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STUDIES ON SOME TRANSITION METAL CHLORANILATES

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Abstract: The present article includes the results of spectrophotometric investigations of the composition and thermodynamic stabilities of some transition metal chelates, [M(II)-Chloranilates], where M(II) refers to Co(II), Ni(II) and Cu(II), in ethanolic-water mixtures 50% w/v.

The results of the studies of the interaction of chloranilic acid with the hydrolysed state of Co(II) are also reported.

solid chloranilates were also prepared and some of their physical properties are discussed.

Introduction

Various methods are reported [1-8] in which coloured organic reagents are used as chelating ligands for the determinations of inorganic transition metal cations. The use of chloranilic acid, 2,5-dichloro-3,6-dihydroxy 1,4-benzoquinone, Ch.A., as an analytical reagent in inorganic chemistry is well known.[9] It is reported that the acid is used for the determinations of certain metal cations.[10-13] References are given for the application of various metal chloranilates for the spectrophotometric determinations of a number of anions. Thus, mercuric chloranilate has been used for the determination of chloride ions [14] and strontium chloranilate has been proposed for the determination of fluoride ions.[15] Data on the sensitivity of the method for these anions and the sulphate anions is reported.[16,17] The application of this acid in the field of microanalytical determinations of some organic compounds and drugs are reported.[18] The acid is also used in blood serum test in disease.[19,20]

EXPERIMENTAL

Chloranilic acid (Merck) was recrystallized from ethanol before use m.p., 305°C. The chlorides used were A.R., reagent grade.

Solution of M(II)-chloranilates were prepared by mixing the appropriate amount of M(II) chloride solution in water- ethanol mixture 50% w/v with that of the acid. The pH value was adjusted to the proper value. Spectrophotometric measurements were carried out after ten minutes of mixing, as this period was found to be sufficient.

On studying the chelation of the hydrolysed state of Co(II) with Ch.A., a series of 6×10^{-4} M solutions of Co(II)-chloride adjusted at different pH values and aged from 24 hours to one month were prepared then the addition of equal volumes of 6×10^{-4} M Ch.A., solution, adjusted at the same pH value was performed. Absorbance were then measured as a function of pH and aging time.

The general method used for the preparations of solid chloranilates involved the addition of an ethyl alcohol solution of the acid to that of the transition metal chloride, applying the mole ratios 1:1 and 1:2. The solid

chloranilates separated out were washed several times with ethanol. Elemental analysis (Table 1) indicated that the reactions proceed in the mole ratio 1:1 only.

Spectrophotometric measurements were carried out on a Perkin-Elmer Lambda 4B and 1B, specord UV-VIS spectrophotometers, using 1 cm quartz cells in an air- conditioned Laboratory at 25°C. pH - adjustments were performed using Broadly-James-Corp model U.S.A., pH-meter with a combined glass-calomel electrode. X-ray diffraction analysis was carried out by means of a PHILIPS type 1390 X-ray powder diffractometer using a Ni-Filter and $Cu_{\alpha}K$ radiation. Other measurements were carried out as mentioned before.(21)
Graphics were drown using computer model Microcat personal computer

Results and Discussions

The interactions between the transition metal cations, M(II) where M=Co, Ni and Cu with Ch.A. were studied spectrophotometrically. The stoichiometry of the formed chelates were determined applying the method of continuous variations (22,23), the mole ratio(24)and the slope ratio methods.(25) The acid reacts with M(II) in 50% w/v water-ethanol mixture, to give adducts which obey Beer's law and absorb in the ultraviolet and visible regions. The addition of water-miscible organic solvent increased the sensitivity of the reaction.It is reported that (26,27) methylcelliosolve and ethanol were found to be useful solvents. The examination of the spectra in the visible region is restricted to concentrated solution due to the low absorption coefficients. As the solubility of the formed chelates are low, hence it was decided to utilise the absorption peak in the ultraviolet region so that one can use dilute solutions.

A shift of the maxima absorption band due to chelation was observed. The results achieved are summarized in Table (2,3) and (4). The data obtained on applying the three methods mentioned indicate the formation of equimolar chelates with the three transition metal cations studied. These chelates are stable in the pH range recorded in Table (5).

Figures (1A, 1B, 1C & 1D) were obtained when the containuous variations method was carried out for Co(II), Ni(II) and Cu(II) applying the total molar concentrations as indicated in the figures. The spectrum of dilute water-ethanolic solution of Cu(II)-Ch.A. of total molar concentration of 8 x 10^{-4} M indicated change in the (U.V.), region, where λ_{max} was found to occure at 353 nm. On studying Job's method of continuous variations using the same total molar concentration and plotting the values of the absorbance as a function of the mole fraction of Cu(II)-Ch.A. chelate. The results revealed the possible formation of two maxima at mole fractions of 1:1,2:1 [2Cu(II)-Ch.A.] Fig. (1D) The intensities of these two maxima are nearly the same. This may be related to the relative stabilities of the different chelated compounds in the reaction mixture at this concentration. On using more dilute solutions of total molar concentration of $6x10^{-4}$ M a more deformed curves was obtained. But when the total molar concentration was raised to 10^{-3}M the result as shown in Fig.(1C) indicated the formation of only one chelate of the mole ratio 1:1. Similar results are reported.(28)

The results obtained from the mole ratio method and slope ratio method are indicated in Figs.(2) and (3). In both cases the results revealed the formation of 1:1 chelates.

The stability constants of the chelated compounds were computed from the continuous variation method.[29] This method is the most widely used due to its simplicity and rapidity. The results obtained are summarized in Table (6).

Spectrophotometric studies of the interaction of chloranilic acid with the hydrolysed state of Co(II)

This studies were carried out to investigate the effect of variations of the pH and aging time on the chelation of the hydrolysed state of Co(II). The spectra of the solutions of the hydrolysed state of Co(II)-chelate after being aged for one, two days and a month are given in Figures (4A, 4B, 4C, 4D & 4E).

A comparison of these spectra with the absorbance - pH graph for a fresh solution of the chelate (Fig.4A) revealed that no change was obvious when the solution mixtures were aged for one day. This means that one day was not sufficient enough for the hydrolysis of Co(II)-chelate. On the other hand, a new maximum appeared in the case of all other spectra. It was observed that all aged solution mixtures have their highest absorbance at pH 8, except for those aged for two days only. This high value of absorbance is presumably due to the complete oxidation of Co(II) with the oxygen of the air in alkaline meduim to give Co(III) which reacts with the acid to give the stable chelate that absorbs at a new wave length.

It is worth mentioning that at higher pH values (9,10) however, the absorbance of the solution mixtures decrease. This may be attributed to the formation of Co(III) hydroxide, thus lowering the extent of chelation with the acid.

The absorption at the new $\lambda_{max} \simeq 215$ nm has its highest values in the case of the solution mixtures aged for one month. Thus it is concluded that one month is a sufficient time for the oxidation of Co(II) - to Co(III) which leads to the formation of a stable chelate of the tervalent state at pH 8. It is to be noticed that for all aging time the spectra of the solution mixtures indicate the presence of characteristic band at 356 nm wich indicates the coexistance of Co(II)-chelate in these solutions. However the intensity of absorption maxiumum is lower than in the case of the fresh solution mixtures. This explain the partial oxidation of Co(II) to Co(III) state and the stability of both chelates in this solution

Infrared spectrometry:

The most interesting change in the infrared spectra of pure chloranilic acid as a ligand and its chelates with Co(II), Co(III), Ni(II), and Cu(II) is that the bands at 1760 and 1630 cm^{-1} which appear as a doublet in the spectrum of the pure ligand, assigned to the stretching frequency of the C=O groups are shifted to the lower frequency and found to be at 1500 cm^{-1}, in the spectra of Co(III), Co(II) and Ni(II)-chelated compounds and at even lower frequency, 1480 cm^{-1}, in the case of Cu(II)-chelate.

A lowering of the frequency of the predominatly C=O stretching mode of carbonyl groups of the ligand upon chelation is an evidence that the donor site is the carbonyl oxygen.[30-33] Similar values are reported.[34] The The

The spectra indicate no splitting for the carbonyl bands which indicates that both C=O are coordinated to the metal cations and the donor behaves as a bidentate ligand.[35]

The M-O bands in the spectra of metal chloranilates, where M=Fe(III) and Cr(III) complexes have been reported [36] to appear in the range of 530-580 cm^{-1}. In the present studies the Co(II)-O band appears at 570 cm^{-1} that for Ni(II)-O band appears at 530 cm^{-1} and the Cu-O band appears at 530 cm^{-1}. This indicates that the strength of the metal oxygen bonds are in the sequence Co(II) and Co(III)≈Ni(II) > Cu(II).

Thermogravimetric Analysis:

Data for the thermal decomposition of chloranilic acid and its cobalt, nickel and copper chelates are recorded, in Table (7). The results of the thermal decomposition of Ch.A., (M.wt. 208.98) indicate a decrease in weight presumably due to the loss of two -OH groups by heating up to 218°C. This is followed by a sudden decrease in weight on heating from 265-350°C, which is actually due to sublimation. the sublimation point of this acid is 266°C.[37]

MCl_2,Ch.A.,$2C_2H_5OH$ chelates start decomposition on gradual heating with the loss of ethanol molecules. Similar behaviour has been reported.[38] The chelates decompose on further heating with the loss of the ligand molecule presumably by sublimation. Further heating is accompained by great decrease in weight with the concomitant formation of the metal.

X-ray spectroscopy:

A survey in the ASTM [39] revealed that X-ray studies are recorded for $CoCl_2,6H_2O$, $NiCl_2,6H_2O$ and $CuCl_2$ "anhydrous", but no crystal structure studies have been made for chloranilic acid. In the absence of such information, we can only make qualitative comparative comparison between the X-ray spectra of Ch.A., and its Co(II), Ni(II) and Cu(II)-chelates which is based on the number and sharpness of lines present. Figs. (5A, 5B & 5C) show the X-ray analyses for the mentioned chlorides, chloranilic acid and its chelates. It is obvious that there are difference in the number of the lines and their intensities as well as the d-spacings in the case of the Ni and Cu-chelates more crystalline than that of Co-chelate.

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Table (1)

Elemental analysis of C, H, for M(II) chloranilates

M(II)-chloranilate	Found (%) C	H	Formula	Calc.(%) C	H
1-Ch.A.,$CoCl_2$,$2C_2H_5OH$	27.4	3.1	$C_{10}H_{14}Cl_4O_6Co$	27.8	3.2
2-Ch.A.,$NiCl_2$,$2C_2H_5OH$	28.3	3.4	$C_{10}H_{14}Cl_4O_6Ni$	27.8	3.2
3-Ch.A.,$CuCl_2$,$2C_2H_5OH$	26.9	3.0	$C_{10}H_{14}Cl_4O_6Cu$	27.5	3.2

Table (2)

The values of absorption spectra of 50% v/v ethanolic-water mixtures of Co(II)-chelate.

Species	Region	λ_{max}(nm)	ε $M^{-1}cm^{-1}$
Co(II)	U.V.	278	16 x 10^2
Co(II)	VIS.	489	41
Ch.A.	U.V.	300	1.4 x 10^3
Ch.A.	VIS.	530	4.4 x 10
Co(II)-Ch.A.	U.V.	356	87 x 10^3

Table (3)

The values of absorption spectra of 50% v/v ethanolic-water mixtures of Ni(II)-chelate

Species	Region	λ_{max} (nm)	ε $M^{-1}cm^{-1}$
Ni(II)	U.V.	341	75
Ch.A.	U.V.	300	1.4 x 10^3
Ch.A.	VIS.	530	4.4 x 10
Ni(II)-Ch.A.	U.V.	360	10.5x 10^3

Table (4)

The values of absorption spectra of 50% v/v ethanolic-water mixtures of Cu-chelate

Species	Region	λ_{max} (nm)	ε M^{-1} cm^{-1}
Cu(II)	U.V.	317	20
Ch.A.	U.V.	300	1.4×10^3
Ch.A.	VIS.	530	4.4×10
Cu(II)-Ch.A.	U.V.	353	10.4×10^3

Table(5)

Values for the absorption spectra of 50% v/v ethanolic - water mixtures of M(II)- chelate at different pH- values.

pH	Co(II) A	pH	Ni(II) A	pH	Cu(II) A
2.2	1.8	4.0-7.0	2.4	3.0	0.3
2.6	1.75	7.7-8.0	2.5	4.0	0.7
2.7	1.80	9.0	2.65	5.0	0.8
3.0	2.4			6.0	0.99
3.6	3.35			6.50	1.40
5.5-7.7	3.4			6.80	1.70
				7.0-7.5	1.90

Where, A : Absorbance.

Table(6)

Formation constants of some transition metal chloranilates chelates

M(II)	λ_{max} (nm)	D_M	D_S	K_S	K_c	ΔF° (K cal)
Co(II)	356	0.58	0.52	5.2×10^{-3}	1.92×10^{4}	-5.9
Ni(II)	360	0.47	0.44	1.3×10^{-3}	7.50×10^{4}	-6.7
Cu(II)	353	1.9	1.6	2.1×10^{-2}	4.63×10^{3}	-5.0

Table(7)

Thermal decomposition of Ch.A., and its M(II)-chloranilates.

Temp.(C)	$M_{obs.}$	Formula	$M_{cal.}$
1- Chloranilic acid, ($C_6H_2Cl_2O_4$)			
20	208.98	$C_6H_2Cl_2O_4$	208.98
20-266	179	$C_6Cl_2O_4$	174.9
218-350	-	Sublimation	-
2- Ch.A.,$CoCl_2$,$2C_2H_5OH$			
20	430.8	Ch.A.,$CoCl_2$,$2C_2H_5OH$	430.8
20 - 266	339.65	Ch.A.,$CoCl_2$	338.7
266 - 372	133	$CoCl_2$	129.9
652- 929	57	Co	58.9
3- Ch.A.,$NiCl_2$,$2C_2H_5OH$			
20	430.6	Ch.A.,$NiCl_2$,$2C_2H_5OH$	430.6
20-332	338.4	Ch.A.,$NiCl_2$	338.5
704 -742	60	Ni	58.7
4- Ch.A.,$CuCl_2$,$2C_2H_5OH$			
20	435.5	Ch.A.,$CuCl_2$,$2C_2H_5OH$	435.5
20-342	343.	Ch.A.,$CuCl_2$	343.
560 - 630	130.2	$CuCl_2$	129.5
750-800	66	Cu	63.5

Where : $M_{obs.}$ = The observed molecular weight.

$M_{cal.}$ = The calculated molecular weight.

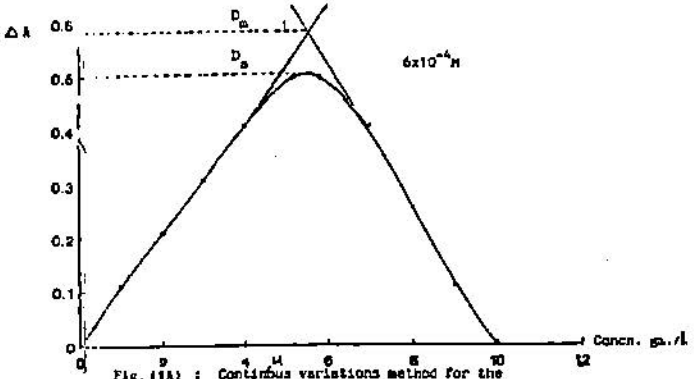

Fig. (1A) : Continous variations method for the determination of 50% W/W, water-ethanol mixtures of [Co(II)-Ch.A] chelate at λ_{max} 356 nm at pH 7 after appropriate corrections.

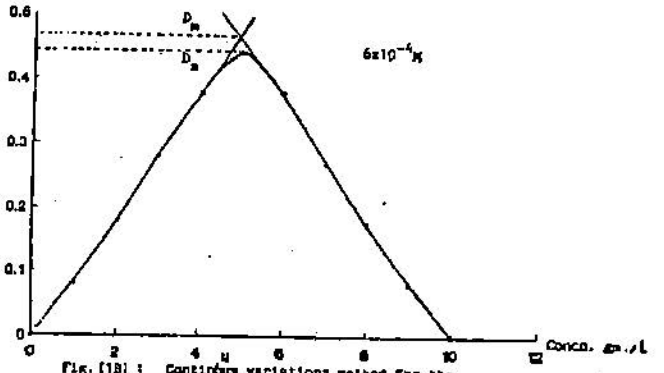

Fig. (1B) : Continous variations method for the determination of 50% W/V, water-ethanol mixtures of [Ni(II)-Ch.A.] chelate at λ_{max} 360 nm at pH 7 after appropriate corrections.

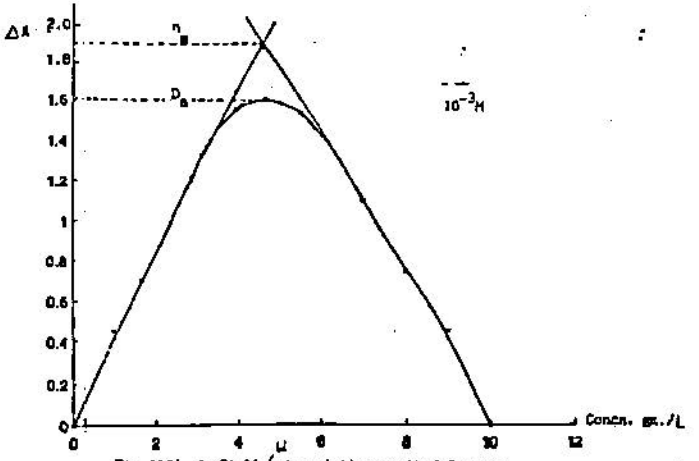

Fig. (1C) : Continous variations method for the determination of 50% W/V, water-ethanol mixtures of [Cu(II)-Ch.A.] chelate at λ_{max} 353 nm. at pH 7 after appropriate corrections.

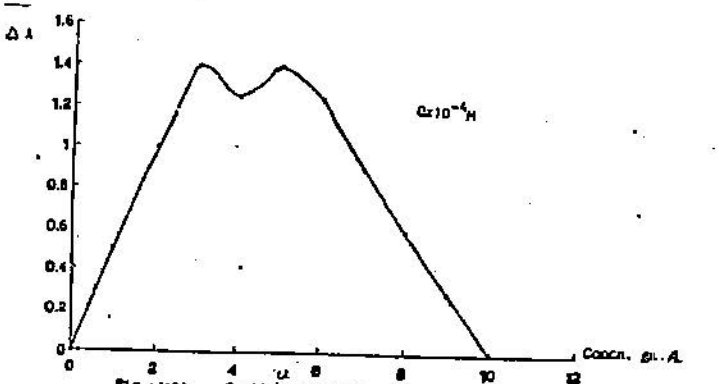

Fig. (1D) Continous variations method for the determination of 50% W/V, water-ethanol mixtures of [Cu(II)-Ch.A.] chelate at λ_{max} 353 nm at pH 7 after appropriate corrections.

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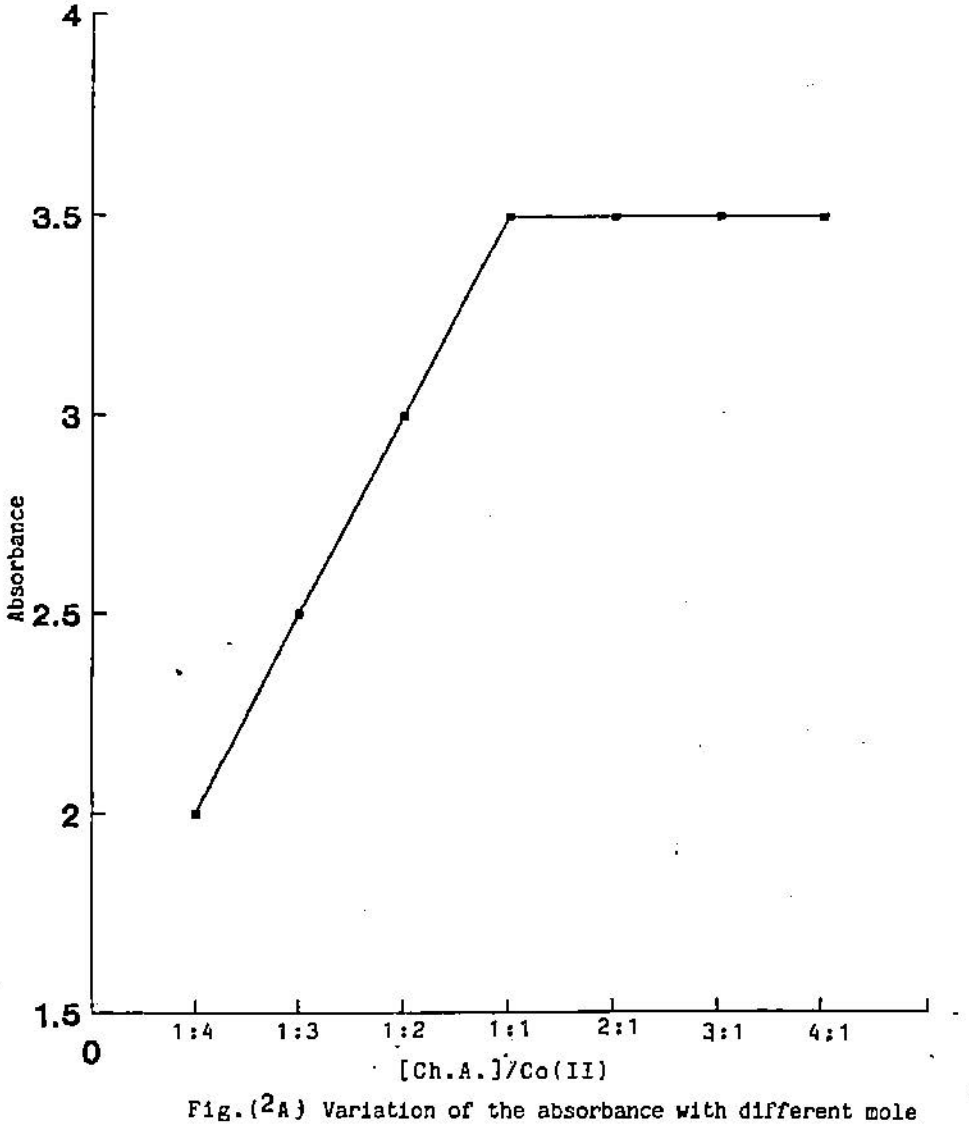

Fig.(2A) Variation of the absorbance with different mole ratio of Co(II) and Ch.A. at λ_{max} 356 nm and at pH 7.

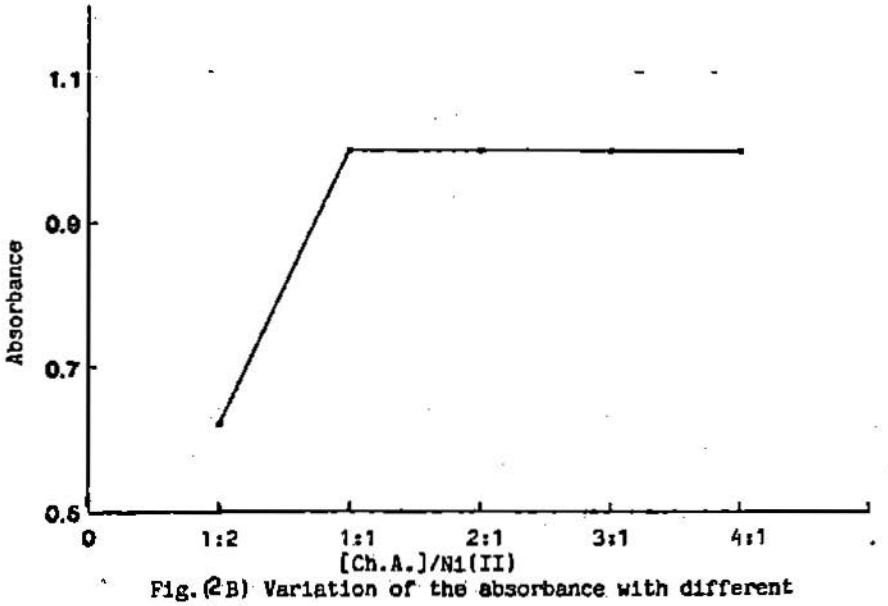

Fig. (2B) Variation of the absorbance with different mole ratio of Ni(II) and Ch.A. at λ_{max} 360 nm and at pH 7.

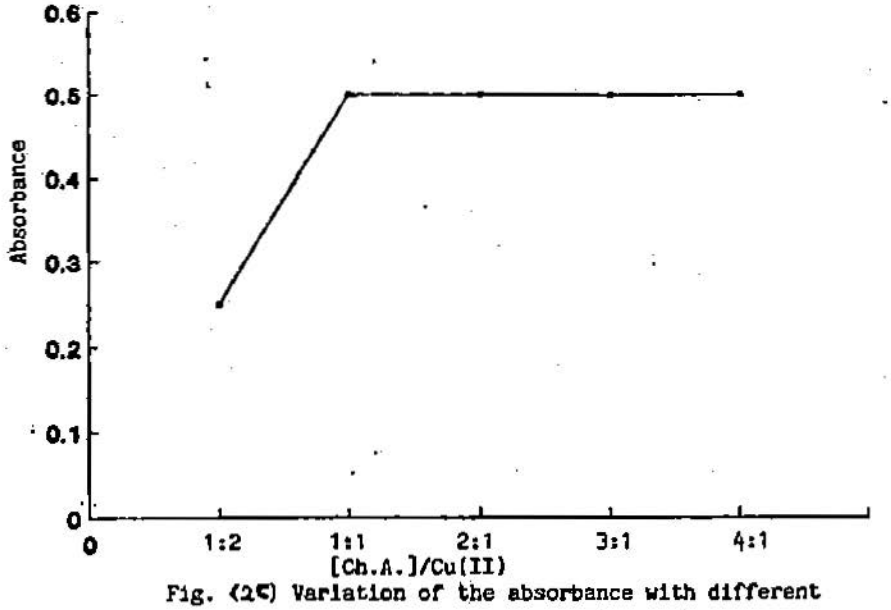

Fig. (2C) Variation of the absorbance with different mole ratio of Cu(II) and Ch.A. at λ_{max} 353 nm and at pH 7

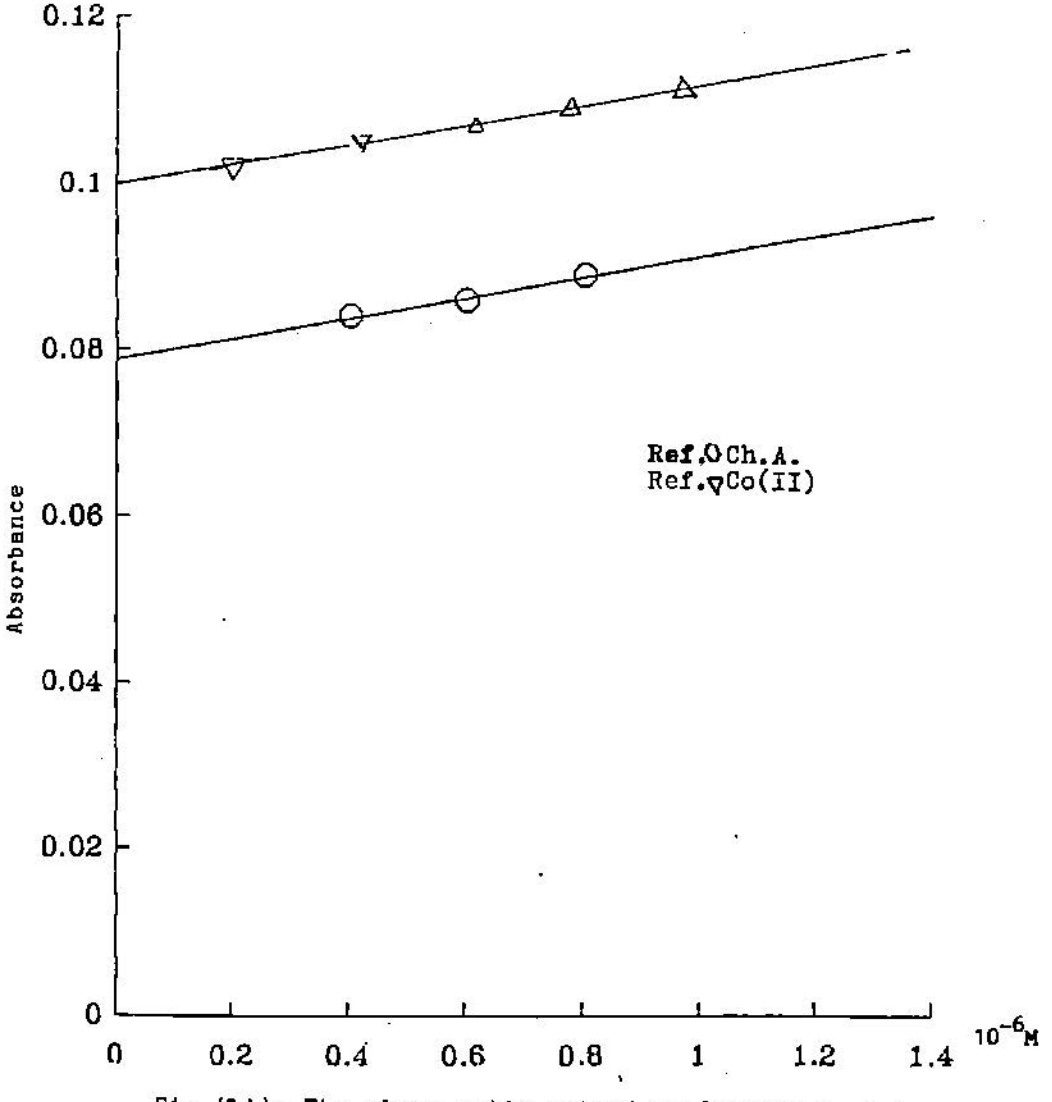

Fig.(3A): The slope ratio method of [Co(II)-Ch.A.] chelate at λ_{max} 356 nm and at pH 7 .

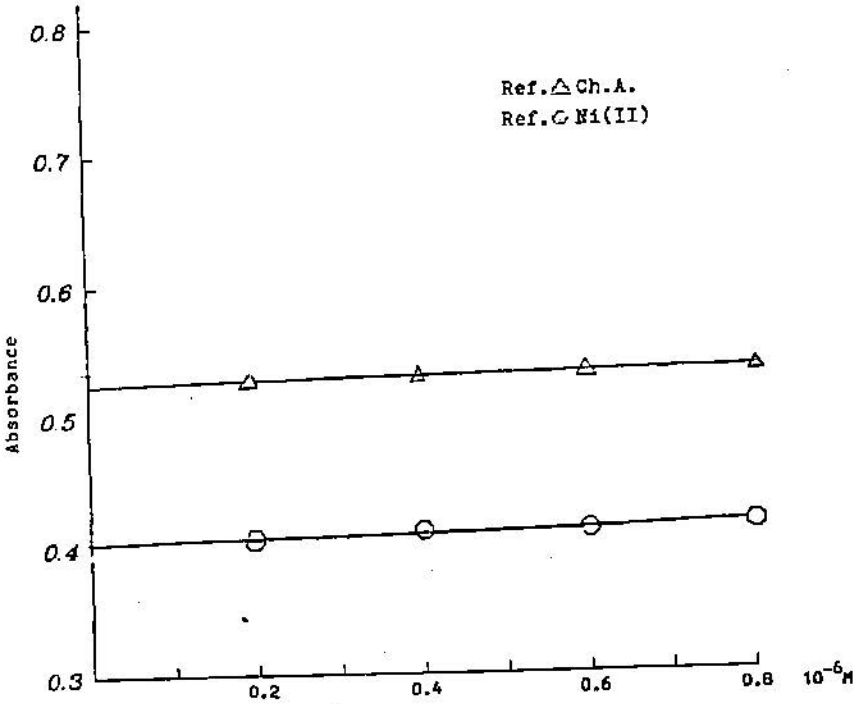

Fig.(3 B): The slope ratio method of [Ni(II)-Ch.A.] chelate at λ_{max} 360 nm and at pH 7 .

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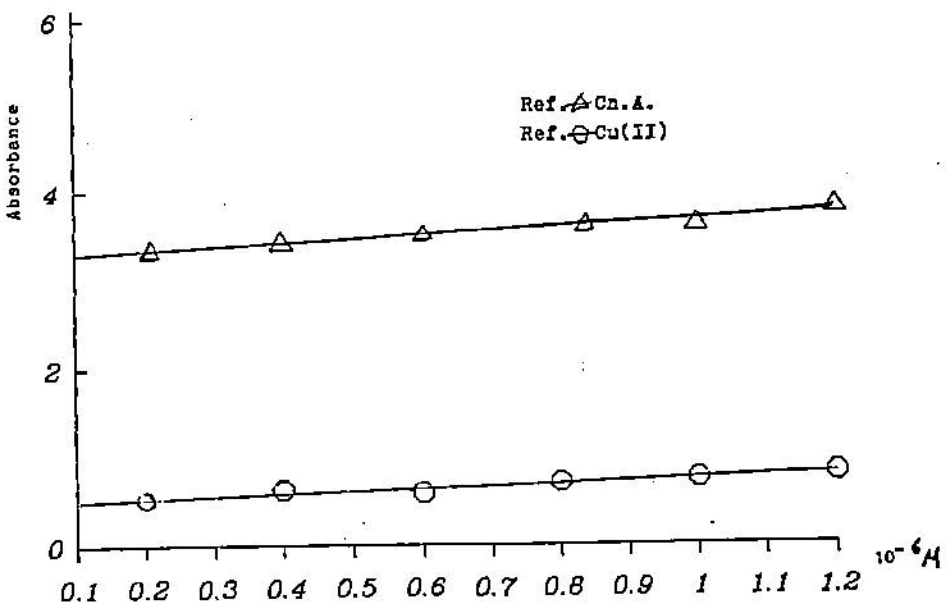

Fig.(3C): The slope ratio method of [Cu(II)-Ch.A.] Chelate at λ_{max} 353 nm and pH 7 .

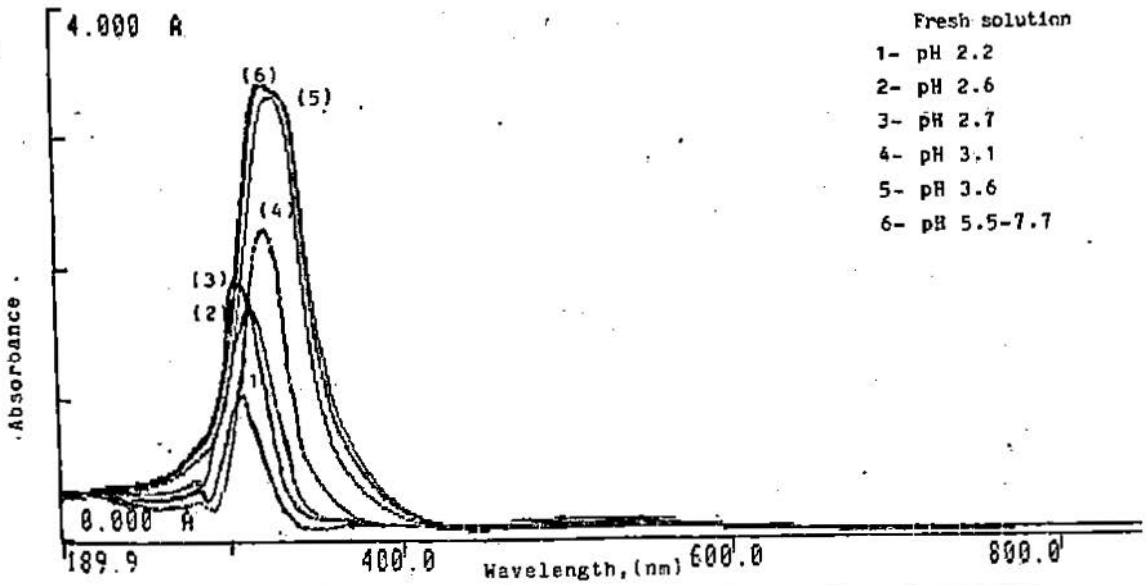

Fig. (4 A) : Variation of the absorption spectra of mixtures of $6x10^{-4}$M Co(II) and $6x10^{-4}$M Ch.A. as a function of pH.

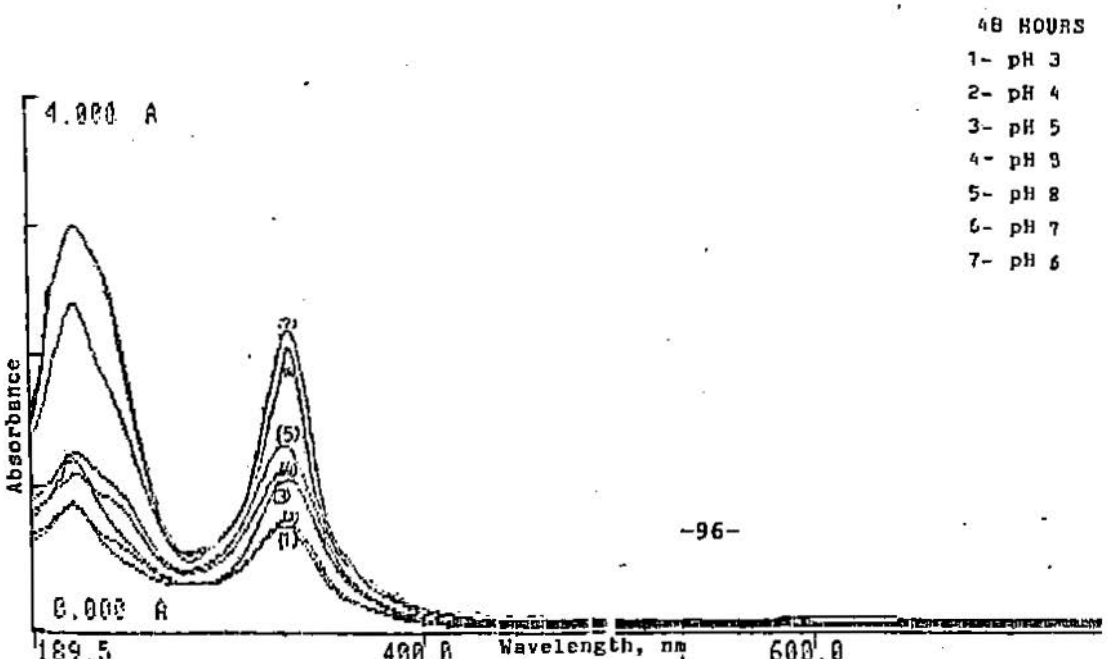

Fig. (4 B) : Variation of the absorption spectra of Co(II)-Ch.A., mixtures aged for 48HOURS as a function of pH.

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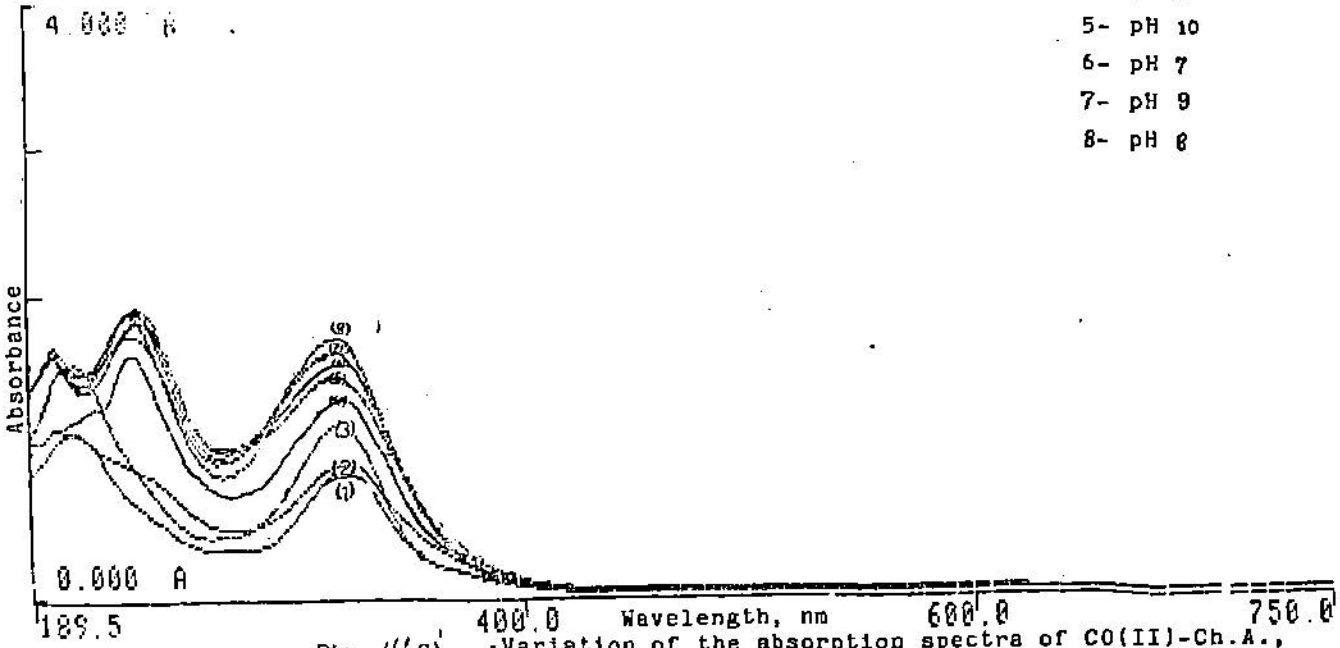

Fig. (4c) :Variation of the absorption spectra of CO(II)-Ch.A., mixtures aged for 'One week" as a function of pH.

Two weeks
1- pH 3
2- pH 4
3- pH 5
4- pH 6
5- pH 7
6- pH 10
7- pH 9
8- pH 8

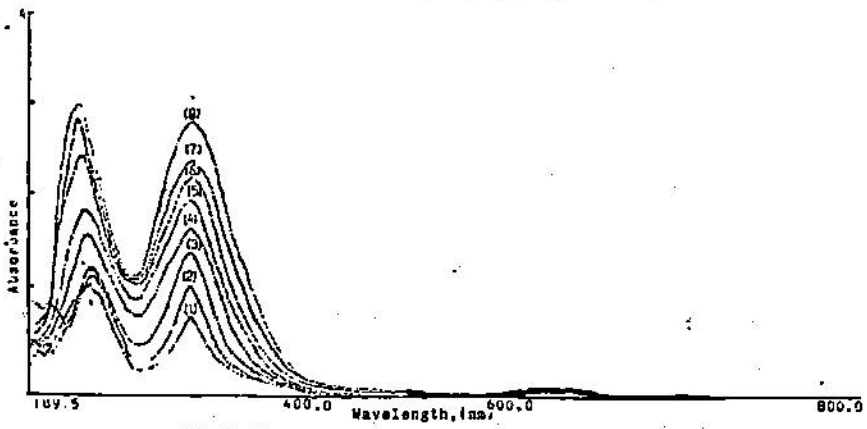

Fig. (4 D): Variation of the absorption spectra of Co(II)-Ch.A., mixtures aged for Two weeks as a function of pH

One month
1- pH 3
2- pH 4
3- pH 5
4- pH 6
5- pH 10
6- pH 7
7- pH 9
8- pH 8

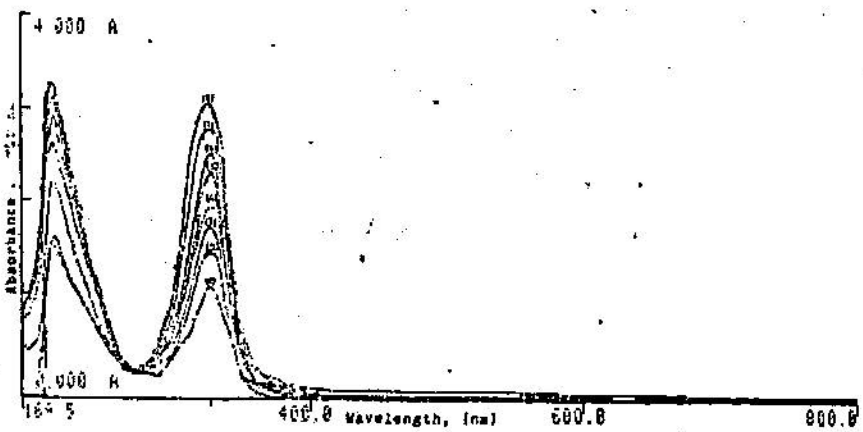

Fig. (4 E) Variation of the absorption spectra of Co(II)-Ch.A., mixtures aged for One month as a function of pH

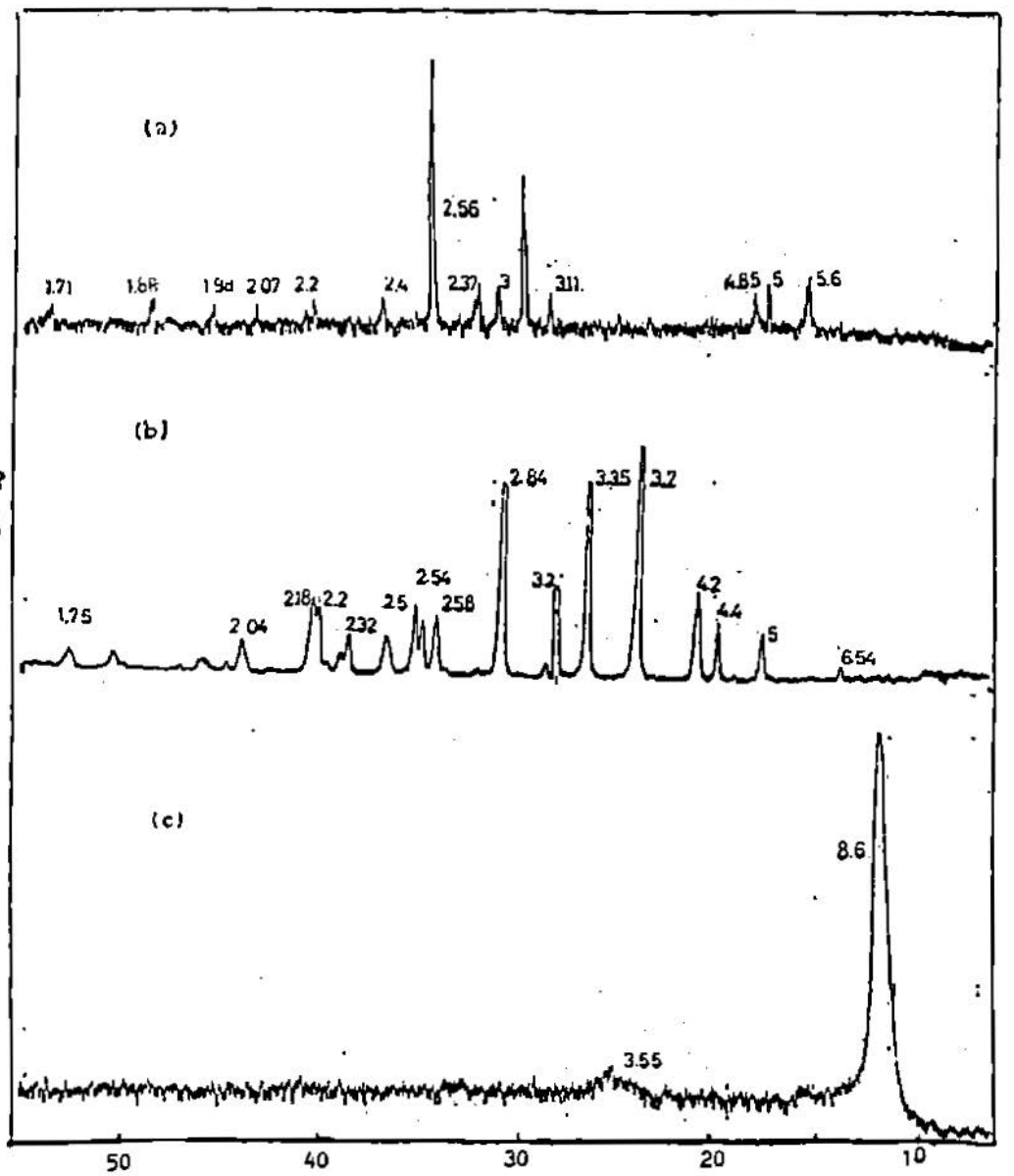

Fig.(5A) X-ray diffraction of (a) $CoCl_2,6H_2O$ (b) Chloranilic acid (c) Ch.A., $CoCl_2,2C_2H_5OH$

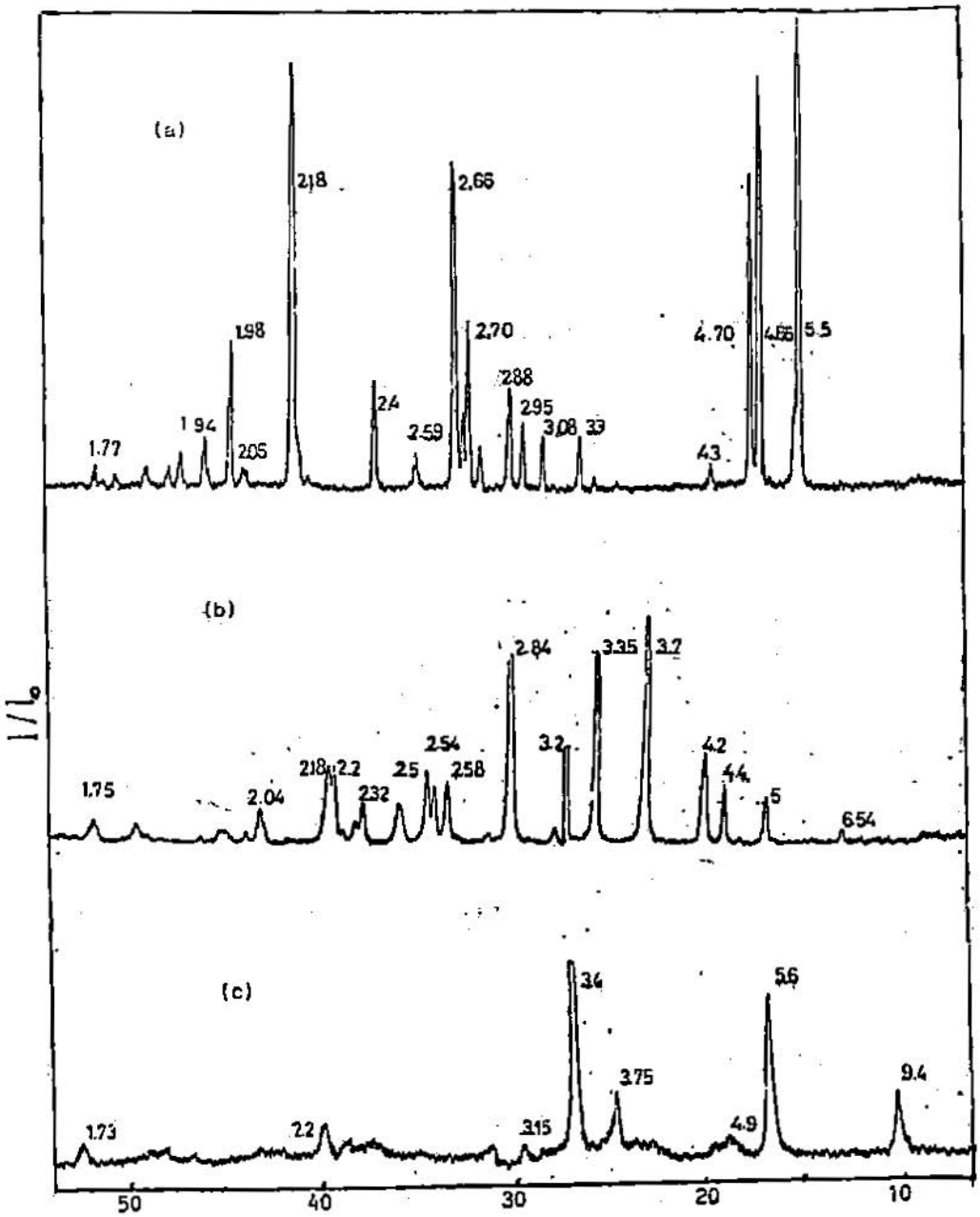

Fig.(5P) X-ray diffraction patterns of (a) $NiCl_2,6H_2O$ (b) Chloranilic acid (c) Ch.A.,$NiCl_2,2C_2H_5OH$

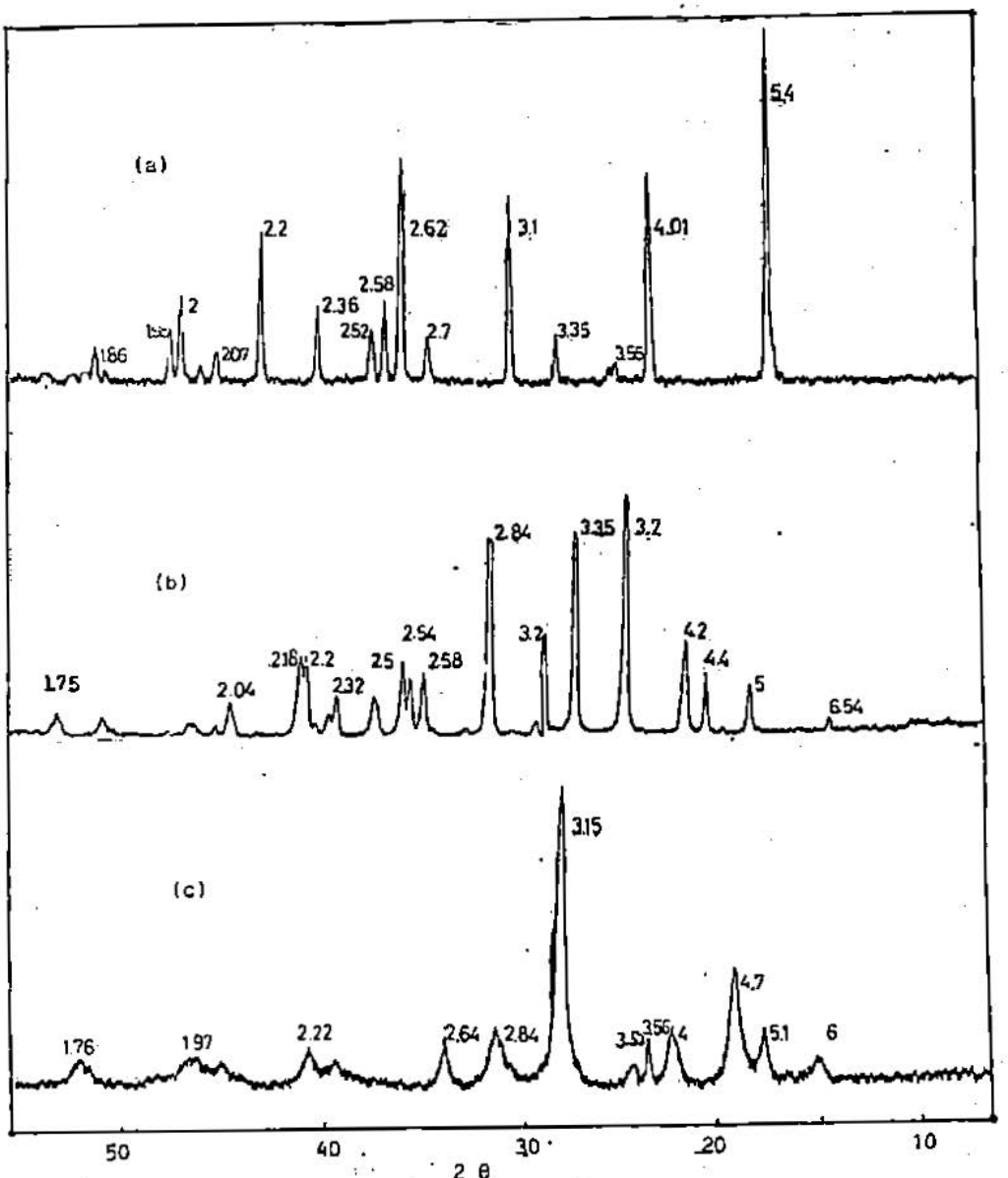

Fig.(5C)X-ray diffraction of (a) $CuCl_2$ anhydrous (b) Chloranilic acid

(c) Ch.A., $CuCl_2, 2C_2H_5OH$

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ملخص للبحث

موضوع هذا البحث يختص بدراسة طيفية لتعيين التركيب الجزئي وحساب ثوابت الاتزان لمتراكبات بعض العناصر الانتقالية ثنائية التكافؤ مثل النحاس النيكل الكوبلت مع حمض الكلورانيليك . ولقد استخدمت طرق تحليلية طيفيه مختلفة لتعيين التركيب الجزئي لمحاليل هذه المتراكبات في مخلوط من الماء المقطر والكحول الايثيلي بنسبة ٥٠٪ .

وقد وجد ان محاليل هذه المتراكبات تتبع قانون Beer's law في مدى معين من التركيز يعتمد على نوع الكاتيون المستخدم كذلك اجريت دراسة لمعرفة مدى تأثير التعيير في pH وكذلك المدى الزمني على تكوين المتراكب مع الكوبلت ثلاثي التكافؤ ووجد ان اعلى قيمة للامتصاص تظهر عند أس هيدروجيني (٨) ما عدا المتراكب الذي يتكون بعد يومين وتعدى قيمة الامتصاص المرتفعة عند هذا الأس الهيدروجيني الى حدوث اكسده من الكوبالت الثنائي الى الكوبالت الثلاثي ويتفاعل بالتالي مع الحمض ليعطي متراكب ثابت . وتم تحضير متراكبات من نفس الكاتيونات مع حمض الكلورانيليك في الحالة الصلبه ودراسة الخواص الطبيعية لها باستخدام الاشعة تحت الحمراء التأثير الحراري وتأثير اشعة اكس ، والبحث يحتوى على رسوم بيانية توضح هذه الدراسة .