

Piperazin ve 1-(2-Aminoetil)Piperazin İçeren Karışık Liganlı Cıva(II) Sakkarin Komplekslerinin Sentezi, Spektroskopik ve Yapısal Özellikleri

Synthesis, Spectroscopic, Thermal and Structural Properties of Mixed Ligand Mercury(II) Saccharin Complexes with Piperazine and 1-(2-Aminoethyl)Piperazine

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ÖZET

Sakkarinat (sac) anyonunun piperazin (ppz) ve N-(2-aminoetil)piperazin (aeppz) ile iki yeni Hg(II) kompleksi olan $[\text{Hg}(\text{sac})_2(\text{ppz})]_n$ (1) ve $[\text{Hg}(\text{sac})_2(\text{aeppz})_2]$ (2) sentezlenmiş ve komplekslerin yapıları element analiz, FT-IR, TGA/DTA, UV-Vis, ve manyetik ölçümler ile belirlenmiştir. Kompleksler $[\text{Hg}(\text{sac})_2]$ ile ppz ve aeppz ligandlarının tepkimesi sonucu sentezlenmiştir. Kompleks 1’de sac’ın Hg(II) iyonuna N atomu üzerinden olarak koordine olduğu, ppz ligandının ise N atomları üzerinden iki Hg(II) arasında köprü koordinasyonu gerçekleştirdiği önerilmiştir. Kompleks 2’de ise sac ligandının karbonil O atomu üzerinden tek dişili olarak koordine olduğu, aeppz ligandının ise halka ve aminoetil N atomlarını kullanarak çift dişli ligand olarak davrandığı önerilmiştir. Komplekslerin IR spektrumu, ppz, aeppz ve sac ligandlarının tipik absorpsiyon bantlarını göstermektedir. Kompleks 1’in termal bozunmasında, ilk aşamada ppz ligandının ekzotermik olarak uzaklaşması gerçekleşirken, sac ligandı daha yüksek sıcaklıklarda iki ekzotermik basamakta bozunmakta ve geriye kalan elementel cıva ise buharlaşarak ortamdan ayrılmaktadır. Kompleks 2’nin termal bozunmasında ise ilk aşamada aeppz ligandının biri ekzotermik, diğeri endotermik iki basamakta uzaklaşması gerçekleşirken, sac ligandı ise daha yüksek sıcaklıklarda iki ekzotermik basamakta bozunmaktadır.

Anahtar Kelimeler: Piperazin, 1-(2-aminoetil)piperazin, sakkarin kompleksleri.

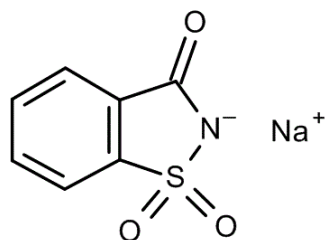
ABSTRACT

Two new Hg(II) complexes of the saccharinate (sac) anion with piperazine (ppz) and N-(2-aminoethyl)piperazine (aeppz), namely $[\text{Hg}(\text{sac})_2(\text{ppz})]_n$ (1) and $[\text{Hg}(\text{sac})_2(\text{aeppz})_2]$ (2), have been synthesized. The structures of these complexes were characterized through various techniques, including elemental analysis, FT-IR spectroscopy, TGA/DTA, UV-Vis spectroscopy, and magnetic susceptibility measurements. The synthesis of the complexes was achieved through the reaction of $[\text{Hg}(\text{sac})_2]$ with the ligands ppz and aeppz. In complex 1, it is suggested that the sac ligand coordinates to the Hg(II) ion through its N atom, while the ppz ligand facilitates bridging coordination between two Hg(II) ions through its N atoms. In complex 2, it is proposed that the sac ligand coordinates in a monodentate manner through its carbonyl O atom, whereas the aeppz ligand acts as a bidentate ligand by utilizing its ring and aminoethyl N atoms. The IR spectrum of the complexes displays the characteristic absorption bands of the ppz, aeppz, and sac ligands. In the thermal decomposition of complex 1, the ppz ligand is exothermically removed in the first stage, while the sac ligand decomposes in two exothermic steps at higher temperatures, leaving elemental mercury to evaporate. In the thermal decomposition of complex 2, one aeppz ligand is removed in two steps, one exothermic and one endothermic, while the sac ligand decomposes in two exothermic stages at higher temperatures.

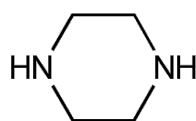
Keywords: Piperazine, 1-(2-aminoethyl)piperazine, Saccharin Complexes.

1. INTRODUCTION

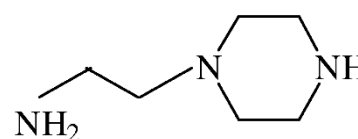
Saccharin is among the most recognized and commonly used artificial sweeteners (Ager et al., 1998). Its imino hydrogen atom is acidic, allowing the molecule to readily convert into the corresponding saccharinate (sac) anion. The sodium salt of saccharin, known as Nasac, is highly soluble in water and is more suitable for use as both a ligand and a sweetener. When Nasac is used as a ligand, the sac anion present in the solution has a negatively charged N atom along with CO and SO₂ groups, allowing it to form either monodentate or bidentate (N, O) coordination through N or O. Additionally, sac can generate more complex polymeric species through the participation of all donor atoms (Baran, 2005). The discovery of anticancer properties in sac complexes has increased interest in these complexes (Ulukaya et al., 2011; Ari et al., 2013; 2014; Al-Jibori et al., 2014).



Sodium Saccharinate



Piperazine



1-(2-Aminoethyl)piperazine

Piperazine derivative compounds are highly interesting ligands due to their excellent bridging abilities. They are commonly used as building blocks for forming coordination polymers (Suen et al., 2002; Ganesan et al., 2004; Zhao et al., 2004; Nolte et al., 2005; Xu et al., 2006). Ppz shows selective binding to various biomolecules of medical significance (Al-Ghorbani et al., 2015; Sharma et al., 2010). Based on this distinctive structure, numerous compounds have been synthesized, demonstrating applications in diverse therapeutic areas, including antifungal, antibacterial, antihistaminic, anticancer, antipsychotic, and antidepressant treatments (Kaur et al., 2022; Limberg et al., 2009; Brito et al., 2019; Aggarwal et al., 2020; Kant et al., 2022). The ppz group also plays a well-known role in medicine as a fundamental component of many commercially available drugs. The importance of piperazines in metal ion-mediated drug delivery has been established (Zhang et al., 2019; Neelakantan et al., 2018).

Our research group has had a long-standing interest in the synthesis and characterization of saccharin metal complexes. In this study, we aimed to synthesize new mixed-ligand mercury(II) saccharinate complexes using ppz and 1-(2-aminoethyl)piperazine (aepz) ligands and to characterize them.

2. MATERIALS AND METHODS

2.1. Materials and Instruments Used

All reagents were acquired from commercial suppliers and were of analytical grade purity. Elemental analyses for carbon, hydrogen, and nitrogen were conducted using a LECO CHNS 932 Elemental Analyzer. The IR spectra were obtained in the range of 4000 to 400 cm⁻¹ using a MATTSON 1000 FT/IR spectrophotometer with KBr pellets. The UV-VIS spectrum was recorded on a Unicam UV2 UV/VIS spectrophotometer, with methanol and ethanol as solvents, in the 200–900 nm range. Thermal analysis curves (TG and DTA) were recorded using Rigaku TG8110 thermal analyzer in a static air environment, with sample sizes ranging from 5 to 10 mg. Magnetic measurements were taken with an MX I Model Sherwood Scientific magnetic susceptibility balance.

2.2. Synthesis

$[\text{Hg}(\text{sac})_2(\text{ppz})]_n$: 1 mmol (0.565 g) of $[\text{Hg}(\text{sac})_2]$ was dissolved in 30 ml of methanol, and a solution prepared by dissolving 2 mmol (0.172 g) of ppz in 10 ml of methanol was added to it. The mixture was stirred on a magnetic stirrer for 1 hour. The complex was obtained in powder form within a few days. Yield: 81%. Decomposition temperature: 176 °C. Calculated values for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_6\text{S}_2\text{Hg}$ (651.08) (%) C, 33.21; H, 2.79; N, 8.60. Found values: C, 32.22; H, 2.21; N, 7.89%.

$[\text{Hg}(\text{sac})_2(\text{aepz})_2]$: 1 mmol (0.565 g) of $[\text{Hg}(\text{sac})_2]$ was dissolved in 30 ml of methanol. Then, 2 mmol (0.258 g) of aepz was added dropwise to the solution, and the mixture was stirred at room temperature for 1 hour. The complex was obtained as a powder. Yield: 85%. Decomposition temperature: 118 °C. Calculated values for $\text{C}_{26}\text{H}_{38}\text{N}_8\text{O}_6\text{S}_2\text{Hg}$ (823.36) (%) C, 37.93; H, 4.65; N, 13.61. Found values: C, 37.90; H, 4.66; N, 13.62%.

3. RESULTS AND DISCUSSION

In the polymeric complex $[\text{Cu}(\text{sac})_2(\text{ppz})(\text{H}_2\text{O})]_n$ synthesized and structurally elucidated by Yılmaz et al. (2008), the Cu(II) ion has a CuN_4O environment formed by four nitrogen atoms from two ppz and two sac ligands and one oxygen atom from an aqua ligand. The sac ligand coordinates monodentately via its negatively charged nitrogen atom, exhibiting the most commonly observed binding mode, while the ppz ligands act as bridging ligands between copper(II) ions through their nitrogen atoms. The $[\text{Hg}(\text{sac})_2(\text{ppz})]_n$ complex is suggested to be polymeric as well, with the Hg(II) ion featuring an HgN_4 environment created by four nitrogen atoms derived from two ppz and two sac ligands. The elemental analysis results for the complex align well with the proposed molecular structure (Figure 1).

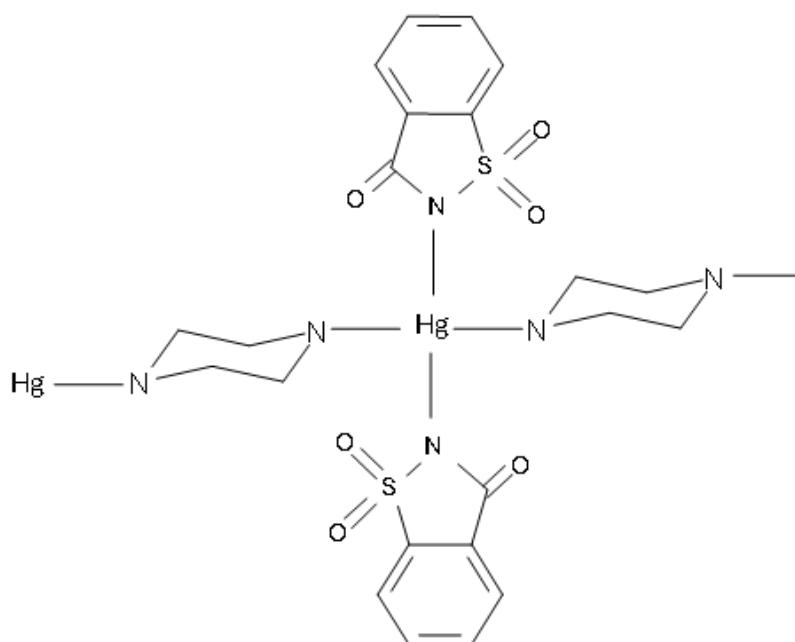


Figure 1. Proposed Molecular Structure of the $[\text{Hg}(\text{sac})_2(\text{ppz})]_n$ Complex

In the complexes $[\text{Ni}(\text{sac})_2(\text{aepz})_2]$ (Güney et al., 2005), $[\text{Cu}(\text{sac})_2(\text{aepz})_2]$ (Yılmaz et al., 2008), $[\text{Zn}(\text{sac})_2(\text{aepz})_2]$, and $[\text{Cd}(\text{sac})_2(\text{aepz})_2]$ (Yılmaz et al., 2005), each metal(II) ion is coordinated by two neutral aepz ligands and two anionic sac ligands. The aepz ligands act as bidentate ligands, coordinating through both their ring nitrogen and aminoethyl nitrogen atoms. In contrast, the sac

ligand coordinates monodentately through its carbonyl oxygen atom, a rarely observed binding mode. The $[\text{Hg}(\text{sac})_2(\text{aep pz})_2]$ complex is proposed to have a similar structure. The elemental analysis results for the complex closely match the calculated values for the proposed molecular structure (Figure 2).

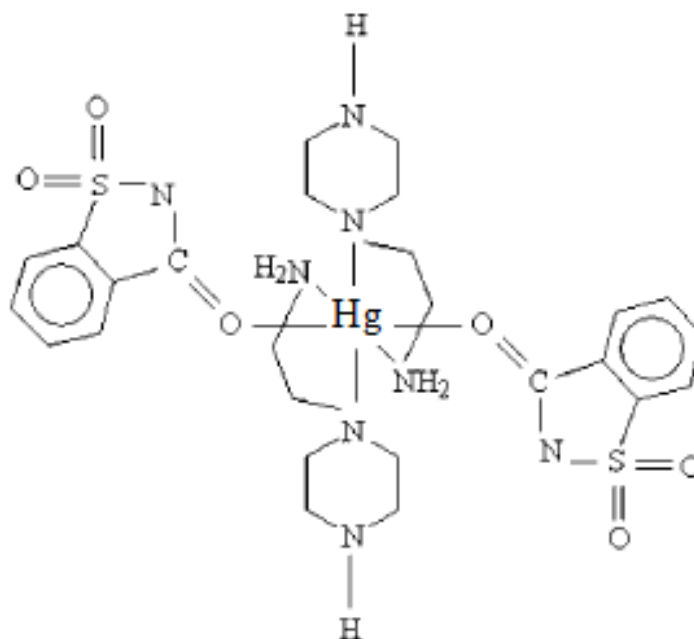


Figure 2. Proposed Molecular Structure of the $[\text{Hg}(\text{sac})_2(\text{aep pz})_2]$

Table 1. IR Spectral Data^a of the Complexes

Assignment	1	2
$\nu(\text{NH})$	3226vs	3325vs; 3298sh
$\nu(\text{CH})$	2920z- 2858z	2945z- 2837z
$\nu(\text{C=O})$	1651vs, 1624vs	1651vs; 1626vs
$\nu_{\text{asim}}(\text{SO}_2)$	1269vs	1286vs
$\nu_{\text{sim}}(\text{SO}_2)$	1153vs	1170vs
$\nu_{\text{sim}}(\text{CNS})$	1336s	1335s
$\nu_{\text{asim}}(\text{CNS})$	951vs	968vs

^aFrequencies in cm^{-1} . w= weak; vs= very strong; s= strong; m= medium; sh=shoulder.

The significant stretching vibrations obtained from the FT-IR spectra of the complexes are presented in Table 1. While the N–H stretching vibration of free ppz is observed in the $3475\text{--}3415\text{ cm}^{-1}$ range, these vibrations are detected in the $3226\text{--}3325\text{ cm}^{-1}$ range in the complexes. This shift can be explained by the strong hydrogen bonds formed between NH groups. Bands arising from C–H vibrations are observed in the approximate range of $2837\text{--}2945\text{ cm}^{-1}$.

In the $[\text{Hg}(\text{sac})_2(\text{ppz})]_n$ complex, the characteristic stretching vibration of the C=O group of the sac ligand appears at $1624\text{--}1651\text{ cm}^{-1}$, which is close to the value observed for the $\text{Hg}(\text{sac})_2$ complex, where sac coordinates to the Hg(II) ion via the N atom. This suggests that in the $[\text{Hg}(\text{sac})_2(\text{ppz})]_n$ complex, sac coordinates through its N atom.

For complexes $[\text{M}(\text{sac})_2(\text{aeppz})_2]$ ($\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}),$ and $\text{Zn}(\text{II})$), where the sac ligand coordinates via the O atom of its CO group, the C=O stretching vibrations are observed at lower frequencies compared to $[\text{M}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ complexes, where sac coordinates through the N atom. This shift is attributed to coordination through the O atom of the CO group (Yılmaz et al., 2008; Güney et al., 2005; Yılmaz et al., 2005). However, in the $[\text{Cd}(\text{sac})_2(\text{aeppz})_2]$ complex, where this shift is not observed, it has also been determined that sac coordinates via the O atom of the CO group (Yılmaz et al., 2005). Therefore, it is proposed that in the $[\text{Hg}(\text{sac})_2(\text{aeppz})_2]$ complex, no shift is observed in the C=O stretching vibration, suggesting coordination through the O atom of the CO group.

The asymmetric stretching vibrations of SO_2 in the complexes are detected below 1300 cm^{-1} , likely as a result of the participation of the SO_2 group in hydrogen bonding.

Strong absorption bands are observed in the UV-Vis spectra of the complexes' solutions in methanol below 300 nm. These bands are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in ppz, aeppz, and sac ligands. As expected, no peaks are observed in the visible region for the complexes.

Magnetic moment measurements at room temperature indicate that the complexes are diamagnetic, as anticipated.

The thermal properties of the complexes were studied with DTA and TG in the temperature range of $20\text{--}1000\text{ }^\circ\text{C}$ in a static air atmosphere. The $[\text{Hg}(\text{sac})_2(\text{ppz})]_n$ complex is thermally stable up to $176\text{ }^\circ\text{C}$, with the ppz ligand dissociating in the first stage (found: 11.9%, calculated: 13.2%). After the exothermic dissociation of the ppz ligand in the $176\text{--}216\text{ }^\circ\text{C}$ range, the metal saccharinates decompose in two exothermic stages in the $216\text{--}520\text{ }^\circ\text{C}$ range (found: 58.0%, calculated: 56.0%). Elemental mercury formed at this temperature volatilizes and leaves the system. The $[\text{Hg}(\text{sac})_2(\text{aeppz})_2]$ complex decomposes in the $118\text{--}336\text{ }^\circ\text{C}$ range, losing two moles of aeppz ligand in two stages, one endothermic and the other exothermic (found: 31.1%, calculated: 31.4%). After the aeppz ligands are removed, two moles of sac ligand are released in two exothermic stages in the $336\text{--}597\text{ }^\circ\text{C}$ range (found: 45.4%, calculated: 44.2%).

4. CONCLUSIONS AND RECOMMENDATIONS

In this research, two novel mixed-ligand Hg(II)-sac complexes featuring ppz and aeppz were synthesized, and their structures were characterized through elemental analysis, UV-VIS and IR spectroscopy, magnetic susceptibility measurements, , as well as thermal analysis techniques. The complexes were obtained with high yield and exhibit stability in air. Despite attempts under various solvents and conditions, single crystals could not be obtained; however, the structures of these complexes could be further investigated in detail by producing single crystals under optimized conditions. Additionally, the biological activities and electrochemical properties of these complexes could be explored as potential research areas.

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