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Synthesis, Characterization and Antimicrobial Screening of Fe (II) And Co (II) Metal Complexes with 2-Thenoyltrifluoroacetone and 2,4-Dinitrophenylhydrazine

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Abstract
Iron (II) and Cobalt (II) complexes were derived from 2-thenoyltrifluoroacetone and 2,4 dinitrophenylhydrazine. The synthesized complexes were characterized by IR and UV-Vis spectral methods. The decomposition temperature ranges from 390-375 ^{o}C and 301-291 ^{o}C for Iron and Cobalt respectively. The conductivity of 0.5bvn88 µS/cm for Iron and 0.684 µS/cm for Cobalt were obtained. The solubility test of both complexes conducted were found to be soluble in acetone, slightly soluble in dinitroethane, 1-propanol, 2-propanol, methanol and ethanol while insoluble in n-hexane and distilled water. The IR spectra observed for both Iron and Cobalt complexes are 3379 cm^{-1}(N-H), 3096 cm^{-1}(C-H), 2344 cm^{-1}(C-H), 1611 cm^{-1}(C=C), 1640 cm^{-1}(N-H), 1540 cm^{-1}(C-H), 1019 cm^{-1}(N-M), 937 cm^{-1}(M-O), 734 cm^{-1}(C-F), 1257 cm^{-1}(C-O) and 3478 cm^{-1}(N-H), 3089 cm^{-1}(C-H), 2113 cm^{-1}(C-H), 1599 cm^{-1}(C=C), 1655 cm^{-1}(N-H), 1544 cm^{-1}(C-H), 992 cm^{-1}(N-M), 836 cm^{-1}(M-O), 743 cm^{-1}(C-F) and 1134 cm^{-1}(C-O) respectively. The complexes have been tested for their antimicrobial screening against bacteria (E. coli). The antimicrobial screening of the complexes was determined in Nutrient Agar Media. Both complexes demonstrate their antibacterial activity, in which not only minimum inhibition zone shown but the complexes dried out the bacteria on all the plates.

Keywords: Synthesis, Characterization, Antimicrobial, Complexes, Inhibition, Decomposition

INTRODUCTION
Due to the development of inorganic chemistry the discovery of derivatives as antimicrobial agent drugs prompted the search for novel metal-based therapeutic agents. Extensive investigations are currently focus on the synthesis of metal complexes with a better chemotherapeutic index in terms of increased bioavailability, more antimicrobial activity, higher selectivity and fewer side effects than the corresponding drugs used. Among the main concept and strategies of medicinal inorganic chemistry, the introduction of metal compounds or metal ions to biological system for therapeutic purpose occupies an important component and several examples exhibit the success of this approach (Scott *et al*., 2009; Hambley, 2007 and Thompson *et al*., 2006). Thus, coordination compounds have found their relevance in the treatment of various diseases e.g., Ehrlich's ancient salvarsan against syphilis, (Lloyd *et al*., 2005) bismuth compounds as antiulcer drugs, (Sun *et al*., 2004) vanadium complexes for the treatment of diabetes (Thompson *et al*., 2019) and in medical diagnostics, as contrast agents

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for magnetic resonance imaging (Hermann *et al*., 2008 and Terreno *et al*., 2010, Hamze *et al*/. 2019) and radio-pharmaceuticals (Rey 2010 and Correia *et al*., 2011, Reiss *et al*., 2021).
The antibacterial metal complexes synthesized are having more advantages compared to the conventional antibiotic drugs as antibacterial. The beautiful thing about these complexes is the novel and multiple modes of action. This action involves the interaction of metal complexes with the nucleic acids, ligand exchange reaction, ROS production and releasing bioactive molecule which interact with the target parts (Evans *et al*., 2021). In complexes, metal ions polarity reduces significantly. The reduction in term of polarity gives the chelate character of increasing the hydrophobicity of the complex and in turn makes permeation possible through the microorganism's lipid layer (Kumar 2021, Devi *et al*., 2022). The ligand activity against bacteria is improved base on complexation and thus the complexation describes the concept of chelation theory (Sulaiman 2021). The applications of metal complexes has gained less attention due to the fact that they do possess potential activity in the treatment of bacteria, fungi, cancer, malaria and neurodegenerative diseases (Frei *et al*., 2020; Jazzar *et al*., 2020; Nolan *et al*., 2022).The challenges faced by health sectors today, is that the current antibiotics produced were becoming more friendly to the bacteria. These lead researchers more especially from the field of inorganic chemistry over the past few years to study the synthesis of metal complexes (Reiss *et al*., 2021; Lindenau *et al*., 2021).

The research intends to synthesize metal complexes with a better chemotherapeutic index in terms of increased bioavailability, more antimicrobial activity, with high selectivity and fewer side effects than the corresponding drugs used.

METHODOLOGY

Materials

Glass wares such as 250 mL round bottom flask. 250 mL, 100 mL and 50 mL beakers, measuring cylinders were used. Analytical weighing balance, filter papers, refluxing apparatus, spatula, magnetic stirrers, Uv Spectroscopy, FTIR Spectroscopy, Conductivity metre, and melting point apparatus were also used. 2-Propanol, 2-Thenoyltrifluoroacetone, 2,4-Dinitrophenylhydrazine, Iron (II) Chloride hexahydrate, Cobalt (II) chloride hexahydrate distilled water, Sodium Sulphate Anhydrous used in the work were all of analytical grade.

Procedure for the synthesis of Fe(II) complex

The 2-Thenoyltrifluoroacetone (1.26 g) was weighed into 250 mL round bottom flask. Then, 100 mL of 2-propanol was added and then stirred, which give a golden yellow colour. About 1.123 g of 2,4 dinitrophenylhydrazine (DNPH) was added to the mixture and which gives orange colour. Furthermore, 1.33 g $FeCl_2.6H_2O$ was weighed into 50 mL beaker and 10 mL of 2-propanol was added and a deep pink colour was formed, and 2mL of distilled water was added to it for complete dissolution of iron (II) salt. The mixture of iron salt from 50 mL beaker was added onto the 250 ml round bottom flask mixture, the colour changed instantaneously to deep brown colour. The mixture was refluxed for two hours and no change in colour during refluxing was observed. The mixture was allowed to cool and 10 g of anhydrous sodium sulphate was added, which in turned absorbed the amount of water added.

$$\text{2-TTA + 2,4-DNPH + } FeCl_2 \xrightarrow[80^oC]{\text{Reflux}} \text{[Fe(TTA)DNPH]Cl + Cl}$$

Procedure for the synthesis of Co (II) complex

The 2-Thenoyltrifluoroacetone (1.23 g) was weighed into 250 mL round bottom flask. 100 ml of 2-propanol was added and then stirred, given a golden yellow colour. About 1.096 g of 2,4-DNPH was added to the mixture which produced an orange colour. About 1.32 g of $CoCl_2.6H_2O$ was weighed into 50 mL beaker and 10 mL of 2-propanol was added which produce a deep pink colour and 2 mL of distilled water was added to it for complete dissolution of Cobalt (II) salt. The mixture of Cobalt salt from 50 mL beaker was added onto the 250 mL round bottom flask mixture, immediately the colour changed to deep brown colour. The mixture was refluxed for two hours and no change in colour during refluxing. The mixture was allowed to cool and 5g of anhydrous sodium sulphate was added, which in turn absorbed the amount of water added.

$$\text{2-TTA + 2,4-DNPH + } CoCl_2 \xrightarrow[80^oC]{\text{Reflux}} \text{[Co(TTA)DNPH]Cl + Cl}$$

The synthesized complexes were heated at 82.14°C to evaporate 2- propanol from the complex, leaving behind the powder complex.

Procedure used for media preparation and growth of the microorganisms

By following the manufacturer's instructions the media was prepared: This medium was originally formulated to be used in antimicrobial susceptibility testing. The agar was prepared by dissolving 30.0g in 1 liter of purified water. It was then heated in boiling water and agitated frequently until completely dissolved and autoclaved for 15 minutes at 121°C. It was then poured into petri-dishes, about 16-18 ml in each and allowed to solidify at room temperature. Both bacteria (E.coli) and fungi were grown by inoculation on seeded dishes, followed by incubation at 37°C for 24 hours (Bacteria) and at 25°C for 72 hours (fungi).

Procedure for antimicrobial screening of the complexes

The complexes were assayed for antimicrobial screening by pouring method, and in which different concentrations were prepared. The culture media employed for the screening of antimicrobial activity is nutrient agar for E.coli (Bacteria). The microorganisms used had been maintained by weekly sub-culturing and incubation at 37°C for bacteria at Rasheed Shekoni, Federal University, Dutse Teaching Hospital. The sterile petri dishes (sterilized at 170°C for 1 hour in hot air oven) were prepared and labeled. About 25 mL of the prepared molten nutrient agar (for bacteria) was poured into the dishes and allowed to solidify. Wells were bored in the seeded dishes with a cork borer (5mm in diameter). Drops of each sample concentrations were poured into the wells formed at the centre of each disc and incubated at 37°C for three days, in which the clear inhibition zone diameter (IZD) base on Minimum Inhibition concentration (MIC) measured and recorded after incubation.

RESULTS AND DISCUSSION

Table 1: Some Physical Properties of the iron and cobalt Complexes

S/N	Complex	FW (g/mol)	Phase State	Color	% Yield
1	Fe-Complex	476.175	Solid	Black	50.63
2	Co-Complex	479.263	Solid	Deep Brown	48.57

Table 2: Results for Magnetic Susceptibility of the iron and cobalt Complexes

S/N	Complex	R_1	R_0	W_0	W_1	L_I C	Xg
1	Fe-Complex	1931	-037	0.754g	0.850g	2.5cm^{-1}	51250 x 10^{-9} M
2	Co-Complex	344 x 10	-037x10	0.664g	0.838g	2.5cm^{-1}	45982.76 x 10^{-9} M

Table 3: IR Spectra of iron and cobalt Complexes

Compound	Fe-Complex	Co-Complex
V(N-H)cm^{-1}stretch	3379	3478
V(C-H)cm^{-1}aromatic stretch	3096	3089
V(C-H)cm^{-1}aldehyde stretch	2344	2113
V(C=C)cm^{-1}stretch	1611	1599
V(N-H)cm^{-1}bending aliphatic	1640	1655
V(C-H)cm^{-1}bending aliphatic	1540	1544
V(C-O)cm^{-1}stretch	1257	1134
V(N-M)cm^{-1}stretch	1019	992
V(M-O)cm^{-1}stretch	937	836
V(C-F)cm^{-1}stretch	732	743

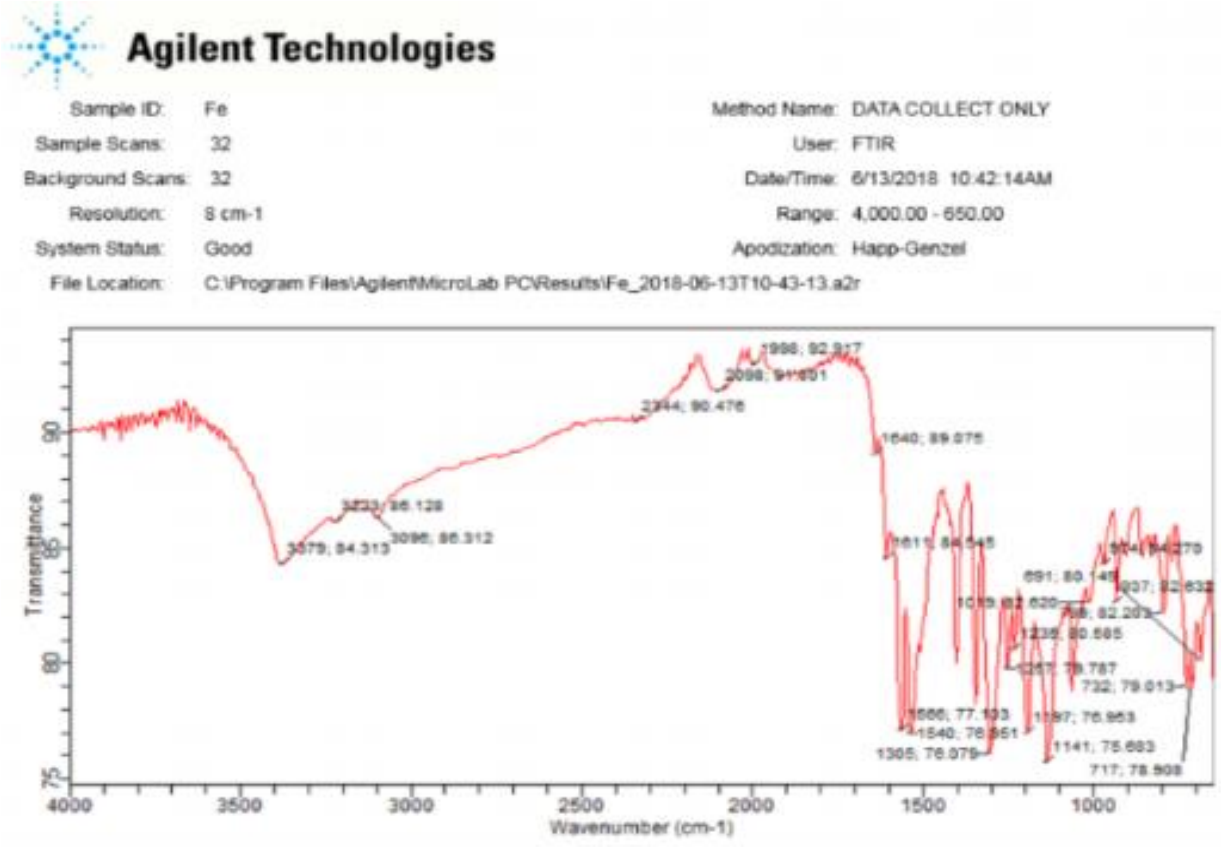

Figure 1: IR Spectra of Fe-complex

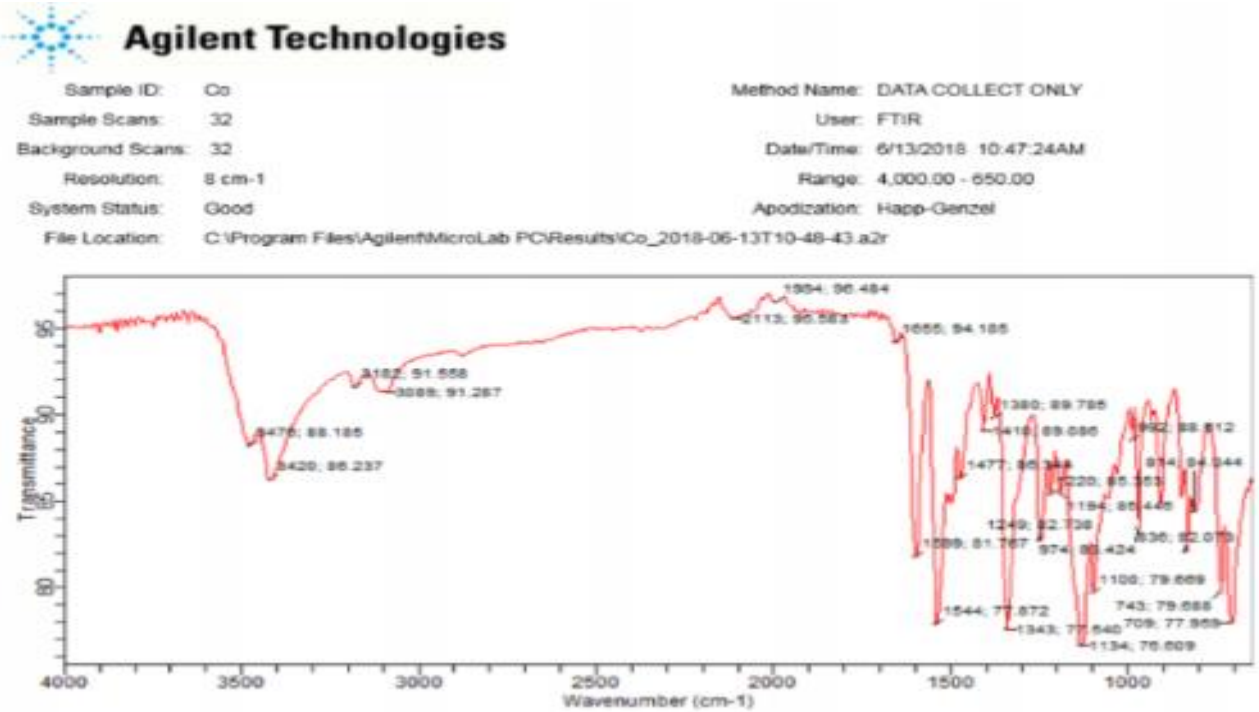

Figure 2: IR Spectra of Co-complex

Table 4: UV-Vis Spectral Data of the iron and cobalt Complexes

Fe-complex Wavelength (nm)	Assignment	Geometry
310.81	n - π*	
364.87	n - π*	square planar
454.03	n – π	
Co-complex Wavelength (nm)	**Assignment**	**Geometry**
317.71	n – π	
364.96	n - π*	square planar
437.85	n - π*	

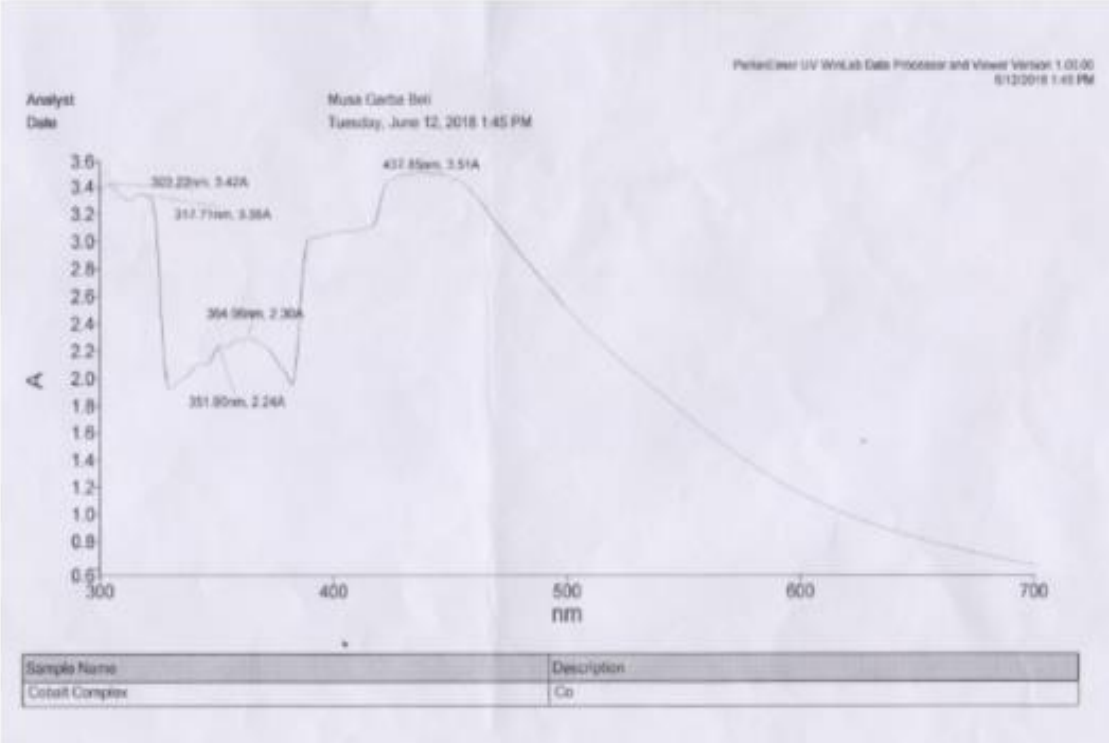

Figure 3: UV Spectra of Co-complex

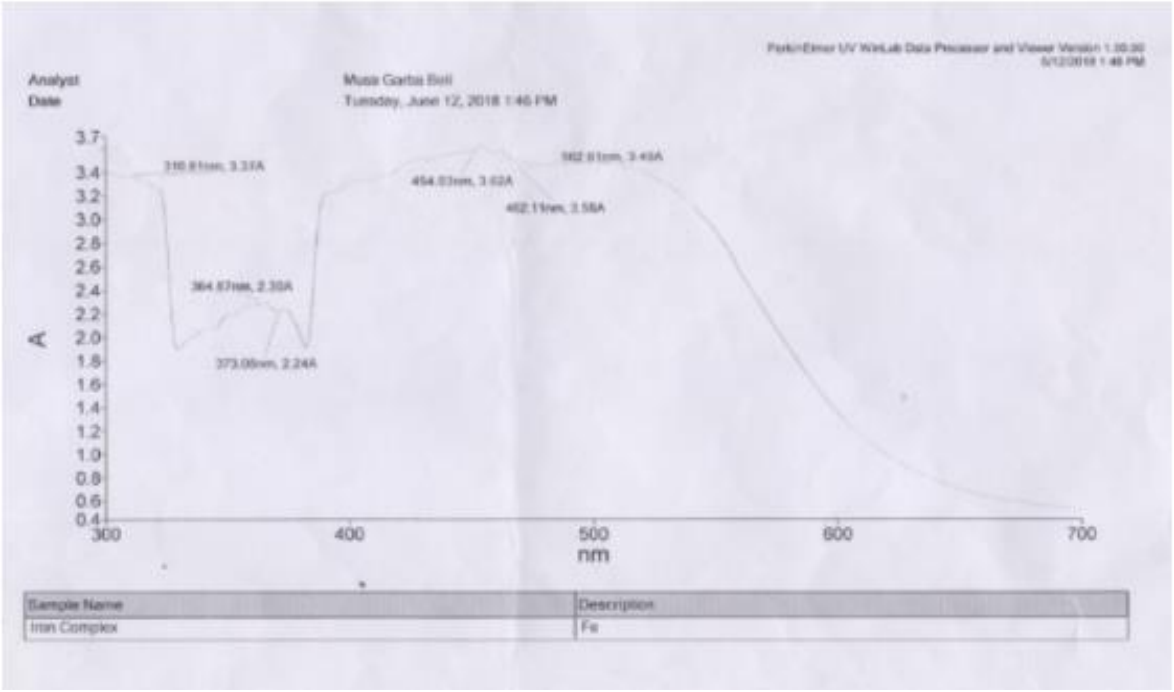

Figure 4: UV Spectra of Fe-complex

Table 5: Solubility Test of the iron and cobalt Complexes

Solvent used	[Fe(TTA) DNPH]Cl	[Co(TTA) DNPH]Cl
Ethanol	Slightly soluble	Insoluble
Methanol	Slightly soluble	Slightly soluble
2-Propanol	Slightly soluble	Insoluble
Distilled H_2O	Insoluble	Insoluble
1-Propanol	Slightly soluble	Insoluble
n-Hexane	Insoluble	Insoluble
Acetone	Soluble	Soluble
Dinitroethane	Slightly soluble	Slightly soluble

Table 6: Conductivity Measurement of the iron and cobalt Complexes

S/N	Name of Complex	Unconverted Conductance µS/cm	Converted Conductance µS/cm
1	[Fe(TTA)DNPH]Cl	0.588	58.5
2	[Co(TTA)DNPH]Cl	0.684	68.4

Table 7: Melting Point Measurement

S/N	Name of Complex	Heat-R MP (°C)
1	[Fe(TTA)DNPH]Cl	5.0 382.5
2	[Co(TTA)DNPH]Cl	5.0 296

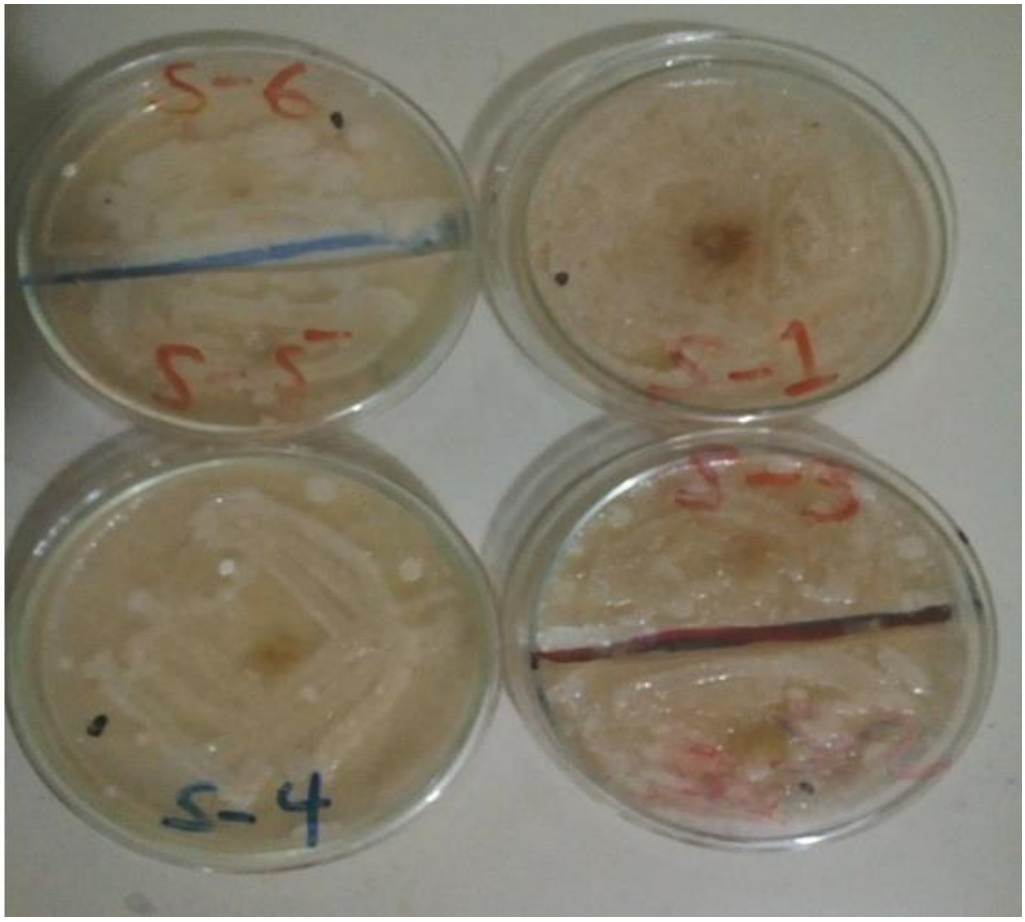

Figure 5: Disc Diffusion Assay showing Zones of Inhibition of the Complexes

Table 8: Antibacterial Screening of Iron and Cobalt Complexes

Tested Organism Isolate	Compound Concentrations 0.01M 0.001M 0.005M
Bacteria E.coli Fe-complex	+ + + + + + +
Bacteria E.coli Co-complex	++ + + + + + +

Table 9: MIC Values of the iron and cobalt Complexes

Tested Organism Isolate	Compound Concentrations 0.01M 0.001M 0.005M
Bacteria E. coli Fe-complex	16 12 12
Bacteria E. coli Co-complex	12 14 14

The synthesized Iron and Cobalt complexes are solids, which have relatively high melting points in the range of 375^{o}C-390^{o}C and 298-301^{o}C respectively. The high melting temperatures of the synthesized complexes shows that they are stable complexes (Mustapha *et al.*, 2014; Sulaiman, 2021 and Reiss 2021).
The iron complex formed a black crystalline solid and the Cobalt complex gave a deep brown powder. The intense color of the complexes is due to the Metal ligand charge transfer (MLCT) (Alberding *et al.*, 2011).

The specific conductance of the complexes of Iron and Cobalt are found to be 0.585 mScm^{-1} and 0.684 mScm^{-1} at 25^{o}C respectively. The above conductance values indicate that the synthesized complexes are electrolyte (Swamy *et al*, 2012).
The significant IR bands for the complexes are compiled and presented in Table 3. From the IR spectra of Fe-complex, the bands observed at 3379 cm^{-1} is assigned to (N-H) mode of amine group, suggesting coordination of amine group to the metal centre. The band observed at 3096 cm^{-1} is assigned to (C-H) stretch in aromatic and as obtained by Reiss (2021) and Sulaiman (2021).These results are in agreement with the Royal Society of Chemistry IR correlation table. Band observed at 1257 cm^{-1} in Table 3 is assigned to (C-O) stretch suggesting coordination of oxygen to metal centre. This result is also in agreement with the results obtained by Mustapha (2014) and Reiss (2021). The band observed at 1019cm^{-1} is assigned to (N-M) and this is also in line with the result obtained by Mustapha (2014); Bin *et al.*, 2014; Scarano *et al.*, 1998. Furthermore, the band observed at 937 cm^{-1} is assigned to (M-O), Scarano *et al.*, 1998 and the band recorded at 732 cm^{-1} is assigned to (C-F) stretch. The band at 2344 cm^{-1} is assigned to (C-H) stretch in aldehyde (Subodh *et al.*, 2009).

For Co-complex, the bands observed at 3478 cm^{-1} is assigned to (N-H) stretch, suggesting coordination of amine group to the metal centre. (Royal Society of Chemistry IR Correlation Table). The bands observed at 1134 cm^{-1}is assigned to (C-O) stretch (Royal society of Chemistry IR correlation table). The band observed at 992 cm^{-1} is assigned to (N-M) and is in agreement with the result obtained by Scarano *et al.*, 1998 and Mustapha (2014). The band seen at 836 cm^{-1} is assigned to (M-O) which is also in line with the result obtained by Mustapha (2014). The band observed at 743 cm^{-1} is assigned to (C-F) stretch. The band observed at 2113 cm^{-1} is assigned to (C-H) stretch in aldehyde (Subodh, 2006, Nolan *et al.*, 2022)

The UV-Vis spectral data of the complexes are presented in Table 3. The electronic absorption spectra of the complexes of Co^{2+} and Fe^{2+} recorded in acetone in the range of (300-700 nm).
The Fe-Complex absorption peaks found at 364.87nm shifted to 373.08nm suggests the transition of TTA as assigned and this is in agreement with result obtained by Chen *et al.*,

(2015); which is approved by Royal Society of Chemistry; King (1951) and Royal Society of Chemistry, RSC (2015). The peak also found at 454.03 nm shifted to 462.11 nm is assigned to DNPH and are in line to the spectra obtained by Subodh, 2006. And the 502.61 nm was assigned to the absorption by the central metal and 310.81 nm is assigned to acetone.

The Co-Complex absorption peaks found at 351.90 nm shifted to 364.96nm is assigned to TTA and the shifts are account for the transition within the TTA. This result is in agreement with results obtained by Chen *et al*., (2015); which is approved by Royal Society of Chemistry, RSC (2015). The peak found at 437.85 nm is assigned to DNPH which is in line with result obtained by Subodh, 2006. And also peak found at 303.22nm shifted to 317.71nm is assigned to acetone. Thus the shifts are due to transition within the solvent.

The synthesized metal complexes of Iron and Cobalt were screened for antimicrobial activity potential. The size of the bacterial growth was observed to spread throughout the discs containing the media. As the complexes were applied by varying concentrations ranging from 0.01M, 0.001 M and 0.005 M indicating that the synthesized complexes had a significant effect on the growth of the bacteria when the growth inhibition was measured (Table 8). For Fe-Complex, 0.01M concentration showed highest activity against E. Coli than other concentrations. The Co-complex of 0.001 M and 0.005 M showed highest activity compared to cobalt complex of 0.01 M concentration. The activity of the complexes spread throughout the discs not restricted to the MIC value the complexes were potent to the extent that it dried the microorganism for the whole discs.

Conclusion

The synthesis of Fe (II) and Co (II) metal complexes derived from 2-thenoyltrifluoroacetone and 2,4-dinitrophenylhydrazine have been reported. The complexes were characterized by spectral methods and analytical data. Based on these square planar geometry has been assigned for both complexes. The antimicrobial screening carried out with the complexes confirmed that they are good antibacterial agents.

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References

Alberding, B. G., Chisholm, M. H., Gallucci, J. C., Ghosh, Y., & Gustafson, T. L. (2011). Electron delocalization in the S 1 and T 1 metal-to-ligand charge transfer states of trans-substituted metal quadruply bonded complexes. *Proceedings of the National Academy of Sciences*, *108*(20), 8152-8156.

Bin, L. K., Helaluddin, A. B. M., Sarker, M. Z. I., Mandal, U. K., & Gaurav, A. (2020). Effect of processing methods on xylitol-starch base co-processed adjuvant for orally disintegrating tablet application. *Pakistan journal of pharmaceutical sciences*, *33*(2).

Chen, C., Liu, W., Wang, Z., Peng, K., Pan, W., & Xie, Q. (2015). Novel form stable phase change materials based on the composites of polyethylene glycol/polymeric solid-solid phase change material. *Solar Energy Materials and Solar Cells*, *134*, 80-88.

Correia, Joao DG, et al. "Radiometallated peptides for molecular imaging and targeted therapy." *Dalton Transactions* 40.23 (2011): 6144-6167.

Devi, Jai, et al. "Synthesis, structural analysis, in vitro antioxidant, antimicrobial activity and molecular docking studies of transition metal complexes derived from Schiff base ligands of 4-(benzyloxy)-2-hydroxybenzaldehyde." *Research on Chemical Intermediates* (2022): 1-36.

Evans, Andris, and Kevin A. Kavanagh. "Evaluation of metal-based antimicrobial compounds for the treatment of bacterial pathogens." *Journal of Medical Microbiology* 70.5 (2021).

Frei, Angelo, et al. "Metal complexes as a promising source for new antibiotics." *Chemical science* 11.10 (2020): 2627-2639.

Hambley, T. W. (2007). Developing new metal-based therapeutics: challenges and opportunities. *Dalton Transactions*, (43), 4929-4937.

Hamze, R., Shi, S., Kapper, S. C., Muthiah Ravinson, D. S., Estergreen, L., Jung, M. C., ... & Thompson, M. E. (2019). "Quick-silver" from a systematic study of highly luminescent, two-coordinate, d10 coinage metal complexes. *Journal of the American Chemical Society*, *141*(21), 8616-8626.

Herrmann, Wolfgang A., et al. "Metal complexes of chiral imidazolin-2-ylidene ligands." *Organometallics* 16.11 (2008): 2472-2477.

Jazzar, Rodolphe, Michele Soleilhavoup, and Guy Bertrand. "Cyclic (alkyl)-and (aryl)-(amino) carbene coinage metal complexes and their applications." *Chemical Reviews* 120.9 (2020): 4141-4168.

King, F. E., & Kidd, D. A. A. (1951). 661. Syntheses from phthalimido-acids. Part III. The preparation of DL-and L-asparagine from phthalyl-DL-and-L-aspartic anhydride. *Journal of the Chemical Society (Resumed)*, 2976-2978.

Kumar, K. Subin, and K. K. Aravindakshan. "Synthesis, cytotoxic, anticancer and antimicrobial activities of some metal complexes of a novel tetradentate Schiff base ligand,(E)-3-((2-((E)-(1-(2-hydroxyphenyl) ethylidene) amino) ethyl) imino)-N-phenylbutanamide." *Results in Chemistry* 3 (2021): 100129.

Lindenau, Kevin, et al. "Synthesis and Characterization of Dinuclear Allenediide Bridged Hafnocene (IV) Complexes." *Organometallics* 40.18 (2021): 3177-3184.

Lloyd, Jon R., and Joanna C. Renshaw. "Microbial transformations of radionuclides: fundamental mechanisms and biogeochemical implications." *Metal ions in biological systems* 44 (2005): 205.

Mustapha, A. N., Ndahi, N. P., Paul, B. B., & Fugu, M. B. (2014). Synthesis, characterization and antimicrobial studies of metal (II) complexes of ciprofloxacin. *J. Chem. Pharm. Res*, *6*(4), 588-593.

Rey, M. A. "Radiometal complexes in molecular imaging and therapy." *Current medicinal chemistry* 17.31 (2010): 3673-3683.

Nolan, Victoria C., et al. "Indole-containing arene-ruthenium complexes with broad spectrum activity against antibiotic-resistant bacteria." *Current research in microbial sciences* 3 (2022): 100099.

Reiss, Aurora, et al. "Bioactive Co (II), Ni (II), and Cu (II) complexes containing a tridentate sulfathiazole-based (ONN) Schiff base." *Molecules* 26.10 (2021): 3062.

Rey, M, A. (2010). Radiometal complexes in molecular imaging and therapy. *Current medicinal chemistry*, *17*(31), 3673-3683.

Scarano, D., Bordiga, S., Lamberti, C., Spoto, G., Ricchiardi, G., Zecchina, A., & Areán, C. O. (1998). FTIR study of the interaction of CO with pure and silica-supported copper (I) oxide. *Surface science*, *411*(3), 272-285.

Scott, Lauren E., and Chris Orvig. "Medicinal inorganic chemistry approaches to passivation and removal of aberrant metal ions in disease." *Chemical Reviews* 109.10 (2009): 4885-4910.

Subodh, G., Deepu, V., Mohanan, P., & Sebastian, M. T. (2009). Polystyrene/Sr2Ce2Ti5O15 composites with low dielectric loss for microwave substrate applications. *Polymer Engineering & Science*, *49*(6), 1218-1224.

Sulaiman, N. N., Ismail, M., Timmiati, S. N., & Lim, K. L. (2021). Improved hydrogen storage performances of LiAlH4+ Mg (BH4) 2 composite with TiF3 addition. *International Journal of Energy Research*, *45*(2), 2882-2898.

Sun, S., Zeng, H., Robinson, D. B., Raoux, S., Rice, P. M., Wang, S. X., & Li, G. (2004). Monodisperse mfe2o4 (m= fe, co, mn) nanoparticles. *Journal of the American chemical society*, *126*(1), 273-279.

Swamy, D. K., Pachling, S. P., & Bhagat, T. M. (2012). Synthesis, characerization, antibacterial and antifungal studies on metal complexes with benzothiazolyl hydrazone. *Rasayan J. Chem.*, *5*, 208-213.

Terreno, Enzo, et al. "Advances in metal-based probes for MR molecular imaging applications." *Current medicinal chemistry* 17.31 (2010): 3684-3700.

Thompson, K. H., Barta, C. A., & Orvig, C. (2006). Metal complexes of maltol and close analogues in medicinal inorganic chemistry. *Chemical Society Reviews*, *35*(6), 545-556.