MAS Journal of Applied Sciences
Uygulamalı Bilimler Dergisi
ISSN: 2757-5675
masjaps.com

OPEN ACCESS

DOI: http://dx.doi.org/10.5281/zenodo.15094019

Research Article

Synthesis, Characterization, and Thermal Properties of Cd(II) and Hg(II) Complexes Containing *N,N′*-bis(2-hydroxyethyl)piperazine and Saccharinate

Serkan GÜNEY [1*]
[1] Ordu University, Ulubey Vocational Higher School, Ordu
*Corresponding author: serkanguney@odu.edu.tr

Received: 08.01.2025 **Accepted**: 25.02.2025

Abstract

New complexes of Cd(II) and Hg(II) incorporating *N,N′*-bis(2-hydroxyethyl)piperazine (bheppz) as a ligand, along with saccharinate (sac), were synthesized. The characterization of these complexes, proposed to have the general structure $[M(sac)_2(bheppz)]n$ (M = Cd(II) or Hg(II)), was conducted using elemental composition determination, FT-IR spectral analysis, and thermal analysis techniques. The complexes were synthesized by reacting $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$ and $[Hg(sac)_2]$ with bheppz. Based on the IR spectra, it has been suggested that the sac ligand coordinates through the N atom, which is its most common coordination mode. Additionally, the bheppz ligand was proposed to act as a bridging ligand via its nitrogen and oxygen donor atoms, leading to the formation of polymeric structures. The immediate precipitation of the complexes as powders during synthesis and their low solubility in common solvents further support their polymeric nature. The IR spectra of the complexes exhibited characteristic absorption bands corresponding to both bheppz and sac ligands. Thermal dissociation studies revealed that the bheppz ligand was exothermically eliminated in the first step, while the sac ligand dissociated in two exothermic steps at higher temperatures. The final decomposition products were identified as CdO for $[Cd(sac)_2(bheppz)]_n$ (1) and elemental mercury for $[Hg(sac)_2(bheppz)]_n$ (2), with mercury volatilizing from the system at elevated temperatures.

Keywords: Thermal analysis, *N,N′*-bis (2-hydroxyethyl) piperazine, saccharin complexes

1. Introduction

Piperazine is a flexible heterocyclic compound that holds significant importance in metal complex formation, as it can stabilize various geometric configurations. The structural adaptability of piperazine allows it to function as a monodentate or bidentate ligand through its nitrogen atoms, and in certain instances, it can serve as a linker connecting two metal centers. Additionally, the introduction of functional groups into the piperazine ring can enhance its coordination ability by providing additional donor atoms (Ciccarese et al., 1998; Zhaoa et al., 2004; Yılmaz et al., 2008a; Yılmaz et al., 2008b). This versatility has led to the widespread use of piperazine-based complexes in catalyst design, material science, and biomedical applications. Recent studies have demonstrated that piperazine and its derivatives exhibit antimicrobial (Gharbi et al., 2023; Adejoh et al., 2024), antibacterial (Kant and Maji, 2023; 2024), antifungal (Nadaf et al., 2020), anticancer (Pait et al., 2014; Nemati et al., 2021; Ragab et al., 2022), and antineurotic (Jaziri et al., 2023) properties, further increasing interest in their coordination chemistry.

Saccharin, an artificial sweetener discovered in 1879 by Remsen and Fahlberg at Johns Hopkins University, is widely used as a sugar substitute due to its intense sweetness, cost-effectiveness, and thermal stability (Anderson and Deskins, 1995). Beyond its applications in food and pharmaceuticals, saccharin has attracted considerable interest in metal complex formation because of its versatile binding capabilities. The sodium salt of saccharin (sodium saccharinate) has excellent solubility in water, with a concentration of 830 g L^{-1} at 20 °C, which further increases its effectiveness in metal complex formation. The sac anion can coordinate to metal centers via its negatively charged nitrogen atom and the oxygen atoms in its carbonyl and sulfonyl groups, allowing for a range of coordination modes (Baran and Yılmaz, 2006).

Recent advancements in mixed-ligand metal complexes have opened new possibilities in chemistry and biochemistry, particularly for systems that incorporate saccharinate (sac) and *N,N′*-bis(2-hydroxyethyl)piperazine (bheppz) as ligands. These complexes exhibit unique biological activity, catalytic potential, and thermal stability, making them attractive for various applications (Ulukaya et al., 2011; Ari et al., 2013; 2014; Al-Jibori et al., 2014; Shehata et al., 2016; İçsel et al., 2024). The bheppz ligand (Figure 1a) contains four donor atoms, allowing it to form strong coordination bonds with metal centers, while the saccharinate anion (Figure 1b) contributes additional stability and electronic effects to the resulting complexes (Yılmaz et al., 2008c; Shehata et al., 2016; Shehata et al., 2019).

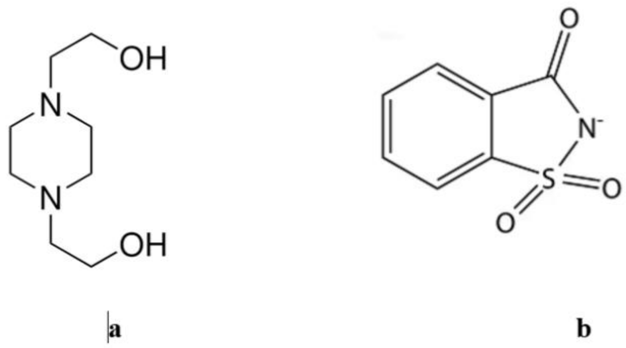

Figure 1. The molecular structures of bheppz (a), sac (b)

This research investigates the preparation, structural analysis, and thermal behavior of polymeric Cd and Hg compounds that incorporate sac and bheppz as ligands. The main objective is to uncover the chemical and physical characteristics of these new coordination materials and assess their possible applications in fields such as catalysis, materials science, and biochemistry.

2. Materials and Methods

2.1. Materials and instruments

All chemicals used in this study were sourced commercially and utilized without further purification. The precursor complexes $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$ and $[Hg(sac)_2]$ were prepared according to methods described in the literature (Biedermann et al., 1971; Kamenar and Jovanovski, 1982; Haider et al., 1985).

Infrared (IR) spectra were recorded using a Mattson 1000 FTIR spectrophotometer. Samples were prepared as KBr pellets, and spectra were obtained within a frequency range of 4000–400 cm^{-1}. Elemental analysis for carbon, hydrogen, and nitrogen was performed with a LECO CHNS 932 Elemental Analyzer. Thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out on a Rigaku TG8110 thermal analyzer under static air conditions, with sample sizes ranging from 5 to 10 mg.

2.2. Synthesis

Complex 1: A solution of bheppz ligand (0.348 g, 2.0 mmol) in 20 ml of methanol was slowly added dropwise to a methanolic solution (20 ml) of $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$ (1.0 mmol) while stirring continuously at room temperature. The mixture was stirred for 1 hour using a magnetic stirrer. After a few days, the powdered complex was obtained. Yield: 90%. Decomposition temperature: 246 °C. Complex 2: It was synthesized in the same way as complex 1 using $[Hg(sac)_2]$ instead of $[Cd(sac)_2(H_2O)_4].2H_2O$. Yield: 82%. Decomposition temperature: 117 °C.

3. Findings and Discussion

In the $[Ag(\mu\text{-}sac)(\mu\text{-}bheppz)]_n$ complex, which was synthesized and structurally analyzed by Yılmaz et al. (2008c), each silver(I) ion is connected by two sac ligands, creating non-planar eight-membered metallo-chelate rings. These dimeric units are additionally linked by bheppz ligands, leading to the formation of a polymeric chain. The bheppz ligand has four donor sites, with each end containing an N atom and an O atom, behaving as a bidentate donor. The sac ligand exhibits bridging coordination through the nitrogen and sulfonyl oxygen atoms. In complexes 1 and 2, the bheppz ligand is also proposed to exhibit a similar bridging coordination. The proposed molecular structure for complexes 1 and 2 is shown in Figure 2. The elemental analysis results given in Table 1 demonstrate that the experimental values are in excellent agreement with the calculated values for the proposed molecular structure.

Table 1. The elemental analysis data of the compounds

Compounds	Molecular Weight	% Composition[a]		
		C	H	N
$[Cd(sac)_2(bheppz)]_n$ $C_{22}H_{26}N_4O_8S_2Cd$	651.01	40.43 (40.59)	3.67 (4.02)	8.46 (8.61)
$[Hg(sac)_2(bheppz)]_n$ $C_{22}H_{26}N_4O_8S_2Hg$	739.19	35.90 (35.75)	3.36 (3.54)	7.62 (7.89)

[a] The calculated values are given in parentheses.

The coordination modes of the sac ligand in the complexes were determined by infrared studies. The complexes were obtained with remarkably high yields. Their immediate precipitation as powders during synthesis and their low solubility in common solvents suggest their polymeric nature. The IR spectra of the complexes are shown in Figure 3, with the key vibration frequencies listed in Table 2. An O-H stretching vibration was detected in the range of 3351–3356 cm^{-1}. The characteristic N-H stretching vibrations of bheppz were overlapped by the O-H band. The bands at 2951–2827 cm^{-1} originate from C-H vibrations. The characteristic C=O stretching band of sac appears very strongly in the range of 1624–1651 cm^{-1}. The C=O stretching vibrations in the complexes were found to be similar to those in the $[Cd(sac)_2(H_2O)_4]\cdot 2H_2O$ and $Hg(sac)_2$ complexes, where sac binds via its N atom. This suggests that sac is also coordinated through its N atom in these complexes. The expected C=N stretching vibration of the pyridine ring around 1600 cm^{-1} was not easily identifiable because it overlapped with the C=O stretching vibration. The asymmetric and symmetric stretching vibrations of SO_2 are observed in the ranges of 1254–1269 cm^{-1} and 1149–1153 cm^{-1}, respectively. The bands in the ranges of 1331–1336 cm^{-1} and 943–966 cm^{-1} correspond to the symmetric and asymmetric CNS stretching vibrations of sac ligands.

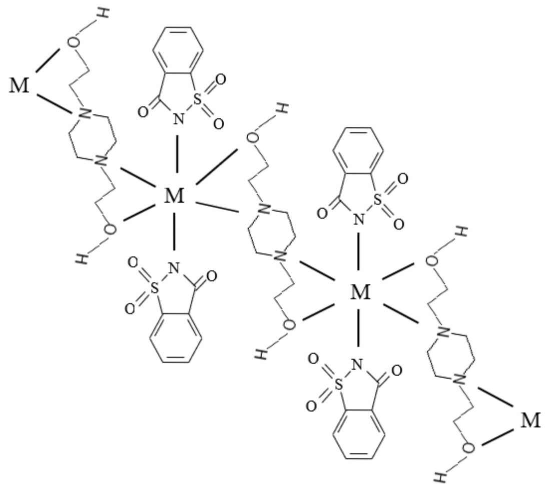

Figure 2. Suggested molecular structure of the compounds

Table 2. IR spectral data[a] of the compounds

Compounds	**ν(OH)**	**ν(CH)**	**ν(C=O)**	**$\nu_{asym}(SO_2)$**	**$\nu_{sym}(SO_2)$**	**ν_{sym}(CNS)**	**ν_{asym}(CNS)**
1	3351s	2951w- 2858w	1651vs-1624 vs	1269vs	1153vs	1336vs	943vs
2	3356b	2943w- 2827w	1647vs	1254vs	1149vs	1331vs	966vs

[a]Frequencies in cm^{-1}. b: broad, vs: very strong. s: strong, w: weak

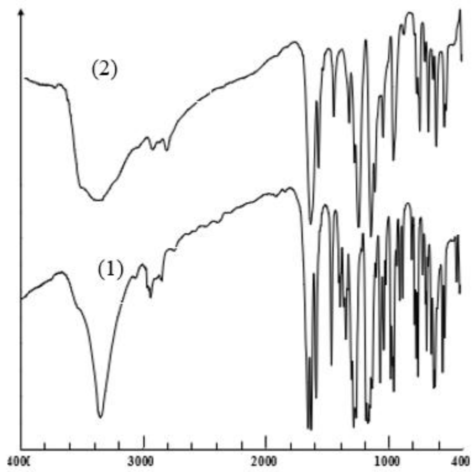

Figure 3. The FT-IR spectra of the compounds

The thermal analysis of the compounds was conducted up to 1000 °C under atmospheric pressure, with the results shown in Table 3. The DTA and TG curves are shown in Figure 4. Complex 1 exhibits thermal stability up to 246 °C. In the first stage, within the 246–346 °C range, the bheppz ligand is released in a single-step exothermic process with a peak maximum at 288 °C (found = 27.2%; calculated = 26.8%). In the subsequent stage, the remaining metal-saccharinate decomposes exothermically within the 346–746 °C range, yielding cadmium oxide (found = 55.1%; calculated = 56.0%). In contrast, Complex 2 remains thermally stable up to 117 °C. During the first stage, between 117–197 °C, it experiences exothermic decomposition with the loss of the bheppz ligand (found = 23.3%; calculated = 23.6%). After the removal of the bheppz ligand, two molar equivalents of the sac ligand are released in a single-step exothermic process within the 197–552 °C range, with a peak maximum at 459 °C, leading to the formation of metallic mercury (found = 49.5%; calculated = 49.3%). At this temperature, the elemental mercury volatilizes and is removed from the system.

Table 3. Thermal analysis results for the compounds

Compounds	**Stage**	**DTA$_{max}$ (°C)** [a]	**Species lost**	**%weight losses**	
				Found	**Calc.**
1	1	288(-)	1bheppz	27.2	26.8
	2	585(-)	2sac	55.1	56.0
	Residue		CdO		
2	1	155(-). 263(-)	1bheppz	23.3	23.6
	2	459(-)	2sac	49.5	49.3
	Residue		-		

[a] (+) indicates endothermic, (-) exothermic processes.

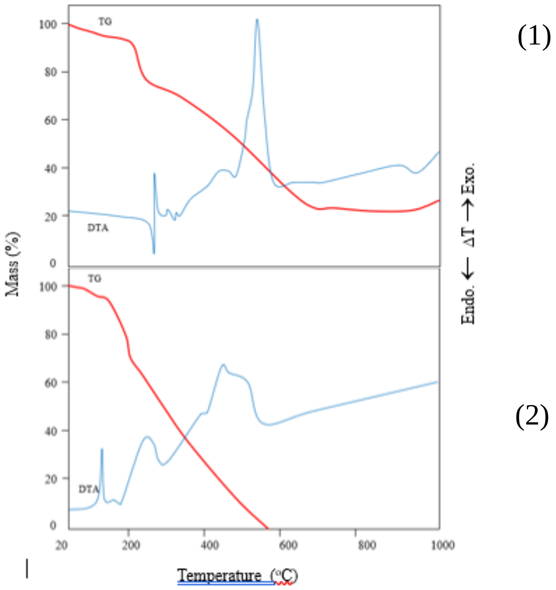

Figure 4. DTA and TG curves of the compounds

4. Conclusions

In this study, two novel Cd(II) and Hg(II) complexes containing bheppz and sac ligands were successfully synthesized and characterized. The synthesis of these complexes was achieved with high yields, and their structural properties were thoroughly analyzed using infrared (IR) spectroscopy, elemental analysis, and thermal analysis (TGA/DTA). The results indicate that both complexes exhibit strong coordination interactions between the metal centers and the ligands, particularly through the nitrogen and oxygen atoms of the sac and bheppz ligands, forming polymeric structures. The IR spectra confirmed the coordination modes of the sac anion and bheppz ligand, with characteristic bands observed for the functional groups involved in coordination. The thermal stability of the complexes was also assessed, with complex 1 demonstrating stability up to 246 °C, while complex 2 showed stability up to 117 °C. The thermal analysis further supported the decomposition patterns of the complexes, with the release of ligands and metal salts occurring in distinct steps. These findings contribute to the understanding of the thermal behaviors and stability of the synthesized complexes. Overall, the results from this study highlight the potential applications of these Cd(II) and Hg(II) complexes in catalysis, materials science, and biochemistry. The presence of the bheppz and sac ligands provides versatility in coordination chemistry, which could lead to the development of new materials with desirable properties. Furthermore, the antimicrobial, anticancer, and neurotic properties of the ligands and their potential synergy with metal centers warrant further exploration for possible therapeutic applications. Future research should focus on exploring the biological activities of these complexes, particularly their anticancer and antimicrobial properties. In addition, further investigations into the mechanistic pathways of their catalytic activities could open new avenues for their use in environmental and industrial applications. It is also recommended to investigate the impact of different metal ions on the coordination environment and stability of these complexes to tailor their properties for specific applications.

References

Adejoh, O., Ukoha, P.O., Hosten, E.C., Nnaji, N., Eze, C.O., Anarado, C.J.O., Iwegbue, C.M.A., Jayamoorthy, K., Ujam, O.T., 2024. Synthesis, structure, preliminary antimicrobial and antimalarial studies of 1,1′-(piperazine-1,4-diyl)bis(2-phenylethan-1-one) and its lanthanide, Ce(III), Pr(III), and Nd(III) complexes. *Journal of Molecular Structure*, 1300: 137287.

Al-Jibori, S.A., Al-Jibori, G.H., Al-Hayaly, L.J., Wagner, C., Schmidt, H., Timur, S., Barlas, F.B., Subasi, E., Ghosh, S., Hogar, G., 2014. Combining anti-cancer drugs with artificial sweeteners: Synthesis and anti-cancer activity of saccharinate (sac) and thiosaccharinate (tsac) complexes cis-[Pt(sac)$_2$(NH$_3$)$_2$] and cis-[Pt(tsac)$_2$(NH$_3$)$_2$]. *Journal of Inorganic Biochemistry*, 14: 55-57.

Anderson, J., Deskins, B., 1995. The Nutrition Bible, William Morrow & Company. Inc: New York.

Ari, F., Cevatemre, B., Ikitimur Armutak, E.I., Aztopal, N., Yilmaz, V.T., Ulukaya, E., 2014. Apoptosis-inducing effect of a palladium(II) saccharinate complex of terpyridine on human breast cancer cells in vitro and in vivo. *Bioorganic & Medicinal Chemistry*, 22: 4948-4954.

Ari, F., Ulukaya, E., Sarimahmut, M., Yilmaz, V.T., 2013. Palladium(II) saccharinate complexes with bis(2-pyridylmethyl)amine induce cell death by apoptosis in human breast cancer cells. *Bioorganic & Medicinal Chemistry*, 21: 3016-3021.

Baran, E.J., Yılmaz, V.T., 2006. Metal complexes of saccharin. *Coordination Chemistry Reviews*, 250: 1981-1999.

Biedermann, H.G., Rossmann, G., Schwarzhans, K.E., 1971. Saccharin als Komplexligand/Saccharin as a Complexligand. *Zeitschrift für Naturforschung B*, 26(5): 480-481.

Ciccarese, A., Clemente, D.A., Fanizzi, F.P., Marzotto, A., Valle, G., 1998. Boat versus chair conformation in *N*-methyl- and *N,N'*-dimethylpiperazine platinum (II) complexes studied by X-ray analysis. A rare example of metal chelate piperazine: cis-[PtCl$_2$(Me$_2$ppz)] Part 1. *Inorganica Chimica Acta,* 275: 410–418.

Gharbi, C., Louis, H., Amodu, I.O., Benjamin, I., Fujita, W., Ben Nasr, C., Khedhiri, L., 2023. Single crystal X-ray diffraction analysis, spectroscopic measurement, quantum chemical studies, antimicrobial potency and molecular docking of a new $[Co(NCS)_4]_2(C_6H_{17}N_3)_2{\cdot}4H_2O$ coordination compound based on piperazine-thiocyanate as co-ligand. *Journal of Molecular Structure*, 1298: 136997.

Haider, S.Z., Malik, K.M.A., Ahmed, K.J., Kauffman, G.B., Karbassi, M., 1985. Metal complexes of saccharin. *Inorganic Syntheses*, 23: 47-51.

İçsel, C., Yılmaz, V.T., Yeşilel, O.Z., Harrison, V.T.A., 2024. Metal complexes of saccharin and thiosaccharin as potential anticancer and antimicrobial agents. *European Journal of Medicinal Chemistry Reports,* 12: 100205.

Jaziri, E., Louis, H., Gharbi, C., Lefebvre, F., Kaminsky, W., Agwamba, E.C. Egemonye, T.G.C., Unimuke, T.O., Ikenyirimba, O.J., Mathias, G.E., Ben Nasr, C., Khedhiri, L., 2023. Investigation of crystal structures, spectral (FT-IR and NMR) analysis, DFT, and molecular docking studies of novel piperazine derivatives as antineurotic drugs. *Journal of Molecular Structure*, 1278: 134937.

Kamenar, B., Jovanovski, G., 1982. Manganese (II) saccharinate hexahydrate, Mn $(C_7H_4NO_3S)_2{\cdot}$ H_2O, and isomorphism with the analogous Fe, Co, Ni, Zn and Cd complexes. *Crystal Structure Communication*, 11: 257–261.

Kant, R., Maji, S., 2023. Synthesis, characterization and biological evaluation of piperazine embedded copper complexes. *Inorganica Chimica Acta*, 552: 121515.

Kant, R., Maji, S., 2024. Metal complex with piperazine ring-based ligand and their biological activities. *Materials Today: Proceedings*.

Nadaf, A.Q.A., Najare, M.S., Garbhagudi, M., Mantur, S., Sunagar, M.G., Gaonkar, S., Joshi, S., Khazi, I.A.M., 2020. Synthesis of 6-[4-(4-propoxyphenyl) piperazin-1-yl]-9h-purine derivatives as antimycobacterial and antifungal agents: In vitro evaluation and in silico study. *Chemistry & Biodiversity*, 17(5): e2000053.

Nemati, L., Keypour, H., Shahabadi, N., Hadidi, S., Gable, R.W., 2021. Synthesis, characterization and DNA interaction of a novel Pt(II) macroacyclic Schiff base complex containing the piperazine moiety and its cytotoxicity and molecular docking. *Journal of Molecular Liquids*, 337: 116292.

Pait, M., Kundu, B., Kundu, S.C., Ray, D., 2014. Copper(II) complexes of piperazine based ligand: Synthesis, crystal structure, protein binding and evaluation of anti-cancerous therapeutic potential. *Inorganica Chimica Acta,* 418: 30-41.

Ragab, M.S., Shehata, M.R., Shoukry, M.M., Haukka, M., Ragheb, M.A., 2022. Oxidative DNA cleavage mediated by a new unexpected $[Pd(BAPP)][PdCl_4]$ complex (BAPP = 1,4-bis(3-aminopropyl)piperazine): crystal structure, DNA binding and cytotoxic behavior. *RSC Advances*, 12: 1871.

Shehata, M.R., Shoukry, M.M., Mabrouk, M.A., Kozakiewicz, A., Van Eldik, R., 2019. Studies on Pd(1,4-bis(2-hydroxyethyl)piperazine)-dicarboxylic acid complexes as models for carboplatin with structural features enhancing the interaction with DNA. *Journal of Coordination Chemistry*, 72(12): 2035–2049.

Shehata, M.R., Shoukry, M.M., Mabrouk, M.A., Van Eldik, R., 2016. Synthesis, X-ray structure, DFT and thermodynamic studies of mono- and binuclear palladium(II) complexes involving 1,4-bis(2-hydroxyethyl)piperazine, bio-relevant ligands and 4,4′-bipiperidine. *Journal of Coordination Chemistry*, 69(3): 522–540.

Ulukaya, E., Ari, F., Dimas, K., İkitimur, E.I., Guney, R., Yılmaz, V.T., 2011. Anti-cancer activity of a novel palladium(II) complex on human breast cancer cells in vitro and in vivo. *European Journal of Medicinal Chemistry*, 46: 4957-4963.

Yılmaz, V.T., Güney, S., Kazak, C., 2008a. Copper(II)-saccharinato complexes with piperazine and *N*-(2-aminoethyl)piperazine ligands. *Polyhedron*, 27: 1381-1386.

Yılmaz, V.T., Güney, S., Kazak, C., 2008b. *trans*-Bis[2-(piperazin-1-yl)ethanamine]bis(saccharinato)cobalt(II). *Acta Crystallographica E*, E64: 59-60.

Yılmaz, V.T., Hamamci, S., Büyükgüngör, O., 2008c. One-dimensional silver coordination polymers generated from saccharinate, piperazine and *N,N'*-bis(2-hydroxyethyl)piperazine. *Polyhedron*, 27: 1761–1766.

Zhaoa, X.J., Du, M., Wang, Y., Bu, X.H., 2004. Formation of cobalt(II)–piperazine supramolecular systems under different organic acid mediums: synthesis, characterization and crystal structures. *Journal of Molecular Structure*, 692: 155–161.

To Cite: Güney, S., 2025. Synthesis, Characterization, and Thermal Properties of Cd(II) and Hg(II) Complexes Containing N,N'-bis(2-hydroxyethyl)piperazine and Saccharinate. *MAS Journal of Applied Sciences*, 10(1): 102-109.
DOI: http://dx.doi.org/10.5281/zenodo.15094019.