Adıyaman University Journal of Science

dergipark.gov.tr/adyusci

ADYUSCI

7 (1) (2017) 47-59

The Synthesis, Characterization of a Novel Schiff Base Ligand and Investigation of Its Transition Metal Complexes

Burak OĞUZHAN[1], Erdal CANPOLAT[2,]*, Hakan ŞAHAL[1], Mehmet KAYA[1]

[1]Fırat University, Faculty of Sciences, Department of Chemistry, 23119 Elazığ, Türkiye, Burak.Oguzhan@tremco-illbruck.com, hakan.shl@gmail.com, mehmetkaya08@firat.edu.tr

[2]Fırat University, Faculty of Education, Department of Science Education, 23119, Elazığ, Türkiye, ecanpolat@firat.edu.tr

Abstract

In this study, one new Schiff base ligand and its transition metal complexes were synthesized. Schiff base was found to be bidentate ligand involving the imino nitrogen and carboxyl oxygen atoms in the complexes. Metal to ligand ratio were found 1:2 for all of the complexes. Co(II), Ni(II), Cu(II) and Zn(II) complexes have been found tetrahedral geometry. The complexes are found to have the formulae $[M(L)_2]$. The structure of these compounds were characterized by using elemental analysis, IR, ^{1}H- and ^{13}C-NMR and UV spectroscopy, magnetic susceptibility measurements. In addition, the thermal characterization of the ligand and its complexes were carried out by using TGA technique.

Keywords: Schiff Bases, Transition Metal Complexes, Synthesis.

Yeni Bir Schiff Baz Ligandının Sentezi, Karakterizasyonu ve Geçiş Metal Komplekslerinin İncelenmesi

Özet

Bu çalışmada, bir yeni Schiff bazı ligandı ve onun geçiş metal kompleksleri sentezlenmiştir. Komplekslerde Schiff bazlarının metal iyonuna imin azotu ve fenolik

---

* Corresponding Author

Received: 07 April 2017 Accepted: 05 June 2017

oksijeninden bağlanarak iki dişli şelat olarak davrandığı bulunmuştur. Metal-ligand oranı, tüm kompleksler için 1: 2 bulundu. Co (II), Ni (II), Cu (II) ve Zn (II) kompleksleri tetrahedral geometriye sahiptir. Komplekslerin formülleri [M(L)$_2$] olduğu bulunmuştur. Bileşiklerin yapıları elemental analiz, IR, ^{1}H- ve ^{13}C-NMR ve UV spektroskopisi, manyetik duyarlılık ölçümleri kullanılarak karakterize edildi. Ek olarak, ligand ve komplekslerinin termal karakterizasyonu TGA tekniği kullanılarak gerçekleştirildi.

Anahtar Kelimeler: Schiff Bazı, Geçiş Metal Kompleksleri, Sentez.

1. Introduction

In recent years there has been a great deal of interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands, due to their importance as catalysts for many reactions [1-3]. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most cations [5]. There is considerable interest in the chemistry of transition metal complexes of ligands containing oxygen, nitrogen and sulfur donor atoms due to the carcinostatic, antitumor, antiviral and antibacterial activity and their industrial uses of complexes derived from them [6]. In addition, the presence of nitrogen and oxygen donor atoms in the complexes makes these compounds effective and stereospecific catalyst for oxidation, reduction, hydrolysis, and they also show biological activity and other transformations of organic and inorganic chemistry. It is well known that some drugs have higher activity when administered as metal complexes than as free ligands [6-9].

In our previous studies we have investigated the synthesis and characterization of various transition metal complexes of novel Schiff base ligands [10-13]. In the present article, we report the synthesis and characterization of a new Schiff base ligand and its complexes with Co(II), Ni(II), Cu(II) and Zn(II) ions.

2. Material and Methods

2.1. Material

All reagents use were purchased from Merck or Fluka or Sigma Company and chemically pure.

2.2. Measurements

Elemental Analyses (C, H, N) were performed on a LECO-932 CHNSO elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV Spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

2.3. Synthesis

2.3.1. Preparation of the Ligand (LH)

To a solution of *p*-aminoacetophenoneoxime (1.50 g, 10 mmol) dissolved in 15 mL absolute EtOH, 3-brom-5-chlorosalicylaldehyde (2.35 g, 10 mmol) and *p*-toluene sulfonic acid (0.01 mg) dissolved in 50 mL absolute EtOH were added dropwise at 65 ^{0}C with continuous stirring for 5 h and monitoring of the course of the reaction with IR. The obtained product was filtered off after overnight, washed with cold ethanol and diethyl ether several times and dried in vacuum at 70 ^{0}C.

For LH: IR spectrum (υ, cm^{-1}): 3320 (oxime O-H), 3235 (phenolic O-H), 1625 (phenolic C=N), 1597 (oxime C=N), 1270 (C-O), 1001 (N-O); ^{1}H-NMR ($CDCl_3$-DMSO-*d₆*, δ, ppm): 13.05 (s, 1H, phenolic O$\underline{H}$), 10.72 (s, 1H, oxime O$\underline{H}$), 8.60 (s, 1H, azomethine C$\underline{H}$=N), 7.60-6.80 (m, 6H aromatic $\underline{H}$,), 1.93 (s, 3H, $C\underline{H}_3$); ^{13}C-NMR ($CDCl_3$-DMSO-d_6, δ, ppm): 164.65 (oxime $\underline{C}$=NOH), 163.50 (imin $\underline{C}$H=N), 159.98 (phenolic $\underline{C}$-OH), 155.49-112.50 (aromatic $\underline{C}$), 21.77 ($\underline{C}H_3$).

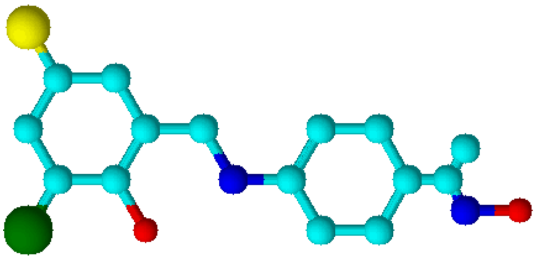
2.3.2. Preparation of the Co(II), Cu(II) and Zn(II) Complexes

A sample of the ligand (LH) (0.73 g, 2.00 mmol) was dissolved in 15 mL absolute ethanol by heating. A solution of the acetate salt of metal $[Co(AcO)_2].4H_2O$ (0.25 g, 1.00 mmol), $[Ni(AcO)_2].4H_2O$ (0.25 g, 1.00 mmol), $[Cu(AcO)_2].H_2O$ (0.20 g, 1.00 mmol), and $[Zn(AcO)_2].2H_2O$ (0.22 g, 1.00 mmol) in 15 mL of hot ethanol were added dropwise to the ligand solution under reflux at 60 ^{0}C with continuous stirring at for 15 h. The precipitated complex was filtered off after overnight, washed with water and cold ethanol several times and dried at room temperature.

For Co(L)$_2$: IR spectrum (υ, cm^{-1}): 3315 (oxime O-H), 1610 (phenolic C=N), 1597 (oxime C=N), 1270 (C-O), 1001 (N-O). For Ni(L)$_2$: IR spectrum (υ, cm^{-1}): 3325 (oxime O-H), 1615 (phenolic C=N), 1600 (oxime C=N), 1325 (C-O), 1005 (N-O). For Cu(L)$_2$: IR spectrum (υ, cm^{-1}): 3325 (oxime O-H), 1615 (phenolic C=N), 1600 (oxime C=N), 1315 (C-O), 1005 (N-O). For Zn(L)$_2$: IR spectrum (υ, cm^{-1}): 3315 (oxime O-H), 1610 (phenolic C=N), 1600 (oxime C=N), 1300 (C-O), 1005 (N-O); ^{1}H-NMR (CDCl$_3$-DMSO-*d*$_6$, δ, ppm): 10.73 (s, 2H, oxime O$\underline{H}$), 8.50 (s, 2H, azomethine C$\underline{H}$=N), 7.64-6.85 (m, 12 H aromatic $\underline{H}$,), 1.92 (s, 6H, C$\underline{H}_3$); ^{13}C-NMR (CDCl$_3$-DMSO-*d*$_6$, δ, ppm): 166.01 (imin $\underline{C}$H=N), 164.66 (oxime $\underline{C}$=NOH), 163.88 (phenolic $\underline{C}$-OH), 155.60-112.56 (aromatic $\underline{C}$), 21.79 ($\underline{C}$H$_3$).

3. Results and Discussion

The ligand (LH) was prepared by reacting equimolar amounts of 3-bromo-5-chlorosalicylaldehyde with *p*-aminoacetophenoneoxime in absolute ethanol. The structures of the ligand and the complexes were established from their IR, ^{1}H and ^{13}C-NMR spectra, electronic spectra, elemental analyses, magnetic susceptibility measurements and thermogravimetric analyses. The general characteristic properties of the complexes and the Schiff base are shown in Table 1. The complexes are intensely colored stable solids.



LH

Figure 1. Conformation of the ligand.

A summary of the elemental analysis data for the ligand and the complexes are given in detail:

For LH: % calculated C, 49.01; H, 3.29; N, 7.62; found C, 48.65; H, 2.94; N, 8.00.

For Co(L)$_2$: % calculated C, 45.49; H, 2.80; N, 7.07; found C, 45.18; H, 2.49; N, 6.69.

For Ni(L)$_2$: % calculated C, 45.50; H, 2.80; N, 7.07; found C, 45.11; H, 2.44; N, 6.72.

For Cu(L)$_2$: % calculated C,45.22; H, 2.78; N, 7.03; found C, 44.86; H, 2.42; N, 6.71.

For Zn(L)$_2$: % calculated C,45.12; H, 2.78; N, 7.02; found C, 44.76; H, 2.39; N, 6.66.

The elemental analysis results agree with the calculated values showing that the complexes have 1:2 metal/ligand ratios. The elemental analysis confirmed the compositions of the above synthesized compounds.

Table 1. Analytical and physical data of the ligand and the complexes.

Compounds	Formula	F.W (g/mol)	Color	Yield (%)
LH	$C_{15}H_{12}N_2O_2BrCl$	367.62	Orange	65
Co(L)$_2$	$CoC_{30}H_{22}N_4O_4Br_2Cl_2$	792.17	Tile Red	60
Ni(L)$_2$	$NiC_{30}H_{22}N_4O_4Br_2Cl_2$	791.92	Green	70
Cu(L)$_2$	$CuC_{30}H_{22}N_4O_4Br_2Cl_2$	796.77	Brown	60
Zn(L)$_2$	$ZnC_{30}H_{22}N_4O_4Br_2Cl_2$	798.62	Yellow	65

The ligand contains four potential donor sites; 1) the phenolic oxygen, 2) the azomethine nitrogen, 3) the oxime oxygen, 4) the oxime nitrogen. In the IR spectrum of the ligand, the most characteristic absorptions are at 3389 cm^{-1} $\upsilon(O\text{-}H)_{oxime}$ [14-17], 3235 cm^{-1} $\upsilon(O\text{-}H)_{phenolic}$, 1625 cm^{-1} $\upsilon(C=N)_{azomethine}$, 1591 cm^{-1} $\upsilon(C=N)_{oxime}$ [18-20], 1270 cm^{-1} $\upsilon(C\text{-}O)$ and 1001 cm^{-1} $\upsilon(N\text{-}O)$. The values are in agreement with similar compounds [6, 21-23].

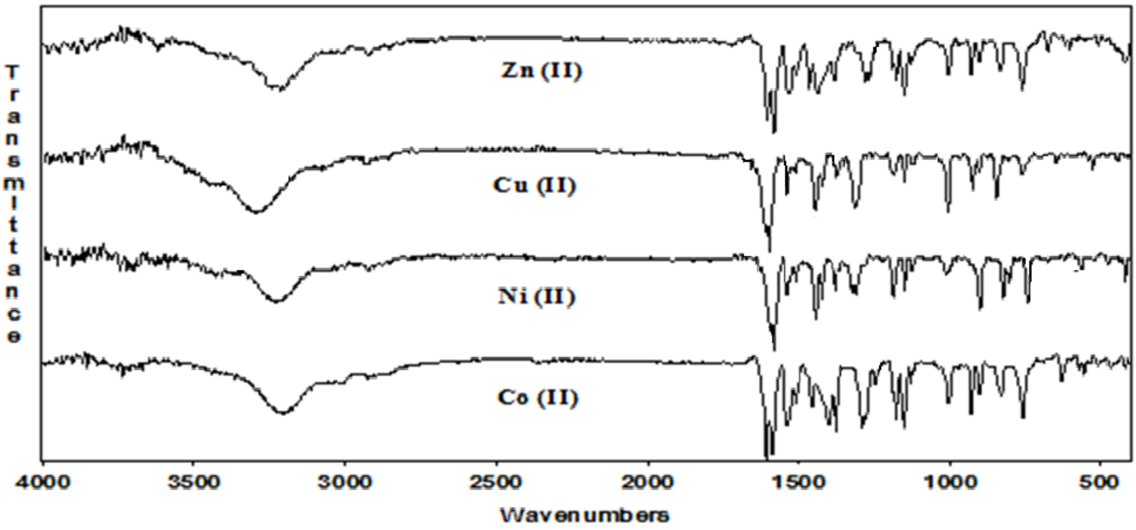


Figure 2. IR spectrum of complexes.

The azomethine vibration of the ligand at 1625 cm^{-1} shifted to lower frequencies after complexation; which is 1610, 1615, 1615 and 1610 cm^{-1} for Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes, respectively. This clearly indicates the coordination of the Schiff bases through the azomethine nitrogen [21, 24-25]. In the free ligand the strong band at 1270 cm^{-1} due to C-O$_{(phenolic)}$ shifts to higher frequency by 25-55 cm^{-1} in the complexes indicating the coordination of the phenolic oxygen atom to the metal ion [6,11]. The practically unchanged O-H at 3320 and C=N at 1597 cm^{-1} reveal that these oxime groups do not coordinated to metal atoms by neither oxygen nor nitrogen atoms.

^{1}H- and ^{13}C-NMR spectrum of the ligand (LH) and its zinc(II) complex were recorded in CDCl$_3$/DMSO-d6. In the spectra of the Zn(II) complex a sharp singlet appeared at 8.50 ppm and has been assigned to the azomethine proton (CH=N). The position of the azomethine signal in the complexes are downfield in comparison with that of the free ligand, suggesting deshielding of the azomethine proton due to is coordination to zinc through the azomethine nitrogen [6, 12]. Comparison of the chemical shifts of the ligand with those of the complex shows that the signal due to the phenolic proton (OH) is absent in the complex, suggesting the coordination of the phenolic oxygen to the metal ion after deprotonation [6, 12]. More detailed information about the structures of the ligand and its Zn(II) complex were provided by ^{13}C-NMR spectra data that C-OH, CH=N and C-N carbon atoms are observed at 163.88, 166.01 and 164.66 ppm. The results confirm the proposed structure of Zn(II) complex.

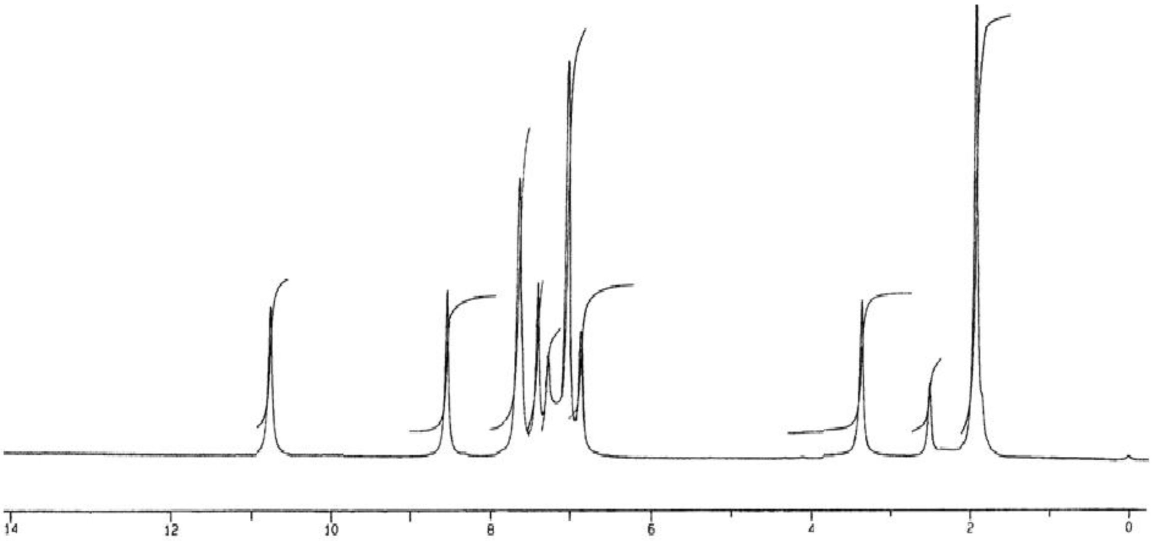


Figure 3. ^{1}H-NMR spectrum of Zn (II) complex.

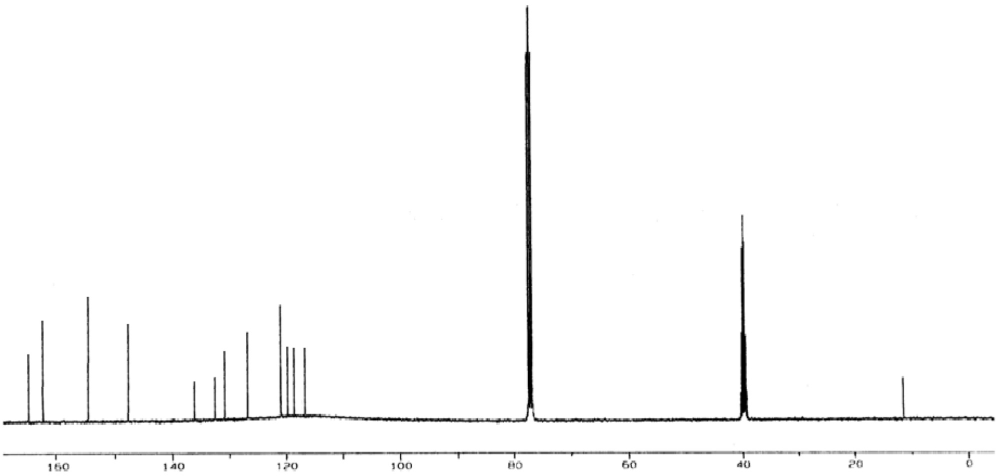


Figure 4. ^{13}C-NMR spectrum of Zn (II) complex.

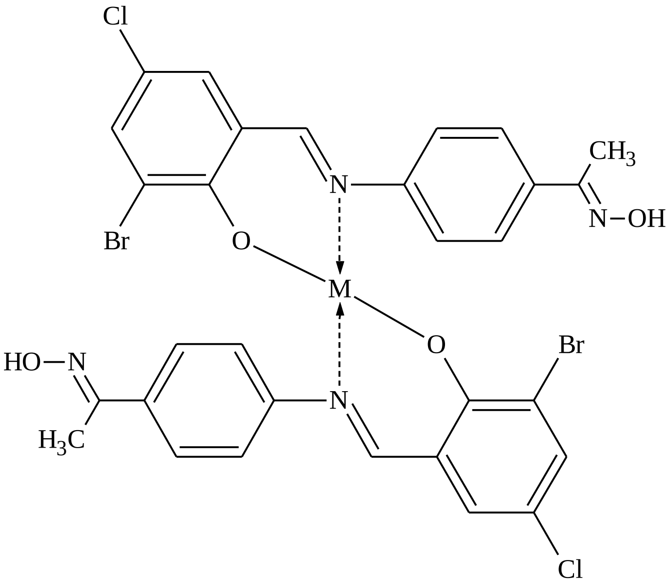
The electronic spectra of the ligand and the Co(II), Ni(II), Cu(II) and Zn(II) complexes were recorded in DMF at room temperature. The electronic spectra of the complexes with their assignments are given in Table 2. The band around 390 nm is due to $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base. The complexes of cobalt(II), nickel(II) and copper(II) show less intense shoulders at *ca.* 590-660 nm (ε = 170-185 L mol^{-1} cm^{-1}), which are assigned as *d-d* transition of the metal ions. The former band is probably due to the $^4A_2 \rightarrow ^4T_1$ (P) for Co(II), $^3A_2 \rightarrow ^3T_2$ (F) for Ni(II) and $^2T_2 \rightarrow ^2E$ (G) for Cu(II) transition of tetrahedral geometry. All the complexes show an intense band at *ca* 375-

385 nm which is assigned to $n \rightarrow \pi^*$ transition associated with azomethine linkage. [12, 26-27].The spectra of all the complexes show intense band at *ca* 415-435 nm (ε = 1.16-4.44 x 10^3 L mol^{-1} cm^{-1}), which can be assigned to charge transfer transition of tetrahedral geometry [12, 28].

Table 2. Magnetic moment and electronic spectral data of the complexes.

Compounds	**μ_{eff} (B. M.)**	**λ_{max} / nm (ε, L mol^{-1} cm^{-1})**		
		d→d	**C-T***	**$n \rightarrow \pi^*_{azomethine}$**
Co(L)$_2$	3.99	660 (ε = 185)	435 (ε = 2.80 x 10^3)	385
Ni(L)$_2$)	2.94	630 (ε = 177)	420 (ε = 3.25 x 10^3)	380
Cu(L)$_2$	1.79	590 (ε = 170)	425 (ε = 1.16 x 10^3)	385
Zn(L)$_2$	dia	-	415 (ε = 4.44 x 10^3)	375

The room temperature magnetic moment values of the complexes are given in Table 2. The synthesized complexes are suggested to have the general structural formulas shown in Figure 5. The Co(II), Ni(II) and Cu(II) complexes are paramagnetic, while the Zn(II) complex is diamagnetic as expected for d^{10} configuration. The magnetic moments of cobalt(II), nickel(II) and copper(II) complexes of the ligand fall in a range of 3.99, 2.94 and 1.79 B.M., respectively. According to results obtained the geometries of the Co(II), Ni(II), Cu(II) and Zn(II) complexes are tetrahedral [11, 12, 29].



M = Co(II), Ni(II), Cu(II) and Zn(II)

Figure 5. Suggested structure of the tetrahedral complexes of ligand.

The thermal behavior of the complexes has been investigated using thermogravimetric techniques in the temperature range from ambient to 800 °C at a heating rate of 10 °C/min. The thermal stability data are listed in Table 3. The decomposition temperature and the weight losses of the complexes were calculated from TGA data. Thermogravimetric studies of the and Co(II), Ni(II), Cu(II) and Zn(II) complexes showed no weight loss up to 230, 270, 265 and 250 °C respectively, indicating absence of the lattice/coordinated water molecules in the complexes [12]. All these complexes oxides, CoO, NiO, CuO and ZnO [30-34].

Table 3. TGA data of the ligand and the complexes.

Compounds	**Decomposition temp. range (^{0}C)**	**Total weight loss (calculated/found), %**	**Residue (calc./found), %**
$Co(L)_2$	230-700	90.54/89.16	9.46/10.84
$Ni(L)_2$)	270-590	90.57/89.25	9.43/10.75
$Cu(L)_2$	265-475	90.20/88.44	9.98/11.56
$Zn(L)_2$	250-400	89.81/88.03	10.19/11.97

4. Conclusions

From the satisfactory analytical data and all the physical-chemical studies it is concluded that the metal:ligand stoichiometric ratio is 1:2 in all the complexes. The general compositions of the transition metal complexes are $[M(L)_2]$ (where M= Co(II), Ni(II), Cu(II) or Zn(II)). The overall spectral studies indicate that the Schiff base ligand behaves in a monobasic bidentate (N, O) manner. According to results obtained, all the complexes are mononuclear and tetrahedral. The proposed structures of the synthesized complexes are shown in Figure 5.

Acknowledgements

This study, Fırat University Scientific Research Projects Coordination (FÜBAP) prepared by the project scope FÜBAP No. 1402 has been prepared summarizing the Master's Thesis.

References

[1] Thangadurai, T. D., Gowri, M., Natarajan, K., *Synthesis and Characterisation of Ruthenium(III) Complexes Containing Monobasic Bidentate Schiff Bases and Their Biological Activities*, Synth. React. Inorg. Met.-Org. Chem., 32, 329-343, 2002.

[2] Serron, S. A., Haar, C. M., Nolan, S. P., Brammer, L., *Synthesis, Characterization and Catalytic Behavior of Ruthenium(II) Schiff Base Complexes*, Organometallics, 16, 5120-5123, 1997.

[3] Mishra, A. P., Khare, M., Gautam, S. K., *Synthesis, Physico-Chemical Characterization and Antibacterial Studies of Some Bioactive Schiff Bases and Their Metal Chelates*, Synth. React. Inorg. Met.-Org. Chem., 32, 1485-1500, 2002.

[4] El-Medani, S. M., *Structural Studies of Some Chromium, Molybdenum and Tungsten Complexes of N-Salicylidene-2-Hydroxyaniline*, J. Coord. Chem., 57, 115-122, 2001.

[5] Salib, K. A. R., Stefan, S. L., Abu El-Wafa, S. M., El-Shafiy. H. F., *Metal Complexes of novel Symmetrical Schiff Base Ligands*, Synth. React. Inorg. Met.-Org. Chem., 31, 895-915, 2003.

[6] Ramesh, R., Sivagamasundari, M., *Synthesis, Spectral and Antifungal Activity of Ru(II) Mixed-Ligand Complexes*, Synth. React. Inorg. Met.-Org. Chem., 33, 899-910, 2003.

[7] Ali, O. A. M., Khalil, M. M. H., Attia, G. M., Ramadan, R. M., *Group VI Dinuclear Oxo Metal Complexes of Salicylideneimine-2-Anisole Schiff Base,* Spectrosc. Lett., 36, 71-82, 2003.

[8] Tuncel, M., Serin, S., *Synthesis and Characterization of Copper(II), Nickel(II), and Cobalt(II) Chelates with Tridentate Schiff Base Ligands Derived from 4-Amino-5-Hydroxynaphthalene-2,7-Disulfonic Acid,* Synth. React. Inorg. Met.-Org. Chem., 33, 985-998, 2003.

[9] Fan, Y. H., Bi, C. F., Li, J. Y., *Thermodecomposition Kinetics of Dy(III) Complex with Schiff Base Derived from Furfural and DL-Alpha-Alanine*, Synth. React. Inorg. Met.-Org. Chem., 33, 137-145, 2003.

[10] Canpolat, E., Kaya, M., *Studies on Mononuclear Chelates Derived from Substituted Schiff Bases Ligands (Part 3): Synthesis and Characterization of a new 5-Nitrosalicyliden-p-Aminoacetophenoneoxime and its Complexes with Co(II), Ni(II), Cu(II) and Zn(II),* Russ. J. Coord. Chem., 31, 415-419, 2005.

[11] Canpolat, E., Kaya, M., *Studies on Mononuclear Chelates Derived from Substituted Schiff Bases Ligands (Part 1): Synthesis and Characterization of a new Salicyliden-p-Aminoacetophenoneoxime and its Complexes with Co(II), Ni(II), Cu(II) and Zn(II),* Polish J. Chem., 79, 959-965, 2005.

[12] Canpolat, E., Yazıcı, A., Kaya, M., Studies on mononuclear chelates derived from substituted Schiff-base Ligands (part 10): *Synthesis and Characterization of a new* 4-*Hydroxysalicyliden-p-Aminoacetophenoneoxime and its Complexes with Co(II), Ni(II), Cu(II) and Zn(II),* J. Coord. Chem., 60, 473-480, 2007.

[13] Şahal, H., Canpolat, E., Kaya, M., Kara, N., *Synthesis, Physico-Chemical Characterization, Antibacterial and Antifungal Activities Studies of a new Schiff Base Ligand and its Transition Metal Complexes*, J. Chem. Soc. Pakistan, 37, 245-251, 2015.

[14] Canpolat, E., Kaya, M., *Synthesis and Characterization of vic-Dioximes Derivatives and Investigation of its Complexes with Ni(II), Co(II), Cu(II) and* UO_2*(VI) Metals*, J. Coord. Chem., 55, 961-968, 2002.

[15] Canpolat, E., Kaya, M., Görgülü, A. O., *The Synthesis and Characterization of 1,2-Dihydroxyimino-3,6-Diaza-8,9-o-Iso-Butylidenenonane and its Complexes with Ni(II), Cu(II), Zn(II) and Cd(II)*, Polish J. Chem., 76, 687-694, 2002.

[16] Canpolat, E., Kaya, M., *The Synthesis and Characterization of a novel (E,E)-Dioxime and its Mononuclear Complexes Containing 1,3-Dioxolane Moieties*, Polish J. Chem., 77, 961-967, 2003.

[17] Kukushkin, V. Y., Tudela, D., Izotova-Belsky, V. K., Stash, A. I., *Structure and Reactivity of [Ptx$_2$(Ketoxime)(2)] Compounds. Cis-Trans Isomerization and X-Ray Structures of Cis-[Ptbr$_2$(Me$_2$C = NOH)(2)] and Trans-[Ptbr$_2$(Me$_2$C=NOH)(2)]Center Dot 2mec(= O)Nme$_2$*, Polyhedron, 17, 2455-2461, 1998.

[18] Güngör, O., Canpolat, E., Kaya, M., *A new Substitued Bis(Vic-Dioxime) of its mono and Dinuclear Complexes*, Polish J. Chem., 77, 403-410, 2003.

[19] Canpolat, E., Kaya, M., Gür, S., *Synthesis, Characterization of Some Co(III) Complexes with vic-Dioxime Ligands and Their Antimicrobial Properties*, Turkish J. Chem., 28, 235-242, 2004.

[20] Canpolat, E., Kaya, M., *Synthesis and Characterization of two vic-Dioximes Containing the 1,3-Dioxolane Ring and 1,4-Diaminobutane and their Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Metal Complexes*, Transit. Metal Chem., 29, 550-556, 2004.

[21] Maurya, R. C., Patel, P., Rajput, S., *Synthesis And Characterization of Mixed-Ligand Complexes of Cu(II), Ni(II), Co(II), Zn(II), Sm(III), and UO$_2$(VI), with a Schiff Base Derived from the Sulfa Drug Sulfamerazine and 2,2'-Bipyridine*, Synth. React. Inorg. Met.-Org. Chem., 33, 817-836, 2003.

[22] Kukushkin, Y. N., Krylov, V. K., Kaplan, S. F., Calligaris, M., Zangrando, E., Pombeiro, A. J. L., Kukushkin, Y. V. *Different Chlorination Modes of Oximes: Chlorination of Salicylaldoxime Coordinated to Platinum*, Inorg. Chim. Acta, 285, 116-121, 1999.

[23] Patel, K. M., Patel, K. N., Patel, N. H., Patel, M. N., *Synthesis, Characterization, and Antimicrobial Activities of some Transition Metal Complexes with a Tridentate Dibasic Schiff Base and Bidentate 2,2'-Bipyridylamine,* Synth. React. Inorg. Met.-Org. Chem., 31, 239-246, 2001.

[24] Arora, K., Sharma, K. P., *Studies on High-Coordination Complexes of Dioxouranium(VI) with a Schiff Base*, Synth. React. Inorg. Met.-Org. Chem., 32, 913-922, 2002.

[25] Patwardhan, H. A., Gopinathan, S., Gopinathan, C., *Chelated Titanium(VI) Compounds of Salicylaldazines*, Indian J. Chem. A., 16, 224-227, 1978.

[26] Rasmussen, J. C., Toftlund, H., Nivorzhkin, A. N., Bourassa, J., Ford, P. C., *Luminescent Tetranuclear Copper(I) Clusters Containing Tetradentate N,S Schiff Base Ligands. X-Ray Crystal Structure of Cu(4)L(2) (L=N,N'-(2,2'-Diphenyl)-Bis(1,3-Diphenyl-4-Iminomethyl-5-Thiopyrazole)*, Inorg. Chim. Acta, 251, 291-298, 1996.

[27] Çelik, C., Tümer, C. M., Serin, S., *Complexes of Tetradentate Schiff Base Ligands with Divalent Transition Metals*, Synth. React. Inorg. Met.-Org. Chem., 32, 1839-1854, 2002.

[28] Yamada, S., Takeuchi, A., *The Conformation and Interconversion of Schiff Base Complexes Of Nickel(II) And Copper(II)*, Coord. Chem. Rev., 43, 187-204, 1982.

[29] Tuncel, M., Serin, S., *Synthesis And Characterization of Copper(II), Nickel(II), and Cobalt(II) Chelates with Tridentate Schiff Base Ligands Derived from 4-Amino-5-Hydroxynaphthalene-2,7-Disulfonic Acid*, Synth. React. Inorg. Met.-Org. Chem., 33, 985-998, 2003.

[30] El-Bindary, A. A., El-Sonbati, A. Z., *Synthesis and Properties of Complexes of Copper(II), Nickel(II), Cobalt(II) and Uranyl Ions with 3-(p-Tolylsulphonamido)Rhodanine*, Polish J. Chem., 74, 615-620, 2000.

[31] Dubler, E., Hanggi, G., *Thermal-Degradation and Crystallographic Data of Metal-Complexes of Oxopurines and Thiopurines*, Thermochim. Acta, 234, 201-219, 1994.

[32] Yasodhai, S., Sivakumar, T., Govindarajan, S., *Preparation, Characterization and Thermal Reactivity of Transition Metal Complexes of Hydrazine with Citric Acid*, Thermochim. Acta, 338, 57-65, 1999.

[33] Dhar, M. L., Singh, O., *Synthesis and Thermal-Decomposition of* UO_2*(II) Complexes with 4,6-Dihydroxycoumaran-3-one and o-Vanillin Oxime*, Thermochim. Acta, 191, 285-291, 1991.

[34] Rakha, T. H. *Mononuclear and Binuclear Chelates of Biacetylmonoxime Picolinoylhydrazone*, Transit. Metal Chem., 24, 659-665, 1999.