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Synthesis and Characterization of Gold(III) Complexes with *bis*-(1,4-Sodium thioglycolate)butane Ligand

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The new ligand *bis*-(1,4-sodium thioglycolate)butane (L) $^{-}O_2CCH_2S(CH_2)_4SCH_2CO_2^{-}$, has been prepared from the reaction of disodium salt of mercaptoacetic acid and 1,4-dichlorobutane. Mono, di and tetranuclear complexes were obtained by direct reaction of the *bis*-(1,4-sodium thioglycolate)butane with $H[AuCl_4]$ in 1:1, 1:2, 2:2 and 4:2 metal:ligand molar ratio. The prepared complexes were characterized by elemental analysis, spectral studies FT-IR and UV-Vis, magnetic measurement, conductivity measurement and ^1H NMR for the ligand. The electrical conductance data indicate that the complexes of the formula $[Au(L)]Cl$, $Na[Au(L)_2]$ and $[Au_3(L)_2Cl_4][AuCl_4]$ are 1:1 electrolyte and $[Au_4(L)_2Cl_6]Cl_2$ is 1:2 electrolyte. Electronic spectra and magnetic moment values indicate the presence of square planner geometry around the Au(III) ion. Molecular modeling program MM2 is used to determine the most stable isomer which coincidence with experimental results.

Key Words: Gold(III) complexes, *Bis*-(1,4-sodium thioglucolate)-butane.

INTRODUCTION

Gold being the most noble of all metals shows low affinity for binding oxygen. Nevertheless a number of compounds with Au-O bonds have been synthesized with gold in the formal oxidation state[1] +1, +2, +3. Generally these compounds are thermally rather unstable as consequence of a mismatch of the hard, basic oxygen ligand with soft gold center which causes a relatively weak Au-O linkage[2]. On the other hand, weak bands are usually highly reactive so that gold compounds containing Au-O bonds are expected to display interesting reaction chemistry. Actually, gold oxygen interactions are thought to be involved in the catalytic activity of gold dispersed on transition metal oxides in some relevant heterogeneous catalytic process[3,4].

Gold(III) complexes with oxygen donor ligands, such as β-dikenes or alkylsiloxides are employed as precursors for chemical vapour deposition[5].

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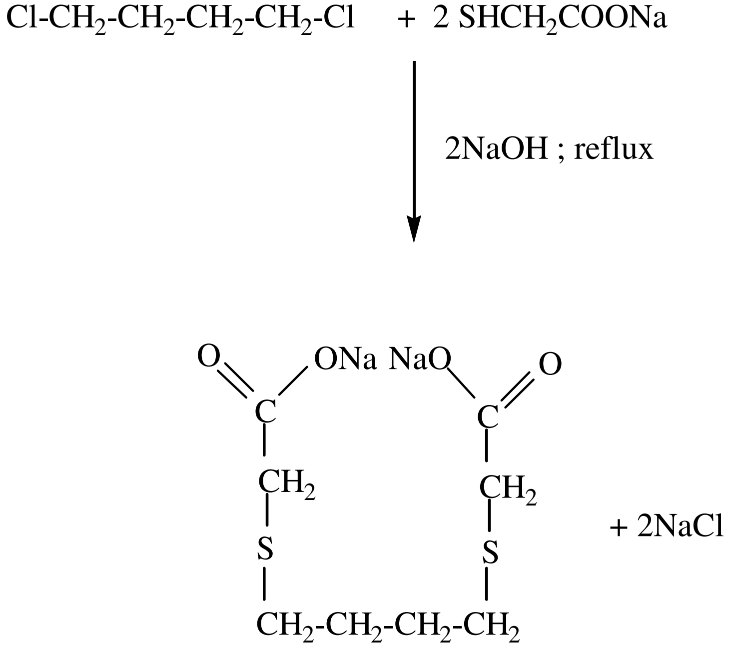
Gold(III) complexes constitute a new class of metallodrugs of potential interest for cancer treatment. During the past decade different kinds of gold(III) complexes have been reported to be appreciably stable under physiological-like conditions and to manifest relevant antiproliferative properties against selected human cell lines[6-8].

Four new $[PPh_4][Au(dithiolene)_2]$ complexes, each involving two symmetrically substituted dithiolene ligands, (SC(H)CRS; R = phenyl, pyridine-2-yl, pyridine-3-yl or pyridine-4-yl), have been synthesized by reacting $K[AuCl_4]$ with the corresponding dithiolene, generated by base hydrolysis of the thione-protected 1,3-dithiolate[9]. A series of new 2-phenyl pyridine Au(III) complexes [Au(ppy)X] with various thiolate ligands has been synthesized and characterized (X = (SCN)(NCS) (**1**), TLC-(thiolactate) (**2**), TSC (thiosalicylate) (**3**), DMP (2,3-dimercapto-1-propanol) (**4**), DMS (2,3-dimercaptosuccinicacid) (**5**), CYC (cysteine) (**6**). The crystal structure of [Au(ppy)(SCN)(NCS)] (**1**) shows the two soft carbanion and sulfur donors mutually *cis* to each other[10].

Metal complexes with sulphur rich ligands are very interesting and in continuation of our studies on Pd and Pt metal ions with sulphur contain ligands[11-13], we are presenting here the preparation and characterization of new ligand *bis*-1,4-(sodium thioglycolate)butane **Scheme-I** and its complexes with Au(III) ion in different molar ratios.



Scheme-I: Ligand synthesis

EXPERIMENTAL

All chemicals were of reagent grade quality and were purchased from commercial sources (BDH and Fluka). They were used without further purification.

IR spectra were recorded on Brucker Tensor 27Co. (FTIR) spectrophotometer in the 4000-250 cm^{-1} range using CsI disc. Electronic spectra were recorded on Shimadzu UV 160 spectrophotometer for 10^{-3} M solution of complexes in dimethyl formamide using 1 cm quartz cell. The ^1H NMR spectra were recorded on a BrukerDRX-200 spectrometer in DMSO-d_6 at room temperature. Conductivity measurements were made on 10^{-3} M solution of the complexes in DMF at ambient temperature using conductivity meter 4070 Jenway. The magnetic measurements were carried out at 25 ºC on the solid state by Faraday's method using Bruker BM6 instrument. Metal content analyses were made on Shimadzu AA670 atomic absorption spectrophotometer.

Synthesis of the compounds

Preparation of *bis*-(1,4-sodium thioglycolate)butane: The ligand was prepared according to the following general method: The reaction of disodium thioglycolate {prepared *in situ* from the reaction of an equivalent amount of NaOH (0.01 mol) and (0.01 mol) mercaptoacetic acid sodium salt in 30 mL ethanol} with 1,4-dichlorobutane (0.01 mol) in 10 mL ethanol. The mixture was boiled under reflux for 5 h. The colourless solution was filtered off and the filtrate was concentrated to dryness and washed with ethanol and diethylether, then dried under vacuum for several hours.

Preparation of the complexes with formulas:

$[Au(^-OOCCH_2S(CH_2)_4SCH_2COO^-)]Cl$ (**1**)

$[Au_2(^-OOCCH_2S(CH_2)_4SCH_2COO^-)_2Cl_2]$ (**2**)

A solution of 1.0 or 2.0 mmol $H[AuCl_4]$ in 15 mL ethanol was added to a stirred solution of the ligand, *bis*(1,4-sodium thioglycolate) butane dissolved in 15 mL ethanol, in molar ratio 1:1 or 2:2, (M:L). The addition was continued for 0.5 h and the reaction mixture was refluxed for 3 h and then the mixture was left 24 h at room temperature to give the precipitate which was filtered off, washed with ethanol and diethyl ether and then dried under vacuum for 4 h, the filtrate of the mixture was reduced to 1/3 and left for 3 days in cooling bath to give the precipitate $[Au_2(^-OOCCH_2S(CH_2)_4SCH_2COO^-)_2Cl_2]$ (**2**), which was filtered off, washed and dried.

Preparation of the complexes with formulas:

$[Au_2(^-OOCCH_2S(CH_2)_4SCH_2COO^-)Cl_4]$ (**3**)

$[Au_3(^-OOCCH_2S(CH_2)_4SCH_2COO^-)_2][AuCl_4]$ (**4**)

$[Au_4(^-OOCCH_2S(CH_2)_4SCH_2COO^-)_2Cl_6]Cl_2$ (**5**)

A solution of $H[AuCl_4]$ in 20 mL ethanol was added to an ethanolic solution of the ligand in 2:1 or 4:2 molar ratios (M:L). The reaction mixture was stirred under reflux for 3 h and left after the reflux 24 h at room temperature to give precipitate, $[Au_2(^-OOCCH_2S(CH_2)_4SCH_2COO^-)Cl]$ (**1**), which was filtered off, washed with ethanol and diethyl ether and then dried under vacuum for several hours. The filtrate of the mixture was left 2 days in cooling bath give brown precipitate, $[Au_3(^-OOCCH_2S(CH_2)_4SCH_2COO^-)_2][AuCl_4]$ (**4**)[14], which was filtered off, washed and dried and the filtrate was reduced to one-third and left for one week in cooling bath to give the pale brown precipitate, $[Au_4(^-OOCCH_2S(CH_2)_4SCH_2COO^-)_2Cl_6]Cl_2$ (**5**), which was also filtered, washed and dried under vacuum for 4 h.

Preparation of $Na[Au(^-OOCCH_2S(CH_2)_4SCH_2COO^-)_2]$ (6): A solution of 2.0 mmol of the ligand *bis*(1,4-sodium thioglycolate) butane in 15 mL ethanol was mixed with a solution of 1.0 mmol of $H[AuCl_4]$ in 15 mL ethanol in molar ratio 1:2 (M:L). The reaction mixture was refluxed for 2 h, the mixture was left 24 h at room temperature to give a brown precipitate, which was filtered off, washed with ethanol and diethyl ether and then dried under vacuum for several hours.

RESULTS AND DISCUSSION

Treatment of mercaptoacetic acid sodium salt with 1,4-dichlorobutane in basic medium gives the ligand *bis*-1,4-(sodium thioglycolate)butane in high percentage yield (90 %) as shown in **Scheme-I**. The reaction of $H[AuCl_4]$ with above ligand in different molar ratio gave the complexes of the general formula $[Au(L)]Cl$ $[Au_2(L)Cl_4]$, $Na[Au_2(L)_2]$, $[Au_2(L)_2Cl_2]$, $[Au_3(L)_2Cl_4][AuCl_4]$ and $[Au_4(L)_2Cl_6]Cl_2$. All the complexes are non-hygroscopic and stable in air, but are insoluble in common organic solvents and hence their crystal structures were not determined.

The analytical data of the complexes are given in Table-1. These data are in a good agreement with the proposed formula. All the complexes are stable at room temperature and insoluble in the common organic solvent but they are soluble in

TABLE-1
PHYSICAL PROPERTIES OF THE LIGAND AND THEIR COMPLEXES

No.	Complex (colour)	Yield % / (m.p., °C)	Elemental analysis (%): Found (calcd.)				Λ ohm^{-1} cm^2 mol^{-1}	μ_{eff} (BM)
			C	H	N	Au		
L	$(C_8H_{12}O_4S_2Na_2)$ (White)	90 (–)	34.00 (34.04)	4.26 (4.26)	22.67 (22.69)	---	---	Dia
1	$[Au(L)]Cl$ (Dark brown)	80 (293^d)	20.34 (20.51)	2.55 (2.56)	13.61 (13.67)	42.00 (42.09)	99	Dia
2	$[Au_2(L)_2Cl_2]$ (Brown)	33 (266)	20.41 (20.49)	2.55 (2.57)	13.56 (13.66)	42.01 (42.05)	50	Dia
3	$[Au_2(L)Cl_4]$ (Golden brown)	85 (300^d)	12.41 (12.43)	1.54 (1.55)	8.27 (8.29)	51.01 (51.10)	30	Dia
4	$[Au_3(L)_2Cl_4][AuCl_4]$ (Brown)	55 (>360)	12.39 (12.44)	1.51 (1.55)	8.24 (8.29)	51.00 (51.04)	120	Dia
5	$[[Au_4(L)_2Cl_6]Cl_2$ (Pale brown)	20 (275^d)	12.40 (12.44)	1.50 (1.55)	8.26 (8.29)	51.01 (51.05)	170	Dia
6	$Na[Au(L)_2]$ (Pale brown)	72 (307)	27.69 (27.74)	3.42 (3.47)	18.41 (18.49)	28.39 (28.46)	110	Dia

d = Decomposition temperature, Dia = Diamagnetic.

dimethyl formamide (DMF). The electrical molar conductance of the complexes in 10^{-3} M DMF solution are with in the range 30-50 ohm^{-1} mol^{-1} cm^2 for complexes **2** and **3** indicate the non electrolytic nature of the complexes, whereas the complexes 1, 4 and 6 are in the range of 99-120 ohm^{-1} mol^{-1} cm^2 which indicate that these complexes are (1:1) electrolyte, while the complex **5** is (1:2) electrolyte[15]. This is consistent with stoichiometry assumed for the complexes on the basis of analytical data.

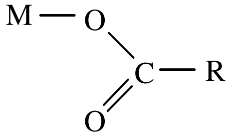
The most important diagnostic features of IR spectrum are listed in Table-2. The ligand band due to carboxylate group may be coordinated to Au(III) ions either in a unidentate or in bidentate manner.

TABLE-2
ELECTRONIC AND INFRARED SPECTRAL DATA AND COMPUTATIONAL STERIC ENERGIES OF THE LIGAND AND THEIR COMPLEXES

No.	λ_{max} (cm^{-1})	$\nu_{as}(COO^-)$	$\nu_{sym}(COO^-)$	$\Delta(\nu_{as}-\nu_{sym})$	ν(C–S)	ν(Au–O)	ν(Au–S)	ν(Au–Cl)	Steric energy (Kcal/mol)
L	36232	1640s	1460s	–	864m	–	–	–	30.08
1	32000,27248,44050	1617s	1399s	218*	842m	480m	340w	300w	340.56
2	30110,28000,25500	1638s	1480s	158**	840s	490 m	345m	280w	274.13
3	32845,27000	1638s	1398s	240*	850m	430m	360w	290w	338.82
4	30000,27248,44050	1617s	1464s	153**	839m	450m	358m	310w	1147.76
5	29500,25000	1610s	1460s	150**	845m	465m	360w	295w	1030.44
6	26666,25000	1618s	1470s	148**	845s	460m	350w	300w	56.26

**Monodentate, *bidentate, s = strong, m = medium, w = weak

The FTIR is consistent with the formation of well defined compound with the above composition. The carboxylate group is able to coordinate to metal ions by different modes[16].



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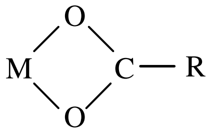


II

When the carboxylate group coordinate the metal ion in a monodentate manner, the difference between the wave number of the formula (I) asymmetric and symmetric stretching band, Δν (=$\nu_{asym}COO^- - \nu_{sym}COO^-$), is lager than that observed for ionic compounds.

When the ligand chelates as in the formula (II), ΔV is considerably smaller than that for ionic compounds, while on the asymmetric bidentate coordination, the value is in the range characteristic of monodentate coordination[17].

Two bands are observed 1638-1610 and 1482-1398 cm^{-1} and the differences in $\Delta\nu COO^-$ (174-210) (Table-2) are indicative of the monodentate or bidentate nature of the carboxylate group[18]. However, the bands observed at 1700-1680 cm^{-1} for some complexes may be as signal to the free carboxylic group. The another ligand band which appeared at 864 cm^{-1} due ν(C-S) stretching is shifted to lower field in the complexes. This is usually indicates that the ν(C-S) group involved in coordination with Au(III) ion through sulfur atom[19]. The appearance of two additional low frequency bands in the region 360-340 and 490-430 cm^{-1} are assignable to ν(Au-S) and ν(Au-O), respectively, further supporting the coordination through the sulfur and oxygen atoms of the ligand. Further more the IR spectra of the complexes showed another band with in the range of 310-280 cm^{-1} range which may be assigned to ν(Au-Cl)[20].

^{1}H NMR spectra of ligand exhibits a singlet band at 3.61 ppm due to methyl protons of the S-CH_2-COO^- and a triplet band at 2.53 ppm assigned to methyl protons C-CH_2-S and a quintet band at 1.71 ppm due to the methyl protons of the R-C-CH_2-C-S.

The diamagnetic nature of the Au(III) complexes is consistent with the normal square-planner geometry around Au(III) ion[21].

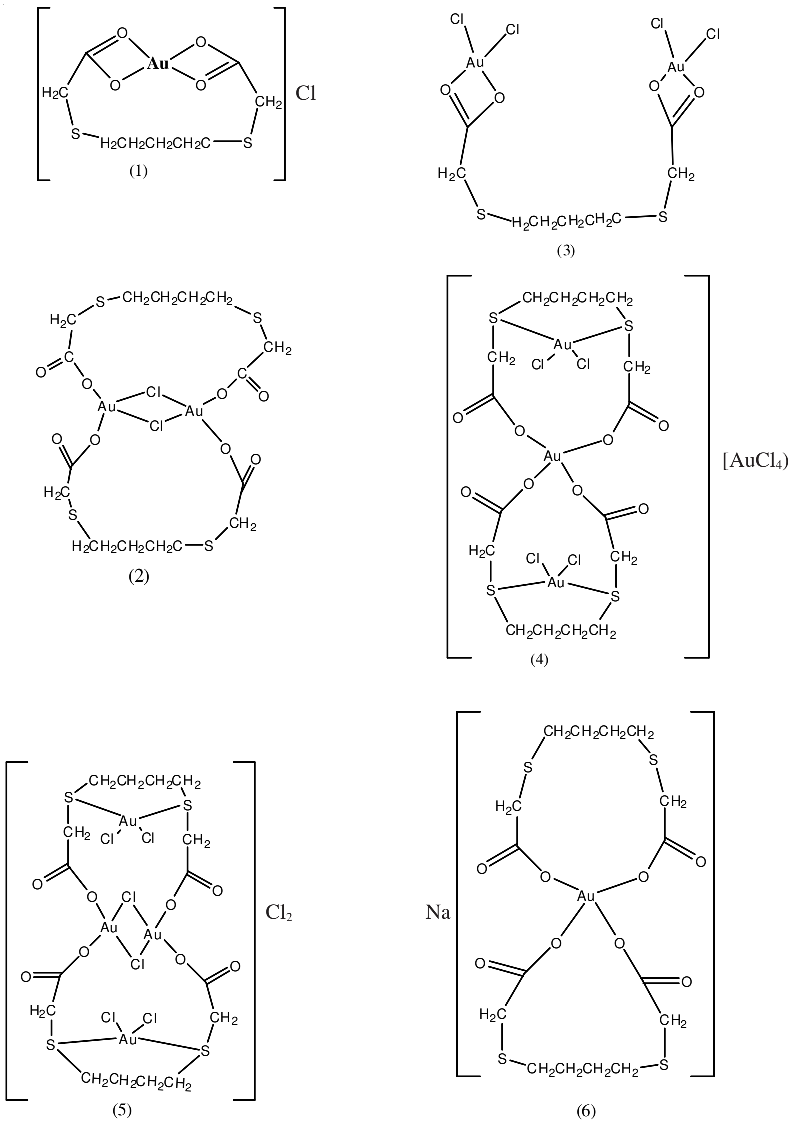
Electronic absorption spectra of the complexes in dimethyl formamide are listed in Table-2. In the spectrum of the ligand the π-π^* transition is observed at 36,232 cm^{-1}. The spectrum of the complexes show new band at 32,845-27,248 and 25,000-26,666 cm^{-1} assigned to the $^1A_{1g}\rightarrow{}^1A_{2u}$ and $^1A_{1g}\rightarrow{}^1Eu$ transition, respectively[22]. These bands correspond fairly well to a square planar geometry around the Au(III) ion. Also the band at 44,050 cm^{-1} is tentatively assigned as ligand charge transfer transition. Similar results were found in Pt(II) and Au(III) complexes of the [M(diimine) (dithiolate] type[23].

TABLE-3
SOME SELECTED PARAMETERS OF THE COMPLEX **1**

	Selected calculated parameter	Value
Bond length (Å)	Au-O1	1.96
	Au-O4	2.05
	C-O3	1.20
	C-O4	1.33
Bond angle (°)	O1-Au-O2	79.34
	O1-Au-O3	167.12
	O3-Au-O4	96.87
	O2-Au-O3	98.67

The ligand has different donor sites through sulfur or oxygen atoms, so in complexation we have different isomers for each complex. MM2 molecular modeling program was used in this study to calculate the steric energy for each isomer. According to the minimum values of steric energy (Table-2) and the optimized geometry we could determine the most stable isomers. All the data obtained are consistent with the experimental data which indicate that the donor atoms in the complexes adopted distorted square planar geometry around the Au(III) ion. The configuration of complex **1**, Fig. 2, was drawn here, as an example, with some selected bond lengths and angles (Table-3)[24,25].

The ligand used in this study, coordinate to the Au(III) ion in bidentate or tetradentate fashion from both oxygen atoms of the carboxylate group and sulfur atoms. The suggested structure of the prepared complexes is according the reaction molar ratio and all the physico-chemical properties as in the following Fig. 1.



(1) (3) (2) (4) (5) (6)

Fig. 1. Suggested structure of the complexes

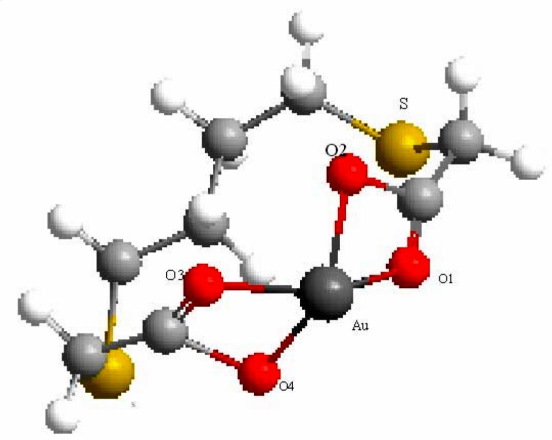


Fig. 2. Optimized geometry for the complex **1**, $[Au(^{-}OOCCH_2S(CH_2)_4SCH_2COO^{-})]^{-}$

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