Structure of the First Tetranuclear Ni(II) Complex Derived from *N*-(2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine

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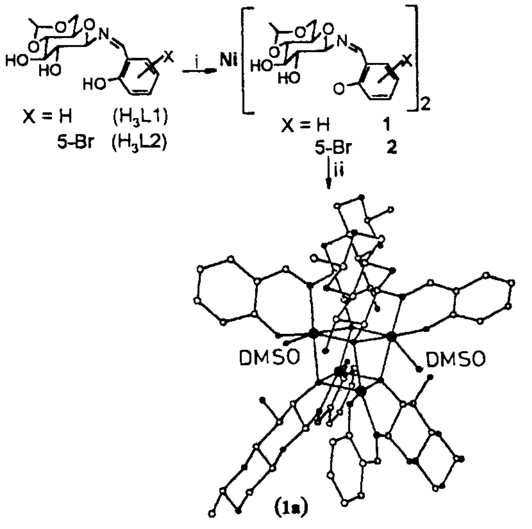
In order to understand the binding nature of the glycosylamines possessing imine functionality, a novel tetranuclear Ni(II) complex of *N*-(2-hydroxybenzylidene)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine having twisted Ni_4O_4 cubane core was synthesized and structurally characterized.

Although in recent times the Ni(II) is gaining importance in bioinorganic chemistry,[1] the knowledge regarding its interaction with bio-important ligand such as saccharide is in its infancy stage. Recently, only Yano's group reported the mono- and dinuclear complexes of glycosylamines with Ni(II).[2] However, during our recent efforts, we have established the structure of K^+ ion complex of *N*-(*o*-carboxyphenyl)-4,6-*O*-ethylidene-*β*-D-glucopyranosylamine.[3] Also reported were the structures of the glycosylamines and those possessing imine functionality (saccharide–C1–N=C–) derived from 4,6-*O*-ethylidene-*β*-D-glucopyranosylamine[4] and the products obtained from their interactions with *cis*-VO_2^+, *cis*-MoO_2^{2+} and *trans*-UO_2^{2+} species by single crystal X-ray diffraction (XRD) study.[5] In continuation with these efforts, the interaction of these saccharide based ligands with Ni(II) were studied, which resulted for the first time the formation of a tetranuclear cubane like structure with Ni_4O_4 core.

Metal ion cores suitable for the formation of a bis-chelate were already shown by us[4] structurally in case of the **H_3L2**. Two complexes of Ni(II) (**1** and **2**) resulted from the reaction between the glycosylamine ligands, **H_3L1** and **H_3L2** and $Ni(OAc)_2{\cdot}4H_2O$ in 2:1 ratio in MeOH at rt are shown in Scheme 1. Both the microanalyses and the FAB mass data of the products[6,7] supported the complex formation with metal to ligand composition of 1:2. However, crystallization of **1** dissolved in DMSO at room temperature followed by the diffusion of methanol into this solution resulted in the formation of single crystals, **1a** suitable for XRD studies. The crystal structure of **1a** revealed the Ni(II) to the ligand ratio to be 1:1[8] resulting in the formation of a tetranuclear complex through saccharide–C2–O^- bridging. The formation of **1a** upon crystallization is attributable to the instability of the mononuclear Ni(II) complex, **1** in DMSO solution as demonstrated by UV–vis absorption spectra. The UV–vis study revealed the breakage of **1** and **2** to result in the release of a Ni(II) species with metal to ligand ratio of 1:1 and the free ligand. The association of such Ni(II) species present in the solution would be responsible for the formation of a tetranuclear complex upon diffusion of MeOH into the DMSO solution.



Scheme 1. Syntheses of Ni(II) complexes: (i) $Ni(OAc)_2{\cdot}4H_2O$/MeOH; (ii) Dissolved in DMSO at rt followed by the diffusion of MeOH. Small dark circles represent oxygens and the big dark one represent Ni(II).

Single crystal XRD study of **1a** revealed a novel twisted Ni_4O_4 cubane core structure where the alternate corners of the cube were occupied by the Ni(II) and the saccharide–C2–O^-. The planes containing the two Ni(II) centers were making an angle with respect to each other to result in a twisted cube as can be seen from the stereo view (Figure 1a). The **HL1** acted as dianionic, tridentate (binding through phenolate ion, imine nitrogen, and saccharide–C2–O^-) to result in one five membered and another six membered chelates, where the saccharide–C2–O^- further extends two bridged interactions with the adjacent Ni(II) centres (Figure 1b). The $NiLO_{saccharide}$ distances are found in the range, 2.032–2.134 Å, $NiLO_{phenolic}$ distances are in the range 1.935–1.946 Å and the NiLN distances are 1.980–1.995 Å. Out of the four nickel centers, geometry around two were found to be square pyramidal [Ni(3) and Ni(4)] and the other two were found to be octahedral [Ni(1) and Ni(2)] wherein the sixth positions were occupied by DMSO with trans angles in the range 150.4°–175.7°. Ni(1) and Ni(4) (2.803 Å) or Ni(2) and Ni(3) (2.794 Å) form dimeric Ni_2O_2 species stabilized through two intra-complex H-bond interactions, saccharide–C3–O–$HLO_{phenolate}$, reminiscent of that observed in the Ni(II)–dimethylglyoximato complex. Thus the formation of the tetrameric, Ni_4O_4 unit (Figure 1) can be visualized to result through the association of two dimeric units. The remaining NiLNi distances are 3.152, 3.183, 3.194 and 3.197 Å, indicating that the Ni_4O_4 core is indeed distorted.

Even after the complex formation (**1a**), the saccharide moiety maintained its pyranose form with 4- and 6-positions being protected by the ethylidene moiety and C1 being modified via

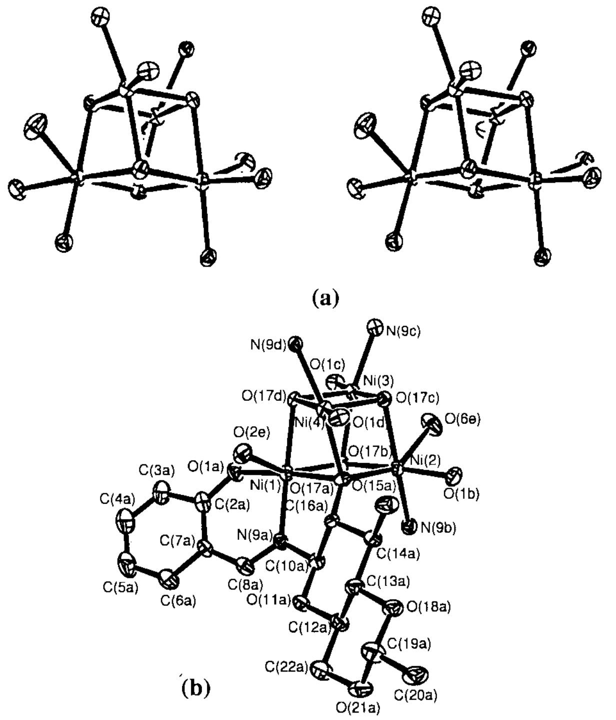


Figure 1. (a) Stereo view of the Ni_4O_4 core of **1a**; (b) ORTEP view of **1a** where only one saccharide molecule is shown for the sake of clarity even though there are four such molecules present.

imine bond formation to result in a $^4C_1$ conformation with double chair. The C1 center of the saccharide moiety exhibited the *β*-anomeric form. In the complex, the aromatic ring and the saccharide moieties were oriented trans with respect to the C=N bond.

In the lattice, the molecule **1a** exhibited four C-HLO type of intermolecular hydrogen bonding interactions where both the bound and free DMSO molecules were involved. The free DMSO molecule acted as hydrogen donor towards one of the pyranose oxygen and also acted as acceptor to the imine, H–C=N– hydrogen. On the other hand the Ni(II) bound DMSO molecule acted as donor towards the saccharide–C3–OH (in both the cases) of the neighbouring molecules to result in a linear network of molecules in the lattice.

In conclusion, we have synthesized and characterized two Ni(II) complexes using 4,6-*O*-ethylidene-*β*-D-glucopyranosylamine based ligand and the structure of one of these was established based on single crystal XRD and this study revealed an interesting core structure of Ni_4O_4. The nuclearity of the complex and the binding mode of the ligand were established based on the structural study. Further studies of these compounds and the related ones are currently under way in our laboratory.

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References and Notes

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6 Analytical Data for **1**: Yield: 73%; mp >250 °C. Anal. Calcd for $C_{30}H_{36}N_2O_{12}Ni\cdot 2H_2O$: C, 50.65; H, 5.67; N, 3.94%. Found: C, 51.13; H, 5.21; N, 3.67%. FABMS *m/z* 675 (65% for $[Ni(\mathbf{H_2L1})_2]^+$) and 731 [100% for $[Ni(\mathbf{H_2L1})_2 + Ni - 2H]^+$. UV–vis, λ_{max}/nm, (ε/$Lmol^{-1}cm^{-1}$): 262(40499), 320(9834), 377(12744), and 600(5).

7 Analytical Data for **2**: Yield: 74%; decomposes above 160 °C. Anal. Calcd for $C_{30}H_{34}N_2Br_2O_{12}Ni\cdot 4H_2O$: C, 39.81; H, 4.68; N, 3.09%. Found: C, 39.79; H, 4.28; N, 3.38%. FABMS *m/z* 833 (60% for $[Ni(\mathbf{H_2L2})_2]^+$ and 890 (40 % for $[Ni(\mathbf{H_2L2})_2 + Ni - 2H]^+$]. UV–vis, λ_{max}/nm, (ε/$Lmol^{-1}cm^{-1}$): 261(38360), 336(5929), 391(16996), and 600(3).

8 Crystal data for **1a**. Empirical Formula: $C_{69}H_{100}N_4Ni_4O_{31}S_3$; fw: 1812.55; Crystal system: Orthorhombic, $P2_12_12_1$; Unit cell Dimension (Å): 15.978(1), 19.589(1), 26.594(1); V = 8323.7(7) Å^3; Z = 4; D_c = 1.446 Mg/m^3; Unique reflections: 14502 [R(int) = 0.0666]; Final R [I>2σ (I)] = 0.0650 and R_w = 0.1452.