

## A Spectroscopic study of the interaction between some Ni( II ) -β - thioxoketone complexes with pyridine.

Dhiaa K. M. AL-Taiy

*Open Educational College, Iraq*

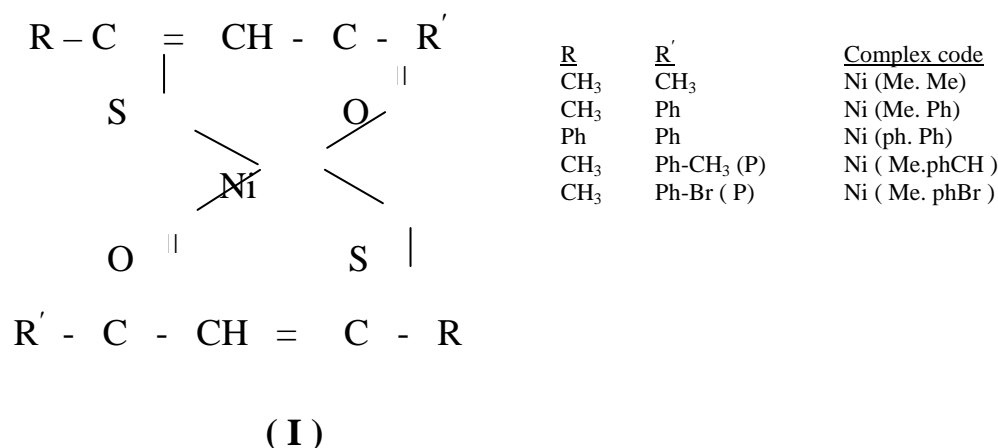
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### Abstract :

For Nickel ( II ) complexes of Ni ( RCSCHCOR )<sub>2</sub> type, in which R=CH<sub>3</sub> , ph ; R = CH<sub>3</sub> , ph , C<sub>6</sub> H<sub>4</sub> – CH<sub>3</sub> ( P ) , C<sub>6</sub> H<sub>4</sub> – Br ( P ) , Lewis acid – base interaction has been studied for these metal complexes as acceptors with pyridine as donor . All the reactions were found as 1 : 1 interactions. Equilibrium constants for these reactions in various solvents have been determined spectroscopically in the visible region. These values were within the range 7.33 – 18.0 L.mol<sup>-1</sup>.

### Introduction :

A number of investigations have been reported on equilibrium constant K<sub>eq</sub> of the Lewis acid – base interaction in various complexes of β-diketonats and related ligands as acceptors with amines as donors using different techniques [ 1 – 4 ]. Despite these studies , a few data have been published about the K<sub>eq</sub> for adduct formation of complexes of monothio-β-diketonats. Thus, the aim of the present work is to investigate interaction of nickel(II) complexes ( structural formula I ) derived from monothio-β-diketonats with pyridine and to calculate k<sub>eq</sub> using spectroscopic method in the visible region and also to observe the effect of variety of solvent and substituents on K<sub>eq</sub> .



### Experimental Section :

**Materials :** all the reagents used were analar pure chemical grade. All the solvents were freshly purified and dried according to standard procedures.

**Preparation of compounds :** Monothio- β -diketonats and their nickel (II) complexes were prepared by the methods reported in the literatures [ 5 , 6 ] , and recrystallized before use. Their physical properties are listed in(Tables 1 and 2.)

**Table ( 1 ) : Form and melting point of monothio-  $\beta$  -diketonates RCSCHCOR' used in the study**

<i>R</i>	<i>R'</i>	<i>Form</i>	<i>M. P. ( C° )</i>
CH <sub>3</sub>	CH <sub>3</sub>	Golden yellow liquid	-
CH <sub>3</sub>	Ph	Orange Crystals	29 – 30
ph	Ph	Red crystals	77 – 78
CH <sub>3</sub>	Ph- CH <sub>3</sub> ( P )	Reddish orange crystals	125 – 126
CH <sub>3</sub>	Ph – Br ( P )	Red crystals	129 - 130

**Table (2) : Colour , melting point and molecular weight of nickel ( II ) complexes**

<i>Complex</i>	<i>Colour</i>	<i>m.p. ( C° )</i>	<i>M. wt found ( cald .)</i>
Ni. (Me. Me)	Yellowish brown	168 – 169	247 ( 269 )
Ni. (Me.ph)	Reddish brown	225 – 226	381 ( 413 )
Ni. ( ph . ph )	Light brown	183 – 184	495 ( 537 )
Ni. ( Me . phCH )	Dark brown	216 – 217	463 ( 441 )
Ni. ( Me . phBr )	Brown	223 – 224	549 ( 571 )

**Physical measurements :** The electronic spectra of the complexes in chloroform , methanol and dichloroethane were recorded on PHILIPS – PU 8620 UV / VIS / NIR Spectrophotometer with 1 cm quartz cell in the range 250 – 700 nm. Infrared spectra were recorded using KBr disc on a pye–unicam Sp<sub>3</sub>-300<sub>s</sub>-infrared spectrophotometer in the range 4000-200cm<sup>-1</sup>. Melting points were recorded with a digital melting point apparatus type Gallenkamp and are uncorrected. Molecular weights were determined using Rast's Camphor method [ 7 ] .

**Equilibrium Constant :** The K<sub>eq</sub> was determined by visible technique as described already [ 8 ] . The measurement was carried out at constant concentration of each complex (0.001M) , while concentrations of pyridine were within the range 0.15 to 0.375 M in various Solvents at 298k using thermostated cell holder type mgw LAUDA k4R electronic with thermometer type PHILIP HARRIS precision + 0.1C<sup>o</sup> .

### Results and Discussion

All the metal complexes were coloured solids. Molecular weight determinations showed that all complexes to be monomeric in solid state. The electronic spectra of the complexes taken in chloroform displayed four bands in the region 650 – 340 nm.

The band around 630-650 nm was assigned to the transition d – d.

The two bands in regions 490 – 555 nm and 430 – 500 nm could be assigned to the transitions M– L and L – M respectively [6,9].

The band in the region 340 – 430 nm to the transition L-L. these data are in good agreement with Cox [ 9 ] and Groy [ 10 ] and the electronic spectra corresponds to square – planar geometry. Infrared spectra of the prepared complexes showed two distinct bands over 1480cm<sup>-1</sup>. The band of higher frequency at 1600-1565 cm<sup>-1</sup> has been assigned to C=O vibration, while the band of lower frequency at 1510-1480 cm<sup>-1</sup> was due to C=C vibration of phenyl ring.

The C=S vibration was observed in the region 1250-1230 cm<sup>-1</sup> [ 5 ] .

The nickel – oxygen and nickel – sulphur frequencies could be noted at 485-435 and 335-295 cm<sup>-1</sup> regions respectively. The analytical data (Table2) and the electronic, Infrared spectra for these complexes have been already reported by many investigators[5,6,9].

**Equilibrium Constants :**

The nickel (II) complexes under study basically prefer a square- planar structure, when solutions of these complexes are treated with Lewis bases such as pyridine ( py ) , the solutions turn yellow and the complexes tend to become pyramidal structure.

The description of this system is given by eq. (1)

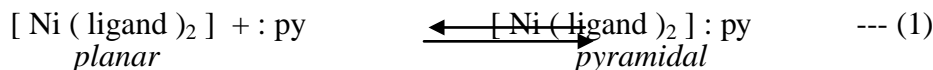
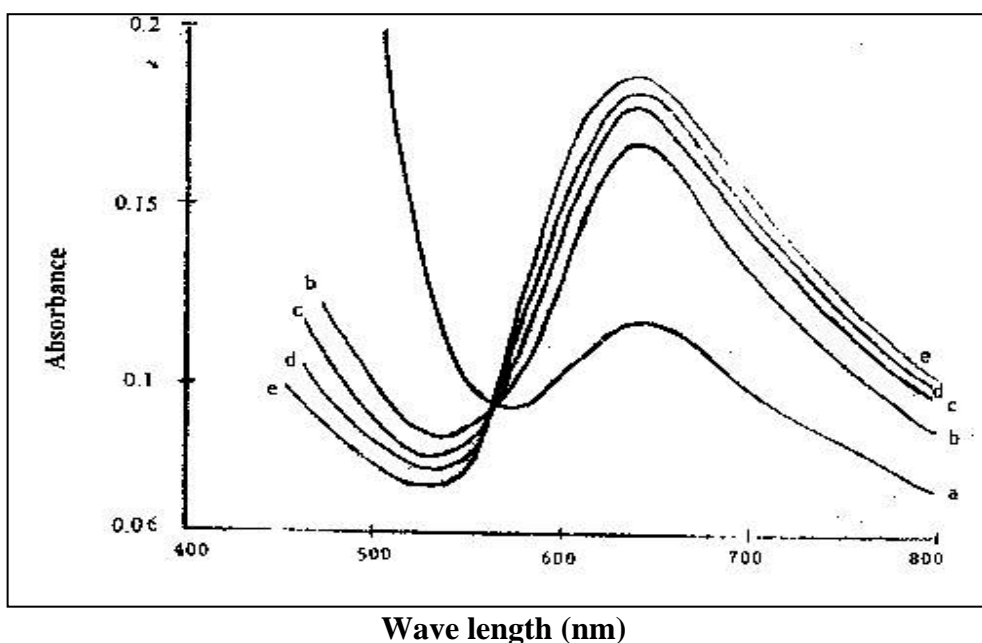


Figure (1) shows electronic spectra of free acceptor Ni ( Me . Me ) and those obtained by adding increasingly concentrations of pyridine. The isosbestic point in this figure is a strongest evidence on adduct formation, and it indicates that the reaction is from type 1 : 1 interaction , and this also appears in the other reactions.



**Figure (1) : electronic spectra of acceptor Ni ( Me . Me ) (a) with increasingly concentrations of pyridine (b) 0.15 (c) 0.225 (d) 0.3 (e) 0.375 M in chloroform.**

The equilibrium constants  $k_{eq}$  were determined by visible technique in various solvents at 298k using Denesi-Hildebrand equation eq. (2) [ 8 ]

$$[C] \ell / A - A_0 = 1/k (\epsilon_c - \epsilon_0) \cdot 1/[D] + 1/\epsilon_c - \epsilon_0 \quad \text{-- (2)}$$

Where [C] , [ D ] = concentrations of the acceptor and donor respectively ;  $\ell$  = cell path length ;  $A_0$  , A = absorbance of the acceptor and adduct respectively ; k = equilibrium constant and,  $\epsilon_0$  ,  $\epsilon_c$  = molar absorptivity of the acceptor and adduct respectively.

Hence a plot of the left – hand side of the eq.2 versus  $1/[D]$  should yield a straight line, from the slope and intercept of which  $k_{eq}$  can be calculated. Figure (2) and (3) show the plots suggested by eq.2 for reaction of some complexes with pyridine, while Table (3) given the results obtained for  $k_{eq}$ .

The  $k_{eq}$  obtained for adduct formation of the complex Ni ( Me . Me ) is smaller (  $k= 10.99 \text{ L.Mol}^{-1}$  ) in chloroform than the complex Ni ( ph . ph ) (  $k = 15.25 \text{ L.mol}^{-1}$  ).

This behaviour is due to the replacement that of phenyl groups in place of methyl groups since this causes increasing electronic deficiency on the metal ion. Also substitutions in phenyl group have a distinct effect on the value of  $k_{eq}$  as to be expected, an electron – withdrawing group (Br) increases the Lewis acidity of metal ion consequently increases value

of  $k_{eq}$  and vice versa. Solvent effect on the interaction showed that the  $k_{eq}$  increased in the direction of dichloroethane chloroform-methanol. This is due to the increasing polarity of the using solvent which probably decreases the Lewis acidity of metal ion and it could be because of interaction between the donor and solvent. This behaviour is in agreement with reported results in the literaries [ 2 ] .

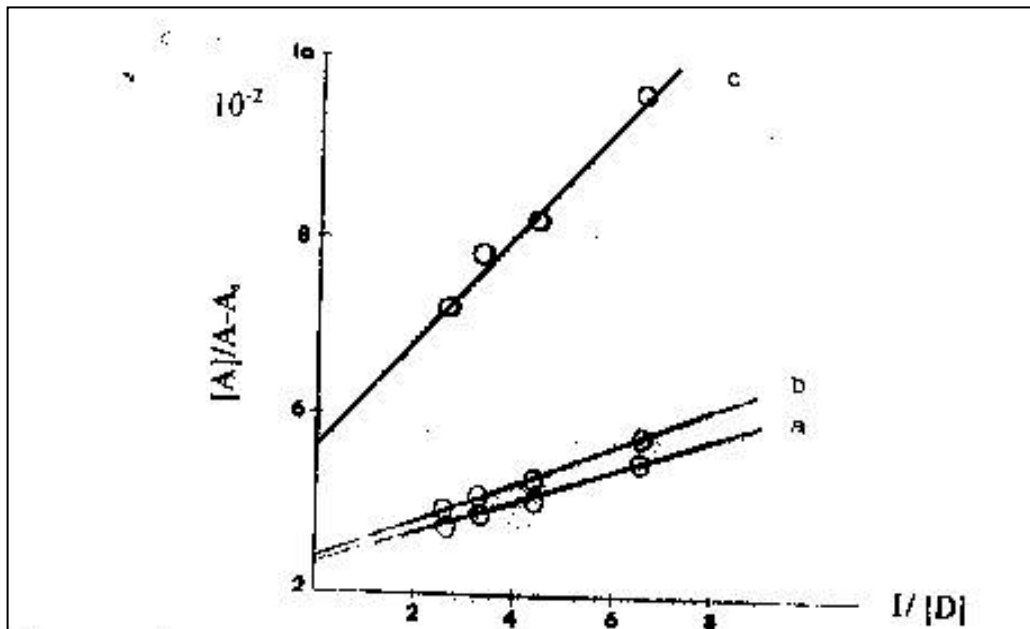


Figure (2) : Plot of equation (2) for interaction Ni ( Me . phCH ) with pyridine (a) dichloroethano (b) chloroform (c) methanol at 298k.

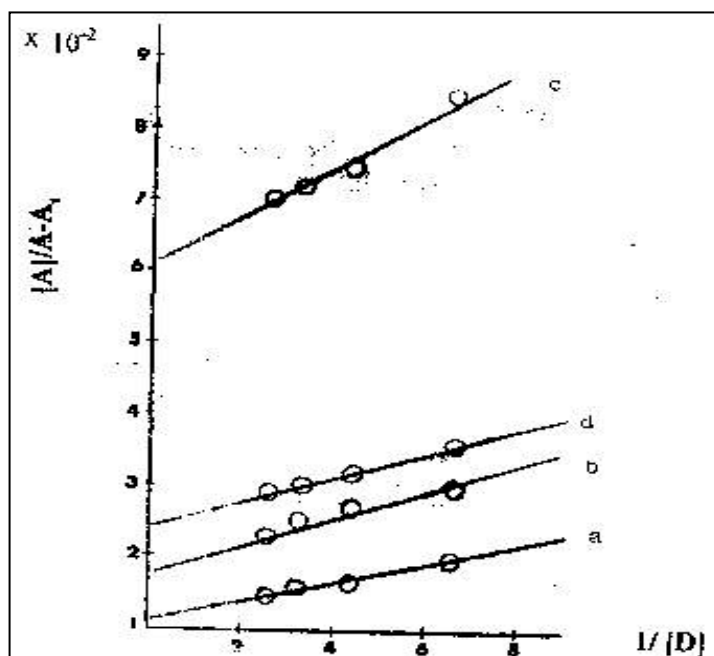


Figure (3) : Plot of equation (2) interaction (a) Ni ( Me . Me ) (b) Ni ( Me . Ph ) (c) Ni ( ph . ph ) (d) Ni ( Me . phBr ) with pyridine in chloroform at 298k.

**Table (3) : Equilibrium constants for the interaction nickel complexes with pyridine in different solvents at 298k.**

Acceptor	Wave length (nm)	$K_{eq} (L.mol^{-1})$ in		
		Dichloroethane	Chloroform	Methanol
Ni (Me.Me)	640	13.14	10.99	9.25
Ni (Me.ph)	645	15.13	11.59	10.75
Ni (ph.ph)	650	18.0	15.25	14.45
Ni (Me.phCH)	635	13.74	10.50	7.33
Ni (Me.phBr)	655	16.75	14.49	11.89

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دراسة طيفية للتداخل بين بعض معقدات نيكل ( II ) بيتا ثايوكسوكيتون مع البريديين .

ضياء كريم مسلم الطائي

الكلية التربوية المفتوحة - العراق .

**خلاصة شديداحت :**

لمعقدات النيكل من نوع  $Ni (RCSCHCOR)$  والتي فيها  $R=CH_3, Ph$  ;  $R= C_6H_4Br(P), C_6H_4CH_3(P), Ph, CH_3$  تم دراسة تداخل حامض - قاعدة لويس لهذه المعقدات كمتقبلات الكترونية مع البريديين كواهب الكتروني وقد وجد ان جميع التداخلات من نوع 1:1 .  
 وتم حساب ثوابت الاتزان لهذه التداخلات وبيان تأثير المذيبات المختلفة كالميثانول والكلوروفورم والثنائي كلوروميثان وكذلك تركيب المعقد عليها باستخدام طريقة طيفية في المنطقة المرئية ، ووجد ان القيم ضمن المدى 33ر7 - 0ر18 لتر / مول .

