Süleyman Demirel Üniversitesi Fen Edebiyat Fakültesi Fen Dergisi

Süleyman Demirel University Faculty of Arts and Sciences Journal of Science

2020, 15(1): 177-193

DOI: 10.29233/sdufeffd.684472

Atıf için / For Citation: E. K. İnal, O. Atakol, M. A. Akay, "The Electron Ionization Mass Spectra of ONO, ONNO and O_3N_3 Type Schiff Base Complexes Containing First Row Transition Metal Ions", *Süleyman Demirel Üniversitesi Fen Edebiyat Fakültesi Fen Dergisi*, 15(1), 177-193, 2020.

The Electron Ionization Mass Spectra of ONO, ONNO and O_3N_3 Type Schiff Base Complexes Containing First Row Transition Metal Ions

Emine Kübra İNAL*[1], Orhan ATAKOL[1], M. Abdulkadir AKAY[1]

[1]*Ankara University, Department of Chemistry, Faculty of Science, 06100, Ankara, Turkey*

**corresponding author e-mail: inal@science.ankara.edu.tr*

(Alınış / Received: 04.02.2020, Kabul / Accepted: 21.05.2020, Yayımlanma / Published: 31.05.2020)

Abstract: Mono-, di- and trinuclear complexes of Fe(III), Co(II), Ni(II), and Cu(II) ions with Bis-N,N'(salicylidene)-1,3-diaminopropane (LH_2), Bis-N,N'(salicylidene)-2,2'-dimethyl-1,3-diaminopropane ($LDMH_2$), N(salicylidene)-2-hydroxyaniline (SAP), and Tris-N,N',N"(salicylidene)-2,2',2"-aminoethylamine (Trensal) were prepared and ionized with 30-110 eV electrons in direct inlet (DI). Compounds with metal-oxygen covalent bonds were observed to give molecular peaks, whereas polynuclear complexes containing coordinative bonds did not have such peaks. It was concluded that the coordinative bonds were dissociated by electron impact (EI). The thermogravimetric analysis reveals that the molecular peak observed for the mononuclear complexes which are stable up to 300 °C is also the base peak. The peaks obtained for the di- and trinuclear complexes that decomposed at these temperatures could not be observed as a molecular signal. The resulting fragments were evaluated and compared with the literature data.

Key words: Schiff base, Transition metal complexes, Mass spectrometry, Electron ionization

Birinci Sıra Geçiş Metali İyonlarını İçeren ONO, ONNO ve O_3N_3 Tipi Schiff Bazı Komplekslerinin Elektron İyonlaştırma Kütle Spektrumları

Özet: Bis-N,N'(salisiliden)-1,3-diaminopropan (LH_2), Bis-N,N'(salisiliden)-2,2'-dimetil-1,3-diaminopropan ($LDMH_2$), N(salisiliden)-2-hidroksianilin (SAP) ve Tris-N,N',N"(salisiliden)-2,2',2"-aminoetilamin (Trensal) ile tek, iki ve üç çekirdekli Fe(III), Co(II), Ni(II) ve Cu(II) kompleksleri hazırlanmış ve direkt inlet (DI) giriş sisteminde 30-110 eV enerjili elektronlarla iyonlaştırılmıştır. Metal-oksijen kovalent bağı içeren bileşiklerde moleküler pik gözlenirken koordinatif bağ içeren çok çekirdekli komplekslerde bu pikler görülmemiştir. Koordinatif bağların elektron etkisi (EI) ile parçalandığı sonucuna varılmıştır. Termogravimetrik analiz, 300 °C'ye kadar kararlı olan tek çekirdekli kompleksler için gözlenen moleküler pikin ayrıca temel pik olduğunu da ortaya koymaktadır. Bu sıcaklıklarda parçalanan iki ve üç çekirdekli kompleksler için elde edilen pikler, moleküler sinyal olarak gözlenememiştir. Elde edilen fragmentler değerlendirilerek literatür verileri ile karşılaştırılmıştır.

Anahtar kelimeler: Schiff bazı, Geçiş metali kompleksleri, Kütle spektrometri, Elektron iyonlaştırma

---

Emine Kübra İNAL, inal@science.ankara.edu.tr, ORCID: https://orcid.org/0000-0001-8334-2791
Orhan ATAKOL, atakol@science.ankara.edu.tr, ORCID: https://orcid.org/0000-0003-0977-6588
M. Abdulkadir AKAY, akay@science.ankara.edu.tr, ORCID: https://orcid.org/0000-0001-5763-4379

1. Introduction

Mass spectrometry has become increasingly popular in the characterization of coordination compounds due to the development of soft ionization methods over the last two decades. However, most of these studies have been carried out with atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI), and especially electrospray ionization (ESI) [1-20]. The studies performed by classical ionization methods are very limited [16, 21-25]. Schiff base transition metal complexes studied extensively by mass spectrometry include Bis-N,N'(salicylidene)-1,2-ethylenediamine complexes. The complexes of this ligand were subjected to a detailed comparative study using soft and hard ionization methods [20]. It has been reported that the number of molecular fragments depends on the valence state of the metals. In light of all these, it was reported that EI method is not suitable for the coordination compounds [20-21]. In salen complexes, trivalent metal ions have been reported to be neutralized by two phenolic oxygens of salen ligand and an additional ligand X such as the AcO^-, Cl^-, BF_4^-. The presence of $[\text{Metalsalen}]^+$ and [MetalsalenX] molecular peaks in the relevant mass spectra have been reported. However, there is no data on the mass fragmentation of di- or trinuclear coordination compounds. A few mass spectra of the complex of N(salicylidene)-2-hydroxyaniline (SAP) by electron ionization have been reported [23-26]. Bis-N,N'(salicylidene)-1,3-diaminopropane (LH_2) is a ligand which easily gives polynuclear complexes. The first di- and trinuclear complexes of this ligand have been reported in 1976 and 1990, respectively [27, 28]. However, since 1990, numerous studies have been conducted on polynuclear complexes and derivatives of this ligand in the literature [29-42]. The structures of Ni(II) and Cu(II) mononuclear complexes of this ligand appeared in the literature in 1985 [43]. These mononuclear complexes can be converted into polynuclear complexes with different anions and cations. These polynuclear coordination compounds are formed by μ-bridges formed by the phenolic oxygens and the oxygens of anions such as AcO^-, NO_3^-, NO_2^-.

In this study, mono, di- and trinuclear coordination compounds were synthesized using LH_2, $LDMH_2$, SAP, and Trensal. Their respective mass spectral data obtained with 30-110 eV electrons were evaluated and compared with the data given in the literature. The molecular structures of most of these compounds were elucidated by X-ray diffraction methods. All studies were carried out by the synthesis procedures of our working group. The structures of the coordination compounds synthesized are given in Figure 1.

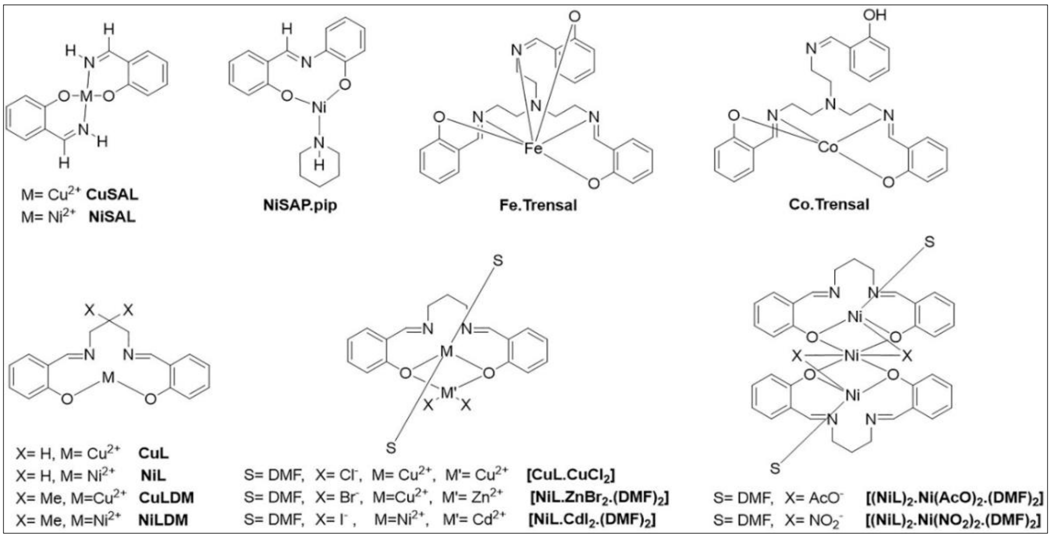


Figure 1. The structural formula of the coordination compounds prepared in this study

The thermogravimetric analysis of the di- and trinuclear complexes prepared from Schiff bases reveals that coordinated solvent molecules are separated from the structure at 120-170°C [33].

2. Material and Method

2.1 Chemicals

All the chemicals used were of high purity grade and were used without further purification. 1,3-diaminopropane, 2,2'-dimethyl-1,3-diaminopropane, Tris(2-aminoethyl)amine, 2-hydroxyaniline, trimethylamine, 1,4-dioxane, salicylaldehyde, piperidine, N,N-dimethylformamide, $NaNO_2$ were purchased from Sigma-Aldrich Chemical Co., $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $FeCl_3.6H_2O$, $CoCl_2.6H_2O$, CdI_2, $Ni(CH_3COO)_2.4H_2O$, $ZnBr_2$, $ZnCl_2$ were purchased from Merck Millipore Chemical Co.

2.2 Instruments

TG-DTA studies were performed with Shimadzu DTG-60H apparatus. The thermogravimetric analysis was carried out in Pt pans at a rate of 10 °C/min under a nitrogen atmosphere. IR spectra of the Schiff base ligands and metal complexes were performed using Shimadzu IRAffinity-1 FTIR spectrometer and all spectra were measured at a resolution of 4 cm^{-1}. C, H, and N analyses were carried out by Eurovector 3018 CHNS analyzer while Ni and Cu analyses were completed by GBC Avanta PM flame atomic absorption spectrometer. NMR spectra of the Schiff bases were recorded on a Varian Mercury 400 MHz using tetramethylsilane as internal. Mass spectra were obtained using direct inlet (DI) unit of Shimadzu QP2010 Plus GCMS apparatus. Ion source and interface temperature were set at 200 °C. The temperature of DI probe was increased to 350 °C at 20 °C/min. Mass spectra were recorded at m/z=40-700. A summary of some of the spectral data and details of the ligands and complexes are given in Tables 1-2.

2.3 Preparation of Schiff Bases

0.1 mole (12.21 g) salicylaldehyde was dissolved in 150 mL of hot EtOH. 50 mL EtOH solution of 0.05 mole (3.71 g) 1,3-diaminopropane for LH_2; 0.05 mole 2,2'-dimethyl-1,3-propanediamine (5.11 g) for $LDMH_2$; 0.033mole Tris(2-aminoethyl)amine (4.83 g) for Trensal and 0.1 mole 2-hydroxyaniline (12.32 g) for SAP were added and heated to the boiling points. After cooling, the Schiff base crystals were filtered.

2.4 Preparation of Mononuclear NiL and NiLDM Complexes

0.01 mole LH_2 (2.82 g) or $LDMH_2$ (3.10 g) was dissolved in 100 mL of hot EtOH. 5 mL concentrated ammonia solution was added and heated to the boiling point. 0.01 mole $NiCl_2.6H_2O$ (2.38 g) in 50 mL of hot water was added, stirred well, the crystals were filtered and dried in air. The resulting complexes were $NiL.NH_3$ and $NiLDM.NH_3$. These complexes were kept at 180 °C for 4 hours to remove the NH_3 from the structure.

2.5 Preparation of Mononuclear CuL and CuLDM Complexes

0.01 mole LH_2 (2.82 g) or $LDMH_2$ (3.10 g) was dissolved in 100 mL of hot EtOH. 1 mL Et_3N was added and heated to the boiling point. 0.01 mole of $CuCl_2.2H_2O$ (1.34 g) in 50 mL of hot water was added, stirred well, the crystals were filtered and dried in air.

2.6 Preparation of NiSAL and CuSAL Complexes

0.02 mole LH_2 (5.64 g) was dissolved in 100 mL of hot EtOH. 5 mL ammonia solution was added and heated to the boiling point. 50 mL of a hot aqueous solution of 0.01 mole

$NiCl_2.6H_2O$ (2.38 g) for NiSAL; 0.01 mole $CuCl_2.2H_2O$ (1.34 g) for CuSAL was added, stirred well, the crystals were filtered and dried at 110 °C for 4 hours.

2.7 Preparation of Fe.Trensal and Co.Trensal Complexes

0.001 mole Trensal (0.46 g) was dissolved in 50 mL of hot dioxane. 0.5 mL Et_3N was added and heated until 80-90 °C. 20 mL of MeOH solution of 0.001 mole $FeCl_3.6H_2O$ (0.27 g) or $CoCl_2.6H_2O$ (0.24 g) was added, stirred well, the crystals were filtered and dried in air.

2.8 Preparation of NiSAP.pip

0.002 mole SAP (0.43 g) was dissolved in 100 mL of hot EtOH. 1.5 mL piperidine was added, heated to 70 °C and 0.002 mole $NiCl_2.6H_2O$ (0.48 g) in 50 mL of MeOH was added, refluxed for 2 hours, the crystals were filtered and dried in air.

2.9 Preparation of Dinuclear Complexes

0.002 mole LH_2 (0.56 g) was dissolved in 50 mL of DMF and heated until 100-110 °C. 0.002 mole $NiCl_2.6H_2O$ (0.48 g) or $CuCl_2.2H_2O$ (0.27 g) in 30 mL of MeOH and a solution of 0.002 mole MX_2 in 20 mL of hot MeOH (M: Cu^{2+}, Zn^{2+}, Cd^{2+}; X= Cl^-, Br^-, I^-) were added, stirred well, the crystals were filtered and dried in air.

2.10 Preparation of Trinuclear Complexes

0.002 mole LH_2 (0.56 g) was dissolved in 50 mL of DMF and heated until 100-110 °C. 0.002 mole $NiCl_2.6H_2O$ (0.48 g) in 30 mL of MeOH and a solution of 0.001 mole $Ni(AcO)_2.4H_2O$ (0.25 g) or 0.001 mole $NiCl_2.6H_2O$ (0.24 g) and 0.002 mole $NaNO_2$ (0.14 g) in 20 mL of hot MeOH were added, stirred well, the crystals were filtered and dried in air.

Table 1. Characteristic Properties and Abbreviations of the Compounds Synthesized

Compounds	**Molecular Weight, g/mol**	**Abbreviation**	**Yield, %**	**Melting Point, °C**
$C_{17}H_{18}N_2O_2$	282	LH_2	87	57
$C_{19}H_{22}N_2O_2$	310	$LDMH_2$	92	97
$C_{27}H_{30}N_4O_3$	458	Trensal	82	92
$C_{13}H_{11}NO_2$	213	SAP	88	182
$C_{17}H_{16}N_2O_2Ni$	338	NiL	90	>300 (decomp:270)
$C_{19}H_{20}N_2O_2Ni$	366	NiLDM	75	>300 (decomp:260)
$C_{17}H_{16}N_2O_2Cu$	343	CuL	65	>300 (decomp:260)
$C_{19}H_{20}N_2O_2Cu$	371	CuLDM	73	>300 (decomp:250)
$C_{14}H_{12}N_2O_2Ni$	298	NiSAL	80	>300 (decomp:240)
$C_{14}H_{12}N_2O_2Cu$	303	CuSAL	80	>300 (decomp:230)
$C_{27}H_{27}N_4O_3Fe$	511	Fe.Trensal	25	decomp:220
$C_{27}H_{28}N_4O_3Co$	515	Co.Trensal	15	decomp:220
$C_{18}H_{20}N_2O_2Ni$	354	NiSAP.pip	30	n.d.
$C_{23}H_{30}N_4O_4NiZnBr_2$	709	$NiL.ZnBr_2$	53	decomp:138
$C_{23}H_{30}N_4O_4NiCdI_2$	850	$NiL.CdI_2$	40	decomp:140
$C_{17}H_{16}N_2O_2Cu_2Cl_2$	526	$CuL.CuCl_2$	55	>300
$C_{44}H_{52}N_6O_{10}Ni_3$	998	$[(NiL)_2.Ni(AcO)_2]$	60	decomp:145
$C_{40}H_{46}N_8O_{10}Ni_3$	972	$[(NiL)_2.Ni(NO_2)_2]$	60	decomp:140

Table 2. A Summary of Elemental Analysis, FTIR and NMR Spectral Data

Compounds	**Elemental Analysis Calculated% (Found%)**						**Important IR Data, cm^{-1}**							
	C	**H**	**N**	**M^1**	**M^2**	$\nu_{\mathrm{N-H}}$	$\nu_{\mathrm{O-H}}$	$\nu_{\mathrm{C-H(Ar)}}$	$\nu_{\mathrm{C-H(Al)}}$	$\nu_{\mathrm{C=O}}$	$\nu_{\mathrm{C=N}}$	$\nu_{\mathrm{C=C(Ar)}}$	$\nu_{\mathrm{C-O(Ph)}}$	$\varepsilon_{\mathrm{C-H(Ar)}}$
LH$_2$	72.32 (71.91)	6.43 (6.45)	9.92 (10.47)	-			2627	3021- 3019	2929- 2862		1629	1608	1274- 1151	762
	^{1}H NMR		13.51 (s)	8.60 (s)	7.43 (d)	7.32 (t)	6.88 (t)	3.68 (t)	2.01 (p)					
	^{13}C NMR		166.6	161.1	132.7	132.1	119.1	118.9	116.9	58.5	31.9			
LDMH$_2$	73.52 (73.41)	7.14 (6.35)	9.02 (8.72)	-			2578	3021- 3019	2929- 2862		1629	1608	1274- 1151	762
	^{1}H NMR		13.58 (s)	8.36 (s)	7.25 (d,t)	7.30 (t,d)	6.97 (d)	6.84 (d,t)	3.49 (s)	1.04 (s)				
	^{13}C NMR		166.99	161.45	132.57	131.61	118.95	118.87	117.20	68.36	34.48	24.61		
Trensal	70.72 (70.39)	6.59 (5.86)	12.21 (11.92)	-			2733- 2654	3051- 3020	2939- 2835		1631	1608- 1581	1276- 1197	754
	^{1}H NMR		13.80 (s)	7.88 (s)	7.27 (m)	6.93 (m)	6.82 (m)	6.54 (m)	3.59 (t)	2.87 (t)				
	^{13}C NMR		167.60	164.92	134.02	133.56	119.55	119.11	118.64	57.85	56.51			
SAP	72.52 (73.77)	5.19 (5.31)	6.56 (6.43)	-			2557	3045	2934- 2839		1625	1612- 1591	1219- 1136	761
	^{1}H NMR		13.80 (s)	8.98 (s)	7.55 (d,t)	7.34 (t,d)	6.97 (d)	6.86 (d,t)						
	^{13}C NMR		165.69	160.53	151.15	134.96	132.82	131.43	130.78	128.17	119.54	118.55	117.96	116.68

Table 2. A Summary of Elemental Analysis, FTIR and NMR Spectral Data (continued)

Compounds	**Elemental Analysis Calculated% (Found%)**					**Important IR Data, cm^{-1}**								
	C	**H**	**N**	**M^1**	**M^2**	$\nu_{N–H}$	ν_{O-H}	$\nu_{C–H(Ar)}$	$\nu_{C–H(Al)}$	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=C(Ar)}$	$\nu_{C–O(Ph)}$	$\varepsilon_{C–H(Ar)}$
NiL	60.28 (60.55)	4.76 (3.17)	8.27 (7.93)	17.33 (17.19)			-	3061-3030	2922-2866		1607	1589-1541	1228-1124	725-744
NiLDM	62.17 (61.84)	5.49 (5.21)	7.62 (7.37)	15.99 (15.69)			-	3049-3021	2924-2866		1608	1586-1535	1221-1120	754
CuL	59.38 (60.07)	4.69 (4.39)	8.14 (7.67)	18.48 (17.76)			-	3052-3031	2930-2866		1608	1592-1544	1235-1124	746
CuLDM	61.37 (61.07)	5.42 (4.37)	7.52 (6.91)	17.09 (17.21)			-	3074-3018	2956-2862		1608	1598-1541	1203-1120	754
NiSAL	56.25 (56.08)	4.04 (3.87)	9.36 (8.95)	19.64 (18.92)		3302	-	3074-3018	-	-	1610	1597-1570	1217-1142	751
CuSAL	55.36 (55.41)	3.97 (3.55)	9.22 (8.71)	20.92 (20.22)		3311	-	3077-3016	-	-	1612	1597-1530	1219-1141	750
Fe.Trensal	63.42 (62.58)	5.32 (4.93)	10.95 (10.41)	10.92 (10.27)		-	-	3049-3022	2941-2848	-	1629	1591-1539	1319-1147	748
Co.Trensal	62.90 (62.87)	5.47 (5.08)	10.86 (10.39)	11.44 (10.89)		-	-	3043-3027	2940-2836	-	1624-1619	1597-1546	1304-1142	750
NiSAP.pip	60.83 (60.89)	5.69 (5.63)	7.80 (7.89)	16.79 (16.15)		3341-3253	-	3053-3017	-	-	1605	1590-1543	1195-1084	751
NiL.ZnBr$_2$	38.88 (37.89)	4.26 (4.03)	7.88 (7.98)	8.26 (7.98)	9.20 (9.16)	-	-	3049-3014	2939-2845	1651	1624	1593	1289-1109	750
NiL.CdI$_2$	32.44 (32.19)	3.55)2.99)	6.58 (6.36)	6.89 (6.49)	13.19 (12.41)				2925-28					
CuL.CuCl$_2$	42.69 (42.08)	3.37 (3.13)	5.85 (5.17)	26.57 (25.48)	-	-	-	3024	2916-2846	-	1622	1595-1540	1294-1116	756
[(NiL)$_2$. Ni(AcO)$_2$]	52.79 (52.37)	5.23 (4.92)	8.39 (7.93)	17.59 (17.23)	-	-	-	3052-3031	2942-2860	1652	1615	1589-1543	1315-1093	752
[(NiL)$_2$. Ni(NO$_2$)$_2$]	49.27 (48.79)	4.75 (4.32)	11.49 (11.07)	18.06 (17.41)	-	-	-	3049-3022	2924-2860	1645	1625	1596-1546	1309-1105	758

3. Results

The aim of this study is to enlighten the MS fragment properties of the 2-hydroxy substituted Schiff base complexes. The most suitable examples for such Schiff bases are those derived from 2-hydroxy benzaldehyde. LH_2 gives CuL and NiL complexes with Cu(II) and Ni(II) ions in an alcoholic medium at high pH values. The MS spectra of LH_2 ligand and its mononuclear complexes obtained by electron ionization method are depicted in Figure 2.

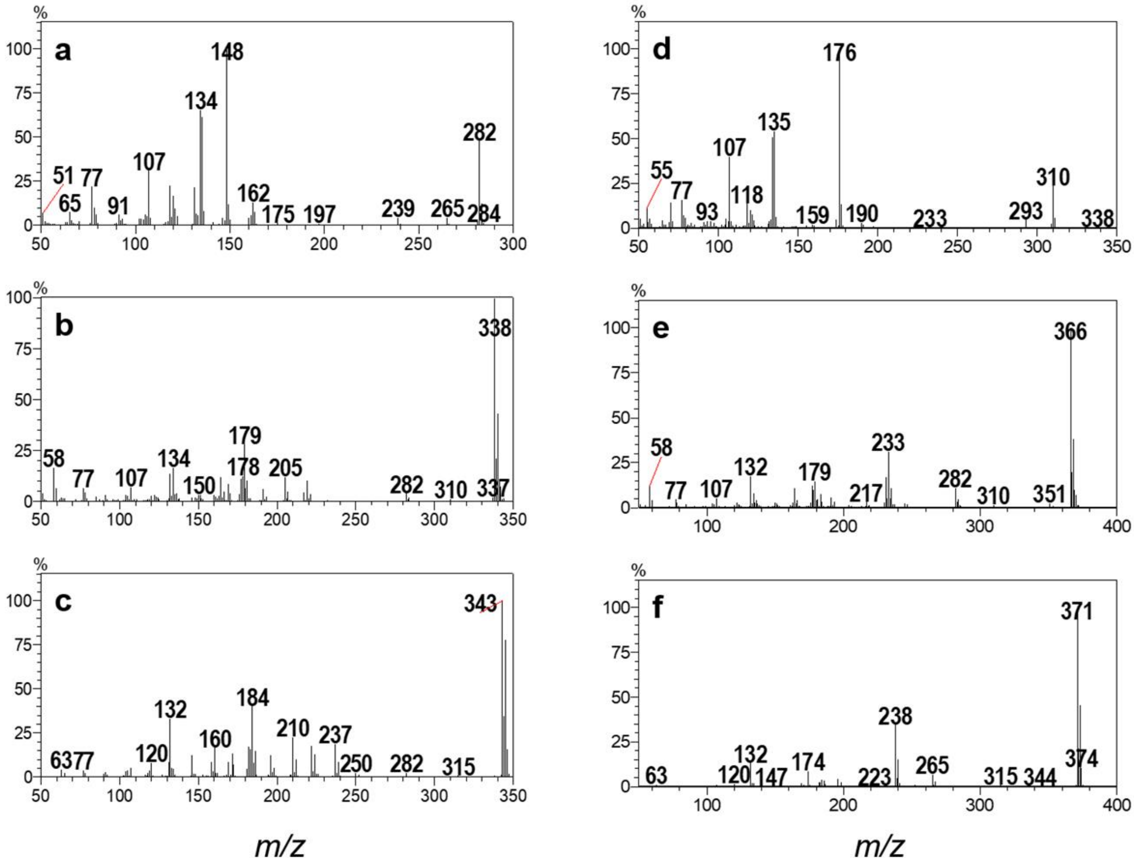
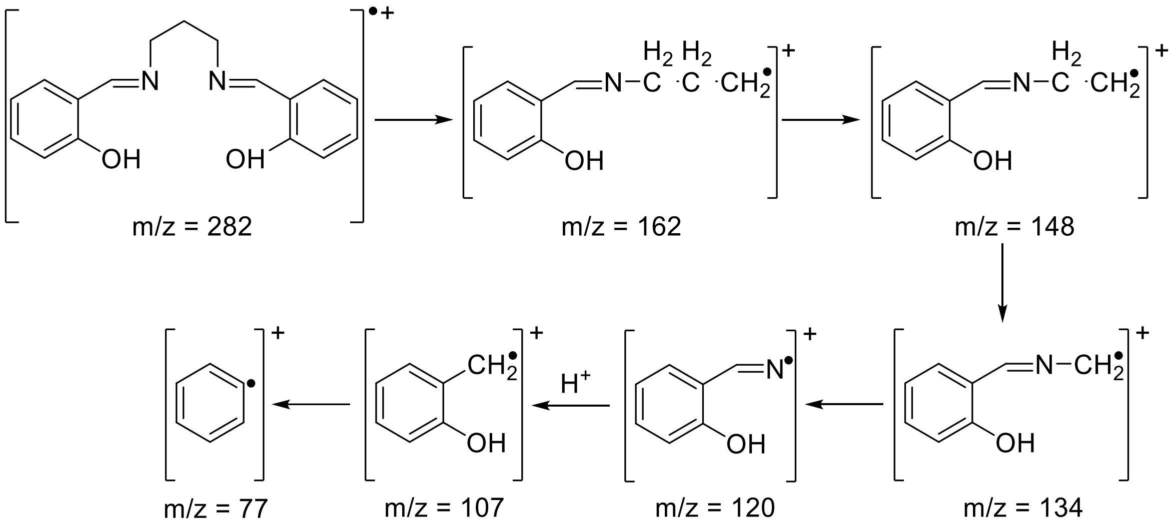


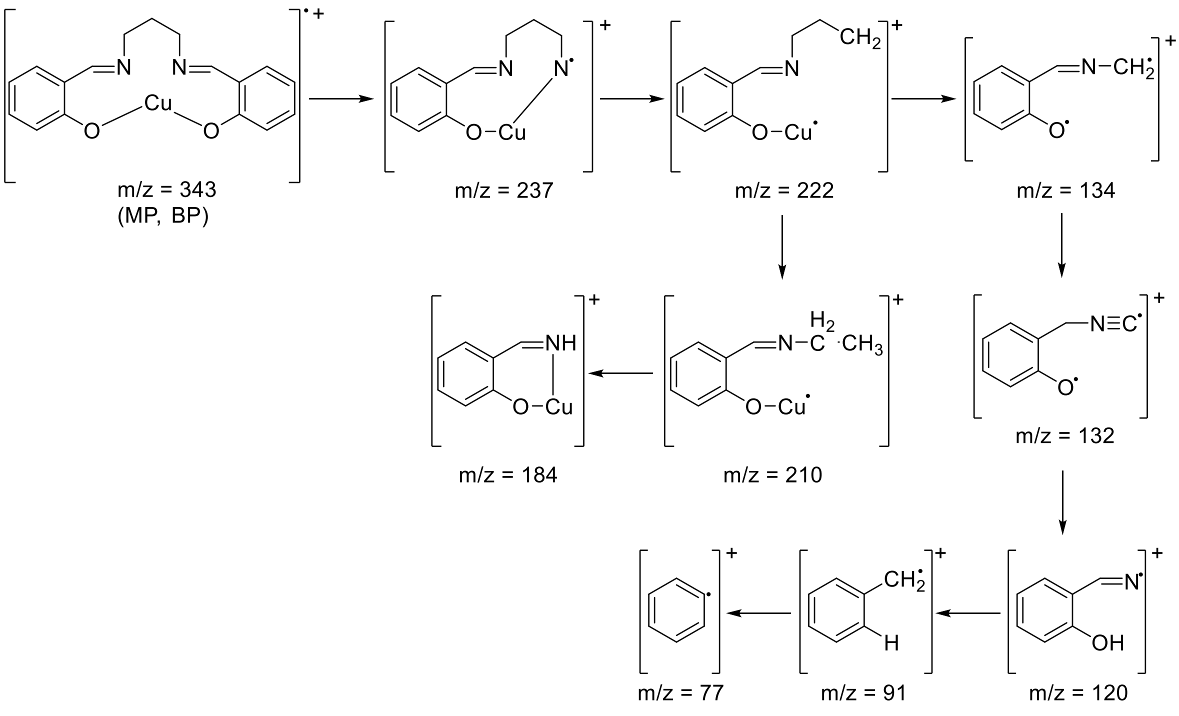
Figure 2. Mass spectra obtained with 70 eV electrons a. LH_2, b. NiL, c. CuL, d. $LDMH_2$, e. NiLDM, f. CuLDM

In Figure 2a the molecular signal of LH_2 ligand appears at m/z=282 in accordance with the nitrogen rule. However, the base peak of the spectra appears at m/z=148. The probable fragments of LH_2 ligand ionized with 70 eV electrons are given in Scheme 1.

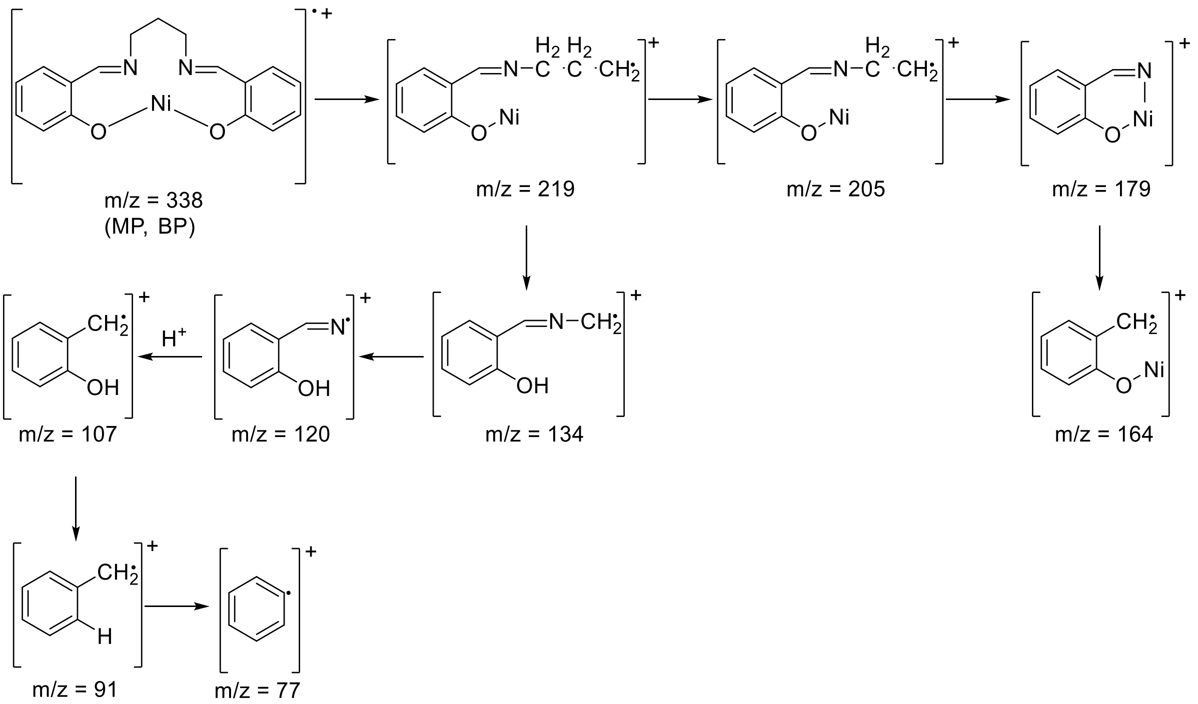


Scheme 1. Proposed fragmentation for LH_2 ligand

On the other hand, the molecular peak is clearly visible in the mass spectra of NiL and CuL mononuclear complexes and it is the most intensive peak in the spectra. The signals of the other fragments are almost negligible. The molecular signals of NiL and CuL appear at m/z=338 and 343, respectively. Since the organic compound is converted into a complex, the nitrogen rule is not expected to be valid. The probable fragments of NiL and CuL complexes are given in Schemes 2-3.



Scheme 2. Proposed fragmentation for CuL complex



Scheme 3. Proposed fragmentation for NiL complex

Similar complexes have been prepared to prove that the expected fragments are true. The mass spectra of $LDMH_2$ ligand and their CuLDM and NiLDM complexes by using 70 eV electrons are given in Figure 2. The ligand of CuSAL and NiSAL complexes is not stable at room temperature and unobtainable but its complexes are stable and synthesized by template synthesis in a medium containing salicylaldehyde and ammonia [44]. Cu.salicylaldehyde and Ni.salicylaldehyde complexes are formed in a weak basic medium containing salicylaldehyde, which have been previously reported in the literature [45].

As shown in Figure 2d the molecular signal appears weakly at m/z=310 and the base peak corresponds to m/z=176 $[HO\text{-}C_6H_4\text{-}CH{=}N\text{-}CH_2\text{-}C(CH_3)_2]^+$ ion. This is an expected result due to the tert-butyl radical, which is one of the most stable radicals [46]. The other signals at m/z=135, 107, 77 are almost the same with those of LH_2 ligand signals.

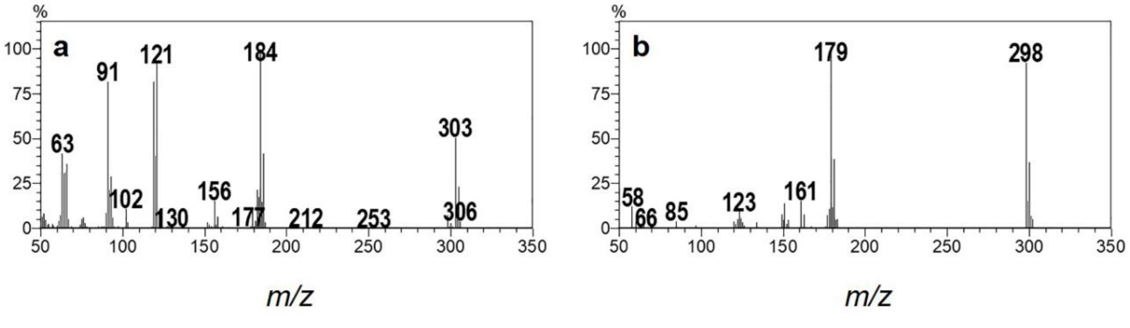


Figure 3. Mass spectra obtained with 70 eV electrons a. CuSAL, b. NiSAL

As seen from Figure 2 the complex state is more stable than the ligand and the molecular signals are also the base peak. In addition, the signals observed at m/z=238 and m/z=233 for CuLDM and NiLDM are similar to signals observed at m/z=184 and m/z=179 for CuSAL and NiSAL complexes and their isotope signals at m/z= 240, 235, 186, 181 correspond to the fragments including fragments Cu and Ni of this complexes.

These signals were attributed to $[CuO\text{-}C_6H_4\text{-}CH{=}N\text{-}CH_2\text{-}C(CH_3)_2]^+$ in CuLDM, $[NiO\text{-}C_6H_4\text{-}CH{=}N\text{-}CH_2\text{-}C(CH_3)_2]^+$ in NiLDM, $[CuO\text{-}C_6H_4\text{-}CH{=}NH]^+$ in CuSAL and $[NiO\text{-}C_6H_4\text{-}CH{=}NH]^+$ fragments in NiSAL.

In this study, an O_3N_3 type Schiff base was used as the hexadentate ligand parallel to the N_2O_2 type Schiff bases. For this goal, an O_3N_3 type Trensal ligand was prepared by using Tris(2,2',2"-aminoethyl)amine and salicylaldehyde. Fe(III) and Co(II) complexes were synthesized using this ligand [47].

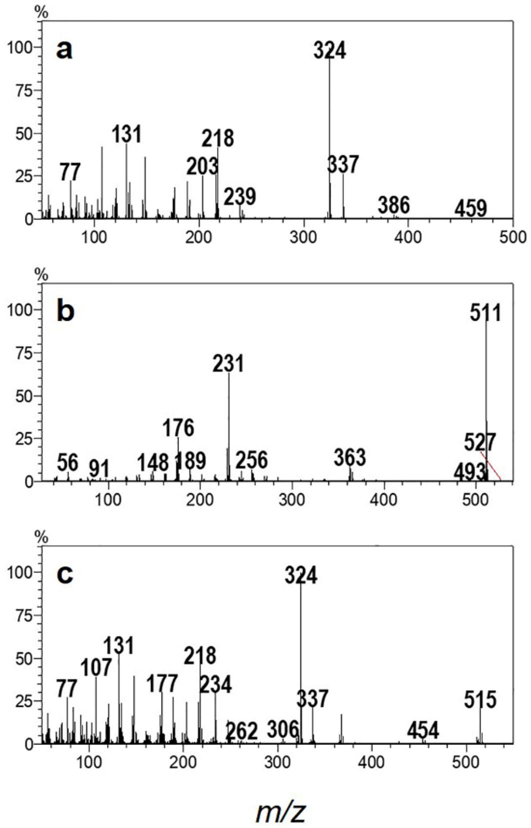
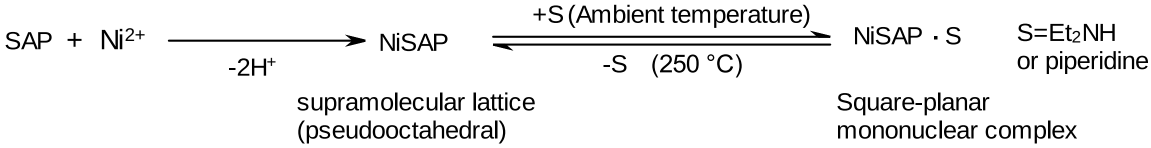


Figure 4. Mass spectra obtained with 70 eV electrons a. Trensal, b. Fe.Trensal, c. Co.Trensal

Due to the fact that Trensal is a fairly large organic molecule so that the base signal of m/z=458 is never observed and the signal which emerges as the base peak at m/z=324 must belong to $[(HO\text{-}C_6H_4\text{-}CH{=}N\text{-}(CH_2)_2\text{-}N\text{-}CH_2{}^{\cdot}]$ radical ion (Figure 4a). Since the compound contains 3 nitrogens, it can be considered that it does not follow the nitrogen rule. However it is not in a molecular, it is a radical ion. The [M+1] isotope peak verifies this structure. The molecular signal of Fe.Trensal complex at m/z=511 is the base peak in the spectrum. The simplicity of the spectrum shows that the complex is highly stable.

Since Co element has only one isotope (^{59}Co) in nature, the isotope peak appears near to m/z=515, the signal must be due to ^{13}C atoms only. As shown in Figure 4c, the signal at m/z=515 is not base peak in the spectrum, it is one of the weak signal in the spectrum. As noted in the experimental part, Co.Trensal complex prepared from Co(II) salts and the resulting complex is a Co(II) complex. It is probable that one phenolic group of the ligand was coordinated to Co(II) ion as phenol (Figure 1). One of the chelate rings of the complex is not formed due to an uncoordinated oxygen atom and decreases the stability of Co.Trensal complex. Since in Fe.Trensal complex all the phenolic oxygen and iminic nitrogens take place in coordination, the resulting chelate rings formed are much more stable. Hence, the molecular peak in Fe.Trensal complex is observed as the base peak. On the other hand, Co.Trensal complex has one phenolic oxygen and one imine group which does not take part in coordination making the molecule much more unstable where no molecular signal is detected.

Another example of mononuclear complexes is the complex that was prepared by using SAP. This ONO type tridentate type ligand gives mononuclear complexes with divalent transition metals. However, it was stated that in solid structure these complexes are plenarily located as dimeric units in the lattice resulting in a supramolecular structure [48]. This complex is not soluble in any common organic solvent and remained intact up to 300 °C. However, these complexes are dissolved by the conversion of mononuclear square-planar or octahedral complexes in the presence of pyridine, NH_3, piperidine, Et_2NH (Scheme 4) [49]. Using this ligand, NiSAP.piperidine complex was prepared and investigated in DI unit. The resulting mass spectra are given in Figure 5.



Scheme 4. Formation of NiSAP complex in the presence of piperidine

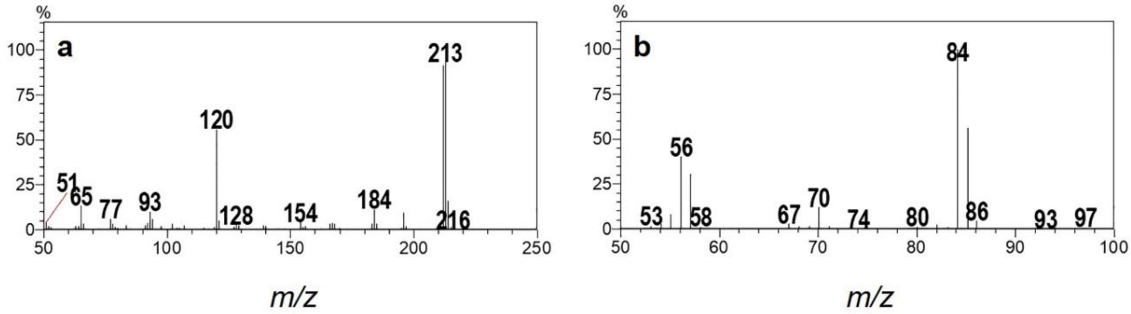


Figure 5. Mass spectra obtained with 70 eV electrons a. SAP, b. NiSAP.piperidine

Figure 5a shows the mass fragments of SAP ligand with 70 eV electrons. The spectrum is very simple showing a molecular [M] signal at m/z=213. The signal that appeared at m/z=214 is [M+1] isotope peak due to ^{13}C atoms and the powerful signal observed at 212 is the signal due to ionization. The signals observed in Figure 5b are solely due to fragments of piperidine coligand. As given in Scheme 4, these remained stable up to 240 °C. After this temperature coligands are removed from the medium in gaseous form leaving a supramolecular complex behind which remained intact up to 300 °C and pyrolyzed around at 320 °C [50]. When DI temperature is between 200-250 °C, all the coligands are evaporated and the fragments originate from amine molecules separated from the structure. The remaining supramolecular structure could not be ionized and volatilized with 70-110 eV electrons. Even the fragments belonging to SAP ligand are absent. However, there is an example in the literature which is very difficult to explain. The authors claimed to have synthesized $ZnSAP.H_2O$ complex observed the molecular signal at m/z=294 with 70 eV electrons [23].

There are an abundant amount of [M+1] and [M+2] signals observed in addition to molecular peak in the spectra of CuL, NiL, CuLDM, NiLDM, CuSAL, NiSAL, Fe.Trensal and Co.Trensal mononuclear complexes. The stable isotopes of Cu in nature are ^{63}Cu and ^{65}Cu with relative abundances of 69.17% and 30.83%. The stable isotopes of Ni are ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni with relative abundances of 68.08%, 26.22%, 1.14%, 3.63% and 0.92% [51]. Therefore the intensity of [M+2] signal in CuL should be 30.83/69.17=1/2.24 of the molecular signal. The corresponding ratio in NiL complex 26.22/68.08=1/2.59. Since there are no stable isotopes of Cu and Ni with a mass number 64 and 59 in nature, the intensity of [M+1] signal is largely determined by ^{13}C atoms. Since there are 17 C atoms in CuL and NiL complexes and if we remember that the relative abundance of ^{13}C atom in nature is 1.07% the intensity [M+1] of this complex must be 17×0.0107=18.2% of the molecular signal. The values found from spectra are comparable to this value. The isotopes of Fe in nature are ^{54}Fe, ^{56}Fe, ^{57}Fe and ^{58}Fe with relative abundances of 5.85%, 91.75%, 2.12% and 0.28% [51]. Co has a single isotope of ^{59}Co. The expected and the experimental values of the molecular signal [M] and isotope signals [M+1] and [M+2] of the mononuclear complexes investigated in this study are listed in Table 3.

Table 3. Molecular/Isotope Ratios of the Mononuclear Complexes Investigated

Compounds	**Molecular Formula**	**[M]/[M+1]**		**[M]/[M+2]**	
		Calculated	**Found**	**Calculated**	**Found**
CuL	$C_{17}H_{16}N_2O_2Cu$	4.98	4.72	2.25	2.12
NiL	$C_{17}H_{16}N_2O_2Ni$	4.98	4.93	2.62	2.56
CuLDM	$C_{19}H_{20}N_2O_2Cu$	4.47	4.50	2.25	2.20
NiLDM	$C_{19}H_{20}N_2O_2Ni$	4.47	4.36	2.62	2.41
CuSAL	$C_{14}H_{10}N_2O_2Cu$	6.42	6.10	2.25	2.14
NiSAL	$C_{14}H_{10}N_2O_2Ni$	6.42	6.19	2.62	2.53
Fe.Trensal	$C_{27}H_{27}N_4O_3Fe$	2.91	2.67	--	--
Co.Trensal	$C_{27}H_{28}N_4O_3Co$	3.10	2.98	--	--

The structural formula of all the coordination compounds investigated in this study are depicted in Figure 1. The structures of most of the compounds were determined with X-ray studies and reported in the literature. In this study, NiL or CuL units of di- or trinuclear complexes used were coordinated by one or two solvent molecules. In dinuclear coordination compounds, the second metal ion only forms μ-bridge with phenolic oxygens. In this case, phenolic oxygens coordinate both metal ions. Similarly, in trinuclear complexes prepared from NiL mononuclear complex, the phenolic oxygens coordinate the metal ions with μ-bridge. There is a second μ-bridge formed between central ion and terminal NiL units is formed by different coligands. These coligands are anions such as formate, acetate, and nitrites. Figure 6 shows the mass fragments of dinuclear coordination compounds of [$CuL.CuCl_2$], [$NiL.ZnBr_2.(DMF)_2$] and [$NiL.CdI_2.(DMF)_2$] with 70 eV electrons. The complexes prepared with Schiff bases thermally release the solvent molecules (DMF) in their structures. This phenomenon is clearly seen in the thermogravimetric analysis [52]. After releasing the coordinative solvent molecules, there remain NiL and halide salts behind.

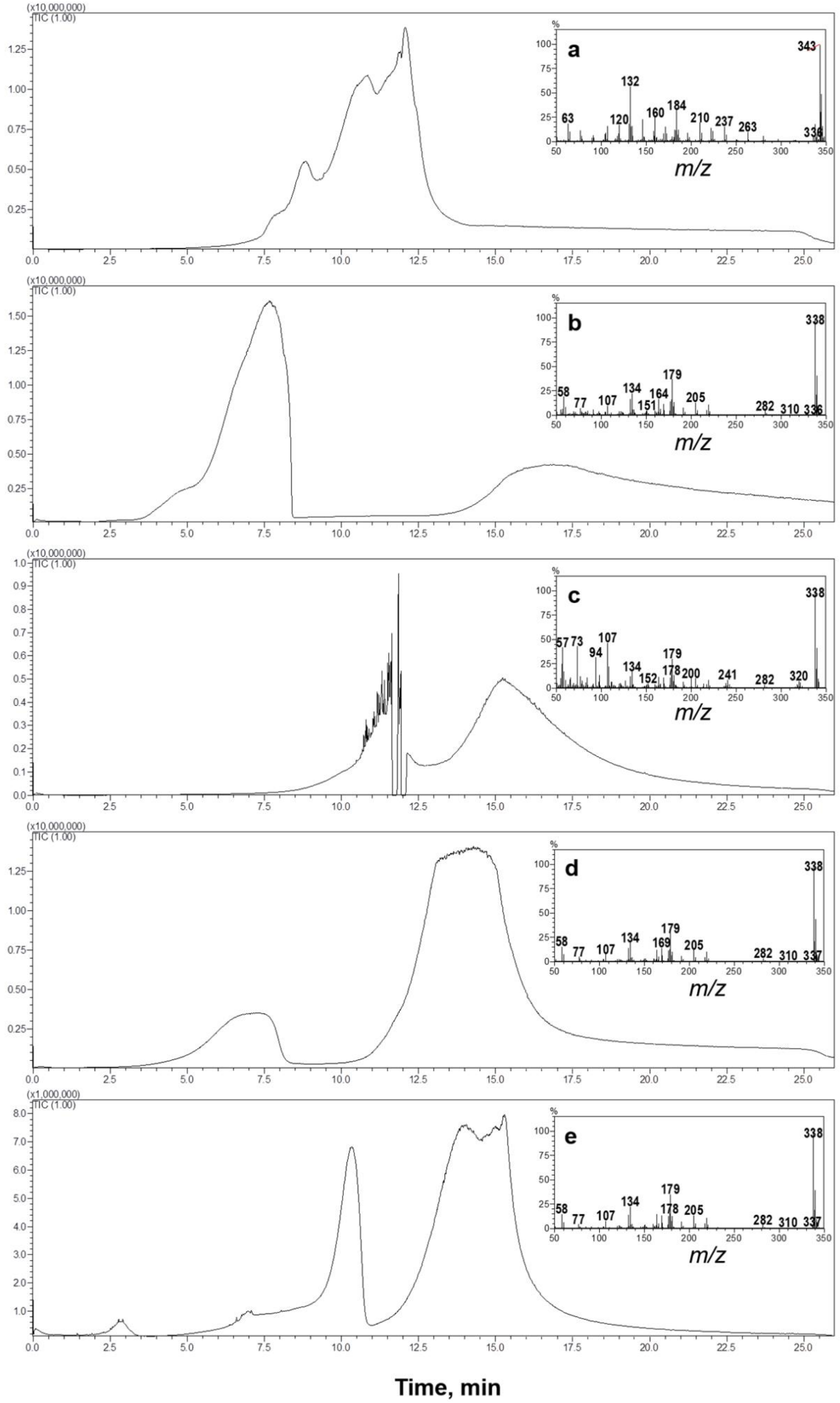


Figure 6. Mass spectra and the ion current at 70 eV a. [$CuL.CuCl_2$], b. [$NiL.ZnBr_2.(DMF)_2$], c. [$NiL.CdI_2.(DMF)_2$], d. [$(NiL)_2.Ni(AcO)_2.(DMF)_2$], e. [$(NiL)_2.Ni(NO_2)_2.(DMF)_2$]

As seen from Figures 6a, 6b and 6c some of the dinuclear complexes prepared with Schiff bases gave two ionic currents. The first one belongs to DMF fragments at m/z=73. The second ionic current which emerges as the temperature of DI is increased is due to CuL or NiL complexes and the resulting thermogram completely fits with that of NiL or CuL.

Trinuclear complexes at DI temperatures under the bombardment of 70 eV electrons leave the DMF from the structure in the gaseous state and get ionized by the electrons. Under these conditions, the complex is completely dissociated. If the complex is a Schiff base type then the complex totally dissociates and the residue contains mononuclear NiL complex and halide salts. With the effect of increasing DI temperature NiL complex is also ionized creating a second ionic current that gives NiL complex fragments. This really is the fact because in Figure 6d and 6e, the first ionic current gives the molecular signal at m/z=73 corresponding to DMF molecule and the signal at m/z=44 due to $[(CH_3)_2N]^+$, the fragment ion of DMF. The second current gives the same mass spectrum with NiL.

The common features of the mononuclear complexes are that they are coordinated to the metal through phenolic oxygen and iminic nitrogen. As a result of each phenolic oxygen-iminic nitrogen coordination, six-membered chelate rings are formed. It is a well-known fact that chelate rings increase the stability of the coordination compounds [53]. That is why in the case that when a neutral complex is formed when the metal ion is connected to all ligands and all probable chelate rings are established it is possible to see the molecular signal of the complex by the use of EI method. So much so that the molecular signal is the base peak in the spectrum. This situation is verified in Figure 2-4. If the chelating rings are formed only by the coordinative bonds, these bonds are broken with ionizing electrons and only ligand-related signals are observed. Under these conditions, the only observable signals or fractions are those belonging to the stable units or the ligands of the complex. This is the case observed in SAP complexes. However, there is an important difference in the complex of this ligand. This ligand is a tridentate ligand and gives supramolecular complexes with transition metals. That is why the mononuclear units of this ligand prefer four and six-membered coordinations with the help of coligands and these mononuclear units are lined up in the crystal lattice to form a supramolecule and that is why mononuclear units are not vaporized. In di- and trinuclear complexes, the mononuclear units are attached to each other with μ-bridges. These μ-bridges form coordinative bonds with metal ions. Coordinative bonds are weaker than covalent bonds and their bond energies are much smaller. That is why these μ-bridges are much more easily broken by 70 eV or more energetic electrons. However, in 2-hydroxy substituted Schiff bases, the metal-ligand coordination takes place through phenolic oxygen and this bond has a comparable strength with a covalent bond and is much stronger than coordinative bond. Also, the formation of chelate rings gives the compound extra stability which makes the mononuclear complex much more stable in its ligand state.

In the literature, it has been reported that EI is not a suitable method for the investigation of coordination compounds. The most preferred method for the investigation of coordination compounds is ESI method. However, this study has proved that EI can be a very convenient method for the investigation of stable coordination compounds. It gives a very clear molecular signal in the coordination compounds coordinated through phenolic oxygen with a completed chelate ring.

Another important point here is that the nitrogen rule used for the organic compounds is not valid for the coordination compounds.

4. Conclusion and Comment

The Schiff base metal complexes containing chelate rings formed through phenolic oxygen and iminic nitrogens have been investigated by using EI method. In contrast to the literature, molecular signal in mononuclear complexes has appeared as the base peak, and these signals are not compatible with the nitrogen rule. It has clearly appeared that EI method is not suitable for the complexes in which mononuclear complexes are attached to each other with coordination bonds over the coligands. In other words, if solid-state supramolecular complexes are formed, the EI method is clearly not suitable.

Author Statement

Emine Kübra İnal: Investigation, Original Draft Writing
Orhan Atakol: Resource/Material/Instrument Supply, Review and Editing
M. Abdulkadir Akay: Supervision, Observation, Advice, Project Administration

Acknowledgment

This research has been supported by Ankara University Scientific Research Projects Coordination Unit [Project Number: 16L0430008, 2016]. Authors thank to TUBITAK for financial support of E. K. İnal (Ph.D. Student).

Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

References

[1] B. Guhathakurta, P. Basu, C. S. Purohit, N. Bandyopadhyay, G. S. Kumar, S. Chowdhury, and J. P. Naskar, “Synthesis, characterization, structure, DNA binding aspects and molecular docking study of a novel Schiff base ligand and its bis(mu-chloro) bridged Cu(II) dimer,” *Polyhedron*, 126, 195-204, 2017.

[2] N. F. Mazlan, L. L. Tan, N. H. Abd Karim, L. Y. Heng, and M. I. H. Reza, “Optical biosensing using newly synthesized metal salphen complexes: A potential DNA diagnostic tool,” *Sensors and Actuators B-Chemical*, 242, 176-188, 2017.

[3] S. Ullmann, R. Schnorr, M. Handke, C. Laube, B. Abel, M. Findeisen, R. Ruger, T. Heine, and B. Kersting, “Zn2+-Ion Sensing by Fluorescent Schiff Base Calix[4]arene Macrocycles,” *Chemistry-A European Journal*, 23, 3824-3827, 2017.

[4] I. A. Ansari, F. Sama, M. Raizada, M. Shahid, R. K. Rajpoot, and Z. A. Siddiqi, “Synthesis and spectral characterization of 2-((2-hydroxybenzylidene)amino)-2-methylpropane-1,3-diol derived complexes: Molecular docking and antimicrobial studies,” *J. Molecular Structure*, 1127, 479-498, 2017.

[5] R. Olar, M. Badea, M. Ferbinteanu, N. Stanica, and I. Alan, “Spectral, magnetic and thermal characterization of new Ni(II), Cu(II), Zn(II) and Cd(II) complexes with a bischelate Schiff base,” *J. Therm. Anal. Cal.*, 127, 709-719, 2017.

[6] N. Kumar, A. K. Asatkar, S. Panda, and S. S. Zade, “Synthesis, characterization and supramolecular building motifs of substituted salphen- and thiasalphen-metal complexes,” *Polyhedron*, 117, 718-728, 2016.

[7] A. Vlad, M. F. Zaltariov, S. Shova, M. Cazacu, M. Avadanei, A. Soroceanu, and P. Samoila, “New Zn(II) and Cu(II) complexes with in situ generated N2O2 siloxane Schiff base ligands,” *Polyhedron*, 115, 76-85, 2016.

[8] F. A. Mautner, R. C. Fischer, M. Spell, A. R. Acevedo, D. H. Tran, and S. S. Massoud, “Metal(II) complexes of compartmental polynuclear Schiff bases containing phenolate and alkoxy groups,” *Crystals*, 6, 91, 2016.

[9] Y. W. Dong, R. Q. Fan, X. M. Wang, P. Wang, H. J. Zhang, L. G. Wei, Y. Song, X. Du, W. Chen, Y. and L. Yang, “Topological evolution in mercury(II) Schiff base complexes tuned through alkyl substitution-synthesis, solid-state structures, and aggregation-induced emission properties,” *European J. Inorg. Chem*., 22, 3598-3610, 2016.

[10] A. N. Srivastva, N. P. Singh, and C. K. Shriwastaw, “In vitro antibacterial and antifungal activities of binuclear transition metal complexes of ONNO Schiff base and 5-methyl-2,6-pyrimidine-dione and their spectroscopic validation,” *Arabian J. Chem*., 9, 48-61, 2016.

[11] M. F. Zaltariov, M. Cazacu, M. Avadanei, S. Shova, M. Balan, N. Vornicu, A. Vlad, A. Dobrov, and C. D. Varganici, “Synthesis, characterization and antimicrobial activity of new Cu(II) and Zn(II) complexes with Schiff bases derived from trimethylsilyl-propyl-p-aminobenzoate,” *Polyhedron*, 100, 121-131, 2015.

[12] B. M. Pires, D. M. Silva, L. C. Visentin, B. L. Rodrigues, N. M. D. Carvalho, and R. B. Faria, “Synthesis and characterization of cobalt(III), nickel(II) and copper(II) mononuclear complexes with the ligand 1,3-bis[(2-aminoethyl)amino]-2-propanol and their catalase-like activity,” *Plos One*, 10, 2015.

[13] G. Y. Nagesh, R. K. Mahendra, and B. H. M. Mruthyunjayaswamy, “Synthesis, characterization, thermal study and biological evaluation of Cu(II), Co(II), Ni(II) and Zn(II) complexes of Schiff base ligand containing thiazole moiety,” *J. Molecular Structure*, 1079, 423-432, 2015.

[14] S. Biswas, and A. Ghosh, “A novel 1D chain of azido bridged copper(II) with a salen-type di-Schiff base ligand,” *J. Molecular Structure*, 1019, 32-36, 2012.

[15] M. K. Panda, M. M. Shaikh, and P. Ghosh, “Controlled oxidation of organic sulfides to sulfoxides under ambient conditions by a series of titanium isopropoxide complexes using environmentally benign H2O2 as an oxidant,” *Dalton Trans*., 39, 2428-2440, 2010.

[16] B. Słomińska, W. Chaładaja, and W. Danikiewicza, “Assessment of the various ionization methods in the analysis of metal salen complexes by mass spectrometry,” *J. Mass Spectrometry*, 49, 392-399, 2014.

[17] Y. Ozkay, Z. Incesu, I. Isikdag, and M. Yesilkaya, “Antiproliferative effects of some N-benzylideneanilines,” *Cell Biochem. and Func*., 26, 102-106, 2008.

[18] A. Mentes, “Molybdenum and tungsten(0) tetracarbonyl complexes with pyridyl amine Schiff base ligands,” *Transition Met. Chem*., 24, 77-80, 1999.

[19] L. Chiang, E. N. Laura, J. Alcantra, M. C. P. Wang, T. Storr, and M. P. Shaver, “Tuning ligand electronics and peripheral substitution on cobalt salen complexes,” *Dalton Trans*., 43, 4295-4304, 2014.

[20] B. Jasiewicz, T. Pospieszny, and E. Wyrzykiewicz, “Mass spectrometry of metal complexes of bis-quinolizidine alkaloids: EI and ESI mass spectral study of Co+2, Ni+2, Cu+2 and Zn+2 2-methylsparteine complexes,” *J. Mass Spectrometry*, 47, 347-351, 2012.

[21] S. M. Schildcrout, S. SriHari, and J. Masnovi, “Comparative chemical ionization and electron ionization mass spectra of salen complexes with metals of the first transition series,” *Inorg. Chem*., 34, 4117-4122, 1995.

[22] D. Blachut, W. Danikiewicz, M. Olejnik, and Z. Czarnocki, “Electron ionization mass spectrometry as a tool for the investigation of the ortho effect in fragmentation of some Schiff bases derived from amphetamine analogs,” *J. Mass Spectrometry*, 39, 966-972, 2004.

[23] S. M. S. Haggag, and I. A. M. Abdel-Hamid, “A tridentate (O,N,O) donor Schiff base zinc(II) nano complex,” *J. Therm. Anal. Cal*., 119, 737-746, 2015.

[24] E. M. Zayed, G. G. Mohamed, and A. M. M. Hindy, “Transition metal complexes of novel Schiff base,” *J. Therm. Anal. Cal*., 120, 893-903, 2015.

[25] W. H. Mahmoud, M. M. Omar, and F. N. Sayed, “Synthesis, spectral characterization, thermal, anticancer and antimicrobial studies of bidentate azo dye metal complexes,” *J. Therm. Anal. Cal*., 124, 1071-1089, 2016.

[26] A. M. A. Omyma, L. H. Abdel-Rahman, and R. M. Ramadan, “Ruthenium carbonyl derivatives of N-salicylidene-2-hydroxyaniline,” *J. Coord. Chem*., 60, 2335-2342, 2007.

[27] R. J. Butcher, and E. Sinn, “Relation between magnetic, spectroscopic and structural properties of Bis[chloro(N-isopropyl-2-hydroxybenzyliden)aminato-μ-O-copper(II)] and Bis(N-isopropyl-2-hydroxybenzylidenaminato)copper(II),” *Inorg. Chem*., 15, 1604-1609, 1976.

[28] C. Fukuhara, K. Tsuneyoshi, N. Matsumoto, S. Kida, M. Mikuriya, and M. Mori, “Synthesis and characterization of trinuclear Schiff base complexes containing sulphurdioxide or hydrogensulphite ions as bridging groups,” *Dalton Trans*., 11, 3473-3479, 1990.

[29] A. Gerli, K. S. Hagen, and L. G. Marzilli, “Nuclearity and formulation of SALPN2-complexes formed from M(O2CCH3)2,” *Inorg. Chem*., 30, 4673-4676, 1991.

[30] S. Uhlenbrock, R. Wegner, and B. Krebs, “Synthesis and characterization of novel tri-and hexanuclear zinc complexes with biomimetic chelate ligands,” *Dalton Trans*., 18, 3731-3736, 1996.

[31] F. Ercan, O. Atakol, I. Svoboda, and H. Fuess, “Three heterotrinuclear Schiff base complexes with cobalt(II), copper(II) and manganese(II),” *Acta. Cryst*., 58, 193-196, 2002.

[32] O. Atakol, R. Boca, I. Ercan, F. Ercan, H. Fuess, W. Haase, and R. Herchel, “Magnetic properties of trinuclear Ni-M-Ni complexes, M = Mn, Co and Ni,” *Chem. Phys. Lett*., 423, 192-196, 2006.

[33] S. Durmuş, Ü. Ergun, J. C. Jaud, K. C. Emregül, H. Fuess, and O. Atakol, “Thermal decomposition of some linear trinuclear Schiff base complexes with acetate bridges,” *J. Therm. Anal. Cal*., 86, 337-346, 2006.

[34] J. Reglinski, M. K. Taylor, and A. R. Kennedy, “Hydrogenated Schiff base ligands,” *Inorg. Chem. Comm*., 9, 736-739, 2006.

[35] D. H. Shi, Z. L. You, C. Xu, Q. Zhang, and H. L. Zhu, “Synthesis, crystal structure and urease inhibitory activities of Schiff base metal complexes,” *Inorg. Chem. Comm*., 10, 404-406, 2007.

[36] P. Mukherjee, C. Biswas, M. G. B. Drew, and A. Ghosh, “Structural variations in Ni(II) complexes of Salen type di Schiff base ligand,” *Polyhedron*, 26, 3121-3128, 2007.

[37] L. K. Das, R. M. Kadam, A. Bauza, A. Frontera, and A. Ghosh, “Differences in nuclearity, molecular shapes and coordination modes of azide in the complexes of Cd(II) and Hg(II) with a metalloligand [CuL] (H2L=N,N’-Bis (salicylidene)-1,3-diaminopropanediamine),” *Inorg. Chem*., 51, 12407-12418, 2012.

[38] S. Saha, S. Sasmal, C. R. Choudhury, C. J. Gomez-Garcia, E. Garribba, and S. Mitra, “A new linear double phenoxide-bridged trinuclear Cu(II) Schiff base complex,” *Polyhedron*, 69, 262-269, 2014.

[39] S. Ghosh, G. Aromi, P. Gamez, and A. Ghosh, “The impact of anion modulated structural variations on the magnetic coupling in trinuclear heterometallic CuII-CoII complexes derived from a salen-type Schiff base ligand,” *Eur. J. Inorg. Chem*., 21, 3341-3349, 2014.

[40] A. Hazari, and A. Ghosh, “Trinuclear complexes of [CuL] with HgX2,” *Polyhedron*, 87, 403-410, 2015.

[41] L. K. Das, C. J. Gomez-Garcia, M. G. B. Drew, and A. Ghosh, “Plying with different metalloligands [NiL] and Hg to [NiL] ratios to tune the nuclearity of Ni(II)-Hg(II) complexes,” *Polyhedron*, 87, 311-320, 2015.

[42] A. Hazari, S. Giri, C. Diaz, and A. Ghosh, “Unusual site selection of NCS- in trinuclear complexes of Cu(II) and Ni(II) with a reduced N2O2 donor Schiff base: Structural, theoretical and magnetic studies,” *Polyhedron*. 118, 70-80, 2016.

[43] M. G. B. Drew, R. N. Prasad, and R. P. Sharma, “Structure of (N,N’-Trimethylenedisalicylidene aminato)nickel(II) and (N,N’-Trimethylenedisalicylideneaminato)copper(II),” *Acta. Cryst*., 41, 1755-1758, 1985.

[44] M. Aksu, S. Durmuş, M. Sari, K. C. Emregül, I. Svoboda, H. Fuess, and O. Atakol, “Investigation of thermal decomposition some heterodinuclear NiII-MII complexes prepared from ONNO type reduced Schiff base compounds,” *J. Therm. Anal. Cal*., 90, 541-547, 2007.

[45] G. N. Tyson Jr, and S. C. Adams, “The configuration of some cupric, nickelous and cobaltus complexes by means of magnetic measurements,” *J. Am. Chem. Soc*., 62, 1228-1229, 1940.

[46] E. Breitmaier, and G. Jung, *Organische Chemie, 6. Überarbeitete Auflage*. Stuttgart: Georg Thieme-Verlag, 1987.

[47] D. M. Kurtz Jr., “Oxo- and hydroxo bridged diiron complexes,” *Chem. Rev*., 90, 585-608, 1990.

[48] F. Maggio, T. Pizzino, V. Romano, and G. Dia, “Adduct formation by sub-coordinated metal complexes,” *J. Inorg. Nucl. Chem*., 38, 599-601, 1976.

[49] Ü. Ergun, O. Atakol, F. Z. Eriş, A. Yücel, and E. Düzgün, “Estimation of coordination bond energies of NH3, H2O and Et2NH ligands in the Ni(II) and Cu(II) complexes,” *J. Therm. Anal. Cal*., 97, 1007-1014, 2009.

[50] O. Atakol, A. Kenar, and M. Kabak, “Some complexes of nickel(II) with ono type Schiff bases and their monoligand adducts,” *Synth. React. Inorg. Met.-Org. Chem*., 27, 29-40, 1997.

[51] N. N. Greenwood, and A. Earnshow, *Chemistry of the Elements, 2nd edition*. Oxford: Elsevier, 1997.

[52] N. Acar, O. Atakol, Ş. B. Sopaci, D. C. Duman, I. Svoboda, and S. Öz, “The investigations of thermal behavior, kinetic analysis, and biological activity of trinuclear complexes prepared ONNO-type Schiff bases with nitrito and nitrato mu-bridges,” *J. Therm. Anal. Cal*., 127, 1319-1337, 2017.

[53] J. Ribas Gispert, *Coordination Chemistry*. Weinheim: Wiley-VCH, 2008.