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Synthesis, Structural Characterization, and Aurophilic Interactions in Gold(I) Thiolate Complexes Supported by Diphosphine Ligands

Kumari Suman

Assistant Professor, Department of Chemistry Pt. D.D.U. Govt. Girls P.G. College, Lucknow, India

Abstract

A comprehensive study on the synthesis and structural characterization of gold(I) thiolate complexes supported by bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) is presented. Reactions of [dppm(AuCl)$_2$] and [dppe(AuCl)$_2$] with heteroaromatic thiols afford discrete dinuclear, tetranuclear, and polymeric gold(I) assemblies. All complexes were characterized by (^{1}H) and (^{31}P) NMR spectroscopy, IR spectroscopy, and single-crystal X-ray diffraction. The structures reveal nearly linear coordination geometries at gold(I) centers and pronounced Au···Au interactions (3.07–3.25 Å), consistent with aurophilic attraction. Ligand steric and electronic effects dictate nuclearity and supramolecular aggregation. These results establish diphosphine-supported gold(I) thiolates as versatile building blocks for polynuclear gold architectures.

Keywords: Gold(I) complexes; thiolates; diphosphine ligands; aurophilic interaction; X-ray crystallography

1. Introduction

Gold exhibits unique chemical behavior due to strong relativistic effects that stabilize the 6s orbital and expand the 5d orbitals, enabling linear coordination and closed-shell Au···Au interactions. Gold(I) complexes commonly adopt linear two-coordinate geometries and display aurophilicity, which strongly influences solid-state organization, photophysical behavior, and cluster formation. Diphosphine ligands such as dppm and dppe are particularly effective in stabilizing gold(I) centers while enabling close metal–metal proximity. Gold(I) thiolate complexes have attracted attention as structural motifs relevant to gold clusters, nanomaterials, catalysis, and medicinal chemistry. Despite extensive work on phosphine–gold(I) systems, structurally characterized thiolate derivatives supported by chelating diphosphines remain comparatively underexplored. This work addresses this gap by systematically investigating the reactions of [dppm(AuCl)$_2$] and [dppe(AuCl)$_2$] with heteroaromatic thiols, focusing on structure–nuclearity relationships and aurophilic interactions.

2. Experimental Section

2.1 General Procedures

All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Commercial reagents were used as received. The synthesis of some starting precursors, as well as newly synthesized species, was analyzed by various physicochemical studies. IR-

spectra were recorded on a spectrometer (Bruker). ^{1}H NMR (300 MHz) and ^{31}P NMR (121MHz) were recorded on AV 300spectrometer (Bruker) in CD_2Cl_2 or $CDCl_3$ at room temperature. Chemical shifts were observed in ppm.

2.1.1. Synthesis of AuCl (THT)

Gold (2.1g) was dissolved in HNO_3 (10 ml) and HCl (30 ml). The reaction mixture was heated up to 100 °C till evolution of brown fumes was observed. Another batch of HNO_3 (10 ml) was added to the reaction mixture. Once the evolution of brown fumes ceased, heating was continued to get half of the volume of the reaction mixture. The reaction solution was cooled to room temperature and diluted with ethanol (50 ml). Tetrahydrothiophene (THT) (9 ml) was 40 added to the reaction mixture, followed by the refluxing at 60 °C to get the AuCl (THT) as a white crystalline solid.

2.1.2 Synthesis of [dppm(AuCl)$_2$]

AuCl (THT) (0.800g, 2.49 mmol) and dppm (0.479g, 1.24 mmol) were stirred in acetone (30 ml) at room temperature for 2 h using a round-bottom flask. The solvent was removed under reduced pressure, and the white precipitate thus obtained was washed with diethyl ether (3 × 15 ml). The species is thus analyzed as [dppm(AuCl)$_2$].

^{1}HNMR (CD2Cl2) δ(ppm): 7.70-7.60(m, 8H, Ph), 7.53-7.45(m, 4H, Ph), 7.43-7.40(m, 8H, Ph), 3.70(t, 2H, -CH_2-).

^{31}P NMR (CD_2Cl_2) δ(ppm): 25.36(s) 5.3.3.

2.1.2.3 Synthesis of [dppe(AuCl$_2$]

AuCl(THT) (0.8020g, 2.5mmol) and dppe (0.499g, 1.25mmol) were stirred in acetone (30ml) at room temperature for 2 h using a round-bottom flask. The solvent was removed under reduced pressure, and the white precipitate thus obtained was washed with diethyl ether (3 × 15 ml). The species is thus analyzed as [dppe(AuCl)$_2$].

^{1}H NMR (CD_2Cl_2) δ(ppm): 7.71-7.61(m, 8H, Ph), 7.57-7.47(m, 12H, Ph), 2.27(s, 4H, CH_2CH_2-).

^{31}P NMR (CD_2Cl_2) δ(ppm): 31.31(s)

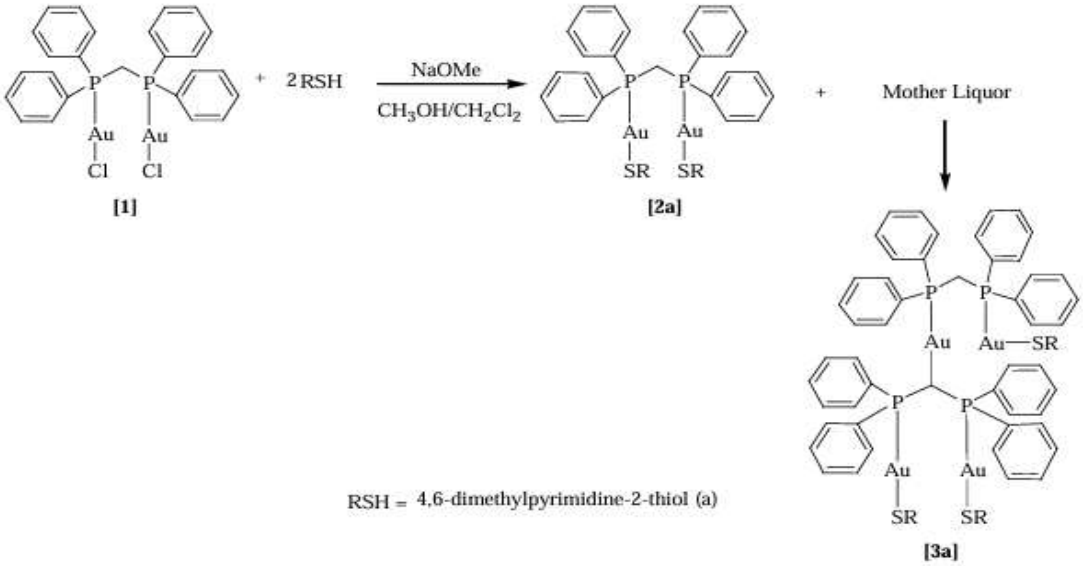
3. Results and Discussion

3.1 Synthesis of Gold(I) Thiolate Complexes

Salt-metathesis reactions of [dppm(AuCl)$_2$] and [dppe(AuCl)$_2$] with heteroaromatic thiols in the presence of NaOMe afford gold(I) thiolate complexes in good yields. The reactions proceed smoothly under ambient conditions using CH_2Cl_2/MeOH solvent mixtures.

3.1.1 Synthesis and characterization of gold(I) thiolate complexes with [dppm(AuCl)$_2$]:

Complexes 2a and 3a were synthesized by the reaction of [dppm(AuCl)$_2$] (1), NaOMe, and 4,6-dimethylpyrimidine-2-thiol (a) in a solvent mixture (CH_2Cl_2-CH_3OH) (4:1). The reaction mixture was stirred for 4 h at room temperature and filtered. The filtrate was left as such for crystallization at room temperature. A crystalline material for X-ray analysis was obtained after 4 days (Scheme 1).



This was characterized by ^{1}H NMR, ^{31}P NMR spectra, and X-ray crystallography, which support the formation of 2a. The ^{31}P NMR spectrum of complex 2a showed a singlet at 28.94 ppm showed a downfield shift of 4 ppm compared to the starting material, which shows a singlet at 25.36 ppm in CD_2Cl_2. ^{31}P NMR of complex 2a and starting material [dppm$(AuCl)_2$] is shown in Figures 1 and 2, respectively.

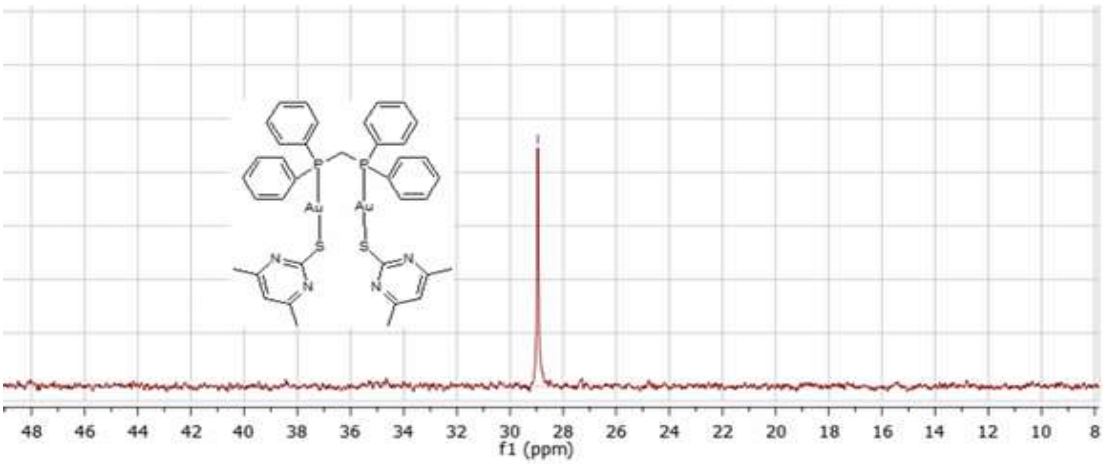


Figure 1: ^{31}P NMR spectrum of complex 2a.

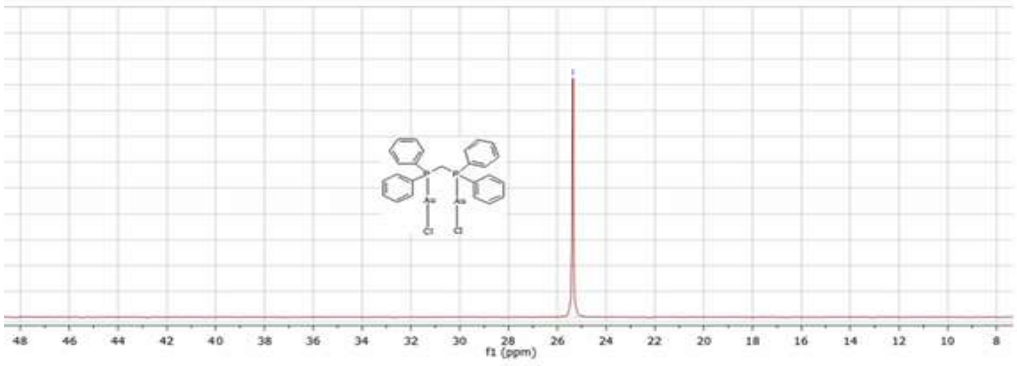


Figure 2: ^{31}P NMR spectrum of [dppm$(AuCl)_2$].

^{1}H NMR of complex 2a exhibited a triplet at 3.74 ppm (2H), singlet at 2.28 ppm (12H), singlet at 6.5 ppm (2H), multiplets at (7.87-7.81) and (7.48-7.36) ppm and were assigned 19 respectively as -CH_2- protons, CH_3- protons, pyrimidine ring protons and phenyl protons of the phosphine. While the ^{1}H NMR of the starting material showed a triplet at 3.72 ppm (2H), a multiplet at (7.70-7.63) and (7.53-7.40) ppm for -CH_2- protons and phenyl rings protons, respectively. ^{1}H NMR spectrum of complex 2a and starting material [dppm$(AuCl)_2$] is shown in Figure 3.

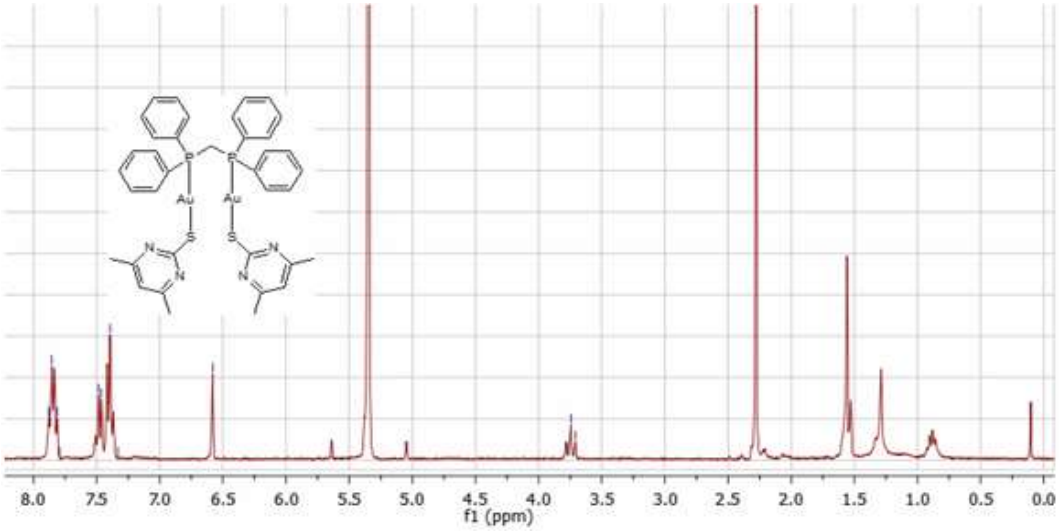


Figure3: ^{1}H NMR spectrum of complex 2a.

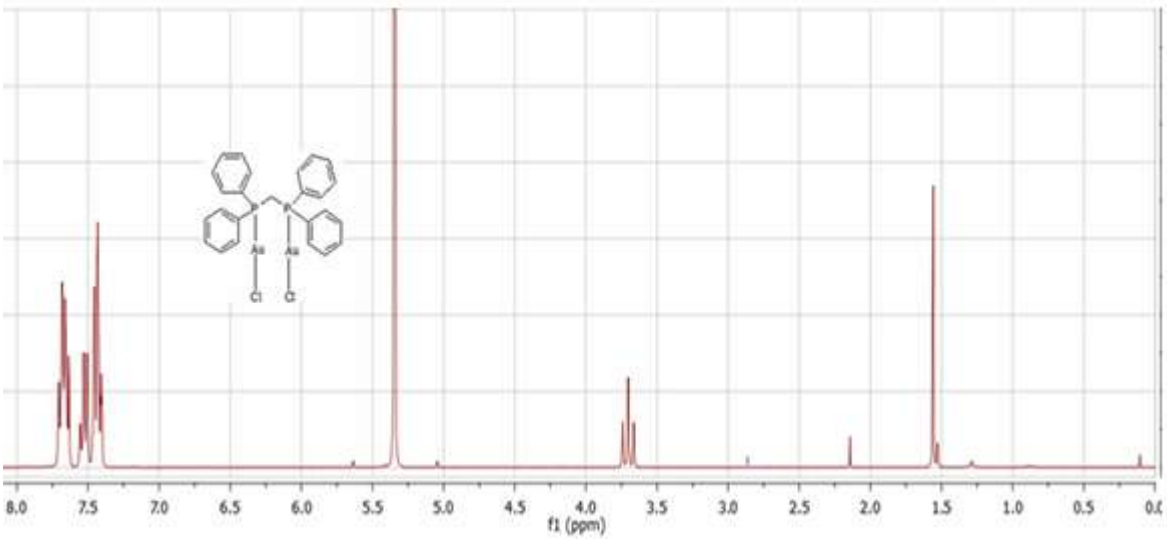


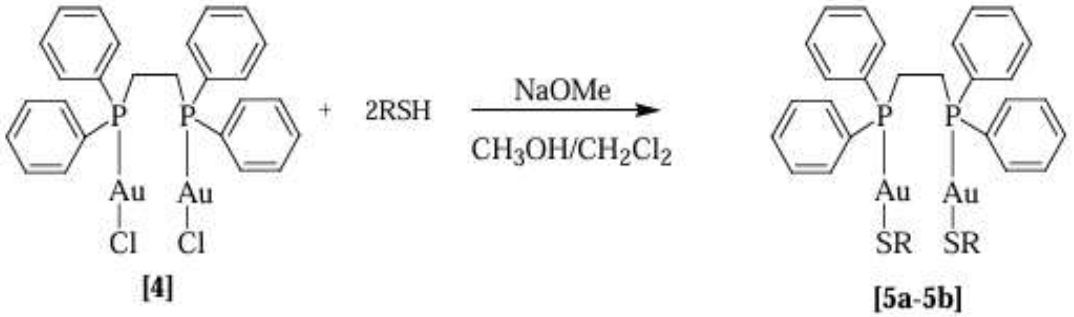
Figure4: ^{1}H NMR spectrum of [dppm$(AuCl)_2$].

^{1}H and ^{31}P NMR of complex 2a is comparable with the known similar complex [{Au (2 $SC_6H_4NH_2$)}$_2$(μ-dppm)] (2-$SC_6H_4NH_2$=2-aminobenzenethiol) which is characterized by Manuel Bardaji, shows a singlet at 29.2 in ^{31}P NMR spectrum, and the ^{1}H NMR spectrum of this complex shows a triplet at 3.69 ppm due to 2H (-CH_2-). The remaining solution of the reaction mixture on crystallization for several days resulted in a crystalline species that was morphologically different from complex 2a. It is interesting to note that

this crystal, on X-ray crystallographic examination, resulted in a structure different from complex 2a and was characterized as complex 3a.

3.1.2 Synthesis and characterization of gold(I) thiolate complexes with [dppe(AuCl)$_2$]:

Complexes 5a and 5b were synthesized by the reaction of [dppe(AuCl)$_2$], NaOMe, and organic thiols 4,6-dimethylpyrimidine-2-thiol (a) and 2-mercaptoquinoline (b) ligands separately in a solvent mixture (CH_2Cl_2-CH_3OH) (4:1). The reaction mixture was stirred for 24 h at room temperature. As shown in Scheme 2.



RSH = 4,6-dimethylpyrimidine-2-thiol (a)
2-mercaptoquinoline (b)

Complexes 5a and 5b were characterized by ^{1}H and ^{31}P NMR spectra. The ^{31}P NMR spectrum of these complexes showed a broad singlet around 35 to 36 ppm showed a downfield shift of 4 ppm compared to the starting material. ^{1}H NMR spectrum of these complexes showed a singlet around 2.8 to 2.9 ppm due to 4H (-CH_2CH_2-) and a multiplet from 7 to 8 ppm due to aromatic protons. These peaks of complex 5a and 5b are comparable with a known complex of Au(I) with dppe, is [dppe($AuSC_7H_7$)$_2$], discovered by Ratnavathany Narayanaswamy, shows a singlet at 36.9 ppm in^{31}P NMR and a singlet at 2.67 ppm for 4H (-CH_2CH_2-) in ^{1}H NMR spectrum. 27 ^{31}P NMR spectrum of complex 5b and starting material [dppe(AuCl)$_2$] shown in Figure 5 and Figure 6, respectively. Complex 5b showed a singlet at 35.90 ppm, and the starting compound [dppe(AuCl)$_2$] showed a singlet at 31.31 ppm.

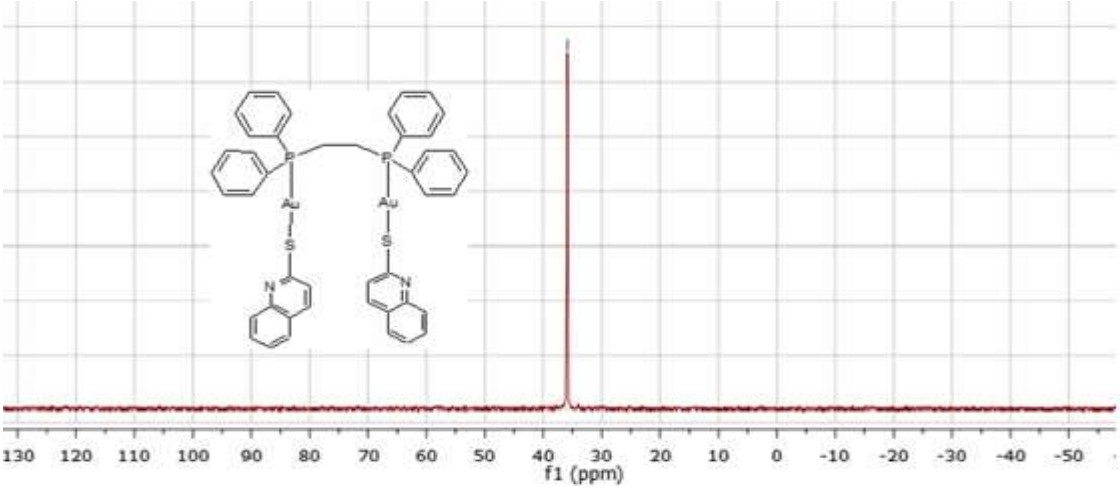


Figure 5: ^{31}P NMR spectrum of Complex 5b.

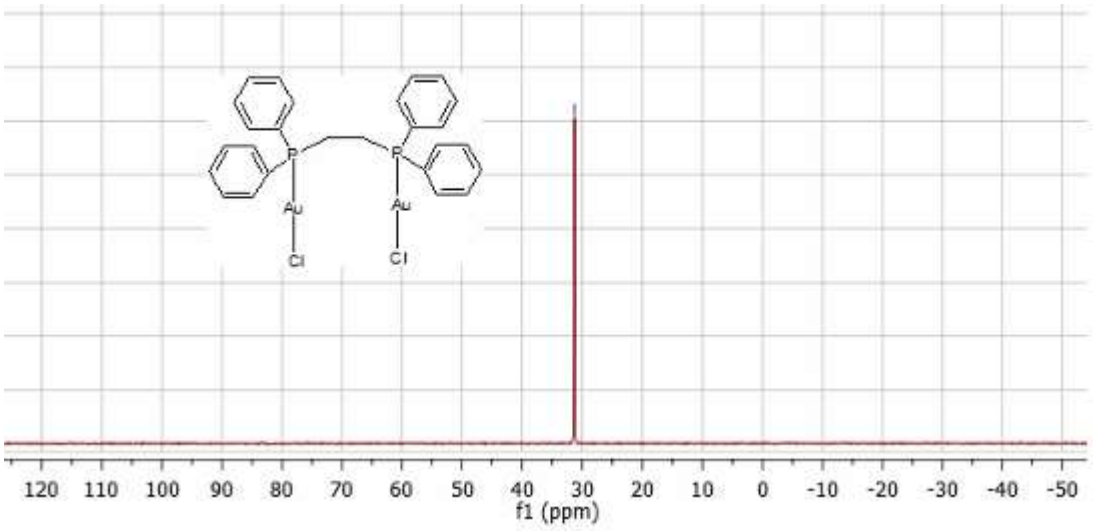


Figure 6:^{31}P NMR spectrum of dppe(AuCl)$_2$.

^{1}H NMR spectrum of complex 5b and starting material [dppe(AuCl)$_2$] is shown in Figure 7 and Figure 8, respectively. Complex 5b showed a singlet at 2.93 ppm, 4H (-CH_2CH_2-) and a multiplet at 7.85-7.28 ppm, 32H (ph and quinoline ring). [dppe(AuCl)$_2$] showed a singlet at 2.71 ppm, 4H (-CH_2CH_2-) and a multiplet at 7.61-7.47 ppm, 20H (ph ring).

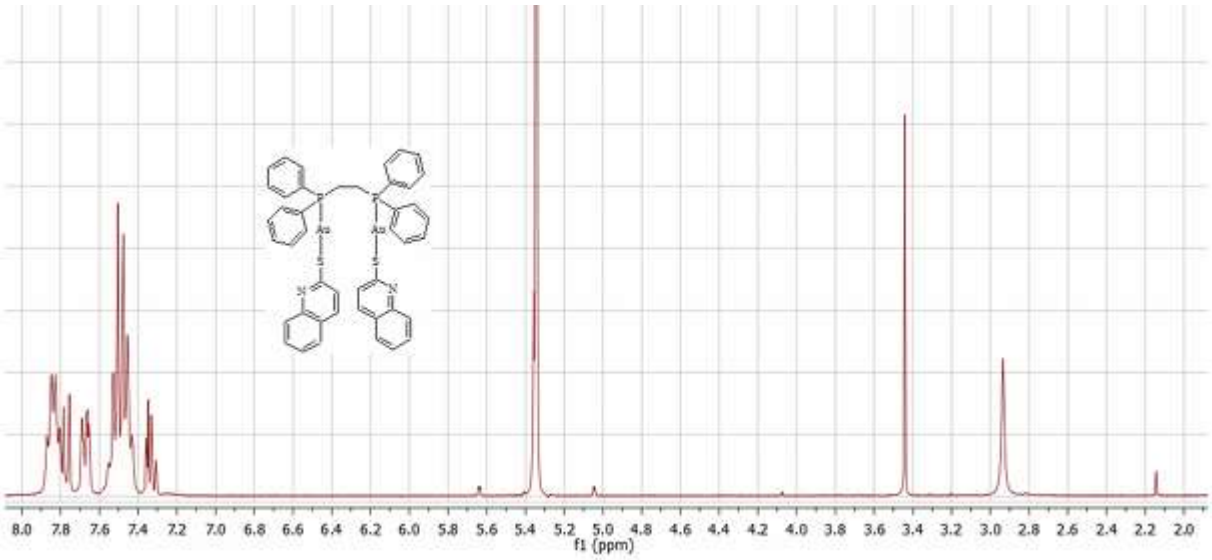


Figure 7 ^{1}H NMR spectrum of Complex 5b.

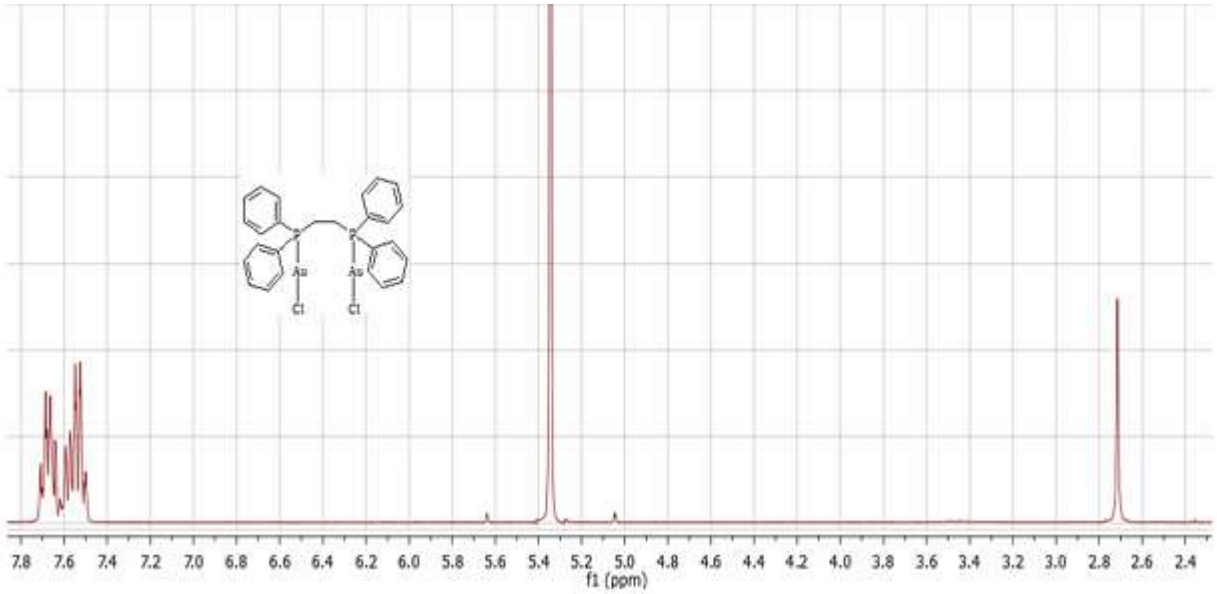


Figure 8 ^{1}H NMR spectrum of [dppe(AuCl)$_2$]

3.2 Molecular Structures

3.2.1 Structure of Complex 2a

Complex 2a crystallizes in the triclinic crystal system (P-1 space group) with two molecules per unit cell. There are two independent molecules in the asymmetric unit with comparable parameters, as shown in the figure 9. Single-crystal X-ray diffraction reveals a dinuclear structure with a bridging dppm ligand. Each gold(I) center exhibits a near-linear P–Au–S coordination geometry. The intramolecular Au···Au separation of ~3.08 Å indicates a significant aurophilic interaction.

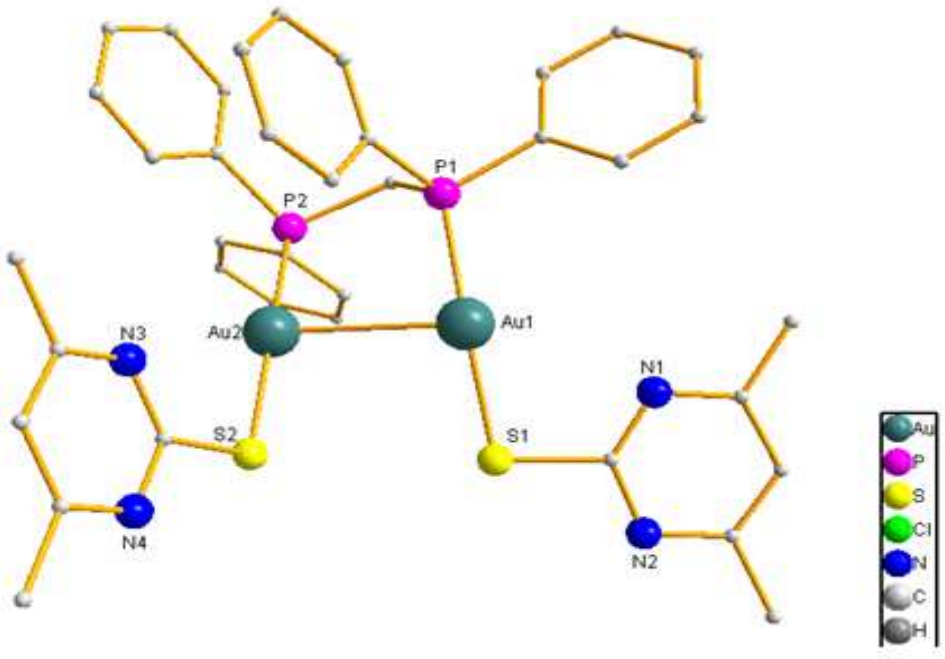


Figure 9. Molecular structure of complex 2a with thermal ellipsoids (50% probability).

3.2.2 Structure of Complex 3a

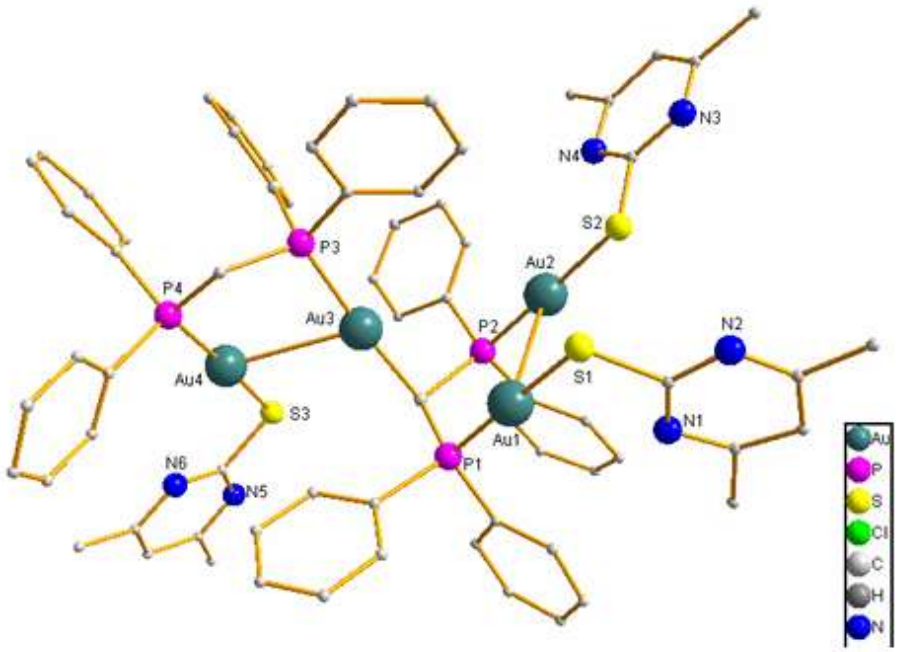


Figure 10. Molecular structure of tetranuclear complex 3a.

Complex 3a forms a tetranuclear gold(I) assembly in which three gold centers are thiolate-bound, while the fourth is bonded to a methylene carbon of a deprotonated dppm ligand. Two distinct Au···Au interactions (3.08–3.17 Å) stabilize the cluster.

3.2.3 Structures of dppe-Supported Complexes 5a and 5b

Complex 5a crystallizes in the monoclinic crystal system (space group P21/c) with two molecules per unit cell. The crystal structure demonstrates two gold atoms, two thiolate ligands, and one dppe ligand. A perspective view of 5a is shown in Figure 2.

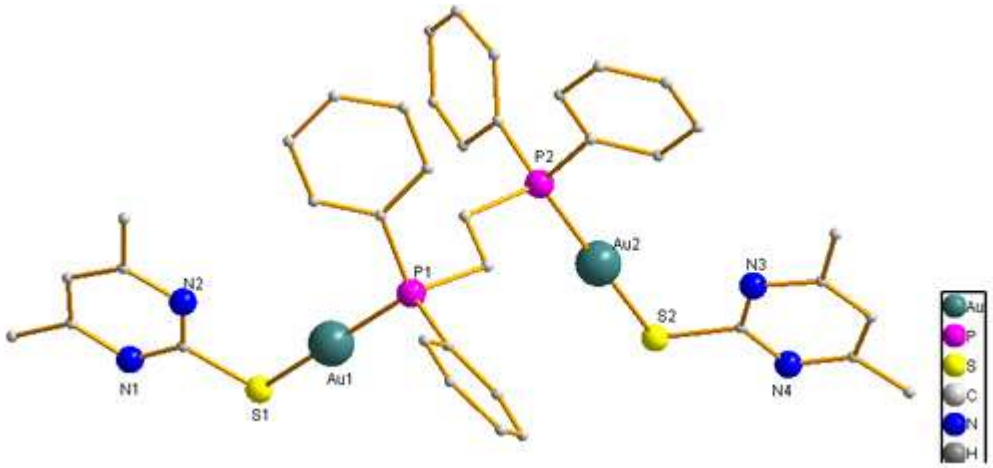


Figure 11: Molecular structure of complex 5a highlighting Au···Au interactions

Complex 5b crystallizes in the triclinic crystal system (P-1 Space group) with two molecules in the unit cell. The complex consists of two gold atoms, two thiolate ligands, and one dppe within the structural framework. A perspective view of 5b is shown in Figure 12.

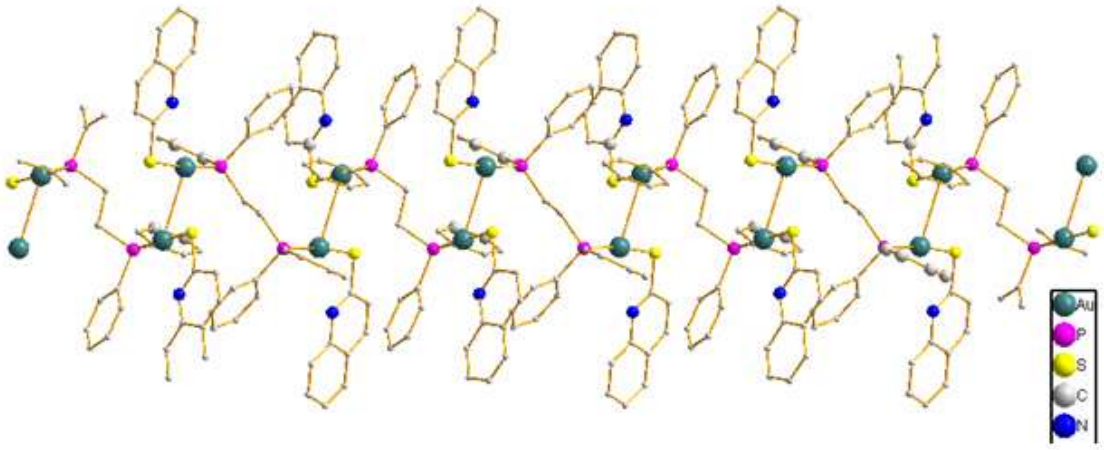


Figure 12: Polymeric Au···Au chain formation in complex 5b

Complex 5a crystallizes as a discrete tetranuclear gold(I) cluster stabilized by aurophilic interactions between dppe-bridged units. In contrast, complex 5b forms extended polymeric chains via intermolecular Au···Au contacts, underscoring the decisive role of thiolate steric and electronic properties.

Table 1: Summary of synthesized gold(I) thiolate complexes.

Complex	Diphosphine	Thiolate ligand	Nuclearity	Structural motif
2a	dppm	4,6-dimethylpyrimi-dine-2-thiolate	Dinuclear	Discrete Au_2
3a	dppm	4,6-dimethylpyrimi-dine-2-thiolate	Tetranuclear	Au_4 cluster
5a	dppe	4,6-dimethylpyrimi-dine-2-thiolate	Tetranuclear	Discrete Au_4
5b	dppe	2-mercaptoquinoline	Polymeric	Au···Au chain

4. Conclusion

Gold complexes with varying thiolate groups exhibit distinct structural features, as seen in complexes 5a and 5b. The discrete tetra-nuclear structure of 5a arises from the sterically bulky 4,6-dimethyl thiopyrimidine group coordinated to the Au(I) center. In contrast, the polynuclear formation of 5b is attributed to the thioquinoline group attached to the Au center. Molecular structures of [dppm$(AuCl)_2$] and [dppe$(AuCl)_2$] derivatives bearing different thiolates consistently show a nearly linear geometry around the gold(I) center, accompanied by notable gold(I)–gold(I) aurophilic interactions. This study demonstrates that diphosphine ligands dppm and dppe effectively direct the assembly of gold(I) thiolate complexes into either discrete or polymeric architectures. Single-crystal X-ray diffraction confirms the linear coordination geometry and significant aurophilic interactions. The nuclearity and aggregation patterns are strongly influenced by the steric and electronic properties of the thiolate ligands. These

findings broaden the understanding of gold(I) thiolate structural chemistry and offer valuable insights for the design of gold clusters.

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