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# Synthesis and characterization of the dihydrosalpren ligand $(H_2L^1)$ and of its trinuclear Ni(II) complex

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#### ABSTRACT

The synthesis of the new unsymmetrical tetradendate Schiff ligand *N*-(2-hydroxybenzyl)-N'-(2-hydroxybenzylidene)-1,3-diaminopropane  $(H_2L^1)$  is reported. The ligand comprises two different coordination moieties: a rigid salicylaldimmine unit and a more flexible (2-hydroxybenzyl)-amino (hydrogenated salicylaldimmine) unit. The reaction of  $H_2L^1$  with Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1:1 molar ratio) leads to the spontaneous formation of a trinuclear complex with composition {[Ni(L<sup>1</sup>)OH<sub>2</sub>]<sub>2</sub>(OAc)<sub>2</sub>Ni}·2H<sub>2</sub>O, characterized by X-ray crystallography, where two [Ni(L<sup>1</sup>)] units act as O,O-bidentate chelate to a Ni(II) ion. © 2009 Elsevier B.V. All rights reserved.

It is known that the mononuclear metal complexes of tetradentate Schiff base ligands  $H_2L$  show the interesting feature of acting as "complex ligands" [1]. This property has been used to prepare and study a wide variety of adducts between transition metal complexes [ML] and alkaline [2], alkaline-earth [3], transition [1,3,4] and *f*-element [5] metal ions. Actually, important research efforts are devoted to the synthesis and characterization of homo- and hetero-trimetallic complexes of  $H_2L$  and relative reduced ligands, due to their applications in various fields [6–9].



Several studies have established that the hosting ability of [ML] complexes is dependent on a fine balance between flexibility and rigidity of the ligand [3]. Conformationally active ligands favour the geometrical disposition of the complex in relation to the guest metal dimensions. On the other hand, the rigidity appears to be an important requirement for the formation of an efficient cage structure. A simple method to favour the flexibility consists of increasing the length of the polymethylene spacer between the nitrogen atoms, leaving the electronic nature of the ligand unaltered. Alter-

natively, it is possible to improve the ligand's flexibility by hydrogenation of the imine bonds [10]. This method drastically modifies the electronic nature of the ligand and its donor strength, as the donor ability of the amine nitrogen is slightly stronger than those of the imine nitrogen atom.

In this paper we report the synthesis of the new unsymmetrical tetradentate ligand N-(2-hydroxybenzyl)-N'-(2-hydroxybenzilid-ene)-1,3-diaminopropane (dihydrosalpren,  $H_2L^1$ ) and a study on its coordination ability.



To the best of our knowledge, no studies are reported in literature on the preparation of the ligand  $H_2L^1$  and related metal complexes, while some reports describe the preparation of the half-hydrogenated salen ligand ( $H_2$ salen) [11–13]. In these studies, the key step in the synthesis of the ligand is the mono-condensation reaction of the salicylaldehyde with an excess of ethylene diamine, followed by the reduction with NaBH<sub>4</sub> or NaBH<sub>3</sub>CN and subsequent imine condensation of the resulted diamine with the salicylaldehyde. Following this suggestion, we carried out the same sequence of reactions using the salicylaldehyde and an excess of 1,3-propandiamine (from 1:4 to 1:10 molar ratio) in high dilution

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Scheme 1. (i) (1) dimethylglyoxime (2 equiv.), MeOH, 30 min, reflux. (2) NaBH<sub>4</sub> (3 equiv.), 2 h, reflux. (ii) salicyladehyde (1 equiv.), MeOH, 2 h, reflux.

conditions. In all the attempts we were able to isolate only the tetrahydrogenated product,  $H_4$ salprn, in high yields (>70%).

To overcome the difficulties we encountered in the mono-condensation of the 1,3-propandiamine with the salicylaldehyde, we considered the known octahedral Ni(II) complex **1** [14] a possible starting material. Thus, using this compound, the ligand  $H_2L^1$  was readily prepared in a one-pot procedure, as outlined in Scheme 1. After demetallation of **1** with dimethylglyoxime and separation from Ni(dmgly)<sub>2</sub> [15], the solution obtained was treated with NaBH<sub>4</sub> to hydrogenate the imine bond. The intermediate **2** obtained was not isolated, but was reacted *in situ* with the salicylaldehyde to give the ligand  $H_2L^1$  in good yield (65%)[16].

The unsymmetrical nature of the ligand was confirmed by IR and <sup>1</sup>H NMR spectroscopy. In particular, the IR spectrum displays a single sharp band at  $3279 \text{ cm}^1$ , due to the NH stretching vibration, and another at  $1629 \text{ cm}^1$ , characteristic of the azomethine (*C*=N) group. The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> is relatively simple and shows a single set of signals, which suggests that a single species exists in solution. The signals of the central methylene of the bridge appear as two triplets around 1.9 ppm, while two multiplets present at 2.7 and 3.7 ppm are attributed to the protons of the methylene units linked to the amine and imine nitrogen atoms, respectively. The signals of the benzylic protons appear as a singlet at 4 ppm and the complex pattern around 7 ppm, attributed to aromatic protons, confirm the unsymmetrical nature of the ligand.



**Fig. 1.** The molecular structure of  $\{[Ni(L^1)OH_2]_2(OAc)_2Ni\}\cdot 2H_2O$ . Hydrogen interactions are represented by dotted lines. Thermal ellipsoids are at 30% probability, '= 1 - x, 1 - y, 1 - z. Bond distances (Å) around Ni atoms: Ni(1)O(2), 2.029(2); Ni(1)O(1), 2.032(2); Ni(1)O(4), 2.050(3); Ni(1)N(1), 2.057(3); Ni(1)N(2), 2.085(3); Ni(1)O(3), 2.165(3); Ni(2)O(2), 2.044(2); Ni(2)O(1), 2.047(2); Ni(2)O(5), 2.130(2).

The slow addition of a nickel acetate solution in H<sub>2</sub>O to a solution of  $H_2L^1$  in methanol (1:1 molar ratio), at room temperature. rapidly afforded a green microcrystalline powder [17]. Recrystallization of this product from CH<sub>3</sub>CN resulted in the formation of crystals suitable for X-ray analysis. The structure of the compound is shown in Fig. 1 [18]. The complex has the formulation  $\{[Ni(L^1)O H_2]_2(OAc)_2Ni$   $H_2O$  and adopts a structural motif common for the tri-nickel acetate complexes of the Salpr and H<sub>4</sub>Salpr ligands [19-21]. The structure shows a trinuclear centrosymmetric complex consisting of three Ni<sup>2+</sup>atoms in a linear array. The Ni(2) ion is located at the inversion centre of the complex in an octahedral environment. This atom is coordinated by the four phenolic oxygen atoms from the two [NiL<sup>1</sup>] moiety that form a plane and, near-perpendicularly to it, by two oxygen atoms from the two acetate bridging ligands that connect the central metal to the outer metal ions. The greatest deviation of the bond angles from those expected for an ideal octahedral geometry is found for O(1)Ni(2)O(2) with 80.07° and O(1)Ni(2)O(2') with 99.93°. The remaining bond angles are close to the ideal values for the octahedral coordination [93.1° for O(1)Ni(2)O(5') and 86.9° for O(1)Ni(2)O(5)]. The bond distances Ni(2)O in the equatorial plane are similar (2.044 and 2.047 Å, respectively), while the axial Ni(2)O(5) bond distance is longer (2.130 Å).

The terminal nickel ions Ni(1) and Ni(1') are in an octahedral environment and are coordinated by two oxygen and two nitrogen atoms of  $(L^1)^2$  in the basal plane, and by two O atoms from one bridging acetate group and one coordinated water molecule in the axial positions. The [NiL<sup>1</sup>] unit are butterfly-shaped, with the dihedral angles formed by the two aryl rings of 58.0°. The greatest deviations from an ideal octahedral geometry are found in the O(1)Ni(1)O(2) (80.78°) and in N(2)Ni(1)N(1) (95.7°) angles. The two equatorial Ni(1)O(phenolic) bond lengths are practically identical (2.029 and 2.032 Å), while the axial Ni(1)O(4) and Ni(1)O(3)distances are rather different (2.050 and 2.165 Å, respectively) thus displaying the relative weakness of the bond with the uncharged water oxygen. Furthermore, the two Ni(1)N bond lengths are only slightly different (2.057 and 2.085 Å), but the N(1)C(benzylic) bond length (1.328 Å) is significantly shorter than the N(2)C(benzylic) bond length (1.451 Å), indicating the different nature of the nitrogen atoms [immine N(1) and amine N(2)].

The short bite of acetate ligand constraints the Ni(1) and Ni(2) coordination octahedra to tilt by 19.4° around the  $O(1) \cdots O(2)$  axis. The presence of the inversion centre on Ni(2) thus produces in the trinuclear complex the stair like structure shown in the figure.

The crystal structure is stabilized by a hydrogen bond network involving the coordinated water molecule (O(3)) and the lattice water (O(6)). The O(3) ligand water molecule behaves as a donor toward O(6) one (O(3)···O(6) 2.689 Å) and alternatively as a donor or acceptor toward the O(3) ligand of the nearest trinuclear complex in the **a** direction (O(3)···O(3'') 2.880 Å, " = -x, 1 - y, 1 - z). The O(6) lattice water molecule accepting a hydrogen bond from

O(3) donates a hydrogen bond to O(5) acetate oxygen  $(O(5)\cdots O(6')$  2.693 Å) as shown by dotted lines in Fig. 1 .

Attempts to isolate the mononuclear complex  $[NiL^1]$  failed. In particular, the use of stoichiometric defects of nickel ion (molar ratio ligand:nickel 1:0.8) or a slow addition of a methanol solution of nickel acetate in to methanol solution of H<sub>2</sub>L, invariably lead to the formation of the trinuclear complex above descript. This indicates a great tendency of  $[NiL^1]$  to act as a "complex ligands" in a similar way as the H<sub>4</sub>Salpr ligand [18], while, for the preparation of the trinickel species of Salpr ligand a stoichiometric excess of nickel ion is needed [20–22].

In conclusion, we have developed a convenient and efficient procedure to synthesize a new unsymmetrical tetradentate Schiff ligand that contains a rigid salycilaldimine coordination unit and more flexible (2-hydroxybenzyl)-amino coordination unit. The Ni<sup>II</sup> complex of this ligand shows a great tendency to act as a "complex ligand", forming trinuclear species. Efforts to investigate other metal complexes based on this new ligand are underway in our laboratory.

#### **Appendix A. Supplementary material**

CCDC 724555 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.inoche.2009.05.003.

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- [17] {[*Ni*(*L*<sup>1</sup>) $\dot{O}H_2$ ]<sub>2</sub>( $\dot{O}Ac$ )<sub>2</sub>*Ni*)<sup>2</sup>*H*<sub>2</sub>O. A water solution (5 mL) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.13 g, 0.52 mmol) was added dropwise to the ligand H<sub>2</sub>L<sup>1</sup> (0.15 g, 0.52 mmol) dissolved in methanol (15 mL). A green solid rapidly precipitated. This was filtered and dried. Yield 0.16 g. Crystals suitable for X-ray analysis were retrieved from acetonitrile solution. M.p.: >320 °C. IR (KBr, nujol): 3256, 3446 ( $v_{OH}$ ) cm<sup>1</sup>; 3282, 3260 ( $v_{NH}$ ) cm<sup>1</sup>; 1636 ( $v_{C=N}$ ) cm<sup>1</sup>; 1590, 1482 ( $v_{COO}$ ) cm<sup>1</sup> Found: C 48.91%, H 5.55%, N 6.12%. Expected for C<sub>38</sub>H<sub>50</sub>N<sub>4</sub>O<sub>12</sub>Ni<sub>3</sub>: C 49.03%, H 5.41%, N 6.02%.
- [18] X-ray Crystal structure determination of {[Ni(L<sup>1</sup>)OH<sub>2</sub>]<sub>2</sub>(OAc)<sub>2</sub>Ni}-2H<sub>2</sub>O: C<sub>38</sub>H<sub>50</sub>N<sub>4</sub>Ni<sub>3</sub>O<sub>12</sub>, *M* = 930.89, triclinic, space group *P*1, *a* = 9.881(2), *b* = 10.415(2), *c* = 10.808(1) Å,  $\alpha = 68.82(1)$ ,  $\beta = 80.47(1)$ ,  $\gamma = 86.60(1)^\circ$ , *V* = 1022.8(3) Å<sup>3</sup>,  $\rho_{calcd} = 1.511$  g cm<sup>3</sup>,  $\mu = 1.028$  m cm<sup>1</sup>, *Z* = 1, Mo K $\alpha$ radiation,  $\lambda = 0.71073$  Å, *T* = 296 K. The unit cell content consists in one {[Ni(L<sup>1</sup>)OH<sub>2</sub>]<sub>2</sub>(OAc)<sub>2</sub>Ni] centrosymmetric molecule and two water lattice molecules. The hydrogen atoms of the acetate ligands have been introduced in the model as statistically disordered on two limit positions. Programmes used: SHELX97 (G.M. Sheldrick, SHELX97, Structure Solution and Refinement Package, Universität Göttinegen, 1997) and WINGX (L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565) suite *R*<sub>1</sub> = 0.0481, *wR*<sub>2</sub> = 0.0901; GOF = 1.053 for 3172 unique reflections and 250 parameters.
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