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Synthesis and spectral studies of Co(II) and Cu(II) complexes with 2-(1-phenyl-2,3-dimethyl-4Amino-5-pyrazolon) Azo Resorcinol ligand

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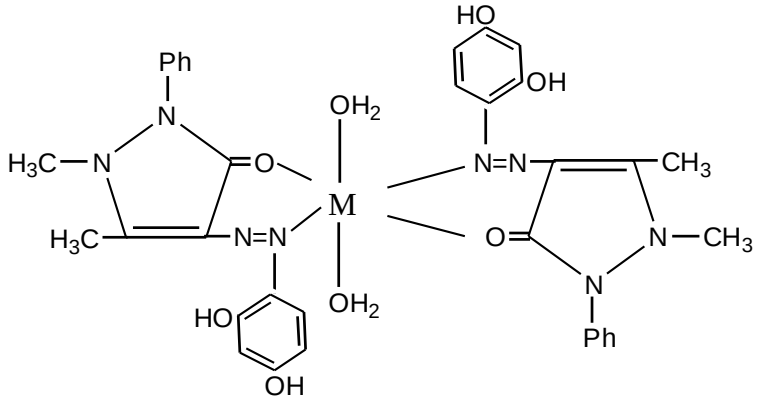
Abstract:

In this study the ligand 2-(1-phenyl-2,3-dimethyl-4-amino-5-pyrazolon) (4-amino antipyrine) azo resorcinol was prepared by the reaction between (1-phenyl-2,3-dimethyl-4-amino -5- pyrazolon) and resorcinol, and it is used for the spectrophotometric determination of Co(II) and Cu(II) complexes .The prepared compounds were characterized by UV-Vis and IR spectrophotometers.

Introduction:

Heterocyclic azo reagents are the most frequently exploited [1,2] as precolumn derivatizing reagents due to formation of chelates with many metal ions of high molar absorbativity , formation of chelates in multicomponent systems and formation of high stability metal complexes . The diazotized of heteroaromatic amines is basically analogous to that of aromatic amines . Among the five membered systems the amino- azoles (pyrroles,diazoles,triazoles,etc) have all been diazotized[3].Azo dyes have N=N group which makes them more reactive toward various metals. These compounds form water-insoluble complexes with most of metal ions ; therefore , their complexes are either dissolved in water or extracted in a suitable solvent for their spectrophotometric determination, which is quite tedious and time consuming , and so there is a need for simpler and more rapid methods[4] .Various spectrophotometric methods for the determination of cobalt(II) and copper(II) have been reported , flow injection teqhnique-[5,6], solvent extraction[7,8], reverse phase-HPLC[9]and the electrical methods[10,11]. In the present work azo ligand has been prepared by the reaction between 1-phenyl-2,3-dimethyl-4-amino-5- pyrazolon and resorcinol Also its complexes with Co(II) and Cu(II) were prepared and characterized. The proposed structure of the complexes is- shown in figure (1).



Fig(1) Proposal structure of the metal complexes (M= Co(II) and Cu(II))

Experimantal

The chemicals used are the following :(1-phenyl-2,3-dimethyl)-4-amino-5-pyrazolon from Riedel-Dehaen AG Seelze-Hannover,cobalt(II)chloride hexahydrate and copper (II) chloride dehydrate from (BDH) . The electronic absorption spectra were determined with Shimadzu Uv-Vis 1650 pc and FT-IR spectra determined with FTIR-8400S using CsI discs in the range 400-4000cm^{-1} the melting points determind by electrothermal Griffin apparatus .

Synthesis of ligand

A diazonium solution was prepared by mixing (1.5 gm , 0.00738 mol) of 1-phenyl-2,3-dimethyl-5- pyrazolon in (2ml) of (11M) hydrochloric acid and (30ml) of de-ionized water and diazotized below 5°C with sodium nitrite (1gm, 0.0144 mol) in de-ionized water(30ml) with drop wise . The diazotized amine coupled with resorcenol (0.8gm 0.00738mol) was dissolved in (20ml) of alkaline de-ionized water below 5°C , the red mixture was allowed to stand overnight , the precipitate was filtered and recrystallized from absolute ethanol .

Synthesis of complexes

All the complexes were prepared by adding an absolut ethanolic solution (0.1626 gm , 5*10^{-4} mol) of the ligand to the solution of the metal salt (0.0426 gm , 2.4*10^{-4} mol) in de- ionized water keeping ligand –metal ratio (1:2),for cobalt and copper complexes a redish- brown precipitate was obtained . The complexes were recrystallized from ethanol, filtared , washed with ethanol and dried .

Results and discussion:

Electronic absorption spectra

Table(1) shows the absorption bands values of the ligand at 412nm and has given bands at 464nm and 469nm for Co(II) and Cu(II) complexes respectively .UV-Vis spectra (Fig.2) indicated abthochromic shift(red shift) for the broad peak in the ligand from 412 to 464 and 469 nm assigned to the formation of the complexes with Co(II) and Cu(II) ions .

Table(1) The physical and spectroscopic data of the ligand and its metal complexes

Compound	Color (complex solution)	λ max (nm)	M : L	Melting Point (^{o}c)
L	Yellow	412	- - - -	164-166
$[CoL_2(H_2O)_2]Cl_2$	Yellowish-Orange	464	1 : 2	225(dec.)
$[CuL_2(H_2O)_2]Cl_2$	Yellowish-Orange	469	1 : 2	194-196

L : azo ligand

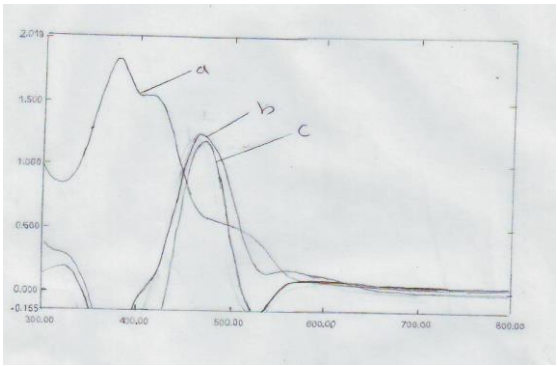


Fig (2) Electronic spectra of (a: ligand , b: cobalt complex, c : copper complex)

IR Spectra

Table (2) shows the most important spectral bounds for the ligand and its metal complexes . IR spectrum of the ligand was compared with the spectra of the metal complexes . The azo ligand shows absorption bands in the regions 3433-3542,1664 and 1492 cm^{-1} refer to υ (O-H) , υ (C=O) and υ (N=N)[5] respectively. Cobalt complex with the ligand shows the important absorption bands in the range 3379-3429, 1590 and 1437 cm^{-1} refer to υ (O-H) , υ (C=O) and υ (N=N), and copper complex shows the important absorption bands in the 3302-3558, 1595 and 1516 cm^{-1} refer to υ (O-H) , υ (C=O) and υ (N=N) respectivly [6,7]. In the spectra of all complexes, the band of υ (C=O) shifted to alower frequency (1614-1516 cm^{-1}) referring to the coordination of the oxygen atom of the carbonyl group with the metal ion and this can be explained by the donation of electrons from oxygen atom to the empty d-orbitals of the metal ion. In the spectra of complexes the band at 3500-3600 cm^{-1} together with a new band at 840-860 cm^{-1} indicating the presence of coordinated water[8] , the nature of metal – ligand bonding confirmed by the newly formed band at 600-655$cm^{-1}$and at 435-451 cm^{-1}which refers to υ (M-N) and υ (M-O) bonds respectively [9].

Table (2) Infrared spectra data for the ligand and the metal complexes (cm^{-1}) .

compounds	ν(OH) Hydrated H_2O	ν(OH) coordinated H_2O	ν(N=N)	ν(C=O)	ν(M-O)	ν(M-N)
L	----	----	1492	1664	----	----
$[CoL_2(H_2O)_2]4H_2O$	3599	844	1437	1590	451	655
$[CuL_2(H_2O)_2]4H_2O$	3558	858	1595	1516	435	607

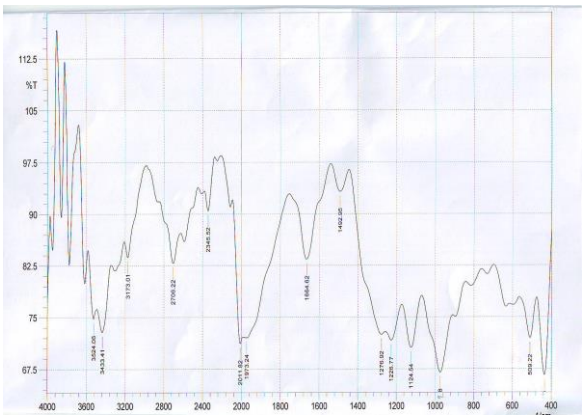
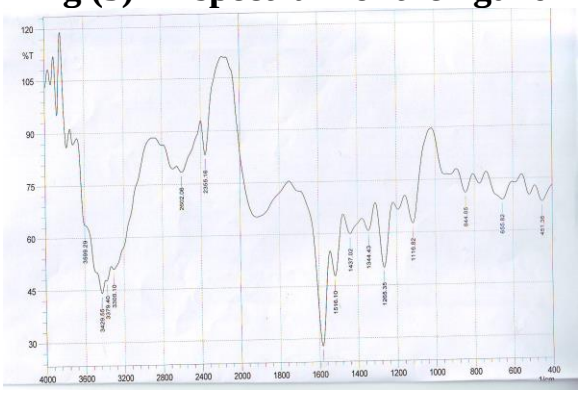
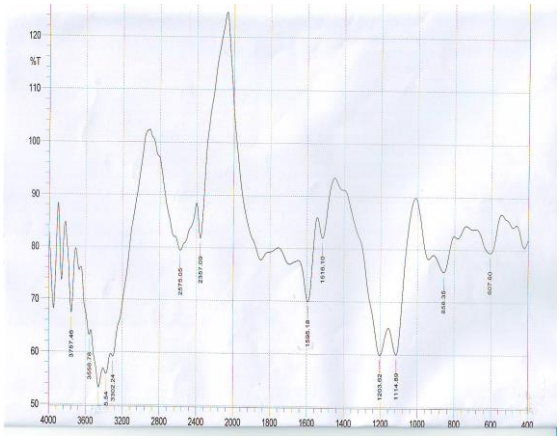


Fig (3) IR spectrum of the ligand



Fig(4) IR spectrum of Co(II) complex



Fig(5) IR spectrum of Cu(II) complex

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تحضير ودراسة الخواص الطيفية لمعقدي الكوبلت الثنائي والنحاس الثنائي مع ليكاند 2- (1- فنيل – 2,3 – ثنائي مثيل -4- أمينو -5- بايرازولون) ازو ريسورسينول

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الخلاصة :

تضمن البحث تحضير صبغة الأزو 2-(1- فنيل-2,3-ثنائي مثيل-4-امينو)-5- بايرازولون أزو ريسورسينول من خلال التفاعل الديدزة بين(1- فنيل-2,3-ثنائي مثيل-4-امينو-5- بايرازولون) والريسورسينول، وأستخدمت هذه الصبغة في تحضير معقدات لايونات العناصر(كوبلت(II) والنحاس(II)) وتم تشخيص المركبات المحضرة بواسطة تقنيات الأشعة المرئية – فوق البنفسجية و الأشعة تحت الحمراء .