American Journal of Biomedicine and Pharmacy
https://biojournals.us/index.php/AJBP
ISSN: 2997-7177

Synthesis, Spectroscopic of Mercury (II) Mixed Ligand Complexes of Benzotriazole with Amines Ligand

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Received: 2024, 15, May
Accepted: 2025, 21, Jun
Published: 2025, 19, Jul

Annotation: In the present work, benzotriazole (Hbta) starting complexes with Phenylmercury(II)acetate ; [PhHg(bta)] (1) were prepared. Treatment of with one mole equivalent of the amines {amines= phenonthroline, bipyridene } afforded mixed ligand complexes of the formula [PhHg(bta)(amines)]; amines = phen (2), bipy (3). The resulting complexes were characterized by elemental analyses, infrared spectra, 1H-NMR spectroscopy. In complexes; (1-3), benzotriazolate link to mercury through its deprotonated nitrogen atom in a monodentate fashion.

Keywords: Benzotriazole; PhHg (II); amines; complexes.

1. Introduction

Coordination complex, coordination compound, or coordination complex in chemistry. There are many branches, including coordination chemistry[1–4]. Coordination chemistry is one of the most important branches concerned with the study of coordination compounds (coordination complexes), their properties, and their reactions[5–7].

Benzotriazole (BTA) is a heterocyclic compound with the chemical formula C6H4N3H. The fusion of benzene and triazole rings forms it. In its pure form, BTA appears as a white solid, although impure samples may take on a brown color[6].. This compound is commonly used as a corrosion inhibitor for copper[8].

Benzotriazole has been used as a binder (or antifog) in photographic emulsions or decorating solutions, and as a reagent for the analytical determination of silver. Most importantly, it has been widely used as a corrosion inhibitor in the atmosphere and underwater[8]. BTA can also be used as an antifreeze, in heating and cooling systems, hydraulic fluids, and as a vapor-phase inhibitor[9-19]. The Hbta ligand exhibits several coordination modes[20-21].

(i) monodentate via a neutral nitrogen atom [14–19],

(ii) bidentate via two nitrogen atoms [11, 12, 23],

(iii) tridentate coordination [24], and

(iv) a diverse binding mode, wherein the ligand coordinates in multiple fashions within the same complex.

Experimental part

Materials and instrumentations

Preparation of the [pHg(L)(phen)] complex

A suspension of the Ph-Hg(L) complex (0.600 mmol, 0.300 g) in 5 ml of absolute ethyl alcohol was added to a hot, white suspension of (phen) (0.600 mmol, 0.096 g) in 5 ml of absolute ethyl alcohol. The mixture was heated for three hours at 60-80°C. The resulting precipitate was filtered and allowed to dry at room temperature to obtain a gummy substance. The filtrate was washed with diethyl ether, forming a transparent suspension. (Melting point: 178-180°C, weight: 0.043 g, yield: 89%.

Preparation of the [pHg(L)(bipy)] complex

A suspension of the Ph-Hg(L) complex (0.381 mmol, 0.102 g) in 5 ml of absolute ethyl alcohol was added to a hot, white suspension of (bipy) (0.660 mmol, 0.0730 g) in 5 ml of absolute ethyl alcohol. The mixture was submerged for three hours at 60-80°C. The resulting precipitate was filtered and allowed to dry at room temperature. The filtrate was then washed with ethanol. (Melting point: 139-141°C, weight: 0.231 g, yield: 89%).

Interpretation and Results

Identification of the [Ph-Hg(L)(Phen)] Complex

Infrared Spectrum of the [Ph-Hg(L)(Phen)] Complex

The infrared spectrum of the [Ph-Hg(L)(Phen)] complex showed a medium to weak band at frequencies of 30353058 cm-1, attributed to the vibrational stretching of the aromatic π(C-H) group. The spectrum also showed a band at 1618 cm-1, attributed to the π(C=C) group.[109] A distinct band for the (C=N)υ[110] group, attributed to the ligand (Phen), appeared at a range of 1421 cm-1. The appearance of this band at this location indicates its biconcentric coordination via the two nitrogen atoms in (Phen). The spectrum also showed a distinct band for (Phen) at frequencies of 1421 cm-1. (842 cm-1), and it was found that there is a band at the frequency (cm-11477) that is attributed to the stretching frequency of the υ(N=N) group in the benzotriazole ring, while the band at the frequency (cm-11257) is attributed to the υ(C-N) group.[111] It was found that a band appeared at (cm-11141) in the spectrum of the complex, which is attributed to the stretching of the υ(N-N) group. The spectrum also showed a weak band at the frequency (430 cm-1) that is attributed to the (Hg_N)υ group, as shown in Figure (1)

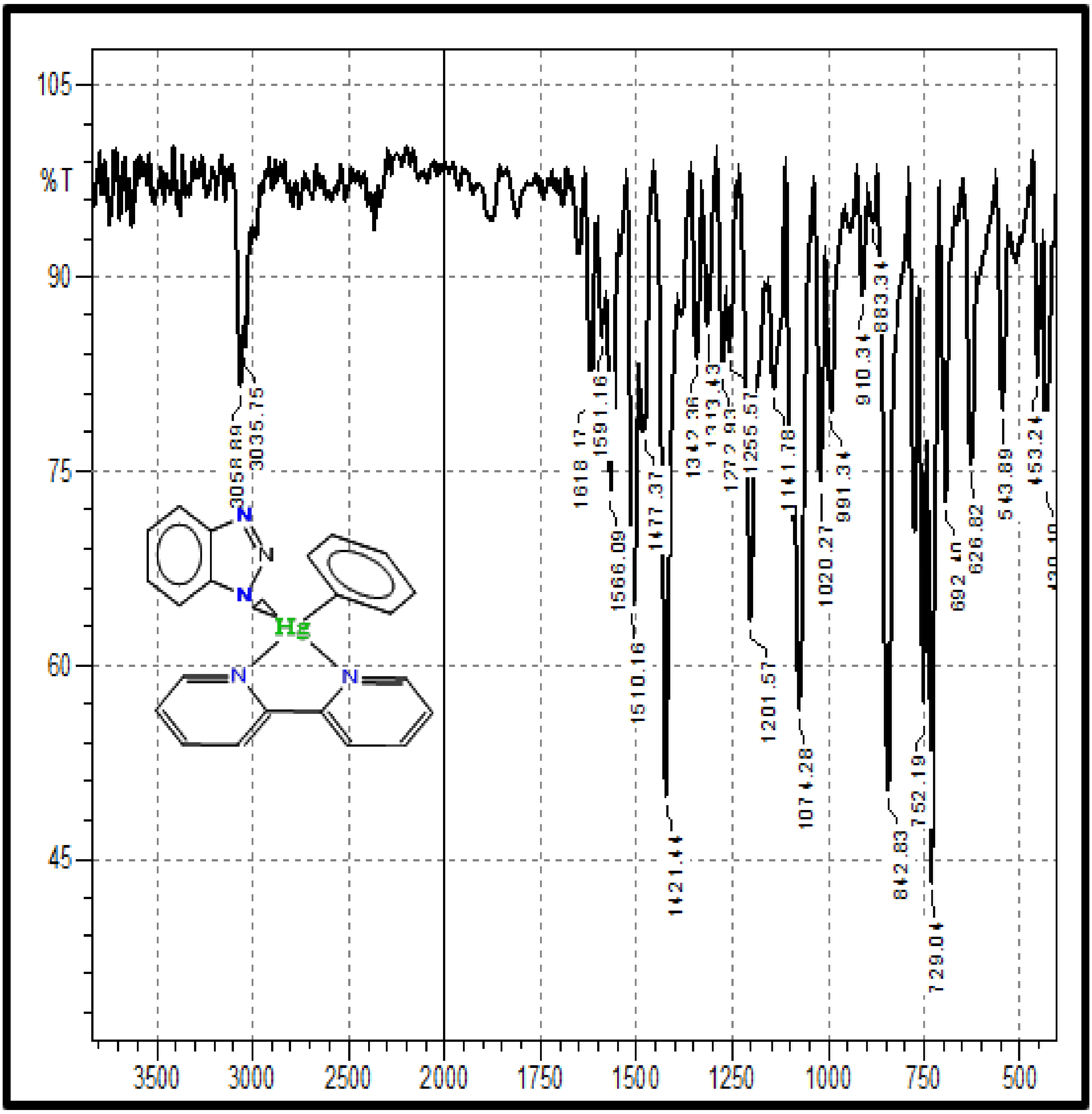

Figure (1) Infrared spectrum of the complex [Ph-Hg(L)(Phen)]

1H-NMR spectrum of the [Ph-Hg(L)(Phen)] complex

The 1H-NMR spectrum of the prepared complex with the formula [Ph-Hg(L)(Phen)] measured in DMSO-d6 solvent showed four separate signals attributed to the protons of the two phenanthroline rings. A single signal appeared at the shift (δH = 9.35 ppm) with the integration of two protons and was attributed to the (H3) proton. Another double signal appeared at the shift (δH = 8.81 ppm with the integration of two protons and was attributed to the (H1) proton. A double signal appeared at the shift (δH = 8.27 ppm with the integration of two protons and was attributed to the (H4) proton. The spectrum also showed a single signal at the shift (δH = 8.08 ppm) and was attributed to the (H4) proton. Proton (H3) and the integration of each of the previous signals indicates that they correspond to two protons of the phenanthroline ring (Phen). Multiple signals also appeared within the range (δH=7.91-7.65 ppm) attributed to the protons of the two phenyl rings, as in Figure (2).

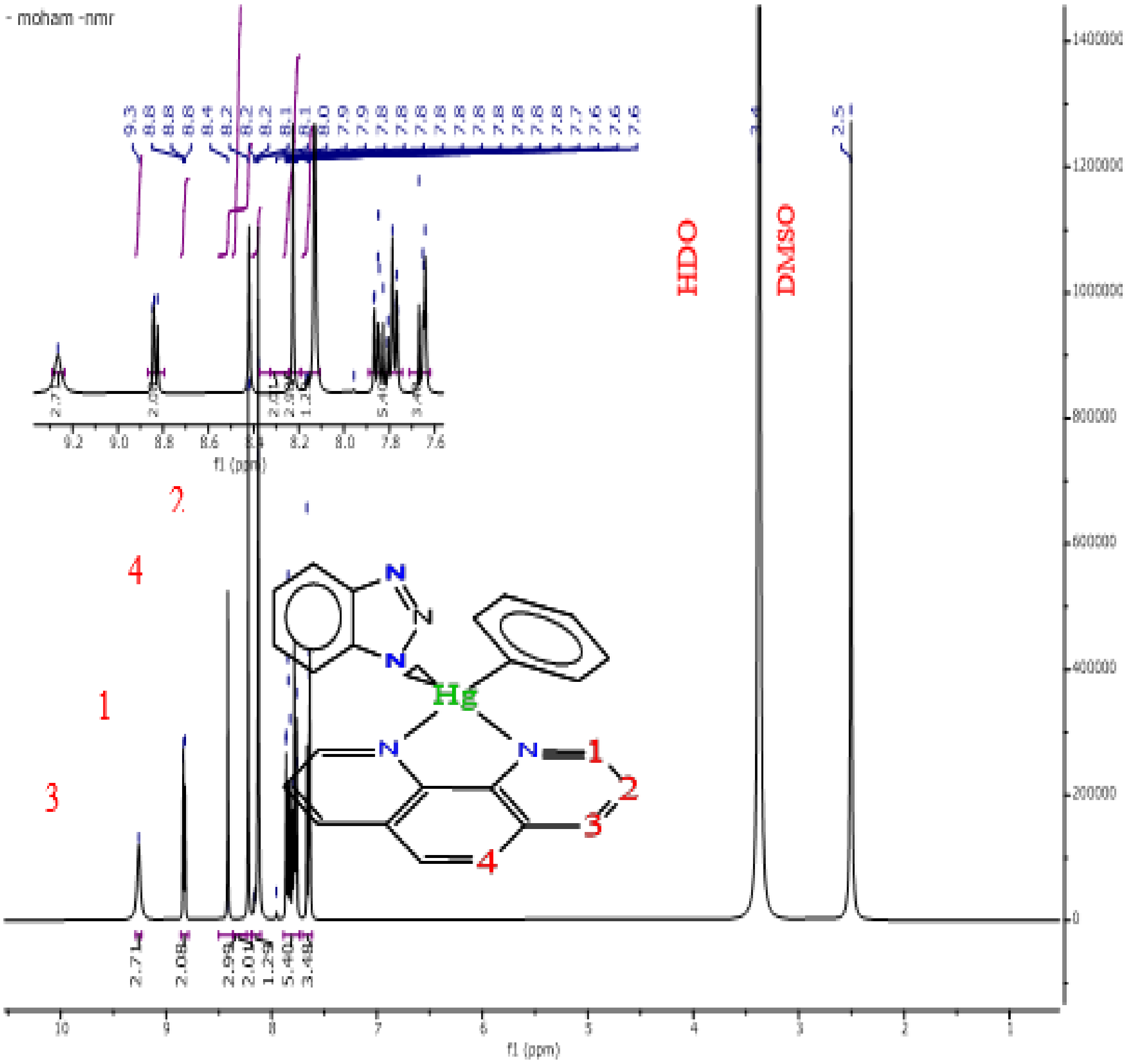

Figure (2) 1H-NMR spectrum of the complex [Ph-Hg(L)(Phen)]

Identification of the [Ph-Hg(L)(Bipy)] complex

Infrared spectrum of the [Ph-Hg(L)(Bipy)] complex

The infrared spectrum of the [Ph-Hg(L)(Bipy)] complex showed a strong band at 3064 cm-1 due to the vibrational stretching of the aromatic π(C-H) group. The spectrum showed a strong band at 1652 cm-1 attributed to the π(C=C) group.[109] A distinct band appeared for the (C=N)υ[110,111] group, which was attributed to the ligand (Bipy), and appeared at a range of 1415 cm-1. The appearance of this band at this location indicates its bidentate coordination via the two nitrogen atoms in (Bipy). The spectrum showed a distinct band for (Bipy) at 1415 cm-1. (742cm-1), and it was found that there is a band at the frequency (cm-11460) due to the stretching frequency of the υ(N=N) group in the benzotriazole ring, while the band at the frequency (cm-11249) is attributed to the υ(C-N) group, and it was found that a band appeared at (cm-11141) in the spectrum of the complex, which is attributed to the stretching of the group, and the spectrum also showed a weak band at the frequency (457cm-1) due to the (Hg_N)υ υ(N-N) group, as shown in Figure (3).

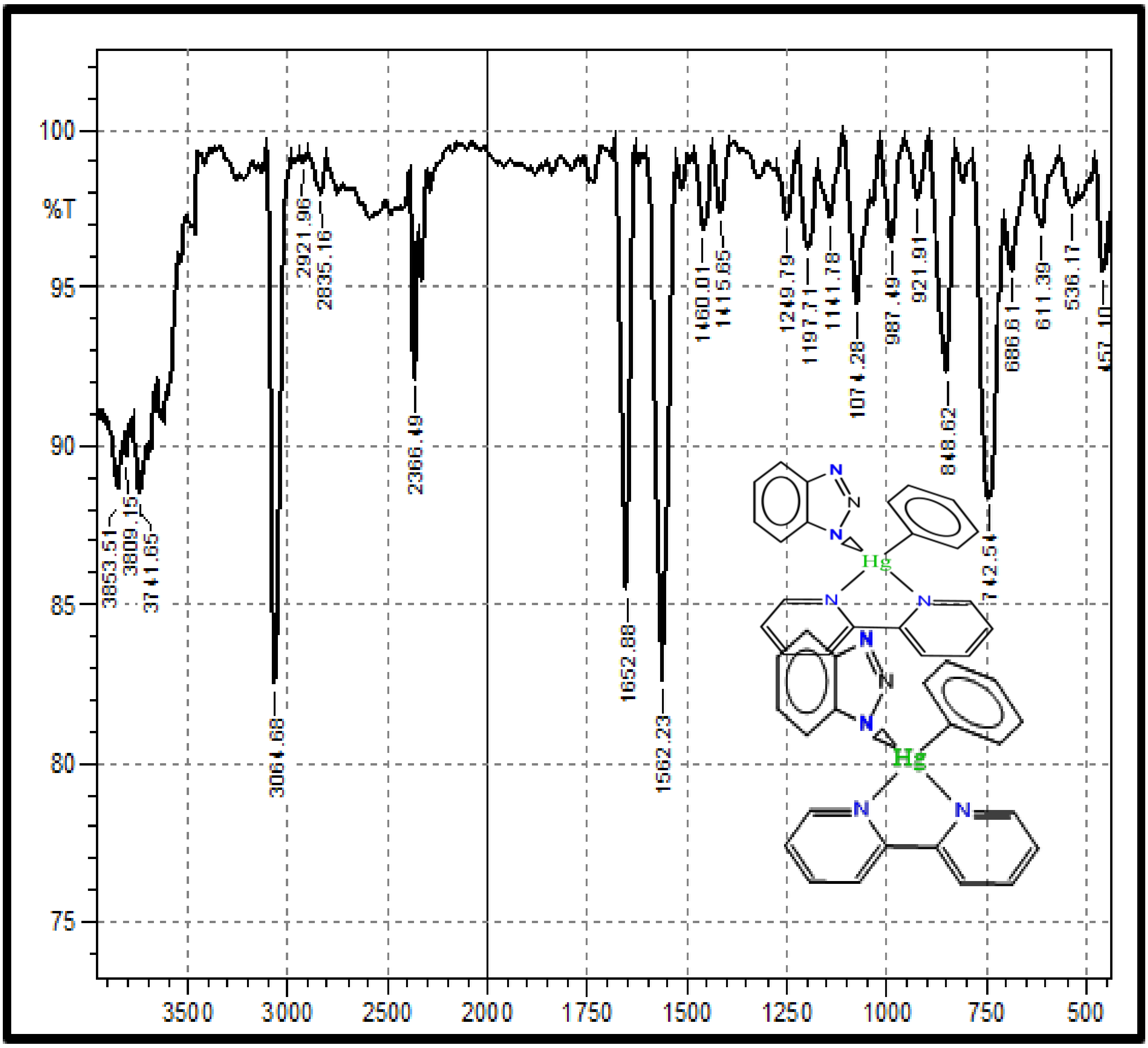

Figure (3) Infrared spectrum of the complex [Ph-Hg(L)(Bipy)]

1H-NMR spectrum of the [Ph-Hg(L)(Bipy)] complex

The 1H-{31P}NMR spectrum of the prepared complex with the formula [Ph-Hg(L)(Bipy)] measured in DMSO-d6 solvent showed four separate signals attributed to the protons of the two bipyridine rings. A doublet signal appeared at the shift (δH = 8.83 ppm) with the integration of two protons and was attributed to the (H1) proton. Another doublet signal appeared at the shift (δH = 8.33 ppm with the integration of two protons and was attributed to the (4H) proton. A triplet signal appeared at the shift (δH = 8.23 ppm with the integration of two protons and was attributed to the (H2) proton. The spectrum also showed a triplet signal at the shift (δH = 8.11 ppm with the integration of two protons. It was attributed to two protons (H3), and the integration of each of the previous signals indicates that they correspond to two protons of the bipyridine ring (Bipy). Multiple signals also appeared in the range (δH=7.81-7.64 ppm). They were attributed to the protons of the two phenyl rings, as in Figure (4).

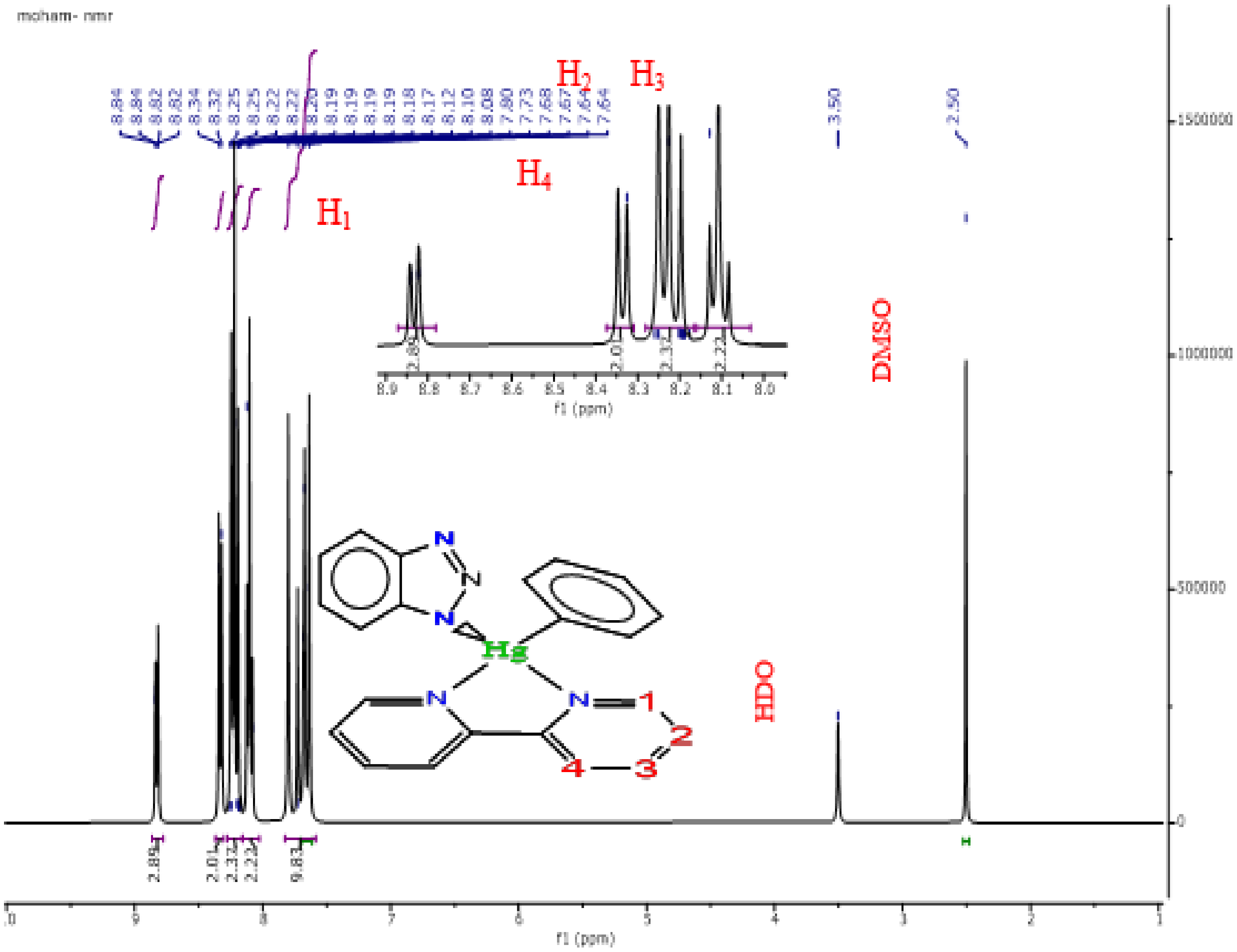

Figure (4) 1H-NMR spectrum of the complex [Ph-Hg(L)(Bipy)]

Antibacterial activity

The results of antibacterial activity of the prepared complexes **1**, **2**, **3** were tested against two bacterial types *staphlycocas aureus* (gram positive) *Citrobacter freundii* (gram negative) and compared with the antibiotic Amikacin exclusive.

The hole methods used to tested of the prepared complexes and three concentration from the prepared complexes (1x10^{-1}, $10^{-3}$and 10^{-5} M) while the DMSO used as solvent and control [33], the antibacterial activity was determined by measuring inhibition zone diameter (IZD) in millimeter (mm) to Amikacin and complexes **1**, **2, 3.** The results are summarized in (Table4). Compared with the antibiotic used by Amikacin, the results of our current study were recorded on Some compounds prepared for the efficacy and growth of the two bacterial species studied, and from the table below, Compounds with strong efficacy and inhibition can be used to treat diseases caused by bacteria, Studied and mentioned above after conducting the histological and anatomical studies of the prepared compounds

No.	**Complexes**	**Concentration**	**Staphlycocas aureus**	***Citrobacter freundii***
1	[PhHg(bta)]	10^{-1}	S	S
		10^{-3}	M	R
		10^{-5}	R	M
2	[PhHg(bta) (phen)]	10^{-1}	R	R

		10^{-3}	S	S
		10^{-5}	R	R
4	[PhHg(bta) (bipy)]	10^{-1}	M	R
		10^{-3}	S	S
		10^{-5}	R	M

Amikacin Inhibition Zone (mm):

- Resistant (R): less than 14 mm
- Moderately susceptible (M): 15-16 mm
- Susceptible (S): greater than 17 mm

Conclusion

This article discusses the preparation and characterization of a new series of mercury complexes that incorporate benzotriazole ligands, with or without amines serving as co-ligands. The characterization methods used demonstrated that the ligand can adopt various coordination patterns, functioning as a monodentate ligand by bonding to either a neutral or deprotonated nitrogen atom. All complexes exhibit stability when exposed to air and can be easily isolated in powder form.

References

1. Nehra, K., Dalal, A., Hooda, A., Bhagwan, S., Saini, R. K., Mari, B.,... & Singh, D. (2022). Lanthanides β-diketonate complexes as energy-efficient emissive materials: A review. Journal of Molecular Structure, 1249, 131531.
2. Zhai, R., Xiao, Y., Gu, Z., & Zhang, J. (2022). Tunable chiroptical application by encapsulating achiral lanthanide complexes into chiral MOF thin films. Nano Research, (2), 1102-1108.
3. Chen, Z., Hu, Y., Wang, J., Shen, Q., Zhang, Y., Ding, C.,... & Gaponik, N. (2020). Boosting photocatalytic CO2 reduction on CsPbBr3 perovskite nanocrystals by immobilizing metal complexes. Chemistry of Materials, 32(4), 1517-1525.
4. Valenti, G., Rampazzo, E., Kesarkar, S., Genovese, D., Fiorani, A., Zanut, A., Prodi, L. (2018). Electrogenerated chemiluminescence from metal complexes-based nanoparticles for highly sensitive sensors applications. Coordination Chemistry Reviews, 367, 65-81.
5. B. V Suma, N.N. Natesh, V. Madhavan, Benzotriazole in medicinal chemistry: An overview, J Chem Pharm Res. 3 (2011) 375–381.
6. C. Sease, Benzotriazole: a review for conservators, Stud. Conserv. 23 (1978) 76–85.
7. A. Solehudin, Performance of benzotriazole as corrosion inhibitors of carbon steel in chloride solution containing hydrogen sulfide, Int. Ref. J. Eng. Sci. 1 (2012) 21–26.
8. Y.-S. Liu, G.-G. Ying, A. Shareef, R.S. Kookana, Biodegradation of three selected benzotriazoles in aquifer materials under aerobic and anaerobic conditions, J. Contam. Hydrol. 151 (2013) 131–139.
9. A. Solehudin, "Performance Of Benzotriazole As Corrosion Inhibitors Of Carbon Steel In Chloride Solution Containing Hydrogen Sulfide," vol. 1, no. 4, pp. 21–26, 2012.
10. Y.-S. Liu, G.-G. Ying, A. Shareef, and R. S. Kookana, "Biodegradation of three selected benzotriazoles in aquifer materials under aerobic and anaerobic conditions," *J. Contam. Hydrol.*, vol. 151, pp. 131–139, 2013.
11. Y. Ren, L. Zhang, C. Zhou, and R. Geng, "Recent Development of Benzotriazole-based Medicinal Drugs," vol. 4, no. 9, pp. 640–662, 2014.

12. X. Wu, N. Chou, D. Lupher, and L. C. Davis, “BENZOTRIAZOLES : TOXICITY AND DEGRADATION,” no. 1977, pp. 374–382, 1998.
13. E. Nielsen, “Benzotriazole and Tolyltriazole,” no. 1526, 2013.
14. A. Palumbo Piccionello and A. Guarcello, “Bioactive compounds containing benzoxadiazole, benzothiadiazole, benzotriazole,” *Curr. Bioact. Compd.*, vol. 6, no. 4, pp. 266–283, 2010.
15. G. Singh, R. Kumar, J. Swett, and B. Zajc, “Modular synthesis of N-vinyl benzotriazoles,” *Org. Lett.*, vol. 15, no. 16, pp. 4086–4089, 2013.
16. Y. Ren, L. Zhang, C.-H. Zhou, and R. X. Geng, “Recent development of benzotriazole-based medicinal drugs,” *Med. chem*, vol. 4, no. 9, pp. 640–662, 2014.
17. I. Sotofte, K. Nielsen, Benzotriazole complexes. IV. The crystal structure of bis (benzotriazole) silver (I) nitrate, Acta Chem. Scand. Ser. A. Phys. Inorg. Chem. 37 (1983) 891–895.
18. J. Reedijk, A.R. Siedle, R.A. Velapoldi, J.A.M. Van Hest, Coordination compounds of benzotriazole and related ligands, Inorganica Chim. Acta. 74 (1983) 109–118.
19. K. Müller-Buschbaum, Y. Mokaddem, Rare Earth Benzotriazolates: Coordination Polymers Incorporating Decomposition Products from Ammonia to 1, 2-Diaminobenzene in $_{\infty}[\mathrm{Ln(Btz)_3(BtzH)}]$(Ln= Ce, Pr), $_{\infty}[\mathrm{Ln(Btz)_3\{Ph(NH_2)_2\}}]$(Ln= Nd, Tb, Yb), and $_{\infty}[\mathrm{Ho_2(Btz)_6(BtzH)(NH_3)}]$, Eur. J. Inorg. Chem. 2006 (2006) 2000–2010.
20. L. Li, X. Wang, G. Shen, R. Wang, and D. Shen, “Synthesis and crystal structure of Zn [(C6H5N3) 4 (H2O) 2](ClO4) 2 and Cu [(C6H5N3) 4 (H2O) 2](ClO4) 2,” *Inorg. Chem. Commun.*, vol. 5, no. 7, pp. 453–457, 2002.
21. P. Ramadevi, S. Kumaresan, and K. W. Muir, “mer-Tris (1H-benzotriazole-κN)(pyridine-2, 6-dicarboxylato-κ3N, O, O′) nickel (II),” *Acta Crystallogr. Sect. E Struct. Reports Online*, vol. 61, no. 9, pp. m1749–m1751, 2005.
22. M. Murrie, C. D. Garner, P. A. Tasker, and S. S. Turner, “Synthesis \ structure