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SPECTROPHOTOMETRIC STUDIES ON COPPER (II) AND NICKEL (II)-O-CARBOXY-PHENYLHYDRAZO-ETHYLACETOACETATE COMPLEXES.

by

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SPECTROPHOTOMETRIC STUDIES ON COPPER (II) AND NICKEL (II)-O-CARBOXY-PHENYLHYDRAZO-ETHYLACETOACETATE COMPLEXES.

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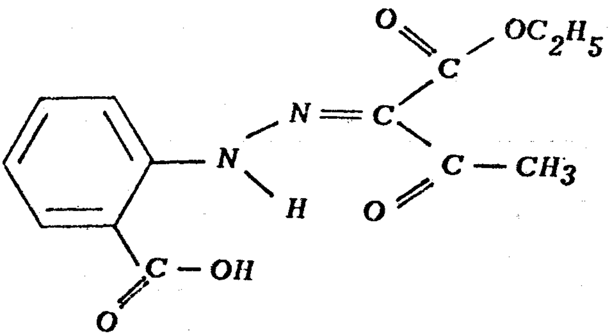
SUMMARY

The composition and the stability constants of Cu(II) and Ni (II) complexes with o-carboxyphenylh drazo ethylacetoacetate ligand (o-CPHEA) were studied spectrophotometrically. Also the isolated solid complexes were investigated using uv & visible and infrared spectra.

INTRODUCTION

The complexing ability of ethylacetoacetate as well as the azo compounds with transition metals [1,2] are well known. Therefore, the coupling product o-carboxyphenylhydrazo-ethylacetoacetate were prepared and used as complexing agents [3a].

In this connection, the composition and the stability constants of Cu (II) and Ni (II) ions with o-carboxyphenylhydrazo-ethylacetoacetate ligand, abbreviated by (o-CPHEA) were determinated in aqueous and in solid states.



o–Carboxyphenylhydrazo–ethylacetoacetate (o–CPHEA)

EXPERIMENTAL

Measurements: The infrared spectra for the isolated solid complexes and the ligand were taken in KBr technique in the range 200–4000 Cm^{-1} using Perkin Elmer model 437 spectrophotometer. The absorption spectra were carried out at room temperature using Perkin Elmer 550S spectrophotometer with one centimeter quartz or glass cells. pH - measurements were carried out using Expandomatic SS^R 2–Beckman pH meter.

Materials: Cu (II), Ni (II) and Co (II) nitrates A.R. grade were used in preparation of solution which standardized as mentioned previously [3b]. All other reagents were purified as recommended method for purification. The potassium salt of the organic ligand 2×10^{-2} M was prepared as mentioned previously [4].

The solid complexes of metal ions with organic ligand were prepared as following: An aqueous solution of metal ions (Cu (II), Ni (II) and Co (II)) 1×10^{-1} M. were mixed with a potassium salt of the organic ligand (o-CPHEA) 2×10^{-2} M. at 70 – 80°C and pH between 5–6. Deep green, pale green and buff crystals were obtained for copper (II), nickel (II) and cobalt (II) complexes respectively.

RESULTS AND DISCUSSION

The elemental analysis of the solid complexes was agree with the composition 1:1 for Cu (II): ligand complex while a composition 1:2 metal: ligand ratio for both Ni (II) and Co (II) ions respectively as indicated in Table 1. The solid complexes are soluble in organic solvents and decomposed by effect of concentrated mineral acids.

Table (1)
Elemental analysis data on ligand-metal complexes studied.

Complexes	Elements %			Melting point °C	Colour
	C	H	N		
$[Cu(C_{13}H_{12}N_2O_5)H_2O]$	43.69	3.90	7.80*	over	green
	44.01	4.10	7.60**	230°	
$[Ni(C_{13}H_{12}N_2O_5)_2H_2O]\ Na_2$	45.05	3.75	8.08*	Charing	Pale
	44.80	4.01	7.65**	at 152°	green
$[Co(C_{13}H_{12}N_2O_5)_2H_2O]\ Na_2$	45.05	3.75	8.08*	Charing	Buff
	45.95	4.00	8.08**	at 150°	

* Calculated

** Found

I. Spectrophotometric Studies:

1. Copper (II) - o - carboxyphenylhydrazo-ethylacetoacetate (-o-CPHEA) complex:

On adding of o-CPHEA (sodium salt) ligand solution to that of copper (II) nitrate solution, a faint green colour is produced. The measurement of the spectra were done after mixing spontaneously the components in the range 400–500 nm. against ligand as reference inspite the absorbance of o-CPHEA in this region is negligable. Fig. (1) illustrates the effect of pH in the range 2.8 to 8.9. It can be noticed that the absorbance of the solution have a maximum at 430 nm increases gradually

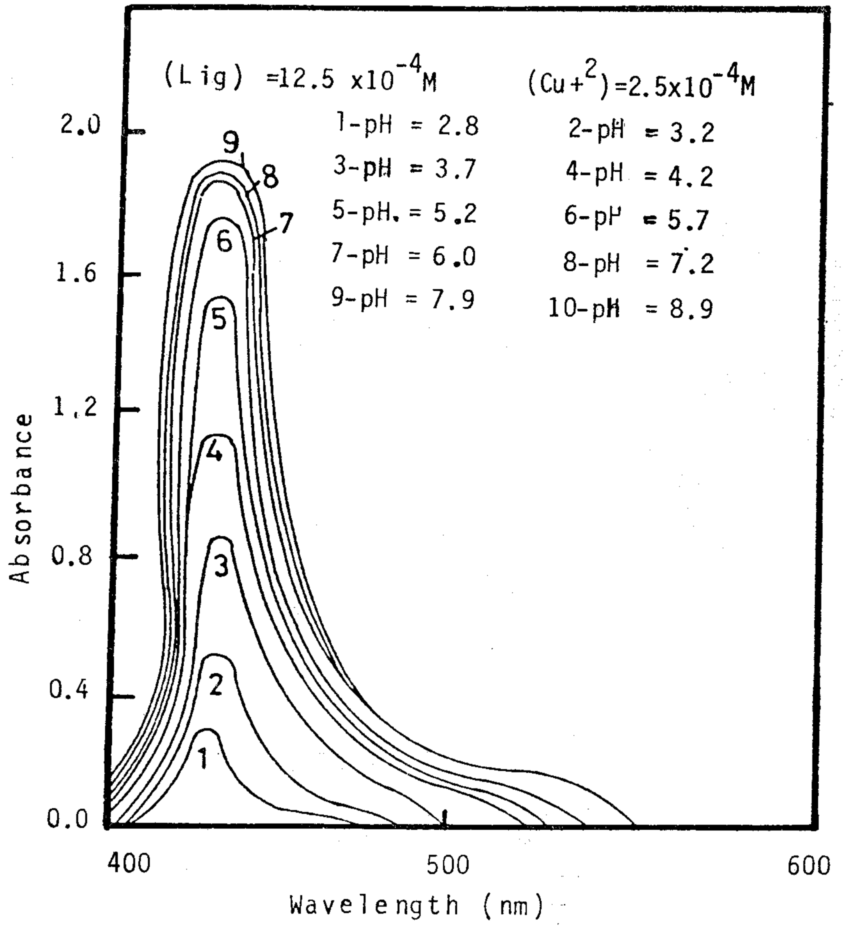


Fig. (1) Effect of pH on the absorption spectra of Cu-o-CPHEA complex.

with increasing pH till pH 6.0, indicating an increase in amount of complexation. Above pH 6 .0 the increase of absorbance is negligable as well as below pH 2 .8 the rate of complex formation is very low.

2 . Nickel (II)-o-carboxyphenylhydrazo-ethylacetoacetate complex: Addition of o-CPHEA to nickel (II) nitrate solution is accompanied by a change in colour from yellow to yellowish green. The spectra of the solution mixtures were measured after 3 hours of mixing the components at room temperature in the range 400–500 nm. against ligand as reference. The complex formation Ni-o-CPHEA is completely developed if the solution was boiled for 5 minutes. From Fig. (2) it is clear that the

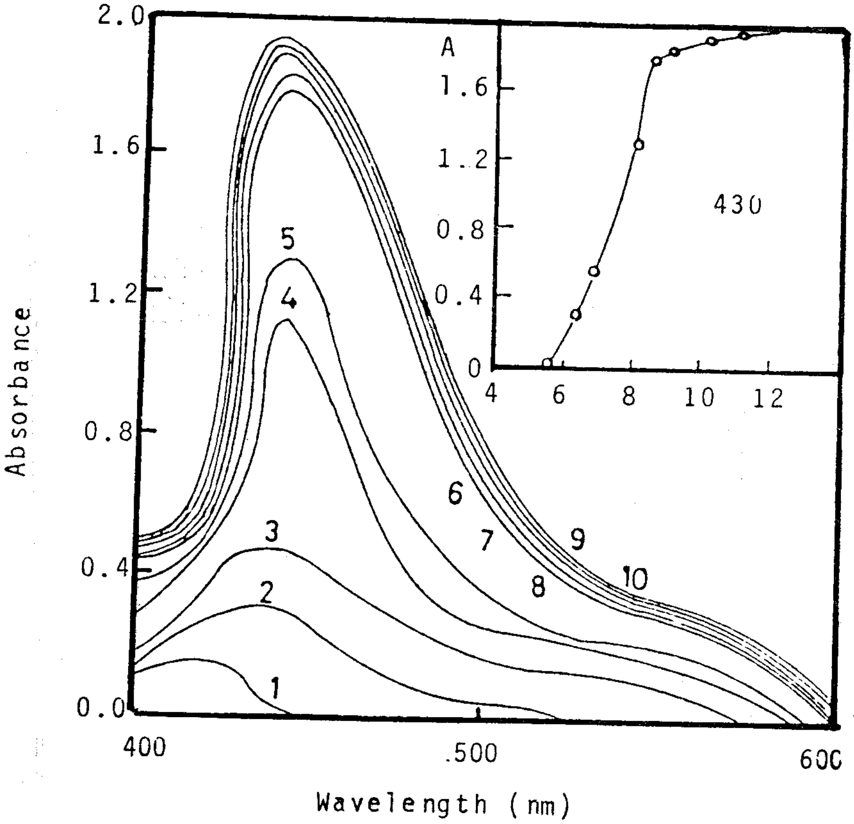


Fig. (2) Effect of pH on the absorption of Ni-o-CPHEA.

1–5.75	2–6.4	3– 6.8
4–7.2	5–8.0	6– 8.5
7–9.0	8–9.5	9–10.0
		10–11.0

complex formation is completed at pH 8 .0 since the increase in the absorbence by further increase of pH is neglected. The effect of increase the concentration of ligand on solution containing constant Ni(II) in aqueous buffered solution at pH 8 .5 shows a fixed maximum at 440 nm. which indicate that only one kind of complex is formed (Fig. 3).

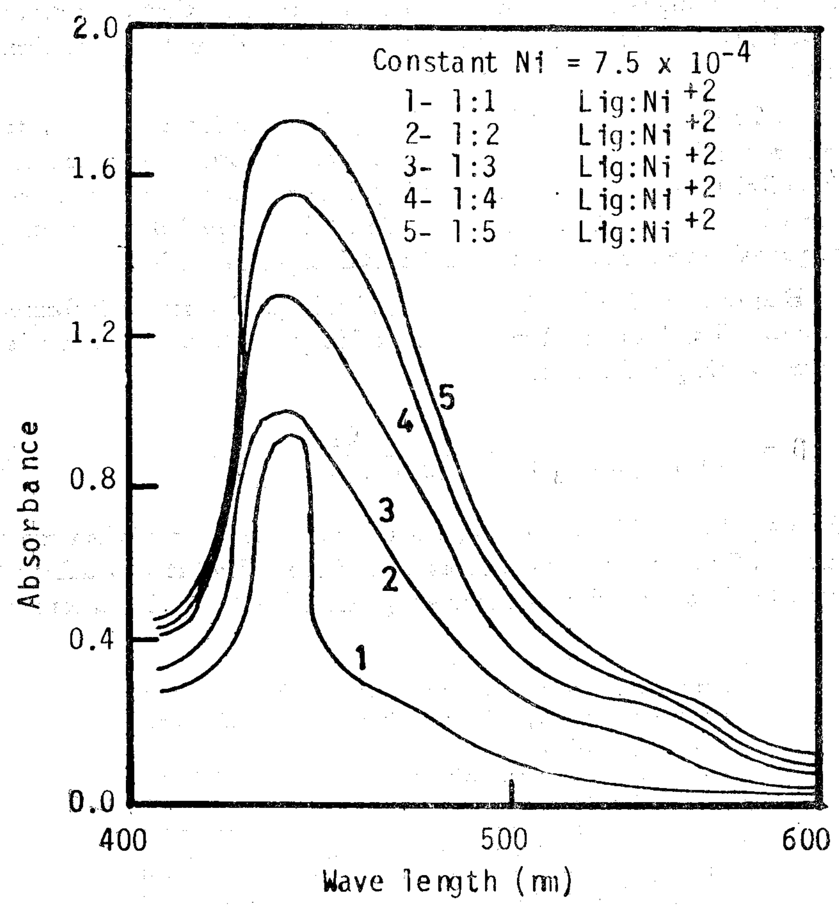


Fig.(3) Effect of concentration of o-CPHEA on the absorption spectra of Ni^{-}_{2} = 7.5x10^{-}_{2} pH = 8.5 .

3 . The composition and stability of the complexes: The composition of the formed complexes have been established by Job's [5], molar ratio [6], slope ratio [7], straight line [8] and Hyaman's [9] methods. Measurements were carried out in unbuffered in solution in case of cop-

per (II)-o-CPHEA mixture and in ammonia buffer in case of nickel (II)-o-CPHEA mixture. All methods are confirmed that the complexes have 1:1 composition solution.

Also the spectrophotometric methods are commenly used in determination of the stability constant for the complexes. However such methods are approximately since one usually assumes that the activity coefficients of both components of the complex do not deviate from unity.

(i) The stability constant is calculated concerning the data obtained in continuous variation method at two different concentrations ($C_t = 2x10^{-3}$ M. and $C'_t = 1x10^{-3}$ M.). The represented results shows a broad maximum at mole fraction of metal ion equal 0 .5 indicating the propable presence of a type 1:1 metal: ligand complexes.

Hagenmullar [10,11] showed that, if only (ML) complex is formed i.e. x = 0.5 and n = 1, therefore the stability constant can be calculated using simple formula:

$$\beta = \frac{C_3}{(0.5\ C_t - C_3)^2} = \frac{C_3}{(0.5\ C'_t - C'_3)^2} \qquad (2)$$

where $A/A' = C_3/C_3'$, C_3 and C'_3 are the concentrations of the formed complex. The results of continuous variation method at two different concentrations for both metal ions are given in Table (2). The absorban-

Table (2)

Application of continuous variation method for stoichiometry determination of copper (II) and nickel (II)-o-CPHEA complex in aqueous solution.

a = total molar concentration of M(II)-o-CPHEA=$2x10^{-3}$ M.

b = total molar concentration of M(II)-o-CPHEA=$1x10^{-3}$ M.

mole fraction of M(II)	Absorbance at different λ = 440 nm.			
	Cu(II) complex		Ni(II) complex	
	a	b	a	b
0.9	0.53	0.33	p.30	0.16
0.8	0.79	0.48	0.53	0.26
0.7	1.05	0.55	0.81	0.37
0.6	1.10	0.60	1.01	0.47
0.5	1.10	0.60	1.11	0.46
0.4	0.58	0.43	1.10	0.54
0.3	0.57	0.29	1.01	0.53
0.2	0.40	0.20	0.81	0.43
0.1	0.25	0.10	0.54	0.30

ces $A = 1.33$ and $A' = 0.7$ were found at 440 nm. in Cu (II)-o-CPHEA complex. In case Ni(II)-o-CPHEA, complex the absorbances $A = 1.38$ and $A' = 0.68$ are at 440 nm. as shown in Fig. (4). The values of the stability constants calculated are 4 .81, 4 .81 and 5 .94, 5 .93 at two different concentrations 2×10^{-3} M. and 1×10^{-3} M. for copper (II) and nickel (II) complexes respectively.

(ii) Also the stability constant calculated using the spectrophotometric method of Yoe and Jones [6[as the following:

$$K = \frac{A/A_m}{(b - a\,A/A_m)\,(1 - A/A_m)} \tag{3}$$

where A_m the absorbance of complexes arrived a constant value in presence of excess ligand. Assuming that one choosen a wave length at which ligand does not absorb; therefore, the absorbance for the complex "A" is proportional to its concentration. "a" and "b" are the original concentration of ligand, and metal ion respectively. The mean value of the stability constants of Cu-o-CPHEA complex is 4.506 Table 3.

Table (3)
The stability constant of 1:1 Cu-o-CPHEA complex using Yoe and Jones method at pH = 6.0 and λ = 430 nm. Cu(II) = [b] = 2.5×10^{-4} M. $A_m = 1.86$

[o-CPHEA] x 10^4M. = a	A	K x 10^{-4}	Log K
5.5	1.50	1.385	4.141
6.0	1.60	1.596	4.203
6.5	1.70	2.525	4.402
7.0	1.75	3.434	4.536
7.5	1.87	7.100	4.850
8.0	1.82	8.016	4.904

The obtained results for Ni(II) o-CPHEA complex confirming the formation of 1:1 complex and it stability constant is equal 4 .32.

II– Infrared and u.v. visible spectra:

The infrared spectra of the solid organic ligand and its solid complexes were investigated. A broad medium bands at 3300–3550 cm^{-1} and 3000 cm^{-1} due to frequency of OH and NH [13] in free ligand were appeared. The OH and NH vibration bands were disappeared in the spectra of the solid complexes. In the same time a strong broad band at 3200–3600 and 3000–3500 cm^{-1} were appeared in the spectra of copper and both nickel & cobalt complexes respectively which may be due to

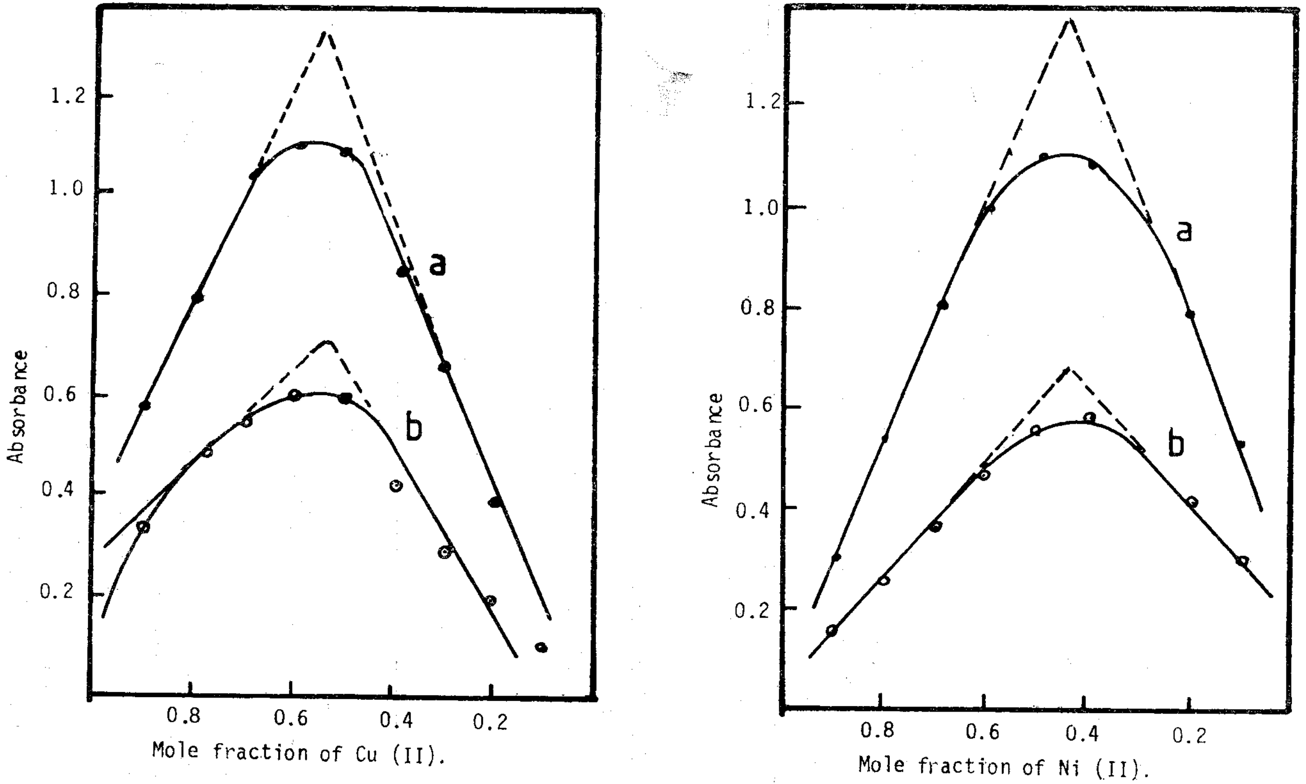


Fig.(4) Job's method at two different concentration a & b and at λ440 nm.

the presence of water of crystalization [13] coordinated to central metal ion. Also, a new medium band were in low frequency region at 580 cm^{-1}. This band may be due to M—N [14] vibration band indicating that the hydrogen atom of hydrazo group in the ligand is replaced by metal ion complex formation.

The observed 1690 cm^{-1} strong band which is always attributed to vibration of carbonyl [15] and other modes of vibration in spectrum of ligand was shifted to other frequency at 1710 cm^{-1} in case of copper complex and at 1697 cm^{-1} for nickel and cobalt complexes. This shifted indicated that oxygen atom of carboxyl group is linked to metal ion, at the same time a new band was appeared at 370 cm^{-1} and 445 cm^{-1} for Cu (II) and both Ni (II), Co (II) complexes. This band was assigned to M—O stretching frequency [15].

Also, the band position of conjugated C = N [13,16] was variable in region 1590–1650 cm^{-1} and depended on substituted groups in the molecule. This band at 1507 cm^{-1} in free ligand was shifted in the corresponding metal complexes as shown in Table 4. A new band appears between 600–500 cm^{-1} which may be due to the presence of M—N (metal-nitrogen) band [17].

Table (4)

Representative results for analysis of ir spectra of o-carboxyphenylhydrazo ethylacetoacetate and their metal complexes.

Frequency of groups Compound	Water molecule	> NH — OH	>C=O	>C=N	M—N	M—O
o-CPHEA ligand	—	2950–3100 m.b.b.	1690	1505	—	—
Cu-o-CPHEA complex	3200–3600 s.b.b.	—	1705 s.b.	1515 s.b.	585 s.b.	370 m.b.
Ni-o-CPHEA complex	3000–3500 s.b.b.	—	1697 s.sh.b.	1494 s.sh.b.	570 s.sh.	445 s.b.
Co-o-CPHEA complex	300–3500 s.b.b.	—	1695 s.sh.b.	1494 s.sh.b.	580 m.b.	445 s.b.

C. Strong, b.b. broad band., Sh. Shoulder m-medium.

Also the electronic absorption spectra of both solid ligand and solid complexes in DMF show that the absorption band maxima at 364 nm. attributed to the hydrazo groups [18] in the ligand, suffered a red shift, to lower frequency confirming that hydrazo group playing a role in chelation process. The ethylacetoacetate band [18] in the ligand at 265 is increase in its absorption as shown in Table 5 indicate that the carbonyl group is shairing in chelation process.

Table (5)

U.V. and visible Absorption maxima for metal-complexes and their organic ligand in DMF solvent at room temperature.

Compound	o-CPHEA		Cu-o-CPHEA		Ni-o-CPHEA		Co-o-CPHEA	
λmax.nm.	258	364	256	392	256	339	256	342
Log ε	4.009	24.292	4.365	4.326	4.046	4.468	4.134	4.505

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