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Synthesis and Spectral Study of New Azo - Azomethine Dyes and its Copper (II) Complexes Derived from Resorcinol, 4-Aminobenzoylhydrazone and 4-Amino antipyrine

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Abstract

Four new azo dyes **L**1, L2, L3 and **L**4, were prepared by linking benzaldehyde *p*-aminobenzoylhydrazone (**3**), *p*-hydroxybenzaldehyde *p*-amino- benzoylhydrazone (**4**), naphthaldehyde *p*-aminobenzoylhydrazone (5) and *p*-methoxybenzaldehyde *p*-aminobenzoylhydrazone (6) to resorcinol and through diazo-coupling reactions. Mixed-ligand dinuclear complexes with general stoichiometry $[Cu_2L(\text{amino antipy.})_2]Cl_2$ (11, 12, 13 and 14) was synthesed from azo ligands and bidentate ligand (4-aminoantipyrine) with copper. The structures of both azo dyes and their complexes were identified by elemental analyses (C.H.N), FTIR, ^{1}H-NMR, UV-Vis, atomic absorbtion and magnetic susceptibility.

Keywords: Azo-dyes, copper(II) complexes, hydrazone, mixed-ligand.

Introduction

p-Acceptor ligands such as azo-containing compounds or an imines are capable of stabilizing metals in formally low oxidation states [1,2].

4-Aminobenzoylhydrazone contain imine group (schiff's bases) which are considered as ‘privileged ligands’ have the ability to stabilize different metals in different oxidation states and thus regulate the performance of metals in a large variety of catalytic transformations [3]. The catalytic activity of the Schiff base complexes is highly dependant on the environment about the metal center and their conformational flexibility [4]. Therefore it is to be expected that the introduction of bulky substituents near the coordination sites might lead to low symmetry complexes with enhanced catalytic properties [5].

The well-known Cu (II) ion forms a series of coordination compounds with well defined structures [6]. It plays an important role in the numerous biological processes that involve electron transfer reactions or the activation of some anti-tumor substances [7].

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for a long time. [8]

In this work, we synthesized four new azo-dyes by bringing together two important chemical compounds, resorcinol, hydrazone, copper (II) complexes by using these dyes and 4-amino antipyrine. The chemical structures of both azo dyes and azo metal complexes were spectral studied.

Experimental

Instrumental

Melting points were determined on a Gallenkamp melting point apparatus. Infrared spectra (in KBr pellets were recorded with a 8300 shimadzu spectrometer). ^{1}H-NMR spectra were recorded on a *Brüker ACF 300* spectrometer operating at 300MHz in DMSO-d^6 using TMS as an internal reference. The electronic spectra of the ligands and complexes were recorded on a UV-1650 Shimadzu spectrophotometer in ethanol. Magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility Balance of Burke Magnet B.M.6, England. Metal concentrations were determined with a GBC Avanta Atomic Absorption Spectrometer in solution. Elemental (C, H and N) analyses were carried out on a Perkin-Elmer automatic equipment model 240B.

Schiff's Bases: 4-Aminobenzohydrazide (2) was prepared by refluxing ethyl *p*-aminobenzoate (1) (0.01 mol, 1.51 g) with hydrazine hydrate (2.5 ml) for 4 hrs.[9], then the prepared compound (2) (0.01 mol) and appropriate aldehyde (0.01 mol) with two drops of glacial acetic acid were heated under reflux in ethanol for 4-6 hrs. The Schiff's bases crystallized out on cooling and were recrystallised from ethanol for purification. Melting points are illustrated in Table (1).

Table (1)
Physical data of the prepared compounds.

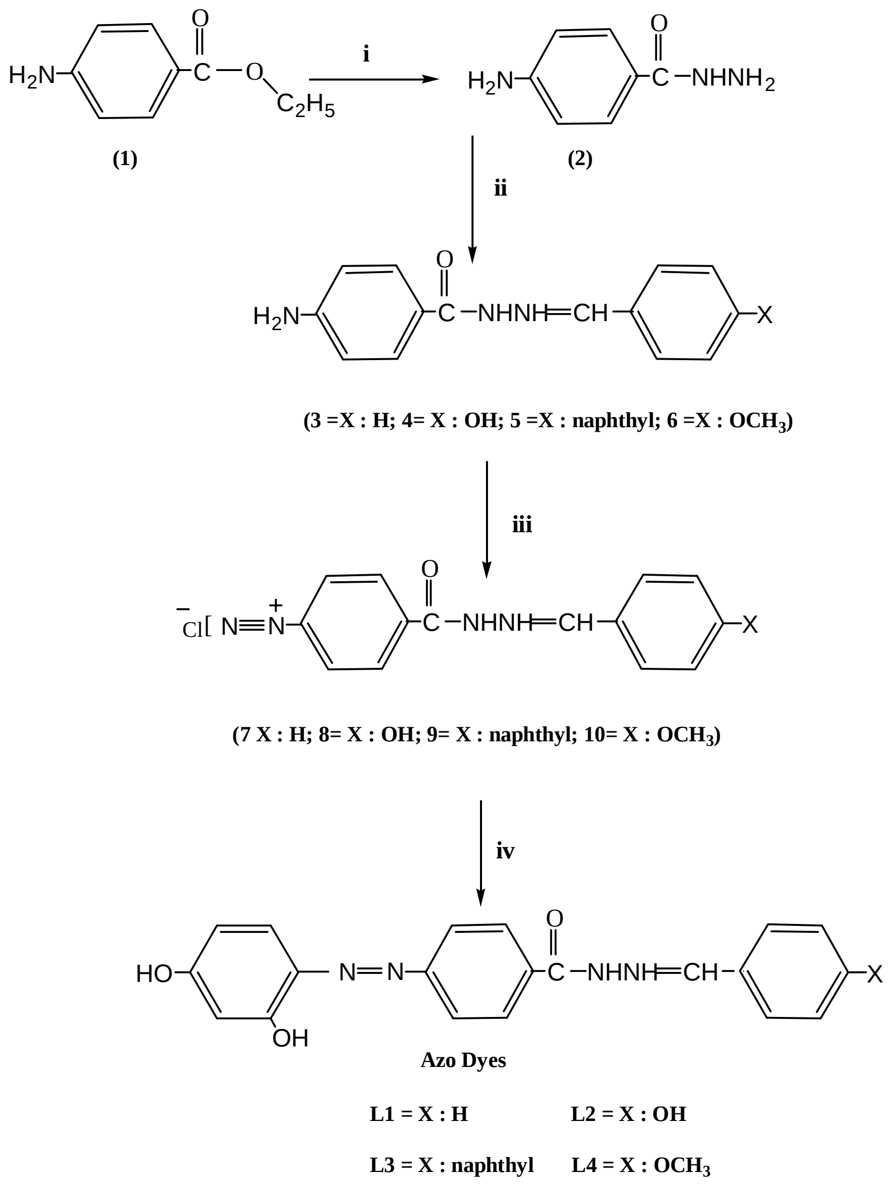
Dyes	***Formula***	***Mp. (°C)***	***Yield (%)***	***Color***	***Calculated (found) %***			
					C	***H***	***N***	***Cu***
L1	$C_{20}H_{17}N_4O_3$	265-267	71	Red				
11	$C_{42}H_{36}N_{10}O_5Cl_2Cu_2$	220-224	78	Black	52.61 (52.58)	3.75 (3.66)	14.61 (14.57)	13.25 (13.18)
L2	$C_{20}H_{16}N_4O_4$	215-219	68	Dark red				
12	$C_{42}H_{36}N_{10}O_6Cl_2Cu_2$	261-264	76	Black	51.75 (51.79)	3.69 (3.61)	14.37 (14.42)	13.04 (12.98)
L3	$C_{24}H_{21}N_4O_3$	173-175	72	Brown				
13	$C_{46}H_{39}N_{10}O_5Cl_2Cu_2$	250-255	80	Green	54.71 (54.76)	3.86 (3.90)	13.87 (13.82)	12.58 (12.64)
L4	$C_{21}H_{19}N_4O_4$	120-125	69	Brown				
14	$C_{42}H_{38}N_{10}O_6Cl_2Cu_2$	280-284	75	Green	51.64 (51.59)	3.89 (3.75)	14.34 (14.48)	13.01 (12.93)

Diazotization

Benzaldehyde 4-aminobenzoyl-hydrazone **(3),** 4-hydroxybenzaldehyde 4-aminobenzoylhydrazone **(4)**, *p*-naphthaldehyde *p*-aminobenzoylhydrazone (5) and *p*-methoxybenzaldehyde *p*-aminobenzoylhydrazone (6) (0.01 mol) were dissolved in 5 mL of 2 M HCl. The solution was then cooled to 0-5 °C in an ice-bath and maintained at this temperature. Sodium nitrite (0.005 mol, 0.345 g) solution in water (5 ml) was then added dropwise. Stirring was continued for 30 min to produce diazonium salts **7, 8, 9** and **10** at the same temperature [10].

Preparation of 4-[2´,4´-dihydroxyphenyl-1-yl)diazenyl]-N´-[phenyl-methylene]benzohydrazide (L1), 4-[2´,4´-dihydroxy phenyl-1-yl)diazenyl]-N-[4´´hydroxyphenyl)-methylene]benzohydrazide (L2), 4-[2´,4´dihydroxyphenyl-1-yl)diazenyl]-N-[naphthal-methylene]benzohydrazide (L3) and 4[2´,4´-dihydroxyphenyl-1-yl)diazenyl]-N-[4´´methoxyphenyl)methylene]benzohydrazide(L4)

The diazonium solution of **7, 8, 9** and **10** was added portion wise to the coupling component solution prepared by mixing a suspension of resorcinol (0.005 mol, 0.55 g) in (40 ml) of water with sodium carbonate (0.015 mol, 1.6 g) dissolved in (40 ml) of water. During the procedure the pH value was maintained within 9-10, and the temperature at 0-5 °C. The mixture was stirred for 6 hrs., and then the pH value was decreased to ~6. The mixture was left overnight. The precipitated crude dyes were collected by filtration, and washed with water, ethanol, and acetone.



Scheme (I) i = $NH_2NH_2.H_2O$, reflux 4 hrs.; ii= benzaldehyde, p-hydroxybenzaldehyde, naphthaldehyde, or p-anisaldehyde, EtOH, HOAc, reflux 1 hr.; iii) $NaNO_2$, HCl, 0-5° C; iv) resorcinol, Na_2CO_3, 0-5° C, 6 hrs.

Preparation of copper (II) complexes (11, 12, 13 and 14)

To a solution of $CuCl_2.2H_2O$ (0.002 mol, 0.35 g) in methanol (10 ml) was added dropwise a solution of 4-amino antipyrine (antipyr) (0.002 mol, 0.406 g) in (10 ml) of methanol with constant stirring. The resulting colored suspension was stirred and heated for 15 min. Then 1 mmol of ligand [**L1** (0.001 mol, 0.361 g for complex **11**) or **L2** (0.001 mol, 0.377 g for complex **12**)] or **L3** (0.001 mol, 0.394 g for complex **13**)] or **L4** (0.001 mol, 0.391 g for complex **14**)] dissolved as a suspension in the same solvent (25 ml) was added and the resulting mixture was refluxed for 5 hrs. The colored precipitate was filtered off and washed several times with methanol and dried in vacuo [11].

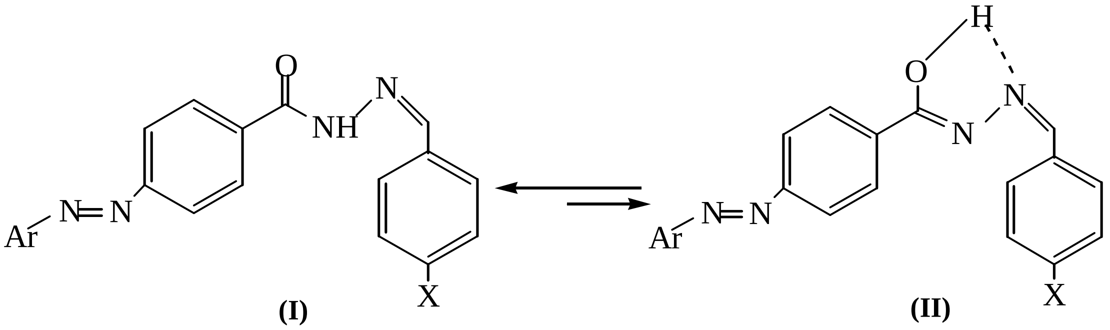
Results and Discussion

The infrared spectra of azo-dyes show intense bands appearing at 1667.0 cm^{-1} for L1, 1675.5 cm^{-1} for L2, 1654.2 cm^{-1} for L3 and 1659.7 cm^{-1} for L4. These peaks are attributed to carbonyl group of the amide group [12]. A broad hydroxyl (-OH) peak is observed within the region 3207-3338 cm^{-1}. The low frequency and the broadening of these bands suggest that these ligands have a strong hydrogen bonding (O-H…..N) in the solid state.[7]The peaks appearing in the region 1598 - 1610 cm^{-1} are attributed to ν(C=N) stretching vibration. The peaks appearing in the region 1422-1453 cm^{-1} are attributed to ν(N=N) stretching vibration [13]. The band belonging to ν (N-H) stretching vibration observed in the region 3433-3462 cm^{-1} [13]. The hydrazone side of the azo-dyes can be exist in keto (**I**) or enol (**II**) tautomeric form in the solid state (Scheme II).[14] The absorption of the strong ν(C=O) absorption band around 1676-1623 cm^{-1} in the infrared spectra of the azo dyes suggests that the hydrazone side of the azo-dyes is in the keto form (**I**) in the solid state.[15] The other characteristic peaks such as IR data of these compounds are given in Table (2). These data are in agreement with those previously reported for similar compounds.[16]

^{1}H-NMR (ppm) L1: 14.20 (s, 1H, O-H….N), 11.12 (s, 1H, N-H), 8.53 (s, 1H, N=CH), 9.20 and 9.10 (s, 1H, OH), 7.6 (s, 5H, Ar-H), 8.01 (d, 2H, Ar-H), 7.42 (d, 2H, Ar-H), 7.5 (d, 2H, Ar-H), 6.86 (s, 1H, Ar-H). UV (λ*max*, nm, ethanol): 214, 321, and 424. ^{1}H-NMR (ppm) L2: 15.21 (s, 1H, O-H· · ··N), 11.20 (s, 1H, N-H), 9.89 (s, 1H, O-H), 9.21 and 9.08 (s, 1H, OH), 8.22 (s, 1H, N=CH), 8.2 (d, 2H, Ar-H), 8.00 (d, 2H, Ar-H), 7.7 (d, 2H, Ar-H), 7.5 (d, 2H, Ar-H), 7.4 (d, 2H, Ar-H), 7.2 (d, 2H, Ar-H), 6.89 (s, 1H, Ar-H). UV (λ*max*, nm, ethanol): 222, 327, and 420. ^{1}H-NMR (ppm) L3: 14.61 (s, 1H, O-H· · ··N), 11.10 (s, 1H, N-H), 9.23 and 9.06 (s, 1H, OH), 8.32 (s, 1H, N=CH), 7.6 – 8.1 (m, 7H, Ar-H), 8.32 (d, 2H, Ar-H), 8.01 (d, 2H, Ar-H), 7.65 (d, 2H, Ar-H), 7.02 (s, 1H, Ar-H). UV (λ*max*, nm, ethanol): 224, 325, and 431.

^{1}H-NMR (ppm) L4: 14.66 (s, 1H, O-H· · ··N), 11.22 (s, 1H, N-H), 9.11 and 8.96 (s, 1H, OH), 8.35 (s, 1H, N=CH), 8.31 (d, 2H, Ar-H), 8.22 (d, 2H, Ar-H), 7.83 (d, 2H, Ar-H), 7.79 (d, 2H, Ar-H), 7.4 (d, 2H, Ar-H), 6.92 (s, 1H, Ar-H), 3.86 (s, 3H, OCH$_3$). UV (λ*max*, nm, ethanol): 224, 340, and 412.

The tautomeric keto forms of the dyes are also indicated by ^{1}HNMR spectroscopy. The enolic OH signals of the enol forms of the compounds are not observed while the amide NH signals of the keto forms appear around 11.10-11.22 ppm.



Scheme (II) Tautomeric forms of the hydrazone moiety of the azo-dyes.

Table (2)
The IR spectral data of the azo-dyes and their complexes, (KBr, cm^{-1}).

Compound No.	*υ (N-H)*	*υ (O-H)*	*υ (C-H alph.)*	*υ (N=CH)*	*υ (C=O)*	*υ (N=N)*
L1	3435.1	3321.8	2943.8	1604.7	1667.0	1453.5
11	3344.4	3214.8	2927.7	1600.8	1623.3	1440.7
L2	3433.7	3215.1	2937.1	1610.3	1675.5	1438.6
12	3233.5	3170.8	2929.7	1596.9	1676.0	1424.6
L3	3458.8	3207.4	2927.7	1602.7	1654.2	1429.2
13	3225.1	3122.9	2918.6	1612.3	1670.5	1445.3
L4	3462.0	3338.6	2960.2	1598.9	1659.7	1422.4
14	3351.3	3260.1	2963.6	1600.8	1665.7	1448.2

The ^{1}H-NMR spectra of azo-dyes show a singlet due to the hydrogen bonded OH proton in the region of 15.11-14.20 ppm. It is well known that hydrogen bonded OH proton resonance appears at a lower field than that of NH proton resonance [13]. Therefore, it may be concluded that these compounds also exist in the azo form (III) in solutions.[11] On the other hand, the resonance of the phenolic OH proton of all ligands are observed as a singlet at a relatively higher field, at 9.93 ppm and 9.94 ppm, respectively. Two singlet peaks between 11.52 and 11.90 ppm owing to NH protons, at the 1- and 3- positions of pyrimidine ring, are observed for **L**1 and **L**3 dyes. The proton of the amide group (NH) at the hydrazone side appears also as a singlet in the region of 11.35-11.87 ppm for all azo-dyes.[12] The other resonances observed for azo-dyes are given in the Experimental section. The results of the infrared data (Table (2)) and 1HNMR are in good agreement with those required for the proposed structure. Uv-Vis. Spectra of the azo-dyes have three strong absorption bands (Fig.(1)), the shortest wavelength, appearing at 222-224 nm, may be attributed to $\pi \rightarrow \pi^*$ transition of the benzenoid moiety [17] of the compounds and intra-ligand $\pi \rightarrow \pi^*$ transition. The second band, observed in the region of 321-340 nm, is attributed n→ π^* electronic transition of the –N=N- group [18]. The third band, appearing in the visible region (412-431 nm), can be assigned to $\pi \rightarrow \pi^*$ transition involving the whole electronic system of the azo-dyes [18].

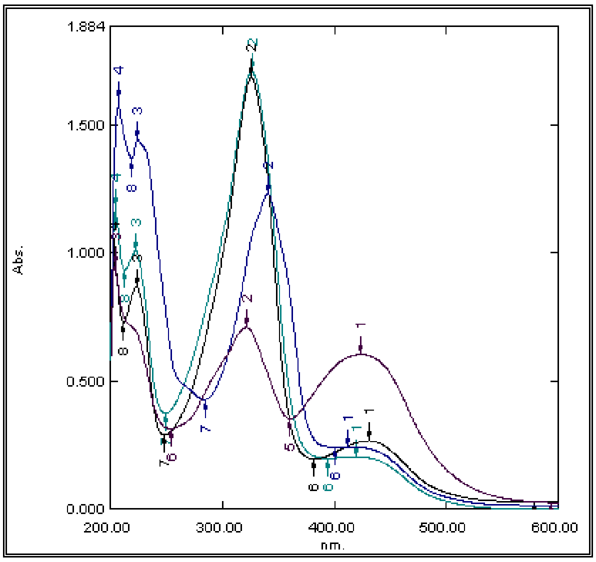


Fig. (1) Electronic Absorption spectra of azo-dyes.

Structure identification of azo-metal complexes

The reaction of copper (II) chloride with 4-aminoantipyrine azo-dyes in methanol gives mixed-ligand dinuclear copper (II) complexes with the general formula $[Cu_2L(antipy)_2]Cl_2$. Magnetic susceptibility, and IR spectroscopies were used to characterize the azo-copper complexes. The characteristic IR frequency values of the azo-dyes and their copper complexes are given in Table (2). The IR spectra of the complexes showed significant differences from those of the free dyes. In the IR spectra of the complexes, two strong carbonyl absorptions were observed in the region of 1751-1663 cm^{-1}. The third carbonyl absorption band and υ(C=N) stretching band at the hydrazone moiety of the azo-dyes appearing in the spectra of metal free azo compounds were not observed but a new band appeared between 1607 and 1620 cm^{-1} probably due to >C=N-N=C< stretching vibration suggesting that the NH proton of the hydrazone side of the dyes was lost via enolazition and the resulting enolic oxygen and the azomethine nitrogen are involved in coordination. The IR spectra of the complexes derived from **L3** and **L4** show a broad band at 3437 cm^{-1} and 3407 cm^{-1}, respectively, which can be attributed to the free OH stretching, indicating non-involvement of the phenolic OH group in coordination.[19] The movement of υ(N=N) stretch of the complexes to relatively lower energy ~10 cm^{-1} compared to that of free dyes indicates coordination via the N=N group.[20] The *υ*(C=N) vibration of the phenanthroline ring could not be assigned since the spectra were complicated by many bands in the 1300-1600 cm^{-1} region. On the basis of IR spectral data we concluded that the barbituric acid side of azo-dyes exists in diketoazo form during complexation, while the hydrazone side exists in enol tautomeric form. In the complexes, the azo-dyes act as dianionic tetradentate ligands (Fig.(2)).

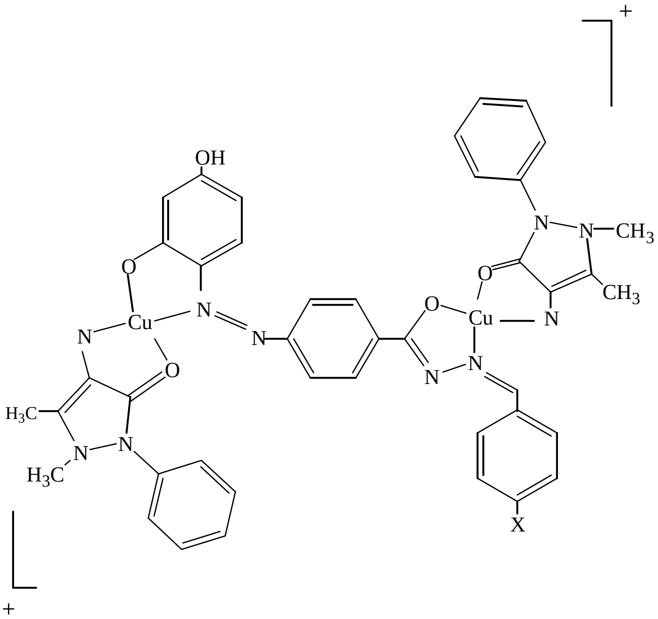


Fig.(2) Proposed structure for the mixed-ligand dinuclear complexes.

The magnetic moment data of the solid state complexes at room temperature are reported in Table (1). The magnetic moment values of the copper (II) complexes are in the region of 2.06-1.90 *μB* at 298 K. It is seen that these magnetic moment values of copper complexes are slightly higher than the theoretical value of 1.73 *μB* for one d^9 copper ion, while they are also lower than that expected for dinuclear copper (II) complexes. These subnormal magnetic moment values of the dinuclear complexes may be explained by a weak antiferromagnetic intramolecular interaction since this situation can occur when two equivalent metal ions are coupled via an exchange interaction in a polynuclear complex.[21]

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الخلاصة

يتضمن هذا البحث تحضير اربع مركبات آزو جديدة (L1, L2, L3 and L4) عن طريق ارتباط الريسورسينول مع p-benzaldehyde p-aminobenzoylhydrazone (**3**), p-hydroxybenzaldehyde p-amino-benzoylhydrazone (**4**), naphthaldehyde p-aminobenzoylhydrazone (5) and p-methoxybenzaldehyde p-aminobenzoylhydrazone (6) من خلال تفاعل الازدواج.

تم تحضير معقد mixed ذو الصيغة $[Cu_2L(\text{amino antipy.})_2]Cl_2$ من مفاعلة النحاس الثنائي مع صبغة الازو وليكند ثنائي الارتباط وهو الامينو الانتيبايرين. تم دراسة تراكيب الصبغات والمعقدات المحضرة بأستخدام تحليل العناصر C.H.N. ومطيافية الاشعة تحت الحمراء و الرنين النووي المغناطيسي ومطيافية الاشعة الفوق بنفسجية والامتصاص الذري ودراسة الحساسية المغناطيسية.