

Synthesis and Characterization of Tetrakis(2-amino-3-methylpyridine)di(aqua)nickel(II)

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Abstrak. Complex of tetrakis(2-amino-3-methylpyridine)-di(aqua)Nickel(II) nitrate had been synthesized by adding dropwise solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0,580 g ; 2 mmol) in 10 mL methanol into the solution of L (L=tetrakis(2-amino-3-methylpyridine)(0,864 g ; 8 mmol) in 30 mL methanol and stirring continuously for one hour at room temperature. The complex formula predicted is $[\text{Ni}(\text{L})_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$. The infrared spectral data indicates that nitrogen atom of C=Npyr and oxygen atom of H_2O are coordinated to the central ion Ni^{2+} . The complex is paramagnetic and shows two maximum peaks which are ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transition. Complex predicted has an octahedral geometry.

1. Introduction

Complex compounds have an important role in the application of science such as biology, analytical, medical, clinical, industrial and other fields. Some of the complex indicate that the N atom in the pyridine cluster(C=N) and N atom outside of pyridine (as NH primary) have the ability to be coordinated to the central atom of either one of the primary NH or pyridine cluster and is jointly coordinated to the central atom [1,2,3,4]. Pyridine derivatives, such as nicotinamide, nicotinalide, benzoylhydrazin and 2-amino-3-Methylpyridine (2-amino-3-picoline), have an N-donor atoms in primary NH groups and N atom in the pyridine cluster (C=N), both have the ability to be coordinated to the central atom. The most common structure is an octahedral and square-planar. The complex of Ni(II) with 2-amino-3-Methylpyridine (L)is expected to form an octahedral structure which can be used as an antibacterial material or other purposes.

2. Experimental

All chemicals were purchased from E.Merck and used without further purification. The Infrared spectra were recorded on a Spectrophotometers Prestige-21 Shimadzu. The nickel content was determined by Atomic Absorption Spectrometer (AAS) Shimadzu AA-6650. Spectra UV-VIS was performed with a Shimadzu UV-3601 spectrophotometer. Molar conductivity (Λ^*_m) of 1 mM solution in methanol was measured at 25° C with a Jenway CE 4071 conductivity meter. The magnetic moment was measured with Auto Sherwood Scientific 10169 Magnetic Susceptibility Balance.

2.1. Complex Synthesis



A solution of nickel(II) nitrate hexahydrate (0,58 g; 2 mmol) in methanol (10 mL) was added dropwise to a solution of the ligand L (0,864 g; 8 mmol) in methanol (30 mL) and the mixture was stirred for 1 hour. The volume was reduced to third and left for about 72 hours. The green precipitate, which was separated, is washed with methanol and dried under vacuum.

3. Result and Discussion

3.1. Complex Synthesis

The mixture of solution $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0,580 g ; 2 mmol) in methanol (10 mL) and solution L (2-amino-3-methylpyridine) (0,864 g ; 8 mmol) in methanol (30 mL) creates a green crystal. The electronic spectrum can be seen in Figure 1.

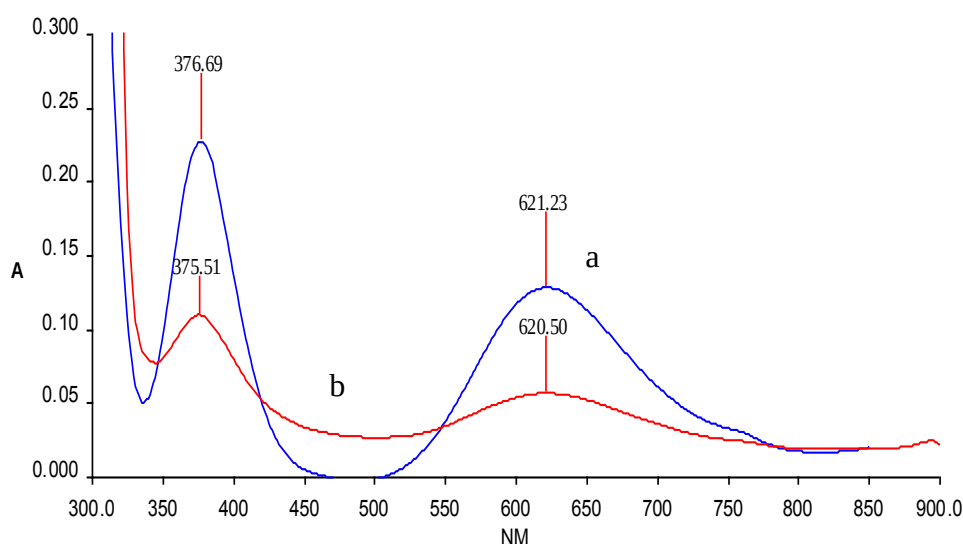


Figure 1. Electronic spectrum (a) solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (b) solution of complex $\text{Ni}(\text{II})\text{L}$ within DMSO

Figure 1 shows a shift of maximum wavelength absorbance of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (621 nm and 376 nm) to a smaller wavelength (620 nm and 375 nm) in the complex of $\text{Ni}(\text{II})\text{L}$. The shift of λ_{max} reveals the formation of complexes between $\text{Ni}(\text{II})$ and L and also reveals that L is a stronger ligand than H_2O . The small shift of maximum wavelength indicates that the ligand L is a weak crystal field as H_2O . Probably the ligand L and H_2O both are coordinated to $\text{Ni}(\text{II})$ which is also in the complex $[\text{Ni}(\text{L}^1)_2(\text{H}_2\text{O})_2]$ ($\text{L}_1 = 3\text{-methyl-4-nitro-1-phenyl-5-pyrazolone}$) [5] and $[\text{Ni}(\text{L}^2)(\text{H}_2\text{O})]$ ($\text{L}^2 = 1,1\text{-diaminobutane-Schiff base}$) [6] as shown in Figure 2 and Figure 3.

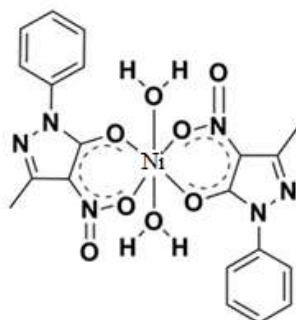


Figure 2. The complex structure of $[\text{Ni}(\text{L}^1)_2(\text{H}_2\text{O})_2]$ ($\text{L}^1 = 3\text{-methyl-4-nitro-1-phenyl-5-pyrazolone}$) [5].

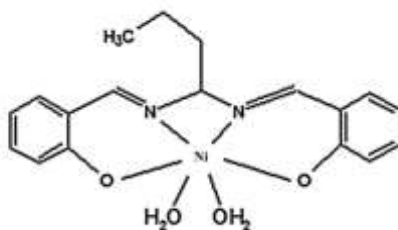


Figure 3. The complex structure of $[\text{Ni}(\text{L}^2)(\text{H}_2\text{O})]$ ($\text{L}^2 = 1,1\text{-diaminobutane-Schiff base}$) [6]

3.2. Determination of Formula and Characteristics of The Complex

The measurements of the amount of Ni in the complex of Ni(II)L is of $9.28 \pm 0.22\%$. If the result of the measurement is compared to the theoretical amount of Cu (9.27%), the estimated complex compound formula for Ni(II)L is possibly $\text{Ni}(\text{L})_4(\text{NO}_3)_2$.

3.3. Electrolytic Conductivity Measurement

The electrolytic conductivity measurement is shown in Table 1.

Table 1. The Electrolytic Conductivity of Standard Solution and complex $\text{Ni}(\text{L})_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \pm 1.10^{-3} \text{ M}$ in methanol

Solution	Λ_m^* ($\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$)	Number of ions
Metanol	0	-
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	5.8 ± 0.2	1 : 1
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	6.9 ± 0.1	1 : 1
$\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$	77.3 ± 0.7	1 : 2
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	93.6 ± 0.6	1 : 2
$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	218.6 ± 0.4	1 : 3
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	273.6 ± 1.4	1 : 3
Ni-L	87.3 ± 0.7	1 : 2

The Electrolytic Conductivity of the complex $\text{Ni}(\text{L})_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ of copper(II) chloride and nickel(II) chloride indicates that the complex is electrolyte corresponds to 1 : 2 electrolyte and the nitrate is a counter ion and not coordinated to Ni(II) as in the $[\text{Co}(\text{Hisn})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$, Hisn =

acetone isonicotinoyl hydrazone [7]. Therefore, the complex may be formulated as $[\text{NiL}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$.

3.4. Infra-Red Spectra

The infrared spectra of 2-amino-3-methylpyridine and complex $[\text{NiL}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$ are shown in Figure 4 and Figure 5 while infrared absorption bands are shown in Table 2.

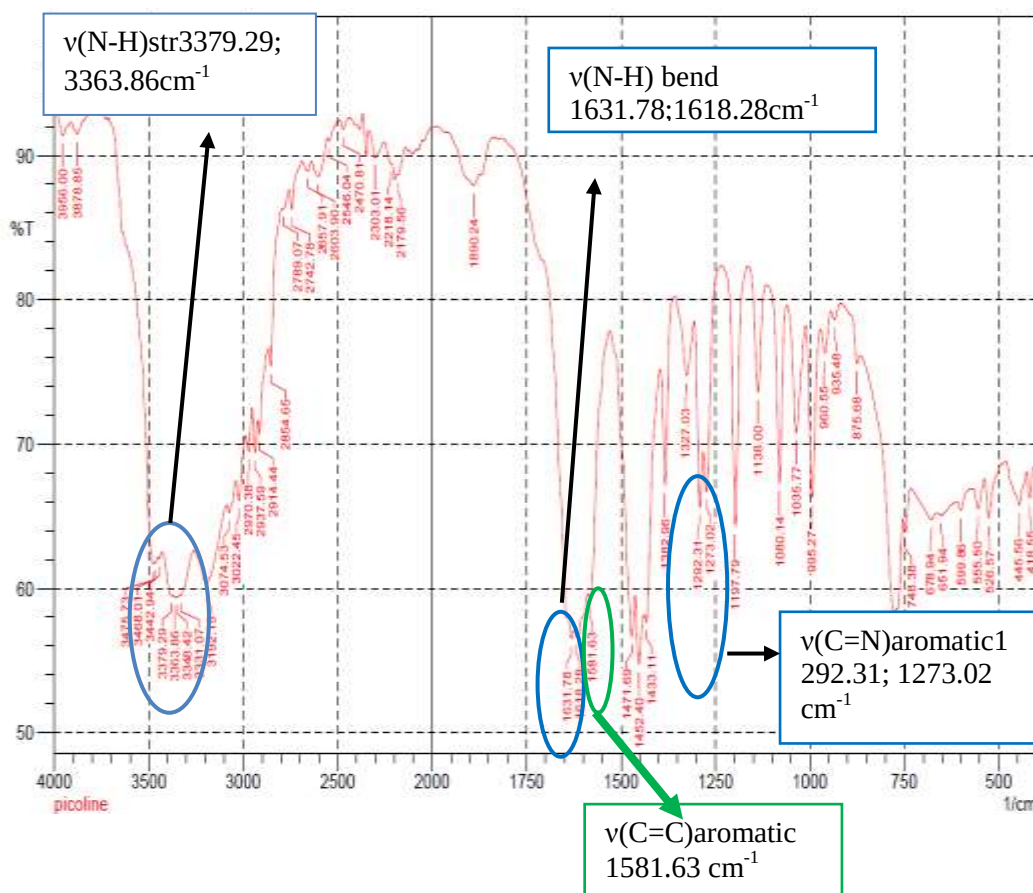


Figure 4. The infrared spectra of L

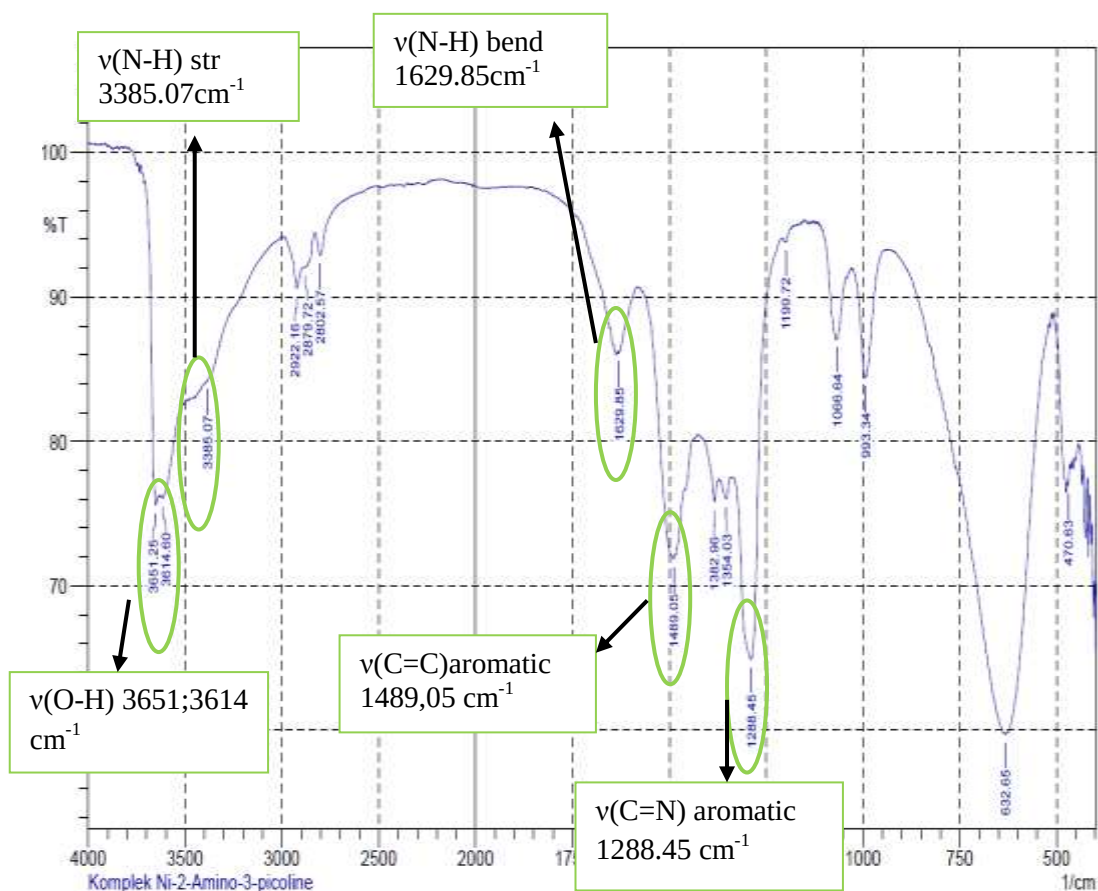


Figure 5. The infrared spectra of $[\text{NiL}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$

Table 2. IR absorption bands (cm^{-1}) of 2-amino-3-methylpyridine and complex $[\text{Ni}(\text{L})_4](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$.

Compound	IR Band Spectra (cm^{-1})			
	(C=N)	(O-H)	(N-H)str	(N-H)bend
L	1292127	-	3379	1631
(2-amino-3-Methylpyridine)	3	-	3363	1618
$[\text{Ni}(\text{L})_4](\text{NO}_3)_2$	1288	3651 3614	3385	1629

Figure 3 and 4 or Table 2 shows the shift of the IR spectra of NH stretching on the area 3379 cm^{-1} and 3363 cm^{-1} to 3385 cm^{-1} , NH bending is at 1631 cm^{-1} and 1618 cm^{-1} to 1629 cm^{-1} . Spectra in the area of 3651 cm^{-1} and 3614 cm^{-1} indicates O-H group. The existence of the O-H group absorption in the complex indicates H_2O molecules are in the complex of $[\text{NiL}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$. The shift of the IR absorption of C=N in this complex indicates that the nitrogen atom on the C=N group is coordinated to the central ion Ni^{2+} as in the complex $[\text{NiL}^3]$, $\text{L}^3 = 4\text{-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol}$ [8].

3.5. Magnetic properties

Effective magnetic moment measurements of the solid complex gave magnetic moments of 2.65 BM, which shows that the nickel(II) is in a high spin with two unpaired electrons. This value is similar to that of other complexes which have an octahedral geometry such as in $[\text{Ni}(\text{L}^4)_2\text{Cl}_2]$, $\text{L}^4 = 3\text{-aminocoumarin}$ which has magnetic moments of 2.6 BM and with an octahedral geometry [9], $[\text{Ni}(\text{OCOCH}_3)_2(\text{isn})_2(\text{H}_2\text{O})]\text{C}_3\text{H}_7\text{NO}$ (isn = isonicotinamide) (2.6 BM) an octahedral geometry [10]. Therefore the expected geometry of the complex $[\text{NiL}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$ is also an octahedral.

3.6. Electronic Spectra

The electronic spectra of the complex recorded in DMSO and the maximum wavelength (λ_{max}), absorbance (A) and absorptivity molar (ϵ) with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are shown in Table 2. The electronic spectra of $[\text{NiL}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$ shows two wide absorption at 620 nm (16116 cm^{-1}) and 375 nm (26630 cm^{-1}). The absorption bands indicated $d-d$ transition ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, as in the octahedral complex of $[\text{Ni}(\text{HL}^5)_2]$, $\text{L}^5 = 2\text{-Chloromethyl-3-(8-hydroxyquinolin-5-yl)-3(H)-quinazolin-4-one}$ which shows absorption at 14962 cm^{-1} and 24548 cm^{-1} , $[\text{Ni}(\text{HL}^6)_2]$, $\text{L}^6 = 6\text{-bromo-2}[(4\text{-phenyl-1-yl)methyl-3-[8-hydroxyquinoline-5-yl]quinazolin-4-one}$ at 14896 cm^{-1} and 22800 cm^{-1} [11].

3.7. Complex Structure

The suggested structure of $[\text{Ni}(\text{2-amino-3-methylpyridine})_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$ complex is an octahedral geometry with (C=N) and H_2O coordinated to nickel(II) ion as shown in Figure 6.

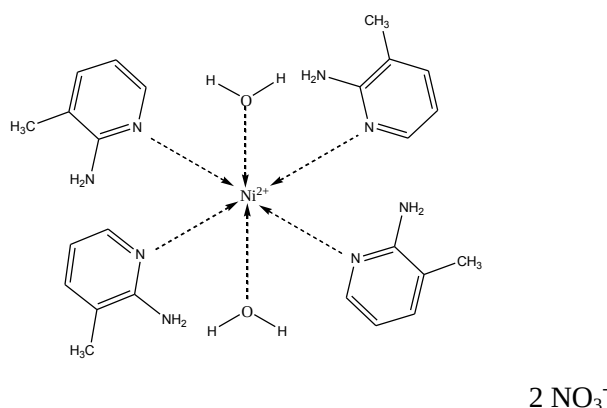


Figure 6. The suggested structure of $[\text{Ni}_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$ complex

According to IUPAC nomenclature, the suggested complex is named by *tetrakis-(2-amino-3-methylpyridine)diaquanickel(II) nitrate*.

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