Inorganic Chemistry Communications 62 (2015) 55–59

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Pro-oxidant activity of nickel (II) pyridoxal complexes. Synthesis, characterization and peroxidase activity assays

Liniquer Andre Fontana, Mônica Stüker, Gelson Manzoni Oliveira, Bernardo Almeida Iglesias *, Davi Fernando Back *

Departamento de Química, Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, UFSM, 97115-900 Santa Maria,RS, Brazil

ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form 14 October 2015
Accepted 16 October 2015
Available online 20 October 2015

Keywords:
Pyridoxal
Nickel complexes
Peroxidase mimetization

ABSTRACT

The synthesis of Ni (II) complexes with pro-oxidant applications has demonstrated many advantages, such as accelerated reactions, solution stability and with high selectivity reactions. In this work we describe the synthesis, characterization and structural analysis of nickel ($[(Ni)(C_{30}H_{28}N_4O_4S_2)]$);($[(Ni)(C_{31}H_{30}N_4O_4S_2)]$) and ($[(Ni)(C_{33}H_{37}N_4O_4S_2)]\cdot$DMF — complex 3) complexes with ligands obtained from the condensation of pyridoxal and aryl-thiol amines and their application as a pro-oxidant in the reaction of the phenol-aminoantipyrine adduct. The complexes show variation in carbon spacers between pyridoxal molecules: ethane, propane and butane. It was found that the spacer two carbons containing the most significant as the pro-oxidant activity.

The peroxidases are a class of enzymes that act mainly on the decomposition of hydrogen peroxide and the oxidation of certain substrates [1]. These enzymes are targets of numerous studies for its use in catalysis [2] and the generation of pro-oxidant species in the degradation of certain substrates [3]. The direct use of the enzyme for this purpose is usually disadvantageous due to the high costs involved in obtaining large scale, as well, the specific reaction conditions to avoid denaturation and ensure good performance [4]. To overcome these limitations, several chemical species have been studied for use as enzyme peroxidase mimics, particularly involving these species, coordination complexes [5], inorganic polymers and nanoparticles [6]. The use of ligands that have mixed donor atoms O, N and S, wherein the oxygen group is a hydroxyl, the nitrogen group was a iminic and the sulfur atom was a thioether are of great interest in the enzymatic synthesis of mimics due to the similarity of complex formed with the active site of certain metalloenzymes [7]. The metal complexes formed with these ligands exhibit electrochemical [8] magnetic [9], catalytic [10], and pharmacological [11] properties, thereby justifying the great interest in its coordination chemistry.

The 2-aminothiophenol may be used as a building block versatile for the synthesis of these ligands, because the selective derivatization can be performed in the –SH and –NH_2 groups. These ligands used in this study were synthesized by alkylation of thiols with di-alkyl halides and the subsequent formation of Schiff bases with the amino group. Pyridoxal is an aldehyde derivative of vitamin B_6, a cofactor and various enzymatic reactions involving the metabolism of proteins, especially for the transamination reactions of [12], racemization [13] and decarboxylation [14] amino acid. Under the supramolecular view, Schiff bases derived from pyridoxal exhibit rich coordination chemistry, intermediate hard coordinate site [15], and a variety of potential intermolecular interactions [16].

Therefore, in this manuscript we describe the synthesis [17–19] structural characterization [20–22] and electrochemical [23] behavior of novel complexes of nickel(II) using ONS donor ligands derivatives pyridoxal. As well as, the evaluation of these Ni(II)-complexes as mimic peroxidase [24–27] enzyme.

In the complexes 1, 2, and 3 the ligands act with three coordination sites; phenolate oxygen, iminic nitrogen and the thiol In complex 1 and 2 the symmetry operator (2-x, y, 0.5 is the complex z-1 and 1-x, y, z 0.5 is the complex 2) completed the coordination shown in the Figs. 1, 2 and 3. Crystal data and more details of the data collection and refinements of the complexes 1, 2 and 3 are contained in Table 1a (see in supplementary information).

The metal center Ni (II) has coordination number six (C.N. = 6) giving it a coordination geometry in the form of a distorted octahedron, this distortion can be evidenced by the angles with the metal center and the ligands: complex 1(O1–Ni–S1 = 169.61(8);N2–Ni–N(2)# = 177.05(19); O(1)#-N2–S1 = 99.57(4)) Complex 2 ((O1–Ni–S1 = 167.91(9); N2–Ni–N(2)# = 172.7(2);O(1)#-N2–S1 = 101.23(2)) and complex 3 (O1–Ni–S1 = 167.44(14); O3–Ni–S2 = 171.57(14); N2–Ni–N3 = 175.8(2); O1–N2–S1 = 101.82(3); O3–Ni3–S2 = 100.85(2)). In this context, the bonding distances involving the nickel atom with atoms of oxygen, nitrogen and sulfur may also be compared: complex 1 (N1–Ni = 2.053(3); O1–Ni = 2.002(3); S–Ni = 2.4404(14))

---

* Corresponding authors
E-mail addresses: bernardopgq@gmail.com (B.A. Iglesias), daviback@gmail.com (D.F. Back).

http://dx.doi.org/10.1016/j.inoche.2015.10.027
1387-7003/

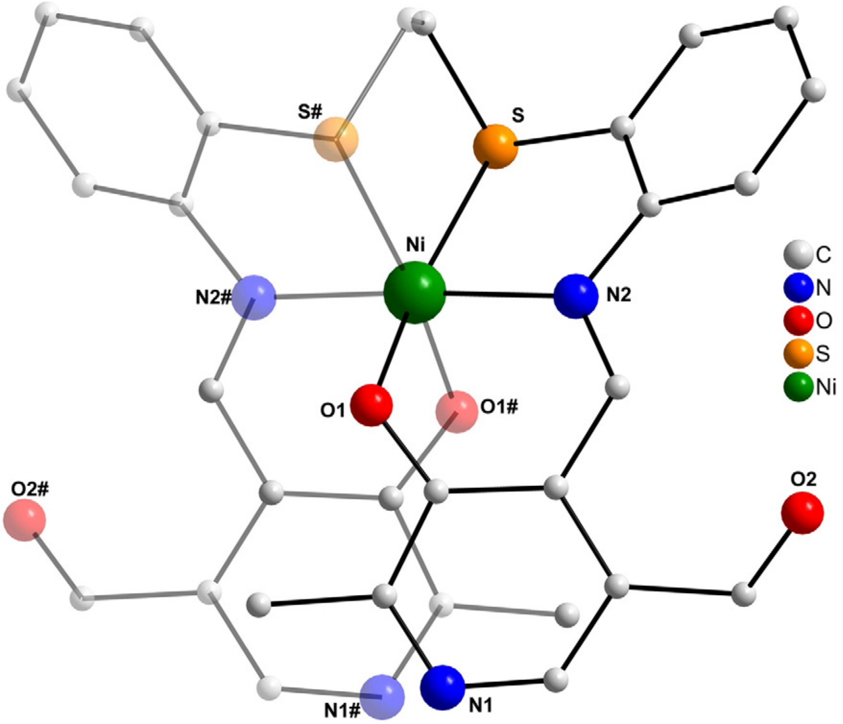

Fig. 1. Molecular structure of the nickel (II) complex (1). For greater clarity, hydrogen atoms are omitted. Symmetry operations used to generate equivalent atoms: (#1) 2-*x*, *y*, 0.5-*z*.

complex 2 (N1–Ni = 2.034(3); O1–Ni = 1.998(3); S–Ni = 2.4992(14)) and complex 3 (N2–Ni = 2.031(5); N3–Ni = 2.022(5); O1–Ni = 2.020(4); O3–Ni = 1.989(4); S1–Ni = 2.4710(19); S2–Ni = 2.5323(19)).

These values are consistent with the values found in the literature, and are referred to as Ni–N (iminic) 1.988 to 2.045 Å, Ni-O (phenol) 2.027 to 2.045 Å and Ni–S (thioether) 2.414 to 2.4776 Å [28–30]. The other bonding length values and relevant angles obtained by the structural analysis of compounds 1, 2 and 3 are listed in supplementary information (Tables 2, 3 and 4 respectively).

In the structure of complex 2, one of the carbon atoms is disordered. This atom C16 was modeled using 50% occupancy for each position,

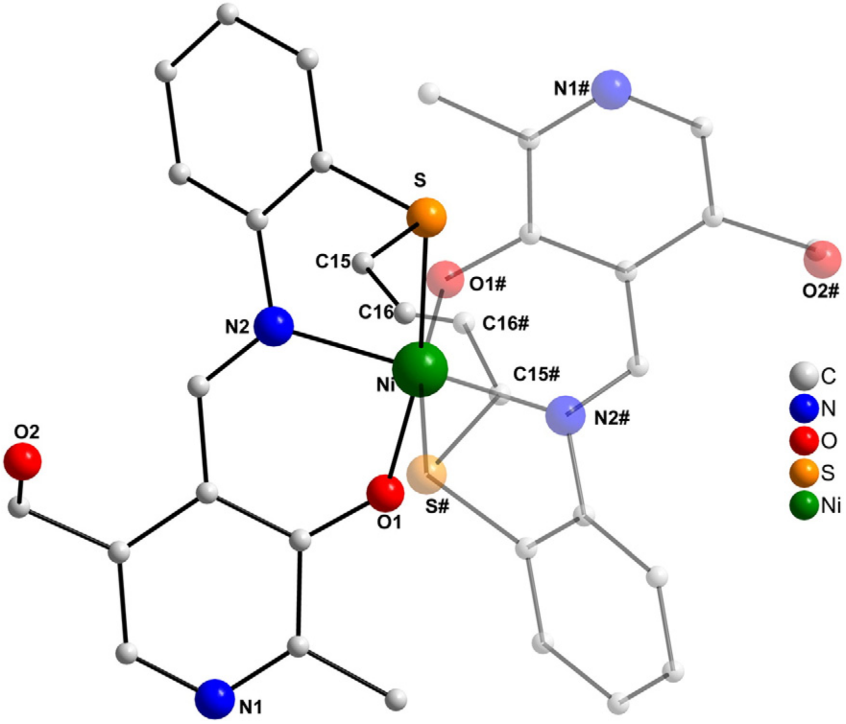

Fig. 2. Molecular structure of the nickel (II) complex (2). For greater clarity, hydrogen atoms are omitted. Symmetry operations used to generate equivalent atoms: (#1) 1-*x*, *y*, 0.5-*z*.