

Coordination chemistry of pyrazole derivatives

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Azole is the suffix used for five-membered ring containing two or more hetero-atoms, at least one of which is nitrogen for example pyrazoles and pyrazole derivatives such as 5-pyrazalones which were formed by reaction between hydrazines and β -Ketonic esters, e.g 3-methyl-1-phenylpyrazolone from phenylhydrazine and ethyleaceto acetate. This, on methylation gives antipyrine (phenazone, 2,3-dimethyl-1-phenylpyrazol-5-one), which is used in medicine as a febrifuge ^[1,2].



The coordination chemistry of pyrazolin-5-ones has attracted much attention by virtue of their applicability as potential ligands for a large number of metal ions^[3-13]. The metal chelates thus produced are well known for their analytical and biological uses. The 4-position of pyrazolin-5-one system is highly reactive and undergoes coupling reactions with diazonium salts to give 4-arylazo derivatives^[14-16]. These azo-derivatives of 5-pyrazolones as well as their metal complexes have wide applications in the dye industry as well as analytical reagents for micro determination of metals^[17]



Different methods were reported for the syntheses of 4-arylazo-5-pyrazolones^[18-25]. The electronic, IR and ¹H NMR spectra of some arylazopyrazolones were obtained^[26] in pure organic solvents and buffer solutions and absorption bands in the UV and visible spectra were assigned. The IR and ¹H NMR spectra confirmed that the investigated compounds exit mainly as hydrazo-keto tautomers. The pK_a values were obtained using spectrophotometric and potentiometric methods, X-ray diffraction and spectral studies of 1-phenyl-3-methyl-4-(2,4-dimethylphenylazo)-5-pyrazolone indicated that it exists as tautomer **1** in its crystals^[27]. The pyrazole ring and its substituents are nearly coplanar, and an intramolecular NH-O bond forms a 6-membered ring.



The infrared spectra of thirteen substituted 4-benzenehydrazo-5-pyrazolones were investigated^[28]. The N-H vibration of the arylhydrazo pyrazolones was undectable as the NH absorption was broad and weak due to hydrogen bonding. A strong absorption band at 1525-1550 cm⁻¹ was assigned to NH—N vibration coupled with the C=C vibration. It was found that the v_{N-NH} frequencies correlate with σ -Hammett function of the substituents of the phenylhydrazo moiety. The C=O, C=N were located at 1635-1650 and 1570-1585cm⁻¹, respectively.

The electronic spectra of some 3-amino-4-arylazo-2-pyrazolin-5-ones **2** were investigated in pure organic solvents of varying polarities^[29]. In terms of the molecular structures of azo compounds and the solvents characteristics, the different absorption bands observed in the UV-visible spectra of the studied compounds were assigned to locally or to predominantly intra-and inter-molecular charge transfer electronic transitions. It was confirmed that these compounds exist mainly as a chelated hydrazo-keto structure **3**. Furthermore, it was concluded that, under the influence of high electron accepting substituents (NO₂) and in high polar solvents (DMF), the azopyrazolone compound was liable to exist in hydrazone-azo tautomeric equilibrium.



Nuclear magnetic resonance was used to determine the tautomeric forms of arylazo -3-, -4- and -5-pyrazolones and several related azo heterocycles in chloroform^[30]. the assignment of the hydrazone structure to the 5-pyrazolones was supported by infrared data. several conclusions emerged from the NMR spectra: (a) in the heterocyclic system studied the hydrazone NH resonance comes from 3-5 ppm lower than the azohydroxy OH resonance and (b) the hydrazone NH resonance of structurally similar azo heterocycles falls within a 2-ppm range.

Mass specral fragmentation of the phenylazopyrazolones 4 and 5



(for 4, R=Me, R^1 =H, p-CH₃, p-OH, o-OH) was found^[31] to occur primarily via rupture of the phenyl N-bond and less readily via rupture of the pyrazole-oxocyclic N bond. Compound **5** where R=AcNH; R^1 =H, p-CH₃, p-NO₂, p-CF₃, fragmented primarily via loss of ketene and secondarily via rupture of the ring –azo group bonds, while for R= H, NH₂, CH₃; R^1 = H, NH₂, fragmentation occurred in the ring or by loss of CH₃.

The mass spectra of the compounds having the general formula 6



(R = H, o-, p-CH₃, -OCH₃, -NO₂, -COOH, -Cl)



were determined and the fragmentation rationalized from high resolution and metastable mass measurements^[32]. Intense molecular ions and ions formed by consecutive decomposition of the N-containing part of the molecule were observed. In addition, ions with aniline-type structures and their decomposition products were also observed.

The mass spectra of 7 (R= CH₃, AcNH; R¹=H, (CH₃)₂N, OH, OCH₃, Cl, NO₂, etc) were given^[33]. Compound 7 cleaved on either side of the azo group. Rearrangement processes leading to arylamine radical ions were also described.



The electronic absorption and IR spectra of some 4-arylhydrazone-3-methyl-5pyrazolones were assigned and correlated to its molecular structure^[34]. The electronic spectra in ethanol comprise four absorption bands. The first three bands located near 253-260 and 335 nm, being characterized by high molar absorptivities, were assigned to π - π^* type transition. The first two bands were assigned to $({}^{1}L_{a}\rightarrow 1A)$ and $({}^{1}L_{b}\leftarrow 1A)$ transition, respectively. The third band was assigned to a π - π^* transition involving the whole molecule influenced by C.T. interaction of the band on the longer wavelength side (400-438 nm) is broad, solvent sensitive and corresponds to a charge transfer (C.T.) transition. The C.T. originates from the phenyl ring to the carbonyl group by resonance and from the hetero ring by induction. The authors noticed that this band was highly influenced by the nature and position of the substituent on the phenyl ring, donor group cause a red shift while acceptor groups cause a counter–shift relative to the non-substituted compound. These compounds display azo-hydrazo tautomerism.





A theoretical explanation of this order was given considering the ionic radii of the metal ions regardless of their respective coordination numbers or geometry. The abnormal high stability of the Fe^{2+} pyrazolone complex is attributed to the know orbital stabilization which occurs in Fe^{2+} ion during complex formation.

The relative stabilities of the metal complexes (Cu, Ni, Co and Zn) of simple arylazo pyrazolones having the formula:



(R = p-Br, p-I, m-CH₃, m-Br, m-Cl and NO₂)

were measured potentiometrically in 75% by volume dioxane^[40]. For a given substituent X, the order of decreasing stability was found to be Cu > Ni > Co > Zn. The $log\beta_2$ values were greater than $log \beta_2$ values .

Stability constants of the copper complexes with investigated dyes was found, to depend on the substituent and increase in the order, $NO < (Cl, Br) < I < OCH_3 < CH_3 < H$. with the exception of the methoxy derivative the order followed the electron attracting power of the substituent group. In case of the methoxy group the inductive effect prevailed over the resonance effect.

Dissociation constants of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one (PAP) and 4-(2-pyridyl-3-hydroxyazo)-1-phenyl-3-methyl -2-pyrazolin-5-one (PMP) and stability constants of their chelates with Th(IV), Zr(IV), Ce(III), Y(III), La(III) and UO₂(II) were determined potentiometrically in 20% (v/v) EtOH-H₂O at an ionic strength of 0.1 mol dm⁻³ (NaClO₄)^[41]. The order of the stabilities is: $Zr(IV) > Th(IV) > UO_2(II) > Y(III) > Ce(III) > La(III)$.

The reaction of La(III), Ce(III), Th(IV) and UO₂(II) with some heterocyclic azopyrazolones was studied by the spectrophotometric molar ratio and continuous variation methods and IR spectra^[42]. The solid complexes were prepared and studied by elemental analysis and conductance measurements. The azopyrazolones studied act as neutral or



monobasic bidentate ligands and bonded to the metal ions through the O atom of the carbonyl group and the α -N of the arylazo group. All solid chelates prepared behave as non electrolytes in DMF solutions.

Kinetic studies of the thermal decomposition of metal chelates of substituted hydrazopyrazolone **9** were done^[43] by TG, DTG and DTA.



 $(R = OH, COOH, OCH_3)$

Complexation was strongest with the hydroxy derivative and the relative order of thermal stability was $UO_2^{2^+} > Fe^{3^+} > Cu^{2^+} > Hg^{2^+}$. The results were used to explain the stabilization of such chelates by dative π -bonding between M^{n_+} and the ligand .

Metal chelates of pyridine azopyrazolin-5-one derivatives with



 $(X = H (L_1, L_2), C_6H_5 (L_3), Y = NH_2(L_1), CH_3 (L_2, L_3)$

Zr(IV), La(III), Y(III) and UO₂(II) have been prepared and characterized by electronic, IR, ¹H NMR spectra and thermogravimetric analyses^[17]. Electronic absorption spectra of the free ligands exhibit mainly two bands in the ranges 234-250 and 350-380 nm. The former one may be attributed to π - π^* electronic transition in the conjugated system of the ligands, while the latter one corresponding to n- π^* transition in the azo (L₁, L₃) or hydrazo (L₂) bond involving C.T. However, the broad band at 405 nm for (L₂) was assigned to Keto–hydrazone intramolecular hydrogen bonding confirming thus its hydrazone structure. The above two bands were red shifted in the presence of the metal ions studied. The visible band shifts decreased in the order Zr(IV) > UO₂(II) > Y(III) > La(III). The stoichiometry of the different metal complexes was determined by applying conventional spectrophotometric methods. The results revealed the possibility of both 1:1 and 1:2 metal ion to ligand adducts. These results were confirmed by conductimetric titrations of each metal ion using the ligands as titrants. Definite evidence for the structure and coordination sites of the ligands was obtained from infrared data. The keto structure of the free ligands and their complexes was confirmed by ¹H NMR data which revealed that there is no signal for the OH proton. Broad band at ~5.8 and 4,4 ppm for L₁ and L₂ was ascribed to the NH proton of the pyrazolone ring. The pyridyl (L₁, L₂) and phenyl (L₃) protons resonate downfield in the δ 7.1-9.1 ppm range. The δ NH₂ (L₁) and δ CH₃ (L₂, L₃) signals appearing at 4.03 and 2.5 ppm were up field shifted, indicating that the shielding was increased as a result of complex formation. The signal around 3.4 ppm in the NMR of all complexes was assigned to the associated water molecules. This assumption was supported by thermogravimetric analysis which indicated loss of water molecules in the range 120-230 °C confirming that water molecules are coordinated. It was concluded that L₁ and L₃ act as neutral bidentate ligands while ligand L₂ can act as monobasic bidentate.

Structural studies of transition metal complexes of Co(II), Ni(II), Cu(II), and Pd(II) with 3-amino-4-(substituted-arylazo)-5-(1H) pyrazolone compounds were discussed^[44]. the stoichiometries of the complexes reported are 1:1, 2:3 Co(II), 1:1 Ni(II), 1:1, 2:1 Cu(II) and 1:2 Pd(II). The investigators suggested rhombic symmetry with 4- or -5-coordinate Co(II), square planar and tetrahedral configuration for Ni(II), tetrahedral Cu(II) and square planar for Pd(II) Complexes. The complexes contained no anions .

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