Chapter 3

Synthesis and characterization of pyrrole, phenanthroline and picolinamide based heterocyclic ligands and its gold(III) complexes
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3. Synthesis and characterization of pyrrole, phenanthroline and picolinamide based heterocyclic ligands and its gold(III) complexes

3.1. General

This chapter deals with the synthesis and characterization of various substituted bidentate/tridentate ligands of pyrrole, phenanthroline and picolinamide derivatives and its gold(III) complexes. The development of synthetic methodologies for N-donor ligands is of paramount importance in chemistry due to their applications in key areas such as photovoltaics [1], OLEDs [2,3], molecular sensors [4,5], DNA interactions [6,7], molecular wires [8] and supramolecular structures (network, helical, box etc.) [9]. N,N-Bidentate ligands with mixed five- and six-membered heterocycles are a desirable class of compounds in the pursuit of structural diversity. In particular, phenanthroline with their versatile applications in the areas like coordination chemistry, redox mediator in biosensor, catalyst of oxidative organic synthesis, metallopeptidase inhibitor, molecular chemistry, disease diagnosis and treatment, water treatment, photolysis chemistry and microbiology; make it centre of interest in medicinal inorganic chemistry.

Dipyrromethanes are important building blocks for the organic synthesis and pharmaceucials [10,11]. They were also widely used as ligands in organometallic synthesis and catalysis [12,13]. 2,2′-Dipyridylamine (dpa) and 2,2′-dipyridylketone (dpk) are aromatic amine in some ways similar to bipyridines (bpy), but the central amine unit introduces several differences: (1) dpa and dpk coordinate with six-membered chelate ring instead of five-membered ring for bpy, (2) the coordinated pyridine rings are not necessarily forced to near coplanarity as in bpy and (3) the ligand field strength of dpa and dpk is greater than ethylenediamine, but closer to that of a single aromatic amine [14]. 2,2′-Dipyridylamine and their derivatives are efficient blue emitters when irradiated by UV light [15].

Gold(III) compounds are emerging as a new class of metal complexes with outstanding cytotoxic properties and are presently being evaluated as potential antitumor agents. Interest in gold coordination chemistry has been growing in recent years with the successful use of ‘Auranofin’ in oral administration, for the treatment of rheumatoid arthritis [16]. Apart from their traditional use in medicine as antiarthritic agents, gold compounds are obvious candidates as a possible alternative to antitumor platinum drugs. However, relatively little attention has been paid to the gold(III) complexes being isoelectronic and isostructural in nature with platinum(II) complexes, even though some gold(III) complexes exhibit anticancer activity [17]. Evidence suggests that gold(III) complexes bind to DNA [18,19] and some Au(I) and Au(III) complexes can bind to DNA via the guanine and cytosine bases [20,21]. The interest for gold(III) complexes can be judged from the increased number of gold(III) complexes synthesized using N-donor ligands [22,23].

3.2. Materials and methods
All the chemicals and solvents were of reagent grade and used as purchased. Chloroauric acid, 4-chloroaniline, 2-aminopyridine, TFA (trifluoroacetic acid) and sodium borohydride were purchased from S.d. fine-chem Ltd. (India). 2,2'-Dipyridylamine (A\textsuperscript{33}) was purchased from Lancaster (England). Di(2-pyridyl)ketone (A\textsuperscript{34}) was purchased from Sigma Aldrich (Germany). Pyrrole was purchased from Spectrochem Pvt. Ltd. (India). 2-Picolinic acid and 2,6-dipicolinic acid was purchased from Alfa Aesar (England).

Infrared spectra were recorded on ABB Bomen MB 3000, FT–IR spectrophotometer as KBr pellets in the range 4000–400 cm\textsuperscript{-1}. The LC-MS were recorded using Thermo Scientific mass spectrophotometer (USA). The \textsuperscript{1}H NMR and \textsuperscript{13}C NMR were recorded on a Bruker Advance (400 MHz, Germany). The peaks at 7.26 ppm and ~1.5 ppm in \textsuperscript{1}H-NMR spectra are obtained due to CDCl\textsubscript{3} (solvent) and water impurity in the solvent, respectively. The peaks at 2.50 ppm and ~3.4 ppm in \textsuperscript{1}H-NMR spectra are obtained due to (CD\textsubscript{3})\textsubscript{2}SO (solvent) and water impurity in the solvent, respectively. The peak at 77.0 ppm and 39.5 ppm in \textsuperscript{13}C-NMR spectra is obtained due to CDCl\textsubscript{3} and (CD\textsubscript{3})\textsubscript{2}SO (solvent), respectively. The electronic spectra were recorded on a TCC-240 A, UV–Vis spectrophotometer, Shimadzu (Japan). The molar conductance were carried out on Equip-Tronics EQ-660A, conductivity meter (India). Thermal DNA denaturation study was performed using Agilent 8453 UV–Vis spectrophotometer. C, H and N elemental analyses were performed with a model 240 Perkin Elmer elemental analyzer.

### 3.3. Synthesis of ligands

#### 3.3.1 2-(4-Chlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (A\textsuperscript{35})

The 1,10-phenanthroline-5,6-dione was prepared by oxidizing 1,10-phenanthroline using a mixture of concentrated sulfuric and nitric acids [15]. The mixture of \textit{p}-chlorobenzaldehyde (1 mM), 1,10-phenanthroline-5,6-dione (1 mM) and ammonium acetate (20 mM) in glacial acetic acid (20 mL) was stirred and refluxed for 4 h. Mixture was cooled to room temperature and the product was precipitated during neutralization with ammonium hydroxide (5 mL). The product precipitates were washed with water and diethyl ether followed by crystallization in methanol.

\[ \text{Scheme 3.1: Synthesis of phenanthroline derivatives} \]
3.3.2 2-(4-Bromophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (A\textsuperscript{36})

It was prepared following the same procedure in the section 3.3.1, by taking p-bromobenzaldehyde as aldehyde.

3.3.3 \(N^2,N^6\)-Bis(pyridin-2-yl)pyridine-2,6-dicarboxamide (A\textsuperscript{37})

It is synthesized through the procedure reported by Gudasi \textit{et al} \textsuperscript{[24]}. A mixture of dipicolinic acid (10 mmol) and thionylchloride (20 ml) were refluxed for 4–5 h, till the evolution of HCl gas ceases, under anhydrous condition. Excess thionylchloride was removed under reduced pressure. The resulting solution was cooled in an ice bath for 15 min. Dry toluene (25–30 ml) followed by 2-aminopyridine (20 mmol) was added to the above solution and further refluxed until no more HCl was evolved. The solvent was removed under reduced pressure and the resultant white solid was washed with petroleum ether and neutralized with 5% NaHCO\textsubscript{3}. It was filtered, washed with water and then alcohol. Recrystallization from chloroform and ethanol yield silky needles.

Scheme 3.2: Synthesis of \(N^2,N^6\)-bis(pyridin-2-yl)pyridine-2,6-dicarboxamide

3.3.4 \(N\)-(Pyridin-2-yl)picolinamide (A\textsuperscript{38})

It was prepared following the same procedure in the section 3.3.3, by taking 2-picolinic acid as starting reactant in equal mole with 2-amino pyridine.

Scheme 3.3: Synthesis of \(N\)-(pyridin-2-yl)picolinamide

3.3.5 4-Chloro-\(N\)-(pyridin-2-ylmethyl)aniline (A\textsuperscript{39})

4-Chloroaniline (14.8 mmol) and pyridine-2-carbaldehyde (7.40 mmol) were dissolved in 50 mL of absolute ethanol to give a brownish-yellow solution, which was stirred for 1 h. Sodium borohydride in 10-fold excess (37.0 mmol) was added in portions to the ethanolic solution at 0 °C, and stirring was continued for 20 min. The solution was then refluxed for 30 min. After cooling of the yellow solution, the ethanol was removed by evaporation. Water (200 mL) was added to give a yellow solution with some precipitate present. Concentrated HCl (~ 2 mL) was added to neutralize the solution (pH ~ 6-7), causing the colour of the solution to lighten and giving an off-white precipitate. The solid mass was collected and dried.
Scheme 3.4: Synthesis of 4-chloro-N-(pyridin-2-ylmethyl)aniline

3.3.6 2,2’-(Phenylmethylene)bis(1H-pyrrole) (A<sup>40</sup>)

2,2’-(Phenylmethylene)bis(1H-pyrrole) was prepared via condensation of the benzaldehyde and pyrrole under TFA catalysis [25,26]. A solution of distilled pyrrole (150 mL, 2.16 mol) and benzaldehyde (6.0 mL, 59 mmol) were taken in a 250 mL two necked round bottomed flask, equipped with a magnetic stir bar and fitted with a gas outlet. The second neck of the flask is sealed with a rubber septum and the mixture is deoxygenated by bubbling dry nitrogen through it for 15 min. TFA (0.45 mL, 5.8 mmol) is added in one portion and the resulting mixture is stirred magnetically for 15 min at room temperature. Excess pyrrole is removed by evaporation with warming (60 °C) to yield dark oil. The oil is taken up in a required amount (~ 10 mL) of dichloromethane, and charged onto the top of a chromatography column. The major fraction containing ligand and some higher oligomers is eluted with dichloromethane and collected (TLC is monitored with visualization using iodine chamber, Ligand turns bright red/orange, and the higher oligomers show a brown spots of lower R<sub>f</sub>). Rotary evaporation of the solvent yields the oil. To allow residual pyrrole and solvent to escape, a slow heating rate is maintained until visible sublimation sets in at approximately 120 °C. After sublimation ceases, the white crystalline sublimate consisting of ligand is collected.

Scheme 3.5: Synthesis of dipyrrromethane derivatives

3.3.7 2,2’-((4-Chlorophenyl)methylene)bis(1H-pyrrole) (A<sup>41</sup>)

It was prepared following the same procedure in the section 3.3.6, by taking p-chlorobenzaldehyde as starting reactant [25,26].
3.4. Characterization of ligands

3.4.1 2-(4-Chlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (A\textsuperscript{35})

Yield: 35%
Melting point: 163 °C
Molecular formula (mol. wt.): C\textsubscript{19}H\textsubscript{11}ClN\textsubscript{4} (330.77 g/mol)

Microanalysis data:
Calc. (%): C, 68.99; H, 3.35; N, 16.94
Found (%): C, 68.84; H, 3.26; N, 16.73

\textbf{FT-IR (KBr, cm\textsuperscript{-1})}: ν(N–H), 3240; ν(C–H), 3110; ν(C=C), 1462; ν(C=N), 1437; ν(C–Cl), 1040; δ(C–H), 745.

\textbf{\textsuperscript{1}H NMR (DMSO, 400 MHz) δ/ppm}: 13.744 (s, 1H, -NH), 9.014 (dd, 2H, H\textsubscript{2,10}), 8.872 (dd, 2H, H\textsubscript{4,8}), 8.205 (d, 2H, H\textsubscript{2',6'}), 8.025 (t, 2H, H\textsubscript{3,9}), 7.793 (d, 2H, H\textsubscript{3',5'}).
13C NMR (CDCl₃, 100 MHz) δ/ppm: 155.43 (C₄₆,1₆a), 151.83 (C₆), 149.74 (C₂,1₀),
134.62 (C₄), 132.90 (C₁), 132.32 (C₄,₈), 129.23 (C₃,₅), 128.23 (C₂,₆), 126.45
(C₅₆,7₆a), 124.15 (C₃,₉), 122.82 (C₄₆a,₈₆a).

3.4.2 2-(4-Bromophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (A³⁶)

Yield: 31%
Melting point: 170 °C
Molecular formula (mol. wt.): C₁₉H₁₁BrN₄ (375.22 g/mol)
Microanalysis data:
Calc. (%): C, 60.22; H, 2.95; N, 14.93
Found (%): C, 60.39; H, 2.81; N, 14.76

FT-IR (KBr, cm⁻¹): ν(N–H), 3234; ν(C–H), 3125; ν(C=C), 1445; ν(C=N), 1419;
ν(C–Br), 1030; δ(C–H), 745.
3.4.3 \(N^2,N^6\text{-bis(pyridin-2-yl)pyridine-2,6-dicarboxamide (A}^{37}\)

Yield: 88%
Melting point: 219 °C
Molecular formula (mol. wt.): \(C_{17}H_{13}N_5O_2\) (319.32 g/mol)
Microanalysis data:
Calc. (%): C, 63.94; H, 4.10; N, 21.93
Found (%): C, 63.80; H, 4.22; N, 21.78
FT-IR (KBr, cm⁻¹): ν(N–H), 3390; ν(C–H), 3050; ν(C=O), 1710; ν(C=C), 1320; ν(C=N), 1240; δ(C–H), 670.

¹H NMR (CDCl₃, 400 MHz) δ/ppm: 11.263 (s, 2H, -NH), 8.564-8.519 (complex, 4H, H₃,₅,₆',₆''), 8.398 (dd, 2H, H₃',₃''), 8.174 (t, 1H, H₄), 7.828 (dt, 2H, H₄',₄''), 7.139 (t, 2H, H₅',₅'').

¹³C NMR (CDCl₃, 100 MHz) δ/ppm: 164.92 (C CO), 150.40 (C₂,₂'), 149.78 (C₂₆), 148.55 (C₆',₆''), 142.47 (C₄), 140.35 (C₄',₄''), 126.92 (C₃,₅), 120.06 (C₅',₅''), 115.21 (C₃',₃'').
3.4.4 N-(Pyridin-2-yl)picolinamide (A^38)

Yield: 83%
Melting point: 163 °C
Molecular formula (mol. wt.): C_{11}H_{9}N_{3}O (199.21 g/mol)
Microanalysis data:
Calc. (%): C, 66.32; H, 4.55; N, 21.09
Found (%): C, 66.56; H, 4.74; N, 21.20

FT-IR (KBr, cm^{-1}): \nu(N-H), 3350; \nu(C-H), 3060; \nu(C=O), 1690; \nu(C=C), 1300; \nu(C=N), 1220; \delta(C-H), 690.

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta/\text{ppm}\): 10.449 (s, 1H, -NH), 8.558 (d, 1H, H\(_6\)), 8.450 (d, 1H, H\(_5\)), 8.397 (t, 1H, H\(_4\)), 8.317 (d, 1H, H\(_6^\prime\)), 7.930 (t, 1H, H\(_5^\prime\)), 7.787 (t, 1H, H\(_4^\prime\)), 7.513 (dt, 1H, H\(_5^\prime\)), 7.106 (dd, 1H, H\(_3^\prime\)).
$^{13}$C NMR (CDCl$_3$, 100 MHz) δ/ppm: 160.75 (C$_{CO}$), 150.38 (C$_{2'}$), 149.78 (C$_2$), 148.55 (C$_6$), 148.24 (C$_6$), 143.48 (C$_4'$), 140.01 (C$_4$), 130.59 (C$_3$), 128.53 (C$_3$), 118.25 (C$_5$), 115.68 (C$_{3'}$).

### 3.4.5 4-Chloro-N-(pyridin-2-ylmethyl)aniline (A$_{39}$)

![Chemical structure of 4-Chloro-N-(pyridin-2-ylmethyl)aniline](image)

Yield: 81%
Melting point: 136 °C
Molecular formula (mol. wt.): C$_{12}$H$_{11}$ClN$_2$ (218.68 g/mol)

**Microanalysis data:**
Calc. (%): C, 65.91; H, 5.07; N, 12.81
Found (%): C, 65.83; H, 4.89; N, 12.94

**FT-IR (KBr, cm$^{-1}$):** ν(N–H), 3330; ν(C–H), 3010; ν(C=C), 1320; ν(C=N), 1280; ν(C-Cl), 1140; δ(C–H), 740.
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta/\text{ppm}\): 8.604 (d, 1H, H\(_6\)), 7.674 (tt, 1H, H\(_4\)), 7.328 (d, 1H, H\(_3\)), 7.216 (t, 1H, H\(_5\)), 7.138 (ddd, 2H, H\(_{3',5'}\)), 6.612 (ddd, 2H, H\(_{2',6'}\)), 4.860 (s, 1H, -NH), 4.446 (d, 2H, CH\(_2\)).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta/\text{ppm}\): 155.26 (C\(_2\)), 148.31 (C\(_6\)), 147.58 (C\(_1'\)), 141.60 (C\(_4\)), 136.74 (C\(_{3',5'}\)), 130.46 (C\(_3\)), 122.53 (C\(_3\)), 121.72 (C\(_5\)), 116.02 (C\(_{2',6'}\)), 47.04 (C\(_{\text{CH}}\)).

3.4.6 2,2'-\((\text{Phenylmethylene})\text{bis(1H-pyrrole)}\) \((A^{40})\)

Yield: 29%
Melting point: 128 °C
Molecular formula (mol. wt.): C\(_{15}\)H\(_{14}\)N\(_2\) (222.29 g/mol)

Microanalysis data:
Calc. (%): C, 81.05; H, 6.35; N, 12.60
Found (%): C, 81.24; H, 6.52; N, 12.47
FT-IR (KBr, cm\(^{-1}\)): \(\nu(N-H), 3420; \nu(C-H), 3060; \nu(C=C), 1380; \nu(C=N), 1120; \delta(C-H), 720.\)

\(^1\)H NMR (DMSO, 400 MHz) \(\delta/\text{ppm}:\) 7.387 (d, 2H, H\(_{3'',5''}\)), 7.275 (d, 2H, H\(_{2'',6''}\)), 7.176 (t, 1H, H\(_{4''}\)), 6.372-6.363 (complex, 2H, H\(_{5,5'}\)), 5.935 (t, 2H, H\(_{4,4'}\)), 5.774 (d, 2H, H\(_{3,3'}\)), 5.273 (s, 2H, -NH), 5.148 (s, 1H, -CH).

\(^{13}\)C NMR (DMSO, 100 MHz) \(\delta/\text{ppm}:\) 146.07 (C\(_{1''}\)), 139.35 (C\(_{2,2'}\)), 137.92 (C\(_{2'',6''}\)), 136.48 (C\(_{3'',5''}\)), 133.80 (C\(_{4''}\)), 126.36 (C\(_{5,5'}\)), 114.57 (C\(_{4,4'}\)), 112.49 (C\(_{3,3'}\)), 48.19 (C\(_{\text{CH}}\)).
3.4.7 2,2’-((4-Chlorophenyl)methylene)bis(1H-pyrrole) (A$^{41}$)

Yield: 26%
Melting point: 135 °C
Molecular formula (mol. wt.): C$_{15}$H$_{13}$ClN$_2$ (256.73 g/mol)
Microanalysis data:
Calc. (%): C, 70.18; H, 5.10; N, 10.91
Found (%): C, 70.35; H, 5.23; N, 11.02

FT-IR (KBr, cm$^{-1}$): ν(N–H), 3430; ν(C–H), 3080; ν(C=C), 1390; ν(C=N), 1120; ν(C–Cl), 1060; δ(C–H), 720.

$^1$H NMR (DMSO, 400 MHz) δ/ppm: 7.428 (d, 2H, H$_{3',5'}$), 7.282 (d, 2H, H$_{2',6'}$), 6.365-6.355 (complex, 2H, H$_{5,5'}$), 5.929 (t, 2H, H$_{4,4'}$), 5.769 (d, 2H, H$_{3,3'}$), 5.264 (s, 2H, -NH), 5.139 (s, 1H, -CH).
3.5. Synthesis of gold(III) complexes

Mixture of H[AuCl₄]·3H₂O (0.5 mmol) and ligand (A¹³⁻¹⁻⁴¹) (0.5 mmol) in absolute ethanol (20 mL) were stirred at 60 °C until formation of light orange precipitate (~2 hr). The product was isolated by filtration, washed with ether and dried.

\[
A^{33-41} + H[AuCl_4]·3H_2O \xrightleftharpoons[\text{Ethanol, 60 °C}]{\text{[Au(A^{33-41})(Cl)_x].Cl_y}} \\
\text{Ligand} \quad \text{Chloroaauric acid} \\
A^{37} = \text{tridentate} \\
A^{33-36, 38-41} = \text{bidentate} \\
A^{37}, x = 1, y = 2 \\
A^{33-36, 38-41}, x = 2, y = 1
\]

Scheme 3.6: Reaction outline for the synthesis of gold(III) complexes

3.6. Characterization of gold(III) complexes

3.6.1 [Au(A¹³)Cl₂].Cl (1)

| Yield: 87% |
| Melting point: 248 °C |
| Molecular formula (mol. wt.): C₁₀H₉AuCl₃N₃ (474.52 g/mol) |
| Am (1 x 10⁻³ mol L⁻¹ in DMF): 99 ฿ cm² mole⁻¹ |
| Microanalysis data: |
| Calc. (%): C, 25.31; H, 1.91; N, 8.86 |
| Found (%): C, 25.20; H, 1.77; N, 8.99 |
FT-IR (KBr, cm\(^{-1}\)): \(\nu(\text{N–H}), 3290\); \(\nu(\text{C–H}), 3120\); \(\nu(\text{C=C}), 1490\); \(\nu(\text{C=N}), 1450\); \(\delta(\text{C–H}), 770\).

\(^1\)H NMR (DMSO, 400 MHz) \(\delta/\text{ppm}: 16.036\) (s, 1H, -NH), 8.406 (d, 2H, H\(_6,6'\)), 8.101 (t, 2H, H\(_5,5'\)), 7.328 (d, 2H, H\(_3,3'\)), 7.289 (t, 2H, H\(_4,4'\)).

\(^{13}\)C NMR (DMSO, 100 MHz) \(\delta/\text{ppm}: 159.17\) (C\(_{2,2'}\)), 148.96 (C\(_{6,6'}\)), 139.20 (C\(_{4,4'}\)), 115.48 (C\(_{5,5'}\)), 111.89 (C\(_{3,3'}\)).
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, $^1$H and $^{13}$C NMR spectroscopy were used to evaluate structure of the complex 1.
Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value 99 \( \mu \text{cm}^2 \text{mole}^{-1} \) reveals that the complex 1 is 1:1 electrolyte [27].

In IR spectrum of complex 1, the appearance of the bands \( \nu(\text{N–H}) \) at 3290 \( \text{cm}^{-1} \) withdraw the possibility of deprotonation of \( \text{–NH} \) group during complexation of ligand. The shifting of \( \nu(\text{C=\text{N}}) \) band from 1310 (ligand) to 1450 (complex) \( \text{cm}^{-1} \) suggest N atoms of pyridyl rings as coordinating atoms.

In \(^1\text{H}-\text{NMR}\) spectrum of complex 1, the appearance of \( \nu(\text{\text{–NH}}) \) peak at 16.036 ppm supports the IR data. The coordination of ligand results in shifting of all \(^1\text{H}-\text{NMR}\) peaks in the downfield region. The maximum shifting is observed for \( \text{H}_{6,6'} \) from 8.299 (ligand) to 8.406 (complex) ppm. This suggests that coordination occur through nearby N atoms where coordination has maximum effect.

The \(^{13}\text{C}-\text{NMR}\) data also supports the data obtained for the 2,2’-dipyridylamine.

The LC-MS spectrum of complex 1 validates the proposed structure of complex 1 from above analytical techniques. The LC-MS spectrum of complex 1 shows peaks at 438, 403, 368 and 171; which can be assigned for the fragments shown in Scheme 3.7. The peaks 438, 440, 442 i.e. M, M+2, M+4 suggest two attached chlorine atoms.

The above analytical and spectroscopic data suggest that coordination occur through two N atoms of pyridine rings of ligand while two chloride atoms are covalently attached with gold ion and one chloride atom in outer sphere making the complex mono cationic in nature.

The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data has clearly revealed the existence of a common and well-conserved structural motif comprising the gold centre, two chloride atoms and two N-donor atoms of 2,2’-dipyridylamine within a square planar arrangement with one chloride ion in outer sphere.

### 3.6.2 \([\text{Au}(\text{A}^{34}_3\text{Cl}_2)].\text{Cl} \) (2)

![Structural formula of \([\text{Au}(\text{A}^{34}_3\text{Cl}_2)].\text{Cl} \) (2)]

**Yield**: 84%

**Melting point**: 251 °C

**Molecular formula (mol. wt.)**: \( \text{C}_{11}\text{H}_8\text{AuCl}_3\text{N}_2\text{O} \) (487.52 g/mol)

**\( \Lambda_m \) (1 x 10\(^{-3}\) mol L\(^{-1}\) in DMF)**: 103 \( \mu \text{cm}^2 \text{mole}^{-1} \)

**Microanalysis data**:

**Calc. (%):** C, 27.10; H, 1.65; N, 5.75

**Found (%):** C, 27.01; H, 1.76; N, 5.63
FT-IR (KBr, cm⁻¹): ν(C–H), 3090; ν(C=O), 1690; ν(C=C), 1520; ν(C=N), 1440; δ(C–H), 740.

¹H NMR (DMSO, 400 MHz) δ/ppm: 8.770 (d, 2H, H₆,₆'), 8.182 (t, 4H, H₄,₄',₅,₅'), 7.789-7.761 (complex, 2H, H₃,₃').

¹³C NMR (DMSO, 100 MHz) δ/ppm: 181.52 (C₇Ọ), 154.51 (C₂,₂'), 152.95 (C₆,₆'), 136.77 (C₄,₄'), 130.53 (C₅,₅), 128.07 (C₃,₃').
LC-MS spectroscopy:

Scheme 3.8: Probable fragments of complex 2

- Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, $^1$H and $^{13}$C NMR spectroscopy were used to evaluate structure of the complex 2.
- Elemental analysis data are in good agreement with the proposed structure.
- The molar conductivity value $103 \ \mu\text{cm}^2\text{.mole}^{-1}$ reveals that the complex 2 is 1:1 electrolyte [27].
In IR spectrum of complex 2, the appearance of band at 1690 cm\(^{-1}\) shows presence of carbonyl group. The shifting of \(\nu(C=\text{N})\) band from 1320 (ligand) to 1440 (complex) cm\(^{-1}\) suggest N atoms of pyridyl rings as coordinating atoms.

The coordination of ligand results in shifting of all \(^1\text{H}-\text{NMR}\) peaks in the downfield region. The maximum shifting is observed for \(H_{6,6'}\) from 8.742 (ligand) to 8.770 (complex) ppm. This suggests that coordination occur through nearby N atoms where coordination has maximum effect.

The \(^{13}\text{C}-\text{NMR}\) data also supports the data obtained for the di(2-pyridyl)-ketone.

The LC-MS spectrum of complex 2 validates the proposed structure of complex 2 from above analytical techniques. The LC-MS spectrum of complex 2 shows peaks at 451, 416 and 381; which can be assigned for the fragments shown in Scheme 3.8. The peaks 451, 453, 455 i.e. M, M+2, M+4 suggest two attached chlorine atoms.

The above analytical and spectroscopic data suggest that coordination occur through two N atoms of pyridine rings of ligand while two chloride atoms are covalently attached with gold ion and one chloride atom in outer sphere, making the complex mono cationic in nature.

The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data has clearly revealed the existence of a common and well-conserved structural motif comprising the gold centre, two chloride atoms and two N-donor atoms of di(2-pyridyl)ketone within a square planar arrangement with one chloride ion in outer sphere.

3.6.3 \([\text{Au}(\text{A}^{35}\text{Cl})_2]\text{Cl}\) (3)

Yield : 89%
Melting point: >280 °C
Molecular formula (mol. wt.): C\(_{19}\)H\(_{11}\)AuCl\(_4\)N\(_4\) (634.10 g/mol)
\(\Lambda m\) (1 x 10\(^3\) mol L\(^{-1}\) in DMF): 96 \(\mu\) cm\(^2\) mole\(^{-1}\)
Microanalysis data:
Calc. (%): C, 35.99; H, 1.75; N, 8.84
Found (%): C, 35.87; H, 1.62; N, 8.97
FT-IR (KBr, cm$^{-1}$): $\nu$(N–H), 3262; $\nu$(C–H), 3128; $\nu$(C=C), 1494; $\nu$(C=N), 1486; $\nu$(C–Cl), 1056; $\delta$(C–H), 758.

$^1$H NMR (DMSO, 400 MHz) $\delta$/ppm: 14.750 (s, 1H, -NH), 9.527 (d, 2H, H$_{2,10}$), 9.190 (d, 2H, H$_{4,8}$), 8.287 (d, 2H, H$_{2',6'}$), 8.237 (t, 2H, H$_{3,9}$), 7.748 (dd, 2H, H$_{3',5'}$).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$/ppm: 159.27 (C$_{1\text{a},1\text{la}}$), 153.44 (C$_6$), 151.72 (C$_{2,10}$), 135.34 (C$_4$), 134.11 (C$_{1\text{r}}$), 132.52 (C$_{4,8}$), 129.51 (C$_{3',5'}$), 128.29 (C$_{2',6'}$), 126.56 (C$_{5\text{a},7\text{a}}$), 124.17 (C$_{3,9}$), 122.89 (C$_{4\text{a},8\text{a}}$).
LC-MS spectroscopy

Scheme 3.9: Probable fragments of complex 3
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, $^1$H and $^{13}$C-NMR spectroscopy were used to evaluate structure of the complex 3.

Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value 96 \( \text{\mu} \text{cm}^2\text{mole}^{-1} \) reveals that complex 3 is 1:1 electrolyte [27].

In IR spectrum of complex 3, the appearance of the band \( \nu(\text{N–H}) \) at 3262 cm\(^{-1} \) withdraw the possibility of deprotonation of –NH group. The shifting of \( \nu(\text{C=\text{N}}) \) band from 1419 (ligand) to 1486 (complex) cm\(^{-1} \) suggest N atoms of pyridyl rings as coordinating atoms.

In \(^1\text{H-NMR} \) spectrum of complex 3, the appearance of –NH peak at 14.750 ppm supports the IR data. The coordination of ligand results in shifting of all \(^1\text{H-NMR} \) peaks in the downfield region. The maximum shifting is observed for H\(_{2,10}\) from 9.014 (ligand) to 9.527 (complex) ppm. This suggests that coordination occur through nearby N atoms where coordination has maximum effect.

The coordination of ligand results in shifting of all \(^{13}\text{C-NMR} \) peaks in the upfield or downfield region. The shifting of C\(_{2,10}\) and C\(_{1a,11a}\) from 149.74 and 155.43 (ligand) to 151.72 and 159.27 (complex) ppm, respectively; suggest that coordination occur through nearby N atom where coordination has maximum effect.

The LC-MS spectrum of complex 3 validates the structure of complex proposed by above analytical and spectroscopic techniques. The LC-MS spectrum of complex 3 shows peaks at 597, 562, 527 and 330; which can be assigned for the fragments shown in Scheme 3.9. The peaks 597, 599, 601 i.e. M, M+2 and M+4 suggest three attached chlorine atoms.

The above analytical and spectroscopic data suggest that coordination occur through two N atoms of pyridyl ring of phenanthroline derivative while two chloride atoms are covalently attached with gold ion and one chloride atom in outer sphere making the complex mono cationic in nature.

The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data, has clearly revealed the existence of a common and well-conserved structural motif comprising the gold centre, two chloride atoms and two N-donor atoms of 2-(4-chlorophenyl)-1H-imidazo[4,5-f][1,10]-phenanthroline ligand within a square planar arrangement with one chloride ion in outer sphere.
3.6.4 \[\text{Au}(\text{A}^{36})\text{Cl}_2].\text{Cl} \ (4)\]

Yield : 88%
Melting point: >280 °C
Molecular formula (mol. wt.): C_{19}H_{11}AuBrCl_{3}N_{4} (678.55 g/mol)
\(\Lambda_m \ (1 \times 10^{-3} \text{ mol L}^{-1} \text{ in DMF}) \): 98 \(\mu\) cm² mole⁻¹
Microanalysis data:
Calc. (%): C, 33.63; H, 1.63; N, 8.26
Found (%): C, 33.49; H, 1.74; N, 8.35

\[\text{FT-IR (KBr, cm}^{-1}\):} \nu(\text{N–H}), 3265; \nu(\text{C–H}), 3038; \nu(\text{C=C}), 1480; \nu(\text{C=N}), 1472; \nu(\text{C–Br}), 1048; \delta(\text{C–H}), 752.\]

\[\text{\(^1\text{H NMR (DMSO, 400 MHz) \delta/ppm:}} \] 14.676 (s, 1H, -NH), 9.636 (d, 2H, H_{2,10}), 9.294 (d, 2H, H_{4,8}), 8.307 (d, 2H, H_{2',6'}), 8.252 (t, 2H, H_{3,9}), 7.743 (dd, 2H, H_{3',5'}).\]
$^{13}$C NMR (DMSO, 100 MHz) δ/ppm: 158.86 (C$_{1a,11a}$), 155.32 (C$_6$), 150.99 (C$_{2,10}$), 134.26 (C$_1$), 132.65 (C$_{3',5'}$), 132.30 (C$_{2',6'}$), 131.47 (C$_4$), 126.98 (C$_{5a,7a}$), 123.19 (C$_{4,8}$), 122.91 (C$_{3,9}$), 121.34 (C$_{4a,8a}$).

**LC-MS spectroscopy**
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, \(^1\)H and \(^{13}\)C-NMR spectroscopy were used to evaluate structure of the complex 4.

Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value 98 \( \text{\Omega} \cdot \text{cm}^2 \cdot \text{mole}^{-1} \) reveals that the complex 4 is 1:1 electrolyte [27].

In IR spectrum of complex 4, the appearance of the band \( \nu(N–H) \) at 3265 cm\(^{-1} \) withdraw the possibility of deprotonation of –NH group. The shifting of \( \nu(C=N) \) band from 1419 (ligand) to 1472 (complex) cm\(^{-1} \) suggest N atoms of pyridyl rings as coordinating atoms.

In \(^1\)H-NMR spectrum of complex 4, the appearance of –NH peak at 14.676 ppm supports the IR data. The coordination of ligand results in shifting of all \(^1\)H-NMR peaks in the downfield region. The maximum shifting is observed for \( H_{2,10} \) from 9.042 (ligand) to 9.636 (complex) ppm. This suggests that coordination occur through nearby N atoms where coordination has maximum effect.

The coordination of ligand results in shifting of all \(^{13}\)C-NMR peaks in the upfield or downfield region. The shifting of \( C_{2,10} \) and \( C_{1a,11a} \) from 149.80 and 154.67 (ligand) to 150.99 and 158.86 (complex) ppm, respectively; suggest that coordination occur through nearby N atom where coordination has maximum effect.

The LC-MS spectrum of complex 4 validates the structure of complex proposed by above analytical and spectroscopic techniques. The LC-MS spectrum of complex 4 shows peaks at 643, 608, 571 and 374; which can be
assigned for the fragments shown in Scheme 3.10. The peaks 643, 645, 647 i.e. M, M+2, M+4 suggest two attached chlorine atoms.

- The above analytical and spectroscopic data suggest that coordination occurs through two N atoms of pyridyl ring of phenanthroline derivative while two chloride atoms are covalently attached with gold ion and one chloride atom in outer sphere, making the complex mono cationic in nature.

- The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data, has clearly revealed the existence of a common and well-conserved structural motif comprising the gold centre, two chloride atoms and two N-donor atoms of 2-(4-bromophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline ligand within a square planar arrangement with one chloride ion in outer sphere.

3.6.5 \([Au(A^{37})Cl].Cl_2\) (5)

![Structure of \([Au(A^{37})Cl].Cl_2\) (5)](image)

Yield : 91%

Melting point: 277 °C

Molecular formula (mol. wt.): \(C_{17}H_{13}AuCl_3N_5O_2\) (622.64 g/mol)

\(\text{Am (1 x 10}^{-3}\text{ mol L}^{-1}\text{ in DMF): 138 }\mu \text{ cm}^2\text{ mole}^{-1}\)

**Microanalysis data:**

Calc. (%): C, 32.79; H, 2.10; N, 11.25

Found (%): C, 32.67; H, 2.22; N, 11.10

**FT-IR (KBr, cm\(^{-1}\))**: \(\nu(N-H), 3600; \nu(C-H), 3080; \nu(C=O), 1720; \nu(C=C), 1440; \nu(C=N), 1340; \delta(C-H), 680.\)
$^1$H NMR (DMSO, 400 MHz) $\delta$/ppm: 12.075 (s, 2H, -NH), 8.550 (d, 4H, H$_{3,5,6',6''}$), 8.477 (dd, 2H, H$_{3',3''}$), 8.364 (t, 1H, H$_4$), 8.122 (dt, 2H, H$_{4',4''}$), 7.400 (t, 2H, H$_{5',5''}$).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$/ppm: 171.25 (C$_{CO}$), 152.64 (C$_{4',4''}$), 152.12 (C$_4$), 149.60 (C$_{2,6}$), 139.33 (C$_{6',6''}$), 136.17 (C$_{2',2''}$), 131.89 (C$_{3,5}$), 129.43 (C$_{5',5''}$), 114.51 (C$_{3',3''}$).
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, \(^1\)H and \(^{13}\)C-NMR spectroscopy were used to evaluate structure of the complex 5.

Scheme 3.11: Probable fragments of complex 5
Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value $138 \text{ cm}^2 \cdot \text{mole}^{-1}$ reveals that complex 5 is 1:2 electrolyte [27].

In IR spectrum of complex 5, shifting of the band $\nu(\text{N–H})$ from 3390 (ligand) to 3600 (complex) cm$^{-1}$, withdraw the possibility of deprotonation of –NH group and suggest the N atom of –NH groups as coordinating atoms. The shifting of $\nu(\text{C=N})$ band from 1240 (ligand) to 1340 (complex) cm$^{-1}$ suggest N atom of central pyridyl ring as a coordinating atom. The involvement of N atoms of side pyridine units as coordinating atoms can be ruled out because coordination from that N atoms produce distortion in structure and hence bring instability in the structure. The $\nu(\text{C=O})$ band shifting from 1710 (ligand) to 1720 (complex) cm$^{-1}$ ruled out the possibility of participation of keto group in coordination. The low shifting in $\nu(\text{C=O})$ band also suggest that coordination has less effect in stretching of nearby groups.

In $^1$H-NMR spectrum of complex 5, the shifting of –NH peak from 11.263 (ligand) to 12.075 (complex) ppm supports the IR data. The coordination of ligand results in moderate shifting in other $^1$H-NMR peaks to the downfield region. So the $^1$H-NMR data suggests that coordination occur through N atom of –NH groups.

The coordination of ligand results in moderate shifting in all $^{13}$C-NMR peaks to the upfield or downfield region. The shifting of $\text{C=O}$ from 164.92 (ligand) to 171.25 (complex) ppm suggest that coordination occur through nearby N atom of –NH groups, where coordination has maximum effect. The large shifting of $\text{C=O}$ in $^{13}$C-NMR also suggest that coordination produces drastic changes in the magnetic environment of coordinating atoms.

The LC-MS spectrum validates the structure of complex 5 proposed by above analytical and spectroscopic techniques. The LC-MS spectrum of complex 5 shows peaks at 551, 516 and 319; which can be assigned for the fragments shown in Scheme 3.11. The peaks 551, 553 i.e. M, M+2 suggest one attached chlorine atom.

The above analytical and spectroscopic data suggest that coordination occur through N atoms of two aliphatic –NH groups and N atom of central pyridine ring of ligand while one chlorine atom is covalently attached with gold ion and two chloride atoms in outer sphere, making the complex di cationic in nature.

The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data has clearly revealed the existence of a common and well-conserved structural motif comprising the gold centre, one chlorine atom and three N-donor atoms of N$^2$N$^6$-bis(pyridin-2-yl)pyridine-2,6-dicarboxamide ligand within a square planar arrangement with two chloride ion in outer sphere.
3.6.6 [Au(A$^{38}$)Cl$_2$.Cl (6)

Yield : 82%
Melting point: 243 °C
Molecular formula (mol. wt.): C$_{11}$H$_9$AuCl$_3$N$_3$O (502.53) g/mol
Am (1 x 10$^{-3}$ mol L$^{-1}$ in DMF): 102 $\tilde{\mu}$ cm$^2$ mole$^{-1}$
Microanalysis data:
Calc. (%): C, 26.29; H, 1.81; N, 8.36
Found (%): C, 26.14; H, 1.97; N, 8.51

\[ \text{FT-IR (KBr, cm$^{-1}$): } \nu(N-H), 3600; \nu(C-H), 3090; \nu(C=O), 1690; \nu(C=C), 1440; \nu(C=N), 1340; \delta(C-H), 690. \]

\[ \text{H NMR (CDCl$_3$, 400 MHz) } \delta/\text{ppm: } 10.574 \text{ (s, 1H, -NH), 8.660 (d, 1H, H$_6$), 8.460 (d, 1H, H$_3$), 8.406 (t, 1H, H$_4$), 8.330 (d, 1H, H$_6'$), 7.943 (t, 1H, H$_3$), 7.799 (t, 1H, H$_4$), 7.521 (dt, 1H, H$_5$), 7.117 (dd, 1H, H$_3'$).} \]
$^{13}$C NMR (CDCl$_3$, 100 MHz) δ/ppm: 168.34 (C$_{CO}$), 153.60 (C$_{4'}$), 152.05 (C$_4$), 149.89 (C$_2$), 144.61 (C$_6$), 137.42 (C$_{6'}$), 134.59 (C$_{2'}$), 132.94 (C$_3$), 130.70 (C$_5$), 128.28 (C$_3$), 115.77 (C$_{3'}$).

**LC-MS spectroscopy**
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, $^1$H and $^{13}$C-NMR spectroscopy were used to evaluate structure of the complex 6.

Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value $102 \ \text{\mu cm}^2\text{.mole}^{-1}$ reveals that the complex 6 is 1:1 electrolyte [27].

In IR spectrum of complex 6, shifting of the band $\nu$(N–H) from 3350 (ligand) to 3600 (complex) cm$^{-1}$ withdraw the possibility of deprotonation of –NH group and suggest the N atom of –NH group as a coordinating atom. The shifting of $\nu$(C=N) band from 1220 (ligand) to 1340 (complex) cm$^{-1}$ suggest N atom of pyridine ring attached with keto group as a coordinating atom. The involvement of N atoms of pyridine units attached with –NH group as coordinating atoms can be ruled out because coordination from N atom of pyridine ring directly attached with –NH group results in formation of unstable four member chelate ring and hence bring instability in the structure.

In $^1$H-NMR spectrum of complex 6, the shifting of –NH peak from 10.449 to 10.574 ppm supports the IR data. The coordination of ligand results in shifting of other $^1$H-NMR peaks to the downfield region. So the $^1$H-NMR
data suggests that coordination occur through N atom of –NH group and with N atom of pyridine ring attached with keto group.

- The coordination of ligand results in shifting of all $^{13}$C-NMR peaks to the upfield or downfield region. The shifting of $C_{C=O}$ from 160.75 (ligand) to 168.34 (complex) ppm suggest that coordination occur through nearby N atom of –NH group, where coordination has maximum effect. The large shifting of $C_{C=O}$ in $^{13}$C-NMR also suggest that coordination produces drastic changes in the magnetic environment of coordinating atoms.

- The LC-MS spectrum of complex 6 validates the structure of complex proposed by above analytical and spectroscopic techniques. The LC-MS spectrum of complex 6 shows peaks at 466, 431 and 396; which can be assigned for the fragments shown in Scheme 3.12. The peaks 466, 468, 470 i.e. M, M+2, M+4 suggest two attached chlorine atoms.

- The above analytical and spectroscopic data suggest that coordination occur through N atom of aliphatic –NH group and N atom of pyridine ring attached with keto group of ligand while two chlorine atoms are covalently attached with gold(III) ion and one chloride ion in outer sphere making the complex mono cationic in nature.

- The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data has clearly revealed the existence of a common and well-conserved structural motif comprising the gold(III) centre, two chlorine atoms and two N-donor atoms of N-(pyridin-2-yl)picolinamide ligand within a square planar arrangement with one chloride ion in outer sphere.

3.6.7 $[\text{Au}(\text{A}^{39})\text{Cl}_2].\text{Cl}$ (7)

<table>
<thead>
<tr>
<th>Yield</th>
<th>84%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>238 °C</td>
</tr>
<tr>
<td>Molecular formula (mol. wt.)</td>
<td>$\text{C}<em>{12}\text{H}</em>{11}\text{AuCl}_4\text{N}_2$ (522.01 g/mol)</td>
</tr>
<tr>
<td>Am (1 x $10^{-3}$ mol L$^{-1}$ in DMF)</td>
<td>97 ν cm$^2$ mole$^{-1}$</td>
</tr>
<tr>
<td>Microanalysis data:</td>
<td></td>
</tr>
<tr>
<td>Calc. (%)</td>
<td>C, 27.61; H, 2.12; N, 5.37</td>
</tr>
<tr>
<td>Found (%)</td>
<td>C, 27.77; H, 1.99; N, 5.59</td>
</tr>
</tbody>
</table>
FT-IR (KBr, cm\(^{-1}\)): \(\nu(N-H), 3410; \nu(C-H), 3020; \nu(C=C), 1370; \nu(C=N), 1320; \nu(C-Cl), 1190; \delta(C-H), 740.\)

\(^1H\) NMR (CDCl\(_3\), 400 MHz) \(\delta/\text{ppm}: 8.759\ (d, 1H, H\(_6\)), 7.866\ (t, 1H, H\(_4\)), 8.622\ (d, 1H, H\(_3\)), 7.480\ (t, 1H, H\(_5\)), 7.346\ (dd, 2H, H\(_3'\), H\(_5'\)) , 6.843\ (dd, 2H, H\(_2'\), H\(_6'\)) , 6.174\ (s, 1H, -NH) , 4.776\ (d, 2H, -CH\(_2\)).

\(^13C\) NMR (CDCl\(_3\), 100 MHz) \(\delta/\text{ppm}: 154.30\ (C\(_2\)), 149.76\ (C\(_4\)), 144.48\ (C\(_6\)), 139.88\ (C\(_1\)), 135.97\ (C\(_4'\)), 129.76\ (C\(_3'\), C\(_5'\)), 126.82\ (C\(_3\)), 126.05\ (C\(_5\)), 124.53\ (C\(_2'\), C\(_6'\)), 47.63\ (C\(_{CH}\)).
**LC-MS spectroscopy**

![LC-MS Spectrogram](image)

**Scheme 3.13:** Probable fragments of complex 7
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, $^1$H and $^{13}$C-NMR spectroscopy were used to evaluate structure of the complex 7.

Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value 97 $\mu$ cm$^2$.mole$^{-1}$ reveals that the complex 7 is 1:1 electrolyte [27].

In IR spectrum of complex 7, shifting of the band $\nu$(N–H) from 3330 (ligand) to 3410 (complex) cm$^{-1}$ withdraw the possibility of deprotonation of –NH group and suggest the N atom of –NH group as coordinating atom. The shifting of $\nu$(C=N) band from 1280 (ligand) to 1320 (complex) cm$^{-1}$ suggest N atom of pyridine ring as a coordinating atom.

In $^1$H-NMR spectrum of complex 7, the shifting of –NH peak from 4.860 (ligand) to 6.174 (complex) ppm supports the IR data. The coordination of ligand results in shifting of other $^1$H-NMR peaks to the downfield region. So the $^1$H-NMR data suggests that coordination occur through N atom of –NH group and with N atom of pyridine ring.

The coordination of ligand results in shifting of all $^{13}$C-NMR peaks to the upfield or downfield region.

The LC-MS spectrum of complex 7 validates the structure of complex proposed by above analytical and spectroscopic techniques. The LC-MS spectrum of complex 7 shows peaks at 485, 450, 415 and 381; which can be assigned for the fragments shown in Scheme 3.13. The peaks 485, 487, 489 i.e. M, M+2, M+4 suggest three attached chlorine atoms.

The above analytical and spectroscopic data suggest that coordination occur through N atom of aliphatic –NH group and N atom of pyridine ring of ligand while two chlorine atoms are covalently attached with gold(III) ion and one chloride ion in outer sphere making the complex mono cationic in nature.

The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data, has clearly revealed the existence of a common and well-conserved structural motif comprising the gold(III) centre, two chlorine atoms and two N-donor atoms of 4-chloro-N-(pyridin-2-ylmethyl)aniline ligand within a square planar arrangement with one chloride ion in outer sphere.
3.6.8 [Au(Au₄)Cl₂].Cl (8)

Yield : 82%
Melting point: 226 °C
Molecular formula (mol. wt.): C₁₅H₁₄AuCl₃N₂ (525.61 g/mol)
Λm (1 x 10⁻³ mol L⁻¹ in DMF): 91 𝜇 cm² mole⁻¹
Microanalysis data:
Calc. (%): C, 34.28; H, 2.68; N, 5.33
Found (%): C, 34.46; H, 2.81; N, 5.20

FT-IR (KBr, cm⁻¹): ν(N–H), 3490; ν(C–H), 3070; ν(C=C), 1400; ν(C=N), 1180; δ(C–H), 730.

¹H NMR (DMSO, 400 MHz) δ/ppm: 7.504 (d, 2H, H₂″,₅″), 7.362 (d, 2H, H₂″,₆″), 7.244 (t, 1H, H₄″), 6.792-6.783 (complex, 2H, H₅₅″), 6.197 (s, 2H, -NH), 6.050 (t, 2H, H₄₄), 5.986 (d, 2H, H₃₃″), 5.205 (s, 1H, -CH).
\(^{13}\)C NMR (DMSO, 100 MHz) δ/ppm: 151.24 (C\(_{1''}\)), 141.37 (C\(_{3,3''}\)), 136.59 (C\(_{2,2''}\)), 135.77 (C\(_{3'',5''}\)), 135.38 (C\(_{2'',6''}\)), 134.12 (C\(_{4''}\)), 130.32 (C\(_{5,5'}\)), 115.95 (C\(_{4,4'}\)), 52.67 (C\(_{CH}\)).

**LC-MS spectroscopy**
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, $^1$H and $^{13}$C-NMR spectroscopy were used to evaluate structure of the complex 8.

Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value $91 \ \text{\Omega}.\text{cm}^2.\text{mole}^{-1}$ reveals that the complex 8 is 1:1 electrolyte [27].

In IR spectrum of complex 8, shifting of the band $\nu$(N–H) from 3420 (ligand) to 3490 (complex) cm$^{-1}$ withdraw the possibility of deprotonation of $–\text{NH}$ group and suggest the N atom of pyrrole rings as coordinating atoms.

In $^1$H-NMR spectrum of complex 8, the shifting of $–\text{NH}$ peak from 5.273 (ligand) to 6.197 (complex) ppm supports the IR data. The coordination of ligand results in shifting of other $^1$H-NMR peaks to the downfield region. The maximum shifting is observed for H$_{5,5'}$ from 6.372-6.363 (ligand) to 6.792-6.783 (complex) ppm. This suggests that coordination occur through nearby N atoms where coordination has maximum effect.

The coordination of ligand results in shifting of all $^{13}$C-NMR peaks in the upfield or downfield region.

The LC-MS spectrum of complex 8 validates the structure of complex proposed by above analytical and spectroscopic techniques. The LC-MS spectrum of complex 8 shows peaks at 489, 459 and 419; which can be assigned for the fragments shown in Scheme 3.14. The peaks 489, 491, 493 i.e. M, M+2 and M+4 suggest two attached chlorine atoms.
The above analytical and spectroscopic data suggest that coordination occurs through two N atoms of pyrrole rings of ligand while two chloride atoms are covalently attached with gold(III) ion and one chloride atom in outer sphere making the complex mono cationic in nature.

The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data, has clearly revealed the existence of a common and well-conserved structural motif comprising the gold(III) centre, two chloride atoms and two N-donor atoms of 2,2'-(phenylmethylene)bis(1H-pyrrole) ligand within a square planar arrangement with one chloride ion in outer sphere.

3.6.9 \([\text{Au}(\text{A}^4\text{I})\text{Cl}_2]\).\(\text{Cl} (9)\)

Yield : 81%
Melting point: 226 °C
Molecular formula (mol. wt.): \(\text{C}_{15}\text{H}_{13}\text{AuCl}_4\text{N}_2 (560.06 \text{ g/mol})\)
\(\Lambda\mu (1 \times 10^{-3} \text{ mol L}^{-1} \text{ in DMF}): 89 \sigma \text{ cm}^2 \text{ mole}^{-1}\)
Microanalysis data:
Calc. (%): C, 32.17; H, 2.34; N, 5.00
Found (%): C, 31.94; H, 2.51; N, 5.11

FT-IR (KBr, cm\(^{-1}\)):
\(\nu(\text{N–H}), 3490; \nu(\text{C–H}), 3090; \nu(\text{C=C}), 1400; \nu(\text{C=N}), 1180; \nu(\text{C–Cl}), 1080; \delta(\text{C–H}), 730.\)
\[ ^1H \text{ NMR (DMSO, 400 MHz)} \delta/\text{ppm}: 7.489 \text{ (d, 2H, H}_3^{''},5^{''}), 7.373 \text{ (d, 2H, H}_2^{''},6^{''}), 6.793-6.784 \text{ (complex, 2H, H}_5,5^{'}), 6.092 \text{ (s, 2H, -NH)}, 5.947 \text{ (t, 2H, H}_4,4^{'}), 5.847 \text{ (d, 2H, H}_3,3^{'}), 5.307 \text{ (s, 1H, -CH)}. \]

\[ ^{13}C \text{ NMR (DMSO, 100 MHz)} \delta/\text{ppm}: 152.33 \text{ (C}_1^{''}), 141.84 \text{ (C}_3,5^{'}), 140.66 \text{ (C}_4^{''}), 139.58 \text{ (C}_2^{''},6^{''}), 138.24 \text{ (C}_2,2^{'}), 136.73 \text{ (C}_3^{''},5^{'}), 130.95 \text{ (C}_5,5^{'}), 117.40 \text{ (C}_4,4^{'}), 52.88 \text{ (CCH)}. \]
**Scheme 3.15:** Probable fragments of complex 9
Several analytical and spectroscopic techniques like molar conductivity measurement, C,H,N elemental analysis, LC–MS, IR, $^1$H and $^{13}$C-NMR spectroscopy were used to evaluate structure of the complex 9.

Elemental analysis data are in good agreement with the proposed structure.

The molar conductivity value $89 \mu\text{cm}^2\text{mole}^{-1}$ reveals that the complex 9 is 1:1 electrolyte [27].

In IR spectrum of complex 9, shifting of the band $\nu$(N–H) from 3430 (ligand) to 3490 (complex) cm$^{-1}$ withdraw the possibility of deprotonation of –NH group and suggest the N atom of pyrrole rings as coordinating atoms.

In $^1$H-NMR spectrum of complex 9, the shifting of –NH peak from 5.264 (ligand) to 6.092 (complex) ppm supports the IR data. The coordination of ligand results in shifting of other $^1$H-NMR peaks to the downfield region. The maximum shifting is observed for H$_{5,5'}$ from 6.365-6.355 (ligand) to 6.793-6.784 (complex) ppm. This suggests that coordination occur through nearby N atoms where coordination has maximum effect.

The coordination of ligand results in shifting of all $^{13}$C-NMR peaks in the upfield or downfield region.

The LC-MS spectrum of complex 9 validates the structure of complex proposed by above analytical and spectroscopic techniques. The LC-MS spectrum of complex 3 shows peaks at 523, 488, 453 and 256; which can be assigned for the fragments shown in Scheme 3.15. The peaks 523, 525, 527 i.e. M, M+2 and M+4 suggest three attached chlorine atoms.

The above analytical and spectroscopic data suggest that coordination occur through two N atoms of pyrrole rings of ligand while two chloride atoms are covalently attached with gold(III) ion and one chloride atom in outer sphere, making the complex mono cationic in nature.

The structural analysis that we have performed on mononuclear gold(III) complexes, relying on the availability of different spectroscopic and analytical data, has clearly revealed the existence of a common and well-conserved structural motif comprising the gold(III) centre, two chloride atoms and two N-donor atoms of 2,2'-(chlorophenylmethylene)bis(1H-pyrrole) ligand within a square planar arrangement with one chloride ion in outer sphere.
3.7. References


