

## ***Synthesis and Characterization of 4-(4-Nirto benzene azo)-3-amino benzoic acid Complexes with Selected Metal Ions***

**H.H.AL-TAWEEL**

**Suhad Shakir**

Department of Chemistry, Ibn-Al-Haitham Education College

**Zainab Abdul Razzaq Jabarah al Mousawy**

Agriculture College, University of Baghdad

### **Abstract**

Coupling reaction of 4-nitroaniline with 3-aminobenzoic acid gave bidentate azo ligand. The prepared ligand was identified by Microelemental Analysis, FT-IR and UV-VIS spectroscopic techniques. Treatment of the prepared ligand with the following metal ions ( $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Hg}^{\text{II}}$ ) in aqueous ethanol with a 1:2 M:L ratio, 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. From the obtained data the tetrahedral structure was suggested for all prepared complexes.

### **Introduction**

Synthetic dyes are produced in large amounts and are used in different industrial branches including the textile industry. After the process, the excess of dye remains in the effluent, which must be treated before release in to the environment<sup>(1,2)</sup>. The development of new structure of azo dyes has been a subject of interest and many novel structure of these dyes, useful in the commercial application to polyester, polyamide or polyacrylic as well as their blends with other fibres<sup>(3)</sup>. Azo containing polymers are macromolecules azo groups in the main chain or side chain polymers with azo benzene moiety have good stability and usually show high glass transition temperature(Tg). Introducing azo benzene linkages in the polymeric main chain can improve thermal stability and allow application as an engineering plastic<sup>(4,5)</sup>. In recent years we have interested in the coordination chemistry of the azo ligand<sup>(6-8)</sup>. Metal complexes of azo compounds containing hetroaryl ring sistems find various application, for example indicator in complexometric, dyes and pigments in textile industry<sup>(9)</sup>. In this work, we synthesized azo dye derived from 4-nitro aniline as diazo component and 3-amino benzoic acid as coupling

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agent. The complex of this ligand with some metal ions has also been studied and characterized physicochemically.

## Experimental

### Instrumentation

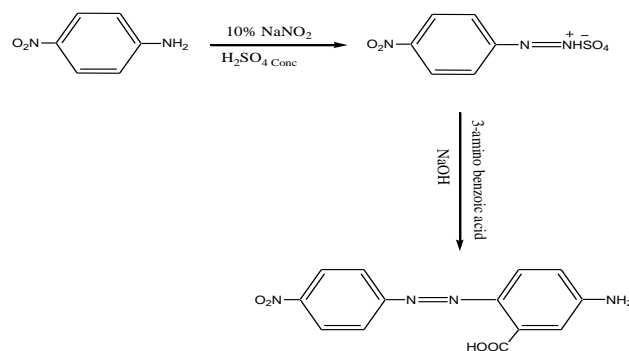
UV-VIS spectra were recorded on a (Shimadzu UV- 160A) Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a (Shimadzu, FT-IR-8400S) Fourier Transform Infrared Spectrophotometer (4000- 400)  $\text{cm}^{-1}$  with samples prepared as KBr discs. Atomic absorption were obtain using a(Shimadzu 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  $10^{-3}\text{M}$  of complexes in ethanol at  $25^{\circ}\text{C}$  using (Philips PW- Digital Conductimeter). Magnetic susceptibilities were performed by using (Brucker Magnet B.M.6) instrument at  $25^{\circ}\text{C}$ . In addition, melting points were obtained using (Stuart Melting Point Apparatus).

### Materials and Reagents

The following chemicals were used as received from suppliers; copper chloride dihydrate 98%, zinc chloride 98.8%, cadmium chloride monohydrate 99.9%, mercury chloride 98% (Merck) 4-nitro aniline, 3-amino benzoic acid (B. D. H).

### Preparation of the Ligand<sup>(10)</sup>

(0.342g,1mmole) of 4- nitroaniline was dissolved in a mixture of (2 ml) sulphuric acid, (10 ml) ethanol and (10 ml) distilled water, and diazotized at  $5^{\circ}\text{C}$  with sodium nitrite solution. The diazo solution was added drop wise with stirring to a cooled ethanolic solution of (0.345g, 1mmole) of 3-aminobenzoic acid. (25 ml) of (1M) 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 scheme (1), while (Table-1) describes the physical properties and elemental analysis.



Scheme (1): Preparation of the Ligand.

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### Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing 0.085g, 0.068g, 0.10g and 0.135g (1mmole) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{HgCl}_2$  respectively was added gradually with stirring to the ethanolic KOH solution of the ligand (0.286g, 2mmole). 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 3-amino benzoic acid with the appropriate diazotate in alkaline solution. The ligand sparingly soluble in water but soluble in organic solvents, stable toward air and moisture.

The synthesized ligand was characterized by Microelemental Analysis (C.H.N), FT-IR and UV-VIS spectroscopic technique.

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

The molar conductance of the complexes as ( $10^{-3}$  M) in ethanol indicating their non- electrolytic nature<sup>(11)</sup>, the data were recorded in (Table- 2).

The effective magnetic moments (Table-2) of  $\text{Cu}^{\text{II}}$  complex exhibit ( $\mu_{\text{eff.}}$ ) value at (1.73 B.M). This value refers to a paramagnetic (high spin) which has been reported for most tetrahedral geometry. In case of  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Hg}^{\text{II}}$  complexes because of filled-d orbital, therefore the magnetic moments ( $\mu=0$ ) are diamagnetic<sup>(12)</sup>.

The UV-VIS spectra data for free ligand and all prepared complexes are listed in (Table-2). The UV- VIS spectrum of an ethanolic solution of the ligand ( $10^{-3}$  M) (Fig.1) display mainly two peaks, the first peak was observed at  $37735 \text{ cm}^{-1}$  was assigned to the moderate energy  $\pi - \pi^*$  transition of the aromatic rings. The third peak ( $\lambda_{\text{max}}$ ) was observed at the  $24691 \text{ cm}^{-1}$  was referred to the  $\pi - \pi^*$  transition of intermolecular charge-transfer taken place from benzene through the azo group  $(-\text{N}=\text{N})$ <sup>(13)</sup>. The spectrum of  $\text{Cu}^{\text{II}}$  complex gave absorption peak at  $32154 \text{ cm}^{-1}$  due to charge transfer. Other peak at  $22573 \text{ cm}^{-1}$  was caused by electronic transition<sup>(14)</sup>  $^2\text{T} \rightarrow ^2\text{E}$ . The spectra of  $\text{Zn}^{\text{II}}$  (Fig.2),  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  complexes showed absorption peaks at  $30303 \text{ cm}^{-1}$ ,  $27855 \text{ cm}^{-1}$  and  $34246 \text{ cm}^{-1}$  respectively were assigned to charge transfer. The absence of absorption peaks in visible region indicated no (d-d) electronic transition happened, therefore a good results for tetrahedral complexes<sup>(15)</sup>.

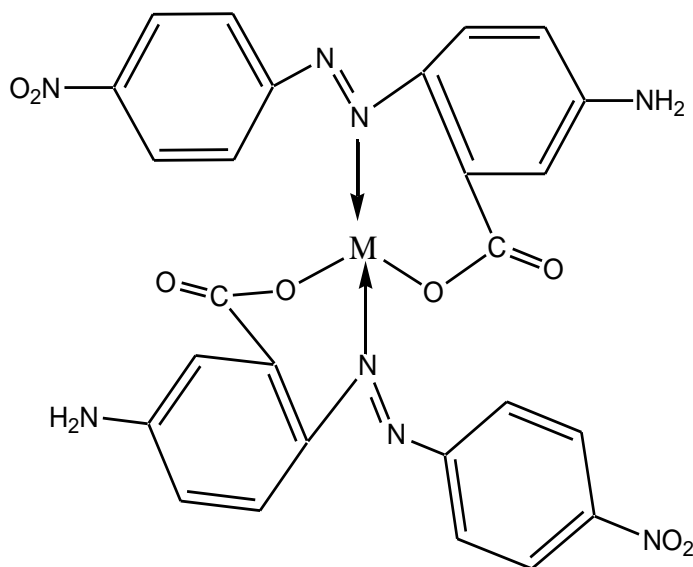
In order to study the binding mode of the ligand with the metal ions, a comparison have been made for the FT. IR spectra of the free ligand and the

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prepared complexes and the data was tabulated in (Table-3). The IR spectrum of the ligand (Fig.3) exhibited broad band at  $3379\text{ cm}^{-1}$  was assigned to the stretching vibration of  $\nu(\text{OH})$  group, absent this band in the spectra of all prepared complexes, which indicated deprotonation and involvement of the enol O in chelation<sup>(16)</sup>. The bands at  $3296\text{ cm}^{-1}$  and  $3116\text{ cm}^{-1}$  due to the stretching mode of  $\nu(\text{NH}_2)$ . Since no change in these bands was noticed, the possibility that coordination occur via the donation atom in this group was excluded<sup>(17)</sup>. The strong band in the free ligand spectrum at  $1666\text{ cm}^{-1}$  due to  $\nu_{\text{as}}(\text{COO})$  asymmetric vibration, significant change in the intensity and in position to lower frequency was observed on complexation with metal ion (Fig.4). The band at  $1558\text{ cm}^{-1}$  in the spectrum of the ligand was assigned to the  $\nu_{\text{s}}(\text{COO})$  symmetric, suffered a great change to higher frequency on complexation with metal ion<sup>(18)</sup>. Band characteristic of the azo bridge vibration at  $1489\text{ cm}^{-1}$ , on complexes shifted to lower frequency with change in shape was observed indication the engagement of this group in the coordination with the metal ion<sup>(19,20)</sup>. The absence of new band at  $(450-578)\text{ cm}^{-1}$  are tentatively assigned to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  (Metal-Ligand) stretching bands<sup>(21-23)</sup>.

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



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**Table (1):- Physical Properties and Elemental Analysis of the Complexes.**

Compound s	Color	M.P °C	Yield%	Analysis Calc.(Found)			
				M%(Metal)	C%	H%	N%
Ligand	Orange	224	77	-	54.54 (53.65)	3.49 (3.21)	19.58 (18.53)
[Cu(L) <sub>2</sub> ]	Deep Brown	>360	68	10.09 (9.74)	49.21 (48.47)	3.15 (2.87)	17.66 (16.37)
[Zn(L) <sub>2</sub> ]	Red	>360	82	10.23 (9.55)	49.13 (48.23)	3.14 (2.77)	17.63 (16.33)
[Cd(L) <sub>2</sub> ]	Yellow	>360	73	16.42 (15.76)	45.74 (44.72)	2.93 (2.17)	16.42 (15.62)
[Hg(L) <sub>2</sub> ]	Yellowish Orange	>360	87	26.07 (25.32)	40.46 (39.56)	2.59 (2.04)	14.52 (13.45)

**Table (2):- UV-Vis, Magnetic Susceptibility and Conductance Measurements Data.**

Compounds	( $\lambda_{max}$ ) nm	ABS	Wave number ( $cm^{-1}$ )	$\epsilon_{max}$ ( $L.mol^{-1}.cm^{-1}$ )	$\Lambda_m(S.cm^2.mol^{-1})$ In Absolute ethanol	$\mu_{eff}$ (B.M)
Ligand	265 405	0.786 2.437	37735 24691	786 2437	-	-
[Cu(L) <sub>2</sub> ]	311 443	1.918 0.217	32154 22573	1918 217	9.74	1.73
[Zn(L) <sub>2</sub> ]	330	1.685	30303	1685	10.17	Dia
[Cd(L) <sub>2</sub> ]	359	1.576	27855	1576	6.87	Dia
[Hg(L) <sub>2</sub> ]	292	1.791	34246	1791	10.34	Dia

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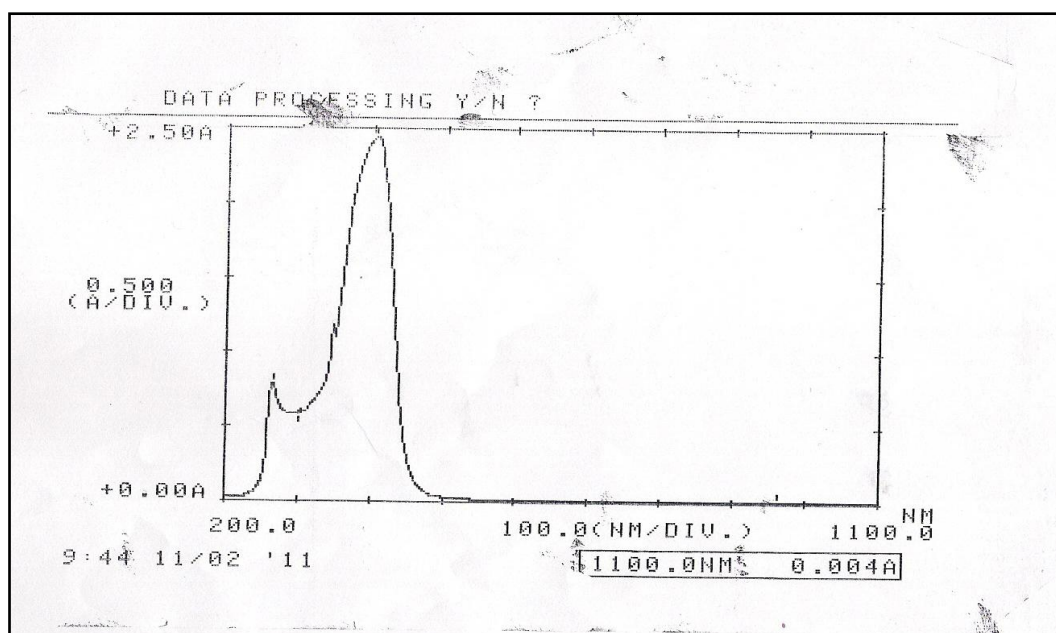
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**Table (3): - The Main Frequencies of the Ligand and Their Complexes (cm<sup>-1</sup>).**

Compounds	$\nu$ (OH) + $\nu$ (NH <sub>2</sub> )	$\nu_{as}$ (COO) + $\nu_s$ (COO)	$\nu$ (-N=N-)	$\nu$ (M-O)	$\nu$ (M-N)
Ligand	3379 br. 3296 br. 3116 sh.	1666 s. 1558 sh.	1489 sh.	-	-
[Cu(L) <sub>2</sub> ]	- 3292 s. 3114 s.	1656 s. 1570 sh.	1471 sh.	560 w.	470 w.
[Zn(L) <sub>2</sub> ]	- 3294 s. 3116 s.	1651 sh. 1597 s.	1479 s.	578 w.	475 w.
[Cd(L) <sub>2</sub> ]	- 3291 sh. 3113 sh.	1630 sh. 1580 s.	1460 s.	563 w.	480 w.
[Hg(L) <sub>2</sub> ]	- 3295 sh. 3117 sh.	1640 s. 1575 sh.	1473 sh.	557 w.	450 w.

br = broad, s= strong, , sh = sharp, sho = shoulder, w = weak, as=asymmetric , s=symmetric

**Fig.(1):- UV-VIS Spectrum of the Ligand.**



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Fig.(2):- UV-VIS Spectrum of the  $[Cu(L)_2]$  Complex.

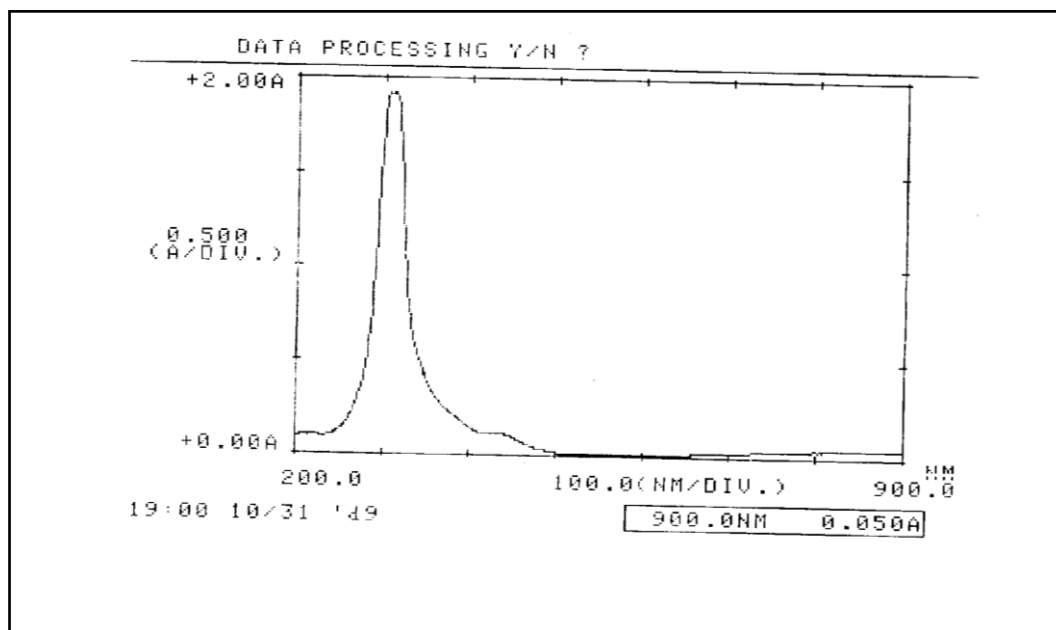
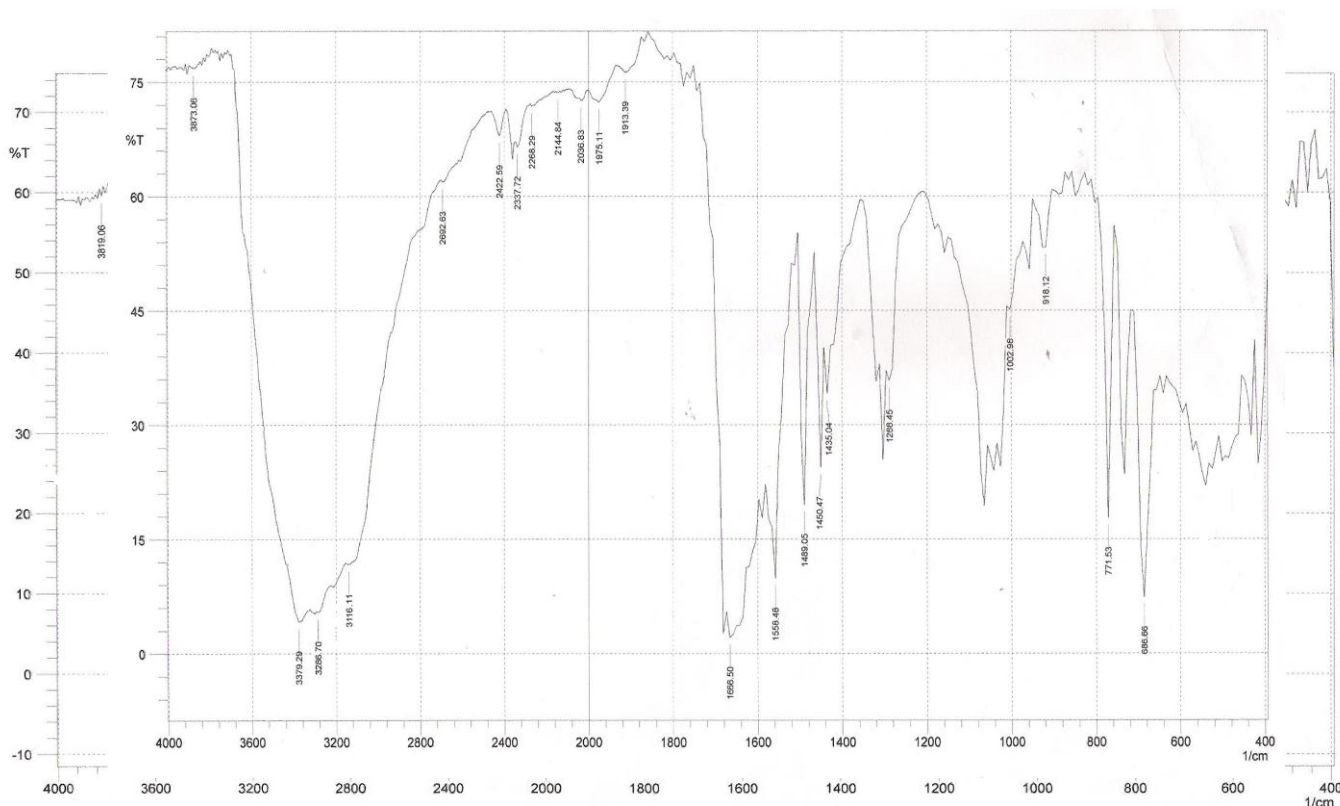


Fig.(3):- FT-IR Spectrum of the Ligand.



**تحضير وتشخيص معقدات 4-(4-نايترو بنزين ازو)-3-امينو بنزويك اسد  
مع بعض الأيونات الفلزية المنتخبة.**

حسام حيدر الطويل، سهاد شاكر محمد،\* زينب عبد الرزاق جبارة الموسوي

قسم الكيمياء، كلية التربية / ابن الهيثم، جامعة بغداد

\*شعبة العلوم الاساسية / كلية الزراعة ، جامعة بغداد

**الخلاصة**

حضرت الليكاند 4-(4-نايترو بنزين ازو)-3-امينو بنزويك اسد من تفاعل ازدواج 4-نايترو انيلين مع 3-امينو بنزويك اسد. شخص الليكاند المحضر بوساطة أطيايف الأشعة تحت الحمراء وفوق البنفسجية- المرئية والتحليل الدقيق للعناصر (C.H.N). تمت مفاعلة الليكاند مع بعض الأيونات الفلزية المنتخبة ( $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ , and  $\text{Hg}^{\text{II}}$ ) في وسط ايثانول - ماء وبنسبة فلز: ليكاند (2:1) وتم الحصول على سلسلة من المعقدات ذات الصيغة العامة  $[\text{M}(\text{L})_2]$ . شخصت هذه المعقدات باستخدام تقنية الامتصاص الذري اللهب، أطيايف الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية والتحليل الدقيق للعناصر (C.H.N). فضلا عن قياسات التوصيلية الكهربائية والحساسية المغناطيسية، ومن النتائج المحصول عليها تم اقتراح الشكل رباعي السطوح للمعقدات المحضرة.