Düzce University Journal of Science & Technology

Research Article

Synthesis and Characterization of Amido-Thiourea Based *p-tert-*butylcalix[4]arene Compound and Investigation of Transition Metal Complex Properties

Sevil SÖYLEYİCİ [a,*]

[a] *Kimya Bölümü, Fen Fakültesi, Pamukkale Üniversitesi, Denizli, TÜRKİYE*
* *Sorumlu yazarın e-posta adresi: szencir@pau.edu.tr*

ABSTRACT

In host-guest complexes, the compatibility of the size and shape of the host cavity and the guest molecule is essential in the formation of the host-guest complex. Considered third-generation macrocyclic hosts, calixarenes attract the attention of researchers in supramolecular chemistry as they offer a wide range of applications in fields such as biocatalysis, enzyme analysis, pharmaceuticals, and biosensing. The synthesis of host molecules for anionic and cationic guest compounds has a very important place in coordination chemistry. Calixarenes are known as one of the important types of supramolecular compounds and are an important class of easily synthesized compounds that can act as a suitable receptors for cations, anions, and organic molecules. When calixarene compounds, which have an important place in host-guest chemistry, are derivatized appropriately, the coordination ability of the molecule against metal cations increases. These derivatizations gained importance due to the sensory properties of the molecule, and different studies were started considering that a larger cavity and functional group are required for more guest molecules. In this study, a new ligand of 1,3-disubstituted p-tert-butylcalix[4]arene derivative with increased donor atomic number with amide and thiourea groups in its structure was synthesized. Co(II), Ni(II), Cu(II), and Zn(II) complexes were synthesized with the compound and the structures of the compounds were characterized by UV-vis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectrometry.

Keywords: p-tert-butylcalix[4]arene, Transition Metal Complex, Amide, Thiourea

Amido-Tiyoüre Bazlı *p-tert*-bütilkaliks[4]aren Bileşiğinin Sentezi, Karakterizasyonu ve Geçiş Metal Kompleks Özelliklerinin Araştırılması

Öz

Konak-konuk kompleks bileşiklerinde, konakçı boşluğunun ve konuk molekülün boyut ve şeklinin uyumluluğu, konak-konuk kompleksinin oluşumunda esastır. Üçüncü nesil makrosiklik konakçılar olarak kabul edilen kaliksarenler, biyokataliz, enzim analizi, farmasötikler ve biyoalgılama gibi alanlarda geniş bir uygulama yelpazesi sunmaları nedeniyle supramoleküler kimya araştırmacılarının ilgisini çekmektedir. Koordinasyon kimyasında anyonik ve katyonik misafir bileşikler için ev sahibi moleküllerin sentezi oldukça önemli yer tutmaktadır. Kaliksareneler supramoleküler bileşiklerin önemli türlerinden biri olarak bilinmekte ve katyon, anyon ve organik moleküller için uygun bir reseptör olarak görev alabilen ve kolay sentezlenebilen önemli bir bileşik sınıfıdır. Ev sahibi-konuk kimyasında önemli bir yeri olan kaliksaren bileşikleri uygun şekilde türevlendirildiklerinde, molekülün metal katyonlarına karşı koordinasyon yeteneği artmaktadır. Bu türevlendirmeler molekülün sensör özelliği göstermesi ile önem kazanmış ve daha çok misafir molekülü için daha büyük kavite ve fonksiyonel grup gerektiği düşünülerek farklı çalışmalar başlamıştır. Bu çalışmada da katyon seçimliliği arttırılmış, yapısında amit grupları taşıyan 1,3-disübstitüe kaliks[4]aren türevi bileşik ve bu bileşiğin Co(II), Ni(II), Cu(II) ve Zn(II)

kompleksleri sentezlenerek bileşiklerin yapıları UV-vis, FT-IR, ^{1}H-NMR, ^{13}C-NMR kütle spektrometresi ile aydınlatılmıştır.

Anahtar Kelimeler: *p-tert-butilkaliks[4]aren, Geçiş Metal Kompleksi, Amit, Tiyoüre*

I. INTRODUCTION

Calixarenes are defined as third-generation compounds after crown ethers and cyclodextrins, which are referred to as first and second-generation compounds in supramolecular chemistry. They belong to the metacyclophan class of compounds and consist of phenol and methylene units, similar to cyclodextrins which consist of glucose units, and crown ethers which consist of ethylene units. Calixarene compounds are macromolecules with flexible structural properties formed as a result of the reaction between formaldehyde and phenol in a base-catalyzed environment. They contain two regions suitable for derivatization, called the upper (*tert*-butyl bonded region) and lower rim (the region where the -OH group is attached). The contribution of *tert*-butyl groups to the solubility of the compound should not be ignored [1]–[3]. The phenolic oxygen portion functionalized with active groups to bind many different species is used for the purpose [4]–[6]. Many calixarene derivatives are encountered in studies of receptors sensitive to changing their spectroscopic properties, especially with the group it interacts with [7]–[9]. Coordination chemistry is widely used in the synthesis of organic structures containing metal cations, which have many application areas and properties [10]–[17]. In many published studies, the anion and cation selectivity of calixarene derivatives was investigated. Although it is tried to focus on the metal-ligand coordination preferences of the synthesized compounds, this seems to be limited. It is seen that metal coordination ligands with a certain geometry are effective to a certain extent, in which there is a binding based on supramolecular interactions instead of strong coordination bonds. Calixarene-derived ligands offer a wide spectrum for designing reagents with such metal selectivity. In the literature, there are compounds derived from the phenolic hydroxy region to include amide groups, and mostly metal extraction studies have been carried out [7]–[9], [18]–[21]. In this study, a new *p-tert*-butyl calix[4]arene derivative with the added sulfur group was synthesized, in addition to similar structures synthesized in the literature [14]-[15]. Instead of investigating the metal selectivity of this compound, its complexes were synthesized with some 2+ charged transition metal cations and characterized by spectroscopic methods.

II. MATERIALS AND METHODS

A. EXPERIMENTAL

Melting point determinations were made and verified with an Electrothermal IA9100) device. ^{1}H-NMR spectra were taken with Varian UNITY INOVA 500MHz NMR and TMS was used as standard. Chemical shift values (δ) in the NMR spectrum are expressed in ppm. IR spectra were taken as KBr discs from the FT-IR (Perkin Elmer 60X FT-IR spectrophotometer. UV spectra were taken on a UV-vis Shimadzu UV-1601 UV-visible. Mass spectra were taken (Bruker Microflex LT MALDI-TOF MS Spectrometer) and elemental analysis LECO CHNS 932 analyzer, DTA-TG (Shimadzu DTG-60H), and magnetic susceptibility (Sherwood Scientific). All chemicals were purchased from Merck, Fluka, and Carlo Erba company and were used without further purifications.

A. 1. Synthesis Of Calix[4]arene Derivatives

A.1.1. Synthesis Of Compound (2)

9.8 g (0.023 mol) *p-tert*-butylcalix[4]arene, 3.5 g (0.026 mol) K_2CO_3, and 300 mL dry acetonitrile were added to a 250 mL two-necked flask. 5.7 mL of ethyl bromoacetate was added to the mixture and it was boiled under reflux for 24 hours. The mixture was evaporated to dryness. The remaining material in the flask was removed by dissolving it with dichloromethane. The dichloromethane phase was washed twice with water and once with brine to be taken into the flask. Anhydrous $MgSO_4$ was added and left to stand for one day. The organic phase was filtered and its solvent was evaporated. Crystallized from chloroform and methanol [24]. Yield: 10,36 g (%78), m.p: 175-177 ºC, FT-IR v_{max}(KBr)/cm^{-1}: 3427 (OH streching), 1753 (C=O streching), ^{1}H-NMR δ_H (500 MHz, CDCl$_3$, 298 K): 1.28 (t, 6H, -CH$_3$), (1.37 (s, 18H, -CH$_3$), 1.32 (s, 18H, -CH$_3$), 3.44 (d, J = 13 Hz, 4H, ArCH$_2$Ar), 4.25 (q, 4H, O-CH$_2$), 4.35 (d, J = 13 Hz, 4H, ArCH$_2$Ar), 4.85 (s, 4H, CH$_2$-C=O), 6.65-7.15 (m, 8 H, ArH), 7.69 (s, 2H, ArOH).

A.1.2. Synthesis of Compound (3)

2 g (3.35.10^{-3} mol) diester *p-tert*-butylcalix[4]arene, which was placed in a single-necked 100 mL flask, was added and mixed with 50 mL of methanol-toluene (1:1). 5 mL of hydrazine hydrate was added and the reaction mixture was heated in the oil bath at 40 °C. After one hour the white solid was precipitated. The cooled mixture was evaporated without filtration. 25 mL of water and 15 mL of methanol were added to the white solid and the resulting white precipitate was filtered and dried [22]. The ptoduct was used with any purification process. Yield: %90, m.p: 263-265ºC, FT-IR $_{vmax}$(KBr)/cm^{-1}: 3313 (OH streching), 1664 (C=O streching), ^{1}H-NMR δ_H (500 MHz, DMSO-d$_6$, 298 K): 1.36 (s, 18H, -CH$_3$), 1.32 (s, 18H, -CH$_3$), 3.47 (d, 4H, ArCH$_2$Ar), 4.21 (d, 4H, ArCH$_2$Ar), 4.80 (br. 4H, NH$_2$), 6.58-7.16 (m, 8H, ArH), 8.28 (s, 2H, NH-NH$_2$), 9.51 (s, 2H, ArOH). MALDI-TOF-MS (m/z) = 913 [M$^+$+ H$^+$+Toluen]

A.1.3. Synthesis of Compound (4)

Reaction of compound **3** with 4-nitroisothiocyanate under inert atmosphere with dry CH$_2$Cl$_2$ at room temperature overnight gave compound **4** as described in the literature [21], [22]. Yield:%52, m.p: 237-239ºC, C$_{46}$H$_{40}$N$_8$O$_{10}$S$_2$, $_{vmax}$(KBr)/cm^{-1}: 3398 (-OH), 3359 (-NH), 1656 (C=O), 1591 (N-O), 735 (C=S), ^{1}H-NMR δ_H (500 MHz, DMSO-d$_6$, 298 K): 1,36 (s, 18H, -CH$_3$), 1,39 (s, 18H, -CH$_3$), 3.49 (d, J = 13.4 Hz, 4H, ArCH$_2$Ar), 4.26 (d, J = 13.4 Hz, 4H, ArCH$_2$Ar), 4.83 (s, 4H, OCH$_2$), 7.06-7.12 (m, 8H, ArH), 7.26 (d, J= 9.2, 4H, ArH-nitrophenyl), 7.74 (d, J= 9.2, 4H, ArH-nitrophenyl), 8.29 (s, 2H, OH), 8.77 (br, 2H, CONH-amide), 9.64 (s, 2H, NH thiourea), 10.12 (s, 2H, NH thiourea) ^{13}C-NMR (100 MHz, DMSO-d$_6$): 155.3, 153.2, 147.5, 140.2, 136.2, 135.5, 129.4, 127.8, 126.3,123.6, 122.1,120.0, 116.7,114.9, 75.3, 33.2, 31.5. MALDI-TOF-MS (m/z) = 1154 [M+ H$^+$]

A.1.4. Synthesis of Metal Complexes

Compound **4** (0.57 g, 1.00 mmol) was dissolved in DMF (20 mL) by heating and placed in a reaction flask. To this solution, 1.00 mmol metal salt (metal (II) acetates were used) solution in 15 mL DMF was added dropwise and mixed. The mixture was heated without reflux until precipitation was occurred. The resulting colored product was left to stand at room temperature overnight and filtered. It was washed with water, ethanol and dried.
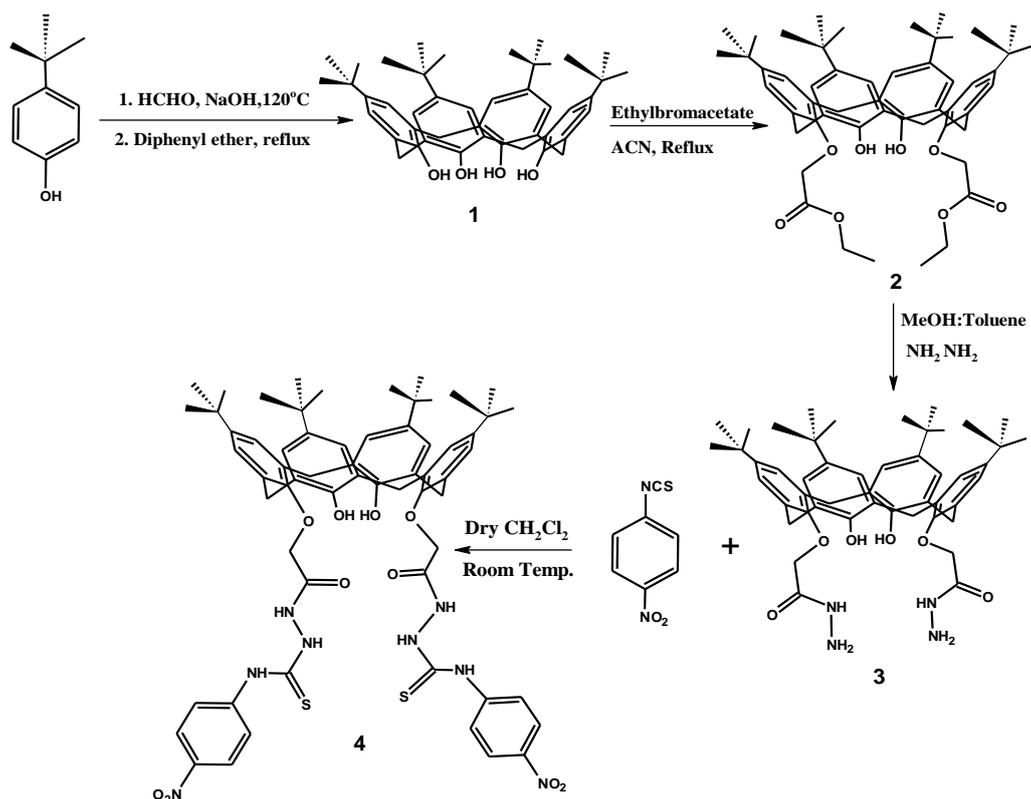
Figure 1. *The synthetic procedure of ligand* ***4***

III. RESULTS AND DISCUSSION

In this study, 1,3-disubstituted p-tert-butylcalix[4]arene and Co(II), Ni(II), Cu(II), and Zn(II) complexes were synthesized. Similar structures have been synthesized before and extraction studies have been carried out with these compounds. Unlike other derivatives, compound **4** has a sulfur donor group in its structure. The structures of the synthesized compounds were characterized by UV-vis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectrometry, and complex synthesis was performed differently. Since the compound is best dissolved in DMF solvent, studies have been done in this solvent environment. The physical data of compound **4** and complexes are given in Table 1.

Table 1*. The physical data of ligands and complexes*

Compound	Formula	M.A (g/mol)	Color	μ_{eff} (B.M)	Elemental Analysis, Calculated (Found) %			
					C	H	N	S
4	$C_{62}H_{72}N_8O_{10}S_2$	1153.42	Beige	-	64.50 (64.66)	6.24 (6.69)	9.71 (11.51)	5.54 (6.58)
[Co(4)(H$_2$O)$_2$]	$CoC_{62}H_{74}N_8O_{12}S_2$	1246.36	Dark brown	4,52	59.69 (56.39)	5.94 (6,57)	8.98 (10.53)	5.13 (6.02)
[Ni(4)(H$_2$O)$_2$]	$NiC_{72}H_{74}N_8O_{12}S_2$	1246.12	Brown	3,20	59.70 (56.40)	5.93 (4,57)	8.98 (10.52)	5.12 (6.01)
[Cu(4)(H$_2$O)$_2$]	$CuC_{72}H_{74}N_8O_{12}S_2$	1250.98	Dark Green	1,74	59.47 (56.15)	5.91 (4.56)	8.95 (10.48)	6,17 (5,99)
[Zn(4)(H$_2$O)$_2$]	$ZnC_{72}H_{74}N_8O_{12}S_2$	1252.82	Light Brown	-	59.38 (56.05)	5.90 (4.55)	8.94 (10.46)	5.11 (5.98)

The characteristic IR peaks of **4** in the spectrum are the peaks of NH-C=O, C=S, and O-H stretching vibrations. Other peaks are C=C and C=O stretching vibrations, aliphatic C-H, aromatic C-H and -NO$_2$ stretching vibrations. In the IR spectrum of the ligand, the stretching vibration of the phenolic –OH group is seen at 3398 cm^{-1}, and the NH-C=O stretching vibration peak of the amide group is seen as a broad peak at 3359 and a sharp peak at 1656 cm^{-1}. The peaks of aromatic and aliphatic C-H stretching vibrations were observed at 3052 cm^{-1} and 2912 cm^{-1}, respectively. -NO$_2$ stretching vibration was observed at 1591 cm^{-1} and C=S stretching vibration was observed at 735 cm^{-1} (Table 2). These bands support the completion of the ligand formation reaction and the results are in agreement with the values given in the literature [25]. The most significant changes in the IR spectra of the metal complexes were observed in the stretching vibrations of the phenolic –OH of the *p-tert*-butylcalix[4]arene and the NH-C=O of the amide group. During the formation of the metal complex of the ligand, the vibration frequency of the amide group -NH-C=O and the strong band observed at 1254 cm^{-1}, which is characteristic of the phenolic C-O stretching vibration in the ligand are both weakened in complex structures and shifted to the high-frequency region as high as 30-35 cm^{-1}. The absence of a significant change in the C=S frequency value indicates that sulfur was not included as a donor atom in the complex formation. This shift shows that deprotonated phenolic oxygen enters coordination with metal ions during the formation of the complex [26], [27]. FT-IR spectrum of compound **4** and Zn^{2+} complex are given in Figure **2**.
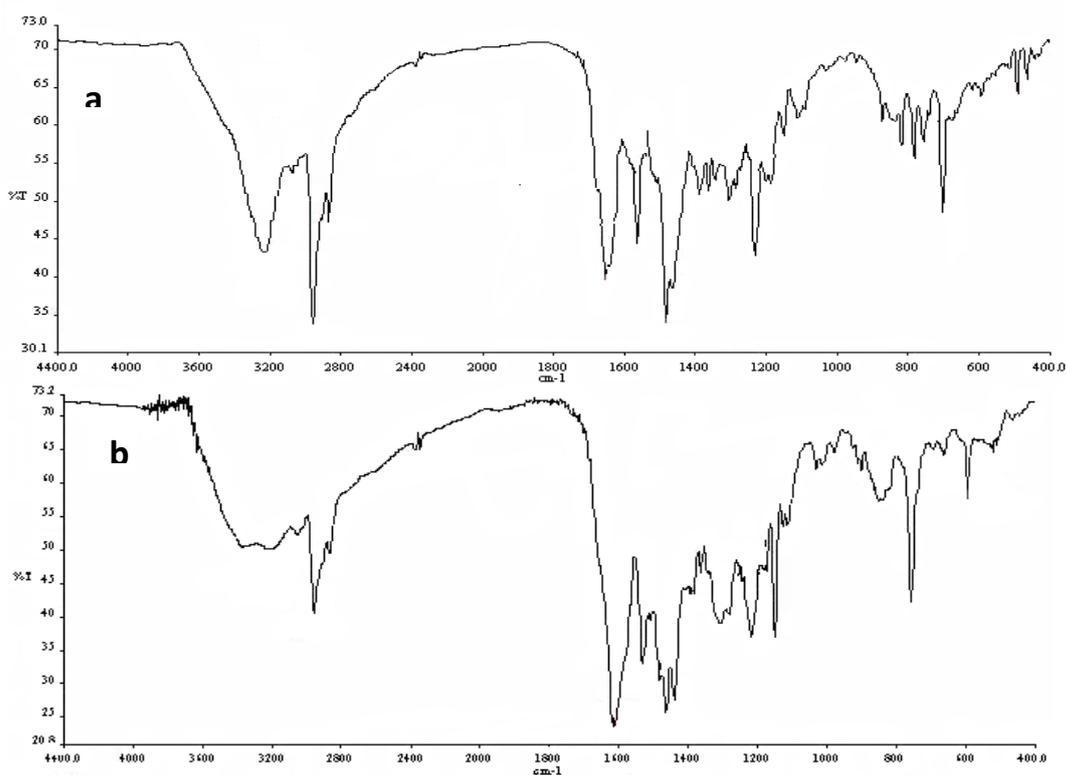

Figure 2. *FT-IR spectra of **a**: compound **4**, **b**: [Zn(**4**)(H$_2$O)$_2$]*

Table 2. *Characteristic IR spectrum data of ligand and complexes*

Compound	ν(-OH) (cm^{-1})	ν(H$_2$O) (cm^{-1})	ν(NH-C=O) (cm^{-1})	ν(-NO$_2$) (cm^{-1})	ν(C-O) (cm^{-1})	ν(C=S) (cm^{-1})	ν(M-O) (cm^{-1})
4	3398	-	1656	1591	1254	735	-
[Co(**4**)(H$_2$O)$_2$]	-	3400-3500	1636	1586	1224	736	586
[Ni(**4**)(H$_2$O)$_2$]	-	3400-3500	1639	1590	1221	735	588
[Cu(**4**)(H$_2$O)$_2$]	-	3400-3500	1631	1574	1224	738	584
[Zn(**4**)(H$_2$O)$_2$]	-	3400-3500	1636	1590	1220	736	599

When we indicate the 1H-NMR spectra of compounds **3**, **4,** and **Zn complex** in the spectrum of compounds **3** and **4**, the peak observed at 8.29 ppm belonging to the hydrazide amine in compound **3** is not seen in compound **4**. This indicates that the ligand is formed. In addition, the other peaks belonging to the **4** are the -NH peaks of the thiourea group in the structure with chemical shift values of 10.12 and 9.64 ppm. Diffuse peaks belonging to -OH and amide -NH proton groups were observed at 8.29 ppm and 8.77 ppm, respectively, and 7.06-7.74 ppm for aromatic protons. The bridge between the aromatic groups in the calixarene compound, which is observed at 4.26 and 3.49 ppm belongs to the Ar-CH$_2$-Ar and this splitting shows us that the compound **4** conformation is cone [4]. The ^{1}H-NMR spectrum of the Zn complex shows that the peak in the -OH group has disappeared in the ligand compound. This indicates that in the synthesis of the complex, it is not the thiourea group that is in the possible binding site, but the phenol oxygen of calixarene. Chemical shifts of C=S, C=O, and C-O carbons in the 13C-NMR spectrum of the ligand were observed at 155.3, 153.2, and 147.5 ppm, respectively. The resonance observed at 75.3 ppm belongs to the O–CH$_2$ carbon and peaks of other aromatic ring carbons were observed at 129.4-114.9 ppm [28]–[30].

When the electronic absorption spectrum of the ligand taken in DMF solution was examined, bands in the range of 300-400 nm were observed to belong $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$. These bands are transitions originating from aromatic rings and unpaired electrons. When the electronic absorption spectra of the Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes of the ligand were taken in DMF solution compared with the spectrum of the ligand, some differences were observed. Three transitions were observed at 347, and 443 nm in the Co^{2+} (d^7) complex. The absorption peak was at 275, and 395 nm, and the shoulder was observed at 455 nm in the Ni^{2+} (d^8) complex. Absorption peaks were observed at 360 and 425 nm in the Cu^{2+} (d^9) complex. Due to the d^{10} structure of the Zn complex, d-d transitions could not be observed [31]. UV-vis spectrum of compound 4 and Ni^{2+} complex is given in Figure **3**.
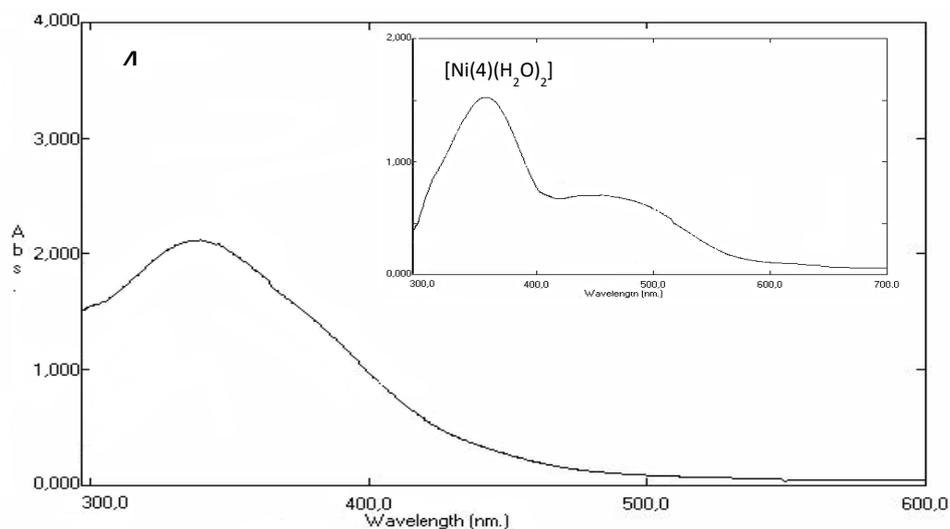
Figure 3. *Absorbtion spectrum of compound **4**. Inset: The absorption spectrum of Ni^{2+} complex*

MALDI-TOF analysis was also used for the structure determination of the synthesized ligand. In this way, it is another technique that determines the molecular weights of the compound and shows whether the targeted compound is formed. In this direction, as a result of the analysis, the molecular weight value of the compound was seen in the spectrum of compound **4** (**Figure 4**). The mass value of the decomposition product formed by the cleavage of tert-butyl groups in the compound is also included in the spectrum as the peak value at 930.86. The MALDI-TOF analysis results of the compound confirm the proposed structure of compound **4**.
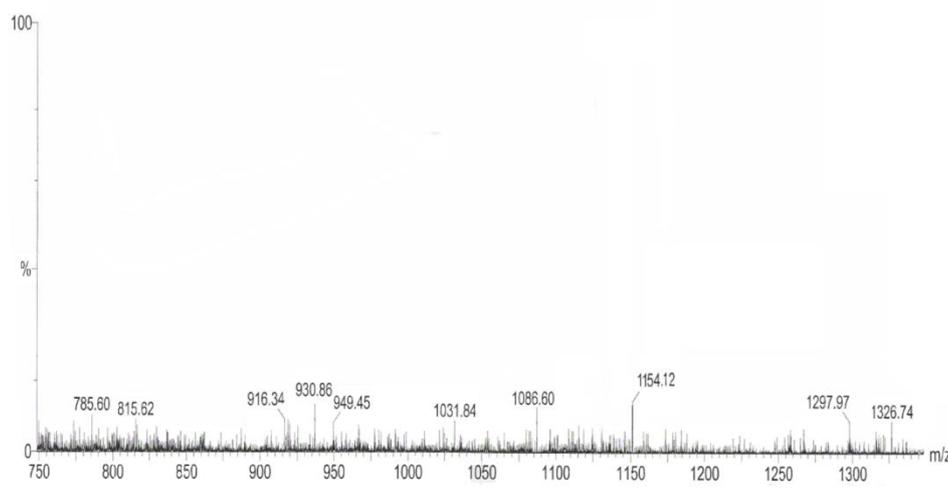

Figure 4. *Mass spectrum of compound **4**.*

Magnetic susceptibility is the ratio of the magnetic intensity caused by a substance to the magnetizing force. It is a very useful technique for identifying unpaired electrons in paramagnetic complexes and helps to suggest the structure of complexes. In the present study, by determining the magnetic susceptibility of metal complexes, it was tried to determine whether the complexes are paramagnetic or diamagnetic, and thus the probable geometry. The measurement results show us that the complex for zinc is diamagnetic as expected, which means that there are no unscreened electrons in the formation of the complex. These values should be higher if the electrons are unpaired. These values for copper, nickel, and cobalt showed that they were close to the values in the literature for unpaired electrons and that all

864

metals were in the +2 oxidation state [27]. The magnetic moment value of the Ni(II) complex reported here is 3.20, within the magnetic moment value range (μeff = 2.9-3.3 B.M) given at room temperature for the octahedral Ni(II) complexes. In the observed normal range, the complex has high spin, indicating that the Ni(II) complex has a 6-coordinated octahedral geometry. The magnetic susceptibility measurement of Co(II) is 4.52, which is within the normal range for octahedral Co(II) complexes (4.3-5.2 B.M). The magnetic moment value of 1.74 in the copper complex is among the data supporting the octahedral geometry for the Cu(II) complex. The complex of Zn(II) is diamagnetic. According to the empirical formulas of these complexes, an octahedral geometry has also been proposed for the complexes [32].
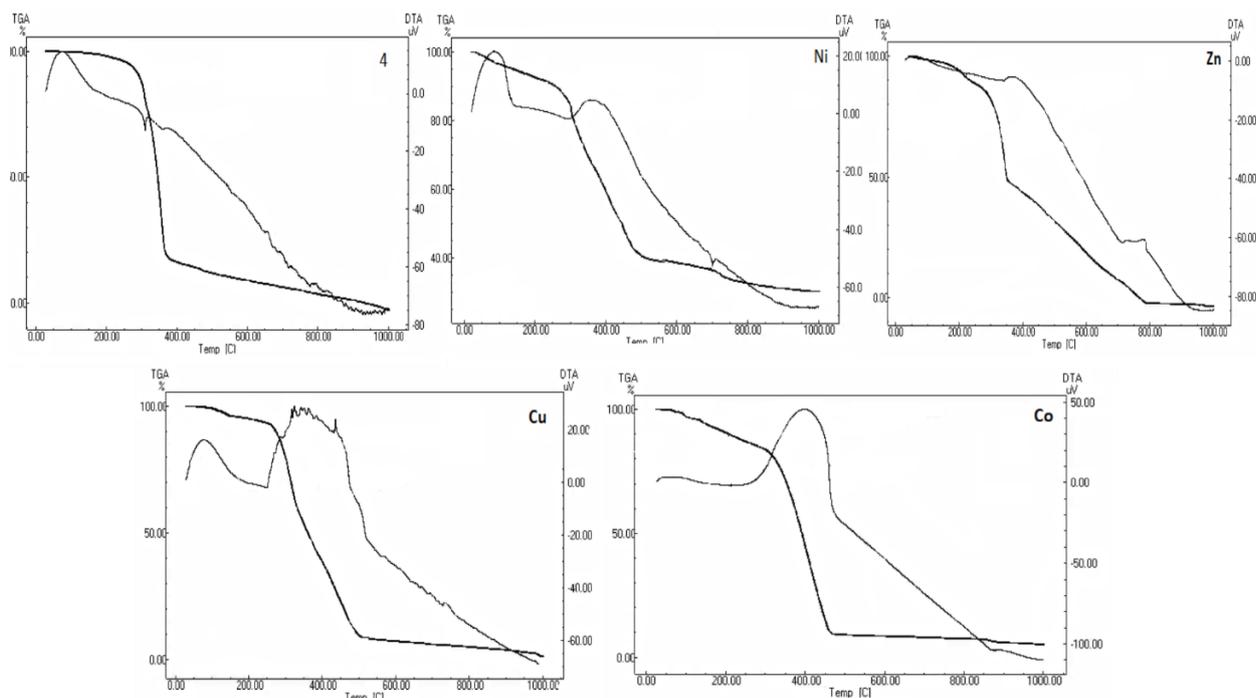

Figure 5. *DTA-TG diagrams of compound 4 and metal complexes*

Thermogravimetric analysis is important in terms of understanding the relationship between these two data by examining the TG/DTA curves of ligands and complexes, as well as the weight reduction and decomposition temperatures. It is also possible to comment on the decomposition products based on the mass loss. In this study, the thermal analysis results of the complexes were calculated with a mass loss of 2,89 % in Co(II) and Ni(II) complexes, 2.87 % in Cu(II) and Zn(II) complexes. These data have shown us that the water molecules in the complexes are separated in the first decomposition step, and the organic structure decomposes in the following steps. As a result of decomposition, it was determined that metal oxides remained from the complexes. The mass loss in the range of 25-250 ºC in the thermogram shows us that there is crystal water in the structure. The presence of water molecules in the structure proves that the complex with octahedral geometry supported by magnetic susceptibility is composed of four oxygen donors and 2 moles of water. The proposed structure of the complex was shown in Figure 6.
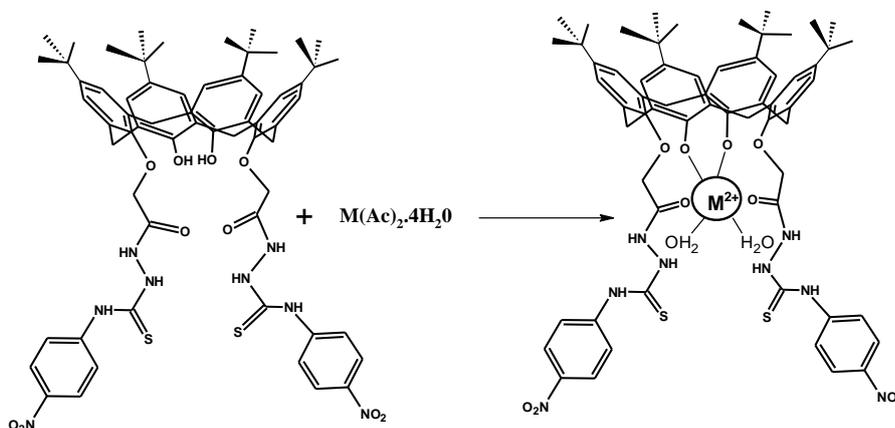
Figure 6. Synthesis of metal complexes and the proposed structure for the metal bonding site

IV. CONCLUSION

In this study, firstly the diester derivative of *p-tert*-butylcalix[4]arene (compound 2) and the hydrazide derivative of this compound (compound 3), and finally compound 4 were synthesized. Previously, similar structures were synthesized but metal extraction studies were carried out with these compounds. In this study, sulfur was added to the structure as a different donor group and it was tried to determine whether sulfur affected complexation. Complexes were synthesized from the reaction of the synthesized ligand with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} acetates. The structures of the obtained compounds and their complexes were characterized using elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, magnetic susceptibility, and thermogravimetric analysis techniques. From the data obtained, it was seen that sulfur was not involved in the formation of the complex, but instead, the binding was from the -OH groups in the calixarene body. It was determined that Co(II), Ni(II), Cu(II), and Zn(II) complexes were in octahedral structure. It also seems possible for compound **4** to perform new ion selection studies.

V. REFERENCES

[1]   C. D. Gutsche, B. Dhawan, and H. Kwang, "Academic Press," Anal. Chem., vol. 48, no. 3, pp. 339A-339A, 1976.

[2]   C. David Gutsche and J. A. Levine, "Calixarenes. 6. Synthesis of a Functionalizable Calix[4]arene in a Conformationally Rigid Cone Conformation," J. Am. Chem. Soc., no. 104, pp. 2652–2653, 1982.

[3]   C. D. G. and M. Iqbal, "p-tert-BUTYLCALIX[4]ARENE," Org. Synth., vol. 68, no. September, pp. 234, 1990.

[4]   C. D. Gutsche and L. J. Bauer, "Calixarenes. 14. The Conformational Properties of the Ethers and Esters of the Calix[6]arenes and the Calix[8]arenes," J. Am. Chem. Soc., vol. 107, no. 21, pp. 6059–6063, 1985.

[5]   D. Diamond and M. A. Mckervey, "Calixarene-based Sensing Agents," Chemıcal Socıety Revıews, vol. 25, no. 1, pp. 15-24, 1996.

[6]   D. M. Rudkevich, W. Verboom, and D. N. Reinhoudt, "Calix[4]arene Salenes: A Bifunctional Receptor for NaH2PO4," J. Org. Chem., vol. 59, no. 13, pp. 3683–3686, 1994.

[7]   M. F. Arnaud-Neu et al., "Modulation of cation binding in calix[4]arene amides: synthesis, complexation and molecular modelling studies," J. Chem. Soc. Trans. 2, no. 8, pp. 1727–1738, 1999.

[8]   B. Tomapatanaget and T. Tuntulani, "Lower rim tetra-substituted and upper rim ferrocene amide calix[4]arenes: Synthesis, conformation and anion-binding properties," Tetrahedron Lett., vol. 42, no. 45, pp. 8105–8109, 2001.

[9]   R. Ludwig and N. T. K. Dzung, "Calixarene-based molecules for cation recognition," Sensors, vol. 2, no. 10, pp. 397–416, 2002.

[10]   N. Galić, M. Rubčić, K. Magdić, M. Cindrić, and V. Tomišić, "Solution and solid-state studies of complexation of transition-metal cations and Al(III) by aroylhydrazones derived from nicotinic acid hydrazide," Inorganica Chim. Acta, vol. 366, no. 1, pp. 98–104, 2011.

[11]   C. Alkan, Y. Tek, and D. Kahraman, "Preparation and characterization of a series of thiourea derivatives as phase change materials for thermal energy storage," Turkish J. Chem., vol. 35, no. 5, pp. 769–777, 2011.

[12]   C. L. Allen and J. M. J. Williams, "Metal-catalysed approaches to amide bond formation," Chem. Soc. Rev., vol. 40, no. 7, pp. 3405–3415, 2011.

[13]   C. Toussaint, C. Beghidja, and R. Welter, "Cobalt complexes supported by salicylichydrazono derivative ligands and various coordination solvents," Comptes Rendus Chim., vol. 13, no. 3, pp. 343–352, 2010.

[14]   K. Mounika, A. Pragathi, and C. Gyanakumari, "Synthesis¸ Characterization and Biological Activity of a Schiff Base Derived from 3-Ethoxy Salicylaldehyde and 2-Amino Benzoic acid and its Transition Metal Complexes," J. Sci. Res., vol. 2, no. 3, p. 513, 2010

[15]   S. Budagumpi, N. V. Kulkarni, G. S. Kurdekar, M. P. Sathisha, and V. K. Revankar, "Synthesis and spectroscopy of CoII, NiII, CuII and ZnII complexes derived from 3,5-disubstituted-1H-pyrazole derivative: A special emphasis on DNA binding and cleavage studies," Eur. J. Med. Chem., vol. 45, no. 2, pp. 455–462, 2010.

[16]   S. N. Podyachev, N. E. Burmakina, V. V. Syakaev, S. N. Sudakova, R. R. Shagidullin, and A. I. Konovalov, "Synthesis, IR and NMR characterization and ion extraction properties of tetranonylcalix[4]resorcinol bearing acetylhydrazone groups," Tetrahedron, vol. 65, no. 1, pp. 408–417, 2009.

[17]   D. Zhang et al., "A selective fluorescence probe for yttrium(III) based on acylhydrazone Schiff base," Inorg. Chem. Commun., vol. 12, no. 11, pp. 1154–1156, 2009.

[18]   A. Ali and C. P. Rao, "Formation of mono- and di-amide-calix[4]arene derivatives from the reaction of p-tert-butyl-calix[4]arene and α-chloro-N,N-diethylacetamide in the presence of sodium hydride," Indian J. Chem. - Sect. B Org. Med. Chem., vol. 44, no. 3, pp. 549–552, 2005.

[19]   I. Vatsouro, E. Alt, M. Vysotsky, and V. Böhmer, "Guest exchange in dimeric capsules formed by tetra-urea calix[4]arenes," Org. Biomol. Chem., vol. 6, no. 6, pp. 998–1003, 2008.

[20]   A. Yildirim, S. Karakurt, and M. Yilmaz, "Synthesized Two New Water-Soluble Fluorescents Calix[4]arene 4-sulfo-1,8-naphthalimide Derivatives Inhibit Proliferation of Human Colorectal Carcinoma Cells," ChemistrySelect, vol. 6, no. 28, pp. 7093–7097, 2021.

[21]   E. Akceylan, A. Uyanik, S. Eymur, O. Sahin, and M. Yilmaz, "Calixarene-proline functionalized iron oxide magnetite nanoparticles (Calix-Pro-MN): An efficient recyclable

organocatalyst for asymmetric aldol reaction in water," Appl. Catal. A Gen., vol. 499, pp. 205–212, 2015.

[22]   E. Quinlan, S. E. Matthews, and T. Gunnlaugsson, "Anion sensing using colorimetric amidourea based receptors incorporated into a 1,3-disubstituted calix[4]arene," Tetrahedron Lett., vol. 47, no. 52, pp. 9333–9338, 2006.

[23]   S. Bozkurt, A. Karakucuk, A. Sirit, and M. Yilmaz, "Synthesis of two calix[4]arene diamide derivatives for extraction of chromium(VI)," Tetrahedron, vol. 61, no. 44, pp. 10443–10448, 2005.

[24]   E. M. Collins et al., "Chemically modified calix[4]arenes. Regioselective synthesis of 1,3-(distal) derivatives and related compounds. X-ray crystal structure of a diphenol-dinitrile," J. Chem. Soc. Perkin Trans. 1, vol. 3, no. 12, pp. 3137–3142, 1991.

[25]   O. K. Taşkin, Ö. F. Öztürk, and E. Canpolat, "Yeni Bir Schi ff Bazı ve Geçiş Metalleri ile Oluşturdukları Komplekslerin Sentezi ve Karakterizasyonu Synthesis and Characterization of a New Schiff Base and Its Complexes with Some Transition Metals," BEU Fen Bilim. Derg., c. 1, s. 1, ss. 34–39, 2012

[26]   D. N. Hundekar, A.M., Sen, "Preparation & Characterization of Metal Complexes of N-Acetyl-N-aroylferrocenyl Hydrazidest," Indian J. Chem., vol. 23, no. June, pp. 477–479, 1984.

[27]   K. Shoaib, W. Rehman, B. Mohammad, and S. Ali, "Synthesis, characterization and biological applications of transition metal complexes of [no] donor schiff bases," J. Proteomics Bioinforma., vol. 6, no. 7, pp. 153–157, 2013.

[28]   S. TUNA YILDIRIM, "Aromatik Amin İçeren Schiff Bazı Ligandının Sentezi, Karakterizasyonu ve Bazı Geçiş Metal Komplekslerinin İncelenmesi," Erzincan Üniversitesi Fen Bilim. Enstitüsü Derg., c. 12, s. 3, ss. 1329–1340, 2019.

[29]   A. S. El-Tabl, F. A. El-Saied, W. Plass, and A. N. Al-Hakimi, "Synthesis, spectroscopic characterization and biological activity of the metal complexes of the Schiff base derived from phenylaminoacetohydrazide and dibenzoylmethane," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 71, no. 1, pp. 90–99, 2008.

[30]   G. G. Mohamed, M. M. Omar, and A. M. Hindy, "Metal complexes of Schiff bases: Preparation, characterization, and biological activity," Turkish J. Chem., vol. 30, no. 3, pp. 361–382, 2006.

[31]   G. G. Mohamed, M. M. Omar, and Y. M. Ahmed, "Metal complexes of Tridentate Schiff base: Synthesis, Characterization, Biological Activity and Molecular Docking Studies with COVID-19 Protein Receptor," Zeitschrift fur Anorg. und Allg. Chemie, vol. 647, no. 23–24, pp. 2201–2218, 2021.

[32]   Z. T. Omar, S. Jadhav, R. Pathrikar, S. Shejul, and M. Rai, "Synthesis, Magnetic Susceptibility, Thermodynamic Study and Bio-Evaluation of Transition Metal Complexes of New Schiff Base Incorporating INH Pharmacophore," Polycycl. Aromat. Compd., vol. 43, no. 1, pp. 523–537, 2023.