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REACTIVITY OF β-DIKESTONES: STRUCTURE AND STABILITY CONSTANT OF COMPLEXES OF DIMEDONE -2-PHENYLAZO WITH Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, AND Mn^{2+}.

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ABSTRACT

The formation of chelate compounds between dimedone-2-phenylazo and some transition metal ions including Cu, Ni, Co, Zn and Mn was investigated spectrophotometrically, conductometrically and potentiometrically. Solid complexes were prepared, investigated by ir and analysed for their elements. The results claimed to formation of a monoligated complex for the studied ions except in case of Co where a bilagated complex predominates. The stability constant were calculated and found to be in the order: Cu > Ni > Zn > Co > Mn

INTRODUCTION

In the last two decades several investigations were reported on β-diketones and their substituted derivatives. This growing interest lasts in the conflicting tautomerization of this system, also its wide applications in medicinal chemistry as anti-inflammatory agents and miticide. (Gh 1939; Neilands, 1970; Schwarzenbach, 1944; Kilgore, 1942; Molho, 1954; Weiner, 1954; Rosini, 1976; Druden, 1976) Consequently, the chemistry of these compounds have been reviewed by Gudrinice in a book containing over 800 reference (Gudrinice 1977) The polarographic behaviour of the titled compound 5,5-dimethyl-cydohexan-1,3-dione-2-phenylazo (I) (known shortly as dimedone-2-phenylazo) have been recently investigated in our laboratory. (Fahmy) The present paper is intended to investigate further the

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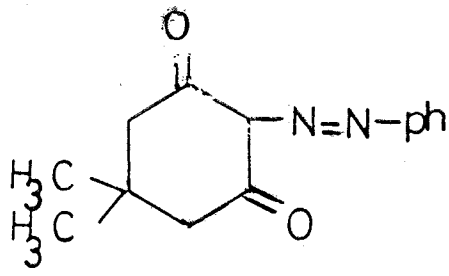
reactivity of this compound towards formation of chelates with Cu^{2+}, Ni^{2+}, Co^{2+}, $Zn^{2+}$and Mn^{2+}. The stability constant and stoichiometry of the formed complexes were examined by UV, conductometric titration, ir and elemental analysis of the separated complexes.



I

EXPERIMENTAL

Organic Synthesis

The ligand compound (I) was prepared following procedures described by Lifschitz by coupling diazotized aniline (from 1.8 gm aniline) with 2.8 gm dimedone in aqueous NaOH (Lifschitz.) The separated product was then filtered off and on recrystallization from alcohol (I) separates as yellow to red fine crystals, m.p. 146°±1°C. Purity of the product was checked by TLC and microanalytical analysis which was found to agree with the theoretical structure.

MATERIALS

Copper, cobalt, nickel, zinc and manganese chloride were AR grade BDH products. Conductivity measurements were carried out using prepared conductivity water of specific conductance 10^{-6} ohm^{-1} cm^{-1}at 25°± 0.02°C. Absolute ethanol special for spectroscopy product of BDH was used as supplied.

MEASUREMENTS

(a) Spectrophotometry: Visible and UV spectra in absolute ethanol were measured by means of PYE UNICAM SP 1800 recor-

ding spectrophotometer using 1 cm fused silica cell. IR absorption spectra were performed applying the KBr disc technique on a PYE UNICAM SP 2000 infrared spectrophotometer.

(b) Conductometric titration: This was performed in a conductivity cell model LTl supplied by W-(WTW)-Germany. Measurements were carried out at 25°C±0.02°C using mg w Lauda RC 20 thermostat with a cooling unit system.

PREPARATION OF SOLID COMPLEXES:

Metal chelates were prepared by mixing 1 m mol of the organic ligand (I) with 0.05 m mol of the metal salt chloride (Cu, Ni, Co, Zn, Mn) both dissolved in the least amount of EtOH. Dilute NaOH was slowly added with stirring to adjust the pH of the solution to 5-7 whereby the metal chelates precipitate. The precipitated complexes were filtered off and washed thoroughly with EtOH-water mixture 1:1. Elemental analysis fo. C, H, Cl and N was carried out in the microanalytical Unit of the University of Cairo, while those for metal content was carried out following well known standard methods described in texts.

pH TITRATION

pH measurements were made using a digital pH meter (Minisis type 5000, Tacusel, France) accurate to ± 0.01 pH unit. Thus ligand solutions which is 40/60 EthOH/H_20 were titrated with 0.01 M NaOH in the presence of different metal ion concentrations.

RESULTS AND DISCUSSION

SPECTROPHOTOMETRIC MEASUREMENTS

The electronic absorption spectra of ethanolic soluttion of the ligand compound (I) show a strong band with a maximum at λ 410 nm which are presumably of π - π*transition. The absorption spectra of the complex solution, using the ligand of the same concentration as in the blank, show a maxima in the 400 nm region with appreciable absorbance. Since the metal ions under consideration have no absorbance at this region, thus one can consider this region suitable for all measurements.

The absorption spectra of the system metal ion-ligand at different concentrations (in the range 1: 0.025 to 1:5, M/L ratio) were recorded for all the metal ions with the ligand. As a representative example Fig. 1 illustrates the results recorded for Cu^{2+}. On keeping the metal ion concentration constant while changing that of the ligand, the optical density increases steadily and finally attains a more or less constant value. In all cases the blank was a solution of the ligand of the same concentration as in the solution of the complexes. The metal

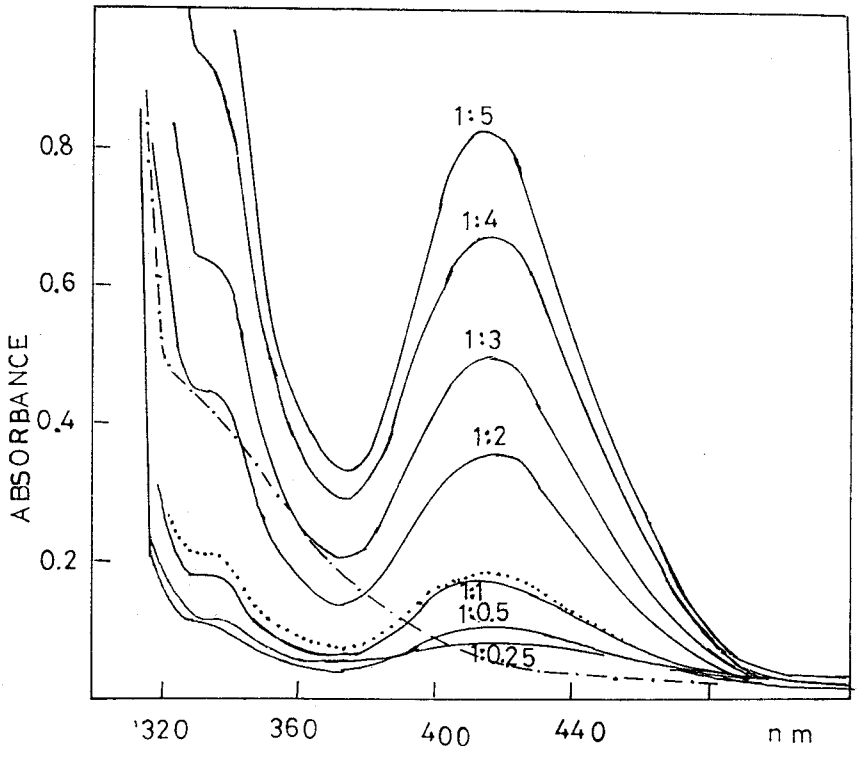


Fig. 1: Absorption spectra of Cu^{2+}-dimedone-2-phenylazo in pure ethanol by the molar ratio method Copper complex (——), free ligand (.....), Cu^{2+}(-.-.-).

ligand stoichiometry were examined following the well known molar ratio method (Yoe, 1944). The results were graphically represented in Fig. 2 where absorption spectra (after correction for absorbance of excess ligand) of M^{z+}-L were plotted against the ligand concentration per mole M^{z+}at the peak. As reflected from the figure a sharp

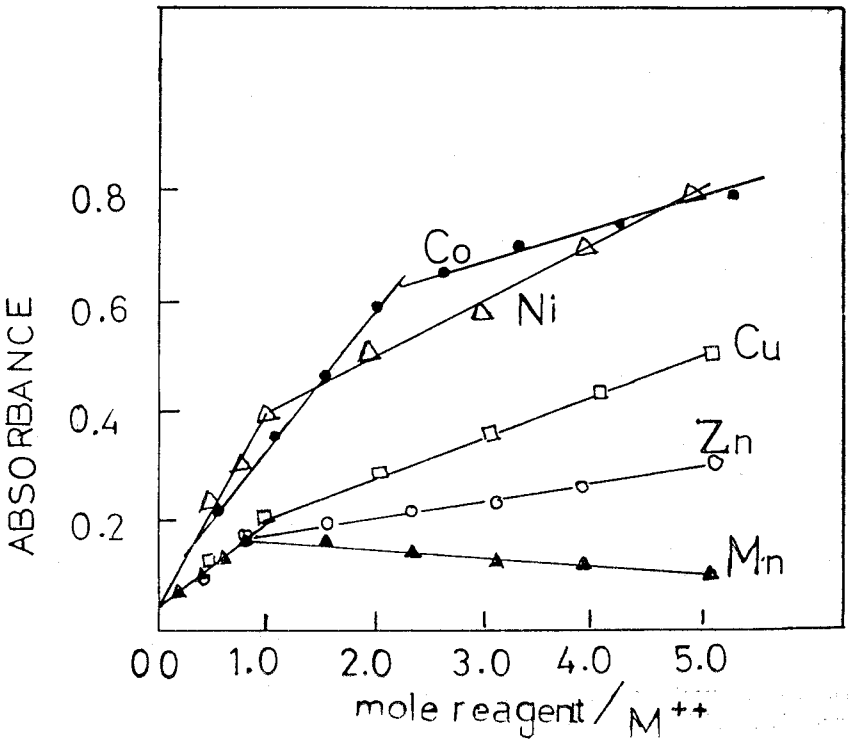


Fig. 2: Composition of metal-ligand complex by the molar ratio method. Cu^{2+}-L (□); Ni^{2+}-L (Δ); Co^{2+}-L (.), Zn^{2+} (O); Mn^{2+}-L (▲).

break could be distinguished at molar ratio 1:1 in case of Cu, Ni, Zn and Mn indicating thus the stability of monoligated complexes in these systems; while with Co a biligated complex predominate. The stoichiometry of the formed complexes were confirmed further applying the straight line and continuous variation methods (Asmus, 1960; Job, 1955; 1962). The results were in good accordance with those obtained by the molar ratio method.

CONDUCTOMETRIC MEASUREMENTS

Conductometric titration of the ligand compound (I) with metal ion solutions were performed in absolute ethanol solution. The specific conductance values determined experimentally were corrected for solvent conductance and volume changes. The results are shown graphically in Fig. 3. As disclosed from the graphs the conductance

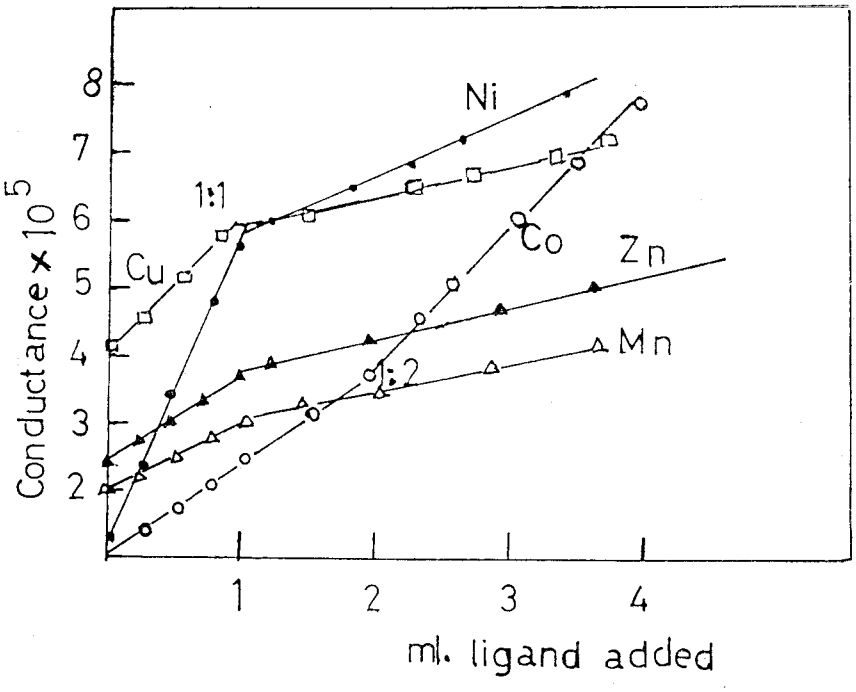


Fig. 3: Conductometric titration of 10 ml metal ions solution (10^{-3}M) against dimedone 2 phenylazo (10^{-2}M)

curves of all metal ions complexes passes by a break corresponding to the composition of 1:1 (metal ion: ligand); in addition a second break corresponding to 1:2 (metal ion: ligand) has been registered in case of Co indicating the stability and predominance of the respective complexe in this solution. These results are concordant with those obtained by spectrophotometric method.

POTENTIOMETRIC TITRATION

The results obtained on titrating 25 ml 2 x 10^{-4} M solutions in absence and presence of the studied metal ions are shown in Fig. 4. For the free ligand a well defined inflection point corresponding to the consumption of one mole base per one mole of ligand is observed. In case of ligand-metal ions mixture a well defined inflection point appears for a 1:1 mixture at a distance from the origin indicating the consumption of two moles of base together with a large initial drop in pH. This is due to the acidification effect produced as a

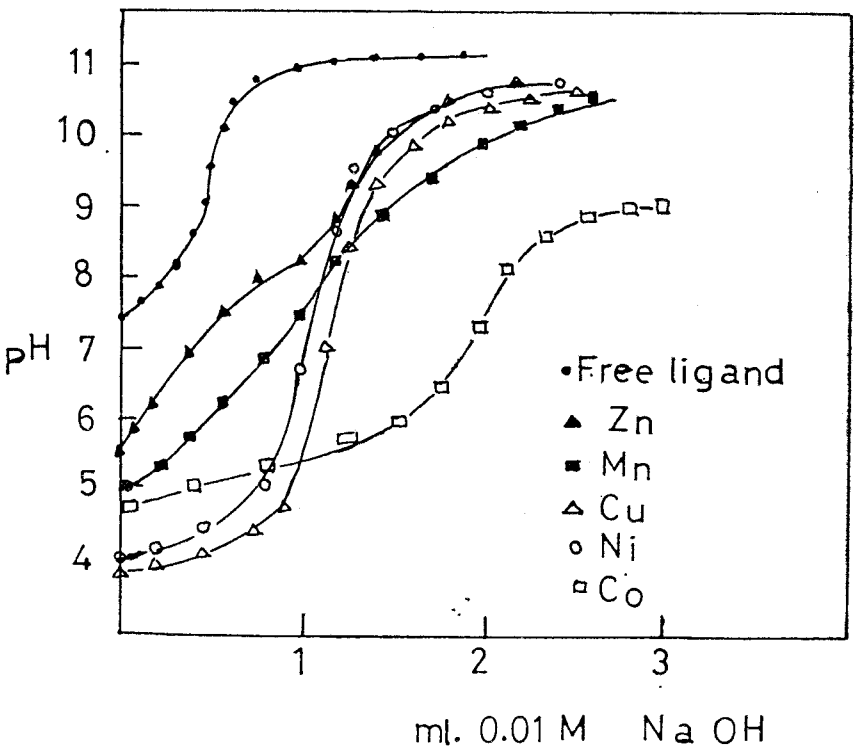


Fig. 4: Titration curves of the ligand 25 ml x 10^{-4}M solutin in presence and absence of metal ions with 0.01M NaOH solution.

result of complex formation. The same inflection point was observed in the titration of a 1:2 molar ratio a fact which supports the presence of only one type of complexes in solution formed by simultaneous displacement of two protons either from two ligand molecules linked to one M^{2+} or from one and the same ligand molecule when it is complexed in the enol form.

IR-SPECTRA

The ir spectra of the free ligand and its metal complexes were run and inspected. Fig. 5 illustrates chart obtained with Cu complex. The free ligand displayed characteristic bands at 3380, 3250 cm^{-1}, which is attributed to a combined absorption for -OH and γ-NH vibration; at 1650 cm^{-1}due to γ C=O and 1640 $cm^{-1}$for = C=N—.

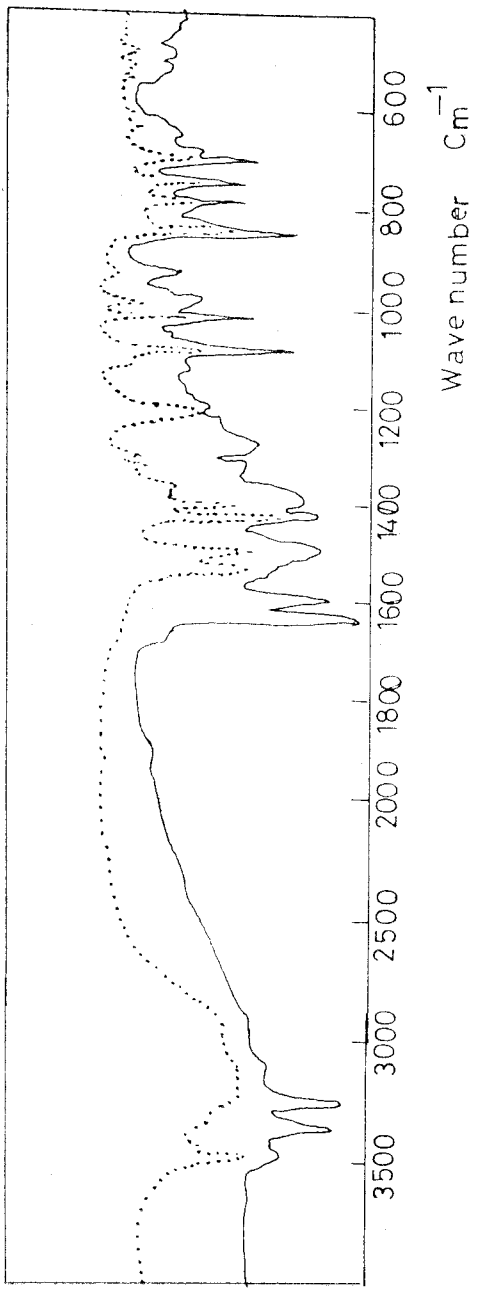
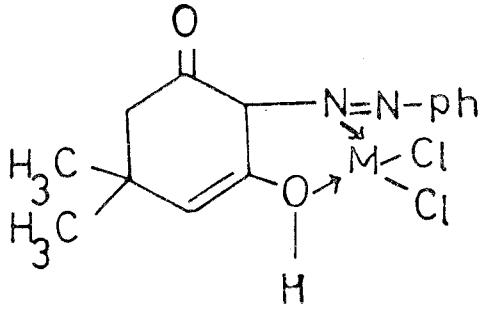


Fig. 5: Infrared absorption spectra of dimedone-2-phenylazo (——) and its copper complex (.....).

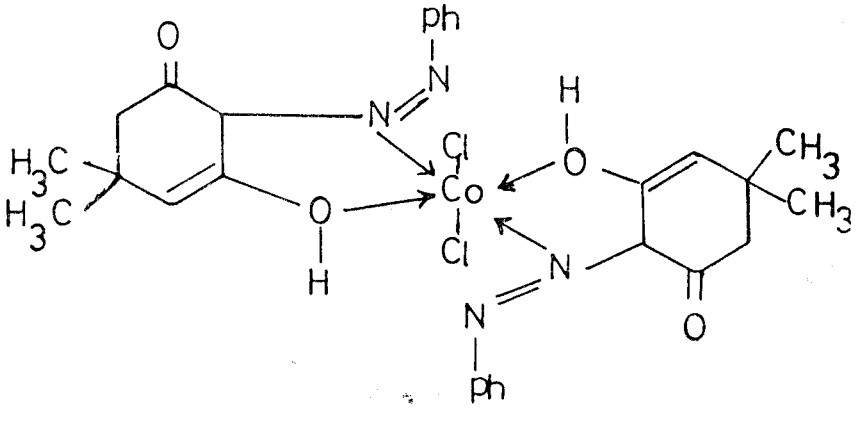
On chelation the bands at 1640 $cm^{-1}$and 1650 cm^{-1}disappears, a fact which suggests that the ligand coordinates with the metal ion in the enol form; also the band corresponding to the hydrazide linkage is shifted to lower frequency. A new hand appeared at 1210 $cm^{-1}$and is assigned to C-O stretching vibration, also a broad band at 3500-3300 cm^{-1}refering to the presence of associated water molecules in the separated complexes.

Taking in consideration the aforesaid discussion the structure of the 1:1 complexes may accordingly represented by



M= Cu , Ni , Zn , Mn

while the 1:2 complex may follow the structure:



Detailed elemental analysis compiled in table 1 support further the proposed structures.

Table 1. Elemental Analysis of Complexes.

Compound	Elemental analysis, % (a)				
	C	H	N	Cl	M
$C_{14}H_{16}O_2N_2Cl_2Cu$	44.01 (44.39)	4.29 (4.26)	7.25 (7.39)	18.32 (18.72)	16.16 (16.77)
$C_{14}H_{16}O_2N_2Cl_2Ni$	44.63 (44.97)	4.19 (4.31)	7.22 (7.49)	18.53 (18.96)	15.22 (15.70)
$C_{14}H_{16}O_2N_2Cl_2Zn$	44.27 (44.18)	4.31 (4.24)	7.19 (7.36)	18.21 (18.63)	17.57 (17.18)
$C_{14}H_{16}O_2N_2Cl_2Mn$	45.17 (45.43)	4.52 (4.36)	7.25 (7.57)	19.41 (19.15)	14.53 (14.84)
$C_{28}H_{32}O_4N_4Cl_2Co$	54.53 (54.38)	5.02 (5.21)	9.23 (9.06)	11.21 (11.46)	9.12 (9.53)

(a) calculated values in parentheses

STABILITY CONSTANT OF THE COMPLEXES

The stability constant of the formed complexes have been calculated as described in Heslop (Heslop, 1970). The calculation were based on the spectrophotometric data applying Job's continuous variation method. The conventional stability constant K for the equilibrium $M+nL \rightleftarrows ML_n$ is given by:

$$K = \frac{[ML_n]}{[M]\,[L]^n}$$

where $[ML_n]$, [M] and [L] are the equilibrium concentrations of the complex, the metal ion and the ligand, respectively. The results were summarized in table 2. The quoted values claimed that

Table 2. Formation Constants of Metal Ions With Dimedone-2-phenylazo.

Metal ion	Type of complex	Formation constant
Cu	1:1	8.52×10^6
Ni	1:1	5.31×10^6
Zn	1:1	2.03×10^6
Co	1:2	8.11×10^5
Mn	1:1	4.31×10^5

Legend of Figures

the formation constants for chelates of the studied metal ions with the ligand underconsideration follow the order:

$$Cu > Ni > Zn > Co > Mn$$

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