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Syntheses and Structure of New Mononuclear Nickel(III) Complex [Ni(L)]·H_2O, where H_3L = [(3-Ethoxy-2-hydroxy-benzylidene)]-[*N*-(3-ethoxy-2-hydroxy-benzylidene)]-1-amino-N-amino-Formimidic Acid

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A new complex [Ni(L)]·H_2O (**1**) ([H_3L = [(3-ethoxy-2-hydroxy-benzylidene)]-[N'-(3-ethoxy-2-hydroxy-benzylidene)]-1-amino-N-amino-Formimidic acid) was synthesized through solvothermal method and it's structure ($C_{19}H_{21}N_3O_6Ni$, Mr = 446.10) was determined by IR spectra, elemental analysis, single-crystal X-ray diffraction analysis. The crystal belongs to monoclinic system, space group $P2_1/n$ with a = 11.4763(4), b = 7.1321(2), c = 24.2433(7) Å, β = 96.578(3)°, V = 1971.26(11), Z = 4, R_1 = 0.0484. The Ni(III) ion is coordinated by two O atoms and two N atoms from a tetradentate L^{3-} in a slightly distorted planar environment. In the crystal structure, the main structure [Ni(L)] seized a solvent water molecule through intramolecular O-H···O hydrogen bond. Ni(III) ion and L^{3-} were attained through *in situ* reaction.

Keywords: Schiff base, Ni(III) Complex, Crystal Structure.

INTRODUCTION

Schiff base ligands derived from aldehydes and amines are one of the most important ligands systems in homogeneous and heterogeneous catalysis, in stereoselective synthesis[1] and their metal complexes exhibit their fascinating structures and functional applications in biological activity, magnetic, electronic, optical, catalytic materials and fluorescent materials[2-9] Thus, it is quite important to have a good understanding of the structure of such metal complexes. In the past years, we have reported a series of complexes with Schiff base ligands and investigated their structure and some relative properties[6,8,10,11].

Ni(III) tetrapyrrolic macrocycles have been intensively studied[12]. Wolberg and Manassen[13] reported on the generation of a Ni(III) porphyrin at 77 K. This reaction was re-examined by Dolphin and his colleagues where it was observed that a Ni(II) porphyrin π-cation radical was formed at room temperature and a low spin Ni(III) porphyrin was generated upon cooling to 77 K, showing intramolecular electron transfer[14]. N-confused porphyrins are porphyrin isomers with an inverted pyrrolic ring and were first reported independently by Latos-Grazynski *et al.*[15] and Furuta *et al.*[16]. They can stabilize transition metals in high oxidation states and some Ni(III) complexes have been repared by Latos-Grazynski[17]. However, crystallographically characterized Ni(III) tetrapyrrolic macrocycles are rare and to the best of our knowledge, the only related example is an oxidized nickel porphyrin $[Ni(OETPP)(BTD)]^+$ (OETPP = β-octaethyl-meso-tetraphenylporphyrin, BTD = 2,1,3-benzothiadiazole) with an EPR spectrum typical of Ni(III)[18]. Herein, we reported a new Ni(III) with open-macrocycle ligand complex (**1**) through *in-situ* reaction formed [(3-ethoxy-2-hydroxy-benzylidene)]-[N'-(3-ethoxy-2-hydroxy-benzylidene)]-1-amino-N-amino-formimidic acid (Fig. 1).

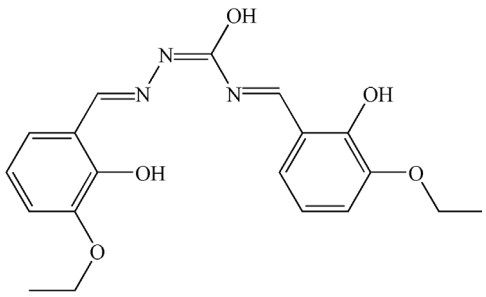


Fig. 1. Structure of H_3L

EXPERIMENTAL

All chemicals were commercially available and used as received without further purification. The C, H, N microanalyses were carried out with a PE 2400 series II elemental analyzer.

The FT-IR spectra were recorded from KBr pellets in the range of 4000-400 cm^{-1} on a PE spectrum one FT-IR spectrometer. The crystal structure was determined by single-crystal X-ray diffraction and using SHELXS-97, SHELXL-97 software for structure solution and refinement, correspondingly.

General procedure: A mixture of Hehbd (0.166 g, 1 mmol, Hehbd is 3-ethoxy-2-hydroxybenzaldehyde), $Ni(ClO_4)_2·6H_2O$ (0.360 g, 1 mmol), carbohydrazide (0.045 g, 0.5 mmol), ethanol (10 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120 ºC for 120 h and then cooled to room temperature. Green block crystals of **1** were obtained. Phase-pure crystals of **1** were obtained by manual separation (Yield: 125.6 mg, 56.4 %, based on Ni). Anal. calcd. (%) for $C_{19}H_{21}N_3O_6Ni$: C, 51.15; H, 4.75; N, 9.41. Found (%): C, 51.12 H, 4.78; N, 9.45. IR data (KBr, ν_{max}, cm^{-1}): 3440(m), 1626(s), 1448(s), 1249(s), 1116(m), 906(m), 741(m), 441(w).

Diffraction data sets were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 293 K using the ω-θ scan mode in the range $2.93° \le \theta \le 25.10°$. Raw frame data were integrated with the SAINT program[19]. The structures were solved by direct methods using SHELXL-97 and refined by fullmatrix least-squares on F^2 using SHELXS-97[19]. An empirical absorption correction was applied with the program SADABS[19]. All non-hydrogen atoms were refined anisotropically. Hydrogenatoms were set in calculated positions and refined by a riding mode. Calculations and graphics were performed with SHELXTL[19]. The crystallographic details are provided in Table-1, while the selected bond distances and angles are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA FOR **1**

Complex	**1**
Formula	$C_{19}H_{20}N_3O_6Ni$
Formula mass	445.09
Colour and form	Green, block
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.4763(4)
b (Å)	7.1321(2)
c (Å)	24.2433(7)
β (°)	96.578(3)
V (Å^3)	1971.26(11)
Z	4
D_{calcd} (g cm^{-3})	1.500
μ (mm^{-1})	1.026
R_{int}	0.0225
GOOf	1.087
Completeness	0.998
F_{000}	924
R_1[a]R ($I > 2\sigma$)	0.0476
wR_2[b]	0.1368
CCDC Number	974753

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w(|F_o^2|)^2]^{1/2}$

RESULTS AND DISCUSSION

Reaction mechanism: Ligand and the Ni(III) ions were attained by *in situ* reaction. The Ni(III) ion was attained by oxidizing reaction. The reaction mechanism of L^{3-} ligand as follows (**Scheme-I**): at first, compound **b** was formed by condensation reaction between Hehbd and carbohydrazide. And **b** further formed **c** through hydrogen transfer reaction, N-N σ bond broke reaction. At last, the H_3L (**d**) ligand was synthesized by condensation reaction between Hehbd and **c**.

Crystal structure of 1: Single-crystal X-ray structure analysis reveals that $[Ni(L)]·H_2O$ crystallizes in a monoclinic system space group $P2_1/n$. it was shown in Fig. 2 that the symmetrical unit contains one nickel atom, one L^{3-} ligand and one solvent water molecule. Ni1 atom is coordinated by two O atoms and two N atoms from one μ_4:η^1:η^1:η^1:η^1-L^{3-} ligand, forming a distorted square-planar geometry. The coordinated bonds of Ni1-O1, Ni1-O2, Ni1-N1, Ni1-N2 are 1.850(2), 1.845(2), 1.824(3), 1.840(3) Å, respectively. The Ni ion is in 3+ oxidation state, as evidenced by bond valence summation calculations, charge balance considerations and the presence of typical bond lengths for a Ni^{3+} ion[18,20]. The L^{3-} ligand was synthesized by *in situ* reaction (**Scheme-I**). In the crystal

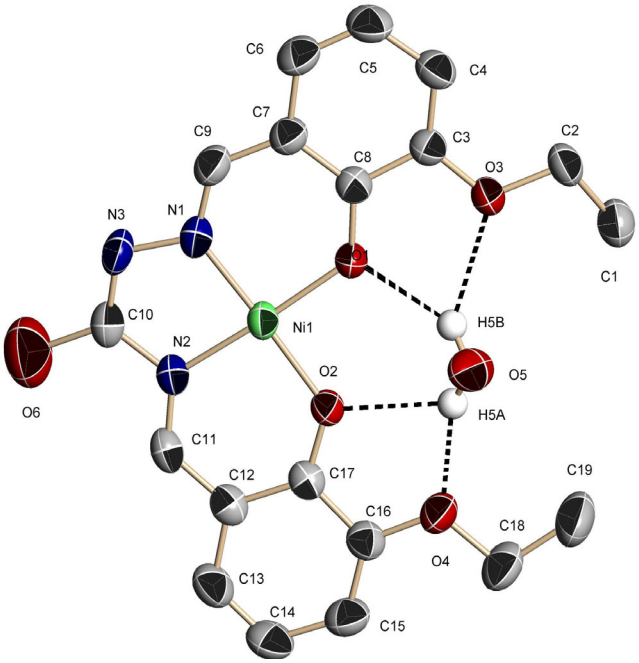
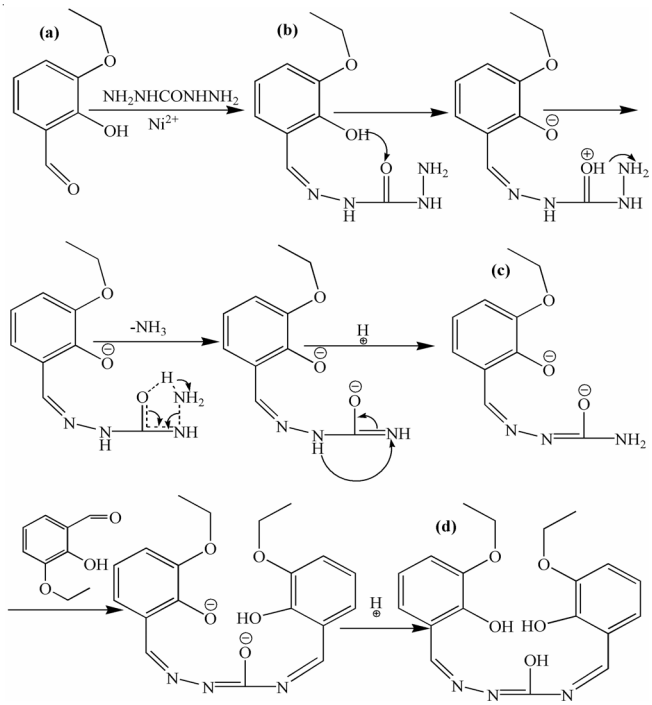


Fig. 2. Structure of **1**, part of hydrogen atoms were omitted

TABLE-2
METAL-LIGAND BOND LENGTHS (Å) AND ANGLES (°) IN **1**

Bond	Distance	Bond	Distance	Bond	Distance (Å)
Ni1–N1	1.824(3)	Ni1–N2	1.840(3)	Ni1–O1	1.850(2)
Ni1–O2	1.845(2)	–	–	–	–
Angle	(°)	Angle	(°)	Angle	(°)
N1–Ni1–N2	82.82(14)	N1–Ni1–O2	177.54(13)	O2–Ni1–O1	87.11(10)
N2–Ni1–O2	95.51(12)	N1–Ni1–O1	94.69(12)	N2–Ni1–O1	175.30(12)



Scheme-I: Reaction mechanism of H_3L ligand

structure, the main structure [Ni(L)] seized a solvent water molecule through intramolecular O-H···O hydrogen bond (O5-H5A···O4, 2.951(4), O5-H5A···O2, 2.981(4), O5-H5B···O1, 2.953(4), O5-H5B···O3, 3.085(4) Å). The molecule formed a dimmer through Ni···N2, Ni···Ni interaction (Ni1···N2A, 3.390(1) Å, Ni1···Ni1A, 3.662(1) Å, symmetry code: (a) 2-x, 1-y, 1-z.). The dimmer further constructed a 2-D network through C-H···O hydrogen bond (C4-H4···O5B, 3.314(1) Å, symmetry code: (B) 1.5-x, -0.5 + y, 0.5-z) (Fig. 3).

IR spectrum: IR spectral data of the compound **1** are shown in Fig. 4. There are indications that broad bands in the range of 3440 cm^{-1} can be assigned to the stretching frequency of solvent water molecules. The strong band located at 1626 cm^{-1} is assigned to C=N bond from L^{3-} ligand[8a,21,22]. The strong band located at 1448 cm^{-1} is assigned to ν(C-O) hydroxyl of the L^{3-} ligand. The two strong bands at 1249 cm^{-1} and at 1116 cm^{-1} may be assigned to the ν(C-N) stretching frequencies. At very low frequencies (500-440 cm^{-1}), a weak band at 441 cm^{-1} is observed from Ni-N bonds. The IR attribution is consistent with the crystal structure determination.

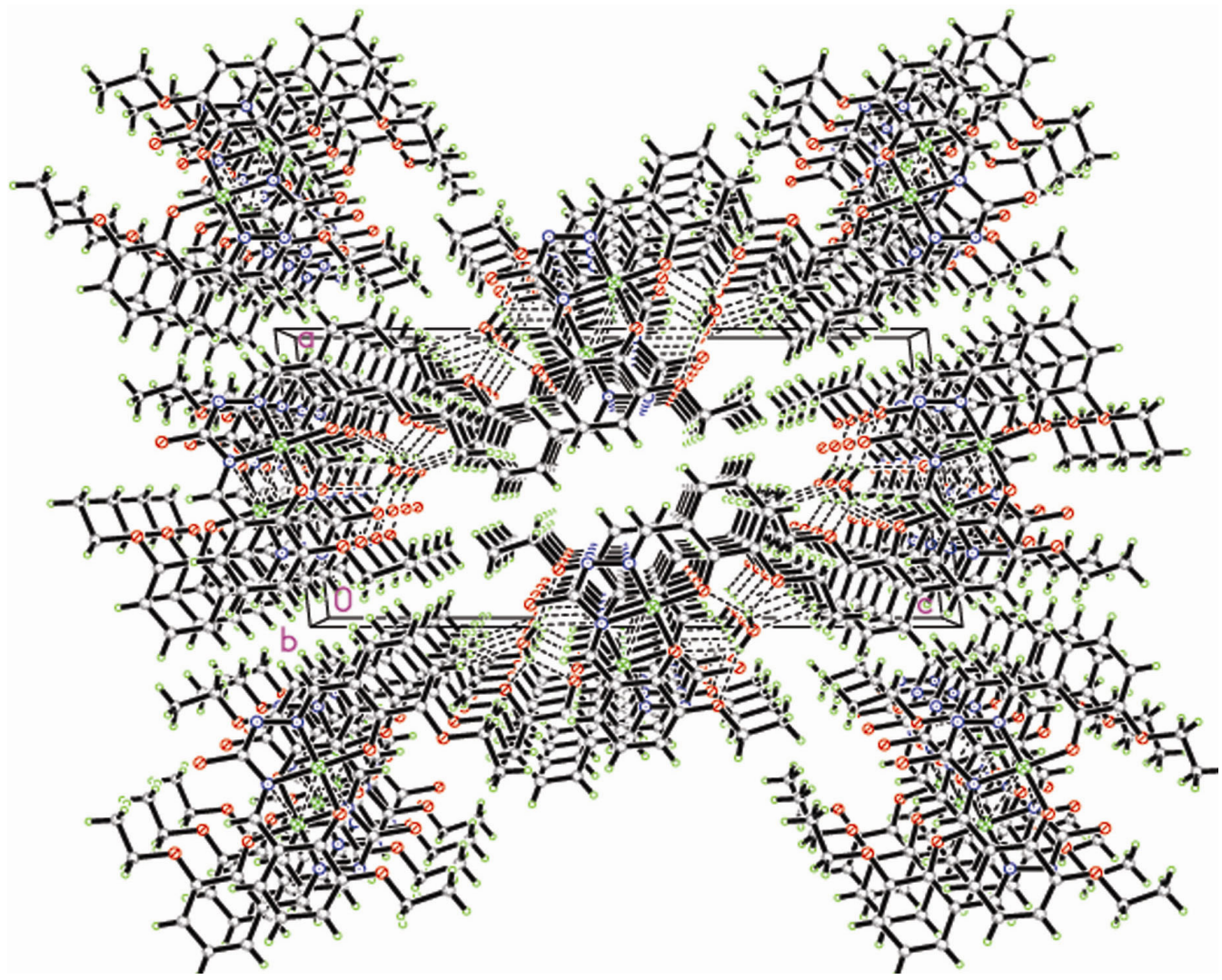


Fig. 3. Parking drawing of **1**

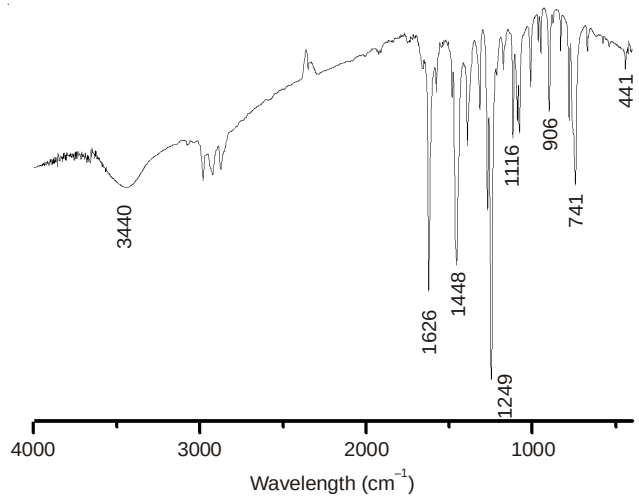


Fig. 4. IR spectra of **1**

Conclusion

Using solvothermal method, a new Ni(III) complex [Ni(L)]·H_2O has been synthesized through *in situ* reaction. At the same time, a new organic ligand has also been formed which is [(3-Ethoxy- 2- hydroxy-benzylidene)-amino]-[N'-(3-ethoxy-2-hydroxy-benzylidene)-hydrazino]-methanol. We reported it's structure and IR spectra.

Notes and references

CCDC 974753 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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