

PREPARATION OF SCHIFF BASES COMPLEXES DERIVED FROM ACETYL ACETONE WITH BENZIDINE, P-PHENYLENEDIAMINE, P-TOLUIDINE AND ANILINE WITH SOME TRANSITION METAL IONS (II) AND (III)

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ABSTRACT

Schiff bases are highly important in industrial and biological fields. The present study has been carried out to investigate the geometrical structure of complexes with M(II) and M(III) ions. The complexes were prepared by condensation of acetyl acetone with benzidine (L), P-phenylene diamine (L₁), P-toluidine (L₂), and aniline (L₃) using different techniques such as elemental analysis, molar conductivity, thermal analysis, IR spectra and magnetic properties.

INTRODUCTION

Schiff bases derived from condensation of aromatic aldehydes, aliphatic or aromatic amines represent an important series of widely studied organic ligands (Holmi *et al.*, 1966 and Yamada, 1966).

Schiff bases compounds are used as chelating agents and have wide applications in biological system and dyes (El-Saied *et al.*, 1989; El-Saied, 1989; El-Bahnasay *et al.*, 1994 and Gaber *et al.*, 1991).

The transition metal complexes of Schiff bases resulted from the condensation of aldehyde group with amine group; Osipov *et al.*, (1967) has studied the luminescent and photochemical properties of Cu (II) complexes of Schiff base derived from some substituted salicyl aldehydes or 2-amino pyridine; Yamada and Yamanouchi (1969) and Parashar (1988) had studied complexes of Cu (II), Zn (II), Pd (II), Co (II) and Ni (II) with the same Schiff base. Salicylaldehyde and anthranilic acid compounds are capable to form chalets with transition metal ions in the form of Schiff bases. The unsymmetrical Schiff base; 1,2-acetonaphthone acetylacetone-ethylene-diamine and its complexes with divalent transition metal ions such as Ni(II), Cu(II) and Pd(II) have been prepared and characterized by elemental analysis, conduct metric measurements, infrared and electronic spectra (Boghaei *et al.*, 2000). Some Schiff base chalets derived from salicylaldehyde with anthranilic acid or o-aminophenol have been prepared and investigated with divalent transition metal ions (Co, Ni and Cu). The chalets were subjected to different chemical analyses using elemental analysis, molar conductance measurements, thermo gravimetric analysis, infrared, electronic and electron paramagnetic resonance spectra. All the analyses show the presence of square planar geometry.

Ayad *et al.* (1991) prepared and studied copper complexes of Schiff bases derived from 3-aminopyridine or 2- amino pyridine, their derivatives with salicylaldehyde and O- hydroxyl naphth aldehyde had been synthesized.

Schiff bases derived from sulphonyl amide have wide applications in biological, clinical and pharmacological system (Ayad *et al.*, 1991; Charles *et al.*, 1971; Hosler *et al.*, 1981 and Meffin *et al.*, 1977).

The complexes of selenium (IV) and tellurium (IV) with sulphonyl amide Schiff bases had been tested for bacteriostatic, anti-inflammatory and hypoglycemic activities (Schmide *et al.*, 1975).

Donia and Ayad (1993) studied the thermal behavior of some crystal solvents of square pyramidal Mn(II) complexes. A number of Mn(III) Schiff base derived from O-phenylenediamine and ethylenediamine complexes (1: 1) had been prepared and characterized (Donia *et al.*, 1991).

Raman *et al.* (2002) studied the synthesis of a new type of tetradentate ligand formed by the condensation of O-phenylenediamine with acetoacetanilide. Some Schiff base chelates derived from salicylaldehyde with anthranilic acid or O-aminophenol have been prepared and investigated with divalent transition metal ions Co, Ni, and Cu. All the analyses show the presence of square planar geometry (Nraman *et al.*, 2002).

MATERIALS AND METHODS

Materials :

The chemicals used in the present study are analytical reagents included acetyl acetone, benzidine, aniline, P-phenylene diamine, P-toluidine, ethyl alcohol, cobalt chloride, zinc chloride chromium chloride, cupric chloride and ferrous chloride.

Preparation of organic ligand :

Refluxing an equimolar mixture of benzidine (L), P-phenylenediamine (L₁), P-toluidine (L₂) and aniline (L₃) with 20-30 ml acetyl acetone respectively in 20 ml ethanol for 10- 12 hrs. A yellow product (L), brown product (L₁ – L₂ – L₃) separated which was left to coagulate and then filtered off, washed by 10 ml of ethanol three times followed by 20 ml diethyl ether. The solid product was recrystallized by 80 % aqueous ethanol.

Preparation of complexes :

An ethanolic 20 ml solution of Schiff base 1.74gm L, 0.55gm L₁, 3.64gm L₂ and 1.75gm L₃ were mixed with metals(II) chlorides respectively in ethanol solution and the mixture was refluxed for 6 hrs. The refluxed material was concentrated and cooled at room temperature. The solid product obtained was filtered off, washed with 50 ml ethanol and dried .

Melting point (M.P), molar conductivity, elemental analysis, thermal analysis, IR spectra and magnetic moments of ligand and Schiff bases complexes using Philip Hars No. B/A-22, HANNA Instrument (HI8733), Perkin – Elmer Model 2400 elemental analyzer, Shimadzu DT-30 thermal analyzer with heating rate of 10 °C /min, Perkin–Elmer 1430 spectrophotometer and a modified Guy type magnetic balance Hertz SG8SHJ, respectively.

RESULTS AND DISCUSSION

The Schiff base and complexes under investigation were formed by the reaction between acetyl acetone, benzidine (L), P-phenyldiamine (L₁), P-toluidine (L₂) and aniline (L₃). The Schiff base complexes were formed by the reaction between these ligands with some 3d- transition metal ions [Cu(II), Ni(II), Co(II), Zn(II), Cr (III) and Fe(III)]. The elemental analysis, color, M.P, and molar or conductivity of ligands and Schiff base complexes are given in Table (1). The obtained data reveal that, the complexes are formed in the ratios (1:1) and (1:2) [L: M]. These Stoichiometric ratio of complexes have the chemical formula of the types: [(L)₂ MX_n.n H₂O] nH₂O n C₂H₅OH, [(L)₂M], [L M₂Xn .nH₂O] nH₂O, [L MX_n] n H₂O and [L MX_n] nH₂O n C₂H₅OH. Where L: Ligand (L₁-L₂-L₃), M: Transition metal ions, X : Chloro and n: no. of water molecules and ethanol molecules.

The conductivities of (10⁻³M) solution in chloroform of the given complexes were measured. The molar conductance is calculated by applying the equation :

$$\Lambda_m = K / C$$

Where K : specific conductance.

C: the concentration of the complexes solution.

The molar or conductivity of the complexes up to 1-4 Cm² mol⁻¹ measured for 10⁻³ M solution in DMF or chloroform indicates the presence of non electrolytic nature. The conductance values in Table (1) taken as an evidence for presence of non- electrolytic nature. The molar conductance values of the complexes show that no inorganic anions (OH⁻) outside the coordination sphere. The non conducting character of these complexes in chloroform solvent show the existence of only one ion and the metal ion in the coordination sphere. Table (2) shows the characteristic IR spectra bands of the ligands and their complexes. The spectra of the free ligand exhibit a strong broad band in the 2442- 3445 Cm⁻¹ region is assigned to the OH⁻ group of the acetyl acetone. The strong absorption in the 1605-1741 Cm⁻¹ region is assigned to the azomethine group present in the Schiff base and the ligand has absorption bands in the 1551-1569 Cm⁻¹ region which is assigned to v(C=C). The IR spectra of the (L)₂ Cu₄Cl₄ .3H₂O, (L)₂ Ni, (L)₂Co.1/2C₂H₅OH, (L)₂Fe₂Cl₂.1/2C₂H₅OH, (L)₂Cr₂Cl₂/2H₂O, (L)Cu₂Cl₂.2H₂O.3H₂O, (L)Ni₂Cl₂.2H₂O.4.5H₂O, (L)ZnCl₂.1.5H₂O and (L)Cu₂Cl₂.2H₂O.4H₂O complexes exhibit bands at 3132, 3440, 3426, 3360, 3411, 3203, 3332, 3336 and 3345 Cm⁻¹ regions, respectively, which attributed to presence of OH⁻ group and it appeared at 3442 Cm⁻¹ region of the free ligand which suggested that the OH⁻ group is involved in chelation with the metal ion. The above complexes showed two bands at 582 and 445, 514 and 440, 517 and 306, 581 and 498, 581 and 365, 514 and 457, 583 and 514, 516 and 448, 518 and 446 and 582 and 331 Cm⁻¹ regions which attributed to v (M-O) and (M-N) vibration, respectively. The IR spectra data show that the coordination to the metal atom is through the oxygen atom of the acetyl acetone. The IR spectra of the (L₁)₂Cu₂Cl₄.4H₂O, (L₁)₂Cu₂Cl₂.2H₂O, (L₂) CuCl₂.4 1/2H₂O, (L₂) CuCl₂.4 1/2H₂O

and (L₃) CuCl₂.1/2 C₂H₅OH 1. 1/2H₂O complexes exhibit bands at 3345, 3337 and 3344 Cm⁻¹ regions, respectively, which attributed to presence of OH⁻ group and it appeared at 3442 Cm⁻¹ region of the free ligands which suggested that the OH⁻ group is involved in chelation with the metal ion. The above complexes showed two bands at 582 and 331, 520 and 382, 517 and 306, 507 and 714 and 513 and 332 Cm⁻¹ regions which attributed to ν (M-O) and (M-N) vibration, respectively.

Table (1): The elemental analysis, color, M.P and molar conductivity of ligands and Schiff base complexes.

Complexes Ligand	Color	M.P °C	M.Wt	Condu- ctance Ω Ms.	Elemental analysis					
					N %		H %		C %	
					C	F	C	F	C	F
L	Yellow	275	348	-	8.04	8.3	6.89	7.06	75.8	74.9
(L) ₂ Cu ₄ Cl ₄ .3H ₂ O	Black	240	1142	4.1	4.4	5.4	4.3	4.1	46.2	46.1
(L) ₂ Ni	Reddish	185	754	2.2	7.2	7.5	6.3	7	69.8	71.5
(L) ₂ Co1/2 C ₂ H ₅ OH	Brown	170	773.5	3.6	7.2	7.5	6.33	7	69.8	71.58
(L) ₂ Fe ₂ Cl ₂ 1/2 C ₂ H ₅ OH	Black	200	898	3.4	6.2	6.8	5.3	5.4	60.13	59.14
(L) ₂ Cr ₂ Cl ₂ 1/2H ₂ O	Gray	180	876	4.0	6.4	6.7	5.1	5	60.2	59.8
(L) Cu ₂ Cl ₂]3 H ₂ O	Black	300<	636	3.1	4.4	4.8	4.1	3.9	41.5	41.1
(L) Ni ₂ Cl ₂ .2H ₂ O 6 _{1/2} H ₂ O	Yellow	300<	651	3.4	4.3	4.1	4.1	4.3	40.5	40.5
(L) ZnCl ₂ 1 _{1/2} H ₂ O	Gray	210	511	3.0	5.4	5.4	5.4	4.52	51.16	51.49
(L) Cu ₂ Cl ₂ .2H ₂ O 4H ₂ O	Brown	300<	653	3.1	4.5	4.5	6.8	6.5	42.8	42.7
L ₁	Brown	145	274	-	10.2	6.85	7.09	7.4	70	75
L ₂	Brown	75	182	-	7.69	7.09	8.24	8.26	73.2	74.7
L ₃	Brown	50	175	-	8.0	7.93	7.4	7.51	75.4	74.5
(L) ₁) ₂ Cu ₂ Cl ₄ .4H ₂ O	Black	250	886	3.2	6.3	5.4	4.5	3.9	43.3	43.2
(L) ₁) ₂ Cu ₂ Cl ₂ .2H ₂ O	Black	300<	505	3.35	4.8	4.8	4.3	4.1	33.2	33.1
(L) ₂) CuCl ₂ .4 1/2H ₂ O	Black	100	404.3	3.5	3.46	3.6	5.7	5.4	35.6	36.3
(L) ₃) CuCl ₂ .1/2 C ₂ H ₅ OH 1. 1/2H ₂ O	Black	300<	359.5	4	3.8	5.2	5	4.75	40.2	39.5

Table (2): The characteristic IR spectra bands of the ligands and their complexes.

Ligand / Complexes	ν M-N	ν M-O	ν C=N	ν C=C	ν OH
L	-	1741	1741	1551	3442
(L) ₂ Cu ₄ Cl ₄ .3H ₂ O	445	1614	1614	1868	3132
(L) ₂ Ni	440	1503	1503	1742	3440
(L) ₂ Co1/2 C ₂ H ₅ OH	306	1502	1502	1774	3426
(L) ₂ Fe ₂ Cl ₂ 1/2 C ₂ H ₅ OH	498	1492	1492	1727	3360
(L) ₂ Cr ₂ Cl ₂ 1/2H ₂ O	365	1529	1529	1794	3411
(L) Cu ₂ Cl ₂]3 H ₂ O	457	1421	1421	1909	3445
(L) Ni ₂ Cl ₂ .2H ₂ O 6 _{1/2} H ₂ O	541	1614	1614	1758	3399
(L) ZnCl ₂ 1 _{1/2} H ₂ O	448	1546	1546	1741	3332
(L) Cu ₂ Cl ₂ .2H ₂ O 4H ₂ O	446	1601	1601	1823	3336
L ₁	-	-	1611	1569	3424
L ₂	-	-	1742	1566	3423
L ₃	-	-	1605	1569	3445
(L) ₁) ₂ Cu ₂ Cl ₄ .4H ₂ O	331	582	1504	1869	3345
(L) ₁) ₂ Cu ₂ Cl ₂ .2H ₂ O	382	520	1616	1771	3346
(L) ₂) CuCl ₂ .4 1/2H ₂ O	713	507	1513	1603	3337
(L) ₃) CuCl ₂ .1/2 C ₂ H ₅ OH 1. 1/2H ₂ O	332	513	1599	1868	3444

Table (3) shows the thermal analysis (DTA and TG) of complexes under investigation, this measurements was carried out with complexes containing water molecules only. The TGA curves for the complexes showed mainly three regions of changes, the first corresponds to the dehydration of the complexes, i.e. elimination of water molecules which take place in two steps when the complexes contain both hydrated and lattice water. Actually, hydrated water is removed from molecules at lower temperature 21-100 °C, while lattice water are stable and volatilize above 130 °C. The DTA curves display broad endothermic peaks in TGA range 21-225 °C corresponding to dehydration and melting of complexes accompanied with partial decomposition by removed HCl or Cl₂. The last region in the TGA curves above 300 °C represents the decomposition of the complexes to the final product which is CuO usually such process take place over a wide range of temperature and the corresponding exothermic peaks in the DTA curves is rather broad. The magnetic moment of the complexes was calculated using the equation :

$$M = 2.84\sqrt{X_M T}$$

Where T: absolute temperature and X_M: molar susceptibility.

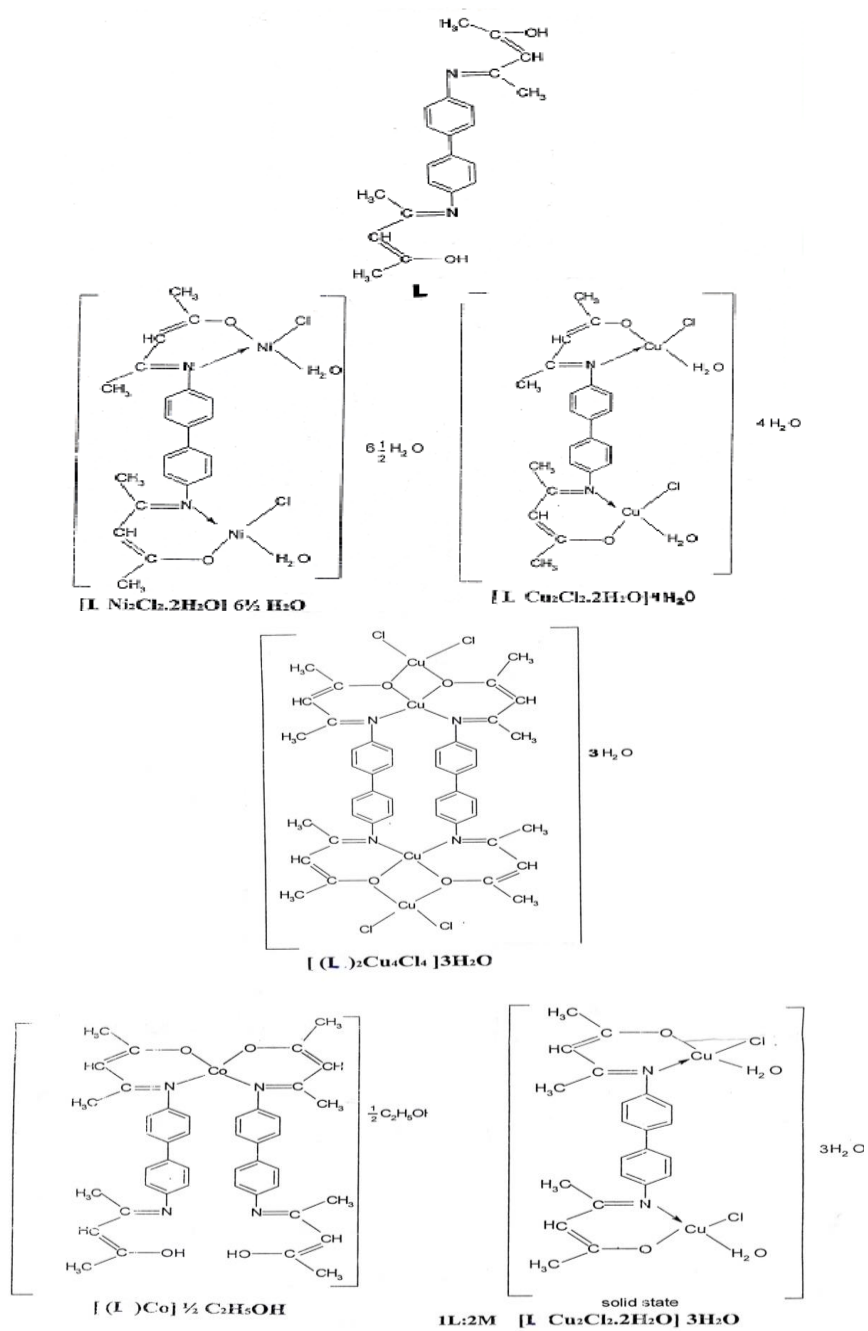
Table (3): Thermal analysis (DTA and TGA) of Cu+2 complex.

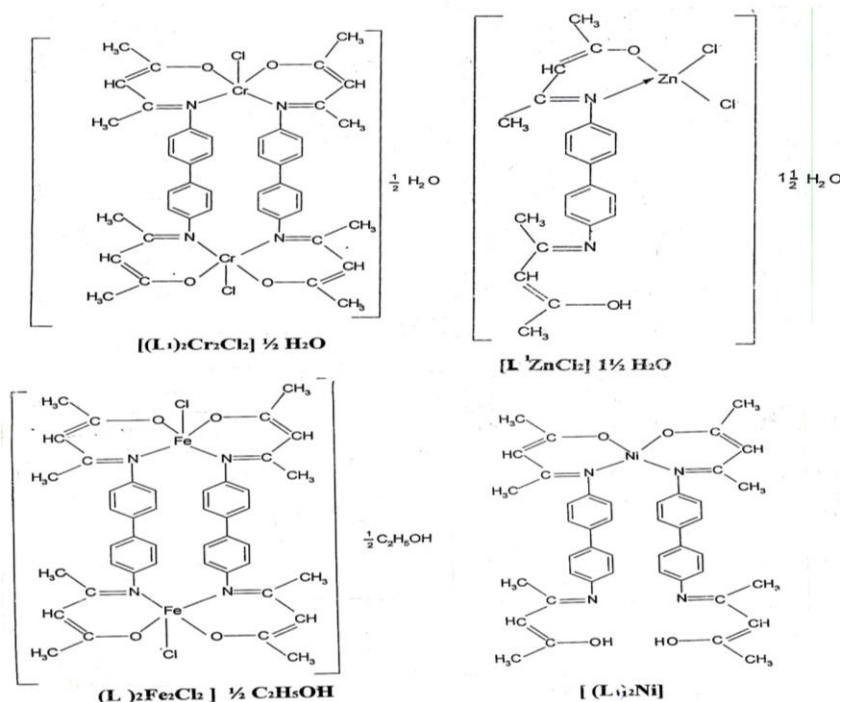
Complexes	Loss (%) TGA		DTA peaks	Temp. °C	Species
	Found	calc			
(L) ₂ Cu ₄ Cl ₄ .3H ₂ O	5.03	4.7	Endo.	100-21	3H ₂ O
(L) ₂ Cu ₄ Cl ₄ .3H ₂ O	11.5	11.7	Endo.	250-100	4HCl
(L) ₂ Cu ₄ Cl ₄ .3H ₂ O	14.7	14.5	Endo.	700-450	Resid
(L) ₁) ₂ Cu ₂ Cl ₄ .4H ₂ O	5.3	5.2	Endo.	130 -28	4H ₂ O
	14.8	14.5	Endo.	250	Melting and 4Cl
(L ₂) CuCl ₂ .4 1/2H ₂ O	5.6	6.6	Endo.	100 -24	4 1/2H ₂ O
	-	14.6	Endo.	250 - 225	Residue formation of
	-	-	Endo.	700 - 438	metal oxide

Table (4): Magnetic properties of complexes under investigation.

Geometry structure	μ _{eff}	Complexes
Octahedral	1.16 B.M	(L) ₂ Cu ₄ Cl ₄ .3H ₂ O
Square planer	0.0	(L) ₂ Ni
Tetrahedral	4.1 B.M	(L) ₂ Co.1/2 C ₂ H ₅ OH
Square planer	1.2 B.M	(L) ₂ Cu ₂ Cl ₂ .2H ₂ O 3H ₂ O
Tetrahedral	3.3 B.M	(L) NiCl ₂ . 2H ₂ O 6 1/2H ₂ O
Square planer and binuclear	1.1 B.M	(L) Cu ₂ Cl ₂ .2H ₂ O 3H ₂ O

The expected structure of the complexes is as follows :





REFERENCES

- Ayad, S.; A. Sallam and H.E. Mabrouk (1991). *Thermo Chimica Acta*, 189, 65.
- Boghaei, M.D.; Sabounchei S.J.S. and Rayati, S. (2000). *Synthesis Reactivity Inorganic Metal-Organic Chemistry*, 30, 1535.
- Charles, G. Ole and F.D. Robert (1971) J.B. Lippincott Company, PA.USA.
- Donia and Ayad (1993). *Monatsheftefur*, 124.
- Donia; Ayad and Issa (1991). *Transition Met. Chem.*
- El-Bahnasay, M.; R.M. El-Saied; A. Azzem and A.K. El-Sawaf (1994). *Polyhedron*, 13,1781.
- El-Saied, J. (1989). *Inorg. Chemic. Acta*, 165, 147.
- El-Saied, M.I.; Ayad and S.A. Aly (1989). *J. Trans. Met. Chem.*, 18, 147.
- Gaber, M.M.; Ayad and M.I. Ayad (1991). *Thermo Chemica Acta*, 176, 21.
- Holmi, G.W.; Everett and A. Chakravorty (1966). F.A. Cotton (Ed) *Proger. Inorg. Chem.*, Inter Science Publication, New York, Vol.7.
- Hosler, C.; T. Schanz; C.E. Hignite and D.L. Azarnoff (1980). *J. Invest*, 74, 15.
- Meffin, R.L.; R.F. Blasckke and M. Rowland (1977). *J. Pharm. Sci.*, 66, 135.
- Nraman; Ypitchaikaniraja and Kuland (2002). *Proc. Indian. Acad. Sci.*, 112(3), 98.
- Osipov, V.I. Minkin; D.Sh. Verkhovodov and M.I. Knyazhanskii (1967). *Russ. J. Inorg. Chem.*, 12, 814.

- Parashar, R.C.Sharma; A. Kumar and G. Mohan (1988). Inorg. Chim. Acta, 151, 201.
- Raman, Mthuraj; Ravichandran and Kuland (2002). Proc. Indian. Acad. Sci., 112.
- Sacconi, L. (1966). Coord. Chem. Rev., 1, 126.
- Schmide, T.P. Prishchep and N.A. Chenova (1975). IZV. Tomak Politekh. Inst., 156.
- Yamada (1966). Coord. Chem. Rev., 1, 415.
- Yamada and K. Yamanouchi (1969). Bull. Chem. Soc. Jpn., 42, 2562.

تحضير معقدات قواعد شيف باستخدام البنزيددين والأسيتيل أسيتون و بارا فينيل ثنائي أمين وباراطولودين والأنيلين مع أيونات بعض العناصر الإنتقالية ثنائية وثلاثية التكافؤ

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قواعد شيف ذات أهمية كبيرة في المجالات الصناعية والبيولوجية ، حيث تستخدم كإصباغ وكعوامل مخلبية لبعض الفلزات. وقد تم في هذا البحث دراسة قواعد شيف المشتقة من تفاعل البنزيددين والأسيتيل أسيتون وكلا من بارا فينيل ثنائي أمين وباراطولودين والأنيلين بعملية التكتيف ، ثم تفاعل هذه الليجانندات مع بعض أيونات العناصر الإنتقالية لتكوين معقدات قواعد شيف وتم التعرف عليها من خلال إستخدام التحليل العنصري والتوصيلية المولارية والتحليل الحراري وأطياف الأشعة تحت الحمراء والخواص المغناطيسية.

قام بتحكيم البحث

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