Kütahya Dumlupınar University
Institute of Graduate Studies

Journal of Scientific
Reports-A
E-ISSN: 2687-6167
Number 49, June 2022

RESEARCH ARTICLE

SYNTHESIS and CHARACTERIZATION of a NOVEL BENZIMIDAZOLE-OXIME LIGAND and ITS Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) COMPLEXES

Halil İLKİMEN*

* Kütahya Dumlupınar University, Faculty of Art and Sciences, Department of Chemistry, halil.ilkimen@dpu.edu.tr,
ORCID: 0000-0003-1747-159X

Receive Date:30.09.2021 *Accepted Date: 18.04.2022*

ABSTRACT

(1*E*, 2*Z*)-2-(1*H*-benzoimidazol-1-yl)-2-(hydroxyimino)acetaldehyde oxime (H_2L) and its metal(II) complexes (**1-5**) (Fe, Co, Ni, Cu and Zn) were obtained using *anti*-monochloroglyoxime (glyox) and 1*H*-benzimidazole (HBI) in absolute ethanol for the first time. The H_2L was characterized by ^{1}H-NMR, elemental analysis, IR, and UV-Vis methods while IR, elemental analysis, UV-Vis, ICP-OES, TGA, molar conductivity and magnetic susceptibility techniques were applied to analyse of metal complexes (**1-5**).

Keywords: 1*H*-benzoimidazole, *vic-dioxime*, *metal complex*

1. INTRODUCTION

The coordination chemistry of vik-dioximes has been studied extensively. Many transition metal complexes of these ligands have been synthesized and continue to be synthesized. Potential applications of vic-dioximes and coordination compounds are useful in chemical industry, biological chemistry, pigment, medicinal chemistry, analytical and model compounds [1-5]. Vicinal dioximate ligands with a conjugated N=C–C=N system often form N,N-chelated metal complexes. The presence of slightly acidic hydroxy groups and slightly basic nitrogen atoms forms adjacent dioxime amphoteric ligands that form square-pyramidal, square-planar, corrine-type or octahedral complexes with metal ions such as cobalt, nickel, copper, zinc, palladium and cadmium as central atoms [6-17].

Benzimidazoles are involved in a great variety of biological processes [18]. They usually coordinate to the metal ions with their nitrogen atoms [19] and some of their complexes derivatives have been proven to possess antibacterial, fungicide and anti-hermitic activities [20-23]. A few reports on synthesis of metal complexes of *di*oxime and benzimidazole derivatives have been synthesized [24-29].

In this study, we prepared *anti*-monochloroglyoxime (glyox) and 1*H*-benzimidazole (HBI) according to literature [30-32] then we combined them to give a novel oxime ligand, named (1*E*, 2*Z*)-2-(1*H*-benzoimidazol-1-yl)-2-(hydroxyimino)acetaldehyde oxime (**1**). In addition, complex compounds of H_2L with metal(II) ions {Fe for **1**, Co for **2**, Ni for **3**, Cu(II) for **4** and Zn(II) for **5** salts were synthesized. The H_2L was characterized by ^{1}H-NMR, elemental analysis, IR, and UV-Vis methods while IR, elemental analysis, UV-Vis, ICP-OES, TGA, molar conductivity and magnetic susceptibility techniques were applied to analyse of metal complexes (**1-5**).

2. EXPERIMENTAL

2.1. General Methods and Materials

All chemicals used were commercially purchased from Merck. Elementar Vario III EL for elemental analyses, Bruker DPX FT NMR for ^{1}H-NMR, Bruker Optics Vertex 70 for IR, Perkin Elmer SII Exstar 6000 TG/DTA 6300 for thermal analyses, SHIMADZU UV-2550 for UV-Vis, Sherwood Scientific Magway MSB MK1 for magnetic moment measurements and WTW Cond 315i/SET for molar conductance instruments were used for the analysis of the structures.

2.2. Synthesis of Ligand H_2L.

We prepared *anti*-monochloroglyoxime (glyox) and 1*H*-benzimidazole (HBI) according to literature [30-32]. A solution of *anti*-monochloroglyoxime (1.22 g) in 25 mL pure ethanol was join to the solution of 1*H*-benzimidazole (1.18 g) in 25 mL pure ethanol. The p*H* of the mixture was adjusted from 3.5 to 7.0 with the addition of 0.1 M KOH solution. The yellow precipated product was filtered and dried (m.p: 140 °C, 1.26 g, 65% yield). The structure of H_2L is given in Fig. 1.

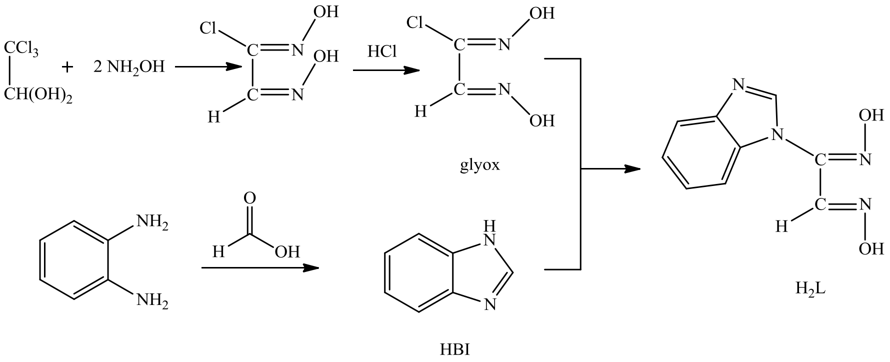


Figure 1. Synthesis of H_2L.

2.3. Synthesis of 1-5.

A solution of 0.139 g $FeSO_4.7H_2O$ for **1**; 0,1245 g $Co(Ac)_2.4H_2O$ for **2**; 0.124 g $Ni(Ac)_2.4H_2O$ for **3**; 0.099 g $Cu(Ac)_2.H_2O$ for **4** and 0.111 g $Zn(Ac)_2.2H_2O$ for **5** in 10 mL water was added to the 0.194 g H_2L in 10 mL ethanol. The solids powder {violet for **1** (0.368 g, 69% yield), as brown for **2** (0.292 g, 70% yield), as red for **3** (0.963 g, 73% yield), as bottle green for **4** (0.372 g, 80% yield) and as yellow for **5** (0.604 g, 77% yield)} that precipitated in the reaction medium was filtered and dried. The structures of **1-5** are given in Figure 2.

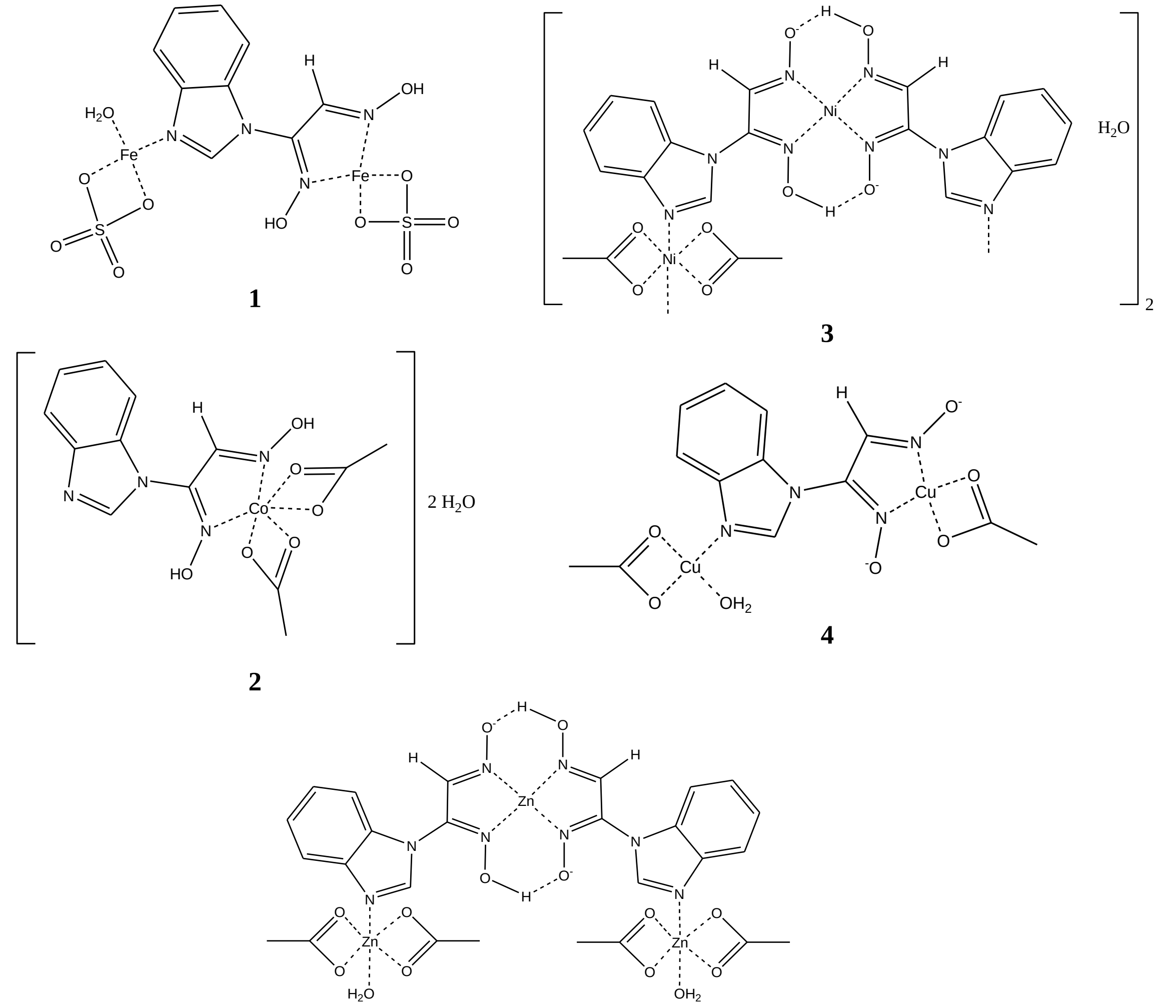


Figure 2. The compound **1-5**.

Anal. Calcd. for **1** ($C_9H_8N_4O_2$) (M = 204.19 g/mol): C, 52.95%, H, 3.97%, N, 27.45%, Found: C, 52.94%, H, 3.95%%, N, 27.44%. Anal. Calcd. for **2** ($C_9H_{10}N_4O_{11}S_2Fe_2$) (M = 526.02 g/mol): C, 20.50%, H, 1.90%, N, 10.65%, S, 12.20%, M, 21.00, Found: C, 20.55%, H, 1.92%, N, 10.65%, S, 12.19%, M, 21.23. Anal. Calcd. for **3** ($C_{13}H_{18}N_4O_8Co$) (M = 417.24 g/mol): C, 37.40%, H, 4.45%, N, 13.40%, M, 14.10, Found: C, 37.42%, H, 4.35%, N, 13.43%, M, 14.12. Anal. Calcd. for **4** ($C_{44}H_{22}N_{16}O_{18}Ni_4$) (M = 1319.69 g/mol): C, 40.01%, H, 3.39%, N, 16.97%, M, 17.70, Found: C, 40.04%, H, 3.36%, N, 16.98%, M, 17.79. Anal. Calcd. for **5** ($C_{13}H_{14}N_4O_7Cu_2$) (M = 465.37 g/mol): C33.57, %, H, 3.04%, N, 12.02%, M, 27.30, Found: C, 33.55%, H, 3.03%, N, 12.04%, M, 27.31. Anal. Calcd. for **6** ($C_{26}H_{30}N_8O_{14}Zn_3$) (M = 784.73 g/mol): C, 35.76%, H, 3.50%, N, 12.80%, M, 22.40, Found, C, 35.70%, H, 3.46%, N, 12.81%, M, 22.43.

3. RESULTS AND DISCUSSION

3.1. ^{1}H-NMR Result of H_2L.

The ^{1}H-NMR spectrum (Figure 3) and ^{1}H-NMR values (Table 1) of H_2L was obtained in d_6-DMSO at 25 ºC.

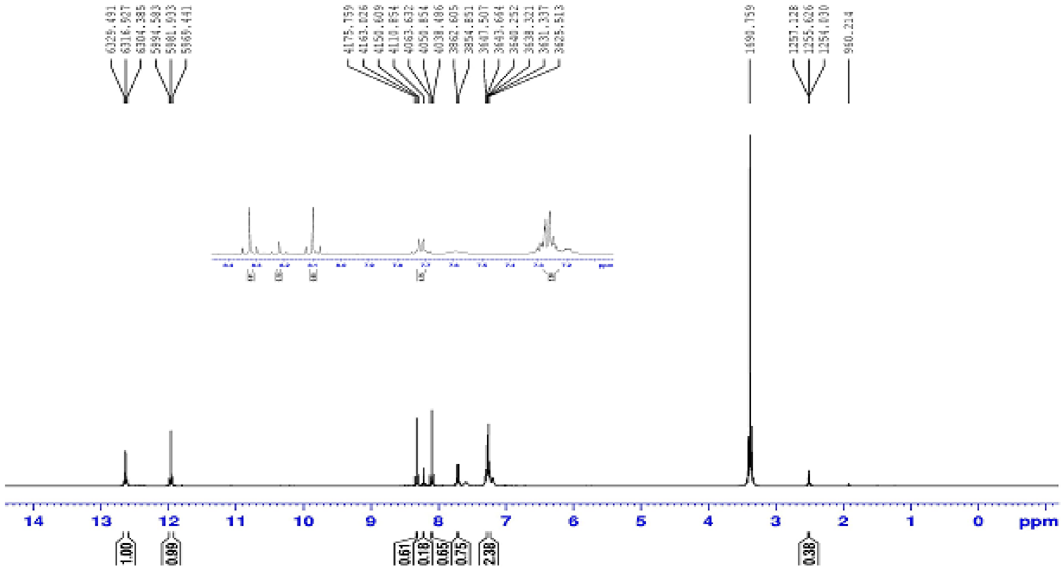
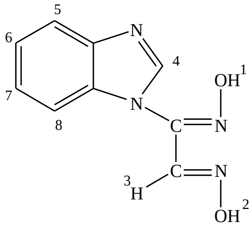


Figure 3. ^{1}H-NMR spectrum of compound H_2L.

Table 1. ^{1}H-NMR values for H_2L.

	
H^1	12.65 (1H, s)
H^2	11.95 (1H, s)
H^4	8.33 (1H, s)
H^3	8.10 (1H, s)
H^8	7.72 (1H, d) [$^3J_{H8\text{-}H7}$ = 7.75 Hz]
H^5, H^6 and H^7	7.28 (3H, m) [$^3J \approx 7$ Hz]

The ^{1}H-NMR spectrum of H_2L also contains two singlet peaks oxime part (H^1 and H^2) at 12.65 ppm and 11.95 ppm, respectively, with the intensity of 1H atom for each. The CH proton of oxime part (H^3) is easily distinguishable as singlet with the intensity of 1H atom at 8.10 ppm. The H^4 proton of H_2L was observed at 7.72 ppm with the intensity of 1H atom. H^5, H^6 and H^7 protons of H_2L are observed at 7.28 ppm ($^3J \approx 7$ Hz) multiple with 3H intensity. H^8 proton of H_2L is doublet as expected and arisen at 7.72 ppm ($^3J_{H8-H7} = 7.75$ Hz) with the intensity of 1H atom.

3.2. FT-IR Results

The IR data of all compounds are given in Table 2. There are broad vibration peaks between 3300 and 3320 cm^{-1} attributed to the ν(OH) vibrations of all compounds (expect HBI). There is a medium vibration peak at 3114 cm^{-1} attributed to the ν(N-H) vibrations of HBI. This peak is not observed in compound H_2L due to replacing H atom of N-H in HBI with oxime group after reaction (Figure 1). υ(C=N) of H_2L and ν(C=N)$_{oxime}$ and/or ν(C=N)$_{HBI}$ of **1-5** vibration are in the range of 1635-1610 cm^{-1} with similar pattern. These frequencies are shifted to higher or lower energies when compared with free glyox (1605 cm^{-1}) and HBI (1615 cm^{-1}) indicating the coordination between metal ion and ν(C=N) groups of H_2L (Figure 2). The peaks at the range of 3022-2823 cm^{-1} (weak), 3100-3055 cm^{-1} (weak), 1405-1587 cm^{-1} (strong) are assigned υ(C-H) methylene, υ(C-H) aromatic (except glyox) and ν(C=C) of all compounds, respectively. In the complexes (**1-5**), the peaks at the range of 475-469 and 579-531 cm^{-1} can be assigned for the ν(M-O) and ν(M-N) modes also showing the coordination between metal ions and H_2L, respectively [33-35].

Table 2. IR data of all compounds (cm^{-1}).

	Glyox	**HBI**	**H_2L**	**1**	**2**	**3**	**4**	**5**
ν(OH)	3298(br)	-	3300(br)	3285(br)	3275(br)	3320(br)	3256(br)	3318(br)
ν(NH)	-	3114(m)	-	-	-	-	-	-
ν(C-H)$_{Ar.}$	-	3061(w)	3055(w)	3050(w)	3065(w)	3100(w)	3059(w)	3059(w)
ν(=C-H)	3022(w)	2939(w)	3000(w)	3005(w)	3007(w)	3023(w)	3000(w)	3000(w)
	2883(w)	2857(w)	2823(w)	2912(w)	2920(w)	2997(w)	2997(w)	2992(w)
				2833(w)	2845(w)	2885(w)	2845(w)	2852(w)
ν(C=N)	1605(s)	1615(s)	1630(s)	1635(s)	1636(s)	1636(s)	1631(s)	1636(s)
			1609(s)	1610(s)	1610(s)	1609(s)	1609(s)	1610(s)
ν(C=C)	-	1587(s)	1542(s)	1542(s)	1545(s)	1548(s)	1559(s)	1548(s)
		1499(s)	1500(s)	1499(s)	1499(s)	1501(s)	1499(s)	1506(s)
		1478(s)	1480(s)	1456(s)	1455(s)	1454(s)	1457(s)	1481(s)
		1456(s)	1457(s)	1412(s)	1420(s)	1412(s)	1405(s)	1456(s)
ν(M-N)	-	-	-	531(w)	548(w)	551(w)	543(w)	579(w)
ν(M-O)	-	-	-	472(w)	475(w)	474(w)	475(w)	469(w)

3.3. Thermal Analyses of Compounds 2-6.

TG-DTG and DTA curves of **1-5** are given in Figure 4-8, respectively, and their values are given in Table 3.

All complexes thermally decomposed in three steps. The endothermic first stage corresponds to the loss of two, two two one and two moles of water molecule for **1-5**. The endothermic second stage is consistent to the loss of $C_9H_8NO_2$, four, four, two and four moles acetate molecules and in the endothermic third stage $S_2N_3O_8$, one, four, one and two moles H_2L for **1-5**. The final product left undecomposed are FeO, CoO, NiO, CuO and ZnO, respectively.

Table 3. Thermal analyses results of compounds **1-5**.

Compound	**Temperature (ºC)**	**DTG_{max} (ºC)**	**Leaving Group**	**Found (%)**	**Calculated (%)**
1	35-157	63	$2H_2O$	3.20	3.42
	157-301	189, 238	$C_9H_8NO_2$	30.70	30.83
	301-800	304, 314	$S_2N_3O_8$	44.60	44.52
	-	-	FeO	21.50	21.23
2	35-195	55	$2H_2O$	7.90	8.55
	195- 401	291	4Ac	28.40	28.32
	401-900	439, 466	H_2L	49.40	49.00
	-	-	CoO	14.30	14.21
3	35-126	78	$2H_2O$	2.80	2.70
	126-300	289	4Ac	17.60	17.80
	300-650	376	4HL	61.70	61.70
	-	-	NiO	17.90	17.78
4	35-143	94	H_2O	3.80	3.88
	143-252	237	2Ac	18.50	18.48
	252-650	266, 271, 301	H_2L	50.50	50.33
	-	-	CuO	27.20	27.31
5	35-164	59	$2H_2O$	4.10	4.12
	164-255	221	4Ac	16.60	16.66
	255- 750	452, 538, 561	$2H_2L$	56.70	56.79
	-	-	ZnO	22.60	22.43

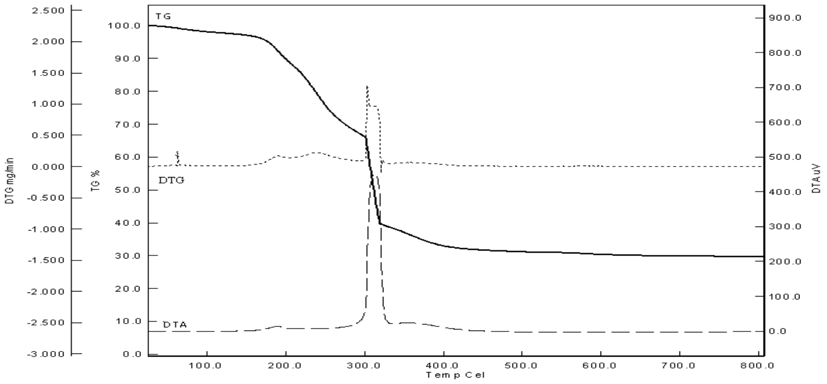


Figure 4. Thermal analysis results of **1**.

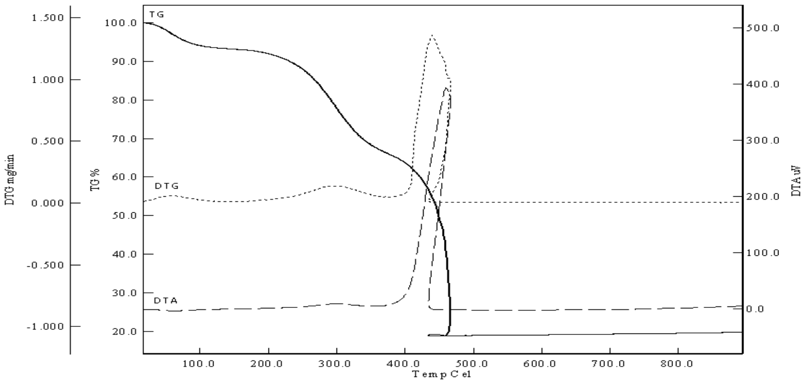


Figure 5. Thermal analysis results of **2**.

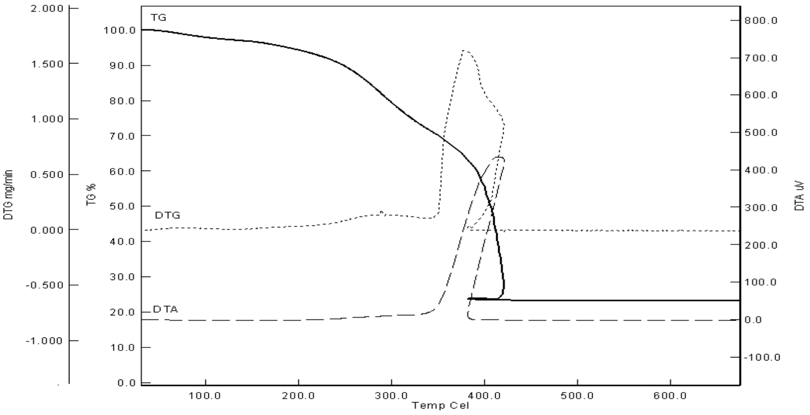


Figure 6. Thermal analysis results of **3**.

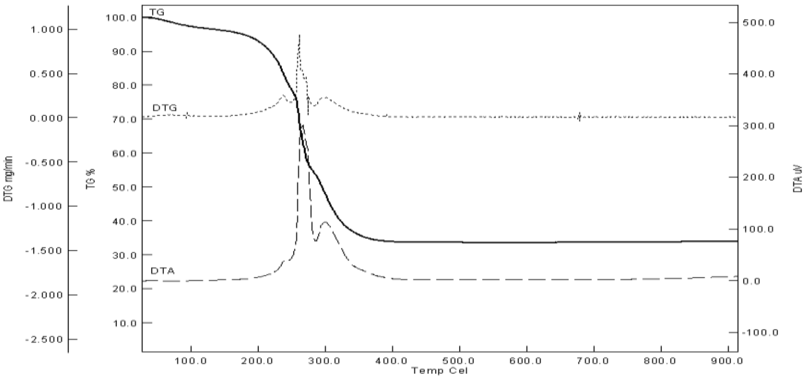


Figure 7. Thermal analysis results of **4**.

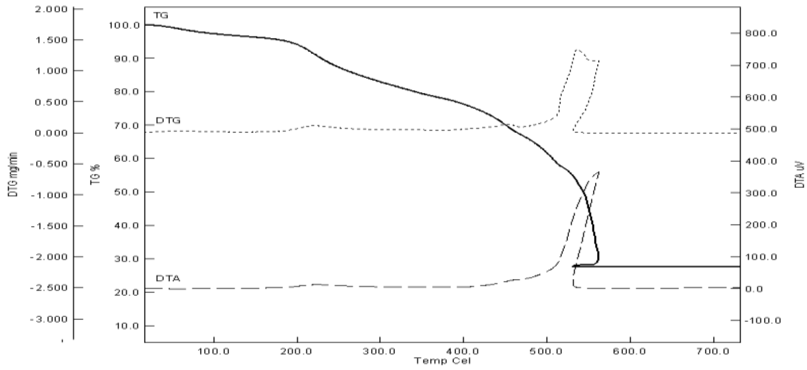


Figure 4. Thermal analysis results of **5**.

3.4. UV-vis Spectra, Molar Conductivities and Magnetic Susceptibilities

The UV-Vis spectra of glyox, HBI, H_2L and **1-5** were recorded in DMSO (1x10^{-3} *M*). The π- π* transitions are seen in the spectra of free ligands glyox (239 and 289 nm) and HBI (288 nm), H_2L (236 and 289 nm), of **1** (236 and 286 nm), of **2** (288 and 294 nm), of **3** (288 and 294 nm), of **4** (294 and 360 nm) and of **5** (289 and 328 nm). The d-d transitions bands of **1-4** are observed at 794, 769, 802 and 821 nm, respectively. The d-d transition for **5** have not been observed due to containing Zn(II) ion (d^{10}).

The molar conductivity data in DMSO of **1-5** is the 0.9, 1.5, 2.0, 0.5 and 3.1 $\Omega^{-1}cm^2$ mol^{-1}, respectively, indicating that **1-5** are non-ionic [36]. These results agree that sulfate ion for **1** and acetate ions for **2-5** complexes are coordinated to the metal ions.

Magnetic moments **1-5** are 4.88, 3.75, 2.79, 1.70 and 0 BM per metal(II) ion, indicating the presence of four, three, two, one and zero unpaired electrons, respectively.

4. CONCLUSIONS

In this study, non-ionic metal(II) complexes (Fe, Co, Ni, Cu and Zn) (**1-5**) with a novel *vic*-dioxime compound, named (1*E*, 2*Z*)-2-(1*H*-benzoimidazol-1-yl)-2-(hydroxyimino)acetaldehyde oxime (H_2L) were prepared and characterized by analysis methods results. According to these results the structures of complexes are proposed tetrahedral (**1** and **4**), octahedral (**2**) and square plane/octahedral (**3** and **5**). Different application areas of the synthesized compounds should be examined.

ACKNOWLEDGEMENT

This work was supported by Dumlupınar University Research Foundation (Grant No: 2010-02) and was carried out at the Chemistry Department of same University. In addition, the author would like to thank Prof. Dr. Cengiz YENİKAYA.

REFERENCES

[1] Coban, B., Eser, N., Babahan, I., (2017), DNA binding by copper (II) complexes of semithiocarbazone containing ligands, Bulgarian Chemical Communications, 49(4), 908-913.

[2] Deveci, P., Taner B., (2013), Synthesis, spectroscopic, and cyclic voltammetric studies of ferrocene containing *vic*-dioxime ligand and its complexes with Ni(II), Cu(II), Co(II), Cd(II) and Zn(II), Inorganica Chimica Acta, 405, 326-330.

[3] Motaleb, M. A., Selim, A. A. (2019), Dioximes: Synthesis and biomedical applications, Bioorganic Chemistry, 82, 145-155.

[4] Tuyun, A. F., Bayrak, N., Yıldırım, H., Yıldız, M., Kara, E. M. Celik, B. O., (2021), Bis(Substituted Phenylamino)Glyoxime derivatives: Synthesis, characterization, and antimicrobial evaluation, Journal of Molecular Structure, 1242, 130812.

[5] Findik, M., Ucar, A., Türkkan E., Pehlivanoglu, S., Ozcan E., (2021), Synthesis of *anti*-4-phenoxyphenylaminoglyoxime and its some transition metal complexes: Spectral, DFT, electrochemical and anticancer activity studies, Journal of Molecular Structure, 1215, 128190.

[6] Deveci, P., Taner, B., Kılıç, Z., Solak, A.O. and Özcan, E., (2012), Synthesis and structural and electrochemical characterization of novel macrocyclic vic-dioxime ligand and its mononuclear transition and nontransition metal complexes, Turkish Journal Of Chemistry, 36, 25-36.

[7] Yenikaya, C., Kaya, M. and Demir, İ., (2008), Synthesis of a imine vic-dioxime ligand and its Ni(II), Co(II), Cu(II) complexes, Asian Journal of Chemistry, 20(7), 5651-5657.

[8] Kaya, M., Demir, İ. and Yenikaya, C., (2008), Synthesis and characterization of complexes of vic-dioxime derivatives with transition metal. Asian Journal of Chemistry, 20(3), 2221-2228.

[9] Kaya, M., Yenikaya, C., Demir, İ. and Kalfa, O.M., (2008), Synthesis and characteristics of N-(glyoxyldioxime)-N′-(2-hydroxybenzylidene)-1,4-diaminonaphthalene and its metal complexes, Russian Journal of General Chemistry, 78(5), 939-945.

[10] Kaya, M., Yenikay,a C., Çolak, A.T. and Çolak, F., (2008), Synthesis, spectral, thermal and biological studies of Co(III) and binuclear Ni(II) complexes with a novel amine-imine-oxime ligand, Russian Journal of General Chemistry, 78(9), 1808-1815.

[11] Canpolat, E., Yazıcı, A., Kaya, M. (2004), Synthesis and Characterization of Co(II), Ni(II), Cu(II), and Zn(II) Complexes with a new vic-dioxime (E,E)-N′-hydroxy-2-(hydroxyimino)-N-(4-{[(2-phenyl-1,3-dioxolan-4yl)methyl]amino}butyl)ethanimidamide. Russian Journal of Coordination Chemistry, 30(2), 87-93.

[12] Poyraz, M., Yenikaya, C. and Çolak, A.T., (2008), Synthesis and Structural Studies of Bidentate Schiff Bases and Their Complexes with Cu(II), Ni(II), Co(II), Cd(II) and Zn(II), Asian Journal of Chemistry, 20(5), 3515-3524.

[13] Gök, Y. and Demirbas, A., (1989), The Synthesis and Complex Formation of Dibenzo [e,k]-2,3-Bis(Hydroxyimino)-1,4-Diaza-7,10-Dithia-2,3,8,9-Tetrahydrocyclododecine, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 19(5), 681-689.

[14] Gül, A. and Bekaroglu, O., (1983), Syntheses of *NN*′-bis(4′-benzo[15-crown-5])diaminoglyoxime and its complexes with copper(II), nickel(II), cobalt(II), cobalt(III), palladium(II), platinum(II), and uranyl(VI), Journal of the Chemical Society, Dalton Transactions, 12, 2537-2541.

[15] Kurtoğlu, M and Serin, S., (2002), Syntheses and characterization of 4-(11-chloro-3,6,9-trioxaundecyloxy) phenylamino-glyoxime and its complexes with copper(II), nickel(II), and cobalt(II), Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 32(3), 629-637.

[16] Durmus, M., Ahsen, V., Luneau, D. and Pécaut, J., (2004), Synthesis and structures of morpholine substituted new *vic*-dioxime ligand and its Ni(II) complexes, Inorganica Chimica Acta, 357(2), 588-594.

[17] Atilla, D., Asma, S. and Gurek, A., (2009), Highly soluble Ni(II) vic-dioxime complexes containing branched thioether with alkyl chains of different lengths:synthesis and characterization, Journal of Coordination Chemistry, 62(18), 3050–3059.

[18] Walia, R., Md, H., Naaz, S.F., Iqbal, K. and Lamba H.S., (2011), Benzimidazole derivatives – an overview, International Journal Of Research In Pharmacy and Chemistry, 1(3):565-573.

[19] Téllez, F., López-Sandoval, H., Castillo-Blum, S.E. and Barba-Behrens, N., (2008), Coordination behavior of benzimidazole, 2-substituted benzimidazoles and benzothiazoles, towards transition metal ions, Arkivoc, (v), 245-275.

[20] Pawar, N.S., Dalal, D.S., Shimpi, S.R. and Mahulikar, P.P., (2004), Studies of antimicrobial activity of N-alkyl and N-acyl 2-(4-thiazolyl)-1H-benzimidazoles, European Journal Of Pharmaceutical Sciences, 21, 115-118.

[21] Özden, S., Atabey, D., Yildiz S. and Göker, H., (2005), Synthesis and potent antimicrobial activity of some novel methyl or ethyl 1*H*-benzimidazole-5-carboxylates derivatives carrying amide or amidine groups, Bioorganic & Medicinal Chemistry, 13(5), 1587-1597.

[22] Ören, I., Temiz, Ö., Yalcin, I., Sener, E. and Altanlar, N., (1998), Synthesis and antimicrobial activity of some novel 2, 5-and/or 6-substituted benzoxazole and benzimidazole derivatives, European Journal Of Pharmaceutical Sciences, 7, 153-160.

[23] He, Y., Ww, B., Yang, J., Robinson, D., Risen, L., Ranken, R., Blyn, L., Sheng, S. and Swayze, E.E., (2003), 2-Piperidin-4-yl-benzimidazoles with broad spectrum antibacterial activities, Bioorganic & Medicinal Chemistry Letters, 13(19): 3253-3256.

[24] Varhelyi, Cs. Jr., Kovacs, A., Nemcsok, D., Nemeth, Z., Kuzmann, E., Vertes, A., Vekey, K., Varhelyi, Cs., Pokol, G., (2007), Spectroscopic and thermal studies of [Fe(dioximato)(amine)]mixed chelates, Journal of Coordination Chemistry 60(4), 379-392.

[25] Gok, Y., Ertepinar, H., (1992), Synthesis and Characterization of Novel Polyamidoxime Transition Metal Complexes. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 22(10), 1495–1505.

[26] Ertepinar, H., Gök, Y., Küçükislamoğlu, M. (1995), Synthesis and characterizations of new polyamidoximes and their crosslinking by metal ions. European Polymer Journal, 31(6), 603–608.

[27] Kraska, J., Czajkowski, W.,(1982), Metal complex pigments, Poland, PL123437 B2

[28] Zsako, J., Varhelyi, C., Demeter-Vodnar, J., Liptay, G., (1992), On the dioxime complexes of transition metals. XCV. New iodo-amino-bis-dimethylglyoximatocobalt(III)-nonelectrolytes, Periodica Polytechnica, Chemical Engineering, 36(4), 271-278.

[29] Zsako, J., Varhelyi, C., Sarvari, T., (1989), On the dioximine complexes of transition metals. LXXIX. Some new chelates of iron with nioxime and trioxime, Studia Universitatis Babes-Bolyai, Chemia, 34(2), 10-15.

[30] Houben, J. and Kaufman, H., (1913), Über Chlor-glyoxime, Oxim-Derivate des Oxalylchlorids und Oxalsäure-halbchlorids und über Cyan-formyl-chloridoxim, Berichte der deutschen chemischen Gesellschaft, 46, 2821-2835.

[31] March, J., (1977), Advanced Organic Chemistry: Reaction, Mechanisms, Structure, 609.

[32] Phillips, M.A., (1931), CCCXVII.—The formation of 2-substituted benziminazoles, Journal of the Chemical Society, 1143-1153.

[33] Ueno, K. and Martell, A.E., (1956), Infrared studies on synthetic oxygen carriers, *The Journal of Physical Chemistry*, 60, 1270-1275.

[34] Nakamoto, K. and Martell, A.E., (1960), Infrared Spectra of Metal Chelate Compounds. VI. A Normal Coordinate Treatment of Oxalato Metal Complexes, The Journal of Chemical Physics, 32, 588-588.

[35] Coleman, W.M. and Taylor, L.T., (1971), Pentadentate ligands. I. Nickel(II) complexes of the linear Schiff base ligands derived from substituted salicylaldehydes and diethylenetriamine and 2,2'-bis(aminopropyl)amine, *Inorganic Chemistry*, 10, 2195-2199.

[36] Geary, W.J., (1971), The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds. Coordination Chemistry Reviews, 7, 81-122.