

# Synthesis, Spectral and Dissociation Thermodynamics Studies of Cobalt (II), Nickel (II) and Copper (II) Complexes with 2-Hydroxyacetophenone Derivatives

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## Abstract

The ketone 2-hydroxyacetophenone was treated with ammonia gas and hydroxylamine hydrochloride for the synthesis of its Schiff base and oxime respectively. The two ligands were used to synthesize Co(II), Ni(II) and Cu(II) complexes. The ligands and complexes have been characterized by IR and UV spectroscopy. Elemental analyses have been performed using C, H, N for ligands and atomic absorption technique for complexes. The limiting molar conductivity of  $[M(\text{HANH})_2]$  and  $[M(\text{HAO})_2]$  complexes in DMF and DMSO at different temperature was measured. The dissociation constant, thermodynamic parameters of dissociation ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) and the activation energy of the transport process ( $E_a$ ) were calculated and discussed. The results show that the dissociation constant values in DMF are larger than that in DMSO. The dissociation process is endothermic for all complexes.

## Introduction

Schiff bases are an important class of ligand in coordination chemistry and find extensive application in different fields [1, 2]. 2-hydroxyacetophenone Schiff bases are Nitrogen and Oxygen donor atoms which potentiate the formation of polydentate ligands [1, 3]. The coordination of these donors ligands with the transition ions give complexes of different geometries and these complexes are widely application in enzymatic reaction [3], catalysis of chemical and the petrochemical industries [4, 5], probing DNA structures [6], biological activities including anti bacterial, anti fungal and anti Cancer [7-9].

Copper complexes are known to have a broad spectrum of biological action. The chemistry of nickel Schiff base complexes has obtained a significant place in bioinorganic chemistry and redox enzyme system [8].

Oximes are versatile ligands [10-11] to form metal complexes with interesting structures.

Transition metal complexes of 2-hydroxyaromatic oximes have attracted much attention as they give cis and trans geometrical isomers. Nickel complexes are known to assume trans structure while cobalt complexes have cis structure [12-13]. The complexation of transition metals as an electron acceptor

with various electron donor bases including (Schiff bases or Oximes) as an acceptor to form charge-transfer complexes have been extensively studied [14]. This complexes show interesting physical properties such as electrical conductance [5, 15].

However, so far there have been no reports about the determination of the dissociation constant, the thermodynamics parameters of dissociation ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) and the activation energy of the transport process ( $E_a$ ) by the limiting molar conductivity of 2-hydroxyacetophenone derivatives complexes.

The present work aims to synthesis, characterization and study the behavior dissociation of  $[M(\text{HANH})_2]$  and  $[M(\text{HAO})_2]$  ( $M = \text{Co}^{+2}$ ,  $\text{Ni}^{+2}$  and  $\text{Cu}^{+2}$ ) complexes in DMF and DMSO solvents at different temperatures using the conductometric technique.

## Experimental

### Ligands:

The ligands were prepared as follows:

HANH (2-hydroxyacetophenone imine); Passed ammonia gas through (0.05) mole (6)ml of EtOH solution 2-hydroxyacetophenone, the mixture was then under glass bath. Yellow needle-like crystals of ligand were recrystallized from EtOH, filtered and dried.

HAO (2-hydroxyacetophenone oxime); A hot EtOH solution of hydroxylamine hydrochloride (0.05) mole (3.47) gm was added to a hot EtOH of the 2-hydroxyacetophenone (0.05) mole (6) ml, added (0.05) mole (2.8) gm EtOH solution of KOH with shaking. The mixture was then boiled under reflux for (15) min. After that the product is cooled and poured to the aqueous solution of  $\text{CH}_3\text{COOH}$  (0.2) Molar. Filtered the precipitate and washed with cold water. The ligand were recrystallized from EtOH, filtered and dried [16].

#### **Metal (II) complexes:**

The metal complexes were prepared by mixing a hot EtOH solution of each ligand (0.02) mole with an aqueous EtOH solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  or  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.01) mole with magnetic stirring. The resulting precipitate was recovered by filtration, washed several time with a hot EtOH and distilled water and dried.

#### **Physical measurements:**

A CECIL model CE7200 spectrophotometer was used to obtain the electronic spectra.

IR spectra in the  $(4000 - 400) \text{ cm}^{-1}$  region were recorded by KBr disk using a SHIMADZU IR prestige-21 FT-IR spectrometer in Ibn-Sina company.

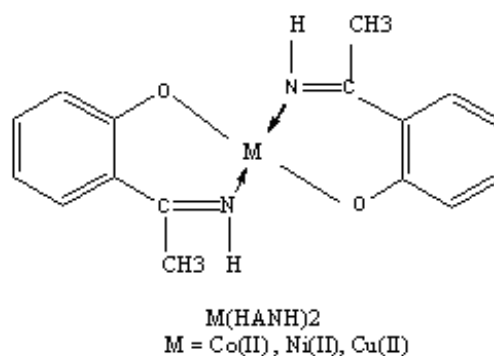
The Element Analysis of the C. H. N. in the ligands was determined by Perkin Elmer Model 2400 in Micro Analytical Center/Cairo University.

The amount of metal in the complexes was determined by SHIMADZU AA-680 atomic absorption/flame emission spectrophotometer in Ibn-Sina company.

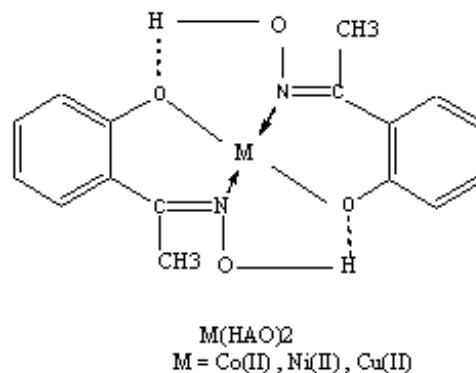
Conductivities were measured in DMF and DMSO solvents using PHILIPS PW9526 digital conductivity meter with a cell constant of  $0.829 \text{ cm}^{-1}$ . Various concentration  $(10^{-3} - 10^{-4})$  molar was measured at 298.15 K, 303.15 K and 308.15K.

## **Result and Discussion**

All the metal chelates are colored, solid and stable towards air moisture. They decompose at high temperature  $(238-310) ^\circ\text{C}$  and they are less soluble in methanol, ethanol and chloroform as solvents but soluble in DMF and DMSO. The suggested structural formulae for complexes study are presented in Figs. (1) and (2) and the characteristics of the complexes and their ligands are recorded in Table (1).



**Fig.(1) Suggested structural formulae of the  $\text{M}(\text{HANH})_2$  complexes.**



**Fig.(2) Suggested structural formulae of the  $\text{M}(\text{HAO})_2$  complexes.**

**Table (1)**  
**The Characteristics and Analyses of the ligands and their complexes.**

Compound	Physical properties	Melting point (°C)	Yield %	M.Wt gm/mole	C% Found (Calc.)	H % Found (Calc.)	N % Found (Calc.)	Metal% Found (Calc.)
HANH	Yellow crystals	193	61	135	71.74 (71.11)	6.91 (6.66)	10.58 (10.37)	—
HAO	White crystals	151	68	151	63.34 (63.57)	6.23 (5.96)	8.86 (9.27)	—
Co(HANH) <sub>2</sub>	Brown powder	280 Dec.	77	328.93	—	—	—	17.65 (17.92)
Ni(HANH) <sub>2</sub>	Brown powder	305 Dec.	72	328.71	—	—	—	18.16 (17.86)
Cu(HANH) <sub>2</sub>	Green powder	238 Dec.	81	333.54	—	—	—	19.42 (19.05)
Co(HAO) <sub>2</sub>	Brown powder	268 Dec.	75	360.93	—	—	—	17.11 (16.33)
Ni(HAO) <sub>2</sub>	Green powder	310 Dec.	83	360.71	—	—	—	16.83 (16.28)
Cu(HAO) <sub>2</sub>	Green powder	296 Dec.	70	365.54	—	—	—	16.97 (17.38)

All the metal chelates have 1:2 (metal: ligand) stoichiometry from the atomic absorption analysis.

#### **Electronic spectra:**

The electronic spectral data of ligands and complexes are presented in Table (2).

**Table (2)**  
**The UV-Visible spectra data of ligands and their complexes  $1 \times 10^{-3} M$  in DMF.**

Compound	$\lambda_{max}$ (I) nm	$I_{max}$ (II) nm	$\lambda_{max}$ (III) nm
HANH	271	319	402
HAO	273	308	—
Co(HANH) <sub>2</sub>	312	375	—
Ni(HANH) <sub>2</sub>	281	327	—
Cu(HANH) <sub>2</sub>	280	329	—
Co(HAO) <sub>2</sub>	329	378	—
Ni(HAO) <sub>2</sub>	321	380	—
Cu(HAO) <sub>2</sub>	289	337	—

In the HANH ligand, the absorption band (I) at (271) nm is attributed to  $\pi \rightarrow \pi^*$  transition

in benzene ring. But the second one (II) at (319) nm suggesting the presence of  $\pi \rightarrow \pi^*$  transition charge transfer between the phenyl ring as a donor group and (C = N) as an acceptor group. While the lowest energy band (III) at (402) nm is attributed to  $\pi \rightarrow \pi^*$  transition in chelating ring [17]. In the HAO ligand, the band (I) appearing in the (273) nm is attributed to benzene  $\pi \rightarrow \pi^*$  transition. Band (II) at lower energy (308) nm is assigned to the azomethine (C = N) chromophore  $\pi \rightarrow \pi^*$  transition.

In the complexes the azomethine  $\pi \rightarrow \pi^*$  transition is shifted to high wave number indicating that the imino nitrogen is involved in coordination to the metal ion [7].

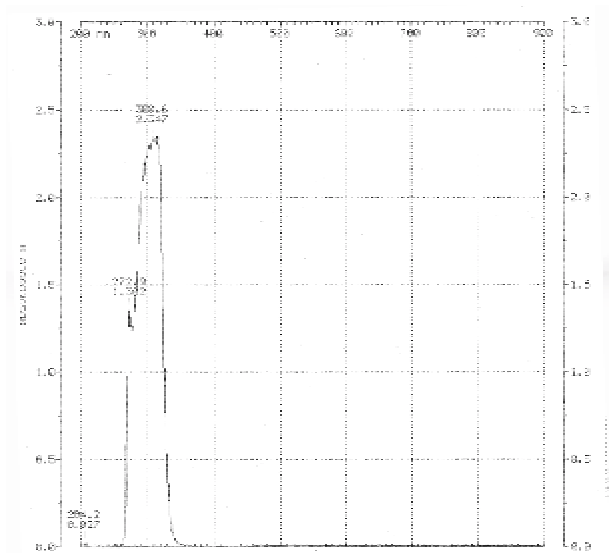


Fig.(3) Electronic absorption spectra of HAO ligand in DMF.

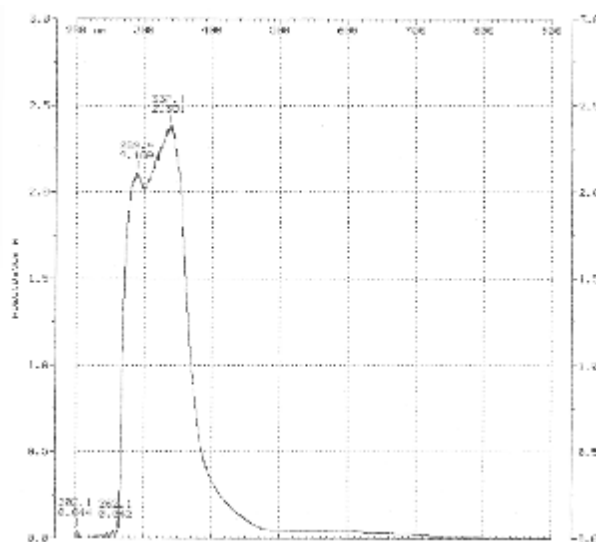


Fig.(4) Electronic absorption spectra of Cu(HAO)<sub>2</sub> complex in DMF.

#### Infrared spectra:

The IR spectra of the ligand and their metal complexes are summarized in Table (3).

Table (3)  
The IR spectra data of ligands and their complexes.

Compound	O-H str. Oxime or N-H str. imine	C = N str.	C=C str. N=H ben.	O-H ben.	C=H ben.
HANH	3400-3200	1612	1523 1473	1334 1288 1249	748 630
HAO	3100-3000	1635	1589 1504 1435	1200 1257	779 748 651
Co(HANH) <sub>2</sub>	3217	1597	1531 1435	1334 1265 1215	748 682
Ni(HANH) <sub>2</sub>	3221	1604	1535 1470 1438	1338 1276 1219	748 675 628
Cu(HANH) <sub>2</sub>	3200	1581	1527 1455 1435	1369 1333 1230	756 725 702
Co(HAO) <sub>2</sub>	2970	1604	1523 1504 1478	1330 1264 1253	770 744 717
Ni(HAO) <sub>2</sub>	3024	1597	1554 1485 1442	1373 1327 1249	790 748 705
Cu(HAO) <sub>2</sub>	3155	1597	1550 1479 1438	1369 1330 1238	779 744 690

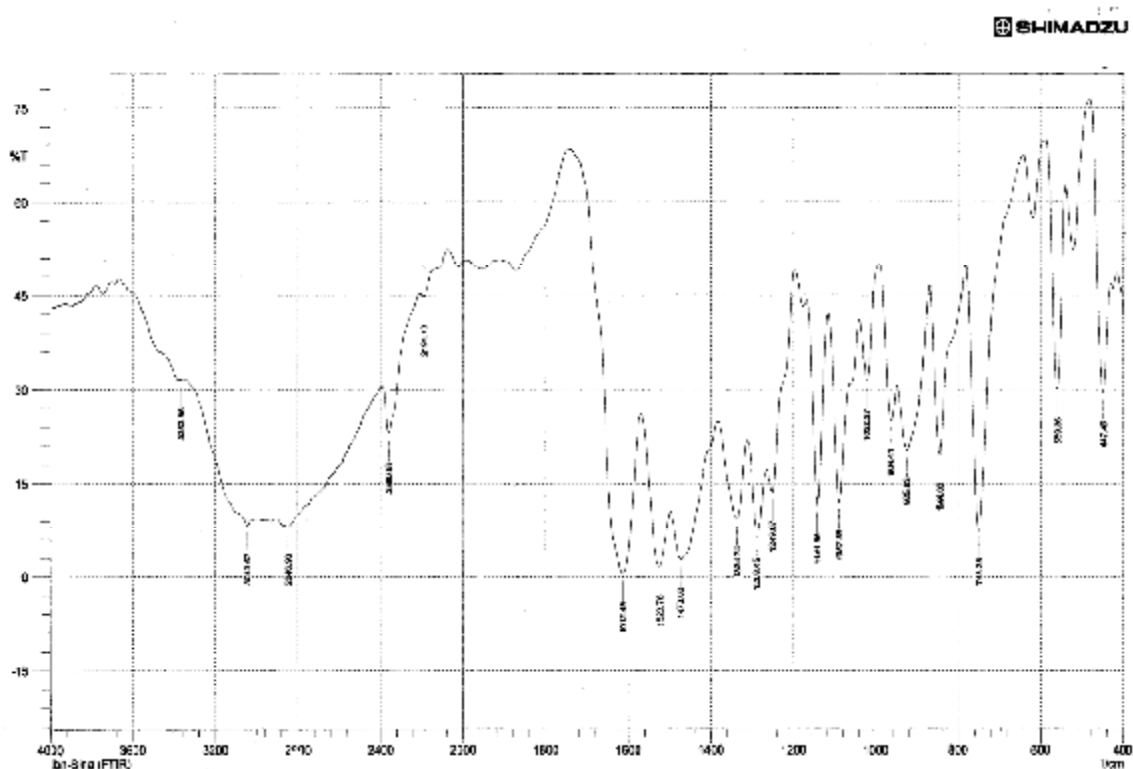
A very broad interaction band at (3400-3200)  $\text{cm}^{-1}$  in ligand HANH is assigned to the phenolic (O-H) and (N-H) stretching vibration, respectively which strongly hydrogen bonded. The disappearance of phenolic (OH) band in the spectra of complexes due to the coordination of phenolic oxygen atom to metal [1, 15]. While the (N-H) band shifted to higher frequencies in metal complexes, indicating coordination of the metal ions imino nitrogen [5, 7].

In the absence of any electron withdrawing group, the  $\nu$  C=O frequencies of free 2-hydroxyacetophenone have been reported at 1650  $\text{cm}^{-1}$  [18]. The ligand NANH band at (1612)  $\text{cm}^{-1}$  is assigned to combination of  $\nu$  (C=N) vibration. In the complexes the band shift to lower frequency by (8-31)  $\text{cm}^{-1}$ , indicating involvement of nitrogen of the azomethine group [5, 7, 14]. The spectra of this ligand show another

absorptions at the range (3043-2360)  $\text{cm}^{-1}$  due to aromatic and aliphatic (C-H) stretching [19].

A broad band in the IR spectra of free ligand HAO observed in the (3400-3200)  $\text{cm}^{-1}$  region is assigned to phenolic (OH). This band is absent in the spectra of metal complexes suggesting the coordination of phenolic oxygen atom to metal. A broad and nearly flat band present in the region (3150- 2900)  $\text{cm}^{-1}$  is assigned to OH group of the  $>\text{C}=\text{N}-\text{OH}$  chromophore involved in strong hydrogen bonding. This band is not effected in the IR spectra of metal complexes indicating no involvement of oxime OH in chelation [10,12].

The  $\nu$  C=N observed at (1635)  $\text{cm}^{-1}$  in ligand is shifted to lower frequency in complexes. This downward shift of C=N stretching band in complexes indicates that the oxime group binds the metal through nitrogen atom.



*Fig.(5) The IR spectra of HANH ligand.*

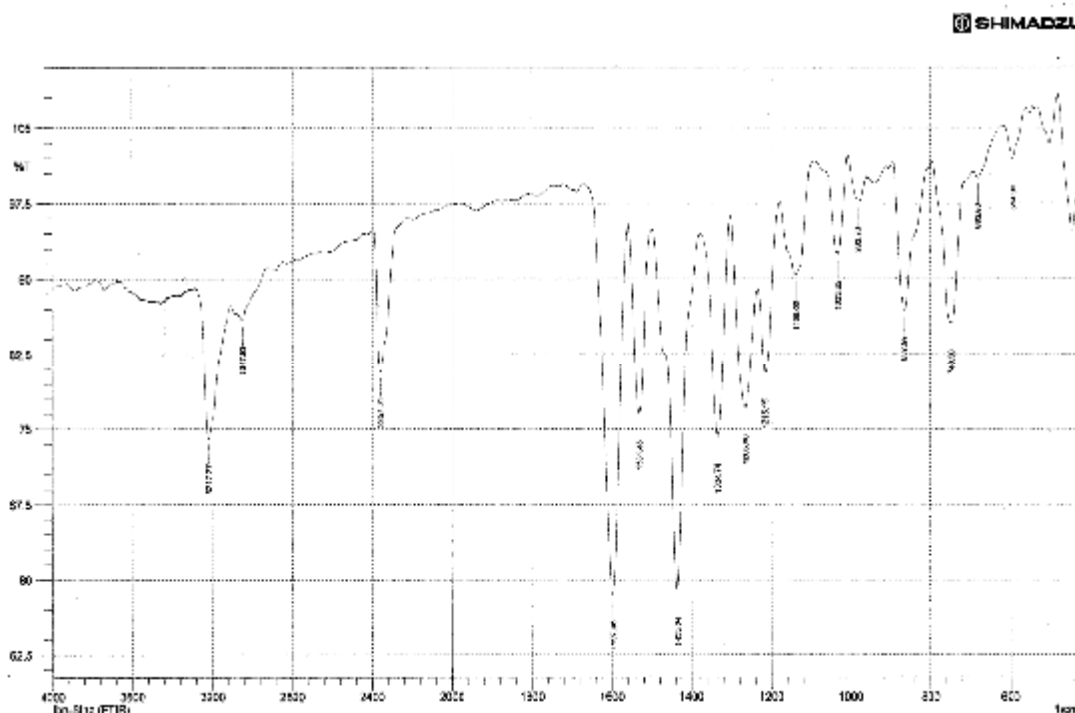


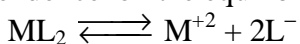
Fig.(6) The IR spectra of [Co (HANH)<sub>2</sub> ] complex.

**Thermodynamics study:**

The specific conductivities ( $\sigma$ ) of the complexes under investigation in DMF and DMSO were measured at 298.15 K, 303.15 K and 308.15 K to various concentration ( $10^{-3}$ - $10^{-4}$ ) molar. The molar conductivities ( $\Lambda$ ) were calculated using the relation (1) [20]:

$$\Lambda = 1000 \times \sigma / C \dots\dots\dots(1)$$

The dissociation of complexes dependence on the equilibrium (metal-ligand):



$$C(1-\alpha) \quad \alpha C \quad 2\alpha C$$

The dissociation constant ( $K_D$ ) of complexes have been evaluated using the following equations [21]:

$$K_D = [M^{+2}] [L^{-}]^2 / [ML_2]$$

and

$$K_D = \alpha C (2\alpha C)^2 / C(1-\alpha) \rightarrow K_D = 4\alpha^3 C^2 / 1-\alpha \rightarrow \{K_D - \alpha K_D = 4\alpha^3 C^2\} \div (\alpha) \rightarrow K_D / \alpha - K_D = 4\alpha^2 C^2$$

when ( $\alpha = \Lambda / \Lambda_0$ )

$$\{\Lambda_0 K_D / \Lambda - K_D = 4\Lambda^2 C^2 / \Lambda_0^2\} \times (\Lambda_0^2 / 4) \rightarrow \Lambda_0^3 K_D / 4\Lambda - \Lambda_0^2 K_D / 4 = \Lambda^2 C^2 \rightarrow \Lambda^2 C^2 = \Lambda_0^3 K_D / 4\Lambda - \Lambda_0^2 K_D / 4 \dots\dots\dots(2)$$

A set of parameters ( $\Lambda_0$ ) and ( $K_D$ ) were derived from the intercept and the slope of the straight line on the plot of  $\Lambda^2 C^2$  versus  $1 / \Lambda$ .

The values of the measured limiting molar conductance  $\Lambda_0$  and the dissociation constant  $K_D$  of the studied complexes at different temperature are given in Table (4).

**Table (4)**

**The limiting molar conductivity  $\Lambda_0 / (S \text{ cm}^2 \text{ mol}^{-1})$  and the dissociation constant  $K_D / (\text{mol dm}^{-3})$  of the complexes at different temperatures.**

Complex ®		Cu(HANH) <sub>2</sub>		Ni(HANH) <sub>2</sub>		Co(HANH) <sub>2</sub>		Cu(HAO) <sub>2</sub>		Ni(HAO) <sub>2</sub>		Co(HAO) <sub>2</sub>	
T/K	Solvent	K <sub>D</sub>	Λ <sub>0</sub>	K <sub>D</sub>	Λ <sub>0</sub>	K <sub>D</sub>	Λ <sub>0</sub>	K <sub>D</sub>	Λ <sub>0</sub>	K <sub>D</sub>	Λ <sub>0</sub>	K <sub>D</sub>	Λ <sub>0</sub>
298.15	DMSO	8	6.05×10 <sup>-6</sup>	8.5	4.31×10 <sup>-6</sup>	8.8	3.75×10 <sup>-6</sup>	10.3	5.38×10 <sup>-6</sup>	13.3	6.75×10 <sup>-6</sup>	13.7	6.46×10 <sup>-6</sup>
	DMF	8.75	20.9×10 <sup>-6</sup>	12.25	10.7×10 <sup>-6</sup>	13.6	6.4×10 <sup>-6</sup>	13.9	17.2×10 <sup>-6</sup>	14.8	10.9×10 <sup>-6</sup>	16.4	7.75×10 <sup>-6</sup>
303.15	DMSO	11	6.13×10 <sup>-6</sup>	12	5.56×10 <sup>-6</sup>	13	5.84×10 <sup>-6</sup>	14	7.47×10 <sup>-6</sup>	14.8	8.15×10 <sup>-6</sup>	15.5	8.51×10 <sup>-6</sup>
	DMF	11.5	36.4×10 <sup>-6</sup>	12.5	20.5×10 <sup>-6</sup>	14	12.2×10 <sup>-6</sup>	15.6	19.8×10 <sup>-6</sup>	16.1	14.7×10 <sup>-6</sup>	18.1	8.66×10 <sup>-6</sup>
308.15	DMSO	14	8.16×10 <sup>-6</sup>	15.7	6.45×10 <sup>-6</sup>	16.7	6.13×10 <sup>-6</sup>	17.4	9.61×10 <sup>-6</sup>	18.5	9.13×10 <sup>-6</sup>	21.5	9.52×10 <sup>-6</sup>
	DMF	14.2	45.8×10 <sup>-6</sup>	17	23.4×10 <sup>-6</sup>	17.5	13.4×10 <sup>-6</sup>	18	11.1×10 <sup>-6</sup>	19.7	16.9×10 <sup>-6</sup>	21.6	9.81×10 <sup>-6</sup>

The data show that the dissociation constant  $K_D$  of all complexes in the DMF solvent is greater than that of the DMSO solvent. This may suggest that the solvation process of the complexes increased in DMF solvent than in DMSO solvent. Furthermore, the results demonstrate that the dissociation constant of complexes increased with raising the temperatures, as a result of increases in dissociation process.

The complexes of oxime  $[M(\text{HAO})_2]$  have been the higher limiting molar conductance  $\Lambda_0$  in comparison with the complexes of Schiff base  $[M(\text{HANH})_2]$ , that attributed to present the O–H group involved in strong hydrogen bonding in the first one. Fig.(7 and 8).

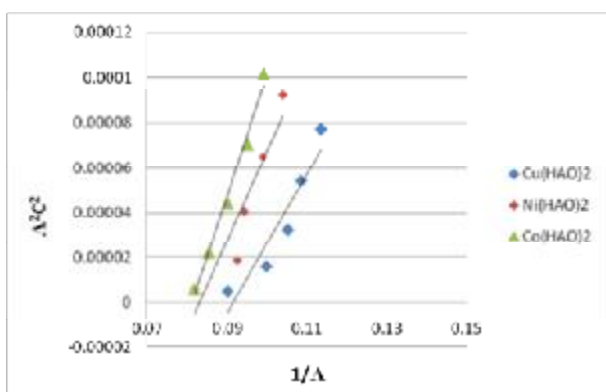


Fig.(7) The  $\Lambda^2C^2$  vs.  $1/\Lambda$  of  $M(\text{HAO})_2$  in DMSO at 298.15K.

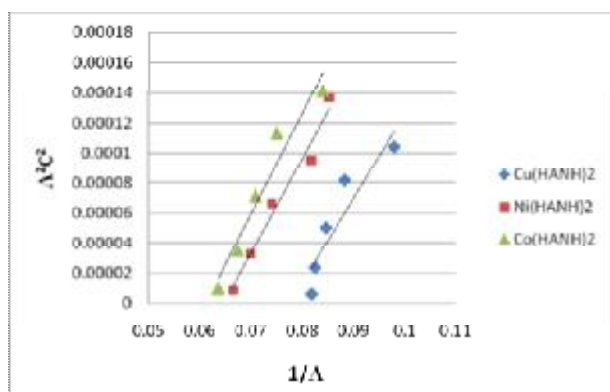


Fig.(8) The  $\Lambda^2C^2$  vs.  $1/\Lambda$  of  $M(\text{HANH})_2$  in DMSO at 308.15K.

The Gibbs energies of dissociation were calculated using the following equation [22]:

$$\Delta G = -RT \ln K_D \dots\dots\dots (3)$$

The enthalpy change  $\Delta H$  of the dissociation process was calculated from the plot of the  $\ln K_D$  versus  $1/T$  [23]. Using the values of  $\Delta H$  and  $\Delta G$ , the value of entropy

change ( $\Delta S$ ) can be found from the relation [20]:

$$\Delta G = \Delta H - T \Delta S \dots\dots\dots (4)$$

Since the conductance of an ion depends mainly on its mobility, it is quite reasonable to treat the rate process taking place with change of temperature on the basis of the Arrhenius equation [21, 24]:

$$\Lambda_0 = A e^{-E_a/RT} \dots\dots\dots (5)$$

where  $A$  is the frequency factor,  $R$  is the gas constant and  $E_a$  is the activation energy of the transfer process. Consequently, from the plot of  $\ln \Lambda_0$  versus  $1/T$ , the  $E_a$  values can be evaluated.

The effect of temperature can be noted from the decreasing in the values of dissociation free energies (decreases the stability of ions species complexes) as the temperature is raised for most complexes except in DMSO solvent (for  $\text{Ni}(\text{HAO})_2$ ) and in DMF solvent (for  $\text{Cu}(\text{HAO})_2$  and  $\text{Co}(\text{HAO})_2$ ). This means that the dissociation process has an endothermic behavior for all complexes in the used solvents. This may be due to the stronger solvent-solvent interaction and weaker ion-solvent interaction for all used complexes [23]. Fig. (9).

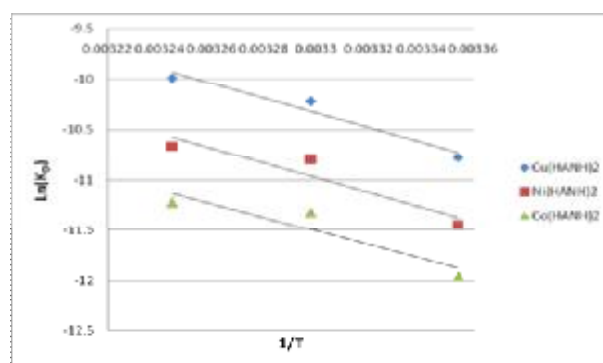


Fig.(9) The enthalpy of  $M(\text{HANH})_2$  in DMF.

The entropy increasing after the dissociation, but some complexes that studies have been negative values. Suggesting these complexes molecules takes different geometries isomers [7, 13]. After dissociation this possibilities are decrease for ions species in solution.

In studying the effect of the solvent on the activation energy of the transport process, it was found that all the values of the activation energy which obtained in DMF solvent is less

than its in DMSO solvent, suggesting a higher solvation and dissociation process in DMF solvent comparison with this in DMSO solvent (Tabs (4, 6)). It is clear that as the ion-solvent interaction increases, the complex molecules require lower activation energy for the transport process [25]. Since a reaction (or step) which requires higher  $E_a$ , is slow at ordinary temperatures, the higher  $E_a$  values indicate lower mobilities of the ions in the solutions and hence lower  $\Lambda_0$  values. Fig.(10).

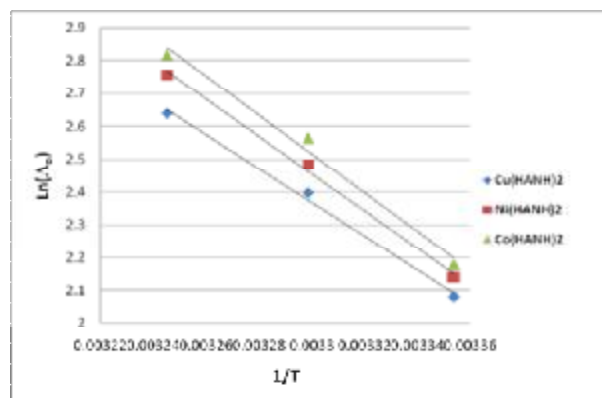


Fig.(10) The activation energy of  $M(HANH)_2$  in DMSO.

Table (5)  
Thermodynamic data of the complexes.

Complex <sup>®</sup>		$Cu(HANH)_2$		$Ni(HANH)_2$		$Co(HANH)_2$		$Cu(HAO)_2$		$Ni(HAO)_2$		$Co(HAO)_2$	
T/K	Solvent	DG	$\Delta S$	DG	$\Delta S$	$\Delta S$	DG	DG	$\Delta S$	DG	$\Delta S$	DG	$\Delta S$
298.15	DMSO	29784	-24.03	30624.75	0.627	30969.75	1.06	30075	47.65	29512.7	-21.57	29621.6	0.25
	DMF	26712.3	111.9	28380	107.1	29644.7	90.84	27194.1	19.09	28324.8	17.52	29170.3	-37.67
303.15	DMSO	30250.5	-25.17	30496.5	1.04	30372.6	24.3	29752	47.94	29532.6	-21.28	29379.7	1.05
	DMF	25760.75	113.2	27207.8	109.2	28515.9	93.06	27295.4	18.44	28046	18.15	29423.7	-37.9
308.15	DMSO	30016.6	-24.01	30619	0.625	30749.5	22.71	29597.5	47.66	29728.8	-21.57	29621.9	0.24
	DMF	25597.1	111.9	27317.6	107.1	28745.8	90.81	29228.3	11.86	28151.3	17.52	29544.8	-37.66

$\Delta G$  and  $\Delta S$  in  $K.Jmol^{-1}$ .

Table (6)  
The enthalpy and the transport activation energy of the complexes.

Complex <sup>®</sup>	$Cu(HANH)_2$		$Ni(HANH)_2$		$Co(HANH)_2$		$Cu(HAO)_2$		$Ni(HAO)_2$		$Co(HAO)_2$	
Solvent ↓	$\Delta H$	$E_a$	$\Delta H$	$E_a$	$\Delta H$	$E_a$	$\Delta H$	$E_a$	$DH$	$E_a$	$\Delta H$	$E_a$
DMSO	22619	42775	30811.7	47139	37747.2	48927	44284.5	49836	23080.5	24964	29696.8	34055
DMF	60082	37237	60313	24907	56729	18800	32886	21269	33549.5	16850	17937.4	21093

$\Delta H$  and  $E_a$  in  $K.Jmol^{-1}$ .

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#### الخلاصة

تمت معاملة 2-هيدروكسي اسيتوفينون مع غاز الأمونيا والهيدروكسيل أمين لتحضير قاعدة شف والأوكزاييم على التوالي. لقد استخدم الليكاندين لتحضير معقدات الكوبلت (II) و النيكل (II) والنحاس (II). شخصلت الليكاندات والمعقدات بمطيفية IR و UV، كما استخدمت تقنية التحليل العنصري الدقيق C,H,N والامتصاص الذري لليكاندات والمعقدات على التوالي. قيسلت التوصيلية المولارية المحددة لمعقدات  $[M(HANH)_2]$  و  $[M(HAO)_2]$  في مذبيي DMF و DMSO عند درجات حرارية مختلفة. تم حساب ثابت التفكك والدوال الثرموديناميكية للتفكك ( $\Delta S, \Delta H, \Delta G$ ) وطاقة التنشيط  $E_a$  لعمليات الأنتقال ثم نوقشت النتائج. لوحظ لجميع المعقدات قيم ثابت التفكك في الـ DMF اكبر من الـ DMSO. وعمليات التفكك ماصة للحرارة لجميع المعقدات.