

Synthesis and Characterization of NiO Nanoparticles by Using Thermal Decompositions of Ni(II) – ONO and ONNO Type Schiff Base Complexes

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Abstract: Five different Nickel (II) complexes were prepared using a ONNO type Schiff base bis-N,N'(salicylidene)-1,3-propanediamine (LH₂) and an ONO type Schiff base N(2-hydroxy)salicylaldimine (SAPH₂) in the presence of NH₃ or amine and NiO nanoparticles were obtained with thermal decomposition of this complexes in air. The prepared complexes and Schiff bases have been characterized by element analysis, IR spectroscopy, Thermogravimetry (TG), ¹HNMR and ¹³CNMR spectroscopy, Mass Spectrometry (MS), Atomic absorption spectrometry (AAS), and Scanning Electron Microscopy (SEM). The surface area of the obtained nanoparticle NiO material was measured by the Brunauer-Emmett-Teller (BET) method. The thermal decomposition products NiO nanoparticles were investigated with XRD, and SEM technics. SEM investigations showed that due to the very little solubility of the prepared two complexes and consequently they were precipitated in the form of nanoparticles. In addition, it observed that this very insoluble complexes are converted to NiO nanoparticles a result of thermal decomposition.

Ni(II) – ONO ve ONNO Tipi Schiff Bazı Komplekslerinin Termal Bozunmalarını Kullanarak NiO Nanopartiküllerinin Sentezi ve Karakterizasyonu

Anahtar Kelimeler

ONO tipi Schiff bazı,
ONNO tipi Schiff bazı,
Schiff bazı kompleksleri,
Termal bozunma,
NiO nanoparçacıkları

Öz: Bir ONNO tipi Schiff bazı olan bis-N,N'(salisiliden)-1,3-propandiamin (LH₂) ve ONO tipi Schiff bazı olan N(2-hidroksi)salisilaldimin (SAPH₂) kullanılarak beş farklı Nikel (II) kompleksi NH₃ veya amin varlığında hazırlandı ve bu komplekslerin havada termal bozunması ile NiO nanoparçacıkları elde edildi. Hazırlanan kompleksler ve Schiff bazları, element analizi, IR spektroskopisi, Termogravimetri (TG), ¹HNMR ve ¹³CNMR spektroskopisi, Kütle Spektrometrisi (MS), Atomik absorpsiyon spektrometrisi (AAS), ve Taramalı Elektron Mikroskobu (SEM) ile karakterize edildi. Elde edilen nanoparçacık NiO malzemenin yüzey alanı Brunauer-Emmett-Teller (BET) yöntemi ile ölçüldü. NiO nanoparçacıklarının termal bozunma ürünleri XRD ve SEM teknikleri ile incelendi. SEM incelemeleri, hazırlanan iki kompleksin çözünürlüğünün çok az olması nedeniyle nanopartiküller halinde çöktüğünü gösterdi. Bu sebepten dolayı çözünmeyen komplekslerin termal bozunma sonucunda NiO nanoparçacıklarına dönüştüğü gözlemlendi.

1. Introduction

Bis-N,N'(salicylidene)-1,3-diaminopropane (LH₂) Schiff base has long been known is a ONNO type tetradentate ligand and this Schiff base gives many mono and polynuclear complexes with some first and second series transition elements [1-21]. The structure of mononuclear complexes given by Ni (II) and Cu (II) ions have been known since 1985, [(NiL) and [CuL]] [22]. Especially, the mononuclear Ni (II)

complex of this ligand can create homo- and hetero-dinuclear [1-3], trinuclear [4-17], tetranuclear [18] and polynuclear [19] complexes with square pyramid or octahedral coordination spheres along with coligands such as picoline, acetate, nitrate and N,N'-dimethylformamide.

The general formula of the dinuclear complexes prepared using the NiL complex is in the form of [NiL.MX₂.(DMF)₂] (M=Cd(II), Zn(II), X= Cl⁻ or Br⁻) and

the trinuclear complexes in the $[(NiL)_2.MX_2.S_z]$ ($M=Mn(II), Fe(II), Cu(II), Ni(II), Cd(II), Zn(II), X= Cl, AcO^-, NO_2^-, NO_3^-, S= Solvent \text{ or } DMF, z= 0 - 2$) form [1-17]. The $[NiL]$ mononuclear complexes are diamagnetic complexes of which molecular structures are illuminated in 1985, and they are soluble in polar solvents at hydrothermal conditions. When a small amount of H_2O is added to this solution, the complex of $[NiL.H_2O]$ is obtained as solid green crystals [21]. In addition, if NH_3 used as coligand with the Schiff base LH_2 , the complexes in the stoichiometry of $[Ni_2L_2(NH_3)_3]$ and $[Ni_2L_2.NH_3]$ is obtained. These complexes can be obtained if we add NH_3 to the NiL complex dissolved in polar solvents. These NH_3 complexes are not found in the literature. The decomposition order of $[Ni_2L_2(NH_3)_3]$ is shown in Fig. 1.

$N(\text{salicylidene})\text{-}2\text{-hydroxyaniline}$ ($SAPH_2$) is a tridentate ligand in the type of ONO and this ligand gives mononuclear complexes with I and II. series transition elements like LH_2 , [23-27]. However, in particular, the $Ni(II)$ complex of this Schiff base is dinuclear coordinated and in crystal lattice supra-molecular structure called pseudo-octahedral in solid state [24, 26]. This supramolecular structure is converted with an amine addition, which is transformed into mononuclear complexes in square plane coordination. The $NiSAP$ complex is a complex that has been studied for many years. It is hardly ever soluble in solvents and could be dissolved, if NH_3 , Et_2NH or $C_5H_{11}N$ (piperidine) is added and it gives the mononuclear and diamagnetic complexes in the stoichiometry of $[NiSAP.NH_3]$, $[NiSAP.Et_2NH]$ or $[NiSAP.C_5H_{11}N]$ (or $[NiSAP.pip]$). In this complex, NH_3 or amine are connected to the metal atom in a coordinated manner. Between $180 - 320^\circ C$, this amine or NH_3 is removed from the structure and transformed into a $[NiSAP]$ complex again, according to the reactions given in Fig. 2 [23-27].

It is known that the $[NiSAP]$ and $[NiL.NH_3)_2.NH_3]$ are very low soluble complexes and they are precipitated as extremely fine particles. The proposed study was carried out in order to be able to produce NiO nanoparticles from these less soluble complexes. Since they are likely to precipitated as nanoparticles, it was investigated that if these nanoparticles are produced as a result of thermal decomposition of precipitation of these low soluble complexes. In this respect, all the complexes were prepared and examined by thermogravimetric (TG) analysis and in addition made thermokinetic analysis using the results of thermogravimetric analysis. Similarly, we also investigated final product of thermal decomposition $[NiSAP.NH_3]$, $[NiSAP.Et_2NH]$ and $[NiSAP.pip]$ complexes. Numerous studies have been reported in the literature to prepare nanoparticles in this way [28-39]. The particle sizes of low soluble complexes were identified by Scanning Electron Microscope (SEM). Also the complexes produced as a result of thermal degradation in the air by heating up to $450^\circ C$ and the obtained NiO was examined with SEM again. Along with the SEM, the X-Ray powder diffraction (XRD) method has been used to examine insoluble complexes and obtained NiO and the particle dimensions were calculated. The surface area of less-soluble complexes and obtained NiO were calculated with the Brunauer-Emmet-Teller (BET) method and the obtained results were compared.

2. Material and Method

The TG-DTA studies were actualized with Shimadzu DTG-60H and these analyses were carried out in Pt pans at different heating rates under nitrogen atmosphere. The IR spectra of the ligands and complexes were actualized by the use of Shimadzu Infinity model FTIR. C, H and N analyses were carried out by Eurovector 3018 CHNS analyzer. Ni analyses of the complexes were made by GBC Avanta PM Model

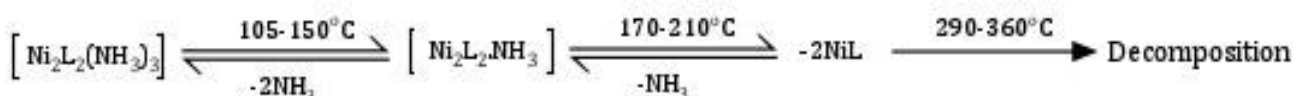


Figure 1. Decomposition order of $[Ni_2L_2(NH_3)_3]$

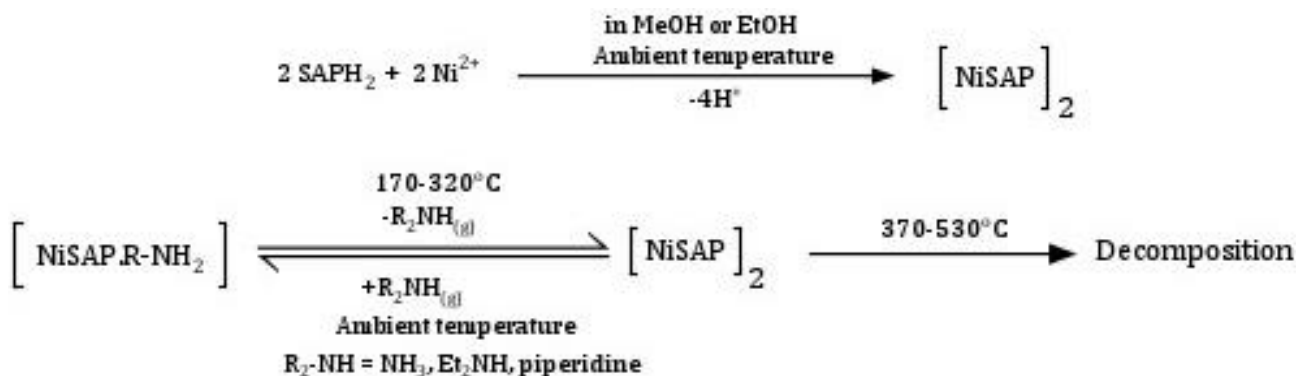


Figure 2. Decomposition of $[NiSAP.R-NH_2]$

flame atomic absorption (FAAS) device. The NMR spectra of the ligands were recorded with a Varian brand Mercury model 400MHz NMR spectrophotometer in d_6 -DMSO. Similarly, were recorded the Mass spectra of the ligands using Shimadzu 2010 Plus GCMS included Direct Inlet (DI) unit. The surface area of complexes and pyrolyzed product NiO were measured by Brunauer-Emmet-Teller method in Quantachrome Nova 2200e device using N_2 with 18 hours degassing time at 110 °C equilibrium temperature

2.1. Ligands

Preparation of Bis-N,N'(salicylidene)-1,3-diaminopropane (LH₂): 2-Hydroxy-benzaldehyde (0.1 mol) has been dissolved in 120 cm³ of warm EtOH. After 0.05 mol of 1, 3-diaminopropane has been added to this solution, heated up to the boiling point. After cooling, it was air-dried and the yellow crystals were filtered. Yield: 90–95%, Melting Point (mp): 58°C.

Elemental Analysis for (LH₂) C₁₇H₁₈N₂O₂: Anal. Calcd. %: C 72.32; H 6.43; N 9.92; Found % C 71.95; H 6.33; N 10.09.

Important IR data (cm⁻¹): ν_{O-H} : 2627, $\nu_{C-H(Ar)}$: 3021-3019, $\nu_{C-H(Aliph)}$: 2929-2862, $\nu_{C=N}$: 1629, $\nu_{C=C(ring)}$: 1608, $\nu_{C-O(Phenol)}$: 1274- 1151, $\delta_{C-H(Ar)}$: 762.

λ_{max} =243nm, ϵ =7045 dm³mol⁻¹cm⁻¹ in DMSO, λ_{max} =242 nm, ϵ =7865 dm³mol⁻¹cm⁻¹ in MeOH.

¹HNMR data in d₆-CH₃COCH₃ (δ , ppm): 13.51 (s) (O-H), 8.60 (s) (-CH=), 7.43 (d) (H_{Ar}), 7.32(t) (H_{Ar}), 6.88 (t) (H_{Ar}), 3.68 (t) (N-CH₂-), 2.01 (p) (-CH₂-).

¹³CNMR data in d₆-CH₃COCH₃ (δ , ppm): 166.6, 161.1, 132.7, 132.1, 119.1, 118.9 (C_{Ar}), 116.9 (-C=N), 58.5 (N-CH₂-), 31.9 (-CH₂-).

MS m/z: 282 [M]⁺, 161 [HO-C₆H₄-CH=N-CH₂-CH₂-CH₂]⁺, 148 [HO-C₆H₄-CH=N-CH₂-CH₂]⁺ (BP), 134 [HO-C₆H₄-CH=N-CH₂]⁺, 120 [HO-C₆H₄-CH=N]⁺, 107 [HO-C₆H₄-CH₂]⁺, 77 [C₆H₅]⁺.

Preparation of N(salicylidene)-2-hydroxyaniline (SAPH₂): This Schiff base was prepared from 0.04 mol salicylaldehyde and 0.04 mol 2-hydroxyaniline in EtOH as given above. Yield: 80%, mp: 183 °C.

Elemental Analysis for C₁₃H₁₁NO₂ Anal. Calcd. %: C: 73.26, H: 5.20, N: 6.56; Found %: C: 72.57, H: 4.79, N: 6.48.

Important IR data (cm⁻¹): ν_{O-H} : 2692-2553, $\nu_{C-H(Ar)}$: 3047, $\nu_{C-H(imin)}$: 2839, $\nu_{C=N}$: 1624, $\nu_{C=C(ring)}$: 1589, $\nu_{C-O(Phenol)}$: 1219- 1111, $\delta_{C-H(Ar)}$: 747.

¹HNMR data in d₆-CH₃COCH₃ (δ , ppm): 13.80 (s, 1H) (OH), 9.93(s, 1H) (OH), 8.78 (s, 1H) (-CH=), 7.63-6.81 (m, 8H) (H_{Ar}).

¹³CNMR data in d₆-CH₃COCH₃ (δ , ppm): 162.2 (C=N), 160.5, 151.2 (C-O), 134.9, 132.9, 132.2, 128.1, 122.3, 119.7, 119.0, 118.9 116.7, 116.4 (C_{Ar}).

MS m/z: 213 [M]⁺ (Base peak), 196 [HO-C₆H₄-CH=N-C₆H₄]⁺, 120 [HO-C₆H₄-CH=N]⁺, 107 [HO-C₆H₄-CH₂]⁺, 93 [HO-C₆H₄]⁺, 77 [C₆H₅]⁺.

2.2. Complexes

Preparation of [Ni₂L₂(NH₃)₃]: 0.05 mol LH₂ has been dissolved in 100 mL EtOH by mixing in 3 different beakers. To these solutions were added 4.0, 10.0 and 20.0 mL concentrated ammonia respectively and heated to boiling point. Then was added a solution of 0.05 mol NiCl₂.6H₂O in 50 mL MeOH to these solutions respectively. After 3-4 hours a light green precipitates have been filtered and dried in air. Yield: 98%, mp: not detected.

Elemental Analysis for C₃₄H₄₁N₇O₄Ni₂: Anal. Calcd. %: C:56.01, H:5.66, N:13.44, Ni:16.01; Found % C: 55.45, H:5.29, N:13.09, Ni:15.73.

Important IR data (cm⁻¹): ν_{N-H} :3309-3219-, $\nu_{C-H(Ar)}$: 3045-3022, $\nu_{C-H(imin)}$: 2941-2854, $\nu_{C=N}$:1616, $\nu_{C=C(ring)}$: 1583-1535, $\nu_{C-O(Phenol)}$: 1195- 1124, $\delta_{C-H(Ar)}$: 750.

Thermogravimetric Analysis: Calculated mass loss of removed NH₃ %: 6.99, found %: 6.95±0.12

Preparation of [NiL]: The [NiL] complex can be prepared in ethanol in the form of NiCl₂ and LH₂ at pH 9, but NiL prepared by this method is obtained as big needle crystals [21]. In this study, NiL was obtained as a result of ammonia loss of [Ni₂L₂(NH₃)₃] light brown complex at 170-190 °C [20,21].

Elemental Analysis for C₁₇H₁₆N₂O₂Ni: Anal. Calcd. %: C: 60.23, H: 4.76, N: 8.33, Ni: 17.33; Found % C: 59.84, H: 4.51, N: 7.99, Ni: 17.19.

Important IR data (cm⁻¹): $\nu_{C-H(Ar)}$: 3051-3033, $\nu_{C-H(Aliph)}$: 2965-2922, $\nu_{C=N}$: 1608, $\nu_{C=C(ring)}$: 1595-1542, δ_{CH_2} : 1475, $\nu_{C-O(Phenol)}$: 1199- 1082, $\delta_{C-H(Ar)}$: 744-725.

Preparation of [NiSAP]: 0.002 mol SAPH₂ was dissolved in 80 mL EtOH under stirring and heating [24]. To this solution, 0.002 mol NiCl₂.6H₂O in 20 mL hot MeOH was added and yellow precipitate filtered and dried in an oven at 80°C. Yield 80%

Elemental Analysis for C₁₃H₉NO₂Ni: Anal. Calcd. %: C: 57.20, H: 3.26, N: 5.36, Ni: 21.82; Found % C: 57.64, H: 3.83, N: 5.22, Ni: 21.98.

Important IR data (cm⁻¹): $\nu_{C-H(Ar)}$: 3047-3025, $\nu_{C=N}$: 1605, $\nu_{C=C(ring)}$: 1595-1541, $\nu_{C-O(Phenol)}$: 1190- 1137, $\delta_{C-H(Ar)}$: 751.

Preparation of [NiSAP.NH₃], [NiSAP.Et₂NH], [NiSAP.pip]: For the [NiSAP.NH₃], 0.002 mol SAPH₂

was dissolved in 80 mL EtOH under stirring and heating. To this solution was added firstly 5 mL concentrated NH_3 then a solution of 0.002 mol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 mL hot MeOH. The mixture was refluxed half an hour. After crystallization, the brown crystals were filtered and dried in air [24-26]. Yield approximately 50%, mp: not determined.

Elemental Analysis for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2\text{Ni}$: Anal. Calcd. %: C: 53.71, H: 4.05, N: 9.28, Ni: 20.42; Found % C: 54.41, H: 4.18, N: 9.76, Ni: 20.48.

Important IR data (cm^{-1}): $\nu_{\text{N-H}}$:3330-3223-, $\nu_{\text{C-H(Ar)}}$: 3052-3018, $\nu_{\text{C=N}}$:1603, $\nu_{\text{C=C(ring)}}$:1587-1545, $\nu_{\text{C-O(Phenol)}}$:1192- 1088, $\delta_{\text{C-H(Ar)}}$:756.

Thermogravimetric Analysis: Calculated mass loss of removed NH_3 %: 5.93, found %: 5.85±0.08

For $[\text{NiSAP} \cdot \text{Et}_2\text{NH}]$ preparation 0.002 mol SAPH_2 , 0.002 mol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 2.0 mL diethylamine, for $[\text{NiSAP} \cdot \text{pip}]$ complex 0.002 mol SAPH_2 , 0.002 mol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 2.0 mL piperidine were used and obtained square planar diamagnetic complexes.

For $[\text{NiSAP} \cdot \text{Et}_2\text{NH}]$ was found the yield approximately % 25, mp: not determined.

Elemental Analysis for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{Ni}$: Anal. Calcd. %: C: 59.55, H: 5.87, N: 8.16, Ni: 17.12; Found % C: 58.93, H: 5.12, N: 7.75, Ni: 16.54.

Important IR data (cm^{-1}): $\nu_{\text{N-H}}$:3346-3257-, $\nu_{\text{C-H(Ar)}}$: 3055-3019, $\nu_{\text{C=N}}$:1606, $\nu_{\text{C=C(ring)}}$:1595-1541, $\nu_{\text{C-O(Phenol)}}$:1208- 1097, $\delta_{\text{C-H(Ar)}}$:756.

Thermogravimetric Analysis: Calculated mass loss of removed Et_2NH %: 21.50, found %: 21.50±0.06.

For $[\text{NiSAP} \cdot \text{pip}]$ was found the yield approximately % 30, mp: not determined.

Elemental Analysis for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{Ni}$: Anal. Calcd. %: C: 60.63, H: 5.69, N: 7.80, Ni: 16.79; Found % C: 60.89, H: 5.63, N: 7.89, Ni: 16.15.

Important IR data (cm^{-1}): $\nu_{\text{N-H}}$:3341-3253-, $\nu_{\text{C-H(Ar)}}$: 3053-3017, $\nu_{\text{C=N}}$:1605, $\nu_{\text{C=C(ring)}}$:1590-1543, $\nu_{\text{C-O(Phenol)}}$:1195- 1084, $\delta_{\text{C-H(Ar)}}$:751.

Thermogravimetric Analysis: Calculated mass loss of removed Et_2NH : 24.20%, found %: 23.87±0.44.

3. Results and Discussion

The results of the element analysis confirm the stoichiometry of the complexes. In addition, the results of thermogravimetric analysis support the stoichiometry of the co-ligand mass losses. The TG curves of the prepared complexes and the thermoanalytical data from these curves were given in Fig. 3-6 and in Table 1. Fig. 3a shows the thermal decomposition of the complex, the $[\text{NiL}]$ complex remaining after two-step ammonia loss up to 300 °C. Mass loss due to thermal decomposition of the $[\text{NiL}]$ complex is observed after 340 °C. The $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ is a paramagnetic complex. The molecular model of this complex has not been determined due to not being able to obtain suitable single crystal and there is no study available about this complex in the literature. The 13.09% of nitrogen were found according to the element analysis of this complex. It is difficult to explain this result. However, sometimes TG is more helpful than element analysis to determine the stoichiometry of complexes [40]. According to TG the NH_3 in the complex $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ is separated into two steps as seen in Fig. 3. There is a mass loss of 6.95% in total, 4.50% of NH_3 removed in the first step, and 2.45% of it leave the structure in the second step and the remaining structure is the $[\text{NiL}]$ mononuclear complex. The total ammonia mass loss indicates that the complex stoichiometry is $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ and the mass loss of 4.50% in the first step shows that the two moles ammonia in this step are separated from the structure and the residual mass is $[\text{Ni}_2\text{L}_2 \cdot \text{NH}_3]$, the expected theoretical mass loss for this first step is 4.66%. The mass loss of 2.45% in the second step shows the last ammonia leaves the structure and the expected mass loss for this first step is 2.33%. In this case, the residual mass is diamagnetic NiL mononuclear complex.

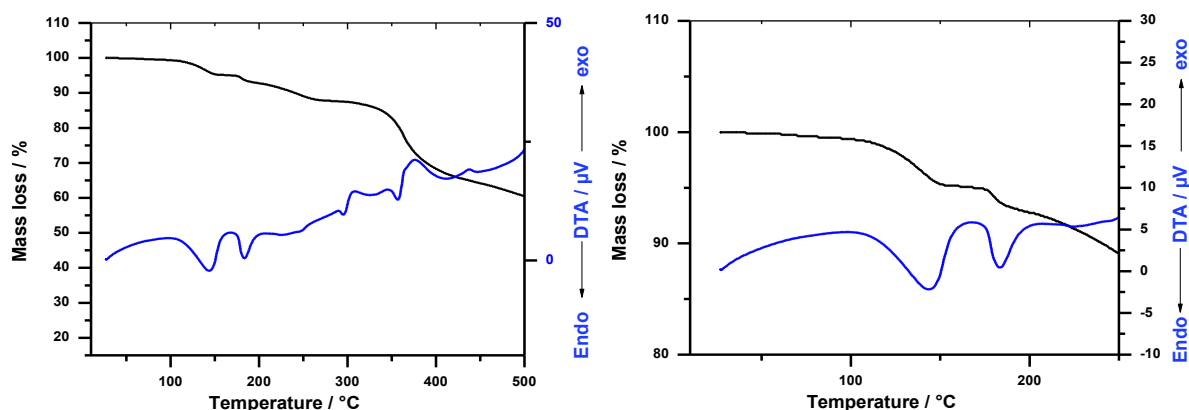


Figure 3. The TG-DTA curves of $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ and zoomed view of NH_3 removal zone.

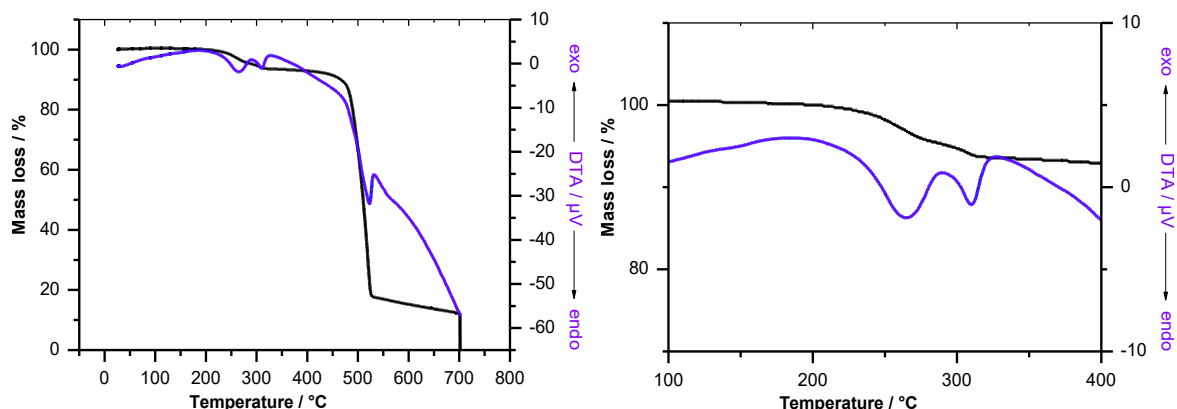


Figure 4. TG-DTA curves of $[\text{NiSAP.NH}_3]$ and zoomed view of the NH_3 removal zone.

In the intermediate product, $[\text{Ni}_2\text{L}_2.\text{NH}_3]$ complex, it is difficult to estimate the coordination but one similar complex structure has been reported in the literature [41]. The structure of the reported complex $[\text{Ni}_2\text{L}_2.\text{NH}_2\text{-CH}_3]$ has been given in the literature. In this complex, the place of NH_3 has been replaced by methylamine. Similarly, the co-ligands of the structures of complexes $[\text{NiSAP.NH}_3]$, $[\text{NiSAP.Et}_2\text{NH}]$ and $[\text{NiSAP.pip}]$ are thermally separated from the structure at the 160-320 °C temperature range Fig. 4-6. As given in Table 1, the mass loss of the co-ligands are expected values and residual mass is corresponds to expected $[\text{NiSAP}]$ mass. The residual $[\text{NiSAP}]$ is thermal decomposed after 370 °C. The $[\text{NiSAP.NH}_3]$, $[\text{NiSAP.Et}_2\text{NH}]$ complexes and very similar complex of $[\text{NiSAP.pip}]$ have been reported in the literature and the X-rays diffraction studies show that their coordination is determined to be square planar [42-44]. Square planar Ni(II) complexes are known as diamagnetic complexes [45]. In the TG curves of these complexes it is seen that approximately between 160-320 °C, the amines or NH_3 which found in the structure, were separated and the mass loss found as it is expected and the residue is paramagnetic $[\text{NiSAP}]$.

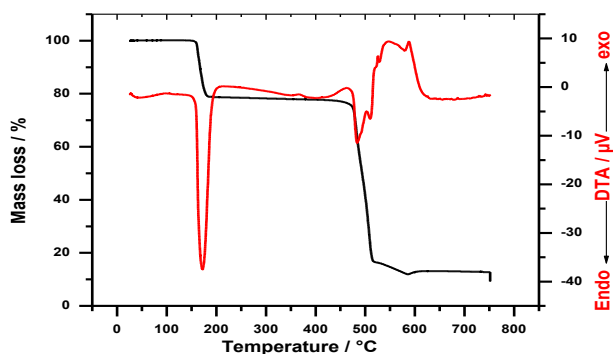


Figure 5. TG-DTA curves of $[\text{NiSAP.Et}_2\text{NH}]$

As seen in Fig. 4, TG signal of the $[\text{NiSAP.NH}_3]$ complex shows that ammonia removing realized in two steps and DTA signals confirms this result. From the element analysis data and the thermoanalytical data given in Table 1, the ratio of $[\text{NiSAP}]/\text{NH}_3$ in the $[\text{NiSAP.NH}_3]$ complex is about 1 and in this case, it is difficult to estimate the structure of the intermediate

product in NH_3 separation observed in thermogravimetric analysis. As can be seen from Fig. 4 and 5, the co-ligands separated from the structure in the $[\text{NiSAP.Et}_2\text{NH}]$ and $[\text{NiSAP.pip}]$ complexes give a single step mass loss of Et_2NH and piperidine and it is seen from Table 1 that these mass losses are expected values. The first aim of this study was to obtain nanoparticle NiO as a result of thermal decomposition in the oxygenated environment of prepared complexes.

It is known that the $[\text{NiSAP}]$ and $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ complexes are insoluble in common solvents, for this reason, it was thought that these complexes to be form in nano-sized, so this study was planned because it is highly probable that the metal oxide compound formed as a result of thermal degradation of the particles obtained in the nanostructure is also nanoparticle.

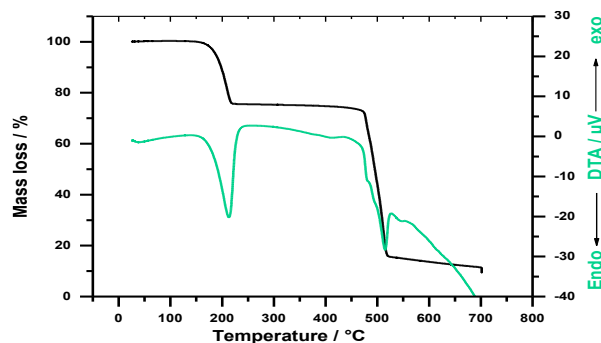


Figure 6. TG-DTA curves of $[\text{NiSAP.pip}]$

The $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ complex was prepared in 3 different NH_3 concentration. The NH_3 concentration adjusted as to be approximately 0.5, 1.5, and 3.0 M to determine the appropriate precipitate. The complexes obtained from these media were examined by the method of Brunauer-Emmett-Teller (BET) and their surface areas were found as 25.910, 25.264 and 22.407 m^2/g respectively. Due to the largest surface area was obtained in 0.5 M NH_3 concentration. Similarly, NiSAP was precipitated directly or the formed from thermal decomposition of the $[\text{NiSAP.NH}_3]$, $[\text{NiSAP.Et}_2\text{NH}]$ and $[\text{NiSAP.pip}]$ complexes.

Table 1. Thermoanalytical data of the prepared complexes

Complex	Thermal reaction of amine loss or first step of ammonia loss			Thermal reaction of second step ammonia loss NH ₃ loss stepwise or degradation of complex			Thermal reaction of the residual complex degradation
	Temperature range/ °C	Calculated mass loss / %	Found mass loss / %	Temperature range/ °C	Calculated mass loss / %	Found mass loss / %	Temperature range/ °C
[Ni ₂ L ₂ (NH ₃) ₃]	5 °C/min. 106.47- 148.72	4.66	4.58-4.49- 4.45-4.48 Average: 4.50±0.06	5 °C/min. 160.11- 200.00	2.33	2.47- 2.19- 2.56- 2.59 Average: 2.45±0.18	5 °C/min. 317.88-382.97
	10 °C/min. 108.65- 164.41			10 °C/min. 166.84- 197.36			10 °C/min. 327.63-388.39
	15 °C/min. 115.78- 172.85			15 °C/min. 179.84- 207.32			15 °C/min. 335.37-398.54
	20 °C/min. 120.85- 186.09			20 °C/min. 199.64- 248.77			20 °C/min. 342.16-403.45
							Melting of NiL: 293-294 °C
							Calculated % NiO: 22.05
							Found NiO: 20.93±1.31
[NiSAP.NH ₃]	10 °C/min. 185.76- 320.80	5.92	5.81-5.97- 5.78 Average: 5.85±0.08	--	--	--	10 °C/min. 471.72- 531.20
	20 °C/min. 192.86- 338.50			--	--	--	20 °C/min. 483.53- 547.86
	30 °C/min. 223.60- 366.48			--	--	--	30 °C/min. 483.40- 553.65
							Calculated % NiO: 26.10
							Found NiO: 24.68±2.07
[NiSAP.Et ₂ NH]	5 °C/min. 148.51 - 183.94	21.50	21.45- 21.45- 21.46- 21.47- 21.56- 21.37 Average: 21.46±0.06	--	---	--	5 °C/min. 434.11-499.16
	10 °C/min. 157.83- 201.96			--	--	--	10 °C/min. 468.77-519.03
	15 °C/min. 157.48- 215.50			--	--	--	15 °C/min. 473.63-521.17
	20 °C/min. 161.79- 232.88			--	--	--	20 °C/min. 484.25-528.35
	25 °C/min. 163.52- 248.76			--	--	--	25 °C/min. 488.23-540.27
							Calculated % NiO: 21.77
						Found % NiO: 20.04±1.26	
[NiSAP.pip]	10 °C/min. 158.94- 237.23	24.19	24.44- 23.36- 23.82 Average: 23.87±0.44	--	--	--	10 °C/min. 472.49-521.19
	20 °C/min. 164.40- 245.35			--	--	--	20 °C/min. 485.45-534.45
	30 °C/min. 181.17- 274.38			--	--	--	30 °C/min. 488.42-552.29
							Calculated % NiO: 21.03
							Found % NiO: 20.51±0.16
[NiSAP]	--	--	--	--	--	--	10 °C/min. 376.69-535.98
							Calculated % NiO: 27.67
							Found % NiO: 26.47±1.09

The all complexes prepared and thermal decomposition products were examined with the scanning electron microscope (SEM) and observed that almost all of the complexes and obtained NiO were obtained in nano-particle size, Fig. 7a-f.

As seen in Fig. 7a, [Ni₂L₂(NH₃)₃] complex precipitated in the form of small sticks and the smallest sticks were precipitated in 0.5 M NH₃ concentration. As it is clearly seen from SEM images, the ones precipitated in 0.5 M NH₃ medium are 110-150 nm, 1.5 M NH₃, 90-320 nm

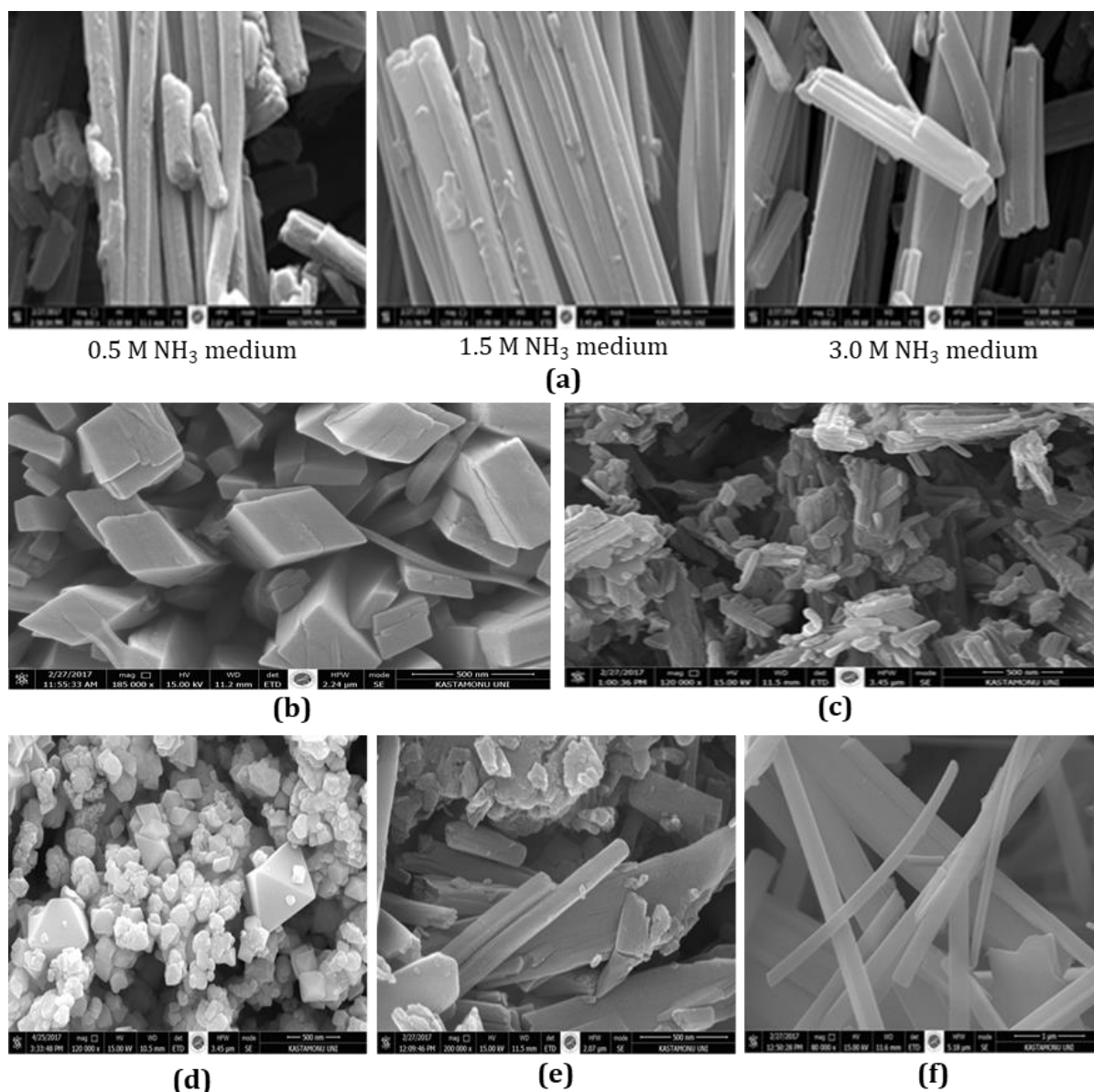


Figure 7. The SEM images of a) $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ complexes precipitated in different NH_3 concentration, b) $[\text{NiSAP}]$ complex from SAPH_2 and $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ prepared, c) $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ precipitated in 0.5 M NH_3 complexes, after thermal degradation at 450 °C, d) $[\text{NiSAP} \cdot \text{NH}_3]$ complex after thermal degradation at 450 °C. e) $[\text{NiSAP}]$ complex after thermal degradation, f) $[\text{NiSAP} \cdot \text{pip}]$ complex after thermal degradation.

and in the 3.0 M NH_3 , 250-430 nm in length. $[\text{NiSAP}]$ complex is a substance which precipitated as small particles and the SEM image of precipitated particles is provided in Fig. 7b. According to the scale, the diameter of these particles of this complex is between 50-330 nm. $[\text{NiSAP} \cdot \text{NH}_3]$, $[\text{NiSAP} \cdot \text{Et}_2\text{NH}]$ and $[\text{NiSAP} \cdot \text{pip}]$ complexes could be crystallized in a few mm diameter. For this reason, these complexes were not measured with SEM method. When these complexes decompose at a temperature of 450 °C, they were turned to NiO particles in air. The SEM images of the remained particles obtained after thermal decomposition are seen in Fig. 7c, 7d, 7e and 7f. After thermal decomposition, $[\text{Ni}_2\text{L}_2(\text{NH}_3)_3]$ complex particles turned into sticks in 35-100 nm diameter and $[\text{NiSAP} \cdot \text{NH}_3]$ complex particles into rhombic particles in 40-220 nm diameters, there is a few rhombic prisms are 580 nm in diameter among these prisms. These

rhombic particles convert into octahedral NiO particles after thermal degradation as seen in Fig. 7d. There are other studies reported for octahedron NiO nanoparticles prepared by thermal method in the literature [33,34,46,47]. As seen in Figure 7e and 7f, the NiSAP and $\text{NiSAP} \cdot \text{pip}$ complex convert into sticks NiO particles with a diameter of 100-415 nm, and the $\text{NiSAP} \cdot \text{pip}$ complex into NiO particles with a diameter of 130-380 nm at the end of thermal decomposition. The particles of the $[\text{NiSAP}]$ complex have grown even more at the end of the thermal decomposition; the $[\text{NiSAP}]$ contains particles of 50-330 nm diameters during the first precipitation, while these particles were transformed into particles of 100-415 nm diameters at the end of the thermal decomposition.

There are examples in the literature for NiO nanoparticles prepared by thermal methods using Ni-

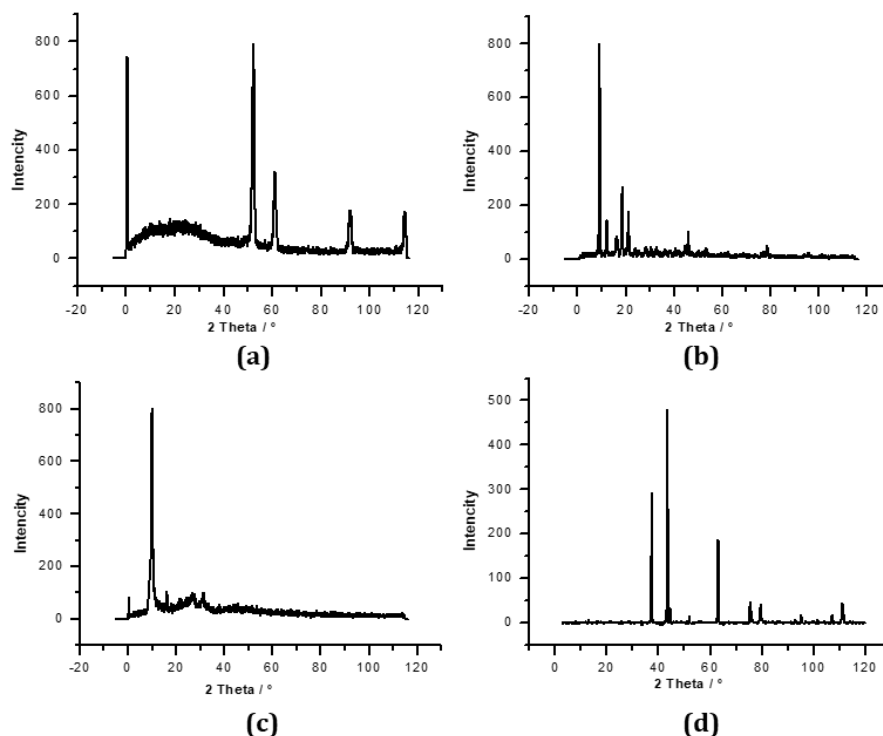


Figure 8. XRD patterns of some complexes prepared and final product NiO prepared from thermal decomposition a) $[Ni_2L_2(NH_3)_3]$ complex obtained from 0.5 M NH_3 media b) NiL c) [NiSAP] d) NiO.

Schiff base complexes. Studies have been published on the production of NiO nanoparticles by thermal decomposition from bidentate Schiff bases - Ni(II) [30, 46-51], tridentate Schiff bases - Ni(II) [34, 51] and tetradentate Schiff bases - Ni(II) complexes [52, 53]. In these studies, the particle diameter was generally calculated from the powder XRD pattern. Diameters of NiO particles prepared from complexes of bidentate ligands were reported as 10-50 nm, while diameters of tetradentate ligands were reported as 20 nm. NiO particle radii that we found in our study are higher but within the nanoparticle frame. Especially NiO octahedral particles are very similar to the two studies in the literature. [46, 47].

In fact, the BET results confirm this observation, when [NiSAP] first precipitated the surface area was 21.510 m^2/g , after the thermal degradation, this surface area

has been calculated as 18.025 m^2/g . The materials prepared were investigated by the powder X-ray diffraction method (XRD) and the diffraction patterns were identified, and the average particle diameter was calculated approximately according to the calculation method given in the literature to support SEM and BET results [54,55]. The average particle diameters obtained from BET and XRD results are given in Table 2 and XRD patterns of some complexes and final product NiO in Fig. 8a-d.

4. Conclusion

Two insoluble and three soluble Ni(II) complexes have been prepared from ONNO and ONO type Schiff Bases in media including of an amine and were thermal decomposed this complexes under air at 450 °C. It was observed that insoluble complexes were precipitated

Table 2. The average diameter of the prepared complexes and pyrolysis products by using SEM and XRD methods.

Complex	Measured diameter / nm	
	SEM	XRD
$[Ni_2L_2(NH_3)_3]$ Precipitated in 0.5 M NH_3	110-150	137.45
$[Ni_2L_2(NH_3)_3]$ Precipitated in 1.0 M NH_3	90-320	142.32
$[Ni_2L_2(NH_3)_3]$ Precipitated in 1.5 M NH_3	250-430	--
[NiL]	30-145	119.67
[NiSAP] obtained by $Ni(AcO)_2$	50-330	42.18
[NiSAP] obtained from NiSAP.pip	130-800	--
[NiSAP] obtained from NiSAP. NH_3	130-470	324.28
[NiSAP] obtained from NiSAP.Et ₂ NH	110-380	--
NiO product of $[Ni_2L_2(NH_3)_3]$	110-249	148.74
NiO product of [NiL.pip]	140-780	--
NiO product of [NiSAP. NH_3]	100-415	162.26
NiO product of [NiSAP.Et ₂ NH]	140-670	--

in the limits of nano particle scale furthermore the thermal decomposition products were also obtained in nanoparticle dimension. The soluble complexes were obtained crystalline but it was seen after the thermal decomposition the NiO particles obtained are the nanoparticles. As a result, thermal decomposition of low soluble complexes can be suggested as an effective method for nanoparticle metal oxides preparation.

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