PHYSICOCHEMICAL STUDIES ON COMPLEXES OF SOME TRANSITION METALS WITH SOME AZO IMIDAZOLE DERIVATIVES

A THESIS

Presented By

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PHYSICOCHEMICAL STUDIES ON COMPLEXES OF SOME TRANSITION METALS WITH SOME AZO IMIDAZOLE DERIVATIVES

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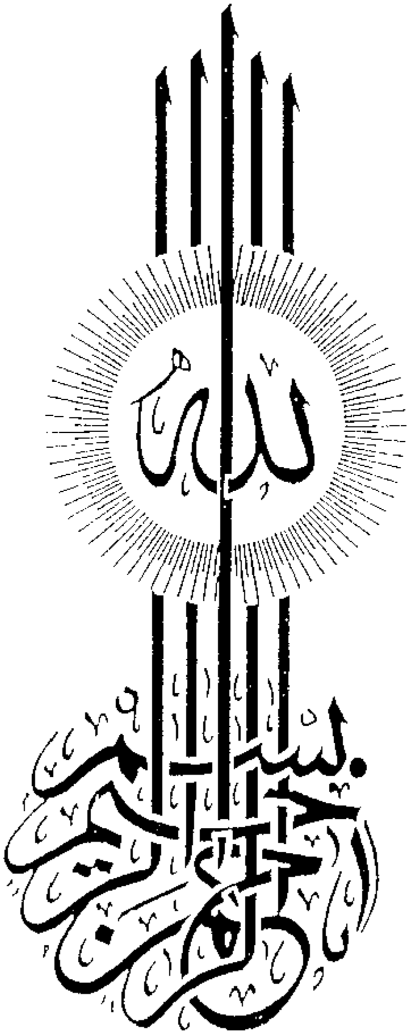
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NOTE

The candidate has attended postgraduate courses for one year in inorganic and physical chemistry covering the following topics :

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TO WHOM THEY LIT
THE CANDLE FOR ME

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Said A. Sayed.

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INTRODUCTION

Literature Survey on Metal Complexes of Imidazole and Its Azo Derivatives:

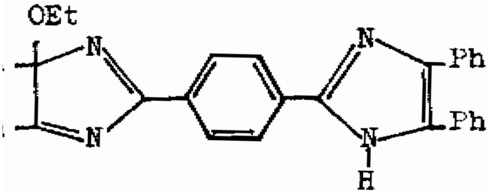
Leandri et al (1) studied the ultraviolet absorption spectra of imidazole, and some of its derivatives. The spectra were discussed in the light of the theory of localized chromophoric groups, and the essential chromophores were characterized in relation to their primary absorption bands. The authors concluded that the absorption of imidazole and methylimidazole in the region of 200 - 202 nm was attributed to "cyclic" excitation, that is, a transition which involves the passage from a symmetrical compound structurally covalent to one which is antisymmetrical and polar. In the case of the nitrobenzimidazoles, the tendency of the spectra towards lower frequencies (300 nm region) was attributed to chromophoric nitrobenzenoid group and the differences in the absorption bands of the derivatives with a $-NO_2$ group in the 4-, 7-, 5-, and 6-position were attributed to the particular effect resulting from the substitution. Furthermore, conclusions were presented with regards to inductive, mesomeric, and steric effects of the various substituents.

Lukton(2) investigated the ir-spectra (2600-3500 and 1600-1800 cm^{-1}) of acetylhistamine (I), methyldihydrourocanate

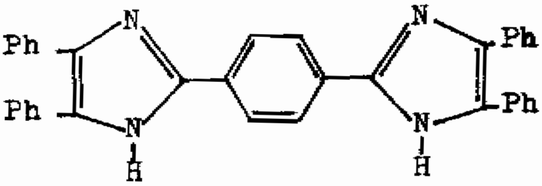
(II), and 1,4-methylhistamine in $CHCl_3$ solutions. He had indicated that the presence of bands at 2967(s), 2878(w), and 3007(vw) cm^{-1} plus the absence of a strong-bonded NH band show that (II) does not contain a H-bond. Furthermore, acetylhistamine forms an internally-bonded ring. In addition, it was deduced that two forms are possible; a 6-membered ring by an (amide) NH---N (ring) bond or an 8-membered ring by a (ring) NH---O (carbonyl) bond.

Russo and Roselli(3) pointed out that the dissociation of 2,4,5-Triphenylimidazole in methanol was induced by addition of sodium methoxide. Apparent molar absorptivities (ϵ) of the anion were determined at various methoxide concentration (C) and pK = 13.83, was calculated by plotting ϵ^{-1} versus C^{-1}. Fluorescent emission in alkaline methanol, at various pH, showed that dissociation occurs in the ground state and not in excited state.

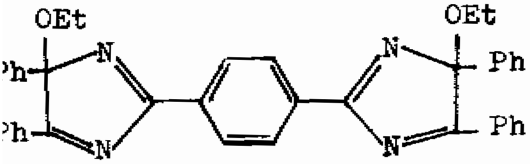
Sakaino and Kakisawa(4) noticed that the longest wavelength electronic absorption band of 2-aryl-4,5-diphenylimidazoles (e.g. I through IV) exhibited a bathochromic shift when more electron-attractive substituents were introduced in 2-Ph group.



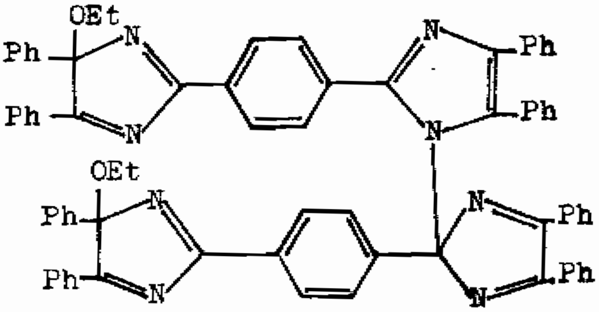
(I)



(II)



(III)



(IV)

Kalman and coworkers$^{(5)}$ indicated that the fairly planar imidazole ring reveals an almost localised double bond (1.308 (3) A) between C(2) and N(3) in accord with position of the tautomeric proton, located unambiguosuly in the neighborhood of N(1).

Edsall et al$^{(6)}$, showed marked changes in the absorption spectra of imidazole when it forms complexes with Cu(II).

Also, investigation of the absorption spectra of Cu(II)-histidine complexes indicated that the imidazole residues of histidine were involved in the linkages formed.

Karkins et al (7) studied the ir spectra for a series of metal chelates of 2-(2-pyridyl) and 2-(o-hydroxyphenyl) derivatives of benzimidazole, imidazoline, benzoxazole, and benzthiazole. They found that the coordination of reagent with a metal ion decreases the N-H streching frequency. This was explained in terms of resonance structure. Evidence was given for an intramolecular chelate structure in 2-(o-hydroxyphenyl)benzimidazole.

Leberman and Rabin(8) studied the titration curves of 3-methylhistamine-di-HCl in the absence and presence of one mole and one-half, respectively of $CuCl_2$. They showed that an additional acid ionization occurs from the 1:1, but not from 2:1, Cu(II) complex. This behaviour was similar to that of histamine and supports the earlier hypothesis that the additional acid ionization occurs from a water molecule coordinated to the 1:1 complex and from the H of the imidazole N. The equilibrium constants for the interactions between the 3-methylhistamine and Cu(II) were not very different from those for histamine.

Hatem-Champy(9) found that, in aqueous solution, within a certain range of concentration, $NiCl_2$ reacts with imidazole to form a soluble complex. However, when $Ni(OH)_2$ was treated with an aqueous solution of imidazole, a yellow-brown insoluble complex was formed. The complex appeared to contain 2 moles of imidazoles to one Ni atom.

Terlon et al(10) found that $CoCl_2$ and imidazole in solution, yielded $[Co(ImH)_6]Cl_2$ and $Co(Im)_2$ complexes; where ImH is imidazole. In the former, the imidazole molecule was linked to Co(II) through one of the atoms of N while in the latter the linkage was through two atoms of N.

Schneider and Schaeg(11) determined the basicity constants of 3-methylhistidine (I), 1-benzylhistinamide (II), and 2-imidazolylalnine (III), 3-pyrazolylalanine (IV), and 3-triazolylalanine (V), as well as the stability constants of their Zn(II), Co(II), and Ni(II) complexes by potentiometric titration and compared with the corresponding values for histidine (VI). The stability of the complexes was found to decrease in the order (VI) > (III) > (IV) > (II). Furthermore it was found that compound (V) forms 1:1 complexes with participation of the imino proton. 4-Imidazolylacetic acid (VII) and 2-pyridylacetic acid, which form 6-ring chelates had lower complex constants than 4-imidazolylcarboxylic acid (VIII) and α-picolinic acid, which form 5-ring chelates.

Relations between stability and ring size of the chelate were discussed$^{(12)}$, and the acidity constants and complex constants of 1:1 complexes of Cu(II), Ni(II), and Zn(II) with some imidazole derivatives were determined by acid-base titration. It was indicated that only 1:1 and 1:2 (metal : ligand) complexes were formed.

The stepwise formation constants pK 1-6 of Ni(II), Co(II) and pK 1-4 of Cu(II) ions with imidazole were determined potentiometrically at 10 - 50$^{o(13)}$. It was found that the formation constants follow the sequence Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II).

The $-\Delta H$ and $-\Delta S$ for complex formation reactions were calculated and discussed in terms of electronic orbitals of transition metals and nature of N-atom donor in the imidazole molecule. On the other hand, potentiometric titrations of $[Cu(MeCN)_4]ClO_4$ with imidazole (I), histamine (II), carnosine (III), glycylhistidine (IV), histidylhistidine (V) revealed the formation of Cu(I) complexes$^{(14)}$. All five ligands gave the monodentate complex, CuL. Moreover, ligands (I), (II), and (III) form CuL, with coordination at imine N.

The ir spectra of imidazole complexes of Ni(II), and Hg(II) were investigated$^{(15)}$ and the vibrational frequencies