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Syntheses, crystal structures, spectroscopy, and catalytic properties of two nickel-based hexaazamacrocyclic complexes with carboxylate ligands

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ABSTRACT

Two new hexaazamacrocyclic nickel(II) complexes with the formula $[NiL^1(4\text{-nba})_2]$ (**1**) and $[NiL^2(sal)_2]$ (**2**) (L^1 = 3,10-dioctyl-1,3,5,8,10,12-hexaazacyclotetradecane, L^2 = 3,10-diisobutyl-1,3,5,8,10,12-hexaazacyclotetradecane, 4-nba = *p*-nitrobenzoate, and sal = salicylate) were synthesized at room temperature. These complexes were characterized by physico-chemical and spectroscopic methods as well as single-crystal X-ray diffraction analysis. The coordination geometry in complexes **1** and **2** exhibit a distorted octahedron around the nickel(II) ion with hexaazamacrocyclic unit in the equatorial positions and two *p*-nitrobenzoate (or salicylate) anions in the axial positions. The degradation of methyl orange by potassium persulfate (KPS) in the presence of complex **1** (or **2**) oxidation system occurred to near completion in 60 min compared to only 55% with KPS alone under UV light irradiation. Thus, both complexes in cooperation with KPS could be an attractive choice for degradation of organic pollutants for environmental remediation.

The increasing world population with growing industrial demands has led to a situation where protection of the environment has become a major problem and an importance factor for several industrial processes. Needless to say, the dye pollutants from textile industry are among those important sources of environmental contaminations. The resulting colored wastewater imposes a major problem for the industry as well as a serious threat to the environment [1,2]. Many studies have been carried out in which chemical and physical processes such as electrochemical process, ion-exchange, flocculation and coagulation technique, biological treatment, adsorption on activated carbon have been applied for color removal from textile wastewater [3–5].

Moreover, the advanced oxidation processes, or the so-called "AOPs", have been widely studied for the treatment of industrial wastewaters. In general, AOPs are mainly based on the generation of the highly reactive oxidizing species, hydroxyl radical, which may be generated by various methods such as UV photolysis of hydrogen peroxide/ozone (H_2O_2/O_3) [6], photochemical catalysis (UV/TiO_2) [7], Fenton's reaction [8], and persulfate oxidation [9,10]. The activated persulfate oxidation uses persulfate anion ($S_2O_8^{2-}$) which is also known as peroxydisulfate or peroxodisulfate. Persulfate salts of $(NH_4)_2S_2O_8$, $Na_2S_2O_8$, and $K_2S_2O_8$ dissociate in water to yield the persulfate anion which is one of the very strong oxidation species with high potential ($E^\circ = 2.01$ V) compared with H_2O_2 ($E^\circ = 1.76$ V). It shows some advantages over other oxidants as being a solid chemical at room temperature with the ease of storage and transport, high stability, high aqueous solubility, and relatively low cost [11]. There are several methods to activate the persulfate anions, such as thermal activation [12], UV irradiation [13], base activation [14], and activation with transition metal catalysts [15], to generate reactive sulfate radicals ($SO_4{}^{\bullet -}$). Activation of persulfate by metal ion catalysis occurs by an oxidation-reduction reaction in which low valent metal ions (M^{n+}) act as electron donors. Heterogeneous catalysis of the nickel(II) complexes with N-donor atoms from the hexaazamacrocyclic and carboxylate mixed ligands have been extensively used in the preparation of coordination polymers (CPs) [16,17]. In the family of aromatic carboxylate ligands, for example, 1,3,5-benzenetricarboxylate (BTC^{3-}), 2,2′-biquinoline-4,4′-dicarboxylate ($BQDC^{2-}$), and isonicotinnate the coordination network through space in one-, two- or three-dimensional architectures have been reported [18,19]. The dimensionality of the resulting coordination network can be increased by non-covalent interactions, such as hydrogen bonding, π⋯π stacking, C—H⋯π, and other van der Waals interactions [20]. The coordination polymers have been an active research area in recent years because it can be applied in many fields such as magnetism, electronics, luminescence, and catalytic activity [21,22].

In this report, we describe the syntheses, characterizations, and crystal structures of two nickel(II) complexes, that is, $[NiL^1(4\text{-nba})_2]$ (**1**) and $[NiL^2(sal)_2]$ (**2**) (L^1 = 3,10-dioctyl-1,3,5,8,10,12-hexaazacyclotetradecane,

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L^2 = 3,10-diisobutyl-1,3,5,8,10,12-hexaazacyclotetra-decane, 4-nba = *p*-nitrobenzoate, and sal = salicylate). In addition, catalytic capabilities of these complexes working in cooperation with persulfate (from KPS) for the degradation of methyl orange (MO) were investigated. For the preparation, **1** and **2** were synthesized at room temperature in mixed $MeCN/H_2O$ solvent with triethylamine added for adjusting the pH of the solution (see supporting information). The carboxylate ligands replaced the perchlorate anions in the axial positions of both complexes. It is worth mentioning that during the reaction of complex **2**, the acetoxy group of the aspirinate ligand underwent hydrolysis process resulting in the cleavage of a covalent bond in a molecule to give the salicylate ligand which was confirmed in the structure by X-ray diffraction technique.

Single crystal X-ray diffraction analysis (See supporting information) showed that **1** crystallizes in the monoclinic space group of *C*2/*c* and containing $[NiL^1]^{2+}$ cation and two *p*-nitrobenzoate anions as shown in Fig. 1a and packing diagram in Fig. 1c. The nickel(II) ion of **1**

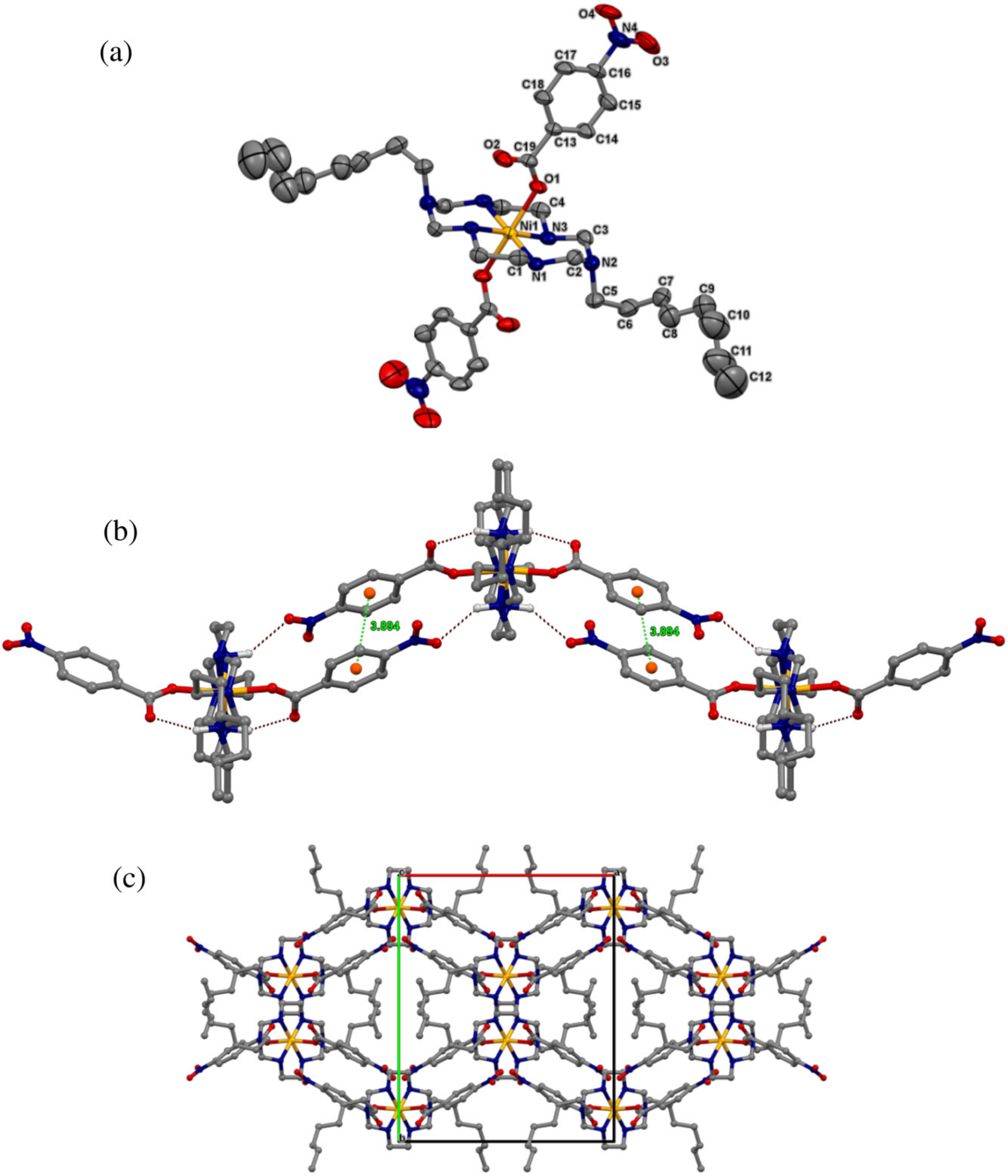

Fig. 1. Molecular structure of **1**, (a) coordination environment of a mononuclear Ni(II) ion with the numbering scheme. (b) The 1D supramolecular network via the H-bonding and π-π stacking interactions. (c) The packing unit cell, viewed along the *a* axis.