

## Spectrophotometric Study on Nickel (II) and Cobalt (II) o-Carboxyphenylhydrazo-diethylmalonate complexes.

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**Summary:** The stability constants for the formation of type 1:1 complex between Ni(II) and Co(II) ions and o-Carboxyphenylhydrazo-diethylmalonate in aqueous medium at pH's 8.6 and 8.8 are 3.43 and 4.08 respectively. The solid complexes were prepared and studied by infrared spectra and ultraviolet to propose their structures.

### Introduction

The azo compounds and diethylmalonate were used widely as complexing agents with transition metals.<sup>1</sup> The coupling product, 3-phenylhydrazo-diethylmalonate<sup>2,3</sup> and carboxyphenyl hydrazo<sup>4a</sup> derivative, were prepared and used as complexing agents<sup>4b</sup>. Also, the complexing ability for similar compounds were studied.<sup>5-7</sup>

In this connection, the composition and the formation constant of nickel (II) and Cobalt (II) ions with o-carboxyphenylhydrazodiethylmalonate abbreviated by (o-CPHM) complexes were studied in aqueous and in solid states.

### Experimental

**Measurements:** The infrared spectra for the isolated solid complexes and the ligand were taken in KBr technique in the range 200-4000  $\text{cm}^{-1}$  using Perkin Elmer model 437 Spectrometer. The absorption spectra were carried out using recording Pye Unicam SP 1800 Spectrometer against the blank. The pH-measurements were carried out using Pye Unicam - 290 pH-meter connecting with a combined electrode. Also Varian atomic absorption was used to determine the percentage of metal in solid complexes.

**Materials:** Nickel (II) and Cobalt (II) nitrates AR grade were used in preparation of solutions which stan-

darized using disodium salt of EDTA in presence of suitable indicator.<sup>8</sup> All other reagents were purified as recommended method for purification. The potassium-salt solution of the ligand  $2 \times 10^{-2}$  M was prepared by mixing the appropriate weight in equivalent amount of KOH and stirred for about 5 hours till the solid was dissolved. The solid complexes were prepared as mentioned before.<sup>4b</sup>

### Results and Discussion

#### 1 Absorption spectra in solution

On adding of o-CPHM (potassium salt) ligand solution, to that of nickel nitrate solution, a greenish-yellow color is produced accompanied by the appearance of a new characteristic band at 419 nm. In o-CPHM - Co(II) complex, a reddish-yellow colour is produced, and a new band at 402 nm. was appeared. The absorption characteristic bands are not shifted by increasing the pH of the solution indicating the formation of the only one absorbing species in solution. Also the intensity of the bands begin to increase at pH more than 6.0 and reached its maximum values at 8.4 and 8.8 for Ni(II) and Co(II) respectively Fig. I. In case of Co-complex Fig. 1.b a decrease in absorption band above pH 9.0, this may be attributed to the decomposition of such com-

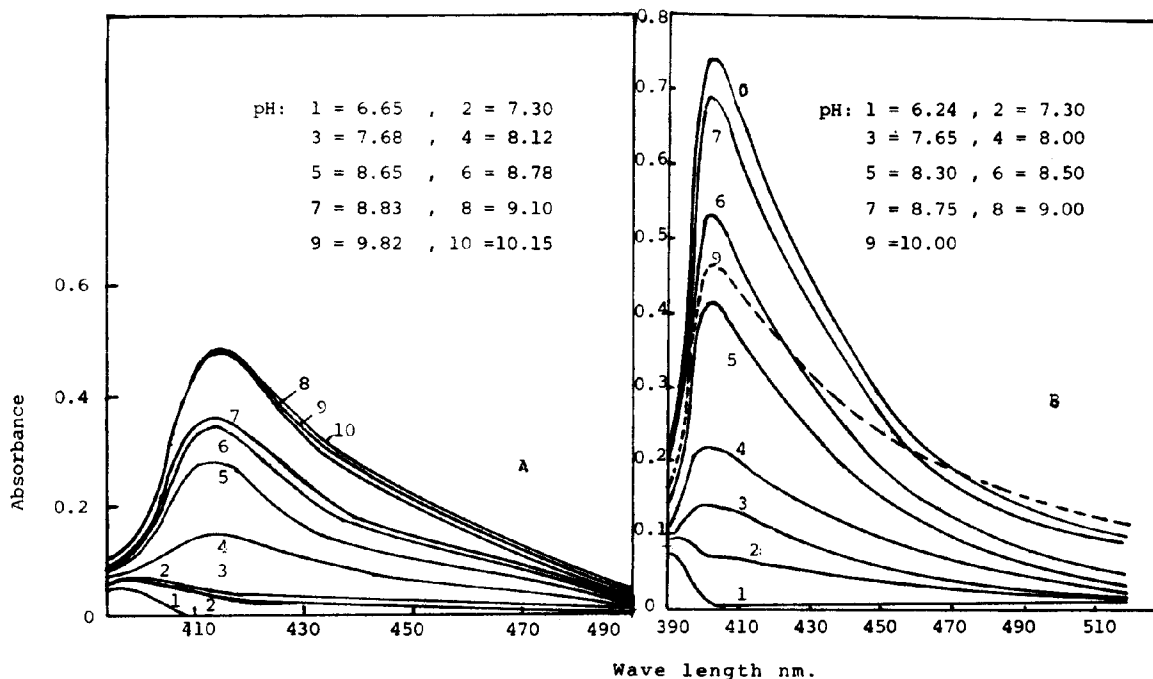


Fig. 1. Effect of the pH on the absorption spectra of:  
 A: Ni-o-CPHM complex [o-CPHM] =  $4.0 \times 10^{-4}$  M., [Ni<sup>2+</sup>] =  $2.0 \times 10^{-4}$  M.  
 B: Co-o-CPHM complex [o-CPHM] =  $2.0 \times 10^{-3}$  M., [Co<sup>2+</sup>] =  $1.0 \times 10^{-3}$  M.

plex.

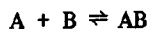
### 11. The composition of the complex

The composition of the complexes for Ni(II) and Co(II) with o-CPHM at pH's 8.6 and 8.8 respectively were determined spectrophotometrically: continuous variation,<sup>9</sup> slope ratio method<sup>10</sup> and the limiting logarithmic method.<sup>11</sup> Measurements were carried out in ammonia buffer, at constant ionic strength 0.1 and at 30°C. All the methods are confirmed that the complex have 1:1 composition in solution.

### 11.1. Stability Constants of Complexes

Spectrophotometric methods are commonly used in the determination of the composition as well as stability constant for complexes. However, such methods are approximate since one usually assumes that the activity coefficients of both component of the complex do not deviate from unity.

Following Haymann's<sup>12</sup> method, the stability constant of the 1:1 nickel or cobalt and o-CPHM complexes can be calculated using the following relations. If:



$$K_{AB} = \frac{c_{AB}}{(C_A - c_{AB})(C_B - c_{AB})} \quad \dots (1)$$

Where  $c_{AB}$  is the concentration of the complex,  $C_A$   $C_B$  are the original concentration of A and B. For small concentrations of A and B, and assuming that the absorbance "D" at specific wave length 424 nm and 430 nm are only due to the Ni(II) and Co(II) complexes respectively, then:

$$D = \epsilon_{AB} c_{AB} \quad (2)$$

$$\frac{C_A C_B}{D} = \frac{1}{K_{AB} \epsilon_{AB}} + \frac{C_A + C_B}{\epsilon_{AB}} - \frac{K_{AB} C_A C_B}{\epsilon_{AB}} \quad (3)$$

Equation (3) is the Scotts<sup>13</sup> form of the Benesi - Hildebrand<sup>14</sup> relation. If  $C_A = C_B$ , and both are small

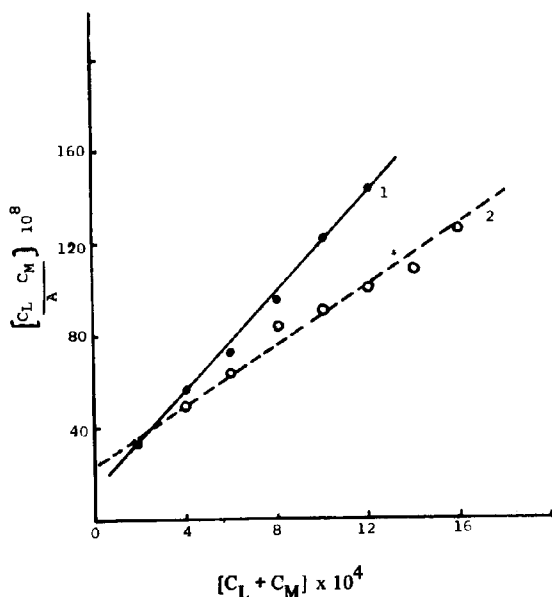


Fig. 2 Haymann's method for determination of stoichiometry of:  
1-Ni-o-CPHM complex at pH 8.6 and 424 nm.  
2-Co-o-CPHM complex at pH 8.8 and 430 nm. in solution.

then the last term in equation (3) can be neglected. Hence a plot of  $C_A C_B/D$  against  $(C_A + C_B)$  will not be completely linear and, according to Scott, the best straight line is drawn through the experimental points after subjecting the data to a least squares analysis of an individual run. From the slope and intercept  $\epsilon_{AB}$  can be computed. Fig. 2 shows the straightline relation between  $C_A C_B/D$  vs.  $C_A + C_B$  confirming the formation 1:1 complexes and from the slope and intercept, the stability constant  $\log K_{AB} = 3.42$  and  $3.97$  for Ni(II) and Co(II) complexes respectively.

The results were confirmed by Yoe and Jones<sup>15</sup> molar ratio method. The stability constant is calculated by the relation

$$K = \frac{A/A_m}{(b-a A/A_m)(1-A/A_m)} \quad (4)$$

where "a" and "b" are the original concentrations of metal ion and o-CPHM Ligand respectively. "A" is absorbance of the mixture for individual concentrations of ligand, and  $A_m$  is the limiting absorbance of the mixture.

The mean value of stability constant, K, calculated for 1:1 complex are  $3.43 \pm 0.19$  and  $4.19 \pm 0.15$  for Ni(II) and Co(II) - o-CPHM complexes respectively.

Nothing is available in literature about the complexing ability of o-carboxyphenylhydrozo-diethylmalonate. The values of stability constants of Ni(II) and Co(II) with o-CPHM complexes are nearly the same as those obtained by Stock and Davies<sup>16</sup> for Ni(II) malonate complex. The studied ligand can behave as a tridentate ligand. Thus, the depression may be attributed to the presence of the ammonia buffer, which can act as a complexing agent.

#### Solid complexes of Ni(II) and Co(II) o-carboxyphenylhydrazodiethylmalonate

##### 1. Preparation and chemical analysis

The solid complexes were prepared by mixing ligand to metal ion in 2:1 ratio in absence of the ammonia buffer at pH 5.5 as mentioned before<sup>4b</sup>. A faint green and buff plates crystals for Ni(II) and Co(II) complexes were obtained respectively. The elemental analysis, were carried out for the solid complexes by standard method, are fairly agree with the composition 2:1 (ligand to metal).

The solid complexes are fairly soluble in most organic solvents, where as completely soluble in dimethylformamide. The solid complexes are shrank at  $110^\circ$  while charred at  $125^\circ\text{C}$ . It decomposed by concentrated mineral acids on heating.

##### II. Infrared spectra

The infrared spectra of the ligand and its Ni(II) and Co(II) complexes Fig. 3 may help to identify the structure of the formed solid complexes inspite of that the complex in solid state have 1:2 (metal: ligand) on contrary the formed complex in solution is 1:1 ratio. This is attributed to the solid complexes prepared at pH 5.5 in absence of the ammonia buffer, while the Spectrophotometric studies are performed between pH 8-9 in ammonia buffer.

The  $\text{-NH}^{17}$  vibration band is broad and weak in the spectrum of the ligand at  $2500 - 2700 \text{ cm}^{-1}$ , which disappeared in their spectra of the complexes. At the same tie a medium band was appeared at  $450 \text{ cm}^{-1}$ . This band may be due to M-N bond<sup>18</sup> indicating that the hydrogen atom of hydrazo group in the ligand is replaced by metal upon complex formation. The observed  $1680 \text{ cm}^{-1}$  strong band which is always attributed to vibration of carbonyl group<sup>19</sup> and other modes of vibration in spec-

TABLE I

Complex	Required				Round			
	C	H	N	M	C	H	N	M
Ni(C <sub>14</sub> H <sub>15</sub> O <sub>6</sub> N <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	47.50	4.79	7.90	8.32	46.80	4.69	7.56	8.25
Co(C <sub>14</sub> H <sub>15</sub> O <sub>6</sub> N <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	47.50	4.70	7.90	8.32	47.10	4.73	7.63	8.40

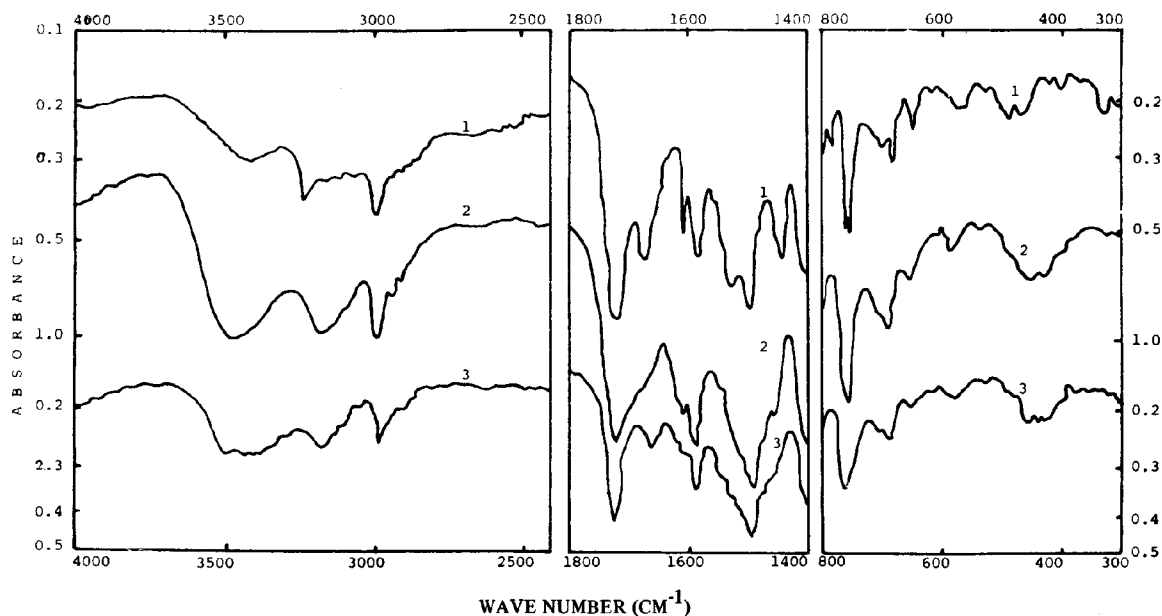


Fig. 3. Infrared Spectra of: 1-*o*-CPHM Ligand 2-Ni(II)-(*o*-CPHM)<sub>2</sub>·2H<sub>2</sub>O Complex 3-Co(II)-(*o*-CPHM)<sub>2</sub>·2H<sub>2</sub>O Complex.

trum of ligand was disappeared in Ni(II) complex. The same band was shifted and became a weak at 1665 cm<sup>-1</sup> in Co(II) complex. This shift indicated that oxygen atom of carbonyl group is linked to metal ion, at the same time a new band was appeared at 430 cm<sup>-1</sup> which was assigned to M-O stretching frequency.<sup>19</sup>

The broad medium bands 3000 – 3420 cm<sup>-1</sup> in ir spectrum of the ligand assigned to OH of carboxy and ethyl<sup>21</sup> groups still appeared in the ir of the solid complexes in the same position. This indicate that carboxy group in the ligand may not be sharing in complexation process. In addition a new strong band appeared at 3500 cm<sup>-1</sup> confirmed the presence of water crystallization<sup>17</sup> in solid Ni(II) and Co(II) complexes.

In addition the electronic absorption spectra of solid ligand and solid Ni (II) and Co(II) complexes in DMF show that the absorption bands maxima at 258 nm, 356 nm for the ligand suffered a red shift to 266 nm, 368 nm. and 266 nm., 362 nm. for Ni(II) and Co(II) respectively. This shift indicate that the carbonyl<sup>22</sup> and hydrazo groups are sharing in coordination process as show in Fig. 4.

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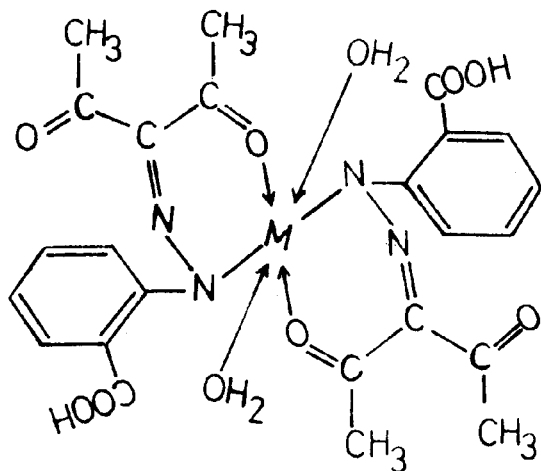


Fig. 4.

## References

1. a. M. Bobtclsky and Bar - Gradda, *Bull. Soc. Chim Fr.*, 276, 9 (1953).  
b. D.P. Graddon, *J. Inorg. Nuc. Chem.*, 7, 73, (1958).  
c. S. Wawzonck and J.B., Fridrickson, *J. Am. Chem. Soc.*, 77, 3985 (1955) d.I. Rusznak, F. Peter and J. Palyi, *Acta Chim. Acad. Sci (Hung)*, 35, 199, (1963).
2. R. Adams "organic Reactions" Vol. 10, John Wiley and Sons Inc., (1959).
3. Y. Yagi, *Bulletin Chemical Soc. of Jap.*, 36, 487, (1962).
4. a. J. Mellor and H.J. Twitchett, *Imperial Chem. Industrial, Britt*, April 2, 811, 113, (1959).  
b. A.M. El-Atrash, B.A. El-Shetary, M.F. El-Shahat and W.H. Mahmoud, *Pakistan J. of Scientific and Industrial Research* (in press).
5. N.N. Ghosh and S. Maulik, *J. Indian Chem. Soc.*, 46, 675, (1969).
6. A.G. Evans, J.C. Evans, B.A. El-Shetary, C.C. Rowlands and P.H. Morgan, *J. Coord. Chem.*, 9, 19, (1979).
7. a. G.A. El-Enanay, B.A., El-Shetary, A. El-Hilali and A.M. El-Atrash, *Pakistan J. of Scientific and Industrial Research (PJSIR)* (in press).  
b. Idem, *J. of General Chem. USSR*.  
b. Idem, *J. of General Chem. USSR*, (in press).  
c. A.M. El-Atrash, G.A. El-Enany, M.F. Ebied, A. El-Hilali and B.A. El-Shetary, *J. Anal. Chem. and Interfacial Electrochem.*, 79, 375 (1977).
8. A.I. Vogel "Quantitative Inorganic Analysis" 3rd Ed. Longmans, (1962).
9. a. P. Job. *Ann. Chim.*, 9, 113, 1928; 11, 97, (1936).  
b. R.K. Gould and W.C. Voshburgh, *ibid*, 64, 1630, (1942).
10. E. Harvey and D.L. Manning, *J. Am. Chem. Soc.*, 72, 4488, (1950).
11. H.E. Bent and G.L. French, *J. Am. Chem. Soc.*, 63, 568, (1941).
12. H. J. Haymann's, *J. Chem. Phys.*, 37, 2290, (1962).
13. R.L. Scott, *Recl. Trav. Chim.*, 75, 787, (1956).
14. H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703, (1949).
15. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem. Analyt.*, 16, 111, (1944).
16. D.I. Stock and C.W. Davies, *J. Chem. Soc.*, 1371, (1949).
17. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Complexes" 2nd Ed., Wiley Interscience, (1970).
18. G.W. Watt and J.F. Knifton, *Inorg. Chem.*, 6, 1010, (1967).
19. K. Nakamoto and A.E. Martell, *J. Chem. Phys.*, 32, 588, (1960).
20. G.T. Belinke and K. Nakamoto, *Inorg. Chem.*, 7, 2030, (1968).
21. L.J. Bellamy "The Infrared Spectra of Complex Molecules" 2nd Edn., Wiley, New York, (1958).
22. R.L. Belford, E.A. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, 2, 11 (1956).