



Microwave Assisted Synthesis and Characterization of 4-Aminothiophenol with Two Mixed Ligands Chelates of Cobalt, Nickel and Mercury

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ABSTRACT

Amino compounds are widely used in medicine, pharmacy, dyes, and industries. In coordination chemistry, these compounds are biologically important. The cobalt, nickel, and mercury metal chelates are derived from 4-aminothiophenol with two mixed ligands, namely sodium benzoate and sodium nitrite. These metal chelates synthesized were characterized by microanalysis, metal estimation, conductivity, magnetic property, Ultraviolet-Visible, Fourier Transform-Infra Red, NMR (proton and carbon), and X-ray diffraction (Powder method). The analytical data show that the metal ligand stoichiometric ration of cobalt and nickel complexes and mercury complexes was confirmed. All the metal chelates were found to be monomeric, neutral, and non-electrolytic. The IR spectral data results show that the 4-ATP acts as monodentate, which can coordinate through the amino group, and another mixed ligand coordinates through the oxygen atom. The results of UV-Visible and magnetic studies predict the octahedral geometry of the cobalt, nickel, and tetrahedral geometry of the mercury complex. The ¹H-NMR and ¹³C-NMR spectra and XRD (Powder pattern) indicate the diamagnetic nature, geometry, crystal structure, and size of the mercury complex. The metal chelates were screened for their biological activities using the Agar disc diffusion. The MIC values that indicate their bio-potential character were found.

Keywords: Metal chelates, 4-Aminothiophenol, Benzoate ion, Nitrite ion, XRD, Bio-potential.

INTRODUCTION

4-ATP is one of the bi-functional molecules used in silver and gold nanoparticles. They form self-assembled monolayers in the development of DNA. Its derivatives, such as Schiff base, have

interesting bio-potential activities such as analgesics, anti-inflammatory, anti-fungal, antibacterial, antioxidant, anticonvulsant, and anticancer¹⁻². Chemo-sensors have many interdisciplinary applications in Chemistry, Chemical Engineering, biology, biochemistry, and environmental sciences.



4-ATP is used in chemosensor material. The microwave-assisted synthetic technique is a promising green chemistry due to its simple, clean, fast, efficient, and low cost³⁻⁴. This technique reduces the reaction time, reduces side reactions, increases yields, and is solvent-free. The nucleophilic centers, viz., oxygen and nitrogen, have free electron pairs available for sharing⁵. Metal complexes containing nitrogen and oxygen donor site chelate ligands pay much attention to biological and pharmacological activities, mainly in metallo-biomolecules⁶. Coordination of such chelate compounds with metal ions like nickel, cobalt, and mercury often enhances their biological activities. They are electrochemically active compounds and catalytically active materials in asymmetric catalysis⁷⁻⁸. The current research aims to synthesize and characterization of cobalt, nickel, and mercury metal complexes of 4-aminothiophenol with two mixed ligands, such as benzoate ion and nitrite ion reported.

MATERIALS AND METHODS

Cobalt nitrate, nickel nitrate, mercury chloride, 4-mercaptoaniline, sodium nitrite, solvent viz. DMSO, methanol, and ethanol were of AR grade. Preparation of metal complexes: Co(II) complex was synthesized by mixing 1.720 g of 4-mercapto aniline in methanol, 0.990 g of sodium benzoate dissolved in water, and adding 1 g of cobalt nitrate dissolved in CH₃OH. The final product was subjected to microwave assisted reaction using microwave oven (Samsung model). The pale pink color metal chelate was filtered and dried in desiccators.

Ni(II) chelate was prepared by the addition of 1.720 g of 4-mercaptoaniline in methanol and 0.686 g of sodium benzoate in water to the corresponding nickel nitrate for 1 g dissolved in CH₃OH. The mixture was subjected to microwave irradiation using the Samsung model. The pale green color complex was dried after filtration.

Mercury complex was prepared by the addition of 0.920 g of 4-mercapto aniline in methanol and 0.500 g of sodium nitrite in water to the corresponding metal chloride like mercury chloride for about 1 g in CH₃OH, and finally the whole mixture was irradiated on a microwave oven for about a few seconds. The pale yellow color complex was filtered and dried.

Characterization

Elemental analysis of the complexes was found using Vario make EL-III model elemental analyzer. Metal ion estimation of the produced complexes was utilized in the standard volumetric and colorimetric analysis. After mixing 10⁻³ M metal complexes with CH₃CN, a Conductivity Bridge was used to evaluate the conductance at room temperature. Metal complexes were subjected to cyclic voltammetry measurements utilizing the Versa Stat model electrochemical workstation in DMSO. Solid state Electronic spectral data was recorded using Varian CARY-5000 model instrument. IR spectral frequencies of the ligand and its metal chelates were recorded using Shimadzu Fourier transform Infra-Red spectrophotometer. The low frequency Far-IR spectral data of the complexes was recorded using Bruker Vertex 80 FTIR equipment. The AVANCE III 500 NMR spectrometer was used to get the zinc complex's NMR spectra. mercury(II) complex powder XRD was performed with the Rigaku model device. The activity of bio-potential: Using *Streptococci*, *Shigella*, *Bacillus candida albicans*, and three different concentrations (50 μ L, 100 μ L, and 150 μ L), the biological activities of 4-ATP and metal chelates were investigated using the Agar disc diffusion method. Three sets of each experiment were conducted. On a millimeter scale, the metal chelates' MIC values were determined.

RESULTS AND DISCUSSION

The synthesized metal chelates are colored except for the mercury complex, which is pale yellow in color. They are non-electrolyte, neutral complexes, and monomeric. They are soluble in organic solvents but insoluble in water; they are stable under room temperature.

Electrochemical property

The electrochemical behavior of cobalt and nickel chelates has been investigated in protic solvents by cyclic voltammetry. From the obtained results, both complexes show electrochemical properties. The cyclic voltammetry of the complexes is shown in Fig. 1, 2. The results indicate that the cobalt complex undergoes one electron transfer redox process with an anodic potential of -0.6079 V and a cathodic peak potential of -1.1393 V with a scan rate of 0.1 V/s in DMSO⁹. This complex shows a redox process with potential separation at -0.5314

V due to the quasi-reversibility of the Co(II)/Co(I) couple. The reversible one electron transfer redox process of the nickel complex shows the anodic peak potential at -0.4656V, and the cathodic potential is -1.1125 V corresponding to the anodic and cathodic current at -2.554 A and -2.076 A, indicating the well electrochemical process. The value of the standard electrode potential is -1.021 V, which indicates the reversibility of the redox reaction¹⁰.

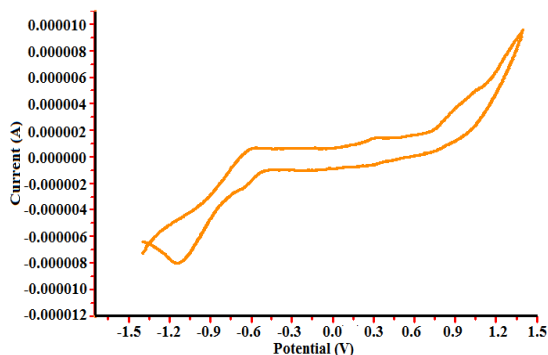


Fig. 1. Electrochemical study of cobalt complex

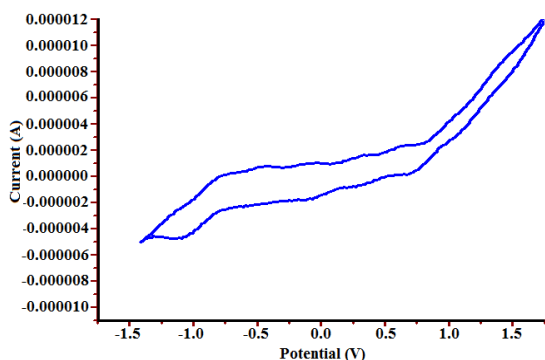


Fig. 2. Electrochemical study of Nickel complex

UV-Visible spectra

The UV-Visible spectrum of the Co(II) complex shows strong, sharp, and highly intense absorption bands at 502nm, 358nm, and 271nm, which are attributed to ${}^4A_{2g} \leftarrow {}^4T_{1g}$, ${}^4T_{2g}(P) \leftarrow {}^4T_{1g}$ and ${}^4T_{2g} \leftarrow {}^4T_{1g}$ electronic transitions respectively. The magnetic moment value of the cobalt complex is 3.55 BM, which indicates the paramagnetic nature of the complex, and it exhibits octahedral geometry. The Ni(II) complex displayed new bands at 591nm, 331nm, and 270nm corresponding to the ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$, ${}^3T_{1g} \leftarrow {}^3A_{2g}$, and ${}^3T_{2g} \leftarrow {}^3A_{2g}$ electronic transitions; the magnetic moment value is 2.94 BM confirms the paramagnetic nature of the complex and the electronic transitions confirming their octahedral geometry around Ni(II) ion. The Hg(II)

complex shows only charge transfer transition at NM, and because of its diamagnetic nature, no magnetic moment value is observed¹¹.

FT-IR Spectra

The FT-IR spectrum is one of the powerful toll to identify the stretching frequencies and coordination mode of the 4-Aminothiophenol to the metal ion. The spectrum of 4-ATP showed sharp bands at 3418 cm^{-1} and 3089 cm^{-1} corresponding to the aromatic N-H (asymmetric and symmetric). The frequency at 3027 cm^{-1} , 3071 cm^{-1} , and 1307 cm^{-1} indicates the C-N, C-H, and C-S stretching frequencies respectively. After coordination of ligand to the cobalt and nickel complexes where shifted to lower or higher frequencies with the corresponding regions¹². The additional stretching frequencies of 1600 cm^{-1} , 1500 cm^{-1} , 3200 cm^{-1} , and 1400 cm^{-1} were exhibited in the cobalt and nickel complexes corresponding to the conjugated C=O(Asy), Conjugated C=O(Sy), C-H (Aromatic stretching) and Ar-C=C (Stretching) respectively to the benzoate ion coordinated to the metal ions through its oxygen atom¹³. In mercury complexes the stretching frequencies were found to at 1400 cm^{-1} , 1300 cm^{-1} , 1450 cm^{-1} , 1050 cm^{-1} and 800 cm^{-1} ranges indicating the ν -NO₂(Stretching), ν_s -NO₂(Stretching), ν (N=O) (Stretching), ν (N-O) (Stretching), and δ -ONO(Stretching) these assignment confirming the coordination of 4-ATP through amino nitrogen and the mixed ligands benzoate ion and nitrite ion coordinated through the oxygen atom. The low frequencies region, which indicates the metal-nitrogen and metal-oxygen coordination mode of the complexes. These frequencies were shown at 400-450 cm^{-1} for the amino coordination of 4-ATP, 460-480 cm^{-1} for the oxygen coordination of benzoate ion and 300-350 cm^{-1} for the oxygen coordination mode of nitrite ion¹⁴.

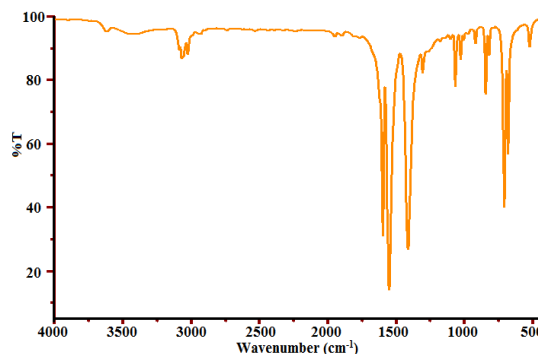


Fig. 3. IR spectrum of 4-Aminothiophenol

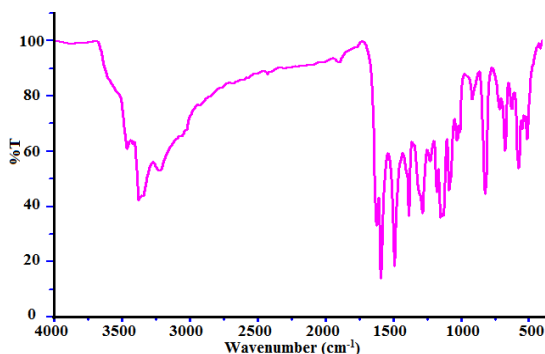


Fig. 4. FT-IR spectrum of cobalt complex

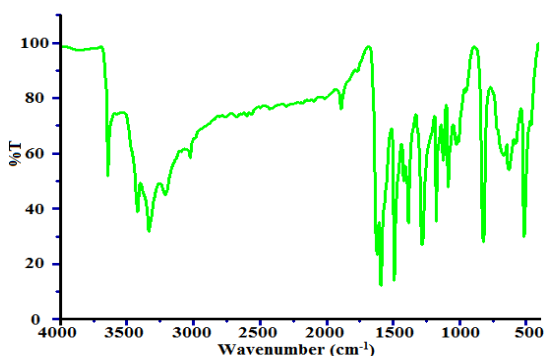


Fig. 5. FT-IR Spectrum of nickel complex

NMR-Spectral study

¹H-NMR spectrum for 4-aminothiophenol shows the signals at (δ =2.503 ppm), (δ =7.873-7.885 ppm), (δ =7.263-7.275 ppm) and (δ =7.100-7.120 ppm) was assigned to the -SH, Aromatic C-H₁, aromatic C-H₂ and NH₂ respectively. In metal complexes, these chemical shift values are shifted to downfield or up-field with the corresponding chemical shift values. The the ¹³C-NMR spectrum of the 4-ATP exhibit four different chemical shift values at 129.03 ppm, 129.51 ppm, 127.50 ppm and 140.86 ppm corresponding to the C-SH, Aromatic C₁, Aromatic C₂, and C-NH₂, in Hg(II) complex these values exhibit at 134.12 ppm, 125.05 ppm, 114.86 ppm and 147.24 ppm respectively indicating the diamagnetic nature of complex and also the probable geometry¹⁵.

Powder XRD of mercury complex

The powder XRD of mercury complex exhibits a crystalline nature. The crystal structure is derived from data like Miller indices (h k l), lattice parameters (a, b, c), and crystal angles (α , β , γ), and the average size. The Hg(II) complex the lattice constant a = 9.377 Å, b = 9.744 Å and c = 4.017 Å, crystal angles of α = 101.37°, β = 98.65°, γ = 93.60° and unit cell volume is 324.11 g/m³. The results are

confirmed by the facts $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$, which indicate the triclinic crystal nature of the complex. (CAS No: 137-18-8)¹⁶.

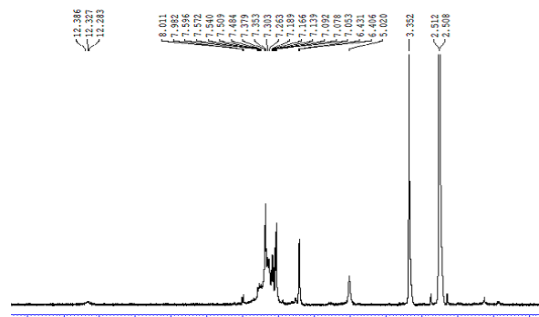


Fig. 6. ¹H-NMR Hg(II) complex

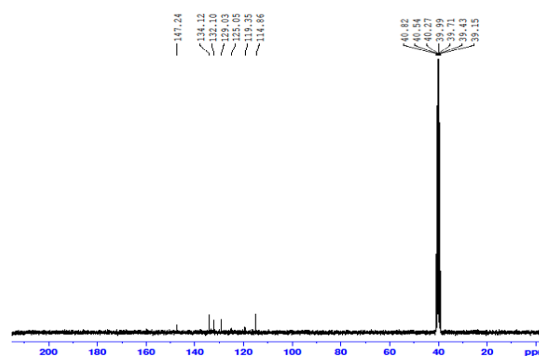


Fig. 7. ¹³C-NMR spectrum of Hg(II) complex

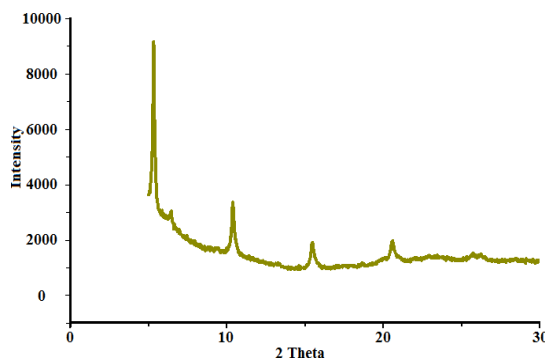


Fig. 8. Powder X-ray diffraction pattern of mercury complex

Table 1: Powder XRD data for mercury complex

Peak number	Angle 2-Theta°	Intensity(cps)	d (Å)	h k l
1	05.3190	8914	33.2025	1 1 0
2	10.4232	3105	16.9606	1 1 0
3	15.5273	1767	11.4045	0 2 0
4	20.5542	1953	08.6352	2 1 0

Bio-potential activities

The metal complexes were found to have higher bio-potential in comparison to

4-aminothiophenol against the tested microorganism under the Agar disc diffusion method. The increased bio-potential properties of the complexes are the reaction of metal ions with bacterial cell. After complexation the polarity reduces the polarity of the metal ions because of partial sharing of the positive charge of the metal ions to the donor ligand. The lipophilicity of metal ion enhanced due to complexation. The permeation of the metal ions through lipid layer of the microorganisms also favoured by the complexation. The other effective factors for bio-potential activities are shape, neutral nature and nature of ligand and central metal ions¹⁷⁻¹⁸.

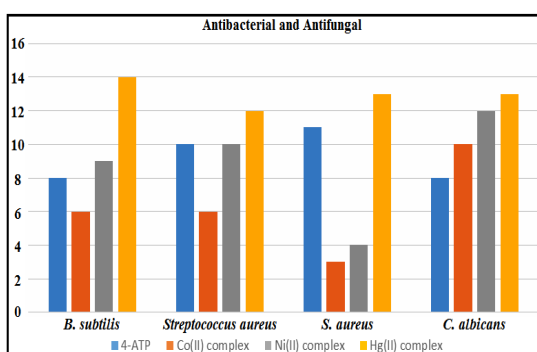


Fig. 9. Bio-potential Data

CONCLUSION

The mixed ligand metal chelates was synthesized under microwave condition and characterized by various physico-chemical and spectroscopic tools. Analytical studies together with spectroscopic studies confirmed by the structure of the complexes. The crystal structure of the mercury complex confirmed by its Powder XRD study. The Bio-potential property of the metal complexes shows enhanced bio-potential activities of the metal chelates.

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Conflict of interest

The author declare that we have no conflict of interest.

REFERENCES

- Mersellem Mohamed.; Hellal Abdelakder.; Benhamou Abdellah., *Journal of Molecular Structure.*, **2021**, 1241, 130666.
- Manish Kumar.; Sonu Chauhan.; Meena Sindhu.; Poonam.; Jangra Darolia.; Anisha Bhardwaj.; Sapana Garg., *Journal of the Indian Chemical Society.*, **2023**, 100(2), 100797.
- Sulakshna Bharti.; Mukesh Choudhary.; Bharti Mohan.; Rawat P.; Sharma SR.; Ahmad K., *Journal of Molecular Structure.*, **2018**, 1164, 137-154.
- Mishra AP.; and Rajendra K. Jain., *Journal of Saudi Chemical Society*, **2014**, 18(6), 814-824.
- Abhinav Jain.; Soumik De.; & Pranjit Barman., *Research on Chemical Intermediates.*, **2022**, 48, 2199–2251.
- Abiola Azeez Jimoh.; Aasif Helal.; Nasiruzzaman Shaikh M.; Abdul Aziz Md.; Zain H. Yamani.; Amir Al-Ahmed.; and Jong-Pil Kim., *Journal of Nanomaterials.*, **2015**, 1-7.
- Mohammad Hassan Motaghedifard.; Mohsen Behpour.; Sayed Mehdi Ghoreishi., *Sensors and Actuators B: Chemical.*, **2014**, 203, 802-811.
- Anilkumar Ambala.; Ch. Abraham Lincoln., *Chemical Data Collections.*, **2020**, 27, 100372.
- Verónica Ferraresi-Curotto.; Gustavo A. Echeverría.; Oscar E. Piro.; Reinaldo Pis-Diez.; Ana C. González-Baró., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.*, **2014**, 118, 279-286.
- Sefa Durmus.; Alparslan Atahan.; Mustafa Zengin., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.*, **2011**, 84(1), 1-5.
- Sulakshna Bharti.; Mukesh Choudhary.; Bharti Mohan.; S. P. Rawat.; S. R. Sharma.; K. Ahmad., *Journal of Molecular Structure.*, **2018**, 1164, 137-154.
- Ahmad Ali Dehghani-Firouzabadi.; Morteza Sobhani.; Behrouz Notash., *Polyhedron.*, **2016**, 119, 49-54.
- Ayman A. Abdel Aziz.; Fatma M. Elantabli.; H. Moustafa.; Samir M. El-Medani., *Journal of Molecular Structure.*, **2017**, 1141, 563-576.

14. Pinar Ekmekcioglu.; Nevin Karabocek.; Serdar Karabocek.; Mustafa Emirik., *Journal of Molecular Structure.*, **2015**, *1099*, 189-196.
15. Hina Zafar.; Anis Ahmad.; Asad U. Khan.; Tahir Ali Khan., *Journal of Molecular Structure.*, **2015**, *1097*, 129-135.
16. Bushra Rafique.; Saima Kalsoom.; Abdulrahim A. Sajini.; Hammad Ismail.; Mudassir Iqbal., *Molecules.*, **2022**, *27*(4), 1352.
17. Manish Kumar.; Sonu Chauhan.; Meena Sindhu.; Poonam Jangra Darolia.; Anisha Bhardwaj.; Sapana Garg., *Journal of the Indian Chemical Society.*, **2023**, *100*(2), 100797.
18. Bitu Shafaatian S.; Sedighe Mousavi.; Sadegh Afshari., *Journal of Molecular Structure.*, **2016**, *1123*, 191-198.