

Synthesis, Physiochemical Studies And Antimicrobial Screening Of Metal Complexes Of Fe(III) & Au(III) With Amino Acids.

Md. Anwar Hossain, M. Saidul Islam, Md. Ashraful Alam, Tipu Sultan

Abstract: Mixed ligand complexes of Iron(III) and Au(III) with succinimide or 8-hydroxyquinoline as primary ligands and amino acids as secondary ligands have been synthesized. The general formula of these complexes are follows: $K[Fe(L)_2(L')_2]$ & $[Au(Q)(L')]$ where $L = C_4H_4O_2N(1-5)$, $Q = C_9H_6NO(6-10)$; $L' = C_6H_{12}NO_2(1,9)$, $C_6H_{10}N_2O_4S_2(2,6)$, $C_3H_6O_2NS(3)$, $C_3H_6NO_3(4,7)$, $C_9H_{10}O_2N(5,8)$. The complexes were prepared in the solid form and characterization by elemental analysis, conductivity, magnetic moment measurement, IR, 1H NMR and electronic spectroscopic studies. The antibacterial and antifungal activities of the ligand and metal complexes have also been investigated. The value of $10 Dq$ was found to be $12250-13965\text{ cm}^{-1}$ for all complexes. The value of B , β and ligand field stabilization energy have also been calculated from the bands obtained in the electronic spectra of the complexes. Electronic and other measurements confirmed their octahedral and square planar structures. The metal complexes showed stronger antibacterial and antifungal activities than the ligand

Key words: Antibacterial, antifungal, Imides, 8-HQ, Amino acids, Metal complexes, 1H NMR and DMSO

1. Introduction

The chemistry of metal complexes is now the most active research field of inorganic chemistry. Today coordination chemistry stands as landmark in the area of scientific advancement embracing most diverse branches of science, engineering and technology. Scanty details on the studies of simple metal imide or metal quinoline complexes are available in the literature but a very little work has been done on their mixed ligand complexes. The salts of imides and 8-HQ with varies metal ions were prepared under anhydrous conditions [1, 2] because of their hydrolysable nature. An extensive work has been carried out on succinimide [3]. The vast literature on structural studies of Schiff-base complexes reveals some interesting features of their coordination behavior [4–8]. Metal complexes with Schiff base ligands have been receiving considerable attention due to the pharmacological properties of both ligands and complexes [9-12]. Gold complexes have been found to act as active homogeneous catalysts in reactions of industrials importance including the hydrogenation [13] hydroformation [14] and oxidative hydrolysis [15] of olefins and carboxylation of methanol. Amino acids have been used as secondary ligands in our studies and however their complexes have great importance in biological fields such as antitumor [16,17], antifungal [18,19] and antibacterial [20, 21] as well known. We report here the preparation and characterization of some mixed ligand complexes of Fe(III) & Au(III) with succinimide or 8-hydroxyquinoline as primary and amino acids, viz. glycine, L-alanine, L-phenylalanine, DL-leucine, L-cystine and L-cystein as secondary ligands.

2. Experimental

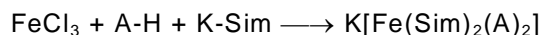
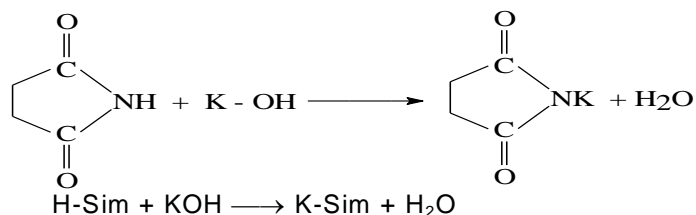
2.1 Physical Measurement

Infrared spectra were recorded on Shimadzu IR-470, Perkin Elmer IR-883 and Genesis Series FTIR TM 9423-240-08061 spectrophotometer as KBr pellets in the region $4500-400\text{ cm}^{-1}$ in the Department of Chemistry, Rajshahi University, Rajshahi. Carbon, hydrogen and analyses were carried out at the Department of Chemistry, University Putra Malaysia. The electronic spectra were run on a Ultrospee K4033 spectrophotometer. Metal was determined by weighing as the oxide produced by direct ignition. The molar conductance of 10^{-3} M solution of the metal complex in amyl alcohol was measured at 30°C using a Jenway 4310 conductivity meter and a dip-cell with platinized electrode (cell constant=1.12). Melting points were determined using an Electrothermal digital melting point apparatus. Magnetic susceptibility was measured with a Jonshon Matthey magnetic susceptibility balance at 298K. 1H NMR (DMSO- d_6) was taken by Varian Gemini 200/MHz pulsed FT NMR spectrometer. TMS was used as the internal standard.

2.1a. Preparation of the Fe(III) complexes:

The alcoholic solutions of Ferric chloride and of potassium succinimide were mixed in the respective molar ratio and refluxed about fifteen minutes with gentle heat. Then aqueous solution of amino acids containing minimum amount of KOH (to make soluble) were mixed in a molar ratio with the previous mixture. To get the precipitate of the complexes, the mixture was then heated at 80°C for forty minutes and then allowed to stand for ten minutes. The precipitates formed were removed by filtration, washed several times with distilled water and then with alcohol and dried in a vacuum desiccator over anhydrous $CaCl_2$.

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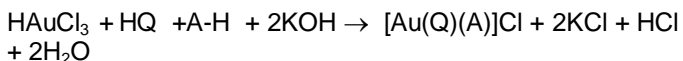


Sim = anions of succinimide

A = anions of amino acids

2.2b. Preparation of the Au(III) complexes:

8-hydroxyquinoline (0.002 mole) was deprotonated by adding KOH (0.002 mole) in 30 cm³ ethanol with constant stirring for ~15 min. Then the amino acid (0.001 mole) was deprotonated by KOH (0.001 mole) in aqueous medium until the pH of the solution was 8-9. Deprotonated amino acid solution was then added dropwise to an alcoholic solution of HAuCl₄ (0.001 mole) with constant stirring. The mixture was then refluxed on water bath for half an hour and then cooled. The solid product that appeared was washed several times with distilled water and finally with ethanol. It was then dried in a vacuum desiccator over anhydrous CaCl₂.



Sim = anions of succinimide

Q = anions of 8- hydroxyquinoline

A= anions of amino acids

2.3. Biological activity technique

The biological screening of the ligand and its Fe(III) and Au(III) complexes were undertaken against the bacteria *E. coli*, *S. aureus* and *S. typhi* by the disc diffusion technique(22) using nutrient agar as medium. In a typical procedure, molten nutrient agar kept at 45°C was then poured into Petridishes and allowed to solidify. Then holes of 4 mm diameter were punched carefully using a sterile cork borer and these were completely filled with the test solutions (40 µg/disc). The plates were incubated for 24h at 37°C. The diameter of the zones of inhibition for all the test compounds was measured and the results were compared with the standard drug ciprofloxacin of the same concentration as that of the test compound under identical conditions. The antifungal activity of the test compounds was evaluated against the *A. niger*, *F. oxysporum* and *T. species* by disc diffusion technique cultured on potato-dextrose agar (PDA) medium adapting similar procedure described above. The plates were incubated for 48h at 28°C. The compounds were measured and the results were compared with the standard drug griseofulvin of the same concentration as that of the test compound under identical conditions. Since all test compounds and standard drugs were prepared in freshly DMSO, its zone of inhibition was found to be very negligible and taken as zero mm

3. Results and discussions:

3.1 Conductivity measurement and elemental analysis:

The complexes of Fe(III) and gold (III) were soluble in benzene, amyl alcohol and DMSO respectively. All the complexes were insoluble in water. The molar conductance of iron(III) and gold (III) were measured in benzene and amyl alcohol and high conductance values were found which indicated that these complexes were highly electrolyte in nature. Some physical properties, viz; colour, melting points, molar conductance are given in table (1). Analytical result for metal, carbon, hydrogen and nitrogen are given in table (2)

Table – 1. Physical properties of the complexes:

Complex No.	Name of the complexes	Colour	Melting points° C	Molar conductance (ohm ⁻¹ cm ² mole ⁻¹)
1	K[Fe(Sim) ₂ (leu) ₂]	Beige	310-315(d)	80
2	K[Fe(Sim) ₂ (cystine) ₂]	reddish	>330	83
3	K[Fe(Sim) ₂ (cystein) ₂]	reddish	>330	81
4	K[Fe(Sim) ₂ (ser) ₂]	Beige	300-305(d)	85
5	K[Fe (Sim) ₂ (phala) ₂]	Beige	315-320)d)	80
6	[Au(Q)(cystine)]Cl	Golden Brown	230-240 (d)	68
7	[Au(Q)(Ser)]Cl	Black	245-250(d)	73
8	[Au(Q) (phala)]Cl	Black	220-225(d)	70
9	[Au(Q)(leu)]Cl	Black	210-215(d)	72

Where, Sim = C₄ H₄O₂N (deprotonated), Q = C₉H₆NO (deprotonated), leu = leucine, Ser = Serine, Phala = Phenylalanine, Cystine = Cystine, Cysteine = Cysteine,

d = decomposition

Table 2. Analytical data of complexes

Complex No.	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
1	10.16 (10.08)	43.67 (43.60)	5.45 (5.35)	10.19 (10.10)
2	7.27 (7.15)	31.26 (31.20)	3.12 (3.06)	7.29 (7.21)
3	10.55 (10.42)	31.73 (31.67)	3.40 (3.32)	10.57 (10.50)
4	11.22 (11.10)	33.78 (33.70)	3.61 (3.56)	11.26 (11.17)
5	9.04 (8.93)	50.52 (50.47)	4.21 (4.14)	9.06 (8.93)
6	32.03 (31.91)	29.27 (29.20)	2.27 (2.19)	4.55 (4.46)
7	41.06 (40.93)	30.01 (29.92)	2.29 (2.20)	5.83 (5.75)
8	36.49 (36.40)	40.01 (39.91)	2.77 (2.68)	5.18 (5.10)
9	38.94 (38.85)	35.58 (35.46)	3.36 (3.28)	5.53 (5.44)

(Observed values are given in the parentheses)

3.2a. Infrared spectra of Fe(III) complexes:

In the free succinimide, the frequency of stretching N-H vibration observed at around 3400 cm^{-1} should disappear in the spectra of the complexes for the coordination of the imino group after deprotonation. The carbonyl stretching frequency of the imides in complexes fall within the range $1517\text{--}1585\text{ cm}^{-1}$ which is well removed from the 1720 cm^{-1} band in the free imide. Although the C=O groups in imides does not take part in coordination, shifts to lower frequency as compared to the non coordinated states may be due to the mass effect of heavy metal ion [25] linked to nitrogen as well as possible

weakening of the C=O linkage. The stretching frequency obtained around 1360 cm^{-1} due to C-N, in the spectrum of succinimide shifted to about 1400 cm^{-1} in the spectra of its complexes indicating thereby N⁻ formation and coordination[24] The stretching frequency of $\nu\text{M-O}$ were observed at around $406\text{--}540\text{ cm}^{-1}$ due to coordination of O⁻ to the metal ion respectively. Two bands at around 770 cm^{-1} and 680 cm^{-1} are due to wagging and rocking mode of carbonyl were observed in the spectra of the complexes (1-5)

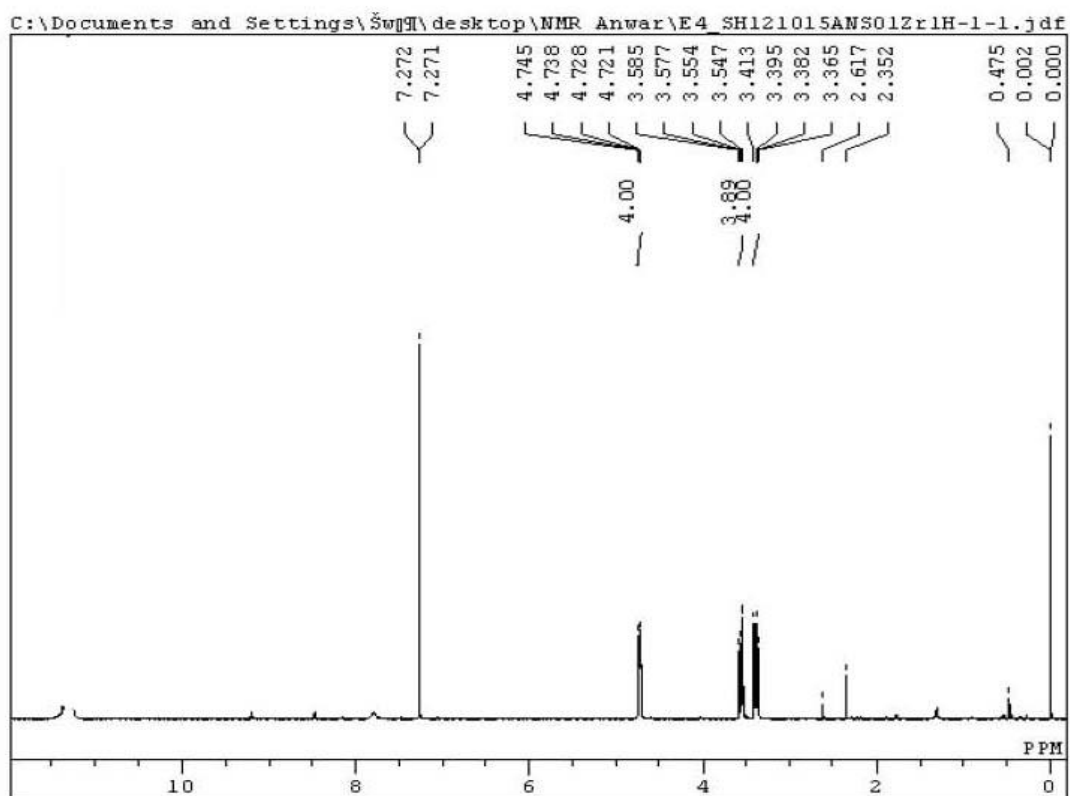
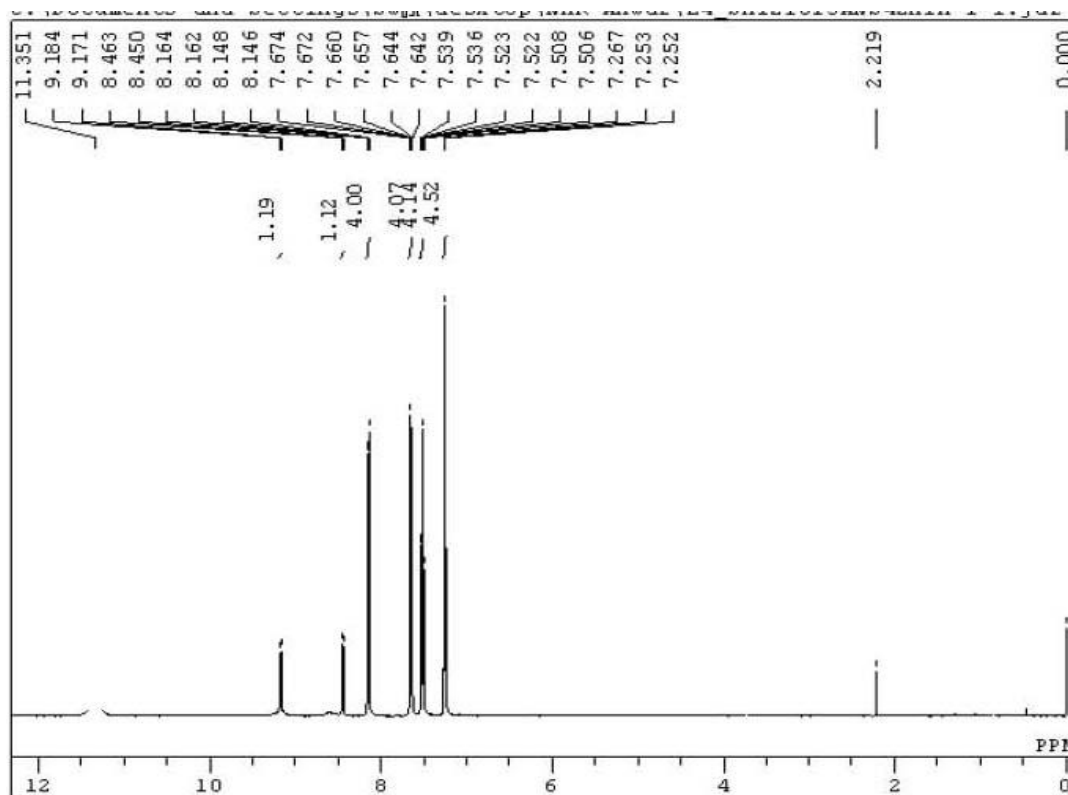
Infrared spectral data of the Fe(III) complexes (Band maxima in cm^{-1})
TABLE -3

Complex	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
1	2938.3	1516.9	1406	534.2	443.6
2	2968.2	1584.4	1407.9	-	540.0
3	2968.2	1584.4	1407.9	-	540
4	2940	1559	1360	546	406
5	2854	1559.2	1407	435.2	422

3.2b. IR studies of Au(III) complexes:

Crystalline amino acids give $\nu(\text{C=O})$ band at $1600\text{--}1630$ and $\nu(\text{C-O})$ band at $1410\text{--}1405\text{ cm}^{-1}$. This antisymmetric stretching frequency of $\nu(\text{C=O})$ and $\nu(\text{C-O})$ are shifted to $1580\text{--}1622$ and $1390\text{--}1370\text{ cm}^{-1}$ respectively in the metal complexes indicating that the coordination of carboxylic acid group via oxygen with metal takes place. Au(III) complexes confirm the coordination of amino group through nitrogen to the metal. The mixing or overlapping of

$\nu(\text{C=O})$ and $\nu(\text{C-O})$ mode of amino acids with characteristic ring vibrational modes of 8-hydroxyquinoline (1600 & 1450 cm^{-1}) hindered the detection of any significant changes of latter modes of the base on complexation. The in-plane and out-of-plane ring deformation modes were observed at ~ 510 and $\sim 780\text{ cm}^{-1}$ respectively undergo a positive shift thereby confirming coordination through nitrogen atom of the base with the metal ions.

Fig1.1: ^1H NMR for complex - 3Fig1.2: ^1H NMR for complex- 6

3.3. ¹H NMR spectral data for complexes Fe(III) and Au(III)

Table -4

Comp.	NMR
1.	¹ H NMR (DMSO-d6): δ 10.03 (2H, s, NH), 7.64 (2H, m, Ar-H), 7.59 (2H, m, Ar-H), 4.51 (2H, s, -CH ₂), 3.70 (3H, s, -CH ₃) ppm.
2.	¹ H NMR (DMSO-d6): δ 9.90 (2H, s, NH), 7.78 (2H, m, Ar-H), 7.50 (2H, m, Ar-H), 4.49 (2H, s, -CH ₂), 3.50 (3H, s, CH ₃) ppm.
3.	¹ H NMR (DMSO-d6): δ 7.27 (2H, m, Ar-H), 4.51 (2H, s, -CH ₂), 3.70 (3H, s, -CH ₃), 2.35 (4H, s, -CH ₃) ppm.
4.	¹ H NMR (DMSO-d6): δ 10.00 (2H, s, NH), 7.59 (2H, m, Ar-H), 4.39 (2H, s, -CH ₂), 3.60 (3H, s, CH ₃) ppm.
5.	¹ H NMR (DMSO-d6): δ 9.95 (2H, s, NH), 7.64 (2H, m, Ar-H), 4.51 (2H, s, -CH ₂), 2.70 (4H, s, CH ₃) ppm.
6.	¹ H NMR (DMSO-d6): δ 9.93 (2H, s, NH), 7.64 (3H, m, Ar-H), 7.59 (3H, m, Ar-H), 2.21 (3H, s, -CH ₃) ppm.
7.	¹ H NMR (DMSO-d6): δ 10.00 (2H, s, NH), 7.77 (3H, m, Ar-H), 7.50 (3H, m, Ar-H), 3.70 (3H, s, CH ₃), 2.21 (3H, s, -CH ₃) ppm.
8.	¹ H NMR (DMSO-d6): δ 9.85 (2H, s, NH), 7.68 (3H, m, Ar-H), 7.52 (3H, m, Ar-H), 4.51 (2H, s, -CH ₂), 3.50 (3H, s, CH ₃) ppm.
9.	¹ H NMR (DMSO-d6): δ 9.98 (2H, s, NH), 7.54 (3H, m, Ar-H), 7.37 (3H, m, Ar-H), 4.41 (2H, s, -CH ₂), 3.40 (3H, s, CH ₃) ppm.

3.4a. Magnetic and electronic spectral studies of Fe(III) complexes:

All the complexes were found to be paramagnetic with magnetic moments 5.40-6.00 B. M. These were the characteristic of high spin Fe(III) complexes. The electronic spectra of all the complexes gave four bands at the range 18115-19011, 21097-21739, 24038-25000 and 25445-

25974 cm⁻¹ corresponding to the transitions ⁶A_{1g}→⁴T_{1g}(G), ⁶A_{1g}→⁴T_{2g}(G), ⁶A_{1g}→⁴E_g(G) and ⁶A_{1g}→⁴A_{1g}(G) respectively. These spectra indicated the octahedral stereo chemistry of Fe(III) complexes. Table-5. contains the data of electronic spectra of Fe(III) complexes.

Table-5: Electronic spectral data of Fe(III) complexes:

Complex	Spectral bands (cm ⁻¹) with assignment			
	⁶ A _{1g} → ⁴ T _{1g} (G)	⁶ A _{1g} → ⁴ T _{2g} (G)	⁶ A _{1g} → ⁴ E _g (G)	⁶ A _{1g} → ⁴ A _{1g} (G)
1	18726	21097	24330	25641
2	19011	21097	24752	25839
3	18726	21096	25000	25974
4	18656	21739	24330	25445
5	18115	21367	24038	25974

3.4b. Magnetic and electronic spectral studies of Au(III) complexes :

The magnetic moment of Au(III) complexes were found 0.2-0.4 indicates that the complexes (6-9) are diamagnetic in character. These complexes exhibit two bands at ~ 33333

and ~ 40000 cm⁻¹ corresponding to the transitions ¹A_{1g} → ³E_{1u} and ¹A_{1u} → ¹A_{2u} respectively. These bands fairly correspond to the square planar geometry of Au(III) complexes.

3.5. Antimicrobial activity

The ligand and its metal complexes were screened against some pathogenic organisms to study their antibacterial and antifungal activities. The ligand showed no activity against the all tested microorganisms under identical experiment conditions. The antibacterial activity results (Table 6) revealed that the complex 5 and 8 showed almost similar activity with the zone of inhibition 22 mm and the complex 4 and 7 displayed maximum activity with the zone of inhibition 18 mm against *E. coli* as compared to standard drug ciprofloxacin, which showed 24 mm inhibition. The complex

5 and 8 exhibited moderate activity with the zone of inhibition 16 mm against *S. aureus* as compared to the standard drug with 22 mm inhibition. The antifungal activity results (Table 7) revealed that the complex 2 and 6 showed very good activity with the zone of inhibition 19 mm against *A. niger* as compared to the standard drug griseofulvin. Besides, the complexes 2, 6 and 8 exhibited moderate activity with 14-16 mm inhibition against *T. species* compared to the standard drug with 26 mm inhibition.

Table 6. Antibacterial activity of the ligand and complexes (inactive: 05 to 07 mm).

Ligand /Complex (No.)	Antibacterial activity (zone of inhibition in mm)		
	<i>E. coli</i> (40 µg/disc)	<i>S. aureus</i> (40 µg/disc)	<i>S. typhi</i> (40 µg/disc)
Ligand (L)	07	06	06
K[Fe(Sim) ₂ (leu) ₂] (1)	05	05	06
K[Fe(Sim) ₂ (cystine) ₂] (2)	10	10	06
K[Fe(Sim) ₂ (cystein) ₂] (3)	06	06	07
K[Fe(Sim) ₂ (ser) ₂] (4)	18	10	12
K[Fe (Sim) ₂ (phala) ₂] (5)	22	16	10
[Au(Q)(cystine)]Cl (6)	09	10	07
[Au(Q)(Ser)]Cl (7)	17	11	13
[Au(Q) (phala)]Cl (8)	21	15	11
[Au(Q)(leu)]Cl (9)	06	06	07
Ciprofloxacin	24	22	22
DMSO (Control)	05	05	05

Table 7. Antifungal activity of the ligand and its complexes (inactive: 05 to 07 mm).

Ligand /Complex (No.)	Antifungal activity (zone of inhibition in mm)		
	<i>A. niger</i> (40 µg/disc)	<i>F. oxysp.</i> (40 µg/disc)	<i>T. species</i> (40 µg/disc)
Ligand (L)	05	06	07
K[Fe(Sim) ₂ (leu) ₂] (1)	07	13	06
K[Fe(Sim) ₂ (cystine) ₂] (2)	19	06	14
K[Fe(Sim) ₂ (cystein) ₂] (3)	05	06	10
K[Fe(Sim) ₂ (ser) ₂] (4)	10	06	06
K[Fe (Sim) ₂ (phala) ₂] (5)	10	11	16
[Au(Q)(cystine)]Cl (6)	20	13	15
[Au(Q)(Ser)]Cl (7)	06	07	10
[Au(Q) (phala)]Cl (8)	18	12	14
[Au(Q)(leu)]Cl (9)	07	10	06
Griseofulvin	24	23	26
DMSO (Control)	05	06	06

Conclusion:

A comparative study of the ligand and its metal complexes indicated that some of the metal chelates exhibited higher antimicrobial activity than the free ligand. The increase in the antimicrobial activity of metal chelates is due to the presence of metal ions in the complexes and however, the acceptable octahedral structure of Fe(III) complexes and square planar structure of Au(III) complexes are given below :

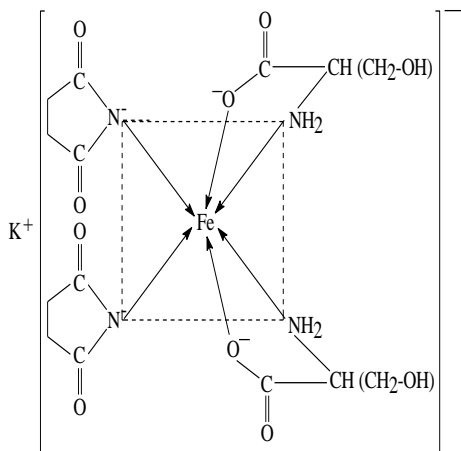


Fig.2.1: Proposed structure of $K[Fe(Sim)_2(Ser)_2]$

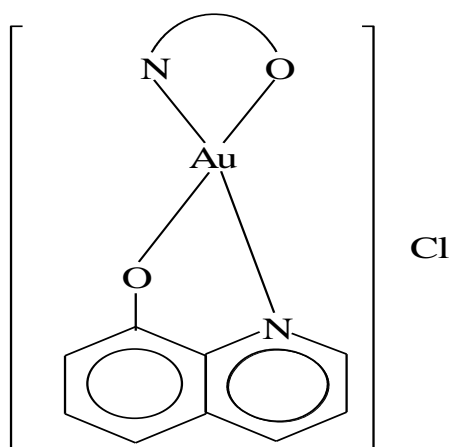


Fig. 2.2: Proposed structure of Au(III) complex.

Acknowledgements

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