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Spectroscopic characterization of N,N'-bis(salicylidene)pentane-1,3-diamine nickel(II) complex

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Abstract The N_2O_2 tetradentate Schiff base ligand, N,N'-bis(salicylidene)pentane-1,3-diamine (Salpn), coupled with 1:2 concentration ratio of 1,3-diaminopentane and salicylaldehyde was used to produce a series of macrocyclic Nikel(Ⅱ) complexes. In the metal complexation, it was observed that Salpn macrocyclic ligand can adopt more than a metal ion giving an unique multinuclear metal complexes including Ni(II)Salpn and $Ni(II)_3(Salpn)_2$. Characteristic IR υ(M-O) peaks for Ni(II)Salpn and $Ni(II)_3(Salpn)_2$ were observed to be 1028cm^{-1} and 1024cm^{-1}, respectively. Characteristic UV-Vis absorption λ_{max} peaks for $Ni(II)_3(Salpn)_2$ were observed to be 241nm and 401 nm. Structural characterization of $Ni(II)_3(Salpn)_2$ by NMR exhibits that the salicylidene ring moiety has two different resonance signals originated from the magnetically asymmetric diligand and trinuclear bis complex. Complete NMR signal assignments and characterizations elucidating structural features of $Ni(II)_3(Salpn)_2$ were described in detail.

Keywords NMR, N_2O_2 donating macrocyclic ligand, Ni(Ⅱ) complex

Introduction

Nitrogen and oxygen donating macrocyclic tetradentate(N_4 or N_2O_2) Schiff base ligand have been received great attention in the studies of enzyme model complexes explaining the biocatalytic active site. [1-2] The oxidation and reduction state of nickel ions in metal-macrocyclic ligand complex are known to be quite important in biological catalytic systems. As an example of N4 ligand, F430 is a Ni-containing coenzyme that functions in the two electron reduction of methyl coenzyme M (2-(methylthio)-ethane sulfonate) to methane and coenzyme M (2-mercapto ethane) in methanogenic bacteria and its model complexes have been studied.[3-8] N_2O_2 Schiff base ligand are also widely used as a Ni-containing model complex since oxido-reduction state, chelate ring size, molecular planarity and ruffling, ligations patterns are similar to the tetraaza or porphyrin macrocyclic nickel complex. [9-11]

In this paper we synthesized a N_2O_2 donating tetradentate macrocyclic ligand,[12] N,N'-bis (salicylidene)pentane-1,3-diamine (Salpn), by utilizing salicylaldehyde and 13-diaminepentane. Unique metal complexes Ni(II)Salpn and $Ni(II)_3(Salpn)_2$ were synthesized and characterized by spectroscopic methods including UV-Vis, FT-IR and NMR. Complete NMR signal assignments and resulting structural features were described in detail

Experimental Methods

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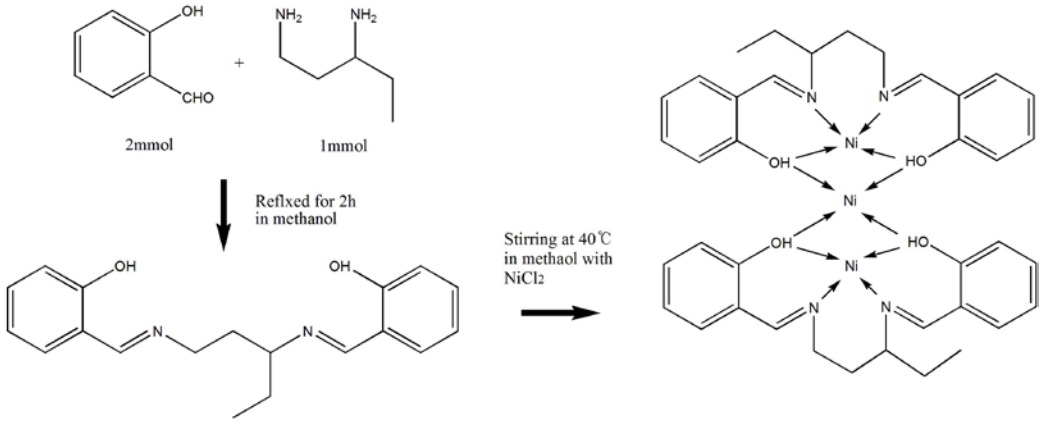
Material. All chemicals used in the synthesis of ligand were all reagent grade. Salicylaldehyde, 1,3-diaminopentane, Ni(II)Cl_2 and all solvents were purchased from Sigma Aldrich and used without further purification. NMR solvents were purchased from Cambridge isotope laboratory.

Synthesis of Ligand and Nickel(Ⅱ) complexes. Synthesis of the N_2O_2 donating macrocyclic Schiff base ligand was prepared by using the reflux condensation of a salicylaldehyde 0.213mL(2mmol) with 1,3-diaminopentane 0.119mL(1mmol) under 40℃ warm methanolic or ethanolic solution for 2hours. Coupling of amine and aldehyde gave rise to yellow colored solutions indicating the formation of the N_2O_2 donating macrocyclic Schiff base, N,N'-bis (salicylidene)pentane-1,3-diamine (Salpn). After fully refluxing, the solution was filtered and slowly evaporated. Now then the yellow emulsion was washed with water and subsequently dried by using freezer-drier as shown in **Scheme 1**.



Scheme 1. Synthesis of the N,N'-bis(salicylidene)pentane-1,3-diamine (Salpn) and its [Ni(Ⅱ)]$_3$(Salpn)$_2$ complex

Various Ni(II)Salpn complexation were attempted with equivalent and unequivalent molar ratio since Salpn can adopt more than a nickel ion. Nickel(II) and N_2O_2 donating Salpn macrocyclic ligand were dissolved in methanol solvent with 1:1 and 3:2 equivalents. The reaction mixture was allowed to stir for 8hr at 40℃. Yellowish Salpn ligand turned into burgundy and dark green color, respectively, when Ni(II) ion were added to Salpn with with 1:1 and 3:2 equivalents. The resulting products were then filtered and dried with roto-evaporator. After washing with water for further purification, the reaction mixtures were recrystallized and subsequently dried by using freezer dryer. Dark reddish powder crystal for 1:1 equivalent and dark green powder crystal for 3:2 Ni(II) to Salpn equivalents were finally obtained.

Spectroscopic measurements. UV-Vis spectra were measured in 200nm-800nm wavelength range by utilizing SINCO UV-Vis spectrometer. The FR-IR spectra were observed in the 4000-650cm^{-1} on a Varian FT-IR 640 spectrophotometer with ATR. Measurements were made for Salpn free ligand and Ni(II)Salpn and Ni(II)$_3$(Salpn)$_2$ complexes and analyzed.

Results and Discussion

UV-Vis spectral analysis. The concentration of metal free ligand N,N'-bis(salicylidene) pentane-1,3 -diamine (Salpn) was 9.0x10^{-5} M in methanol. The concentrations of Ni(II)Salpn and Ni(II)$_3$(Salpn)$_2$ were 7.6x10^{-5} M and 5.5x10^{-5} M, respectively, in methanol. Characteristic absorption peaks of the Salpn were appeared at 255 nm, 317 nm, 401 nm due to the attribution of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition from

the conjugation of salicylidene ring moiety as shown in shown in Figure 1. Characteristic absorption peaks of Ni(II)Salpn complex were observed at 242 nm, 256nm, 318nm. A new strong absorption peak at 242nm represents the origin of the Ni(II) ion chelation to N_2O_2 macrocyclic ligand. Absorption peaks for $Ni(II)_3(Salpn)_2$ were appeared at 241 nm, 257 nm, 321 nm, 401 nm. Although the multinuclear-ligand μ-biscomplex, $Ni(II)_3(Salpn)_2$, exhibits a characteristic 242nm originated from the metal chelation and the 401nm peaks exhibiting yellowish green color and different coordination environment compare to Ni(II)Salpn were observed. Weak absorption band around 600 nm due to d-d transition for both complexes were appeared. All characteristic UV-Vis absorption λ_{max} peaks are summarized in Table 1.

FT-IR spectroscopy. The IR spectra of Salpn, Ni(II)Salpn and $Ni(II)_3(Salpn)_2$ complexes were observed and compared in the region 4000-650cm^{-1} as shown in Figure 2. Characteristic IR peaks of the Ni(II)-free Salpn ligand were observed to be υ(O-H) 3486 cm^{-1}, υ(C-H) 2859 cm^{-1}, υ(C=N) 1629 cm^{-1} and υ(C=C) 1495 cm^{-1}, respectively. The strong C-O absorption band around 1300cm^{-1} was observed but shifted down to near 1250cm^{-1} for Ni(II)salpn complexes. Characteristic Ni(II)-oxygen vibrational absorption peaks were assigned to υ(M-O) 1028 cm^{-1} for Ni(II)Salpn and υ(M-O) 1024 cm^{-1} for $Ni(II)_3(Salpn)_2$ complexes. All characteristic vibrational absorption peaks are summarized in Table 1.

NMR spectroscopy. All NMR measurements including ^1H,^{13}C-NMR, homo and heteronuclear 2D-NMR were obtained by using Varian 500Mhz FT-NMR spectrometer. DEPT, HSQC, COSY, TOCSY NMR measurements were accomplished at 298K for signal assignments and elucidation of structural features of Salpn and its Ni(II)-complexes. NMR spectral data were collected with following conditions: 5.3 mM Salpn, 10.0 mM in DMSO-d_6 solvent; T = 25℃. ^1H and ^{13}C-NMR chemical shifts were referenced to internal DMSO-d_6 (2.5 ppm, ^1H; 39.5 ppm, ^{13}C).

Proton-carbon heteronuclear connectivities and covalent linkages were made by two different ^1H-detected multiple quantum DEPT and HSQC NMR experiments. DEPT spectra provided all protonated carbon NMR signals with clear sorting of CH, CH_2, CH_3 as shown in Figure 3. Proton-carbon one-bond connectivities were made with HSQC pulse sequence which is quite useful for identification of germinal methylene protons since they are connected to a carbon atom.

Starting from the well isolated methyl proton, ^1H-NMR signal were grouped into scalar J-networks with a TOCSY spectrum collected with a relatively long 65ms mixing period. Because COSY NMR spectrum reveals only direct scalar coupling, the proton J-networks associated with 1,3-diamino pentane($^1H\sim^5H$) were simply clarified in signal assignments.

During the Ni(II)-ligand complexation, it was found that N_2O_2 donating N,N'-bis(salicylidene) pentane-1,3-diamine (Salpn) ligand can adopt more than a Ni(II) metal ion so that multinuclear/ligand complexes were obtained. There are similar J-networks patterns are remained in Ni(II)Salpn complex. However, the salicylidene ring moiety has two different resonance signals originated from the magnetically asymmetric diligand and trinuclear bis complex which is $Ni(II)_3(Salpn)_2$. Comparisons of TOCSY spectra of Salpn and $Ni(II)_3(Salpn)_2$ complex exhibit similar proton J-networks but a pair of chemical shifts associated with salicylidene ring moiety due to the Ni(II) ion binding and magnetic equivalence arisen from different structural features as shown in Figure 4.

NMR signal assignments[12-14] and spectral comparison in terms of chemical shift change on Ni(II) metal ion addition to N_2O_2 donating macrocyclic Salpn ligand are shown in Figure 5 and summarized in Table 2, respectively. The chemical shift of H6 (8.56 ppm) of Salpn was shifted down and divided into 8.62 ppm and 10.40 ppm in $Ni(II)_3(Salpn)_2$ complex.

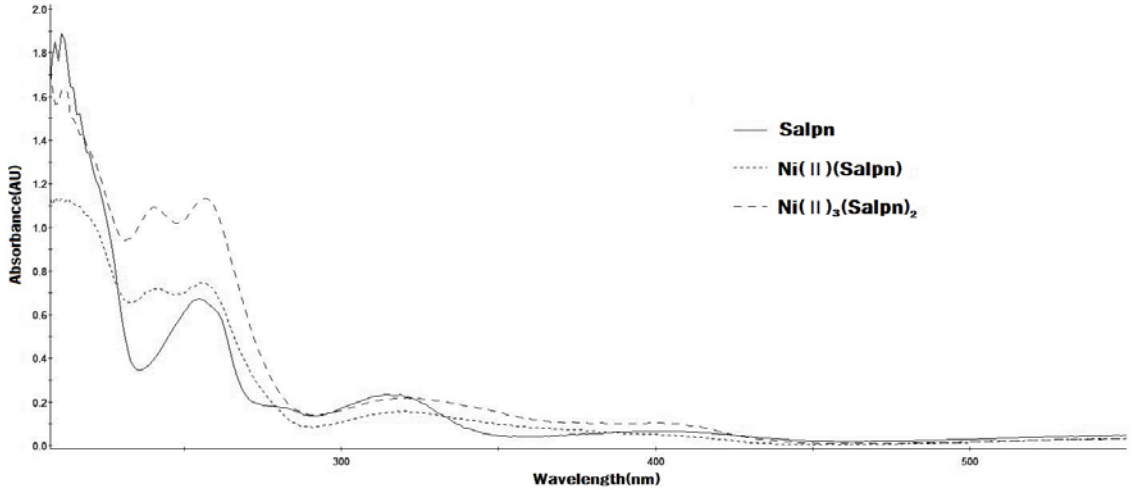


Figure1. UV-Vis spectra of N_2O_2 donating macrocyclic Salpn ligand and Ni(Ⅱ) complexes.

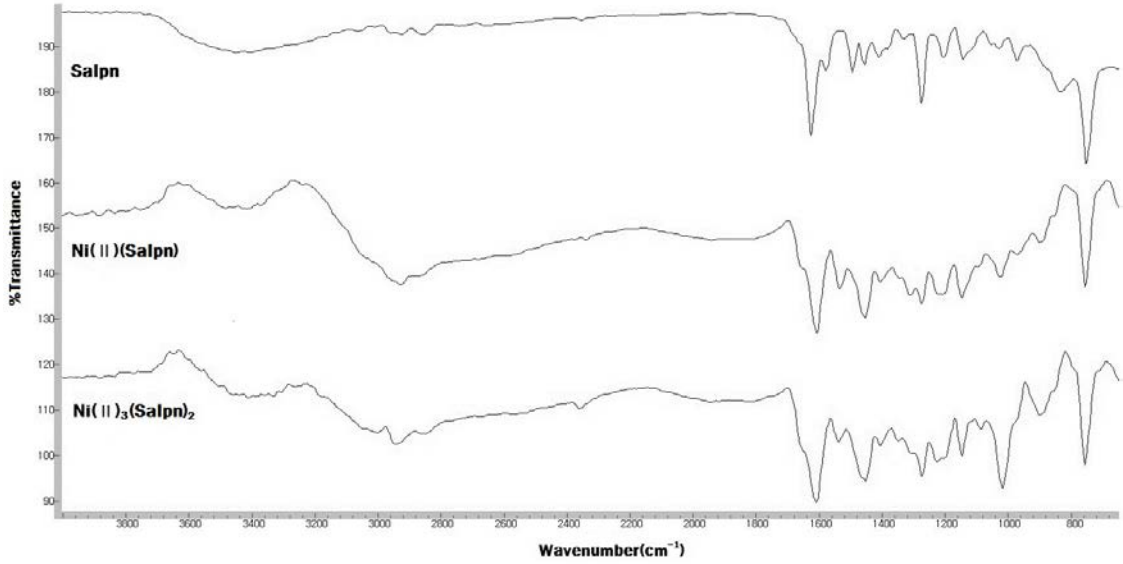


Figure 2. FT-IR spectra of N_2O_2 donating macrocyclic Salpn ligand and Ni(Ⅱ) complexes.

Table 1. IR(cm^{-1}) and UV-Vis(nm) spectral data of Salpn and its Ni(II) complexes

Compound	υ(O-H), υ(C-H), υ(C=N), υ(C=C)	υ(M-O)	λ_{max}
Salpn	3486, 2859, 1629, 1495		255, 317, 401
Ni(II)(Salpn)	3041, 2838, 1625, 1482,	1028	242, 256, 318
$Ni(II)_3(Salpn)_2$	2943, 2943, 1628, 1478,	1024	241, 257, 321, 401

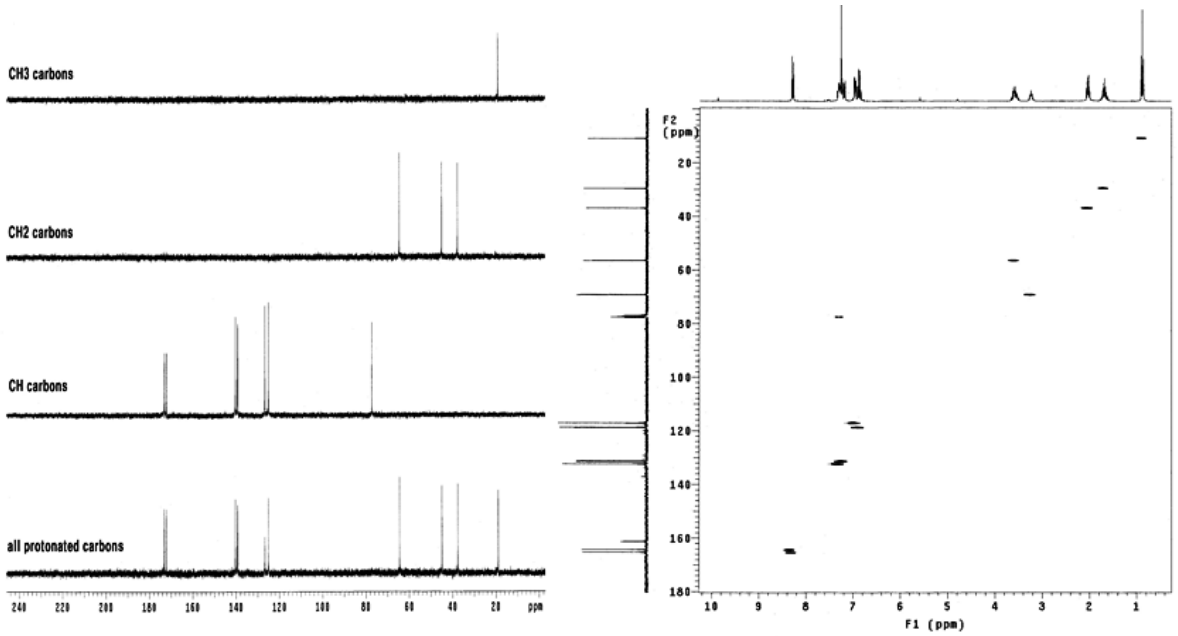


Figure 3. DEPT spectrum of Salpn exhibiting clear sorting of CH, CH_2, CH_3 J-networks(left) and HSQC spectrum exhibiting proton-carbon one-bond J-networks(right)

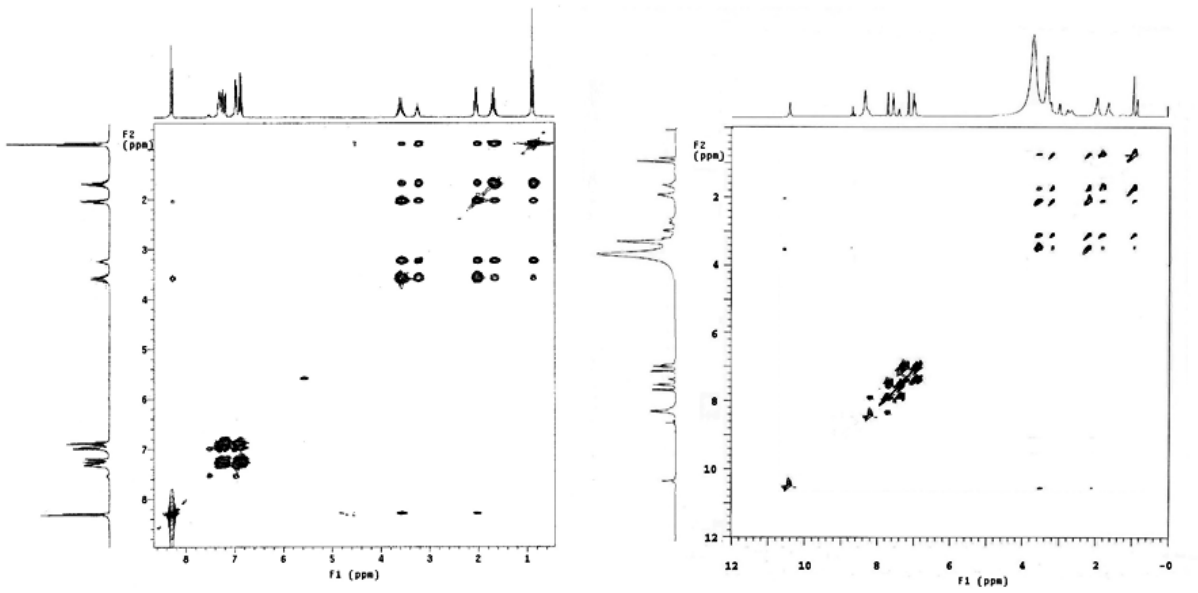


Figure 4. 2D-TOCSY spectra N,N'-bis(salicylidene)pentane-1,3-diamine(left) and $Ni(II)_3(Salpn)_2$ complex(light)

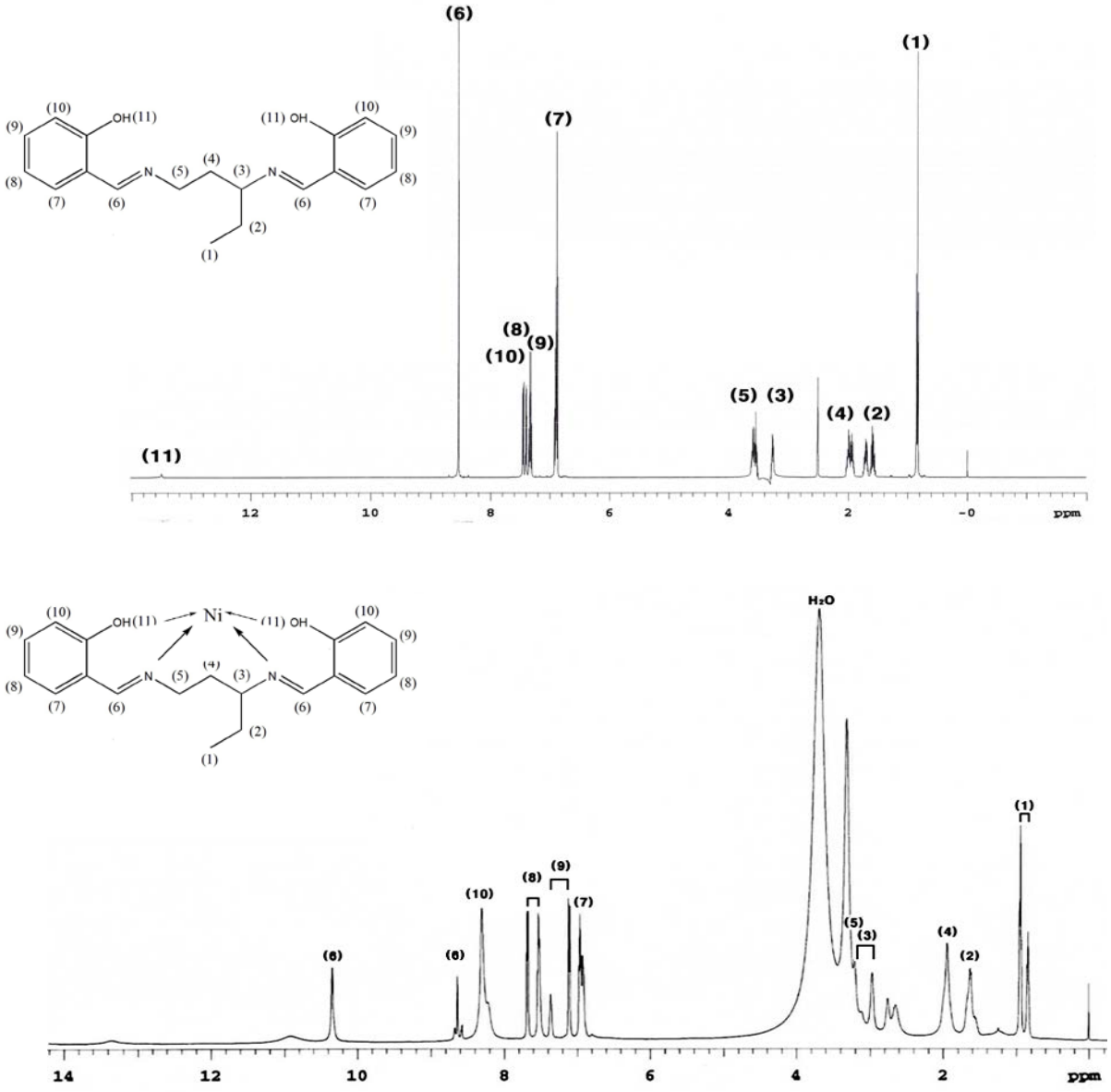


Figure 5. ^{1}H-NMR spectra of N,N'-bis(salicylidene)pentane-1,3-diamine(up) and $Ni(II)_3(Salpn)_2$ complex(down)

Table 2. ^{1}H-NMR data for Schiff base ligand and complex (integration, coupling, number)

	δ (in ppm)
Salpn ligand	0.88(3H, t, (1)), 1.65,1.70(2H, m, (2)), 1,98(2H, m, (4)), 3.26(1H, m, (3)), 3.80(2H, t, (5)), 6.91(2H, d, (7)), 7,32(2H, t, (9)) 7.37(2H, t, (8)), 7.40,7.42(2H, d, (10)), 8.56(2H, s, (6)), 13.50(2H, s, (11))
$Ni(II)_3(Salpn)_2$ complex	0.91,0.98(3H, t, (1)), 1.70(2H, m, (2)), 1.95(2H, m, (4)), 3.08,3.28(1H, m, (3)), 3.52(2H, t, (5)), 3.73(2H, s, H_2O) 7.02,7.13(2H, d, (7)), 7.11,7.40(2H, t, (9)), 7.50,7.65(2H, t, (8)), 8.25,8.30(2H, m, (10)), 8.62,10.40(2H, s,m (6)),

Chemical shift changes from metal free macrocyclic Salpn ligand to $Ni(II)_3(Salpn)_2$ complex in salicylidenyl ring moety were designated as follow: H7(6.91 to 7.02, 7.13 ppm); H8(7.37 to 7.50, 7.65 ppm); H9(7.32 to 7.11, 7.40 ppm); H10(7.42 to 8.25, 8.30 ppm). In the up field region, the chiral proton H3 was changed from 3.26 ppm to 3.08, 3.28 ppm. Spectral changes can be used for explanation of coordination environment and oxidation state of Ni(II) ion. ^{1}H-NMR spectra of Salpn metal free macrocyclic ligand are fairly sharp and well resolved whereas $Ni(II)_3(Salpn)_2$ are quite broaden. Most of chemical shifts associated with salicylidenyl ring moiety exhibits two different resonance signals implying μ-biscomplex.

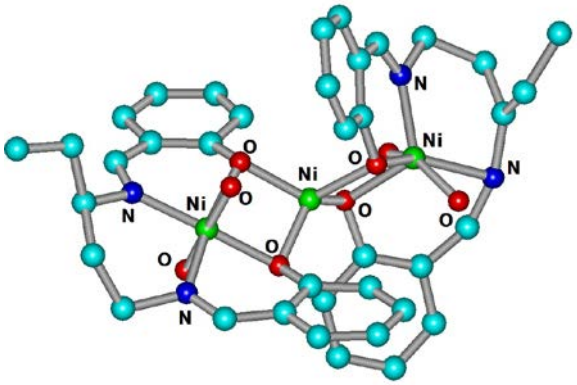


Figure 6. Proposed structure of $Ni(II)_3(Salpn)_2$ complex

Conclusion

A N_2O_2 donating tetradentate macrocyclic ligand, N,N'-bis (salicylidene)pentane-1,3-diamine (Salpn), by utilizing salicylaldehyde and 1,3-diaminepentane. In metal complexation, we were able to find that the Salpn macrocyclic ring can adopt more than a Ni(II) ions. Ni(II)Salpn and multinuclear-ligand complex, $Ni(II)_3(Salpn)_2$ were also synthesized. A strong UV absorption peak at 242nm represents the origin of the Ni(II) ion chelation to N_2O_2 macrocyclic ligand. Characteristic absorption peaks for $Ni(II)_3(Salpn)_2$ were appeared at 241 nm, 257 nm, 321 nm, 401 nm. Characteristic Ni(II)-oxygen vibrational absorption peaks were assigned to υ(M-O) 1028 cm^{-1} for Ni(II)Salpn and υ(M-O) 1024 cm^{-1} for $Ni(II)_3(Salpn)_2$ complexes, respectively. NMR signal assignments and structural elucidations were made by utilizing homonuclear and heteronuclear multiple quantum correlation methods including COSY, TOCSY, DEPT, HSQC experiments.

Weak paramagenetic shifts of resonance signals and peak broadening exhibits that the Ni(II) ions are in octahedral environment with possible water binding or solvent binding low spin state. Molecular modeling of complexes shows that $Ni(II)_3(Salpn)_2$ may have μ-biscomplex similar to other metal complex.[12] Electrochemical studies that can address the biological function of macrocyclic Ni(II) complexes are in progress. Results of X-ray crytallographic study for molecular structure of metal complexes will be published elsewhere.

Acknowledgements

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