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Synthesis and characterization of formyl group containing N-monofunctionalized tetraazamacrocyclic ligand and its nickel(II) complex

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Abstract

New N-functionalized tetraaza macrocyclic ligand [*N*-{(2-hydroxy-3-formyl-5-bromo)benzyl}-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L)] and its nickel(II) complex has been prepared and characterized. The X-ray structural analysis of $[NiL](ClO_4) \cdot H_2O$ showed that the geometry around nickel(II) ion is distorted trigonal bipyramid. Cyclic voltammetric studies of Ni(II) complex show one electron irreversible reduction at $E_{pc} = -1.49$ V and oxidation at $E_{pa} = 1.12$ V. Nickel(II) complex has a room temperature magnetic moment value of $\mu_{eff} = 3.35$ B.M.

Keywords: Tetraaza macrocycle; N-functionalization; Nickel(II) complex; Crystal structure; Electrochemistry

Tetraaza macrocyclic complexes bearing pendant coordination side arms have found applications in various areas such as medical [1], environmental sciences [2], biomimetic chemistry [3], catalysis [4], molecular electronics [5] and their chemistry has accordingly been developed. Pendant arms can enhance the selectivity of the ligand for a given ion and may allow for a fine-tuning the properties of the complex. Our research has focus on the synthesis of N-functionalized "tet a" ligand [6]. The pendant arm in the macrocyclic ligand has a formyl group apart from a phenolic group. In ligand, the pendant donor group is linked to the macrocyclic donors via a methylene group that imparts high degree of ligand conformational flexibility [7,8]. The special feature of this ligand is the presence of formyl group, which can be further condensed with polymers. These macrocycle-appended polymers can be used in metal extraction processes [9] and catalytic applications. The aldehyde group can also be condensed with fluorescent moiety [10] or redox active molecule, which can be used as sensors [11]. This paper deals with synthesis and characterization of N-monofunctionalized "tet a" macrocyclic ligand and its nickel(II) complex.

The ligand was prepared [12] by reacting equimolar amount of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane [13] with 3-chloromethyl-5-bromosalicylaldehyde [14] in acetonitrile and the resulting compound was hydrolyzed with aqueous NaOH solution. The nickel(II) complex [15] was prepared in 72% yield by reacting equimolar amounts of $Ni(ClO_4)_2 \cdot 6H_2O$ with an equimolar amount of L in methanol. Green colored single crystals of $[NiL](ClO_4) \cdot H_2O$ suitable for X-ray diffraction study were grown by the slow evaporation of the methanolic solution. The synthetic route for the preparation of complex is shown in Scheme 1.

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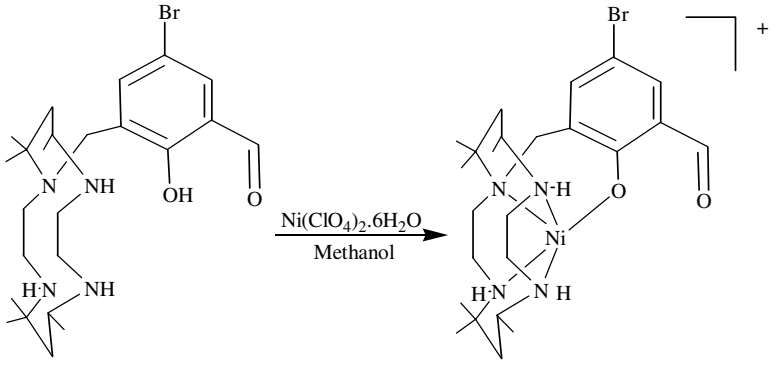

Scheme 1.

An ORTEP diagram of $[NiL](ClO_4) \cdot H_2O$ with the atomic labeling scheme is shown in Fig. 1. The nickel(II) ion is five-coordinated, and the geometry around the nickel ion is distorted trigonal bipyramid [16] with atoms N2, N4 of "tet a" and O6 from pendant phenolic group forming the trigonal plane. The atoms N1 and N3 of "tet a" occupy the axial positions. The phenolic oxygen and amine nitrogen atoms are coordinated to the nickel ion with distance of Ni–N(1) = 2.094(4), Ni–N(2) = 2.095(5), Ni–N(3) = 2.086(5), Ni–N(4) = 2.072(4), Ni–O(6) = 1.954(4) Å. The nickel is pulled out of the basal plane towards N3 by 0.0233(1) Å from trigonal plane. The axial Ni–N1 [2.094(4) Å] bond length is longer than the other axial Ni–N3 bond [2.086(5) Å]. Coordination bond formed by the secondary nitrogen (Ni–N3) is stronger than the tertiary nitrogen atom (Ni–N1). So the Ni ion is shifted towards N3. The angles in the trigonal plane depart significantly from theoretical (120°) value with values of 105.94 (19), 136.56 (18), 117.86 (19)°. The phenyl ring is roughly parallel to the basal plane. The structural index τ, $[\beta - \alpha]/60$ with α and β being two largest angles, is zero for an ideal square pyramid and becomes unity for an ideal trigonal bipyramid [17]. The τ value of nickel(II) complex is 0.67 indicating that the trigonal bipyramid geometry is distorted or deviates towards square pyramid. One uncoordinated perchlorate anion is present in the complex and this ion neutralizes the positive charge of the complex. The water molecule found in the crystal is not coordinated with the Ni(II) ion and occupies the crystal lattice as a free molecule.

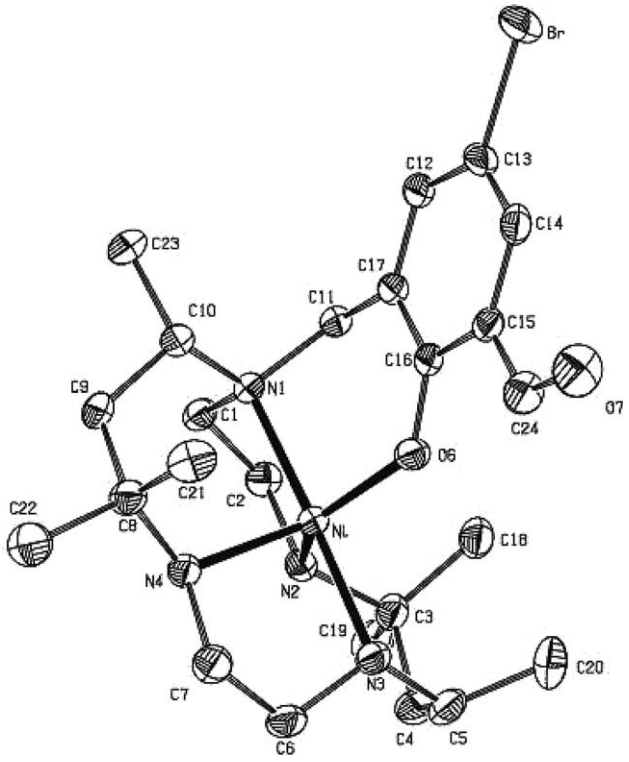

Fig. 1. ORTEP diagram of $[NiL]ClO_4 \cdot H_2O$ with atom labels and numbering scheme (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ni–N(1) 2.094(4), Ni–N(2) 2.095(5), Ni–N(3) 2.086(5), Ni–N(4) 2.072(4), Ni–O(6) 1.954(4) and N(1)–Ni–N(2) 85.64(17), N(3)–Ni–N(2) 91.20(2), N(4)–Ni–N(2) 105.54(19), N(3)–Ni–N(1) 176.53(19), N(4)–Ni–N(1) 93.72(17), O(6)–Ni–N(1) 93.06(16), O(6)–Ni–N(2) 136.56(18), O(6)–Ni–N(3) 90.22(18), O(6)–Ni–N(4) 117.86(19).

The infrared spectrum of ligand shows ν(N–H), ν(C=O) peaks at 3289, 1666 cm^{-1}, respectively. The nickel(II) complex shows ν(N–H), ν(C=O) peaks at 3251, 1655 cm^{-1} respectively. The complex also shows peaks at 1087 and 624 cm^{-1} characteristic of perchlorate anion. The peak at 1087 cm^{-1} is broad without splitting indicates that the perchlorate is not coordinated with the metal ion [18]. The diffusion reflectance spectrum of nickel(II) complex displays an absorption maximum at 965, 750(sh), 625, 400 nm. The electronic spectrum of the complex in DMF exhibits three main transitions. The absorption bands observed at 985 nm ($\varepsilon \sim 25\ M^{-1}cm^{-1}$), 756(sh) nm, 612 nm ($\varepsilon \sim 68\ M^{-1}cm^{-1}$), 398 nm ($\varepsilon \sim 3450\ M^{-1}cm^{-1}$) are attributable to the distorted trigonal bipyramid geometry around Ni(II) ion which is consistent with literature report [19]. The electronic spectrum of the complex in DMF solution has red shift (10–20 nm) when compared to the solid state