

**Spectrophotometric Determination of Nickel (II) Ion by Novel
Route of Calix-4-arenes as Analytical Reagent**

تقدير أيون النيكل (II) طيفيا" باستخدام الكاشف الجديد Calix-4-arenes

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Abstract

A new route of Calix-4-arenes was prepared, a sensitive and selective spectrophotometric method was proposed for the rapid determination of Nickel (II) in analytical sample, The proposed method based on the formation green complex with anew route Calix-4-arenes as a new chromogenic reagent that has a maximum absorption at λ_{max} 403 nm. Where the reaction was instantaneous in basic medium at pH=9.0, the absorbance of complex remains stable for over 24hr . Linearity was observed from 0.74-10.0 $\mu\text{g}.\text{ml}^{-1}$ with detection limit of 0.5 $\mu\text{g}.\text{ml}^{-1}$. Recovery and relative error values of precision and accuracy of method were found to be R.S.D.% = 2.91, Re% =1.12% and Erel = 98.88% . The nature of complex showed that (M:L) ratio was 1:1 at pH=9 and the stability constant of (0.48x10⁸ L¹.mole⁻¹) The effect of chemical and physical parameter and analytical parameter are evaluated . The proposed method was applied successfully to determine Ni(II) in analytical sample.

الخلاصة

حضر المركب الجديد Calix-4-arenes واستخدم في تقدير أيون النيكل (II) طيفيا في النماذج التحليلية, كما اوضحت الطريقة الطيفية المقترحة حساسية وانتقائية وسرعة في التقدير, حيث اعتمدت الطريقة على تكوين معقد اخضر مع الكاشف الجديد الذي يعطي اعلى امتصاص عند الطول الموجي 403 نانوميتر عند دالة حامضية pH=9.0 و حدود الخطية كانت بين 0.74-10.0 $\mu\text{g}.\text{ml}^{-1}$ مع حد كشف مقداره 0.5 $\mu\text{g}.\text{ml}^{-1}$ كما اوضحت استقرار امتصاصية المعقد لاكثر من 24 ساعة كما حسب حساسة الطريقة و ضبطها فكانت (R.S.D.% = 2.91%) و (Re% = 98.88%) و (Erel = 1.12%). كما درست طبيعة المعقد الذائب فكانت نسبة الفلز الى الكاشف (1:1) عند دالة حامضية pH=9 و ثابت استقرارية (0.48x10⁸ L¹.mole⁻¹) . تم تحديد الظروف الفضلى لتكوين المعقد. كما طبقت الطريقة المقترحة بنجاح لتقدير النيكل (II) في النماذج التحليلية .

Introduction

The calixarenes are a class of cyclooligomers formed *via* a phenol-formaldehyde condensation. Their rigid conformation enables calixarenes to act as host molecules as a result of their preformed cavities. By functionally modifying either the upper and/or lower rims it is possible to prepare various derivatives with differing selectivities for various guest ions and small molecules. Calixarenes lend themselves well to many applications because of the multiplicity of options for such structural elaboration. For calixarenes to be used in ion selective electrode (ISE) and bulk optode sensing devices, they must be immobilised into organic membranes ⁽¹⁻³⁾ (films/coatings) which are hydrophobic in nature. Furthermore, if aqueous analysis is desired, the calixarenes must be water insoluble otherwise immobilisation would be undermined by water dissolution of the ionophore from the device. It is essential that the calixarenes used in this way be lipophilic with very low water solubility⁽⁴⁻⁸⁾.

The McKerverey group began work on calixarene synthesis back in the 1980s. Their first major accomplishment in the field involved the modification of the lower rims of the tetra-, hexa- and octa-calixarenes by the introduction of a series of acetate esters. The calixarene ester derivatives were shown to have characteristics which make them attractive agents for use in potentiometric ion sensors. The resulting calixarenes demonstrated outstanding selectivity for various cations. Calixarenes displayed selectivity toward the sodium cation. It was reasoned that the presence of the t-butyl groups in the upper rim forced the calixarene into a permanent cone conformation which allowed the esters to form the necessary cavity for coordination ⁽⁸⁻¹⁰⁾.

The present study reports the synthesis ,characterization and analytical study of new route of Calix-4-arenes where used as organic reagent for spectrophotometric determination of Ni(II), also a new spectrophotometric method is described for the determination of Ni(II) in analytical sample.

Experimental

Apparatus

IR spectrum was recorded using KBr discs 4000-400 cm^{-1} on FT-IR Testscan Shimadzu model 8400. UV-Vis. Spectrum were recorded in ethanol on Unico model 4802UV/Vis double beam spectrophotometer recording. $^1\text{H-NMR}$ spectra in DMSO with TMS as internal standard were obtained from a JeolFX-90Q fourier $^1\text{H-NMR}$ spectrometer at university of London, college of Queen Marry. Molar conductance measurements were determined in DMSO by using WTW-Terminal 740 digital conductivity. pH measurements were carried out using WTW pH meter model 720. Gallen kamp capillary melting point apparatus was used to measure the melting points of the ligand and its complexes.

Reagents

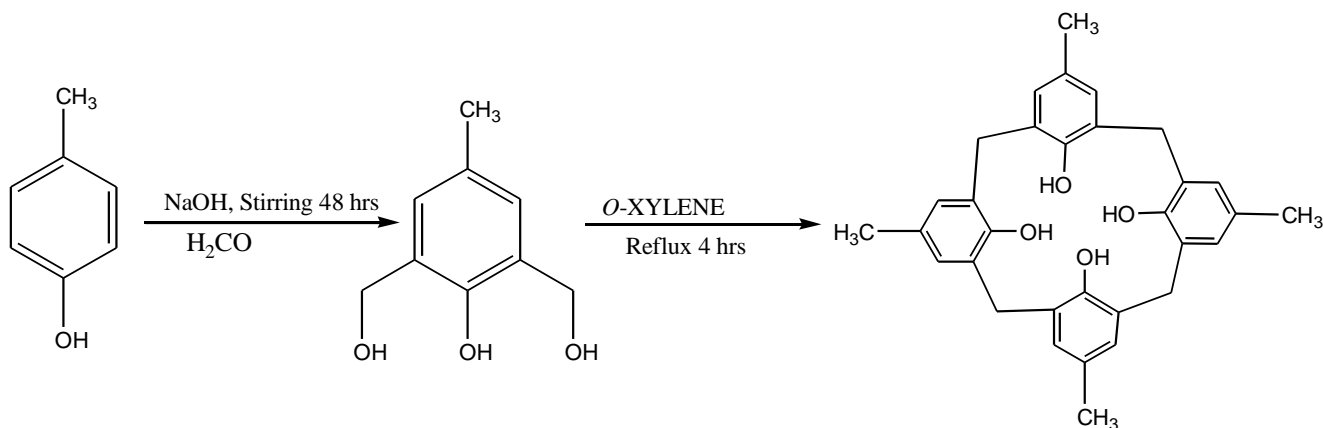
All chemicals were used in the present investigation are of analytical grade. All solutions were prepared with distilled water.

Preparation of [2,6-dimethylol 4-methyl phenol] ⁽¹¹⁾

To a solution of NaOH (50g, 1250mmole) in H_2O (200mL) was added *p*-cresol (108g, 100mmole). The mixture was stirred until a clear brown solution was obtained, stirring was continued while a (37%) solution of (CH_2O) (formaldehyde) (215g, 2651mmole) in H_2O was added. The yellow solution was allowed to stand for 48hrs. , after which time a white solid had precipitated. This was filtered and washed with saturated NaCl solution (200mL). The white precipitate was dried under section. The Na salt [Na(2,6-dimethylol-4-methyl phenolate)] was dissolved in 1.5 times the amount of water and neutralized with dilute acetic acid with stirring. The free alcohol crystallized out as white crystals, recrystallized from acetone- water, filtered and dried to give 130g, (90%) product, melting point (128°C).

Preparation of [Calix]-4- arenes

The condensation reaction of four equivalent of 2,6-dimethylol 4-methyl phenol (400 mmole, 67.2 g) in (200 mL) of *O*-xylene , the mixture was stirred half hour, then allowed to reflux to four hours, the orange precipitate was formed, the result precipitate washed in (5 mL) cold methanol, and (25 mL) 2% citric acid , the two layer solution were obtained, separated by equalized funnel, the organic layer take and dried by MgSO_4 , filtered , the filtrate dried by vacuum, the deep yellow precipitate yielded, 65g, (33%). The preparation of ligand was showed in *Scheme 1*.



Scheme 1. Synthesis route of Calix-4-arenes ligand

Syntheses of solid complex

Weighted 0.1gm of reagent (0.2 mmole) and dissolved in 15ml of ethanol , than weighted 0.0472gm (0.2mmole)of the solid NiCl₂.6H₂O that dissolved previously with minimum amount of ethanol in a 50mL beaker and mixed at room temperature. The complex then filtrated and precipitated at pH=9 used NaOH (0.01M) to control of the pH . The precipitate after purification dried and stored in tightly closed container. Some physical properties of the prepared ligand and it's complex were tabulated in *Table (1)*.

Table 1. Some physical properties of reagent and Ni(II) complex

Compound	Molecular weight(g/mole)	Color	λ_{max} nm	Melting point	Conductivity S.mol ⁻¹ .cm ²
Reagent	480.59	Yellow-brown	306	108 C°	-----
Ni(II)-----	532	Green	403	218 C°	321.4

Results and Discussion

I-Characterization of ligand

Electronic spectra

The ultra violet spectrums of *bis*(hydroxyl methyl) p-cresol and calyx-4-arens *Fig (1)* and *Fig (2)* respectively, appeared peaks at 284nm ($\epsilon_{max} = 1154 \text{ molar}^{-1} \text{ cm}^{-1}$) of starting material and 245, 284 nm ($\epsilon_{max} = 1383, 1135 \text{ molar}^{-1} \text{ cm}^{-1}$) due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively .

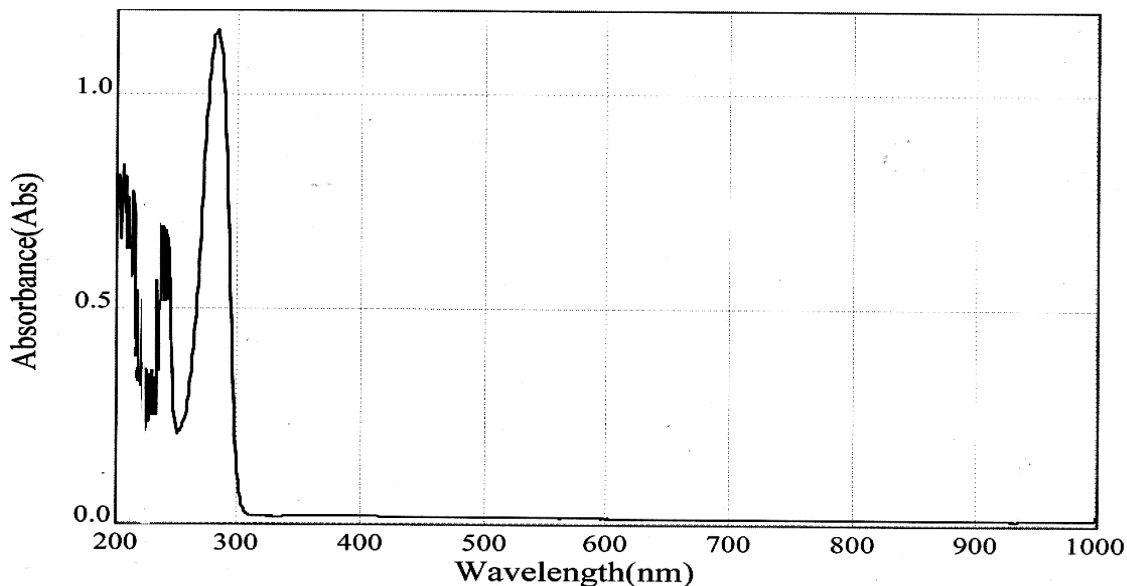


Fig .1. UV-Vis spectrum of *bis*(hydroxyl methyl) p-cresol

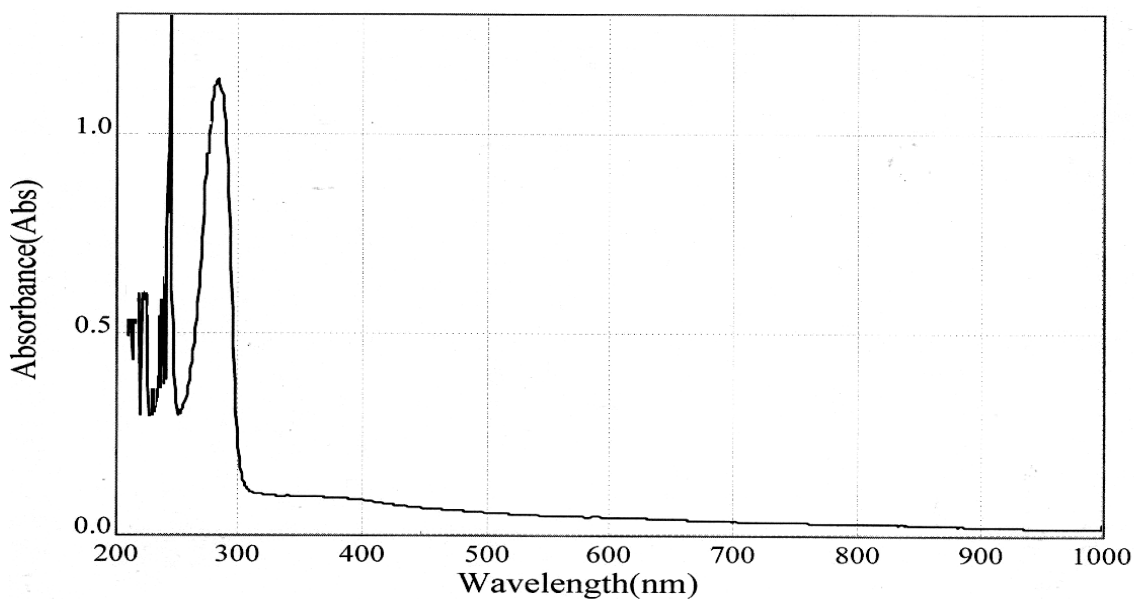


Fig. 2. UV-Vis spectrum of [calix] -4- arenes

¹H NMR spectra

The ¹H NMR spectrum of [calix] -4- arenes *Fig (3)* shows signal at ($\delta=8.35$ ppm ,4H) assigned to Ar-OH groups , The signals at ($\delta=7.10$ ppm ,4H , $\delta= 6.25$ ppm ,4H) attributed to aromatic protons of four benzene rings, due to the aromatic rings are exist in twested configuration the Ar-CH₂ groups appears twin signals at ($\delta=3.50,3.20$ ppm ,8H) and methyl groups Ar-CH₃ shows twin signal at ($\delta=2.25,2.10$ ppm ,12 H),the signal at ($\delta=2.60$ ppm) assigned the solvent DMSO.

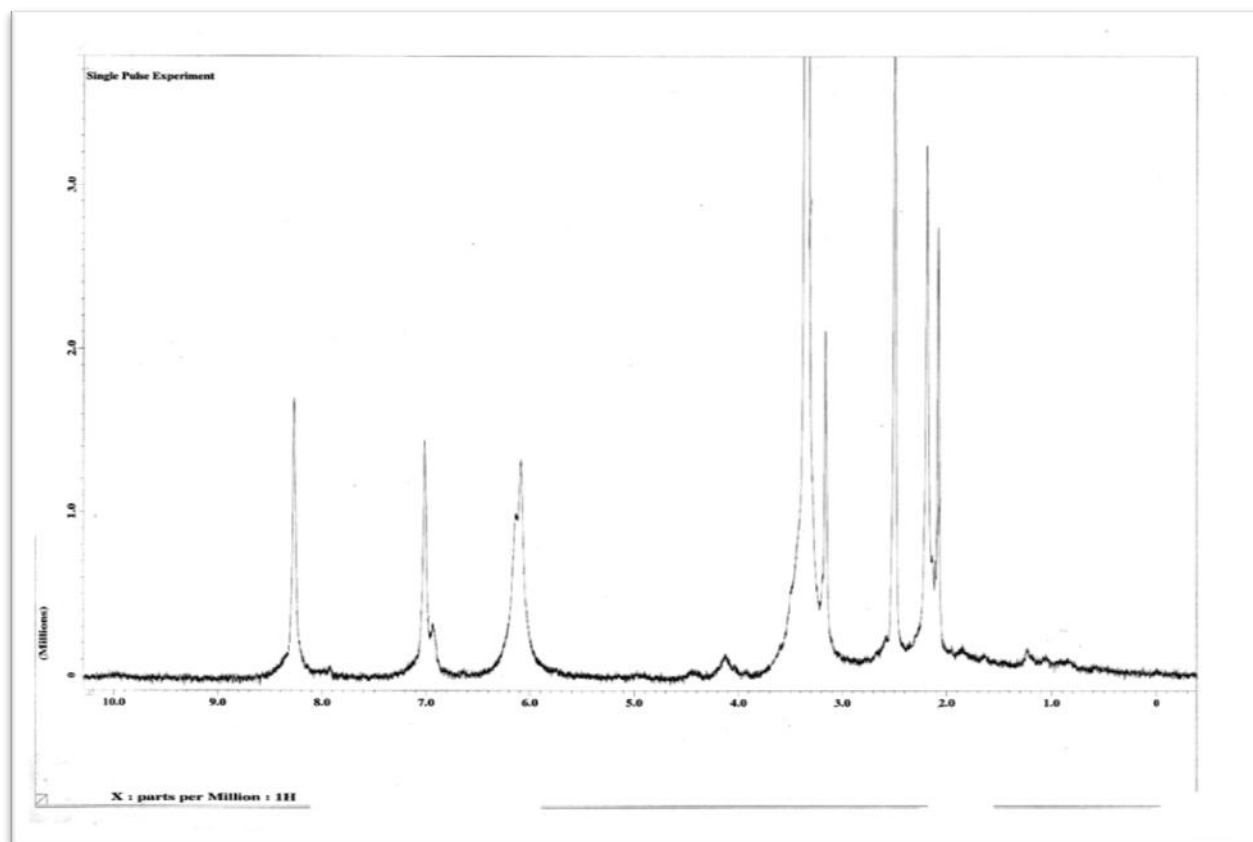


Fig. 3. ¹H NMR spectrum of [calix] -4- arenes

FT-IR spectra

The IR spectrum of *bis* (hydroxyl methyl)-*p* -cresol Fig(4) displayed two bands at 3400cm⁻¹ and 3308 cm⁻¹ can be aromatic and aliphatic hydroxyl groups respectively. The weak bands at 3050 cm⁻¹ and 2893cm⁻¹ assigned to ν(C-H) stretching of aromatic aliphatic (C-H) respectively, the other bands at 1568,1442 and 1205 cm⁻¹ due to the vibration frequencies of rings .While the IR spectra of (calyx)-4-arenes Fig (5) shows the disappearing of band at 3400 cm⁻¹ due to aliphatic (OH) and the shifting of other bands indicating of the obtaining of calix-4- areanes.

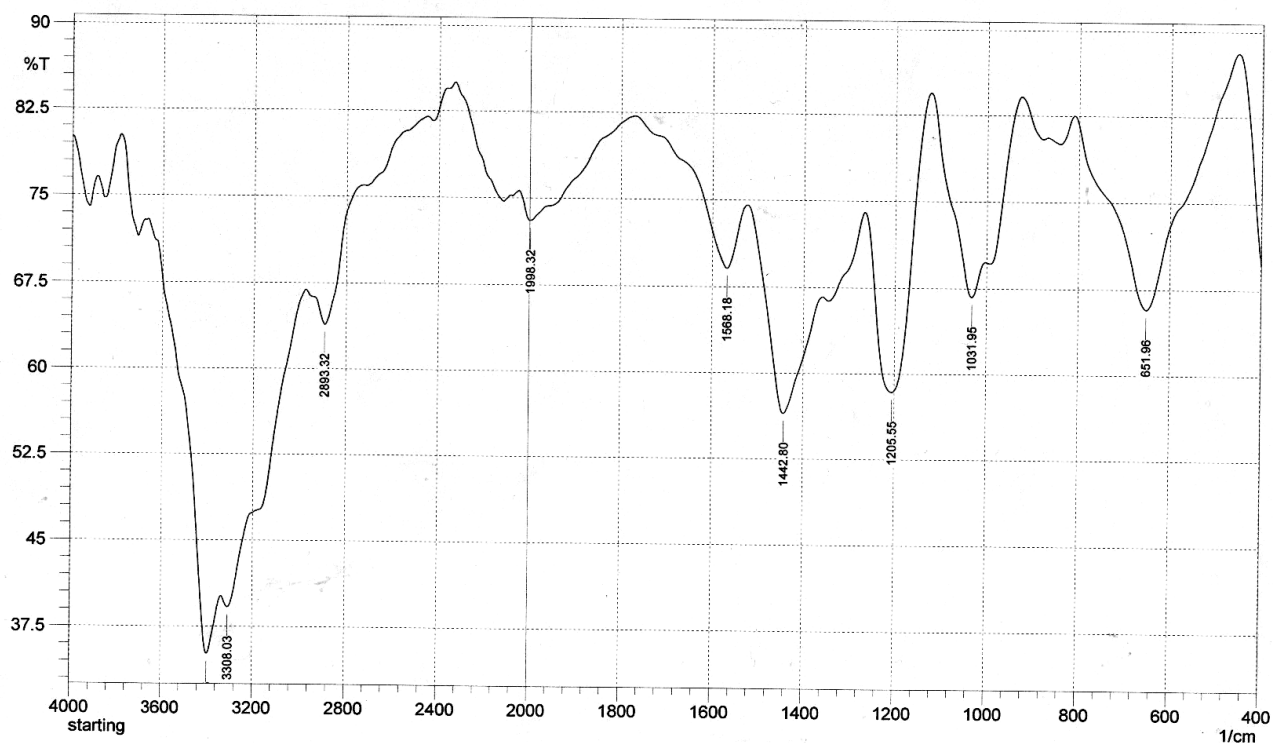


Fig.4. FT-IR spectrum of 2,6-dimethylol 4-methyl phenol

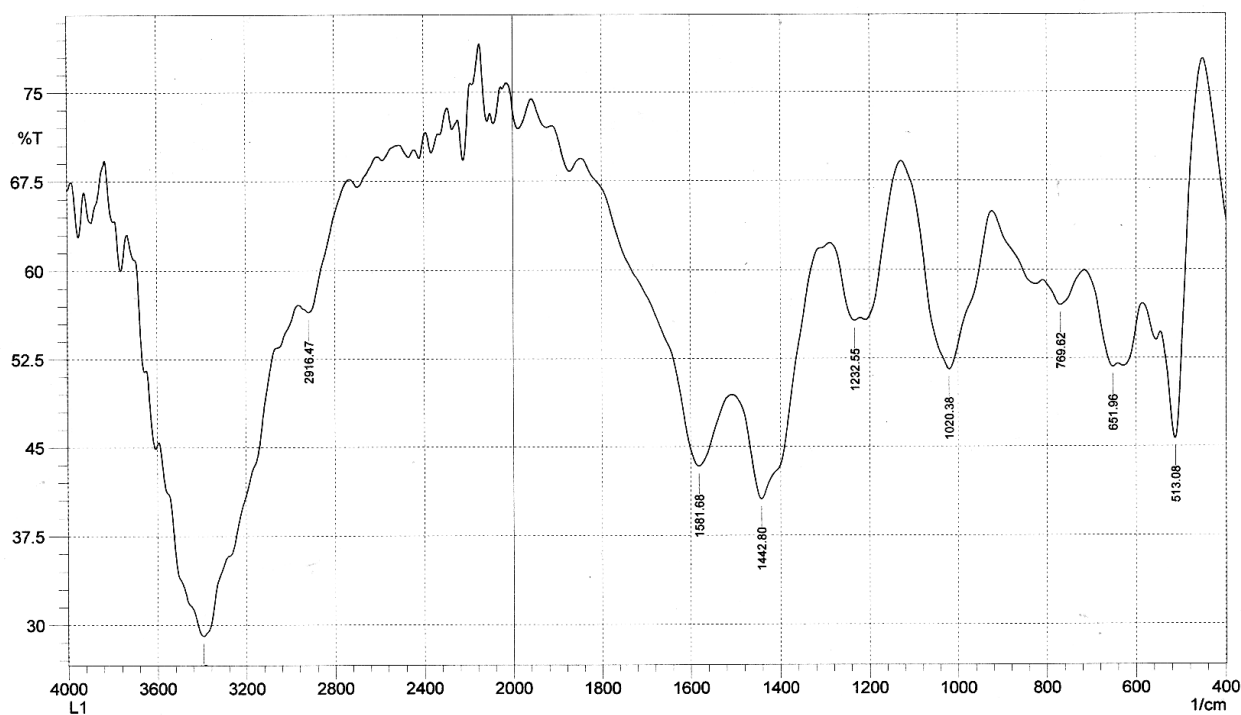


Fig. 5. FT-IR spectrum of [calix] -4- arenes

II-Characterization of complex

Electronic spectra

The UV-Visible spectrum of the ligand, *Fig (2)* shows twin absorption peak at 245 and 284 nm ($\epsilon_{\max} = 1383, 1135 \text{ molar}^{-1} \text{ cm}^{-1}$) due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively⁽¹²⁾. While the electronic spectrum of the complex of Ni^{II}, *Fig (6)* exhibited the following data .

The nickel(II) complex shows peak at 254nm (39370 cm^{-1}) ($\epsilon_{\max} = 720 \text{ molar}^{-1} \text{ cm}^{-1}$) and at 306 nm (32679 cm^{-1}) ($\epsilon_{\max} = 650 \text{ molar}^{-1} \text{ cm}^{-1}$) assigned to intraligand charge transfer and the peak at 403nm (24813 cm^{-1}) ($\epsilon_{\max} = 650 \text{ molar}^{-1} \text{ cm}^{-1}$) attributed to d-d transition type ${}^3A_{2g}^{(F)} \rightarrow {}^3T_{2g}^{(F)}$ and shoulder peaks at 754nm (13262 cm^{-1}) ($\epsilon_{\max} = 42 \text{ molar}^{-1} \text{ cm}^{-1}$) that attributed to d-d transition type ${}^3A_{2g} \rightarrow {}^3T_{1g}$ which that similar to that showed of octahedral d^8 complexes⁽¹³⁾.

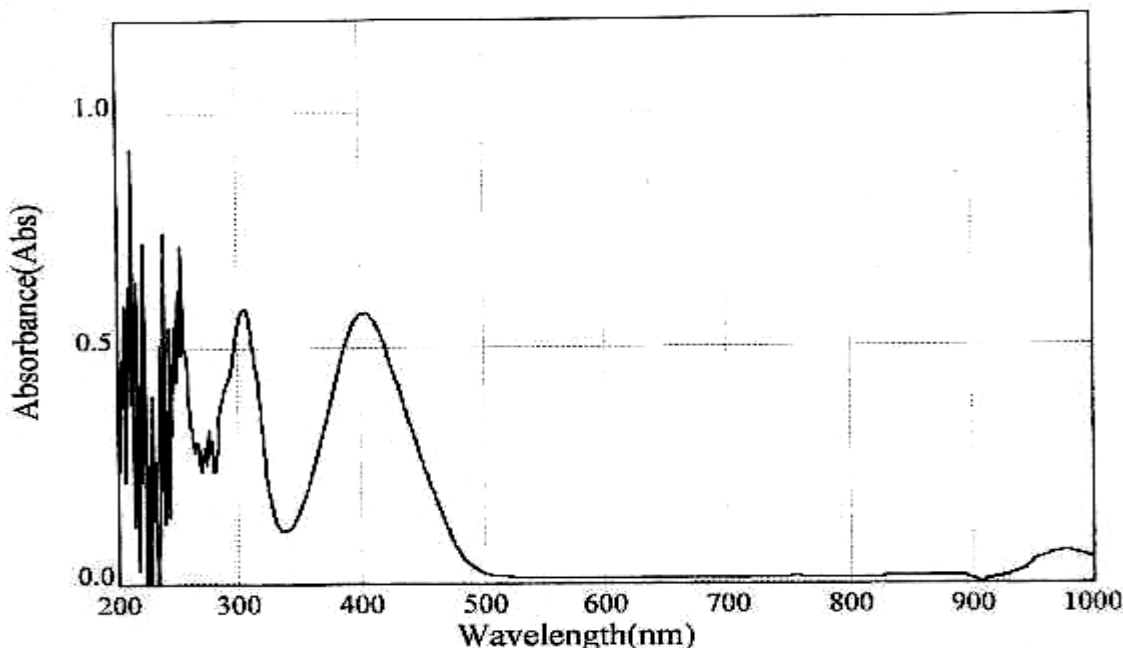


Fig. 6. UV-Vis spectrum of Ni(II)-complex

FT-IR spectra

The IR spectra of the ligand is shown in *Fig (7)* and the IR spectra of the complexes Ni(II) are shown in *Figs.(2)*, that exhibited the following data .

The broad band at 3400 cm^{-1} in the free ligand spectrum which assigned to $\nu(-\text{OH})$ stretching, the lower frequency for $\nu(-\text{OH})$ due to hydrogen bonding⁽¹⁴⁾, these band in IR spectrum of complex was shifted and reduced intensity due to complex formation⁽¹⁵⁾. There is also a shifting noticed in the $\nu(\text{C}-\text{O})$ group of phenol group from 1232 cm^{-1} toward 1267 cm^{-1} producing another evidence about involvement of phenol group in coordination with metal ions via oxygen group.⁽¹⁶⁾ The band at 1232 cm^{-1} attributed to phenolic $\nu(\text{C}-\text{O})$ ⁽¹⁴⁾. New bands at 449 cm^{-1} was assigned in the spectra of metal complexes. These bands were not present in the spectrum of ligand, and it is due to $\nu(\text{M}-\text{O})$ vibrations.⁽¹⁷⁾ The appearance of these bands support the involvement of hydroxyl groups of ligand via oxygen atoms in complexation.

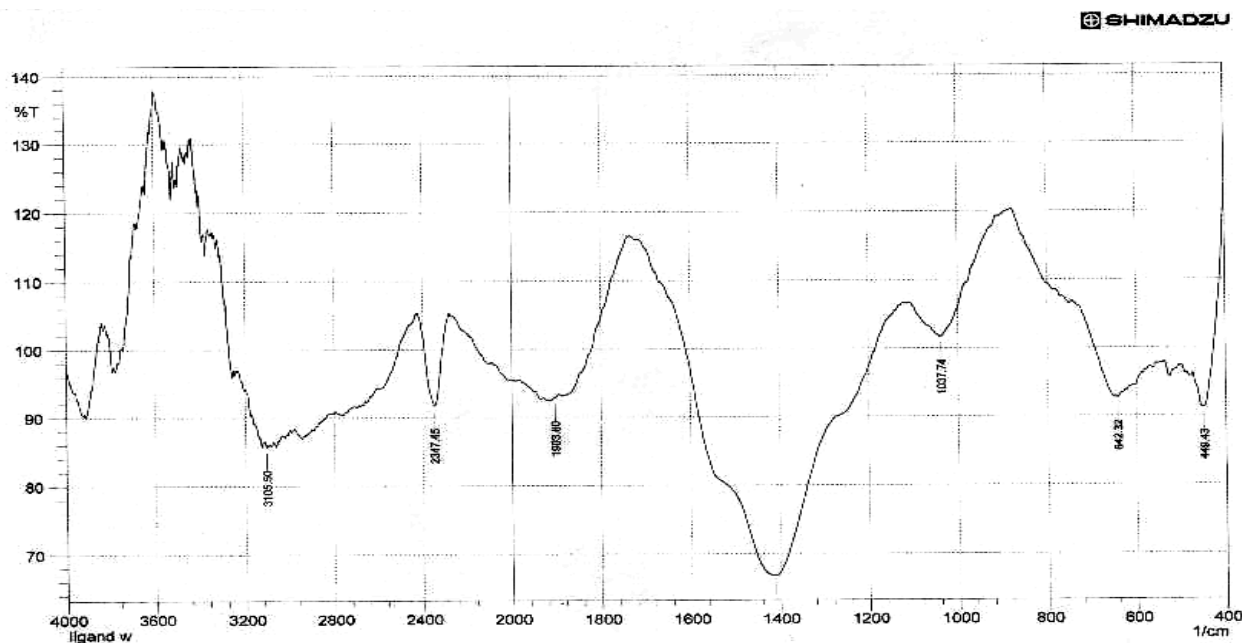


Fig.7. FT-IR spectrum of Ni-complex

Optimum study of complex

Nickel (II) ion react with Calix-4-arenes in neutral medium to form a green complex that has a maximum absorption at λ_{max} 403 nm *Fig (6)*. The absorbance of the green complex is directly related to the concentration of Ni(II) and that can be used for its spectrophotometric determination . The development of the color intensity and stability of complex depends on the reaction condition and were optimize as follows:

Influence of pH

The pH was studied between the rang (3-9), adjusted by means of dilute HCl and NaOH solution, where the maximum absorbance obtained in (pH=9) . At pH > 9 a decreases in absorbance because the precipitation of Ni(II)-complex or form unstable ionic complexes ⁽¹⁸⁾ .

Influence of time

The color intensity reached a maximum after nickel(II) solution had been reacted immediately with reagent and become stable after 25 min. therefore 25 min development time was selected as optimum in the general procedure. The green complex was stable for 24 hr.

Effect of order addition

The effect of order addition in absorbance of formation complex, depended a four sequence that tabulated in *Table 2*

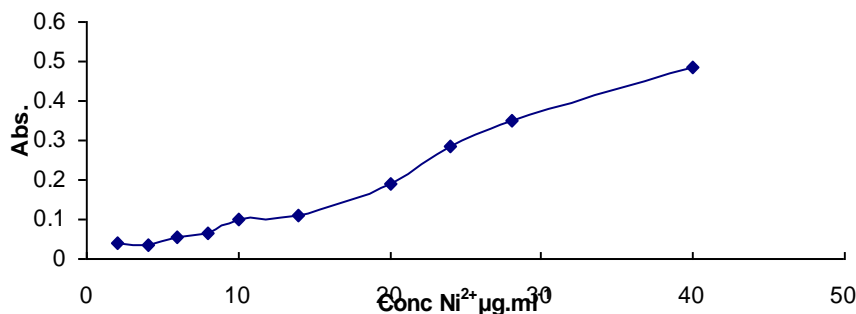
*Table 2.*Effect of order addition, $[Ni^{2+}] = 10 \mu g.ml^{-1}$, $[L] = 200 \mu g.ml^{-1}$ pH=9

No.of test	Sequence of addition	Abs. of Ni(II)-complex
1	M+L+pH	0.049
2	L+M+pH	0.069
3	M+pH+L	0.004
4	L+pH+M	0.059

M= Ni^{2+} ,L=reagent

Concentration of metal effect

When various concentration of metal solution in the range of (1–40 $\mu\text{g.ml}^{-1}$) were added to fixed amount of reagent [Calix]-4- arenes 200 $\mu\text{g.ml}^{-1}$. Concentrations of metal ion 10 $\mu\text{g.ml}^{-1}$ give the highest



absorbance Fig (8) and were for further experiments.

Fig.8. Concentration of metal effect , [L] = 200 $\mu\text{g.ml}^{-1}$, pH=9

Concentration of ligand effect

When various concentration of [Calix]-4- arenes solution in the range of (5 –250 $\mu\text{g.ml}^{-1}$) were added to fixed amount of Ni(II) 10 $\mu\text{g.ml}^{-1}$. Concentrations of reagent 200 $\mu\text{g.ml}^{-1}$ give the highest absorbance Fig (9) and were for further experiments.

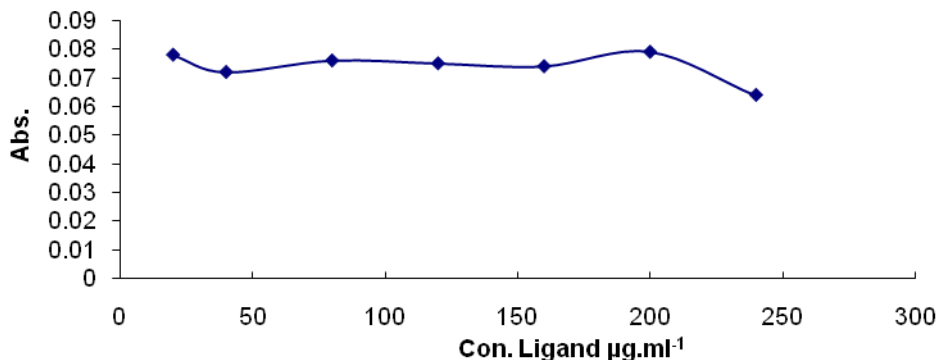


Fig. 9. Concentration of ligand effect , [Ni] = 10 $\mu\text{g.ml}^{-1}$, pH=9

Stoichiometry of complex

The stoichiometry of the complex was investigated using mole – ratio and job method under the optimizes conditions. The result obtained Fig (10) and Fig (11), show a 1:1 metal to reagent complex was formed. The formation of the complex may probable be occur as follows

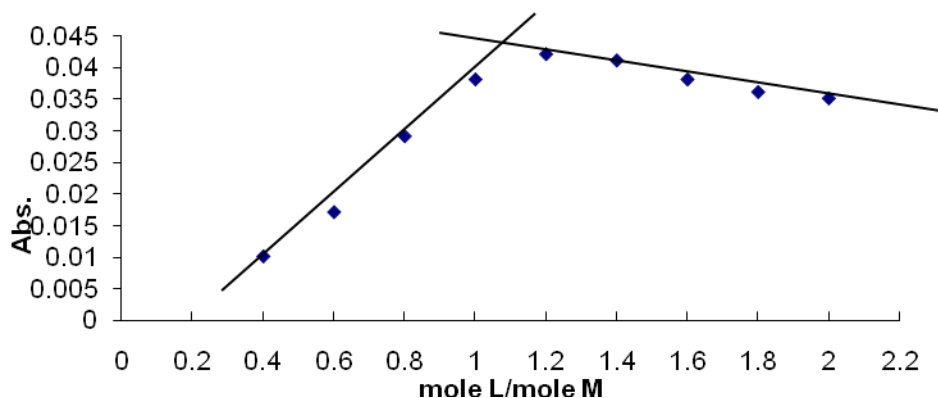


Fig. 10. Mole ratio of Ni(II)-complex

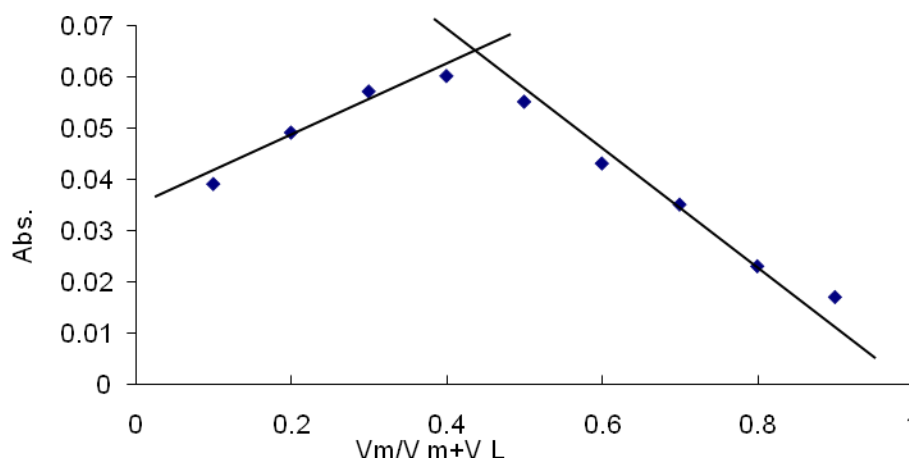


Fig. 11. Job's method of Ni(II)-complex

As applied to the molar ratio method, stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal ion mixture at fixed wavelength λ_{max} and pH values. The degree of formation of the complexes is obtained according to the relationship⁽¹⁹⁾, $K = (1 - \alpha) / \alpha^2 c$, and $\alpha = (A_m - A_s) / A_m$, where A_s and A_m are the absorbance's of the partially and fully formed complex respectively at optimum concentration. The complex have stability constant $0.48 \times 10^8 \text{ L.mole}^{-1}$ that appear the complex highly stability which can used a reagent to spectrometric determination of Ni(II) .

Calibration curve

Under the optimum condition at pH=9 ,time 25 min. and temperature 25 C° . Linear calibration curve *Fig (12)*, was obtained over the concentration range of (0.74-10.0 $\mu\text{g.ml}^{-1}$) .The limited of detection (signal/ noise = 3) was 0.5 $\mu\text{g.ml}^{-1}$ and the correlation coefficient was 0.996.

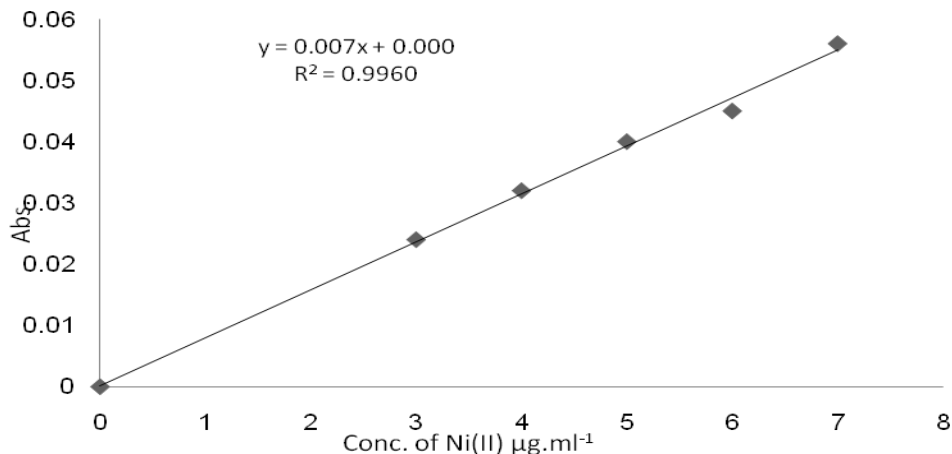


Fig. 13. Calibration curve of Ni(II)-complex

Precision and Accuracy

The relation standard deviation evaluated from five independent determination of $10\mu\text{g.ml}^{-1}$ of Ni(II) was 2.91%, this result show that the method is highly precise. Also the accuracy of the method was determined by calculating the $E_{rel}\%$ and $Re\%$ for $10\mu\text{g.ml}^{-1}$ of Ni(II) which was found to be 1.12% and 98.88% respectively

Influence of foreign ions

The selectivity of the proposed methods was investigated by the determination ($10\mu\text{g.ml}^{-1}$) of Ni(II) in the presence of a series of $10\mu\text{g.ml}^{-1}$ of cations *Table 3* and $200\mu\text{g.ml}^{-1}$ anions *Table 4* the results show the tolerance limit was taken as the amount that caused an error of 0.076 in the absorbance .

Table 3. Determination tolerance limits of some foreign cations

Species	Absorbance of Ni(II) complex	Error %
Complex without addition	0.076	-----
Fe^{3+}	0.143	-88.16
Zr^{4+}	0.041	46.05
Al^{3+}	0.038	50.00
Mn^{2+}	0.112	-47.37
Hg^{2+}	0.041	46.05
Cd^{2+}	0.057	25.00
Mg^{2+}	0.038	50.00

Table 4. Determination tolerance limits of some foreign anions

Species	Absorbance of Ni(II)complex	Error %
Complex without addition	0.076	----
NO_3^-	0.042	44.74
F^-	0.041	46.05
$\text{C}_2\text{O}_4^{=}$	0.048	36.84
Ac^-	0.051	32.89
$\text{SO}_4^{=}$	0.218	-186.84
$\text{CrO}_4^{=}$	0.052	31.58

Which they are also reacting with reagent Calix-4-arenes at the same choosing conditions and they were masked by using suitable masking agent. The results obtained are summarized in *Table 5*.

Table 5. Effect of masking agents

Masking agent 0.5 ml (0.01M)	Absorbance of Ni(II)-complex
Complex without addition	0.076
EDTA	0.033
Thiourea	0.050
Ascorbic acid	0.126
Potassium cyanite	0.079

Analytical application

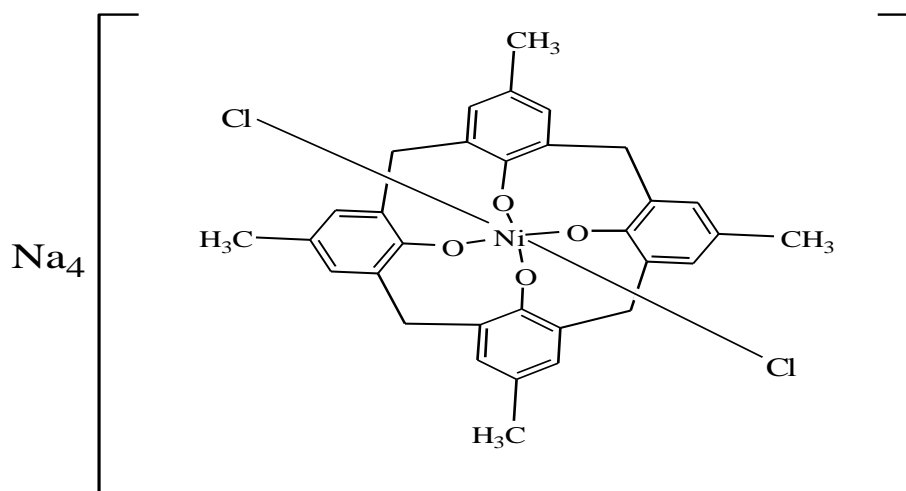
A validity of the method was checked successfully by determine the Ni(II) in 0.5 gm of clay sample dissolve in 1L than prepared solution $10 \mu\text{gml}^{-1}$ of Ni(II) than determined at the optimum conditions of the method this method show a low difference of nickel(II) concentration by using the calibration curve ,the data of application tabulated in *Table 6* .

Table 6. Application data of determination of Ni (II) in clay sample

Sample	Concentration of Ni(II) prepared μgml^{-1}	Absorbance measured	Concentration of Ni(II) measured μgml^{-1}	wt/wt % measured of Ni(II)	Error %
Prepared Ni(II)	10	0.069	9.988	99.45%	1.12%
Clay sample (Pentonite)	-----	0.082	11.88	23.76%	-----

Suggestion structural formula of Ni (II) –complex

According to these results from FT-IR spectrum, absorption spectra study and conductivity measurement while the composition of the complex was studied by Job's method and mole ratio method. Both methods indicated that the ratio of metal ion to ligand molecules was 1:1(M:L). The octahedral geometry around Ni(II) ion can be suggested, as follow



References

1. Calixarenes, C. D. Gutsche, *Royal Society of Chemistry*, Cambridge, 1989.
2. Calixarenes Revisited, C. D. Gutsche, *Royal Society of Chemistry*, Cambridge, 1997.
3. Calixarenes, C. D. Gutsche, *Acc. Chem. Res.*, 1983, 16, 161.
4. Calixarenes, macrocycles with (almost) unlimited possibilities, V. Böhm, *Angew. Chem. Int. Ed. Engl.*, 1995, 34, 713.
5. Formaldehyde polymers 29. Isolation and characterization of calix[5]arene from the condensation product of 4-tert-butylphenol with formaldehyde, A. Ninagawa and H. Matsuda, *Makromol. Chem. – Rapid Commun.*, 1982, 3, 65.
6. Calix[7]arene from 4-tert-butylphenol and formaldehyde, Y. Nakamoto and S. I. Ishida, *Makromol. Chem. – Rapid Commun.*, 1982, 3, 705.
7. Metal complexes of calixarenes, D. M. Roundhill, in *Progress in Inorganic Chemistry*, Vol. 43, K. D. Karlin (ed.), John Wiley & Sons Inc., New York, 1995.
8. Coordination chemistry of the larger calixarenes, C. Redshaw, *Coord. Chem. Rev.*, 2003, 244, 45.
9. Phenol-formaldehyde and allied resins VI: Rational synthesis of a 'cyclic' tetranuclear p-cresol novolak, B. T. Hayes and R. F. Hunter, *J. Appl. Chem.*, 1958, 8, 743.
10. A new synthetic access to cyclic oligonuclear phenolic compounds, V. Böhm, P. Chim and H. Kämmmerer, *Makromol. Chem.*, 1979, 180, 2503.
11. C. N. Verani, L. Rentschler, W. Thomas, E. Bill, and P. Chaudhuri, *J. Chem. Soc., Dalton trans*, 251-258 (2000).
12. Nakamoto K., "Infrared spectra of inorganic and coordination compounds", 4th. Ed. 289, (1996), Wiley, intr., New York.
13. B. P. Lever, "Inorganic Electronic Spectroscopy", 2th, New York, (1984).
14. R. M. Silverstein and F. X. Webster, "Spectrometric Identification of Organic Compounds", 6th. Ed., John Wiley and sons, (1998).
15. C. Dennig and J. Thatcter, *J. Amer. Chem. Soc.*, 1986, 90, 5917.
16. Nakamoto K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, Inc., (1978).
17. El-ajaily M M, Maihub A A, Aboukrisha M and Salem A I, *Jerash for Researches and Studies*, 2002, Part I, 6(2), 7- 20.
18. Burger K, "coordination chemistry "Experimenyal Methods , hondon Butte worth(1967).
19. S. Shibata, M. Furkawa and R. Nakashima, *Anal. Chem. Acta.*, (1976), 81, 131.