

Synthesis and Characterization of New Azo Dye Complexes with Selected Metal Ions

Amer J. Jarad

Department of Chemistry, Ibn-Al-Haithem Education College, University of Baghdad, Baghdad-Iraq.

Abstract

Coupling reaction of 2-amino benzoic acid with phenol gave the new bidentate azo ligand. The prepared ligand was identified by Microelemental Analysis, FT-IR and UV-Vis spectroscopic technique. Treatment of the prepared ligand with the following metal ions (Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}) in aqueous ethanol with a 1:2 M:L ratio and at optimum pH, yielded a series of neutral complexes of the general formula $[\text{M}(\text{L})_2]$. The prepared complexes were characterized using flame atomic absorption, (C.H.N) Analysis, FT-IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. The nature of the complexes formed were studied following the mole ratio and continuous variation methods, Beer's law obeyed over a concentration range (1×10^{-4} - 3×10^{-4} M). High molar absorptivity of the complex solutions were observed. The stability constant of the complexes have also been studied.

Keywords: Azo-dyes, azo-aromatic ligand, synthesis, azo complexes

Introduction

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^[1-3]. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium^[4-7], toner^[8,9], ink-jet printing^[10,11], and oil-soluble lightfast dyes^[12]. Recently, azo metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements and printing systems^[13]. In this respect an attempt has been made to synthesize and characterize a new azo bidentate ligand derived from 2-amino benzoic acid as diazo component, and phenol as coupling agent. The complexes of this ligand with some metal ions has also been studied and characterized physicochemically.

Experimental

Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV- 160A) Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a (Shimadzu, FTI R- 8400S) Fourier Transform Infrared Spectrophotometer (4000 - 400) cm^{-1} with samples prepared as KBr discs. Atomic absorption were obtained using a

(Shimadzu A.A-160A) Atomic Absorption /Flame Emission Spectrophotometer. Microelemental analysis (C. H. N) were performed in Al- al- Bayt University- Jordan using (Euro vector EA 3000A Elemental Analyser). Conductivities were measured for 10^{-3} M of complexes in ethanol at 25°C using (Philips PW-Digital Conductimeter). Magnetic susceptibilities were performed using (Brucker Magnet B. M. 6) instrument at 25°C . In addition melting points were obtained using (Stuart Melting Point Apparatus).

Materials and Reagents

The following chemicals were used as received from suppliers; cobaltous chloride hexahydrate 98.8%, nickel chloride hexahydrate 99.9%, copper chloride dihydrate 98%, zinc chloride 99% (Merck) 2- amino benzoic acid 98.8%, phenol 99% (B. D. H).

The pH of the medium (5-7.5) were adjusted with ammonium acetate –ammonia – glacial acetic acid buffer solution.

Solutions were made of the ligand (1×10^{-5} - 1×10^{-3} M) in absolute ethanol and same concentration range of metals salts in buffer solutions

Preparation of the Ligand

(0.34g, 1mmole) of 2- amino benzoic acid was dissolved in a mixture of (2 ml) sulphuric acid, (10 ml) ethanol and (10 ml) distilled water, and diazotized at 5°C with sodium

nitrite solution. The diazo solution was added dropwise with stirring to a cooled ethanolic solution of (0.23g, 1mmole) of phenol. (25 ml) of (1 M) sodium hydroxide solution was added to the dark colored mixture. The precipitate was filtered off and washed several times with (1: 1) ethanol: water, mixture then left to dry. The reaction is shown in Fig. (1). The physical properties and elemental analysis are listed in Table (1).

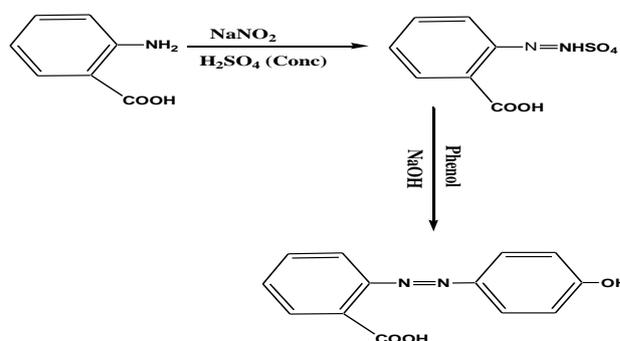


Fig.(1) Preparation of the Ligand.

Table (1)
Physical Properties and Elemental Analysis of the Ligand and Its Complexes.

Compounds	Color	M.P °C	Yield %	Analysis Calc.(Found)			
				M% (Metal)	C%	H%	N%
Ligand	Orange	210	88	-	64.46 (63.95)	4.13 (4.02)	11.57 (11.23)
[Co(L) ₂]	Brown	>360	80	10.90 (10.51)	60.70 (60.05)	3.50 (3.31)	10.34 (9.93)
[Ni(L) ₂]	Reddish Orange	>360	78	10.74 (10.04)	57.77 (57.12)	3.33 (3.01)	10.37 (10.07)
[Cu(L) ₂]	Yellowish Orange	>360	72	11.72 (11.12)	57.14 (56.90)	3.29 (2.98)	10.25 (9.96)
[Zn(L) ₂]	Red	>360	86	11.88 (10.51)	57.03 (56.88)	3.29 (3.03)	10.23 (10.12)

Preparation of Metal Complexes (general procedure)

An ethanolic solution of the ligand (0.24g, 2mmole) was added gradually with stirring to the 0.118g, 0.118g, 0.085g and 0.068g (1mmole) of CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O and ZnCl₂ respectively dissolved in the buffer solution of the required pH. The mixture was cooled until dark color precipitate was formed, filtered and washed several times with (1: 1) water: ethanol then with acetone.

Results and Discussion

The ligand was prepared by coupling phenol with the appropriate diazotate in alkaline solution. The ligand sparingly soluble in water but soluble in organic solvents, stable toward air and moisture.

The ligand was characterized by UV-Vis spectroscopic technique. The spectrum of an ethanolic solution of the ligand (10⁻³ M) display mainly three peaks, the first and second peaks were observed at (253 nm) and

(300 nm) were assigned to the moderate energy π - π^* transition of the aromatic rings. The third peak (λ_{max}) was observed at the (424 nm) was referred to the π - π^* transition of intermolecular charge-transfer taken place from benzene through the azo group (-N=N)^[14].

Interaction of the metal ions (Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) with the prepared ligand has been studied in solution; An aqueous-ethanolic solutions were always performed over wide molar concentration and acidity range. The colors of these mixed solutions were varied from brown or reddish orange to red. (Table (1)) described physical properties and elemental analysis.

The interaction of the metal ion with the ligand manifest itself in the absorption spectra by the appearance of a peak in the range (477-520 nm). A great bathochromic shift in the visible region was detected in the complex solutions spectra with respect to that of the free ligand. The high shift in the (λ_{max}) gave a

good indication for complex formation. (Fig.(2)) showed a comparison between the

spectra of the ligand and Co^{II} mixed solution.

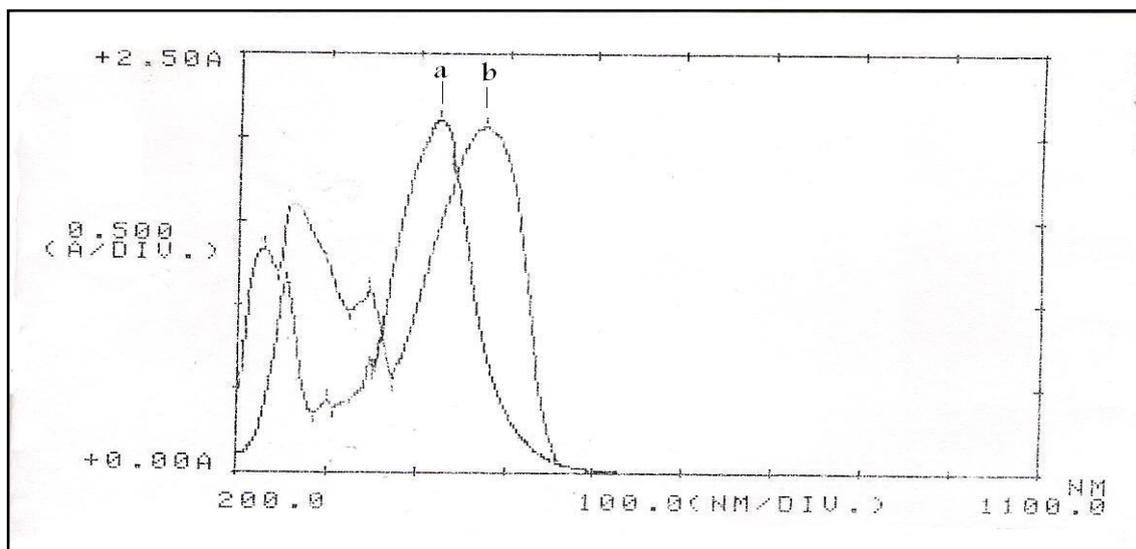


Fig.(2) UV-Vis spectra of a- free Ligand Solution b- Co^{II} - L Mixed Solution.

From the wide studied range of molar concentration (10^{-5} - 10^{-3} M) of the mixed solutions, only concentration of (10^{-4} M) obey Lambert- Beer's law and showed intense color. A calibration curve was plotted on absorbance

against molar concentration in the range (1×10^{-4} - 3×10^{-4} M). Best fit straight lines were obtained (Fig.(3)) with correlation factor $R > 0.998$.

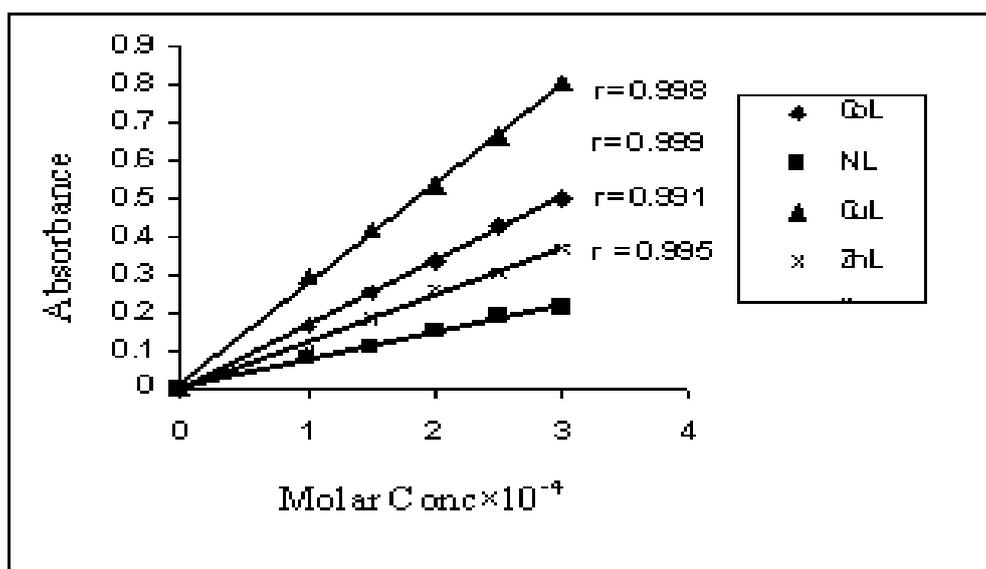


Fig.(3) Linear Relation Between Molar Concentration and Absorbance.

The optimum concentration was chosen for complex solution gave rise to a constant (λ_{max}) at different pH.

The influence of pH was also studied at pH range (5 - 7.5) and the absorbance- pH curves for each metal ion measured at certain (λ_{max}) were plotted. (Fig.(4)) showed a selective pH-absorbance curves. The plateau of the curves

represent the completion of the reaction and consequently represent the optimum pH.

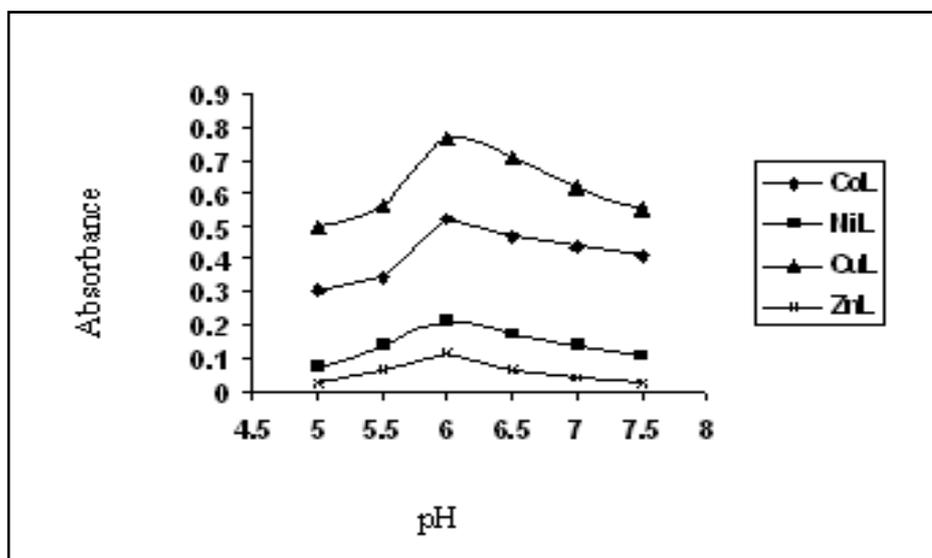


Fig.(4) Effect of pH on Absorbance (λ_{max}) for Complexes.

The composition of the complexes formed in solution has been established by mole ratio and job methods. In both cases the results reveals (1:2) metal to ligand ratio. A chosen plots of were represented in (Fig.(5)).

(Table (2)) summarize the results obtained as a conditions for the preparation of the complexes

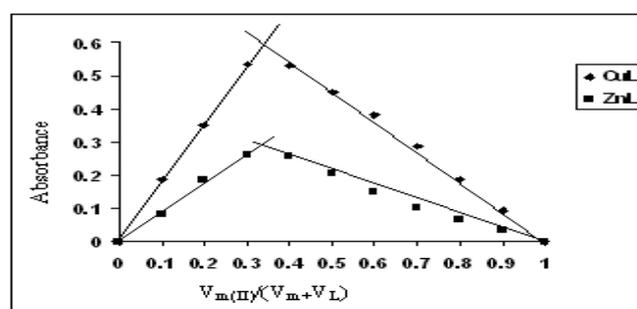
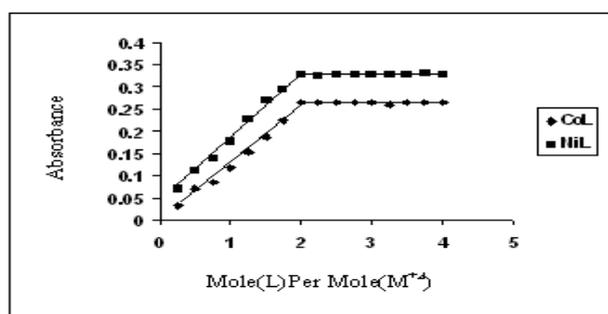


Fig.(5) Mole Ratio and Job Methods for Complexes Solutions.

Table (2)
Conditions for the Preparation of the Complexes and UV-Vis, Magnetic Susceptibility and Conductance Measurements Data.

Compounds	Optimum pH	Optimum Molar Conc $\times 10^{-4}$	M:L Ratio	(λ_{max}) nm	ABS	ϵ_{max} ($L.mol^{-1}.cm^{-1}$)	$A_m(S.cm^2.mol^{-1})$ In Absolute ethanol	μ_{eff} (B.M)
Ligand	-	-	-	424	2.105	2105	-	-
[Co(L) ₂]	6	2.5	1:2	512	0.954	954	13.63	3.81
[Ni(L) ₂]	6	2	1:2	477	1.049	1049	10.86	3.04
[Cu(L) ₂]	6	2.5	1:2	492	0.744	744	8.67	1.61
[Zn(L) ₂]	6	2.5	1:2	520	0.687	687	15.42	-

The apparent stability constant (K) of the (1:2) metal: ligand complex were evaluated spectroscopically using the following equations:

$$K = \frac{1-\alpha}{4\alpha^2 c^2} \quad \alpha = \frac{A_m - A_s}{A_m}$$

Where c = the concentration of the complex solution in mole/ L

A = degree of dissociation, A_s = the absorption of solution containing a stoichiometric amount of ligand and metal

ion and A_m = the absorption of solution containing the same amount of metal and excess of ligand.

The A_s and A_m were measured at (λ_{\max}) of solution. The values of (A_s , A_m , α , K and $\log K$) were tabulated in (Table (3)). The high values of K may reflect the high stability of the prepared complexes ^[15].

Table (3)
Stability Constant of the Prepared Complexes.

Complexes	A_s	A_m	α	k	$\text{Log } k$
[Co(L) ₂]	0.118	0.264	0.553	1.08×10^6	6.033
[Ni(L) ₂]	0.177	0.328	0.460	2.45×10^6	6.390
[Cu(L) ₂]	0.11	0.263	0.581	1.03×10^6	6.012
[Zn(L) ₂]	0.202	0.533	0.546	1.33×10^6	6.123

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions at the optimum pH and in a (M: L) ratio of (1: 2). The (C. H. N) and metal contents of these complexes were in a good agreements with the calculated values.

The molar conductance of the complexes as (10^{-3} M) in ethanol indicating their non-electrolytic nature^[16], the data were recorded in (Table (2)).The effective magnetic moments of the complexes lies in the range (1.61- 3.81) B.M. This value refers to a paramagnetic (high spin) which has been reported for most tetrahedral geometry^[17].

The UV-Vis spectra of the prepared complexes dissolved in ethanol (10^{-3} M) have been measured and the data obtained were included in (Table (2)). Again the large bathochromic shift of the (λ_{\max}) assigned to ($\pi-\pi^*$) transition of the ligand suggesting the involvement of the ligand in the bond formation with the metal ion.

In order to study the binding mode of the new ligand with the metal ions, a comparison have been made for the FT. IR spectra of the free ligand and the prepared complexes and the data was tabulated in (Table (4)).

Table (4)
The Main Frequencies of the Ligand and Their Complexes (cm^{-1}).

Compounds	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu_{as}(\text{COO})$	$\nu_s(\text{COO})$	$\nu(-\text{N}=\text{N}-)$ + $\nu(-\text{C}=\text{N}-\text{N}=\text{C})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
Ligand	3409 br.	1674 s.	1604 m.	1488 s.	1450 sho. 1373 sho.	-	-
$[\text{Co}(\text{L})_2]$	3402 br.	1697 s.	1573 sh.	1492 sh.	1458 s. 1388 sh.	493 w.	439 w.
$[\text{Ni}(\text{L})_2]$	3402 br.	1705sh.	1597 sh.	1492 sh.	1473 sh. 1450 sh. 1408 sho.	505 w.	443 w.
$[\text{Cu}(\text{L})_2]$	3402 br.	1708 s.	1577 sh.	1489 s.	1473 sho. 1450 sh. 1388 s.	509 w.	405 w.
$[\text{Zn}(\text{L})_2]$	3404 br.	1691s.	1589 s.	1489 sh.	1462 s. 1415 sho. 1373 s.	497 w.	430 w.

r = broad, s = strong, m = medium, sh = sharp, sho = shoulder, w = weak, as = asymmetric, s = symmetric

The IR spectrum of the ligand (Fig.(5)) exhibited broad band at (3409 cm^{-1}) was assigned to the stretching vibration of $\nu(\text{OH})$ of the carboxyl and phenol^[18,19].

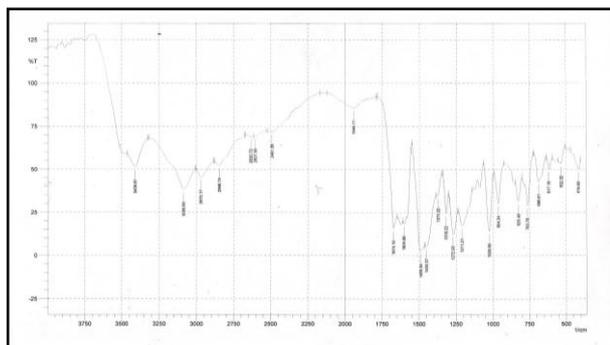


Fig.(6) FT-IR Spectrum of the Ligand .

Strong band in the ligand spectrum was observed at (1674 cm^{-1}) ascribed to the $\nu(\text{C}=\text{O})$ for the carboxyl group. Significant change in the position to higher frequency was also observed on complexation with metal ion. The strong band in the free ligand spectrum at (1604 cm^{-1}) due to $\nu(\text{COO})$ asymmetric vibration, significant change in the intensity and in position to lower frequency was observed on complexation with metal ion (Fig.(6,7)).



Fig.(7) FT-IR Spectrum of the $[\text{Co}(\text{L})_2]$ Complex.

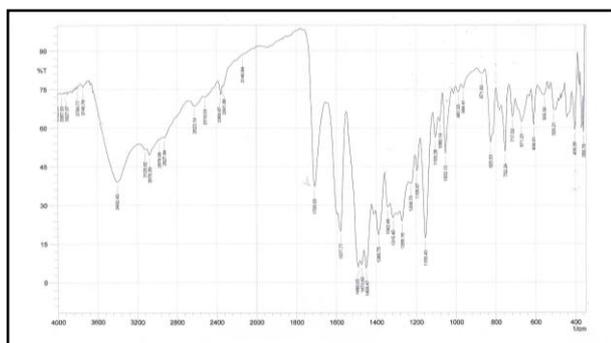
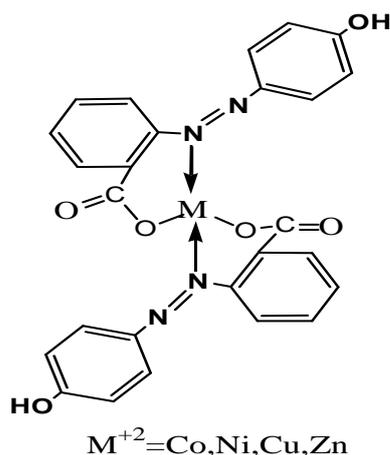


Fig.(8) FT-IR Spectrum of the [Cu(L)₂] Complex.

The band at (1488cm⁻¹) in the spectrum of the ligand was assigned to the $\nu(\text{COO})$ symmetric, suffered a great change to higher frequency on complexation with metal ion [20]. Band characteristic of the azo bridge vibration at (1450 cm⁻¹), on complexation shiften with change in shape or splitting was observed, indicating the engagement of this group in the coordination with metal ion (21). Metal oxygen and nitrogen bands [22,23] further confirmed by the presence of the bands around(493-509) cm⁻¹ and (405-443) cm⁻¹.

According to the results obtained an tetrahedral structure has been suggested to these complexes.



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الخلاصة

حضرت الليكاند ٤-(٢-امينو بنزويك اسد ازو)- فينول من تفاعل ازدواج ٢-امينو حامض البنزويك مع (الفينول). شخص الليكاند المحضر بوساطة أطيف الأشعة تحت الحمراء وفوق البنفسجية- المرئية والتحليل الدقيق للعناصر (C.H.N) تمت مفاعلة الليكاند مع بعض الأيونات أفلزية المنتخبة ($Zn^{II}, Cu^{II}, Ni^{II}, Co^{II}$) في وسط ايثانول - ماء وبنسبة فلز: ليكاند (2:1) وفي الدالة الحامضية المثلى، وخضعت محاليل هذه المعقدات لقانون لامبرت - بير ضمن مدى التراكيز ($1 \times 10^{-4} - 3 \times 10^{-4} M$) شخصت هذه المعقدات باستخدام تقنية الامتصاص الذري اللهبى، أطيف الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية والتحليل الدقيق للعناصر (C.H.N) فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية. درست تراكيب المعقدات باستخدام طريقتي النسب المولية والمتغيرات المستمرة، كما تم حساب استقرارية المعقدات المحضرة.

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