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Synthesis and characterization of gold (III) Complexes of 1,1,2,2-tetrakis (2-substituted-thio) ethyl or propyl thio ethylene ligands

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Abstract: A new multidentate ligands 1,1,2,2-tetrakis {(2-benzylthio) ethylthio} ethylene (L^1) ; 1,1,2,2-tetrakis {(3-benzylthio) propylthio} ethylene (L^2) ;1,1,2,2-tetrakis {2-(o-tolylthio) ethylthio} ethylene (L^3) ;1,1,2,2-tetrakis {3-(o-tolylthio) propylthio} ethylene (L^4) ; 1,1,2,2-tetrakis {2-(4-chloro-pheny-lthio) ethylthio} ethylene (L^5) ; 1,1,2,2-tetrakis {3-(4-chloro-phenylthio) propylthio} ethylene (L^6); 1,1,2,2-tetrakis {2-(o-aminophen-ylthio) ethy-lthio} ethylene (L^7) ; 1,1,2,2-tetrakis {3-(o-aminophen-ylthio) propylthio} ethylene (L^8) , were prepared from the reaction between 1,1,2,2-tetrachloroe-thlene and equimolar amounts of potassium hydroxides and 4-mercapto-2-thia-1-butylbenzene or 4-mercapto-2-thia-1-pentylbenzene or o-methyl-4-mercapto-1-thia-1-butyl benzene or o-methyl -4-mercapto-1- thia-1-pentylbenzene or p-chloro-4-mercapto-1-thia-1-butylbenzene or p-chloro-4-mercapto-1-thia-1-pentylbenzene or o-amino-4-mercapto-1-thia-1-butylbenzene or o-amino-4-mercapto-1-thia-1- pentyl benzene. Complexes of general formula $[Au_2(L)Cl_4]Cl_2$ ($L=L^1$-L^8) were prepared through the direct reaction of the above ligands with $H[AuCl_4]$ in (1:2) ligand to metal molar ratio . The prepared complexes were characterized by their elemental analysis , IR , UV-Vis , spectra magnetic measurements and conductivity measurements .The results of electronic spectra and magnetic measurements indicate that the complexes have a square planar geometry , and the molar conductivity measurements indicate that all the complexesare (1:2) electrolyte.

Keywords: Au (III) complexes , substituted thio ethylene ligands, square planar complexes .

Introduction

The chemistry of gold has grown rapidly in recent years and along with this as improved understanding of gold sulfur bonding [(1)]. An extensive range of bis-dithiolene complexes of Au and their properties have been reported , the majority is $[Au(dithiolene)_2]^-$ complexes with a square planar $[AS_4]$ core , diamagnetic , and generally considered to involve a Au(III) (d^8) centre [(2-4)] . The redox properties of $[Au(dithio\text{-}lene)2]^-$complexes have been investigation and related $[Au(dithiol\text{-}ene)_2]^2$(z=0-2) complexes identified; the electronic structures of these systems , notably the role of the dithiolene ligands in the redox processes , have been probed by a b initio and density functional calculations[(5-7)].

Planar metal complexes of the [M(N-N)(S-S)] type , were [M=Pd(II) , Pt(II) and Au(III) having diimine (N-N) ligand as a π electron acceptor and dithiolate (S-S) ligand as an electron donor are polarized around the metal ions . Metal complexes of this type containing sulfur rich dithiolate ligands are expected to form unique columnar molecular stackings and layered arrangement through electrostatic interactions of the polarized metal center moieties , metal - metal interactions and many (S-S) non-bonded contacts in the solid state , several polarized metal complexes of the type [M(dimmine)(Sulfur rich dithiolate)] ,M=Pd(II) and Pt(II) and their oxidized species behaving as electrical conductors [(8-11)] .

A series of new 2-phenylpyridire Au(III) complexes [Au(ppy)x] with various thiolate ligands has been synthesized and characterized (X=(SCN)(NCS)(1) , tlc(thiolactate)(2) , tsc (thio salicylate)(3) , dmp (2,3-dimercapto-1-propanal((4), dms(2,3-dimercapto succinic acid)(5) , cys (cysteine)(6) . The crystal structure of [Au(ppy)(SCN)(NCS)](1) shows the two soft carbanion and sulfur donor mutually cis to each other in thermodynamically most stable isomcr . Crystal structure of $[Au(ppy)(tsc)]1.5H_2O$(3) and $[Au(ppy)(cys)]0.5(Cl+ClO_4)$(6) show the expected square planar coordinated around the gold atom and the stronger trans inference groups S and C adopting the cis oriented configuration [(12)] .

New group11 metal complexes have been prepared using the tripodal bis (imidazole) thioether ligand (N-methyl-4,5-diphenyl-2-imidazolyl)$_2$C(OMe)C$(CH_3)_2$S(tert-Bu)($\{BIT^{OMe,StBu}\}$),(2) . The Pincer ligand offers a N_2S donor atom set that can be used to coordinate the group11 metals in different oxidation states [Au^1, Au^{111} , Ag^1 , Cu^1 and Cu^{11}] . Thus the new

compounds $[Au\{BIT^{OMe,StBu}\}Cl][AuCl_4]_2$(3) , $[Au\{BIT^{OMe,StBu}\}X]$ X= $OSO_2CF_3^-$(5) , PF_6^- (6) , have been synthesized from reaction of (2) with the appropriate metal precursors [13] .

Reactions of the dinuclear platinum (II) sulfide complex $[Pt_2(\mu\text{-}S)(pph_3)_4]$with a range of gold(III) dichloride complexes $[AuLCl_2]$ containing C,N- or N,N-cyclo aurated ligands L gives new series of dicationic adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Au]^{+2}$, isolated as their PF_6^- salts . The complexes investigated are $[Au\{C_6H_4(CH_2NMe_2)\text{-}2\}C_2]$, $[Au\{C_6H_3(CH_2\text{-}NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Cl_2]$,$[Au\{NC_5H_4(CH_2C_6H_4)\text{-}2\}Cl_2]$,$[Au\{NC_5H_4(CO\text{-}C_6H_4)\text{-}2\}Cl_2]$ and $[Au\{NC_5H_4(CH_2NMe_2)\text{-}2\}Cl_2]$. The complexes are chara-cterized by NMR spectroscopy , electrospray mass spectrometry and micro-elemental analysis and X-ray crystallography [14] .

A new pyridine 5(pyridine -4yl)-5-hydro-6-dihydro-1,4-dithin - 2,3-dithiolate,4-pdddt=5-(pyridin -4-yl)-5-hydrosubstituted clithiolene complex , pph_4 $[Au(4\text{-}pdddt)_2]$ was and characterized cyclic voltametry show three redox process corresponding to the inter conversion between dianionic , monoanionic , neutral and cationic states , as often presented by this type of bis (dithiolene) complexes [15].

In view of these interesting results and as continuation of our compretensive studies on transition metal complexes with sulfur containing ligands [16-19] , we have prepared new multidentate ligands and as well as their dinuclear gold (III) complexes .

Experimental

The reaction were carried out under nitrogen atmosphere using vacuum lime and schlenk techniques . All starting materials used were of analar grade , were purchased from Aldrich or Fluka and used as supplied . Solvents were dried and distilled according to standard procedure .

Physical Measurements

Elemental analysis (C,H,N,S) were carried by the staff of chemical analysis service of Liverpool University (U.K.) , on conductivity measurements were performed at room temperature in 10^{-3}M DMF solution, employing on Jenway 4510 conductivity meter . Infrared spectra were run on Brucker Tensor 27Co FT-IR spectrometer in the range (4000-200 cm^{-1})using CsI disc . Electronic spectra were recorded on Shimadzu UV/1650PC spectrophotometer for 10^{-3} Msolution of complexes in DMF using l cm quartz cell . Melting points or decomposition temperature were determined on a Buchi 510 melting points apparatus and were uncorrected. The magn-etic measurements were carried out at 25°C on the solid state by Feraday's method using Brucker BM6 instrument . ^1H , ^{13}C NMRspectra of the ligands were determined on measured by using DMSO d^6or $CDCl_3$ as solvents at (20°C) by using (BRUCKER AVANCE and DPX 400 MHz) . The chemical shifts being measured relative to tetramethylsilane (TMS) as an internal standard . This measurements were carried out at Department of Chemistry , Liverpool University (UK) .

Synthesis of the ligands

The starting materials were prepared according to the literature [20].

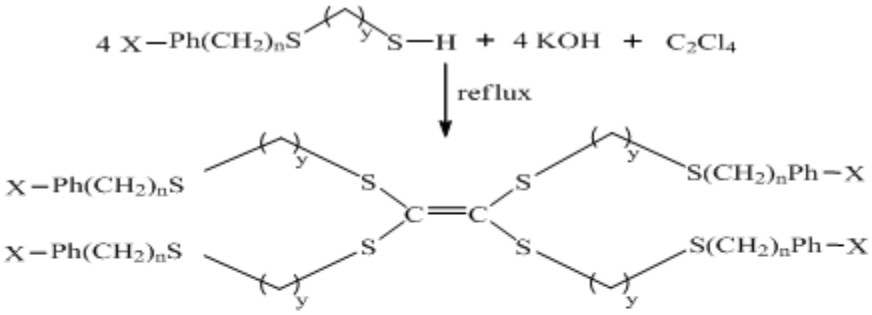
Synthesis of 1,1,2,2-tetrakis (2-benzylthio)ethylthio) ethylene (L^1) :

A solution of 4-mercapto-2-thia-1-butylbenzene (0.73 g , 0.004 mol) in 20 ml toluene was added to a solution of (0.23 g , 0.004 mol) of KOH in 10 ml ethanol , then the mixture was added to a solution of tetrachloroethylene (0.17 g , 0.001 mol) in 10 ml ethanol . The mixture was stirred under reflux for 12 h . On cooling the precipitate was obtained which was filtered off , washed several times with ethanol to remove the formed KCl , then was washed with diethylether and then dried under vacuum for 4h .

Synthesis of 1,1,2,2-tetrakis [3-(benzylthio)propylthio] ethylene (L^2) :

Treatment of a solution of 4-mercapto-2-thia-1-pentylbenzene (0.79 g , 0.004 mol) in (20 ml) toluene with a solution of (0.23 g , 0.004 mol) of KOH in (10 ml) ethanol , then the mixture was added to a solution of tetrachloroethylene (0.17 g , 0.001 mol) in (10 ml) ethanol . The mixture was stirred under reflux for 12h . On cooling the precipitate was obtained which was filtered off , washed several times with ethanol to remove the formed KCl , then it was washed with diethylether and then dried under vacuum for 4h .

The preparation of other ligands (L^3-L^8) using similar procedure , the preparation of the ligands (L^1-L^8) shown in Scheme (1) .



n = 1, X = H ,	y = 2	L^1
n = 1, X = H ,	y = 3	L^2
n = 0, X = *o*-CH_3 ,	y = 2	L^3
n = 0, X = *o*-CH_3 ,	y = 3	L^4
n = 0, X = *p*-Cl ,	y = 2	L^5
n = 0, X = *p*-Cl ,	y = 3	L^6
n = 0, X = *o*-NH_2 ,	y = 2	L^7
n = 0, X = *o*-NH_2 ,	y = 3	L^8

Scheme (1) : Preparation of the ligands (L^1-L^8)

Results and Discussions

The new multidentate ligands (L^1-L^8) were prepared the reaction of equimolar amount of 4-mercapto-2-thia-1-butyl benzene or 4-mercapto-2-thia-1-pentyl benzene or o-methyl-4-mercapto-1-thia-1-butyl benzene or o-methyl -4- mercapto-1- thia-1-pentyl benzene or p-chloro-4-mercapto-1-thia-1-butyl benzene or p-chloro-4-mercapto-1-thia-1-pentyl benzene or o-amino-4-mercapto-1-thia-1-butyl benzene or o-amino-4-mercapto-1-thia-1- penty-lbenzene and KOH with tetrachloroethylene to give the above ligands (Scheme 1) . The physical properties of these ligands are listed in Table (1) . The ligands were characterized by elemental analysis , IR , ^{1}H , ^{13}C NMR spectroscopy and electronic spectra .

The ligands (L^1-L^8) are white to brown in colour , and are isolated in good yield and are fairly pure by elemental analysis and NMR measurements Table (1) . The ^{1}H NMR spectrum of L^1 , L^2 , L^6 , L^7 as follow : The ^{1}H NMR spectrum of (L^1) exhibit the aromatic protons were observed in the region 7.249 - 7.343 (m , 20 H) , 3.945 (t , H) , 3.946 – 3.879 (m , 8H , CH_2), 3.819 (t , 1H) , 3.725 (s, 1H) , 3.146 (m , 3H) , 2.88 – 2.827 (m , 3H) , 2.693 – 2.646 (m , 5H) , 2.572 (d , 2H) . The ^{1}H NMR spectrum of (L^2) exhibit the aromatic protons were observed in the region 7.2-8.2 (m,20H,Ar) , 2.46 (m,8H,CH_2) , 2.70 (t,8H,CH_2) , 3.07 (t,8H,CH_2) , 3.6 (s,8H,CH_2) . The ^{1}H NMR of L^6 exhibit the aromatic proton in the region 8.3-8.5 (m,16H,Ar) , 1.1 (t,8H,CH_2) , 1.7 (t,8H,CH_2), 2.5 (t,8H, CH_2) . The ^{1}H NMR of (L^7) exhibit the aromatic protons were observed in the region 6.840 -7.411 (m , 16H , Ar) , 4.452 (s , 8H , NH_2) , 3.134 (m , 8H , CH_2) , 2.898 (m , 8H , CH_2) , the ^{13}C - NMR spectrum shows peaks at 30.4-35.33 ppm for (a – c) CH_2 , 127.5 for c = c and 128.9 - 139.0 ppm for aromatic carbon for L^1 . The ^{13}C NMR spectrum shows peaks at (26.00-36.11) for (a-d) CH_2 , 125 for C=C and 126-140 ppm for aromatic carbon for L^2 , the ^{13}C NMR spectrum for (L^6) shows peaks at 25.1-31.0 for (a-c)CH_2 , 105.55 for C=C , 129-131 for aromatic carbon . The ^{13}C NMR spectrum for (L^7) shows peaks at 22 . 0-38.2 for (a - c) CH_2 and 125.5 for (C = C) and 128.47-148.0 ppm for aromatic carbon . as in Fig. (1a,1b) .

The complexes were prepared through direct reaction of the gold salts $H[AuCl_4]$ with the above ligands in (2:1) molar ratio , gave the complexes of the general formula $[Au (L) Cl_4]Cl_2$.

The analytical data of the complexes are given in Table (2) . These data were in a good agreement with the proposed formula . All the complexes are colored , solid and stable towards air and moisture at room temperature . They melt or decompose at high temperature and more or less soluble in common organic solvents , they are soluble in DMF and DMSO. The observed molar conductance of the complexes in DMF at room temperature are consistent with (1:2) electrolytic nature of the complexes [21] .

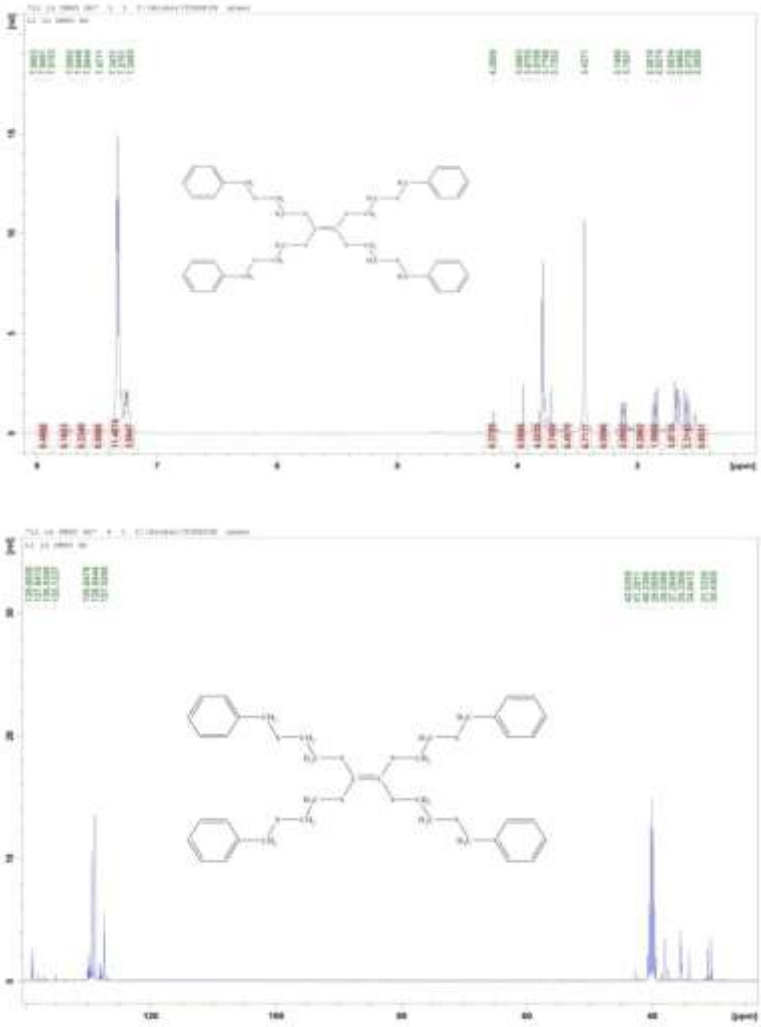
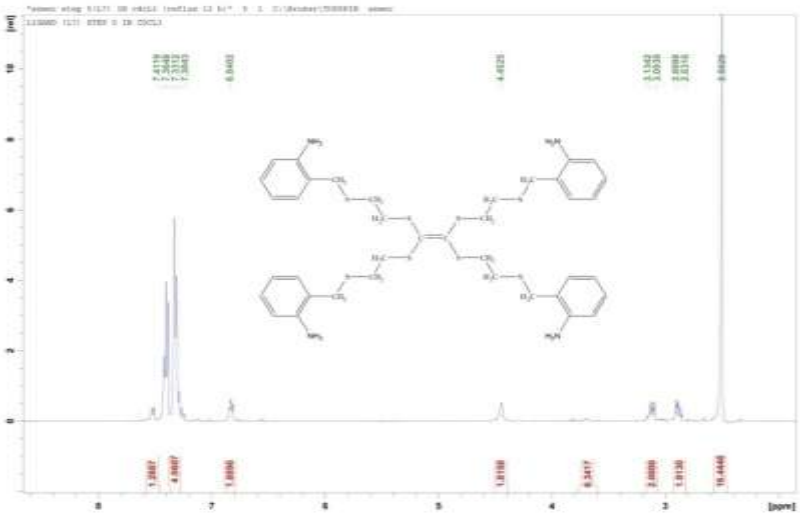


Fig. 1a : $^{1}H,^{13}C$ for ligand (L^{1})



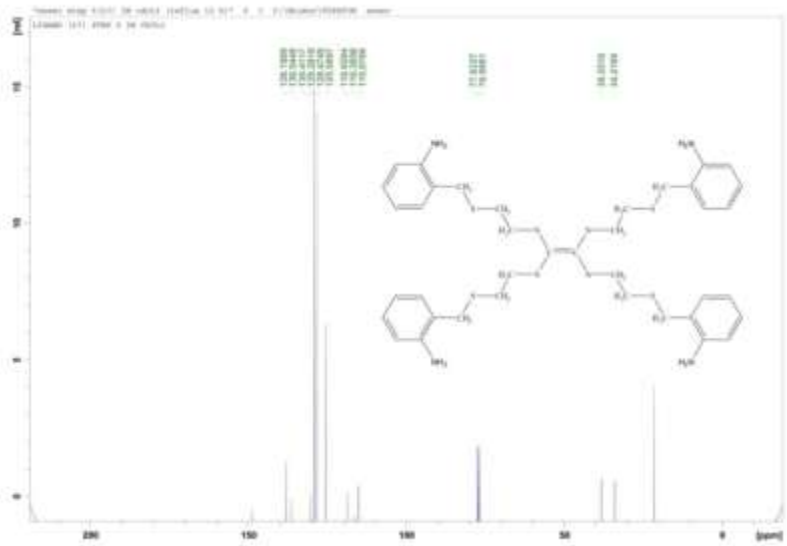


Fig. 1b: $^{1}H,^{13}C$ for ligand (L^{7})

The IR spectra of the complexes were compared with those of the free ligands in order to determine the involvement of coordination sites in chelation. Characteristic peak in the spectra of the ligands and their complexes were considered and compared.

The IR spectrum of the ligands exhibit a band at (1620-1655cm^{-1}) due to the free double bond ν (C=C) . This band does not shift in the spectra of the complexes indicating that it is not involved in the coordination with Au (III) ion . A sharp bands at (829-866 cm^{-1}) are due to the ν (C-S) group . It's position in the complex has been observed at (816-883 cm^{-1}) , indicate that this stretch frequency was shifted upward or downward indicating the involvement of the sulfur atom in coordination[22]. The IR absorption of the NH_2 group of the ligands (L^7 and L^8) remains almost constant upon coordination with A_4 metal , i.e. the coordination had taken place via sulphur atoms of the ligands .
Furthermore , the IR spectra showed a bands in the (352-384 cm^{-1}) region which tentatively assigned to ν (Au-S) . The IR spectra also showed in all complexes two medium to weak brands around (275-320 cm^{-1}) assigned to ν (Au-Cl) in Cis-arrangement [23].

The diamagnetic nature of the Au (III) complexes are consistent with the normal square planar geometry around the Au (III) ion [24].

Electronic absorption spectra of the complexes in DMF are listed Table (3) . In the spectrum of the ligands the π-π* transitions were observed at (35714-32258 cm^{-1}) . In the spectrum of the complexes they show new bands at (15337-22966 cm^{-1}) assignees to $^{1}A_{1}g$ $^{1}A_{2}g$ transition , these bands correspond fairly well to a square planar geometry around Au (III) ion . Similar results were found in Pt (II) and Au (III) complexes of the form [M(diimin) (dithiolate)] [25] . The ligands used in this study , coordinate to the Au (III) ions in tetradentate fashion from the sulphur atoms . The suggested structures of the prepared complexes are show in Fig. (2).

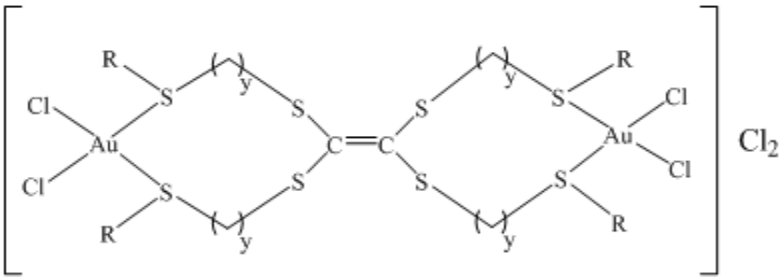


Fig. (2) : Suggested structures of the prepared complexes.

Table (1) : Some physical properties and elemental analysis of the prepared ligands

Ligand	Chemical formula	m . p °C	Color	Yield	Elemental analysis found / (calculated)			
					C%	H%	N%	S%
L^1	$C_{38}H_{44}S_8$	231-233	Beige	65	59.71 (60.31)	5.42 (5.82)	----	33.64 (33.86)
L^2	$C_{42}H_{52}S_8$	236-238	White	67	63.47 (62.06)	6.68 (6.40)	----	31.04 (31.52)
L^3	$C_{38}H_{44}S_8$	285-288	Pale yellow	65	60.20 (60.31)	5.61 (5.82)	----	32.90 (33.86)
L^4	$C_{42}H_{52}S_8$	258-260	Beige	88	61.87 (62.06)	6.35 (6.40)	----	30.92 (31.52)
L^5	$C_{34}H_{32}S_8Cl_4$	255-258	White	63	48.46 (48.68)	3.64 (3.81)	----	30.23 (30.54)
L^6	$C_{38}H_{40}S_8Cl_4$	260-262	White	64	50.81 (51.00)	4.32 (4.47)	----	28.44 (28.63)
L^7	$C_{34}H_{40}N_4S_8$	130^d	Light brown	72	53.99 (53.68)	5.51 (5.26)	7.86 (7.36)	32.74 (33.68)
L^8	$C_{38}H_{48}N_4S_8$	284^d	Beige	62	55.72 (55.88)	5.93 (5.98)	6.51 (6.86)	30.72 (31.37)

d= decomposition temperature

Table (2) : Analytical data and physical properties of the complexes .

No.	Chemical formula	M. P. °C	Color	Yield	Elemental analysis (found) / calculated				Λ (10^{-3}M) $Ohm^{-1}.mol^{-1}.cm^2$
					C%	H%	N%	S%	
1	$[Au_2L^1Cl_4]Cl_2$	170^d	Brown	82	32.81 (33.45)	3.31 (3.22)	----	18.53 (18.78)	122
2	$[Au_2L^2Cl_4]Cl_2$	110-112	Greenish brown	80	35.23 (35.51)	3.58 (3.66)	----	18.21 (18.04)	124
3	$[Au_2L^3Cl_4]Cl_2$	306^d	Light brown	81	32.96 (33.45)	3.41 (3.22)	----	18.46 (18.78)	135
4	$[Au_2L^4Cl_4]Cl_2$	108-110	Dark brown	66	35.62 (35.51)	3.51 (3.66)	----	17.82 (18.04)	142
5	$[Au_2L^5Cl_4]Cl_2$	122^d	Light brown	78	28.12 (28.23)	2.30 (2.21)	----	17.60 (17.71)	155
6	$[Au_2L^6Cl_4]Cl_2$	241-244	Dark brown	52	30.44 (30.38)	2.53 (2.66)	----	17.18 (17.05)	118
7	$[Au_2L^7Cl_4]Cl_2$	161-164	Brown	56	29.64 (29.84)	2.76 (2.92)	4.23 (4.09)	18.61 (18.72)	182
8	$[Au_2L^8Cl_4]Cl_2$	320^d	Dark brown	60	32.20 (32.04)	3.25 (3.37)	3.81 (3.93)	17.85 (17.99)	148

d= decomposition temperature

Table (3) : Infrared , electronic spectra of the free ligands and there metal complexes .

Ligand seq.	Chemical formula	ν(C=C) cm^{-1}	ν (C-S) cm^{-1}	ν (NH_2) cm^{-1}	ν (Au-S) cm^{-1}	ν(Au-Cl) cm^{-1}	UV/Vis ν (cm^{-1})
L^1	$C_{38}H_{44}S_8$	1653(m)	857(m)	----	----	----	34246,37593
L^2	$C_{42}H_{52}S_8$	1620(w)	866(w)	----	----	----	32894
L^3	$C_{38}H_{44}S_8$	1647(m)	839(m)	----	----	----	35211
L^4	$C_{42}H_{52}S_8$	1624(w)	865(w)	----	----	----	32258

L^5	$C_{34}H_{32}S_8Cl_4$	1655(m)	849(m)	----	----	----	40983,35714
L^6	$C_{38}H_{40}S_8Cl_4$	1652(m)	831(w)	----	----	----	32258
L^7	$C_{34}H_{40}N_4S_8$	1618(s)	829(w)	3343(b)	----	----	32467
L^8	$C_{38}H_{48}N_4S_8$	1652(m)	831(w)	3199(b)	----	----	33557
1	$[Au_2L^1Cl_4]Cl_2$	1655(m)	816(w)	----	352(w)	282(m) 302(w)	18518
2	$[Au_2L^2Cl_4]Cl_2$	1625(w)	822(w)	----	356(w)	281(w) 304(w)	15337 , 22702
3	$[Au_2L^3Cl_4]Cl_2$	1642(m)	858(w)	----	373(w)	275(w) 305(w)	18939
4	$[Au_2L^4Cl_4]Cl_2$	1632(w)	872(w)	----	380(w)	291(w) 310(w)	17064
5	$[Au_2L^5Cl_4]Cl_2$	1650(w)	822(w)	----	382(w)	297(w) 315(w)	18315
6	$[Au_2L^6Cl_4]Cl_2$	1648(w)	883(w)	----	377(w)	283(w) 300(w)	15723 , 18248
7	$[Au_2L^7Cl_4]Cl_2$	1624(w)	870(w)	3330(b)	365(w)	302(w) 315(w)	22966
8	$[Au_2L^8Cl_4]Cl_2$	1648(w)	876(w)	3217(b)	384(w)	285(w) 320(w)	15942

w= week , m=medium , s=strong , b=broad.

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