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Spectrophotometric Investigation of Al (III) and Ga (III) Chalcone complexes based on 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one

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Abstract:

Metal complexes of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one with Al (III) and Ga (III) ions in 95% ethanolic solution have been prepared and studied . Ligand to metal ratio for the complexes has been investigated using the mole ratio method. The 3:1 complexes absorb light in the region 200-600 nm. Formation constant also have been determined using corresponding solution method.The spectrophotometric investigation of the metal complexes indicated that the detection limits were $0.97x10^{-6}$ M of Al (III) and $1.35x10^{-6}$ M of Ga (III) ions with linear calibration curves up to $3.0x10^{-4}$ M for both ions. No interferences were noticed with most transition metal under our experimental conditions.

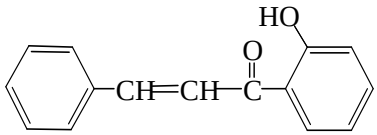
KeyWords: Spectrophotometric Determination of Aluminum and Gallium ions , α,β-unsaturated system , Aldol condensation , Mole Ratio Method , Corresponding solution method .

Introduction :

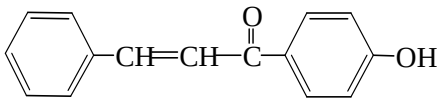
Aldol condensation represents an important class of carbon-carbon bond formation reaction both in nature and synthetic chemistry. Compounds called *chalcones* can be prepared by the aldol condensation of an aromatic ketone and an aldehyde. In a chalcone, two aromatic rings are joined by a 3-carbon α,β-unsaturated system [1, 2]. Several metal complexes of 2`,4`-dihydroxychalcone prepared and studied extensively [3]. Phenolic chalcone was prepared by phenolic aldehydes or ketones, many workers [4-6] have prepared and studied the phenolic chalcones during the past few years and they used this type of chalcone in different applications as biological, industrial and analytical applications. For example a series of chalcones derived from 5-methyl-2-hydroxyacetophenone with different substitutes ketones and aldehydes have been prepared and are found to be antibacterial and have an antifungal activity [7].The aim of the investigation to find specific reagent for Aluminum and Gallium ions and study the complexes formed.

Experimental:

Chalcone **I** and **II** (scheme 1) were prepared by mixing 45 ml of cold ethanol 95% , 25ml of aqueous sodium hydroxide 20% , 0.015 moles of benzaldehyde and 0.015 moles of para (ortho) hydroxyacetophenone. The mixture was stirred for 3 hours in a water bath at (0-5)^{o}C . The reaction mixture was diluted in water and precipitated in acetic acid and can optionally be recrystallised from EtOH : H_2O (1:1). The chalcone **I** and **II** were yellow to brown in color and were obtained in yields of up to 89% of both.



Chalcone I



Chalcone II

Scheme 1

The chalcone **I** and **II** were characterized by IR spectra recorded as KBr discs using Jasco spectrophotometer from Jasco Inc. in Baghdad University. Fig. (1) shows the infrared spectrum of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (Chalcone I) as an example, Table (1) shows most important characterized peaks in the IR spectrum of Chalcone (I).

The chalcone **I** and **II** also characterized by NMR spectra using Brucker (AC 250 MHz) in Germany. Fig. (2) shows the NMR spectra of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (Chalcone I) as an example, Table (2) shows most important characterized peaks in the NMR spectrum of Chalcone (I).All metal salts were as nitrates due to their good solubilities in 95% ethanolic solution. The UV.-Vis spectra of the prepared chalcones and their metal complexes were measured using HEλ105α spectrophotometer from Thermo Spectronic Inc. in Basrah University with a quartz cell of 1 cm path length.

Table (1): Most important characterized peaks in the IR chart of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (Calcone I) measured in cm^{-1}.

Peak	OH st.	C-O (Ar- H)	C=C Olifine or arom.	HC= Bend out of Plane	C=C Arom. st.	C=O
Position (cm^{-1})	3430-3620	1240	1605	845	1450, 1515	1660

Table (2): Most important characterized peaks in the NMR chart of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (Calcone I) by using (DMSO) as a solvent.

Peak	OH	Ar – H and CH=CH
Chemical Shift (ppm)	4.81	6.81 – 8.36

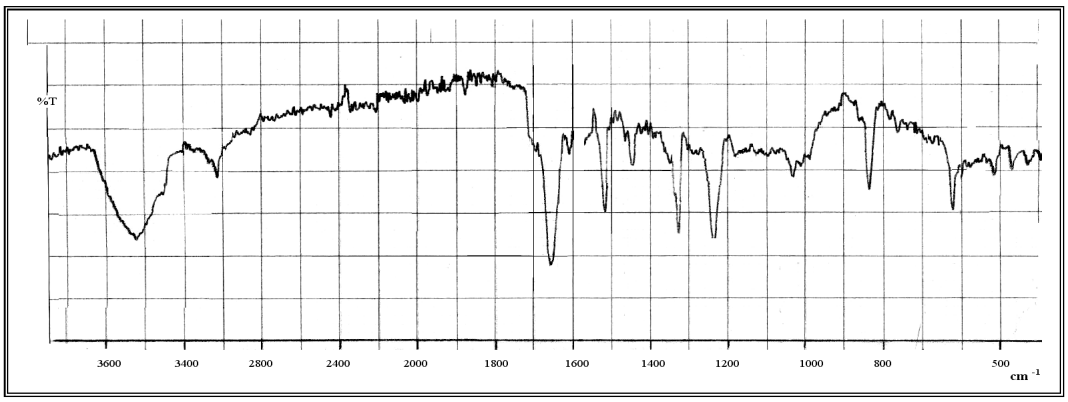


Fig.(1): The IR spectrum of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (Chalcone I).

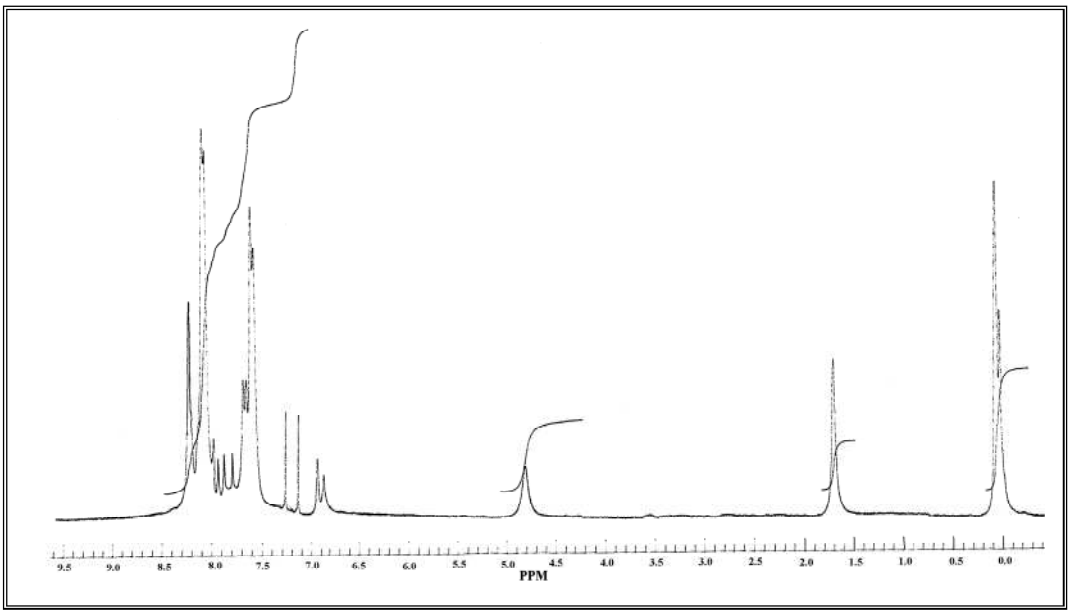


Fig. (2): The NMR spectrum of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (Chalcone I).

Results and Discussion:

Metal Complexes:

Spot test [8] was used for the formation of metal complexes of the prepared chalcones with divalent Pb , Cu , Zn , Mn , Co , Ni , Fe and Cd ; trivalent Cr , Fe , In and Ga ions.

Fe (III) ion gave colored complexes with the prepared chalcones, this could be attributed to the fact that all the prepared chalcones are of phenolic nature. Phenolic compounds usually give complexes with Fe (III) ions [9].The ions which gave colored complexes were Al (III) and Ga (III) ions with only chalcone **I** , thus this chalcone was used as ligand for the spectrophotometric investigation of both Al (III) and Ga (III) ions. Fig. (3,4 and 5) show the absorption spectra of chalcone **I** (used ligand) and its complexes with Al

(III) and Ga (III) ions at λ_{max} = 307, 434, 470nm respectively in 95% ethanolic solution.

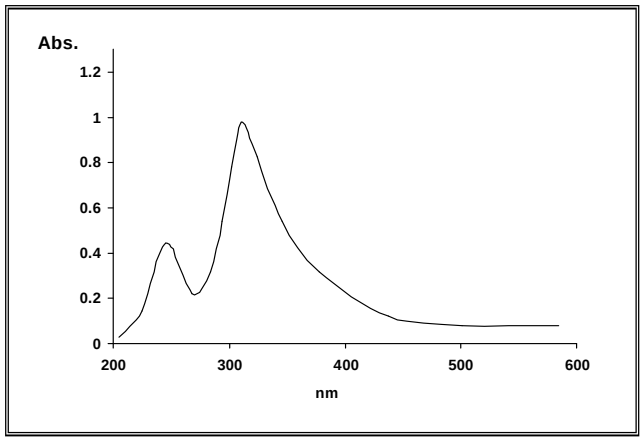


Fig. (3): Absorption spectrum of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (Ligand).

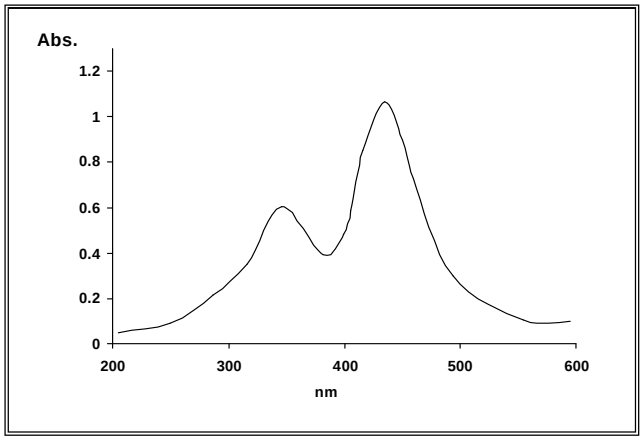


Fig. (4): Absorption spectrum of Al (III) complex.

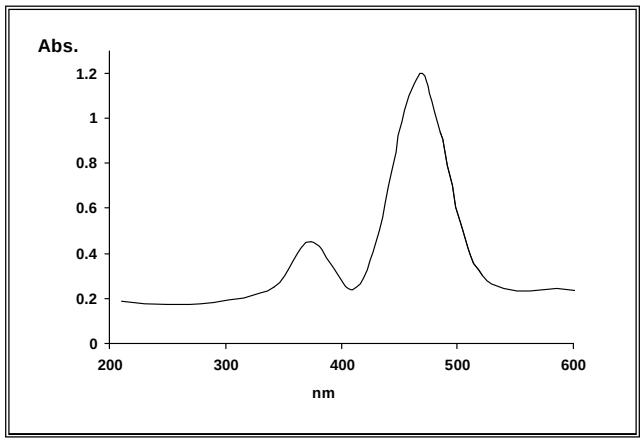


Fig. (5): Absorption spectrum of Ga (III) complex.

Mole Ratio Method :

In this method, series of solutions must be prepared including a constant concentration of metal ion and various concentrations of ligand or inverse [10,11]. A plot of the concentration ratio of chalcone **I** to Al (III) or Ga (III) was draw against the optical density of the formed complexes. Fig. (6 and 7) indicate that the concentrations of 3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one (chalcone **I**) with both Al (III) and Ga (III) ions are of the ratio 3:1 and they may be formed with the ratio 2:1 and 1:1 .

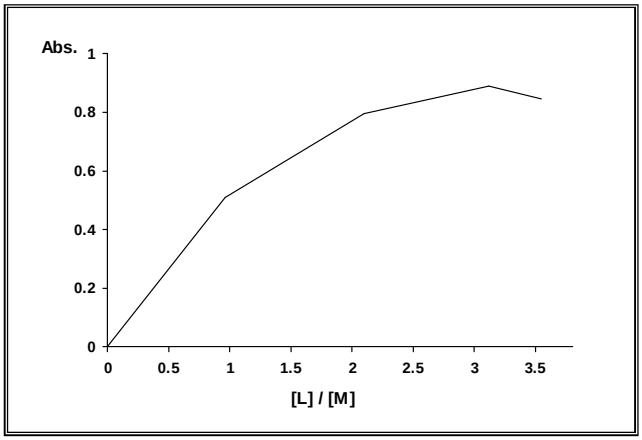


Fig. (6): Mole Ratio Method for Al (III) complex at (□max = 434.8 nm).

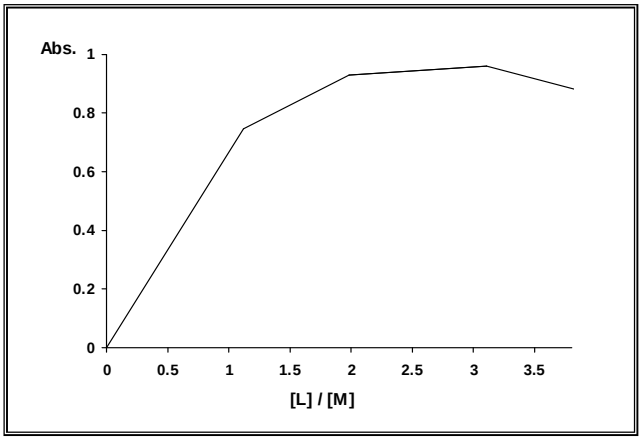


Fig. (7): Mole Ratio Method for Ga (III) complex at (λmax = 470.3 nm).

***Calibration Curves* :**

Calibration curves for both Al (III) and Ga (III) ions were linear in the range ($4.6x10^{-6}$ - $3x10^{-4}$) molar , detection limits were calculated by using the following equation [12,13] :

$$D.L = (2 \times S.D \times [M]) / \bar{x}$$

Where: D.L = Detection Limits ; S.D = Standard Deviation ; [M] = Metal Concentration ; x = Average value of absorbance.

The detection limits for Al (III) and Ga (III) ions were equal to ($1.35x10^{-6}$ and $0.97x10^{-6}$) molar respectively.

Formation Constants :

The initial and final formation constants of the complexes are calculated by using the following equations [14] :

At $\bar{n} = 0.5$, $pL = \log k_1$

At $\bar{n} = 1.5$, $pL = \log k_2$

At $\bar{n} = 2.5$, $pL = \log k_3$

$\log \beta_1 = \log k_1$

$\log \beta_2 = \log k_1 + \log k_2$

$\log \beta_3 = \log k_1 + \log k_2 + \log k_3$

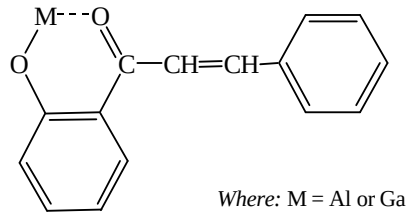
were: L = ligand Concentration , $\bar{n}$ = formation function (ratio of Ligand concentration to Metal concentration) , β_1 , β_2 , β_3 = formation constant of the first step , the second step and the overall formation constant respectively.

The formation curves were obtained by plotting the formation function values (n) vs. the negative logarithm of free ligand concentration (pL) , Fig. (8 and 9) .

From figures (8&9) have found Log β_1 , Log β_2 and Log β_3 these data are shown in Table (3).

Conclusion :

Chalcone **I**(3-phenyl-1-(2-hydroxyphenyl)-2-propene-1-one) gave complexes with Al (III) and Ga (III) ions as a colored solution whereas the other chalcone did not, this may be attributed to the presence of hydroxyl group in ortho position in chalcone I which lead us to expect formation of six-member ring formed by linking metal ion with carbonyl and hydroxyl groups, the suggested structure for the complex shown below:



Where: M = Al or Ga

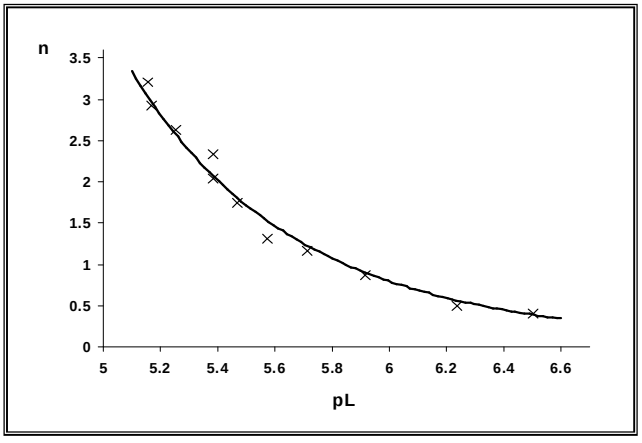


Fig. (8): Half value method for the calculation of formation constant of Al (III) complex.

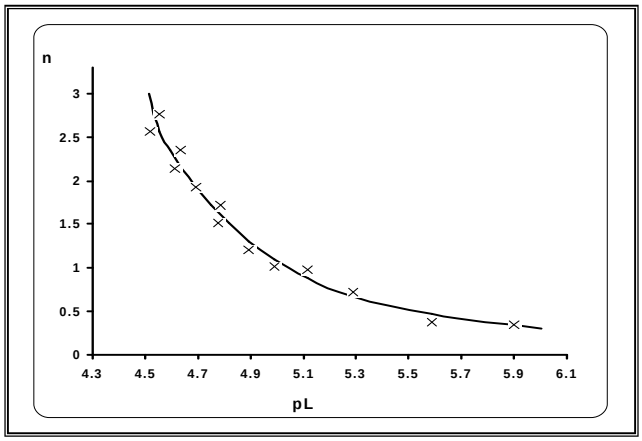


Fig. (9): Half value method for the calculation of formation constant of Ga (III) complex.

Table (3): Formation Constants of Al (III) and Ga (III) Complexes

Complex	$\overline{n}$	pL	Log β_1	Log β_2	Log β_3
Al (III)	0.5	6.31	6.31	-	-
	1.5	5.60	-	11.91	-
	2.5	5.28	-	-	17.19
Ga (III)	0.5	5.55	5.55	-	-
	1.5	4.81	-	10.36	-
	2.5	4.57	-	-	14.93

References:

1- L.D. Hicks, J.K. Han and A.J. Fry, ***J. Tetrahedron Lett.*** , **41**, 7817 (2000).

2- C. Francis, ,, ***Organic Chemistry*** '' 6th ed. , McGraw-Hill , New York (1990).

3- M.L. Dhar, O. Singh , V.K. Gupta and R. Raina , ***J. Iraq Soc.*** , **11**(1) , 42-58 (1986).

4- W.J. Nacy, ***MSc. thesis*** , Basrah University , Iraq (1982).

5- S.B. Gholse and R.B. Kharat, ***J. Article***, **15** , 10-14 (2001).

6- M.L. Dhar, O. Singh , V.K. Gupta and R.Ranina, ***J. Iraqi Soc***. , **11**(1), 42-58 (1986).

7- S.R. Dighade , S.D. Patil , M.M. Chincholkar and N.R. Dighade , ***Ori. J. Chem. , 18*** , 533-538 (2002).

8- A.A. Saeed, H.S. Abbo, H.H. Haddad and G.Y. Matti , ***J. of Spectroscopy*** , 30 , 63-66 (1985).

9- R.M. Silverstein and F.X. Webster, ,, ***Spectrometric Identification of Organic Compounds***'' 6th ed. , John Wiley & Sons. Inc. New York (1998).

10- A.A. Ali, ***Ph.D.thesis*** , Cairo University , Egypt (1984).

11- J. Basset , R. Denney, G. Jeffry and J. Mendham, ,, **Vogel's Text-book of Quantitative Inorganic Analysis** '' Longman Inc. New York edition (1978).

12- D. Harvey , ,, ***Modern Analytical Chemistry***'' , 10th ed. , McGraw-Hill , New York (2000).

13- D.J. Pietrzyk and C.W. Frank, ,, ***Analytical Chemistry***'' Academic Press, New York (1979).

14- M.T. Beck, ,, ***Chemistry of Complex Equiliberia*** '' Akademiai Kido, Budapest (1970).

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التقدير الطيفي لعنصري الألمنيوم والكاليوم في معقديهما مع الجالكون 3-فنيل-1-(2-هيدروكسي فنيل)-2-بروبين-1-ون

علي عبد الرزاق عبد الواحد ، نيران جاسم الصالحي ، علي طه السامرائي

قسم الكيمياء- كلية العلوم – جامعة البصرة – قسم الكيمياء

الخلاصة :

تم تحضير مركبين من الجالكونات المشتقة من تفاعل أورثو (بارا) هيدروكسي أسيتوفينون مع البنزلديهيد وتم الحصول على معقدي الألمنيوم (III) والكاليوم (III) مع المركب 3-فنيل-1-(2-هيدروكسي فنيل)-2- بروبين-1-ون في محلول الأيثانول 95% ، وتمت دراسة نسبة الليكند إلى الفلز للمعقدين بإستخدام طريقة النسب المولية .

لقد أعطت المعقدات المتكونة بنسبة 1:3 أمتصاصاً في المنطقة 200-600 نانومتر ، كما تم حساب ثوابت التكوين للمعقدين المتكونين بطريقة نصف القيمة ، وبإستخدام الطريقة الطيفية أمكن تقدير الألمنيوم (III) بحد كشف $0.97x10^{-6}$ مولاري والكاليوم (III) بحد كشف $1.35x10^{-6}$ مولاري وامتازت الطريقة بعدم وجود متداخلات مع آيونات العناصر الأخرى.