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Preparation and Characterization of Some Gold (III) Complexes with Organic Ligands

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ABSTRACT

A new four Au(III) complexes was prepared by the following steps , 1st synthesis of four ligands tow chalcone ligands (L1, L2) to preparation (M1, M2) complexes and two azo ligands contain hetero cyclic ring (L4, L3) to preparation (M3 , M4) complexes , 2nd synthesis of Au(III) complexes by the reaction of four prepared ligands and gold (III) chloride , Their structures were elucidated using spectroscopic techniques such as FT- IR (Infrared), ^{1}H-NMR , Elemental analysis , UV-Vis and physical properties such as change in color and melting point , the number of ligands in the complexes determined by using molar ratio method ,The percentage of the metal in the complexes determined by using atomic absorption technique . The results show compatibles with the theoretical studies of the proposed formula (square planar) for the synthetic complexes.

Keywords: Gold(III) Complex, Chalcon, Ligands.

INTRODUCTION

The chemistry of gold(III) complexes is far less developed than the corresponding gold(I) complexes. Gold(III) gives stable complexes with C, N, P, S, or even O-donor ligands. Organometallic chemistry is very important because many compounds have been prepared starting from organometallic gold(III) precursors[1-3]. Gold(III) complexes with nitrogen donor ligands are more stable than the corresponding gold(I) species. Several examples with polydentate amine ligands of different types have been reported. Polypyridines such as phenanthroline, terpyridine, pyrazolate ligands, and so on, form square planar gold(III) complexes such as $[AuCl(terpy)]^{2+}$ [4], $[AuMe_2(py_2CHpy)]^+$ [5] or $[AuCl_2(m\text{-}pz)]_2$ or $[Au\{N,N0\text{-}(pz)_3BH\}_2]ClO_4$ [6]. The rigid bidentate ligand phen enables the synthesis of pseudo-pentacoordinate gold(III) derivatives as in $[Au(C_6H_4CH_2NMe_2)(phen)(PPh_3)]^{2+}$ [7]. The cytotoxic activity of some of these complexes with polydentate nitrogen ligands has been tested. The complex $[AuCl_2(phen)]Cl$ has shown to be highly cytotoxic toward the A2780 tumor cell line either sensitive or resistant to cisplatin; solution chemistry studies show that the fragment $[Au^{III}phen]^{3+}$ is stable in solution for several hours, even under physiological conditions. The predominant species existing in solution under physiological conditions is likely to be $[Au(OH_2)_2(phen)]$ [8]. Gold(III) porphyrins have been used as acceptors in porphyrin diads and triads due to their ability to be easily reduced, either chemically or photochemically. A new method for incorporating gold(III) into porphyrins has been described and consists of the disproportionation of

$[Au(tht)_2]BF_4$ in its reaction with the porphyrin in mild conditions [9]. The metallation of 16-hexaphyrin with $NaAuCl_4$ yielded the aromatic gold(III) complexes and the two-electron reduction of the aromatic complexes provided the antiaromatic species [10]. However, a literature survey indicates that Gold (III) complexes are very rare, so, in the present work, we have prepared four Gold (III) complexes with different ligands in order to establish the effect of introducing azomethene, azo and chalcones group instead of other donor groups on the gold (III) complexes formation.

MATERIALS AND METHODS

General: All used starting material were obtained from (Fluka, BDH and Aldrich) without further purification. melting point determined by using Stuart Melting point SMP30, UV – visible spectrum recorded by using the (JENWAY Spectrophotometer 6800 UV / Vis), Infrared spectra were recorded as KBr pellets on a Bruker-Tensor 27 spectrometer , The molar connectivity by using a Conductivity Meter - Model CRISON Basic 30 EC .^{1}H-NMR spectra were recorded on Bruker-500 MHz spectrometer using $CDCl_3$ as a solvent and TMS (TetraMethylSilane $(CH_3)_4Si$) as internal standard. Elemental analyses (C, H, N) were performed Elemental Analyzer Perkin-Elemer 240B. Percentage of the gold metal in the complex performed Atomic absorption technique (Shimadzu AA680 GBC 933 plus).

Synthesis of ligands

Preparation of ligand (L1) 1, 5-bis (2-hydroxyphenyl) penta-1, 4-dien-3-one:

Step 1: In a 50 mL beaker mix 0.05 mol (5.1 mL) of 2 - hydroxy benzaldehyde with 0.025 mol (1.83 mL) of acetone and dissolved in 10 mL of ethanol.

Step 2: In another 250 ml beaker dissolve 5 g of NaOH in 50 mL of distilled water and 40 mL ethanol at room temperature. Then add half of the solution prepared in first step to the solution in the second step, leave for 15 min then add the remaining half and leave the reaction mixture. After constant stirring at room temperature for 1.5 h the solid obtained was filtered washed successively with distilled water and then recrystallized with ethanol. Fig.1. shows the structure of the ligand.

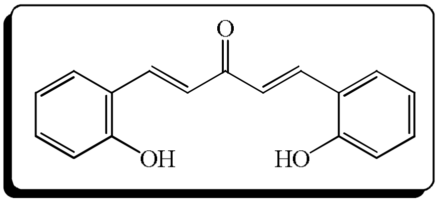


Figure 1. Structure of L1

Synthesis of 3 - (2-hydroxyphenyl) acrylaldehde

Step 1: In a 50 mL beaker mix 0.05 mol (5.1 mL) of salicylaldehyde with 0.05 mol (2.1 mL) of acetaldehyde then dissolve in 10 mL of ethanol .

Step 2: In another 250 mL beaker dissolved 5 g of NaOH in 50 mL of distilled water and 40 mL ethanol at room temperature. Then add half of the solution prepared in first step to the solution in the second step, leave for 15 min and then add the remaining half and leave the reaction mixture. After constant stirring at room temperature for 1.5 h the solid obtained was filtered, washed successively with distilled water and then recrystallized with ethanol. Fig.2. shows the structure of the ligand.

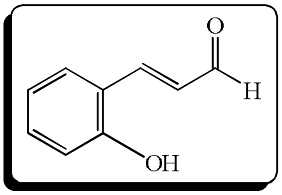


Figure 2. Structure of 3 - (2-hydroxyphenyl) acrylaldehde

Synthesis of Ligand (L2) 2,2'-(1E,1'E,3E,3'E)-3,3'-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(prop-1-ene-1-yl-3-ylidene)diphenol : A solution of 3 - (2-hydroxyphenyl) acrylaldehde (0.02 mol) in 20 mL absolute ethanol was added drop wise into a solution of *O*-phenylenediamine (0.01 mol) in 20 mL absolute ethanol contained in a 100 mL reaction flask. The mixture was refluxed for 3 h with magnetic stirring. The product was filtered, washed several times with water then recrystallized with ethanol. Fig.3. shows the structure of the ligand.

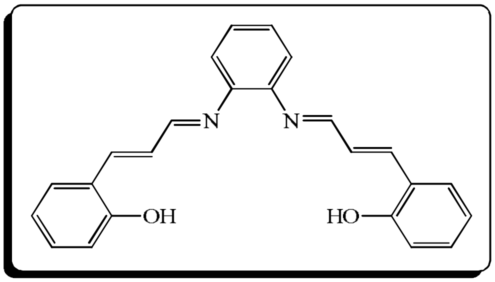


Figure 3.Structure of L2

Synthesis of ligands L3 and L4: Azo compounds were prepared as reported method [11] Fig.4.

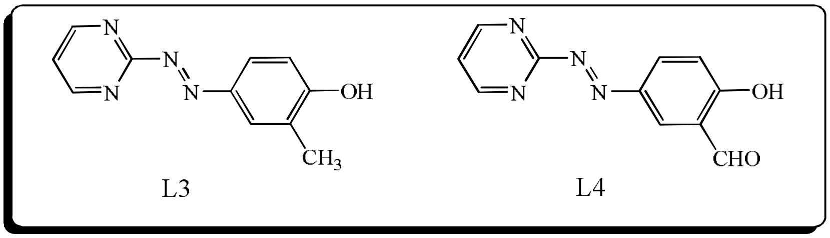


Figure 4. Structure of L3 and L4

Synthesis of complexes M1, M2, M3 and M4: In 50 mL round bottom flask calculated amount of ligand (L1, L2, L3L4) dissolved in 15 mL of ethanol mix with a solution of 0.1 g of gold (III) chloride dissolved in 15 mL of ethanol, the resulting mixture was refluxed for 1.5 h, then cooled to obtained the precipitate then filtered and washed with ethanol and dried.

RESULTS AND DISCUSSION

The prepared ligands identified by FT-IR spectrophotometer. The spectrum of L1 shows the stretching vibration for hydroxyl group (νO-H) absorption band at 3404 cm^{-1},(νC-$H_{arom.}$) at 3054 cm^{-1} , (νC=O) for α β unsaturated ketone at 1602 cm^{-1} and (νC=C_{ring}) at 1596 cm^{-1}, 1488 cm^{-1} [12]. The results for other ligands are given in table 1.

Table 1. FT-IR absorption bands for prepared ligands

Comp.	νO-H	νC-H		νC=O	νC=N	νC=C		N=N
		Arom	Aliph.					
L_1	3404	3054	-	1602	-	1596	1488	-
L_2	3429	3053	-	-	1613	1585	1481	-
L_4	3439	3055	2928	1650	-	1612	1489	1416
L_9	3427	3055	2916	-	-	1619	1479	1421

The prepared ligands identified by ^{1}H-NMR , The spectrums of L1 , L2 , L3 and L4 shows the following signals[12].

<u>L1</u> = [δ=4.94 ppm, (s, 2H), 2(OH)], [δ=7.0-8.53ppm, (m,12H), 2(Ar-CH + CH=CH)].

<u>L2</u> = [δ=3.34 ppm, (s, 2H), 2(OH)], [δ=6.95 ppm, (d, 2H), 2(CH=CH)], [δ=7.66 ppm, (m, 12H), (Ar-H)$_{\text{rings}}$], [δ=7.00-7.49 ppm, (m,2H), 2(CH=N)].

<u>L3</u> = [δ=2.1 ppm, (s, 3H), (CH_3)], [δ=5.5 ppm,(s,H), (OH)], [δ=6.8-8.8 ppm, (m,6H), (Ar-H)$_{\text{rings}}$].

<u>L4</u> = [δ=5.2 ppm, (s,H), (OH)], [δ=7.1-8.9 ppm,(m,6H), (Ar-H)$_{\text{rings}}$], [δ=10.5 ppm,(s,H), (CO-H)].

The prepared complexes identified by FT-IR spectrophotometer. The results are given in table 2.

Table 2. FT-IR absorption bands for prepared complexes

Comp	νO-H	νN-H	νC-H		νC=O	νC=N	νC=C		N=N	M-O	M-N
			Arom	Aliph							
M_1	-	-	3056	-	1603	-	1598	1490	-	948	-
M_2	-	-	3057	-	-	1622	1590	1499	-	910	549
M_4	3442	-	3056	2933	1656	-	1616	1499	1422	-	550
M_9	3426	-	3059	2930	-	-	1629	1486	1423	-	532

The theoretical elementals analysis for prepared ligand and gold (III) complexes shows a good agreement with practical percentage of elements. The results are given in table 2.

Table 3. Elemental Micro Analysis (C.H.N) for ligands and M for complexes prepared

Comp	Molecular formula	Elemental Micro Analysis Theoretical (practical)			
		%C	%H	%N	%Au
L_1	($C_{17}H_{14}O_3$)	76.68 (76.01)	5.30 (4.90)	-	-
L_2	($C_{24}H_{20}N_2O_2$)	78.24 (77.88)	5.47 (5.09)	7.60 (7.30)	-
L_3	($C_{11}H_8N_4O_2$)	57.89 (75.12)	3.35 (2.97)	24.55 (24.15)	-
L_4	($C_{11}H_{10}N_4O$)	61.67(60.98)	4.71(4.09)	26.15(25.48)	
M_1	[Au($C_{17}H_{14}O_3$)$_2$]	56.29 (55.69)	3.33 (2.98)	-	27.15 (26.64)
M_2	[Au($C_{24}H_{20}N_2O_2$)]	51.17 (50.77)	3.22 (3.11)	4.97 (4.26)	34.96 (34.14)
M_3	[Au($C_{11}H_8N_4O_2$)Cl_2]	26.63 (26.09)	1.63 (1.10)	11.29 (10.47)	39.70 (39.06)
M_4	[Au($C_{11}H_{10}N_4O$)Cl_2]	27.40(26.84)	2.09(1.77)	11.62(11.05)	40.86(39.73)

The molar conductivity for prepared complexes at concentration (10^{-3} Molar) as solutions of Dimethyl sulphoxide (DMSO) at room temperature (25°C) The results are given in table 4.

Table 4. Molar conductivity for prepared complexes

No.	M	(ohm $^{-1}$. cm^2 . mol^{-1})
1	[M1]	197.5
2	[M2]	82.2
3	[M4]	49.7
4	[M9]	47.5

Moreover the ligands and complexes identified by UV-Vis spectrum. The results are given in table 5.

Table 5. λ_{max} Values for prepared ligands and complexes

Comp.	Band (1)		Band (2)		Band (3)	
	λ_{max} (nm)	ν (cm^{-1})	λ_{max} (nm)	ν (cm^{-1})	λ_{max} (nm)	ν (cm^{-1})
L_1	528	18939	358	27932	262	38167
L_2	378	26455	330	30303	270	37037

L_3	**470**	**21276**	**325**	**30769**	**264**	**37878**
L4	**455**	**21978**	**320**	**31250**	**260**	**38461**
M_1	**306**	**32679**	**292**	**34246**	**266**	**37593**
M^2	**332**	**30120**	**318**	**31446**	**292**	**34246**
M_3	**458**	**21834**	**305**	**23756**	**261**	**38314**
M_4	**440**	**22727**	**300**	**33333**	**258**	**38759**

The physical properties for prepared ligands and complexes are given in table 6.

Table 6. Physical properties for prepared ligands and complexes

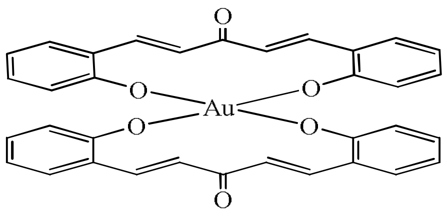
Comp.	Colour	yield%	M.P.
L1	**Violet**	**75**	**221**
L2	**Orange Yellow**	**79**	**163**
L3	**Built-red**	**71**	**224**
L4	**Dark Brown**	**68**	**250(Dec.)**
M1	**Dark purple**	**70**	**>300**
M2	**Light Brown**	**75**	**>300**
M3	**Dark Brown**	**68**	**>300**
M4	**Black**	**65**	**>300**

APPLICATIONS

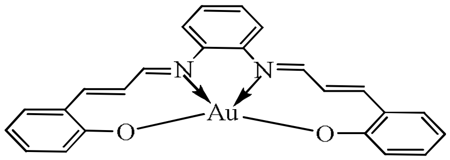
This study is useful for knowing the physical properties for gold (III) complexes and know the suitable ligands to prepare other complexes which have biological activity towards cancer cells.

CONCLUSIONS

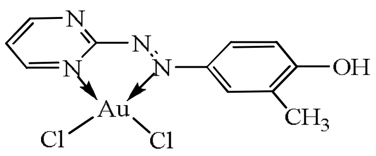
All prepared complexes described by stability and its resistance for heating and air. Physical and spectrophotometry results indicates that the stereo shape for prepared complexes is square planar. L1 use two oxygen atoms to formation the complex M1 therefore the ratio of metal : ligand is (1 : 2), L2 use two oxygen atoms and two azomethene groups nitrogen atom to formation the complex M2 therefore the ratio of metal : ligand is (1 : 1), L3 and L4 use azo group nitrogen atom and hetero aromatic ring nitrogen atom to formation the complex M3 and M4 therefore the ratio of metal : ligand is (1 : 1) .Fig 5. Show the shape for prepared complexes.



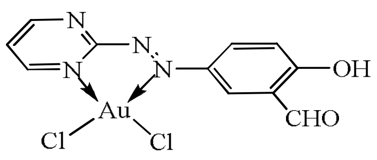
M1



M2



M3



M4

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