SYNTHESES AND CHARACTERIZATION OF COPPER (II) AND PALLADIUM (II) COMPLEXES WITH 2-(ARYLMETHYLENEACETYL)BENZIMIDAZOLE

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ABSTRACT

Metal complexes formed through the reaction of 2-(Arylmethyleneacetyl) benzimidazole (L1-L4) with copper (II) and palladium (II) ions were prepared and characterized by elemental analysis, conductance measurements, infrared spectra, electronic absorption spectra, X-ray diffraction and thermal analyses. The 2-(Arylmethyleneacetyl)benzimidazole (L1-L4) coordinate as neutral bidentate ligands. The final product in all the cases of TG thermogram of the complexes was found to be metal oxides. Complexes of copper (II) and palladium (II) with 2-(Arylmethyleneacetyl)benzimidazole in solution were studied by spectrophotometric methods and the formation constants and stioichiometries of the complexes were calculated to be 1:2 (M : L) as calculated by continuous variations and the mole ratio methods. The stability sequence is in agreement with the Irving-Williams rule.

Keywords: *Copper (II), Palladium (II), Complexes, X-ray diffraction, Thermal analyses, UV–Vis spectroscopy.*

INTRODUCTION

Benzimidazole and its derivatives are interesting heterocycles because of their presence in many medicaments. It has been found that they possess antibacterial, antifungal, antioxidant, antihistaminic, cytostatic, local analgesic, hypotensive antihelmintic, anticancer, antihypertensive, antineoplastic, antiprotozoal, anti-hepatitis B virus and anti-inflammatory activity [1-6]. It was confirmed to have a moderate in vitro anti-HIV activity [7, 8]. Also Benzimidazole as its 5,6-dimethyl derivative is present in vitamin B12 and related biomolecules and benzimidazole derivatives have found wide uses as antihelmintic agents for both human and veterinary purposes[9]. Benzimidazoles are also used extensively in industrial processes as corrosion inhibitors for metal and alloy surfaces particularly of copper[10] and ion exchangers [11].

Complex compounds of transition metal ions with benzimidazole and substituted compounds of these ligands have been studied extensively[12-16]. In the recent time, possible therapeutic properties of the metal complexes have been examined. It was found that the complexes of transition metals with benzimidazole derivatives have a higher antimicrobial activity than the corresponding ligands [17-21].

Synthesis, characterization and antimicrobial activities of transition metal complexes of 1,3-bis(benzimidazolyl/N-methylbenzimidazolyl)benzene have been reported [18-23].

The aim of the present article is to prepare and characterize Copper (II) and palladium (II) complexes with 2-(Arylmethyleneacetyl)benzimidazole derivatives and their characterization by Elemental analysis, conductance measurements, TGA, UV-Visible, IR, thermal analyse as and X-ray diffraction were used to investigate the titled complexes.

Experimental

All the chemicals were of analytical reagent grade; the ligands 2-(Arylmethyleneacetyl)benzimidazole (L_1-L_4) were prepared by procedure of Zeinab [24]. All solutions were prepared with doubly distilled water. The solutions were diluted as necessary to prepare standard working solution.
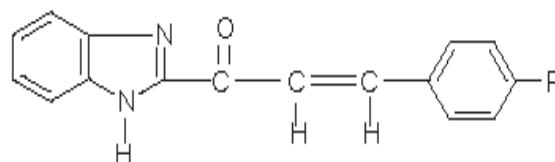
Where R = H (L_1),   p-Cl (L_2),

p- NO_2 (L_3),   p-$N(CH_3)_2$ (L_4)

Fig. 1. Structure of the Ligand 2-(Arylmethyleneacetyl)benzimidazole (L_1-L_4).

Preparation of the solid complexes

A solution of Cu(II) or Pd(II) chloride (0.01 mole dissolved in 25 ml ethanol) was added to a hot ethanolic solution of the ligands (L_1-L_4) (0.02 mole in 25 ml ethanol) in stoichiometric ratio 1:2 (metal ion : ligand). The mixture was refluxed for about 4 hours, the solid complexes were filtered on a water pump and washed several times with ethanol and dried in vacuum over P_4O_{10}.

Physical measurement and analyses

Electronic spectra of solutions of the complexes in DMF were recorded on a Perkin – Elmer Lambada 3B Spectrophotometer. The IR spectra were recorded on a Shimadzu IR 470 (4000-400) spectrophotometer using KBr discs. TGA measurements were carried out with a shimadzu thermal analyses 50, at heating rate of 20ºC/min.

Conductivity was measured in solutions of the complexes in DMF (10^{-3} M) using Hana conductivity bridge (Model) HI 8819 at 25 ºC.

Microanalyses for C, H, N were carried out at the Microanalytical center, Assiut University.

X-ray was carried out with Philips X-ray PW 1710 diffractometer using Ni-filtered CuKα radiation, Assiut University.

RESULT AND DISCUSSION:

The complex formation reaction of the ligands (L_1-L_4) with Cu(II) and Pd(II) halides can be represented by the following equations:

$MX_2 + 2 L \rightarrow [ML_2X_2]$
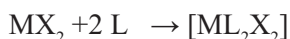
Where M= Cu (II) and Pd (II) , X= Cl

They are soluble in DMF, DMSO, Acetone and slightly soluble in Ethanol, methanol.

The complexes were characterized by chemical analyses, IR and visible spectra, thermal analyses and conductivity measurements.

Molar conductance values for the solid complexes (1×10^{-3} M DMF solution) indicates that the complexes are non-electrolytes [25].

Infrared spectra

The infrared spectra of the free ligand are recorded in the 4000 - 400 cm⁻¹ region and compared with the spectra of the Cu(II) and Pd(II) complexes. The characteristic of the ligand and complexes bands are listed in Table (1).

The IR spectrum of the free ligand display a stretching band at 3250-3450 cm⁻¹ attributed to νNH [24]. Also the free ligands spectrum exhibits a strong band at 1650-1662 cm⁻¹ is due to C=O stretching frequency The band corresponding to υ (C=N) vibration group is shifted to lower or higher values in the spectra of the complexes indicating that the nitrogen atom shared in coordination with metal ion in these complexes . Also other absorption band in the IR spectra of the free ligands at 1580-1595 cm⁻¹ attributed to the C=N group and The υ (C=O) absorption is also shifted to a lower or higher frequency indicating that the ligand is coordinated with the metal ion through the oxygen of the carbonyl group [26].

The IR spectrum also exhibits stretching band of the free ligand at 1485-1540 cm⁻¹ attributed to the C=C of skeletal benzonoid moieties of these ligand, but these bann the complexes are slightly shifted compared to the free ligands.

So the conclusive evidence of the coordination of the 2-(Arylmethyleneacetyl)benzimidazole (L_1-L_4) with the metal ions was shown by the appearance new bands at 482-505 cm⁻¹ and 525-585 cm⁻¹ assigned to the metal nitrogen (M—N) [27-29] and metal-oxygen (M—O) [30] vibrations, respectively. These bands were absent in the spectrum of the ligand itself, thus confirming participation of the O and N atoms in the coordination.

The x-ray powder diffraction patterns for the complexes of Cu(II) and Pd(II) with 2-

(Arylacetyl)benzimidazole are depicted in Figs. 2-4. They indicate that the Pd(II) complexes with L_2 and L_3 are crystalline (Fig. 2), also the Cu(II) complex with L_1, L_2 and L_3 are semi-crystalline(Fig. 3), while the Cu(II) complex with L_4 is amorphous (Fig. 4). This indicates that the polymeric structure of Cu(II) complexes with L_1, L_2, L_3 and L_4 are more convenient, while the Pd(II) complexes with L_2 and L_3 have a monomeric structure.

Table 1. Characteristic infrared bands and λmax electronic absorption bands of the   2-(Arylmethyleneacetyl)benzimidazole (L₁-L₄) and its Cu (II) and Pd (II) complexes.

Compound	νNH	νC=O	νC=N	νC=C	νM-O	νM-N	λ_{max} nm
L$_1$	3250	1650	1580	1510	-	-	330
[Cu (L$_1$)$_2$Cl$_2$]	3450	1655	1695	1517	585	490	430
[Pd (L$_1$)$_2$Cl$_2$]H$_2$O	3150	1670	1600	1400	575	495	460
L$_2$	3420	1662	1595	1485	-	-	332
[Cu (L$_2$)$_2$Cl$_2$]	3340	1650	1585	1485	575	495	413
[Pd (L$_2$)$_2$Cl$_2$]H$_2$O	3100	1678	1590	1483	580	482	455
L$_3$	3300	1658	1585	1508	-	-	340
[Cu (L$_3$)$_2$Cl$_2$]H$_2$O	3450	1655	1590	1510	525	505	423
[Pd (L$_3$)$_2$Cl$_2$]H$_2$O	3150	1682	1587	1510	540	485	64
L$_4$	3450	1658	1595	1540	-	-	436
[Cu (L$_4$)$_2$Cl$_2$]H$_2$O	3350	1640	1585	1525	540	485	435
[Pd (L$_4$)$_2$Cl$_2$]H$_2$O	3150	1620	1590 1560	1520	558	497	480

X-ray powder diffraction
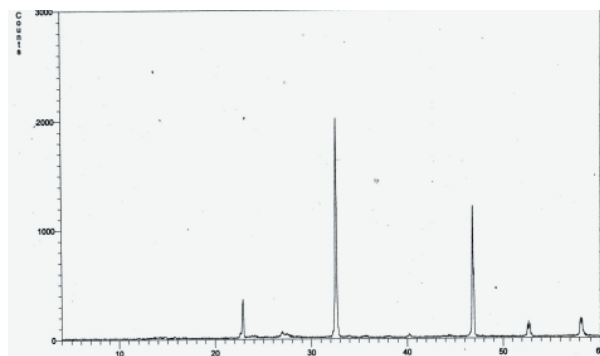
Fig. 2. X-ray powder diffraction pattern of [Pd (L$_3$)$_2$Cl$_2$]H$_2$O complex.
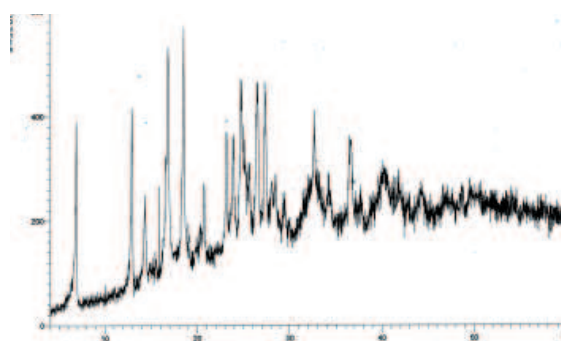
Fig. 3. X-ray powder diffraction pattern of [Cu (L$_3$)$_2$Cl$_2$]H$_2$O complex.
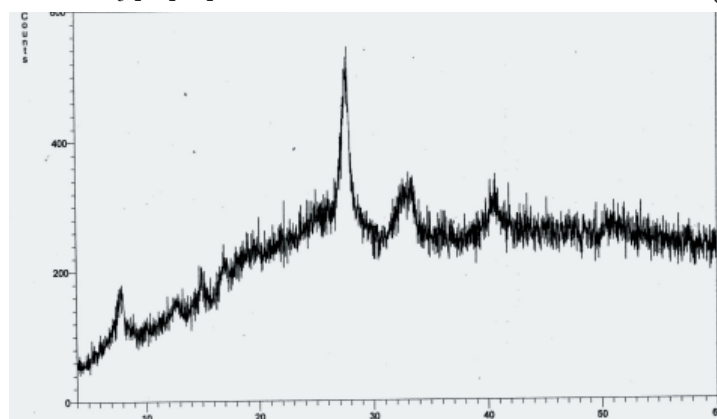
Fig. 3. X-ray powder diffraction pattern of [Cu (L$_4$)2Cl$_2$]H$_2$O complex.

Microanalysis:

The elemental analysis (C.H.N) of the isolated complexes of Cu(II) and Pd(II) with   2-(Arylacetyl)benzimidazole (L$_1$ - L$_4$) were found to be in agreement with calculated values which support the proposed formula of the complexes, Table (2),

These were ascertained by the continuous

Table 2. Elemental analysis result of the Cu(II) and Pd(II) complexes with 2-(Arylme- thyleneacetyl)benzi midazole derivatives.

Complex	Formula	Found (Calc.)%		
		C%	H%	N%
$[Cu\,(L_1)_2Cl_2]$	$C_{32}H_{24}\,N_4O_2Cl_2Cu$	60.50 (60.9)	3.46 (3.83)	8.66 (8.88)
$[Pd\,(L_1)_2Cl_2]\,H_2O$	$C_{32}H_{26}\,N_4O_3Cl_2Pd$	55.20 (55.55)	4.10 (3.78)	8.40 (8.09)
$[Cu\,(L_2)_2Cl_2]$	$C_{32}H_{22}\,N_4O_2C_{14}Cu$	54.50 (54.91)	2.53 (3.16)	7.73 (8.01)
$[Pd\,(L_2)_2C_{12}]\,H_2O$	$C_{32}H_{24}\,N_4O_3Cl_4Pd$	50.80 (50.51)	3.52 (3.17)	6.95 (7.36)
$[Cu\,(L_3)_2C_{12}]H_2O$	$C_{32}H_{24}\,N_6O_7C_{12}Cu$	51.82 (52.00)	2.96 (3.27)	11.58 (11.37)
$[Pd\,(L_3)_2C_{12}]H_2O$	$C_{32}H_{24}\,N_6O_7C_{12}Pd$	49.58 (49.15)	3.31 (3.09))	11.08 (10.74)
$[Cu\,(L_4)_2C_{12}]H_2O$	$C_{36}H_{36}\,N_6O_3Cl_2Cu$	59.10 (58.81)	4.70 (4.93)	10.95 (11.43)
$[Pd\,(L_4)_2C_{12}]H_2O$	$C_{36}H_{36}\,N_6O_3Cl_2Pd$	55.30 (55.57)	4.25 (4.66)	10.90 (10.80)

variation and molar ratio methods. The results reveal that the stoichiometry is 1 : 2 (metal: ligand) ratio for each complex.

Thermal Analyses

Thermal analyses of the $[Pd\,(L_2)_2Cl_2]\,H_2O$ complex (Fig. 5), was studied using the TG technique. The thermo gravimetric studies of the complex were carried out in the temperature range 30-800 °C with a sample heating rate 20°C/min in Nitrogen. The complex become anhydrous at 100 ºC and the loss of weight was equal to 2.3% corresponding to the loss one molecule of water. DTA curve show an endothermic band due to the elimination of water, thus indicating that the water molecule are present in the outer sphere of the complex. The TG curve of $[Pd\,(L_2)_2Cl_2]\,H_2O$ complex also indicate a loss of weight at 150- 400 ºC equal 23.6 % due to the loss of two PhCH. The final step of the decomposition occurs within the temperature range 400-750 0C corresponding to the decomposition of the complexe with the formation of the metal oxide (PdO) as a final product.

The thermal decompositions of $[Cu\,(L_3)_2Cl_2]H_2O$ complex (Fig. 6) displays three steps, the first step in the range 50-300 ºC corresponding to the loss of one water molecule

and two HCl molecules (12.5%). The second decomposition step at 300-450ºC can be attributed to the removal of two molecules of NO_2 (12.4%)[31]. The third decomposition step at 450 – 750ºC (89 %) attributed to complete decomposition of parent molecule leaving copper oxide (CuO) as stable end product.

The TGA characteristic of the $[Cu\,(L_1)_2Cl_2]$ complex have two decomposition steps (Fig. 7). The first step at 200-350 ºC (11.6 %) corresponds to elimination of two HCl molecules [32]. The second weight-loss step between 350-750°C may be attributed to the loss of organic moiety of the complex molecule (87.5 %). The final de-
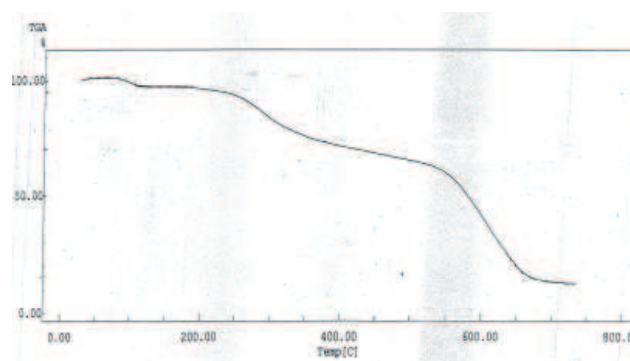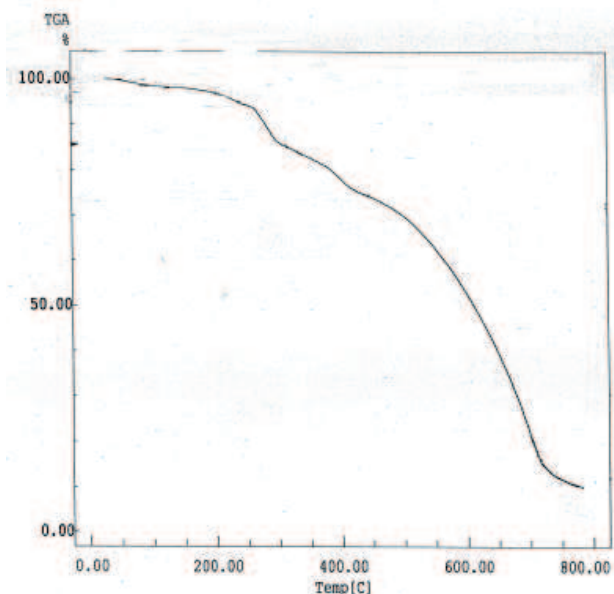

Fig. 5. TG diagram of $[Pd\,(L_2)_2Cl_2]H_2O$ complex.

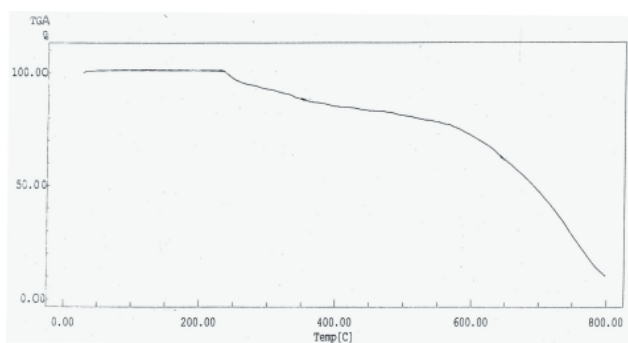**Fig. 6. TG diagram of [Cu (L$_3$)$_2$Cl$_2$]H$_2$O complex.**

Fig. 7. TG diagram of [Cu (L$_1$)$_2$Cl$_2$] complex.

composition continuous up to 800 °C and on further increasing the temperature no weight loss is observed which may be attributed to formation of stable metal oxide (CuO). .

Electronic spectra

The absorption spectra of the 2-(Arylmethyleneacetyl)benzimidazole (L$_1$-L$_4$) in ethanol exhibit a main absorption at 330 nm , 332 nm, 340 nm and 436 nm for L$_1$-L$_4$ respectively. The maximum absorption of bands of the Cu(II) and Pd(II) complexes with 2-(Arylacetyl)benzimidazole (L$_1$-L$_4$) are recorded in Table (1).

Comparison of electronic absorption spectra of free ligands (L$_1$-L$_4$) with that of the chelated Cu(II) and Pd(II), reveals that the addition of metal ion to 2-(Arylacetyl)benzimidazole (L$_1$-L$_4$) ligand solutions results in band shift to longer wavelength, which is an evidence for the formation of the coordination compounds.

Determination of the Stoichiometry and Formation Constants of the Complexes:

Complexes were studied in solution using ethanol as a solvents in order to determine the [M : L] ratio in the complexes. The stoichiometry of the 2-(Arylmethyleneacetyl)benzimidazole (L$_1$-L$_4$) with (Cu(II) and Pd(II)) complexes
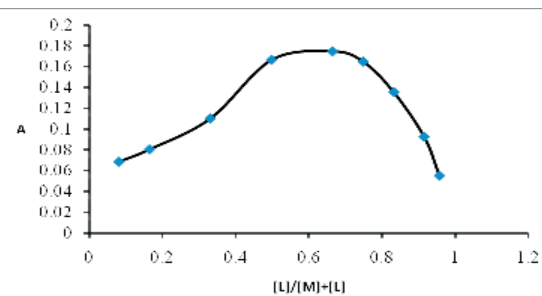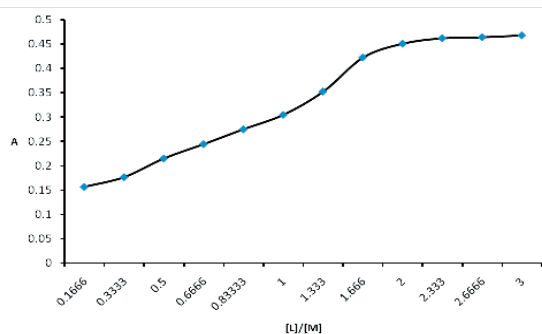

Fig.8. Molar ratio and continuous variation curve for Pd (II) L$_3$ complex.

were verified to be 1:2 (metal : ligand) by applying the two spectrophotometric methods

i- Molar ratio method [33]   ii- Jobs continuous variation method [34]
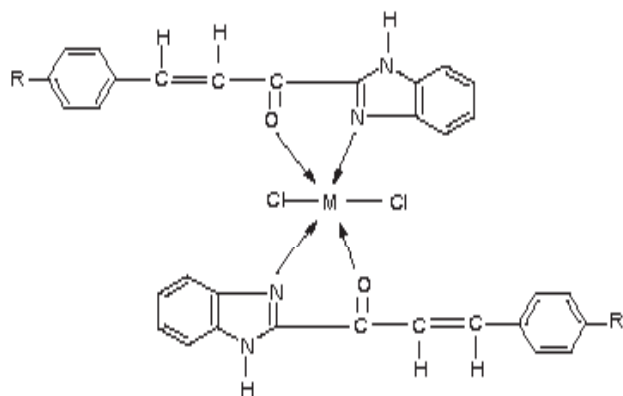
as shown in Figure 8.

The formation constant (K$_f$) of the complexes are determined by using data from the

continuous variation method (Job's plot) and molar ratio method.

The formation constant (K$_f$) is determined by using the following relation [35, 36]:

$$K_f = \frac{A/Am}{4C^2\,(1-A/Am)^3} \quad \ldots\ldots\ldots\ldots(2)$$

The results in Table (3) reveal the following features:

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Where M = Cu (II), Pd (II) and R = L₁ (H), L₂(p-Cl), L₃ (p-NO₂), L₄ (p-N(CH₃)₂)

Fig. 9, Proposed structure of the complexes.

In general, the stability of the complexes of the same ligand goes in order Cu (II) > Pd (II). This order agrees with the conclusions reached by Grinberg and Yatsimirki [37] and by Irving and Williams [38].

Also The complexes stability of the same metals with the different ligands (L₁-L₄) increase in the following order:

L₄ (R= p-N(CH₃)₂) > L₁ (R= H) > L₃ (R= p-NO₂) >L₂(R= p-Cl)
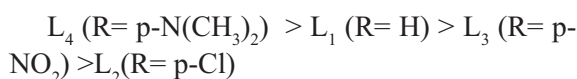
This is in agreement with decreasing electron releasing character of the substituent in the same direction which results in a decrease in the basicity of the azomethine nitrogen of the ligand

Table. 3. Apparent formation constant values (K_f) of the different Cu(II) and Pd(II) complexes with 2-(Arylmethyleneacetyl)benzimidazole derivatives.

Complex	Molar Ratio	Continuous Variation	Mean
Cu- L₁	5.25×10^{10}	9.045×10^{10}	7.14×10^{10}
Cu- L₂	4.45×10^{10}	7.25×10^{10}	5.85×10^{10}
Cu- L₃	4.92×10^{10}	8.75×10^{10}	6.83×10^{10}
Cu- L₄	5.7×10^{10}	9.46×10^{10}	7.58×10^{10}
Pd – L₁	4.23×10^{10}	7.09×10^{10}	5.66×10^{10}
Pd – L₂	4.09×10^{10}	6.36×10^{10}	5.22×10^{10}
Pd – L₃	4.19×10^{10}	6.61×10^{10}	5.44×10^{10}
Pd – L₄	4.29×10^{10}	7.11×10^{10}	5.70×10^{10}

and consequently the tendency toward complex formation is expected to decrease.

Based on the evidence discussed above and various physico-chemical studies, the following structures (Fig. 9) can be proposed about the nature of these complexes.

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الملخص العربى

تحضير وتوصيف ودراسات بيولوجيه على متراكبات أيونات النحاس الثنائى والبلاديوم الثنائى مع مشتقات 2- أريل مثيلين اسيتيل بنزاميدازول.

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يتضمن البحث تحضير متراكبات النحاس الثنائى والبلاديوم الثنائى مع اربع مشتقات 2-اريل مثيلين اسيتيل بنزاميدازول بنسبة مولية 1:2 ليجند :فلز فتكونت ثمانية متراكبات بنفس النسبة المولية السابقة وتم توصيف ودراسة هذه المتراكبات بواسطة التحليل العنصرى والتحليل الحرارى الوزنى ودراسة أطياف الأشعه تحت الحمراء وأشعة أكس والأشعه المرئيه لتحديد صيغ التراكيب الجزيئيه وطريقة الترابط بين الفلزات وهذه المشتقات. أيضا تم دراسة متراكبات النحاس الثنائى والبلاديوم الثنائى مع اربع مشتقات 2-اريل مثيلين اسيتيل بنزاميدازول فى المحاليل بالطرق الطيفيه مثل طريق التغير المستمر والنسبه المولاريه لدراسة نسبه تكون المتراكب وتبين من الدراسه ان نسبة تكون المتراكبات 1:2 (الليجند : الفلز) وتم حساب ثوابت التكوين لهذه المتراكبات. ووضع تصور عن الارتباط بين مشتقات 2-اريل مثيلين اسيتيل بنزاميدازول و ايونات النحاس الثنائى والبلاديوم الثنائى باستخدام الاشعة تحت الحمراء.