salagluc) together with 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (tptz) as capping coligand in a mixture of methanol and chloroform affords the complex [Ni(Hsalagluc)(tptz)]ClO_4 as brown crystals [23]. In presence of one equivalent triethylamine the phenolic hydroxyl group of the H_2salagluc ligand is deprotonated upon

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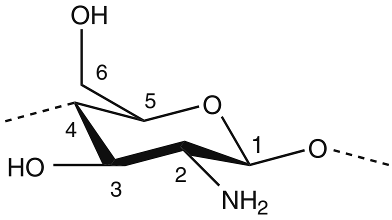

Scheme 1. 2-Aminoglucose building block of chitosan.

complexation and the sugar ligand therefore coordinates in its mono anionic form.

[Ni(Hsalagluc)(tptz)]ClO$_4$ crystallizes enantiomerically pure in the monoclinic space group $P2_1$ with two methanol molecules [24]. In Fig. 1 the molecular structure of one of the two rather similar but crystallographically independent molecules (denoted by the running number *j*) is depicted. The coordination geometry around the nickel(II) centers can be described as distorted octahedral. The tridentate ligands H$_2$salagluc and tptz both coordinate in a meridional fashion forming one six- and three five-membered chelate rings at the nickel(II) centers with bite angles of about 92° (O*j*6–Ni*j*–N*j*1) and 76–81° (N*j*2–Ni*j*–N*j*5, N*j*2–Ni*j*–N*j*6 and O*j*3–Ni*j*–N*j*1), respectively. The distortion of the octahedral geometry is most evident when the bond lengths of the nickel(II) centers are compared, as they fall into two groups of meridional donor sets at distances of about 198 and 217 pm. The donors within the short distance group are given by the salicylidene-based donor sets of the Schiff-base ligand, i.e. the imino nitrogen atom N*j*1 and the phenolic oxygen atom O*j*6, and the triazine nitrogen atom N*j*2 of the tptz coligand. The group of donor atoms with elongated bond lengths consists of the pyridyl nitrogen atoms N*j*5 and N*j*6 of the tptz coligand and the hydroxy oxygen atom O*j*3 of the sugar backbone. This is somewhat unusual, as the bond lengths of both the short and long distance groups are at the lower and upper limits of their expected ranges, respectively.

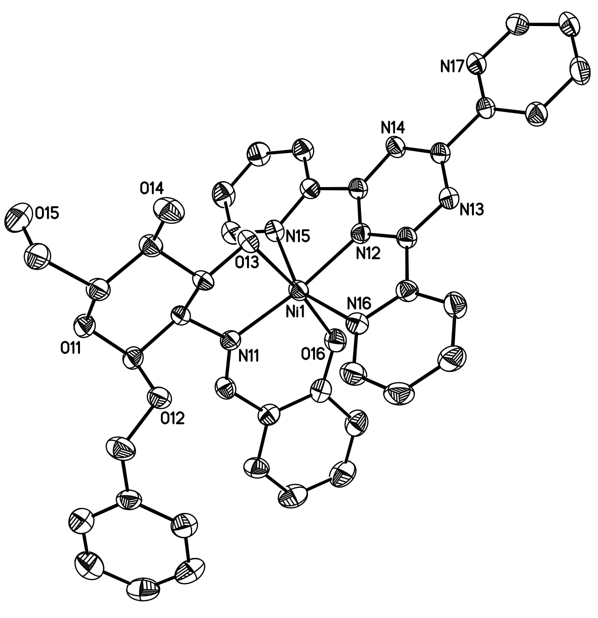

Fig. 1. Molecular structure of one of the two crystallographically independent [Ni(Hsalagluc)(tptz)]$^+$ cations in crystals of [Ni(Hsalagluc)(tptz)]ClO$_4 \cdot$ 2CH$_3$OH. Thermal ellipsoids are drawn at the 50% probability level. Pertinent bond lengths (pm) and angles (°) of both molecules (running number *j*, data are given in the order of *j* = 1,2): Ni*j*–O*j*3 216.1(2), 215.2(2); Ni*j*–O*j*6 199.7(2), 198.7(2); Ni*j*–N*j*1 198.3(3), 198.0(3); Ni*j*–N*j*2 198.0(3), 198.4(2); Ni*j*–N*j*5 217.6(2), 214.8(3); Ni*j*–N*j*6 218.3(2), 216.5(3); O*j*3–Ni*j*–O*j*6 172.93(10), 173.71(8); O*j*3–Ni*j*–N*j*1 81.21(9), 81.44(10); O*j*3–Ni*j*–N*j*2 91.55(9), 93.31(9); O*j*3–Ni*j*–N*j*5 89.27(9), 92.58(9); O*j*3–Ni*j*–N*j*6 90.69(9), 90.44(9); O*j*6–Ni*j*–N*j*1 91.93(10), 92.32(10); O*j*6–Ni*j*–N*j*2 95.35(10), 92.92(10); O*j*6–Ni*j*–N*j*5 93.83(10), 89.65(10); O*j*6–Ni*j*–N*j*6 89.44(9), 90.18(10); N*j*1–Ni*j*–N*j*2 172.61(10), 174.68(12); N*j*1–Ni*j*–N*j*5 102.03(10), 103.92(10); N*j*1–Ni*j*–N*j*6 104.69(10), 102.56(10); N*j*2–Ni*j*–N*j*5 76.23(9), 77.05(10); N*j*2–Ni*j*–N*j*6 76.72(10), 76.50(10); N*j*5–Ni*j*–N*j*6 152.94(10), 153.50(10).

Intermolecular hydrogen bonding interactions between the C3 hydroxy group of the sugar backbone and the nitrogen atom of the dangling pyridyl group of the tptz coligand of an adjacent [Ni(Hsalagluc)(tptz)]$^+$ moiety lead to the formation of dimeric {[Ni(Hsalagluc)(tptz)]$^+$}$_2$ units as depicted in Fig. 2. Two of the methanol molecules of crystallization (O1L and O4L) are involved in hydrogen bonds towards the phenolate oxygen atoms of the Schiff-base ligand. Whereas the other two methanol molecules build a hydrogen bonding relay with the C6 hydroxy group (O25) of the sugar backbone of one of the [Ni(Hsalagluc)(tptz)]$^+$ moieties and the phenyl group of an adjacent moiety of the same type (Ni2) as hydrogen bond acceptor, with an O–H$\cdots\pi$(Ar) distance of 255 pm. Additional hydrogen bonds are observed between the remaining hydroxy groups of the sugar backbone and the perchlorate counterions with OH$\cdots$O distances of about 289 pm. Moreover, within the dimeric units the tptz coligands of the [Ni(Hsalagluc)(tptz)]$^+$ moieties are involved in π–π interactions at distances of 320–350 pm [25–27]. The corresponding mean planes of the triazine fragments are almost coplanar with an angle of 4.8°. Additional π–π stacking of

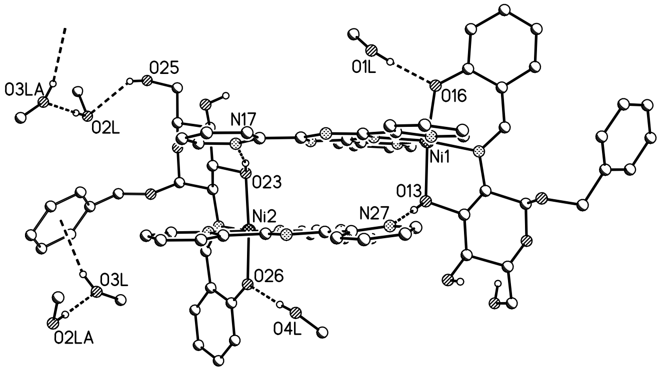

Fig. 2. Representation of the dimeric {[Ni(Hsalagluc)(tptz)]$^+$}$_2$ unit with hydrogen bonding interactions towards the methanol molecules in crystals of [Ni(Hsalagluc)(tptz)]ClO$_4 \cdot$ 2CH$_3$OH. Perchlorate ions and carbon-bound hydrogen atoms are omitted for clarity. Pertinent hydrogen bond distances (pm): O13$\cdots$N27 290.6, O23$\cdots$N17 284.6, O16$\cdots$O1L 271.7, O26$\cdots$O4L 267.8, O25$\cdots$O2L 275.7, O2L$\cdots$O3LA 280.0, O3L$\cdots\pi$(Ar) 357.7.