

## On the Formation of Ni(II)-Anthranilic Acid Anilide Complexes

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**Summary:** The preparation and spectral properties are reported for a series of nine anthranilic acid anilide ligand-Ni(II) complexes. The coordination of the ligands has been demonstrated by ir and electronic spectra. The results indicate octahedral geometry around Ni(II) ion, where EtOH molecule occupy bridged positions which lead to dimeric structure. The formation curves and consequently the stability constants of the complexes in 50% dioxane are determined by potentiometric techniques. The values of the stability constants depend on molecular structure. Deviation of the  $\sigma^*-\log K$  plots slopes from unity is attributed mainly to steric effects,  $\pi$ -electron back donation from the metal ion or structural changes in the ligand.

### Introduction

Although the coordination compounds of Ni(II) with various mono- or bidentate ligands have been studied extensively in the light of their stereochemistry the structure aspects of five coordinate Ni(II) complexes are still under extensive investigation[1-4]. Generally Ni(II) forms octahedral or square planar complexes. There is another possibility of five-coordinated environment around Ni(II) giving square pyramidal or trigonal bipyramidal structures in which one ligand is weaker at the axial position or the solvent molecule may occupy bridged positions.

The aim of the present work, is to prepare Ni(II) complexes with some anthranilic acid anilides. The prepared complexes are subjected to elemental analysis, TGA and some spectroscopic investigations. The composition, nature and stability of the complexes formed in 50% aqueous dioxane are also considered.

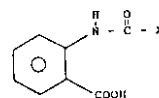
### Experimental

All commercial reagents of high grade were distilled or recrystallized, when necessary, before use.

To a Ni(II) sulphate solution (0.015M), dissolved in the least amount of distilled water, was added a mixture of equimolar quantities of KOH and the anilide ligand solutions (100 ml ethanol) dropwise and the reaction mixture was stirred for about 4 hours. The deep blue solid precipitated was filtered off, washed several times with bidistilled water, ethanol then finally ether and dried in vacuo.

All the prepared complexes were subjected to elemental microanalysis; the results are listed in Table (1).

The ligands used in the present investigation have the following formula (I):



in which X is as follows:

#### Ligand Abbreviation

	X
anben	- C <sub>6</sub> H <sub>5</sub>
annit	- CH <sub>2</sub> CN
aneth	- CH = CH <sub>2</sub>
anacac	- CH <sub>2</sub> COCH <sub>3</sub>
anbenac	- CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub>
anethacet	- CH <sub>2</sub> COOEt
anethprop	- CH <sub>2</sub> CH <sub>2</sub> COOEt
anacet	- CH <sub>2</sub> CONH <sub>2</sub>



The solid complexes are insoluble in most of common organic solvents which prevents their study in solutions. The apparatus and working procedures are the same as described previously[5,6].

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## Results and Discussion

### A) Complexes in the Solid State:

Table (1) summarizes the Ni(II) complexes together with their analytical data. The analytical data correspond to the assigned molecular formula. Weight loss experiments show the presence of solvent molecules coordinated to the central Ni(II) ion which are not removed by static vacuum for four hours at room temperature. This conclusion is also supported by the results of thermogravimetric analysis of Ni(II) complexes which show the dehydration of lattice and coordinated solvent molecules at 70- 80°C and 130-150°C respectively in case of  $\{Ni(\text{anben})_2(\text{H}_2\text{O})_2\} \cdot 7\text{H}_2\text{O}$  and  $\{Ni(\text{aneth})_2(\text{H}_2\text{O})_2\}$  complexes while in the other complexes the removal of coordinated ethanol occurs at 120-140°C.

On examining the ir spectra of the complexes under investigation in comparison to those of the free ligands the following can be pointed out:

The bands located at 3320-3260 and 1680-1670  $\text{cm}^{-1}$  due to  $\nu\text{NH}$  and  $\nu\text{COO}$  respectively, in the spectra of the complex formation by 80- 70 and 40-30  $\text{cm}^{-1}$  respectively. Thus the bonding between the Ni(II) ion and the ligands under investigation would take place through the interaction of COO and NH groups with Ni(II) ion while the band observed at 1625-1590, in the spectra of free ligands, due to  $\nu\text{CO}$  tends to vanish in the spectra of Ni(II) complexes. This will lead us to conclude that in the formation of the Ni(II) complexes, the -CONH- group of the ligand molecule is transformed into C=N group when the ligand molecule reacted with Ni(II) ion and also the enolic OH groups does not participate in the formation of Ni(II) complexes. The existence of coordinated EtOH or H<sub>2</sub>O molecules in all complexes renders it difficult to draw conclusions from the  $\nu\text{OH}$  band of the carboxy group which would be covered by those of EtOH or H<sub>2</sub>O molecules. Actually, the spectra of most complexes exhibit a broad band around 3600-3340  $\text{cm}^{-1}$ . This could be attributed to  $\nu\text{OH}$  of H<sub>2</sub>O or EtOH molecules associated with complexes formation. On comparing the ir spectra of Ni(II) complexes with those of annit, anacet, anacac, anbenac, anethacet, and anethprop ligands. A new band appears at 965-945  $\text{cm}^{-1}$  in the spectra of Ni(II) com-

plexes due to OH out of plane bending mode vibrations of solvent molecules[7]. The band position denotes that the solvent molecules are bridged in such type of complexes[7]. The two new bands observed at 440-480 and 350-380 $\text{cm}^{-1}$  which are not present in the spectra of the free ligands, can be assigned to  $\nu\text{M-O}$  and  $\nu\text{M-N}$  respectively.

It is well known that Ni(II) ion forms a large number of chelates[8,9], with its coordination number varying from four to six. The structure of the six coordinated chelates are generally octahedral and often with slight distortion[10], while those with coordination number four may have tetrahedral or square planar arrangement. Trigonal bipyramidal or square pyramidal structures are usually assigned to many pentacoordinated Ni(II) complexes. The electronic reflectance spectra of Ni(II) complexes with all ligands under investigation, Fig.(1), have the same general features. The complexes exhibit mainly four absorption bands with  $\lambda_{\text{max}}$  within 340-350, 360-370, 390-420 and 550-600 nm ranges. Since the absorption bands for  $\{Ni(\text{aneth})(\text{H}_2\text{O})_2\}$ ,

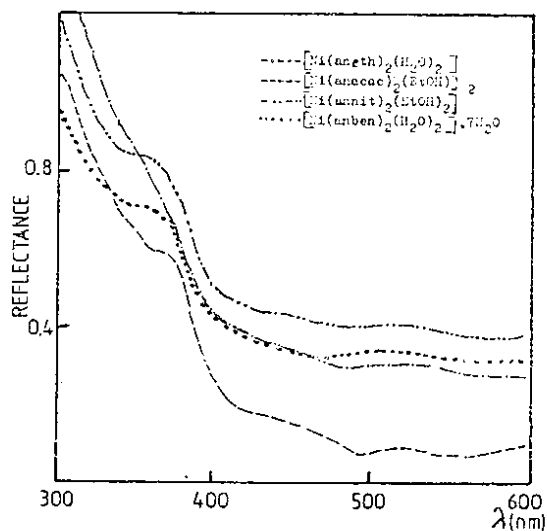


Fig. 1: Reflectance spectra of Ni(II)-anilide complexes.

$[Ni(\text{anben})_2(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}$  and  $[Ni(\text{anisacet})(\text{EtOH})_2]$  are similar to those of the other complexes under investigation one can conclude the following:

- (a) The first two bands correspond to  $\pi \rightarrow \pi^*$  transition within the aromatic ring and anilide part respectively whereas the other two absorption bands can be assigned to:

Table 1: Analytical and conditional stability constants data for Ni(II)-anthranilic acid complexes

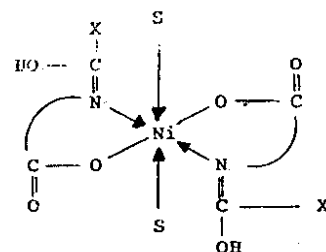
Complexes	Microanalysis Results*				Log K (Ni:L)		
	%C	%H	%N	%Ni	2:1	1:1	1:2
[Ni(annit) <sub>2</sub> (EtOH) <sub>2</sub> ]	50.00 (50.73)	4.30 (4.67)	9.87 (10.05)	10.56 (10.54)	10.25	9.70	9.20
[Ni(anacet) <sub>2</sub> EtOH] <sub>2</sub>	48.70 (48.28)	4.32 (4.38)	9.60 (10.20)	10.56 (10.73)	10.60	10.25	10.05
[Ni(aneth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	51.00 (50.55)	4.29 (4.21)	6.88 (5.89)	12.79 (12.36)	11.85	11.80	11.65
[Ni(anacac) <sub>2</sub> (EtOH) <sub>2</sub> ]	52.09 (52.87)	4.31 (4.77)	5.00 (5.14)	10.56 (10.77)	11.00	10.50	10.15
[Ni(anbenac) <sub>2</sub> EtOH] <sub>2</sub>	61.70 (61.00)	4.77 (4.41)	4.55 (4.18)	9.39 (8.77)	10.75	9.80	9.40
[Ni(anethacet) <sub>2</sub> EtOH] <sub>2</sub>	51.81 (51.54)	4.59 (4.29)	5.00 (5.00)	10.56 (10.50)	10.30	9.80	9.35
[Ni(anbisacet) <sub>2</sub> (EtOH) <sub>2</sub> ]	52.00 (51.40)	4.61 (4.89)	5.33 (5.70)	11.74 (11.96)	11.05	9.60	10.20
[Ni(anethprop) <sub>2</sub> EtOH] <sub>2</sub>	53.59 (53.17)	4.41 (4.77)	4.73 (4.77)	9.97 (10.00)	10.75	10.37	10.35
[Ni(anben) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].7H <sub>2</sub> O	48.40 (48.00)	4.80 (5.42)	3.29 (3.99)	8.21 (8.37)	3.05	3.09	3.11

\* % Found (%. calculated).

and  ${}^3A_{2g} \longrightarrow {}^3T_{1g} (P)$   
 ${}^3A_{2g} \longrightarrow {}^1A_{1g} (G)$  transition  
 respectively.

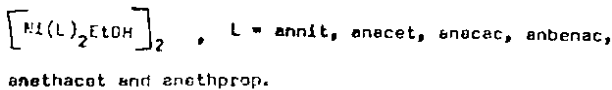
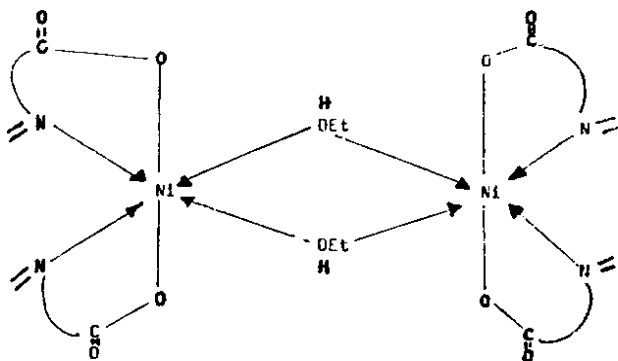
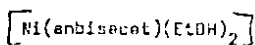
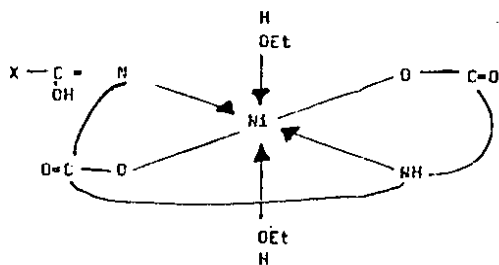
- (b) The spectral pattern of the Ni(II) anilide complexes under investigation is relevant to an octahedral arrangement of the ligands annit, anacac, anbenac, anethacet, anethprop and anacet only five ligated groups are present; the fulfillment of the sixth coordination site can only take place if the EtOH molecule can behave as bridging position which leads to octahedral dimeric structure.

On the basis of the above results Ni(II) - anilide complexes can have the following formula:

S = H<sub>2</sub>O or EtOH

L = aneth and anben

[Ni(L)<sub>2</sub>S<sub>2</sub>].



### Complexes in Solution:

Since the formation of the Ni(II) complexes with anthranilic acid anilides are associated with the liberation of  $\text{H}^+$  ions from the ligands, then it is possible to apply the pH metric method for the

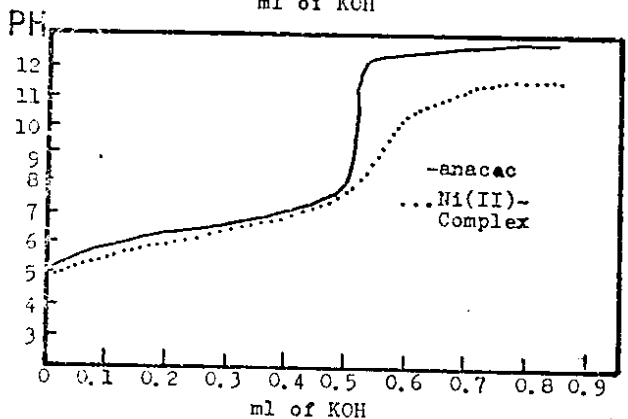
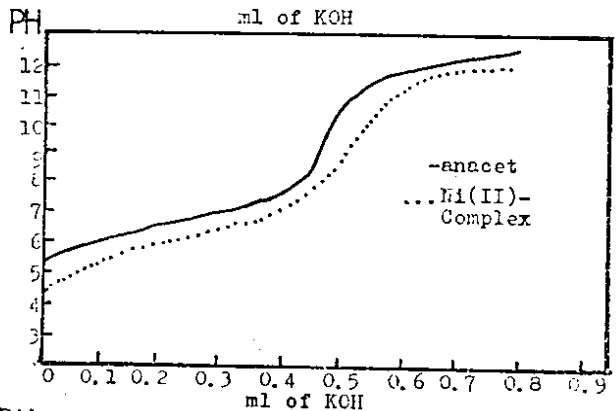
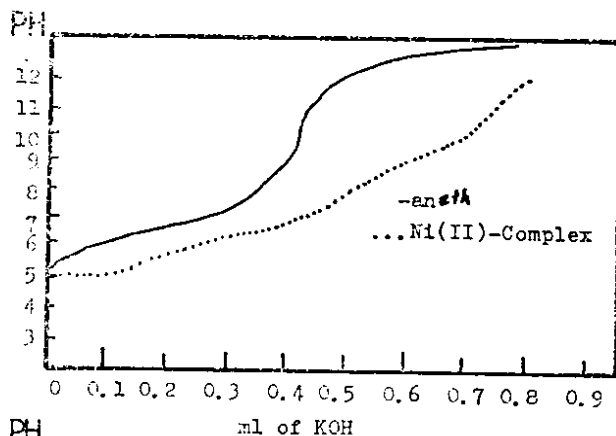
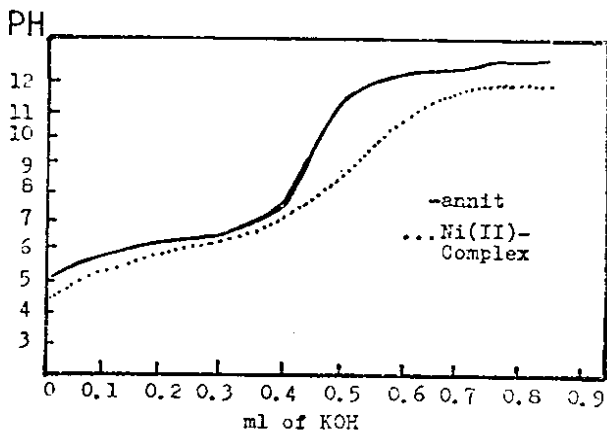


Fig. 2A: Titration curves of Ni(II)-anilide complexes.

determination of the composition and conditional stability constants of the chelates formed in solution[11].

The pH titration curves of the Ni(II) complexes under investigation (Fig.2A) are S-shaped, the volume of alkali consumed in the titration corresponds to the liberation of one or two  $\text{H}^+$  ions per Ni(II) ion or complex formation. The titration curves exhibit one inflection within 7.5-8.4 pH

Table II: Spectral data for Ni(II)-anthranilic acid anilides complexes

Complexes	IR cm-1							UV, visible
	$\nu$ OH	$\nu$ N-H	$\nu$ OHenol	$\nu$ COO	$\nu$ OH def	$\nu$ M-O	$\nu$ M-N	Reflectance $\lambda$ (nm)
[Ni(annit) <sub>2</sub> (EtOH) <sub>2</sub> ]	3340-3560	3080	2890	1610	-	440	360	345-350, 360-370, 410-420 550-600
[Ni(anacet) <sub>2</sub> EtOH] <sub>2</sub>	3340-5490	3100	2950 2920	1600	945	470	360	340-350, 360-370, 410-420, 550-600
[Ni(aneth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3300-3500	3190	2890	1605	-	450	380	345-350, 360-370, 410-420, 550-600
[Ni(anacac) <sub>2</sub> EtOH] <sub>2</sub>	3340-3510	3190	2930 2900	1600	965	460	350	340-350, 360-370, 410-420, 550-600
[Ni(anbenac) <sub>2</sub> EtOH] <sub>2</sub>	3500-3560	3110	2930 2920	1620	955	475	350	340-350, 360-370, 390-420, 550-600
[Ni(anethacet) <sub>2</sub> EtOH] <sub>2</sub> <sup>a</sup>	3340-3510	3110	2940 2920	1625	985	480	360	340-350, 360-370, 390-410, 550-600
[Ni(anbisacet)(EtOH) <sub>2</sub> ] <sub>2</sub> <sup>b</sup>	3340-3500	3280	2910	1630	995	470	380	340-350, 360-370, 390-410, 550-600.
[Ni(anben) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·7H <sub>2</sub> O	3340-3500	3180	2890	1620	-	440	375	340-350, 360-370, 340-410, 550-600

a)  $\nu$  COO free ester at 1700 -1720 cm<sup>-1</sup>  
 b)  $\nu$  C=N at 1600 cm<sup>-1</sup>.

range which can be ascribed to the formation of some different types of complexes, probably the hydroxo type[12].

The formation curves obtained, (Fig.2B) for the different complexes investigated have more than one inflection mostly three indicating three types of chelates are formed having the stoichiometric ratios 2:1, 1:1, 1:2, (Ni<sup>+2</sup>: L).

The conditional stability constants of the three types of complexes log K<sub>1</sub>, log K<sub>2</sub> and log K<sub>3</sub> were determined by the method of Bjerrum[13] and Albert[14] applying the least square method and the graphical representation method (n vs pL), Fig.2B.

The data obtained, Table I, indicate that the values of the conditional stability constants depend on the nature of the ligand where a linear relation is obtained for  $\sigma^*$  vs log K<sub>1</sub>, log K<sub>2</sub> or log K<sub>3</sub> plots,

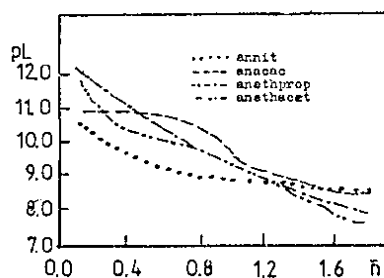


Fig. (2B): Formation curves of Ni(II)-anilide complexes

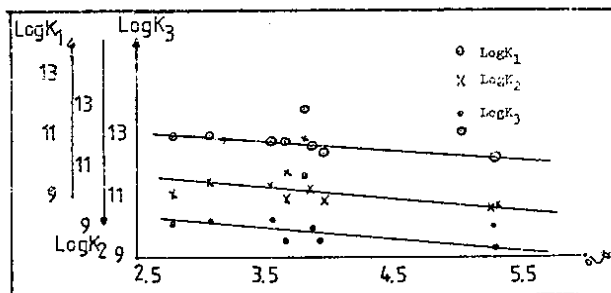
Fig. 3: Effect of LogK<sub>2</sub>, or LogK<sub>3</sub> on the molecular structure of Ni(II)-anilide complexes.

Fig.3. The negative slopes indicate that the complex formation is favoured by increased electron densities at the coordination sites, a factor which favours increased covalent character of the Ni(II)-ligand bond. Deviation from a slope of unity is attributed mainly to steric effect,  $\pi$ -electron back donation from the metal ion or structure changes in the ligand which alter the strength of the donor atom within the ligand[15].

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