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Mikrodalga Destekli Yeni Heterosiklik Schiff Bazlarının Sentezi ve Saldeta/Salpyr Metal Komplekslerinin İncelenmesi

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Makale Bilgisi

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Heterosiklik,
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Schiff baz,
Metal kompleks .

ÖZET

Literatür çalışmalarından elde edilen 2-(4-aminofenil)-1H-benzimidazol çıkış maddesi olarak kullanıldı. Elde edilen bileşik Gentisaldehyde reaksiyona girerek, 2-(((4-(1H-benzimidazolyl)phenyl)imino)methyl)benzene-1,4-diol (25SAPBZ) elde edildi. (25SAPBZ) ligandına etanolde çözülmüş [Fe(saldeta/salpyr)Cl] kompleksi ilave edilerek oksijen köprülü kompleksler elde edildi. Elde edilen ligandların FTIR, elementel analizleri, $^{1}H/^{13}C$-NMR ve kompleks yapıların FTIR, elementel analizleri, manyetik süssebtibilite ölçümleri ile yapılar aydınlatıldı.

The Synthesis of Novel Heterocyclic Schiff Bases Microwave Assisted and Investigation of Saldeta/Salpyr Metal Complexes

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ABSTRACT

2-(4-aminophenyl)-1H-benzimidazole obtained from literature studies was used as the outlet agent. The resulting compound reacted with Gentisaldehyde to get 2-(((4-(1H-benzoimidazoleyl)phenyl)imino)methyl)benzene-1,4-diol (25SAPBZ). Oxygen-bridging complexes were obtained by adding the [Fe(saldeta/salpyr)Cl] complex dissolved in ethanol to the (25SAPBZ) ligand. FTIR, elemental analyses, $^{1}H/^{13}C$-NMR and FTIR of complex structures, elemental analyses, and magnetic susceptibility measurements of the obtained ligands were elucidated.

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INTRODUCTION

Heterocyclic compounds constitute an important class of compounds because they function in biological systems [1]. Natural compounds and drugs contain heterocyclic rings, for which an important part of the scientific studies in organic and inorganic chemistry are those related to heterocyclic compounds [2]. In heterocyclic compounds, one or more of the hetero atoms such as oxygen, nitrogen, and sulfur are found displaced by carbon in the ring [3]. Benzimidazoles are also included in this group, this ring system has a wide range of uses in industry, medicine and pharmaceutical chemistry as it is found in the structure of many substances [4]. The fact that nitrogen atoms in its structure are easily subbalanced under controlled conditions has led researchers to study benzimidazole compounds, especially in recent years [5]. This ring system is of industrial importance as it is found in the structure of many substances such as drugs and dye complexes [6]. Benzimidazoles are also included in this group, this ring system has a wide range of uses in industry, medicine and pharmaceutical chemistry as it is found in the structure of many substances [5]. The fact that nitrogen atoms in its structure are easily sublocated under controlled conditions has led researchers to study benzimidazole compounds, especially in recent years [7, 8]. Therefore, heterocyclic compounds have gained importance in scientific studies due to the prominence of ligand properties in scientific studies in coordination chemistry [9]. The most commonly used method of synthesis of benzimidazole is the reaction of o-phenylenediamines with a solution of 4N HCl or PPA with carboxylic acid or acid anhydride [6]. This method is known as Phillips' benzimidazole synthesis [10].

A lot of research has been done on compounds, also known as Schiff bases and contain a C=N group. Such compounds are important class ligands in coordination chemistry, which have wide applications in different fields [11, 12]. The use of Schiff complexes in the pharmaceutical industry is increasing rapidly [13, 14]. It has been determined that it has antimicrobial activities, especially against some types of bacteria, fungi and tumors. It has been determined that the biological activity of Benzimidazole Schiff bases is mainly related to azomethin bonds [15]. In addition, a Benzimidazole Schiff base metal complexes, which is an anticancer agent for the role of metal complexes, was synthesized [6].

MATERIALS AND METHODS

Elemental analyses (C, H, N) were performed using a Leco, CHNS-932 model analyser. ^{1}H NMR spectra were recorded by the Varian, 400 M spectrometer at room temperature. FTIR spectra were recorded using a Bruker Vertex 70 with Universal ATR Polarization Accessory. Magnetic susceptibilities of the metal samples were measured at 296 K using a Sherwood Scientific MX Gouy magnetic susceptibility apparatus (Gouy method) with $Hg[Co(SCN)_4]$ as a calibration by the constant magnetic field.

Synthesis of 2-(4-Aminophenyl)-1H-benzimidazole (4APBZ)

The (4APBZ) was prepared according to the literature method [10] (Figure 1).

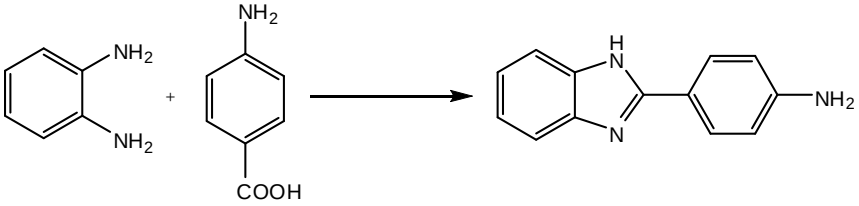

Figure 1
Synthesis of 4-Aminophenylbenzimidazole.

2-(((4-(1H-benzimidazolyl)phenyl)imino)methyl)benzene-1,4-diol (25SAPBZ)

4APBZ (5.00 g, 24 mmol) and Gentisaldehyde (4.00 g. 29 mmol) obtained by the method in the literature were dissolved by heating in ethanol (35 mL) 0.4 N methanol HCl was added as a catalyst and 3-Aº M.S. were added as a desiccant. The mixture was stirred under the back cooler for about 6 hours. Then the solvent of the mixture was evaporated under the evaporator. Recrystallized from ethanol and filtered and dried under vacuum. (25SAPBZ) yield: (55%); M.P.:294 °C; $C_{20}H_{15}N_3O_2$, Found: C, 76.83; H, 4.63; N, 12.72%). Calculated: C, 72.94; H, 4.59; N, 12.76; %). FTIR (cm^{-1}): 2853 (O-H), 2598 (N-H), 2411 (C-H), 1702 (CH=N), 1608 (C=C), 1537 (C=N), 1242 (C-O_{Phen}). ^{1}H NMR (400 MHz, DMSO-d_6) 12.55 (s, H, N-H), 11.26 (s, H, O-H), 8.86 (s, H, CH=N), 8.26-8.19 (d, 2H, C-H_{ar}), 7.23 (t, H, C-H_{ar}), 7.98 (t, H, C-$H_{ar.}$), 7.78-7.66 (d, 2H, C-$H_{ar.}$), 6.75-6.76 (d, 2H, C-$H_{ar.}$), 6.84-7.08 (m, 3H, C-$H_{ar.}$), 5.26 (s, H, O-H). ^{13}C NMR (100 MHz, DMSO–d_6): 195.16, 174,46, 172.45, 163.24, 159.48, 151.41, 149.42, 150.73, 139.51, 130.12, 128.55, 123.39, 120.11, 113.74, 115.23 (Figure 2).

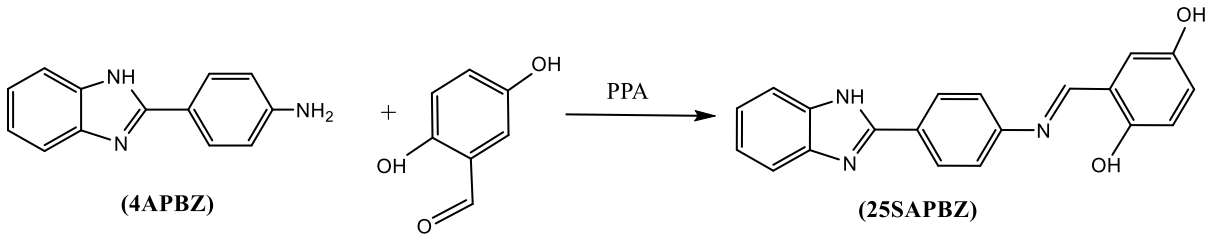

Figure 2
2-(((4-(1H-benzoimidazolyl)phenyl)imino)methyl)benzene-1,4-diol

Synthesis of [Fe(saldeta/salpyr)Cl] complexes

Saldeta (5 mmol, 1.35 g)/salpyr (5 mmol, 1.60 g) is dissolved in 20 mL of methanol under a refrigerant. Anhydrous $FeCl_3$ was dissolved in 20 mL of methanol (5 mmol, 1.62 g) and added dropwise to the prepared solution. Then, the solution was boiled at 50 ºC for 10 minutes. Triethylamine was added to the mixture (10 mmol, 1.5 ml) and mixed under a refrigerant for 1 h and cooled to obtain a black precipitate. After the precipitate was filtered, it was washed in methanol and diethyl ether and dried in a vacuum desiccator. For metals, anhydrous $FeCl_3$ was used, respectively. The resulting [Fe(saldeta/salpyr)Cl] complex is brown M.P.:>300 ºC (Figure 3) [5, 12].

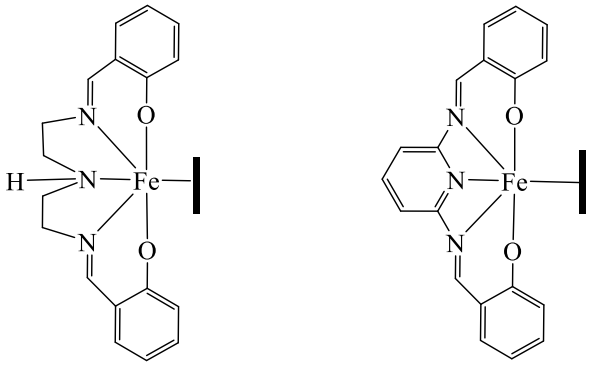

Figure 3
Synthesis of the metal complex of saldeta and salpyr

Synthesis of 2-(((4-(1H-benzoimidazolyl)phenyl)imino)methyl)benzene-1,4-diol (25SAPBZ) [Fe(saldeta/salpyr)Cl] complexes

2-(((4-(1H-benzoimidazolyl)phenyl)imino)methyl)benzene-1,4-diol (25SAPBZ) (1 mmol, 0.33 g) was suspended in 20 mL ethanol in a 100 mL balloon, and (2 mmol 0.75/0.85 g) [Fe(saldeta/salpyr)Cl]

and 20 mL ethanol solution were added to it, respectively. Boiled under a back cooler for 8 h at around 80 ºC. The solvent was evaporated by half and allowed to cool (under room conditions). Then half the water was added, left for a day, filtered in a vacuum and dried in an oven at 105 ºC. Yield: (67%); M.P.: >300 °C; $C_{56}H_{50}N_9O_6Fe_2$, FTIR (cm^{-1}): 2944 (N-H), 2868 (C-H), 1672, 1598 (C=N), 1517 (C=N), 1176 (C-O_{Phen}). $C_{59}H_{42}N_9O_6Fe_2$, FTIR (cm^{-1}): 2853 (C-H), 1665, 1595, 1590 (C=N), 1517 (C=N), 1176 (C-O_{Phen}) (Figure 4).

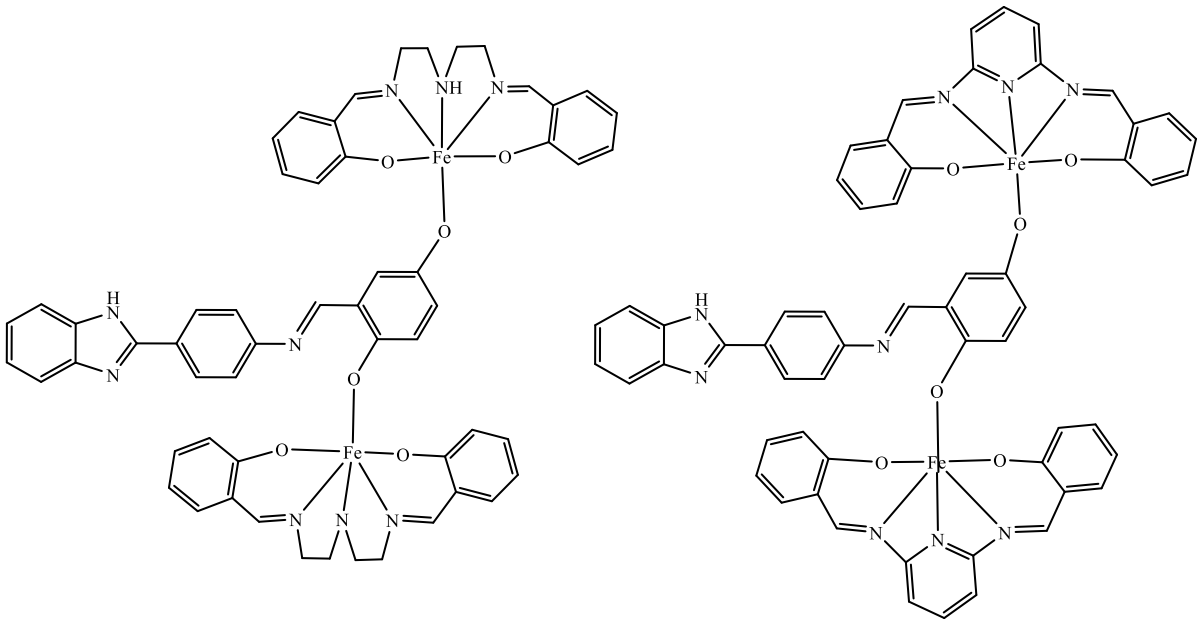

Figure 4
2-(((4-(1H-benzoimidazolyl)phenyl)imino)methyl)benzene-1,4-diol (25SAPBZ) [{Fe(saldeta/salpyr)Cl}]

RESULTS AND DISCUSSION

(4APBZ) was used as the starting material in this study. The melting point of the obtained (4APBZ) was found to be 213-214 ºC as stated in the literature. (4APBZ) was obtained as a result of condensation of this amine group compound with Gentisaldehyde under acid catalysis using the methods given in the literature, and benzimidazole-Schiff base compound (25SAPBZ) was obtained. Ethanol-dissolved [Fe(saldeta/salpyr)Cl] ligand complexes were added to the Benzimidazole-Schiff base ligand to obtain single oxygen-coordinated complexes. As a result, it was the (25SAPBZ) ligand, and the Fe(III), saldeta, and salpyr complexes of these ligands and complexes were isolated. The ligan of the synthesized starting material and ligands were elucidated using ^{1}H NMR, ^{13}C NMR FTIR, and Elemental Analysis. [Fe(saldeta/salpyr)Cl] was added to ligand complexes to obtain single oxygen-coordinated dipodal complexes. The structures of the obtained complex compounds were elucidated by elemental analysis, FTIR spectroscopy, and magnetic susceptibility.

When the ^{1}H NMR studies of ligands were examined, it was observed that NH protons corresponding to NH/OH protons occurred between 12.55/11.25 ppm, respectively, when NH protons in the (25SAPBZ) benzimidazole ring and OH protons in the salicidin ring were examined. It has been observed that it shifts to the lower field by giving a large singlet because it can make intramolecular hydrogen bonds with OH protons and with the effect of electronegativity. In addition, chemical shift values were observed between 8.87 ppm belonging to CH=N aliphatic groups.

FTIR spectra of the synthesized compounds were obtained. FTIR spectral data of the benzimidazole-Schiff base ligand and their metal complexes are given separately in the experimental section. When we examine these values;

The aldehyde found in the starting material of the (25SAPBZ) ligand was observed as C=O at 1702 cm^{-1} and CH=N at 1701 cm^{-1}, respectively. In addition, NH_2 and C=O vibrations at 3340 cm^{-1} from amine compounds were lost. Instead of these vibrations, Schiff base CH=N 1701 cm^{-1} bands were observed.

FTIR bands of coordination compounds obtained from [Fe(saldeta/salpyr)Cl] dissolved in ethanol with 2-(((4-(1H-benzimidazolyl)phenyl)imino)methyl)benzene-1,4-diol ligand were taken and thought to have been synthesized. When the FTIR bands were examined, it was observed that the OH groups observed at 2852 cm^{-1} disappeared after the formation of complex structures in the IR bands. It has been stated in the literature that M-O and M-N bonds are at 655 and 564 cm^{-1}, respectively, considering that they are also bonded in metal complexes [4, 16].

2-(((4-(1H-benzoimidazolyl)phenyl)imino)methyl)benzene-1,4-diol ligand [Fe(saldeta/salpyr)Cl] complexes were observed to have high spin at magnetic susceptibility values measured in single oxygen-coordinated complexes. The [Fe(saldeta/salpyr)Cl] complexes of the benzimidazole-Schiff base ligands in the d^5 ($t_{2g}^3e_g^2$) metal ion arrangement have paramagnetic and high spin values between 5.41-5.25 BM, respectively. According to these results, it is thought that the single oxygen-coordinated complexes are octahedral structure with Fe(III) sp^3d^2 hybridization, unstable structure with external d complex features.

Although there is literature on Benzimidazole-Schiff base ligands, very few studies have been found on Benzimidazole-Schiff base complexes and there is not enough information about the properties of these complexes. The resulting Benzimidazole-Schiff base complexes are soluble in DMSO, THF and DMF. During the formation of the complex, the dissolution and complexation reaction takes place one after the other and it is understood that the complexation is completed with the color change [9]

As a result, benzimidazole-Schiff base ligand and their [Fe(saldeta/salpyr)Cl] complexes were synthesized in this study. Their structures were tried to be elucidated by ^1H NMR, ^{13}C NMR, FTIR, magnetic susceptibility, and elemental analysis methods [17].

Ethical Statement

I declare that I have no other relevant conflict of interest. No writing assistance was utilized in the production of this manuscript.

Conflict of Interest

The author has no conflicts of interest to disclose for this study.

Author Contributions

Research Design (CRediT 1) Z.E.K (%100)
Data Collection (CRediT 2) Z.E.K (%100)
Research - Data Analysis - Validation (CRediT 3-4-6-11) Z.E.K (%100)
Writing the Article (CRediT 12-13) Z.E.K (%100)
Revision and Improvement of the Text (CRediT 14) Z.E.K (%100)

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