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Metal Complexes of Bis (2,6-diamine pyridine 2,5-hexanedione) Macrocyclic Schiff-Base Ligand: Preparation, Characterization and thermal study

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Abstract

New series of Schiff base macrocyclic complexes have been prepared through a new chemical approach. Firstly, ligand Bis (2,6-diamine pyridine 2,5-hexanedione (DP-HD) prepared via reacting of 2,6-diamine pyridine (DP) with 2,5-hexanedione(HD) in molar ration (1DP:1HD). The complexes of this ligand include Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) as central metal ions also prepared with a molar ratio of (1 ligand:1 metal ion). Metals chloride was used as raw materials for this preparation. A variety of spectral and physical techniques were applied to characterize the macrocyclic complexes such as ¹H-NMR, FT-IR, UV-Vis, CHN analysis, conductivity, Atomic absorption and magnetic susceptibility. Depending on spectral and magnetic measurements, the suggested geometrical shapes of these complexes were reported. FT-IR spectroscopy recorded the coordination sites based on the ligand's main group bands that could shift to a lower frequency. Finally, thermal stability has been investigated for ligands and their complexes. While the thermal gravimetric analyses (TGA) and differential thermal analyses (DTA) approved the stability of these compounds if compared to their ligands only.

Keywords: Macrocyclic ligand, transition metal complexes, Schiff base complexes, Thermal stability.

المعقدات الفلزية لقواعد شيف ثنائي (2،6-ثنائي امين بريدين 2،5-هكسادايون) ذات الحلقة الكبيرة، تحضيرها ، تشخيصها، دراسة الاستقرار الحرارية

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الخلاصة

تم في هذا البحث تحضير ليكند لقواعد شيف ذات الحلقات الكبيرة ثنائي(2،6-ثنائي امين بريدين 2،5-هكسادايون) (DP-HD) من خلال مفاعلة نسب مولية متكافئة من المواد الاولية. كذلك تم تحضير معقدات بعض الفلزات (Mn(II),Fe(II),Co(II),Ni(II),Cu(II)) لهذا الليكند وينسب مولية (1:1) من الليكند إلى الفلز باستخدام كلوريد الفلز كمصدر للفلز. تم تشخيص المركبات المحضرة بواسطة العديد من الطرائق الطيفية

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والفيزيائية مثل طيف الرنين النووي المغناطيسي $^1\text{H-NMR}$ ، طيف الأشعة تحت الحمراء FT-IR ، طيف الأشعة فوق البنفسجية والمرئية UV-Vis ، التحليل الدقيق للعناصر CHN ، التوصيلية ، تقنية الامتصاص الذري فضلاً عن قياسات الحساسية المغناطيسية. اقترح الشكل الفراغي للمعقدات المحضرة اعتماداً على القياسات الطيفية و الحساسية المغناطيسية والذي اقترح بهيئة رباعي السطوح وثمانى السطوح. ان دراسة الاستقرار الحرارية (TGA,DTA) بينت ان جميع المركبات المحضرة مستقرة تحت درجة حرارة 300°C وان جميع المعقدات اكثر استقراراً من الليكند عند مقارنتها تحت نفس الظروف الحرارية.

1. Introduction

Schiff bases have been recorded as familiar ligands react with most transition metals to form stable complexes [1, 2]. These complexes have many applications, such as health topics, industrial topics, and other applications [3, 4]. The Macrocyclic Schiff base ligand has unique coordination with the metal ion in the center of cyclic ligand formation. This formation is similar to biological molecules such as hemoglobin, chlorophyll, catalytically enzyme and vitamin B12. Most complexes of macrocyclic Schiff base ligand stable with a high oxidation state of metal ion, slow coordination reaction, and high thermal stability [5, 6].

The development of transition metal reaction with macrocyclic ligand encountered some difficulties; for example, most non-transition metals react with large ring ligands such as Pb(II), Ba(II) and Ag(II), the transmetallation technique has been used to form the same complex with a transition metal, in this case, the complexes of non-transition metal must be dissolved completely in the solvent [2, 7].

Pyridine and its substitution are used widely in macrocyclic Schiff base synthesis, many transition metal complexes prepared by reaction of metals (Cr (III), Mn (II), Fe (III), Co (II), Ni (II) and Cu (II)) with 2,6-diacetyl pyridine once and with 1,2-di(o-amino phenyl) thioethane another once [8]. Non-transition metal complexes prepared in similar way, the dinuclear complex of Pb(II) of pyridine Schiff bases ligands with formula $[\text{Pb}_2(\text{BT})(\text{BI})_2(\text{SCN})_2]$ (BT= Benzotriazole, BI= Benzoimidazole) [8, 9].

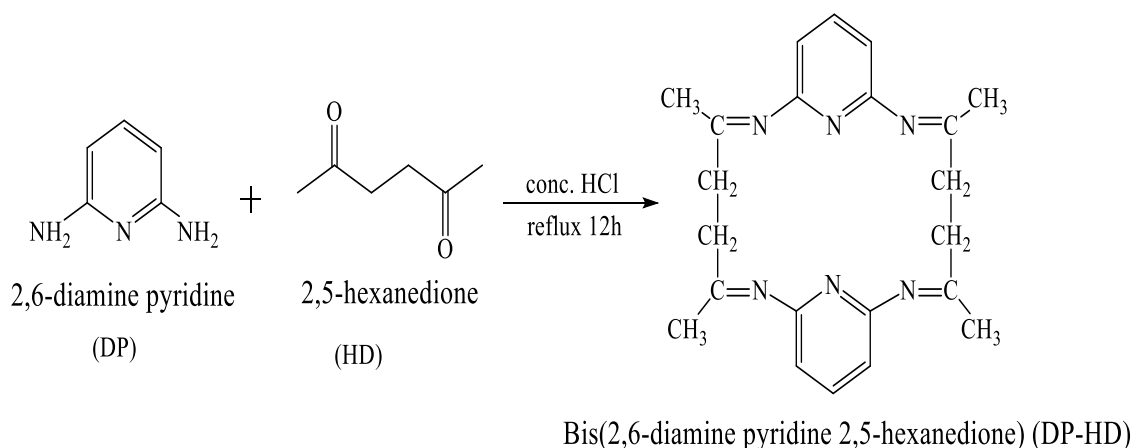
Thermal stability study of complexes very important to indicate the properties and the applications especially in the industrial applications. The thermal gravimetric analysis will be helpful in this study [3]. In this work, we aim to prepare some transition metal complexes with large cycle ligand and study the thermal stability of them in order to indicate the future applications of these complexes.

2. Experimental

All chemicals used are fine chemical and all the compounds are prepared according to literature preparation methods [3, 10-12].

2.1. Preparation of Bis(2,6-diamine pyridine 2,5-hexanedione) (DP-HD):

A solution of 2,6-diamine pyridine (DP) (0.02mol, 2.2g) dissolved in 30ml of warm ethanol was added to (0.02mol, 2.28g) of 2,5-hexanedione (HD) (dissolved in 30ml of warm ethanol too). Then 1ml of concentrated HCl was added to the mixture, and all these content refluxed for 12h. After that, the mixture concentrated to a half volume (approximately 20ml), it left overnight to cool. A dark gray precipitation appeared can be separated by filtration and washed by ethanol and diethyl ether several time. Then after the precipitate was dried at room temperature and then in an oven below 100°C . The filtered solution was concentrated slowly by evaporation at room temperature to obtain more participation. Scheme (1) shows the prepared ligand (DP-HD).



Scheme 1- Prepared Ligand (DP-HD) Bis(2,6-diamine pyridine 2,5-hexanedione)

2.2. Preparation of the complexes:

(0.01mol) of (DP-HD) was dissolved in warm 20ml ethanol and dropwise addition with constant stirring to a solution of (0.01mol) metal ion dissolved in 20ml ethanol (metal as metal chloride) with a molar ratio is 1:1 (ligand: metal), the mixture reflux for 15h, then concentrated to 20ml. The precipitate then was washed with diethyl ether.

2.3. Characterization methods:

Several spectral and physical methods were used to characterize the prepared compounds. The infra red spectroscopy (IR) was carried out by using ALPHA FT-IR spectrometer Bruker, JASCO Canvas FT/IR 4200 (with KBr and CsI desk). At the same time, the conductivity of prepared samples was recorded via the HANNA EC214 conductivity meter. Elemental analysis (CHN) was carried out via Euro EA Elemental Analysis Euro 3000-Italy. Atomic absorption for metal ion analyses was carried out by atomic absorption spectrophotometer of type SensAA GCB scientific equipment system 3000. Proton NMR at NMR 60 pro version (1.0). Electrothermal melting point 9100 was used to determine the melting point. Magnetic susceptibility was tested by using Sherwood MK1. Shimadzu 1800 spectroscopy was used for UV-Vis measurements, for the thermal study were carried out by METTLER TOLEDO TGA\DSC with STARE evaluation software virgin (16.3) at 25-600°C with heat ramping rate 5°C/min to get more accurate results. All compounds were finely characterized. Table 1 shows some physical properties of the prepared compounds.

Table 1- Some physical properties of prepared compounds

No.	Compound	Color	m.p °C	CHN cal./(found)			M% cal./ (found)	Cl% cal./ (found)
				C%	H%	N%		
1	(DP-HD)	Dark gray	80-83	70.58 (69.48)	6.95 (6.64)	22.46 (23.14)	---	---
2	[Mn(DP-HD)(H ₂ O) ₂ Cl ₂]	Dark brown	102-105	45.89 (47.08)	5.47 (5.82)	16.90 (15.34)	10.24 (12.88)	13.2 (14.8)
3	[Fe(DP-HD)Cl ₂]	Black	123-125	52.72 (53.82)	5.23 (4.43)	16.77 (15.91)	11.14 (10.55)	14.1 (13.9)
4	[Co(DP-HD)Cl ₂]	Gray	110-113	52.40 (54.20)	5.20 (4.86)	16.66 (15.36)	11.70 (12.12)	14.0 (14.5)
5	[Ni(DP-HD)Cl ₂]	Dark gray	113-115	52.42 (53.88)	5.20 (5.27)	16.67 (15.33)	11.65 (12.05)	14.0 (13.3)
6	[Cu(DP-HD)Cl ₂]	Dark brown	400<	51.92 (52.75)	5.15 (4.63)	16.51 (15.01)	12.49 (13.22)	13.9 (13.0)

3. Results and discussion

Figure 1 shows $^1\text{H-NMR}$ spectral for ligand (DP-HD) (the solvent used DMSO-d₆ appears at (δ 2.50), δ -1.99 (s, 12H), δ -5.76 (t, 8H, J = 6.0 Hz), δ -6.42 (m, 2H), δ -7.30 (m, 4H), the conductivity measurements carried out by using DMSO as a solvent with concentration 10^{-3} M at 25°C. These results prove that the complexes are nonconductive and the chloride ion is connected directly with the metal ion in the coordination sphere expect the chromium complex. On the other side, the complexes geometrical shape are tetrahedral, which suggested depends on the magnetic susceptibility and spectral data, which a good matching with the literature [10, 13-15]. Table 2 show the conductivity, magnetic data and spectral bands value with their transition bands.

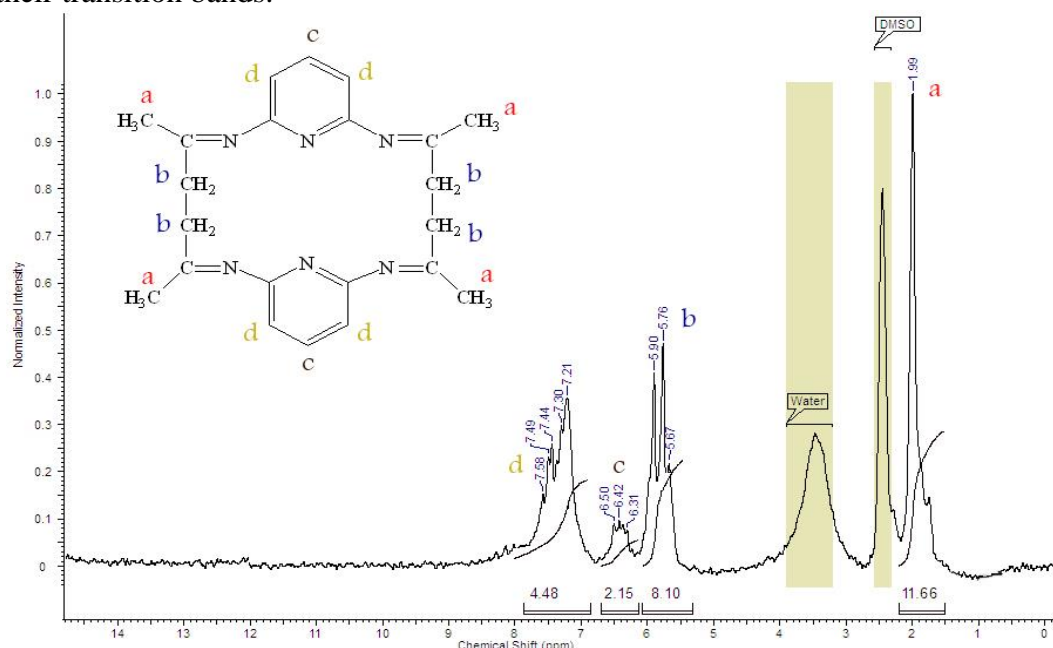


Figure 1- The $^1\text{H-NMR}$ spectral of the ligand (DP-HD)

Table 2- Conductivity, magnetic and spectral data

No.	Compound	Conductivity ($\text{ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$)	$\mu_{\text{eff}}(\text{B.M})$	Bands cm^{-1}	Suggested transitions
1	(DP-HD)	---	---	28248 34602	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
2	$[\text{Mn}(\text{DP-HD})(\text{H}_2\text{O})_2\text{Cl}_2]$	0.22	6.08	18181 23222	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$
3	$[\text{Fe}(\text{DP-HD})\text{Cl}_2]$	0.16	4.73	11961 12562	${}^5\text{E} \rightarrow {}^5\text{T}_2$
4	$[\text{Co}(\text{DP-HD})\text{Cl}_2]$	0.18	3.92	14836 16477 17761	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$
5	$[\text{Ni}(\text{DP-HD})\text{Cl}_2]$	0.31	3.81	12610 14164 14310	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$ ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$
6	$[\text{Cu}(\text{DP-HD})\text{Cl}_2]$	0.20	2.62	14310	${}^2\text{T}_2 \rightarrow {}^2\text{E}$

The infrared results confirm the suggested coordination site and identify the main groups in the prepared compounds. The stretching IR spectrum of ligand show a strong band at (1647cm^{-1}) referring to: $\nu(\text{N}=\text{C})_{\text{am}}$ azomethine group, and that agrees with the literature [3, 16], while the pyridine ring shows the bands at ($1517, 1562\text{cm}^{-1}$) belongs to $\nu(\text{C}=\text{N})_{\text{py}}$ group, and the bands ($1382, 1456\text{cm}^{-1}$) refer to stretching frequency of $\nu(\text{C}=\text{C})_{\text{py}}$ [17]. The other

two bands at (3182 cm^{-1}) and (2975 cm^{-1}) refer to $\nu(\text{C-H})_{\text{ar}}$ and $\nu(\text{C-H})_{\text{a}}$ frequency respectively. For the water band appears at (3357 cm^{-1}) [18-20], Figure 2 show the IR spectrum of the ligand.

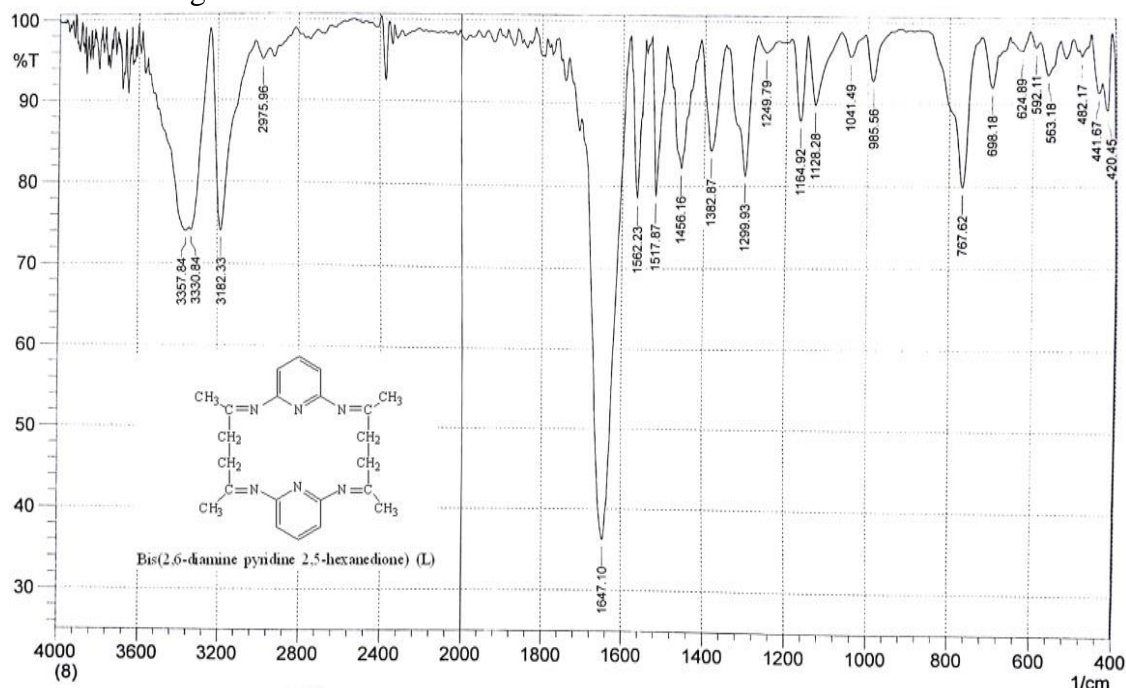


Figure 2- IR spectrum of ligand (DP-HD) Bis(2,6-diamine pyridine 2,5-hexanedione)

In complexes IR spectrum, it was observed that decrease in $\nu(\text{C=N})_{\text{am}}$ value within ($10\text{-}40\text{ cm}^{-1}$). This shifting in this group band indicates the coordination site from the nitrogen atom of azomethine in the ligand, while the $\nu(\text{C=N})_{\text{py}}$ stretching frequency value decries up to (50 cm^{-1}), refer to coordination from the nitrogen atom of pyridine. The stretching frequency of $\nu(\text{M-N})$ and $\nu(\text{M-Cl})$ bands appear at ($430\text{-}465\text{ cm}^{-1}$) ($235\text{-}325\text{ cm}^{-1}$), respectively. The other main group did not show any notable change in their frequency. Table 3 shows the main group's IR band in the prepared compounds.

Table 3- IR spectral data of prepared compounds in cm^{-1}

No.	Compound	$\nu(\text{C=N})_{\text{am}}$	$\nu(\text{C=N})_{\text{py}}$	$\nu(\text{C-H})_{\text{ar}}$	$\nu(\text{C-H})_{\text{alph}}$
1	(DP-HD)	1647	1652,1517	3182	2975
2	[Mn(DP-HD)(H ₂ O) ₂ Cl ₂]	1638	1449	3196	2919
3	[Fe(DP-HD)Cl ₂]	1641	1455	3190	2925
4	[Co(DP-HD)Cl ₂]	1639	1479	3201	2999
5	[Ni(DP-HD)Cl ₂]	1609	1480	3177	2974
6	[Cu(DP-HD)Cl ₂]	1581	1430	3163	2920
No.	Compound	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M-O})$
1	(DP-HD)	---	---	3357	---
2	[Mn(DP-HD)(H ₂ O) ₂ Cl ₂]	435	272	3318	440
3	[Fe(DP-HD)Cl ₂]	442	260	3320	---
4	[Co(DP-HD)Cl ₂]	451	281	3326	---
5	[Ni(DP-HD)Cl ₂]	449	310	3298	---
6	[Cu(DP-HD)Cl ₂]	457	214	3351	---

The suggested structure is shown in Figure 3 from all physical and spectral properties.

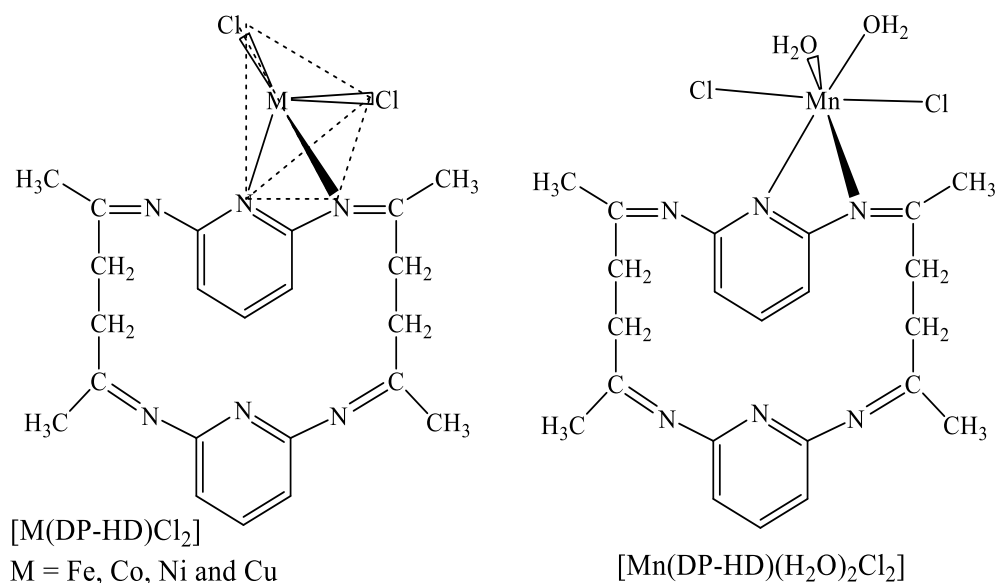


Figure 3- The suggested complexes' structure

This work aims to study the thermal stability of the prepared compounds. The thermal study can be useful to predicate the complex beavers especially when they use in the industrial process such as biological uses, polymer production and other application [3, 21-23]; knowing thermal properties to determine the right decision of identified these compounds in the various and specific application.

Thermal gravimetric analysis (TGA) was carried out, as shown in the experimental part. The (TGA) analyses of the ligand (DP-HD) show that the mass loss process pass through two main steps. The first step includes the remove of the moistness water at a temperature up to 100°C. In contrast, the second step includes the dissociation of the compounds to original parts with temperature from 120°C to 415°C. The (TGA) diagram of the ligand is shown in Figure 4, differential thermal analyses (DTA) is shown in Figure 5 and differential scanning calorimetry (DSC) is shown in Figure 6. Time, temperature and losing mass ratio percentage of the ligand dissociation steps are listed in Table 4.

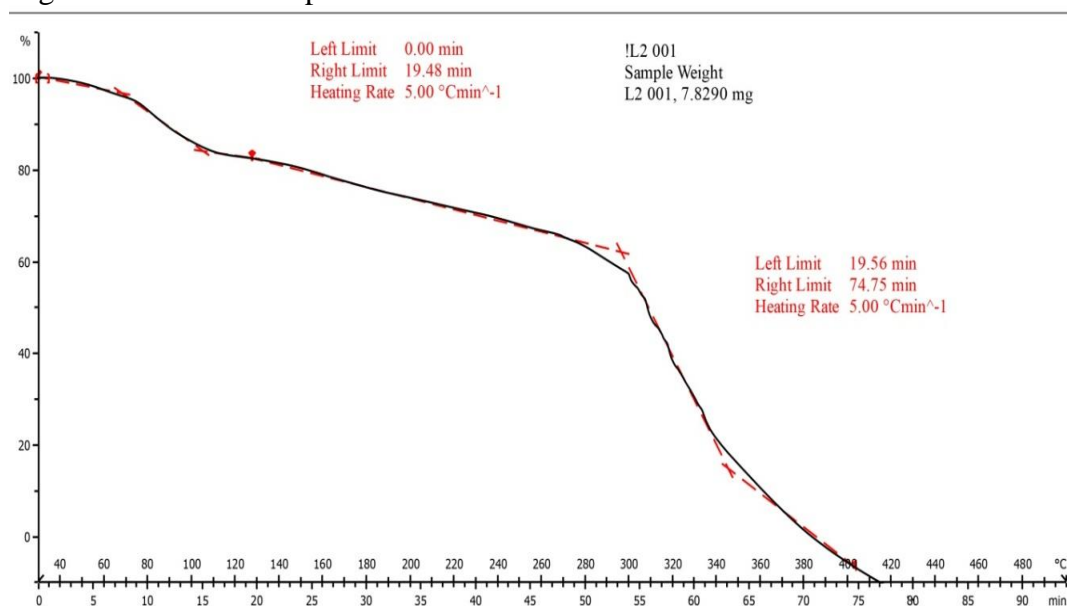


Figure 4- TGA diagram of the ligand (DP-HD) Bis(2,6-diamine pyridine 2,5-hexanedione)

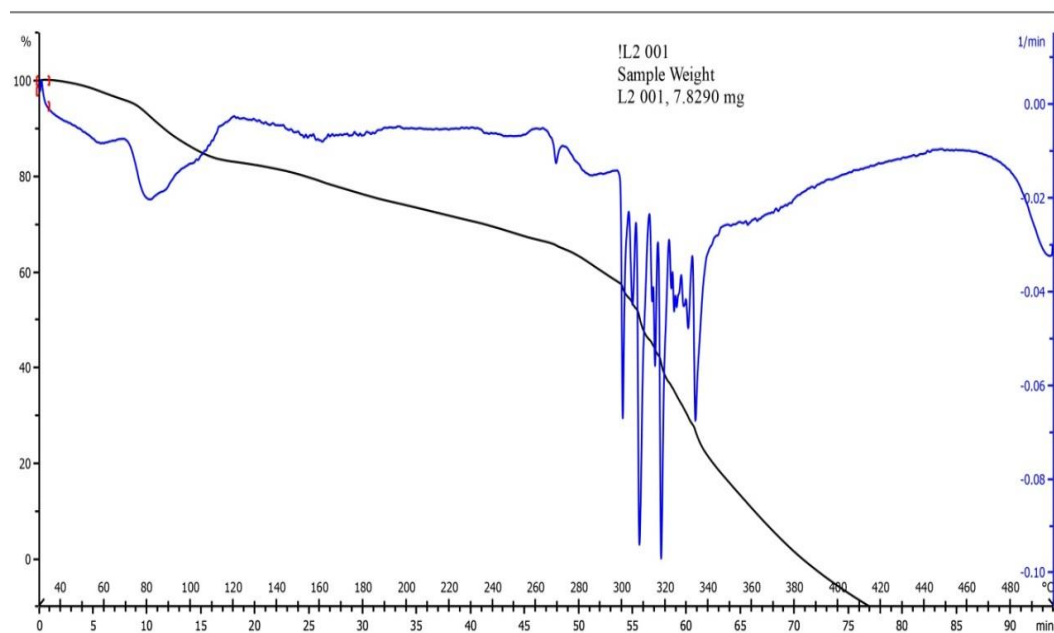


Figure 5- TGA and DTA of the ligand (DP-HD) Bis(2,6-diamine pyridine 2,5-hexanedione)

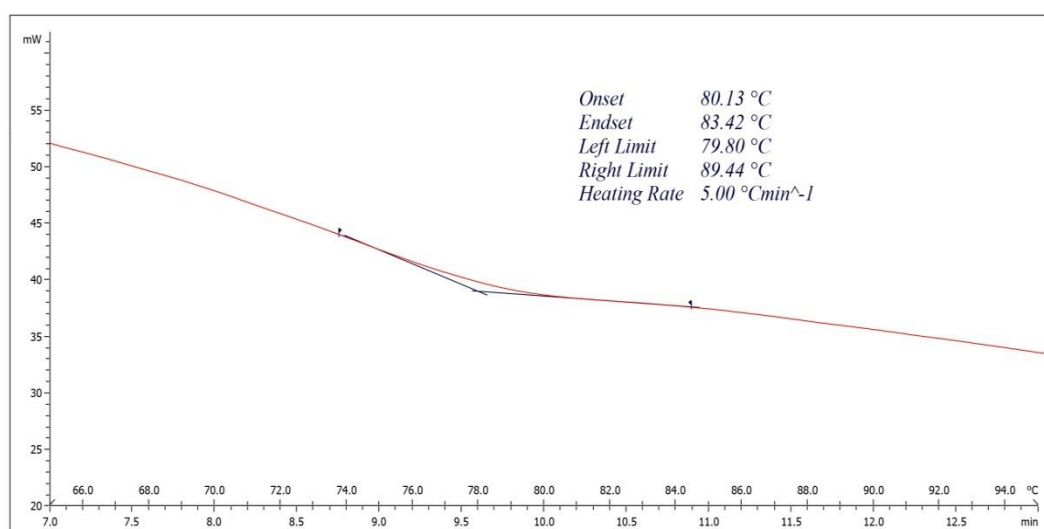


Figure 6- DSC of the ligand (DP-HD) Bis(2,6-diamine pyridine 2,5-hexanedione)

Table 4- TGA data of the ligand (DP-HD)

Steps	Time. min	Temp. °C	Mass Loss%
1 st	0-19	25-120	17.66%
2 nd	19-75	120-400	82.34%

The complexes thermal stability was studied too and compared with the ligand. The results approve all complexes are more stable than ligand, as can be seen in Figure 7, the complex with metal Mn, Fe and Co ions (**2-4**) is more stable than the complex with Ni and Cu metal (**5,6**). All complexes can be applied in an industrial process that needs heat rampage below 300°C.

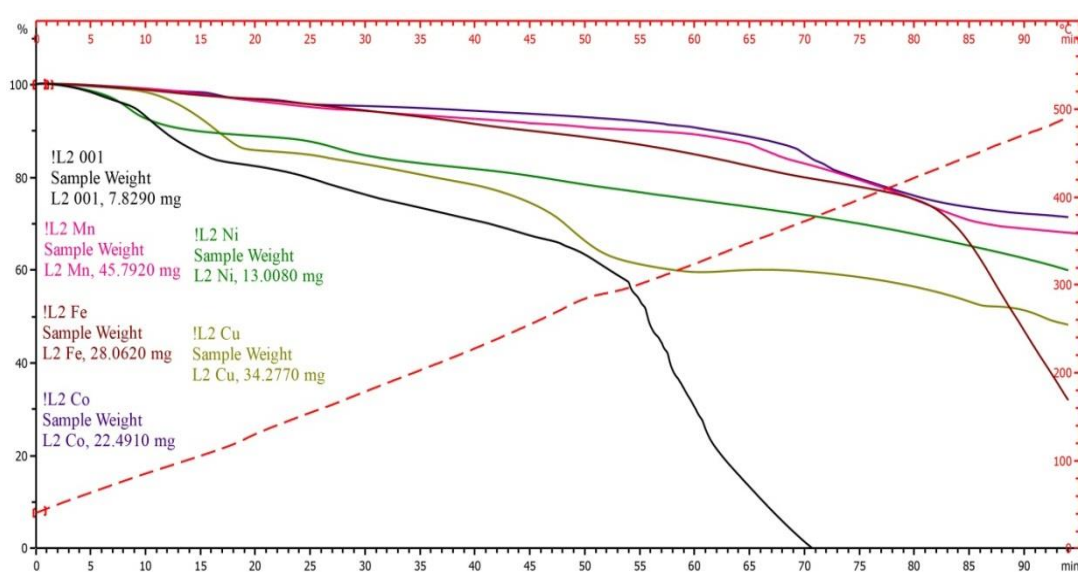


Figure 7- TGA and DTA of the ligand (DP-HD) and its complexes (2-6)

4. Conclusion:

The spectral and magnetic measurements has determined the geometrical shapes of prepared macrocyclic complexes to be an octahedral geometry for Mn(II) complex $[\text{Mn}(\text{DP-HD})(\text{H}_2\text{O})_2\text{Cl}_2]$. At the same time, the other complexes showed tetrahedral geometrical shapes that have a general formula $[\text{M}(\text{L})\text{Cl}_2]$ ($\text{M} = \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$).

The thermal study showed that the ligands were stable below 300°C . While the complexes were more stable than ligands at the same conditions, and they were stable up to 300°C . Complexes (2-4) have good thermal stability compared with complexes (5,6). All the prepared macrocyclic compounds can be utilized in any industrial applications at temperatures below 300°C .

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6. References:

- [1] P. Chakraborty, S. Purkait, S. Mondal, A. Bauzá, A. Frontera, C. Massera, *et al.*, "Exploration of $\text{CH}\cdots\pi$ interactions involving the π -system of pseudohalide coligands in metal complexes of a Schiff-base ligand," *CrystEngComm*, vol. 17, pp. 4680-4690, 2015.
- [2] E. M. Zayed, G. G. Mohamed, and A. M. Hindy, "Transition metal complexes of novel Schiff base," *Journal of Thermal Analysis and Calorimetry*, vol. 120, pp. 893-903, 2015.
- [3] K. Mostafa MH, I. Eman H, M. Gehad G, Z. Ehab M, and B. Ahmed, "Synthesis and characterization of a novel schiff base metal complexes and their application in determination of iron in different types of natural water," *Open Journal of Inorganic Chemistry*, vol. 2012, 2012.
- [4] A. Kareem, M. Arshad, S. A. Nami, and N. Nishat, "Herbo-mineral based Schiff base ligand and its metal complexes: Synthesis, characterization, catalytic potential and biological applications," *Journal of Photochemistry and Photobiology B: Biology*, vol. 160, pp. 163-171, 2016.
- [5] P. Gull and A. A. Hashmi, "Biological activity studies on metal complexes of macrocyclic schiff base ligand: synthesis and spectroscopic characterization," *Journal of the Brazilian Chemical Society*, vol. 26, pp. 1331-1337, 2015.
- [6] R. A. Shiekh, I. Ab Rahman, M. A. Malik, N. Luddin, S. a. M. Masudi, and S. A. Al-Thabaiti, "Transition metal complexes with mixed nitrogensulphur (NS) donor macrocyclic Schiff base ligand: synthesis, spectral, electrochemical and antimicrobial studies," *Int. J. Electrochem. Sci*, vol. 8, pp. 6972-6987, 2013.
- [7] A. Abou-Hussein and W. Linert, "Synthesis, spectroscopic studies and inhibitory activity against

- bacteria and fungi of acyclic and macrocyclic transition metal complexes containing a triamine coumarine Schiff base ligand," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 141, pp. 223-232, 2015.
- [8] M. Rezaeivala and H. Keypour, "Schiff base and non-Schiff base macrocyclic ligands and complexes incorporating the pyridine moiety—The first 50 years," *Coordination Chemistry Reviews*, vol. 280, pp. 203-253, 2014.
- [9] M. N. Uddin, M. A. Salam, and J. Sultana, "Pb (II) complexes of Schiff bases derived from benzoylhydrazine as the antibacterial agents," *Science publishing group*, vol. 3, pp. 7-14, 2015.
- [10] E. Yousif, A. Majeed, K. Al-Sammarae, N. Salih, J. Salimon, and B. Abdullah, "Metal complexes of Schiff base: preparation, characterization and antibacterial activity," *Arabian Journal of Chemistry*, vol. 10, pp. S1639-S1644, 2017.
- [11] A. M. Abu-Dief and I. M. Mohamed, "A review on versatile applications of transition metal complexes incorporating Schiff bases," *Beni-suef university journal of basic and applied sciences*, vol. 4, pp. 119-133, 2015.
- [12] A. Xavier and N. Srividhya, "Synthesis and study of Schiff base ligands," *IOSR Journal of Applied Chemistry*, vol. 7, pp. 06-15, 2014.
- [13] Q.-M. Hasi, Y. Fan, X.-Q. Yao, D.-C. Hu, and J.-C. Liu, "Synthesis, characterization, antioxidant and antimicrobial activities of a bidentate Schiff base ligand and its metal complexes," *Polyhedron*, vol. 109, pp. 75-80, 2016.
- [14] A. Nagajothi, A. Kiruthika, S. Chitra, and K. Parameswari, "Fe (III) complexes with Schiff base ligands: synthesis, characterization, antimicrobial studies," *Research Journal of Chemical Sciences ISSN*, vol. 2231, p. 606X, 2013.
- [15] S. A. Hamed, "Synthesis, Molecular Structure from the X-ray Diffraction Data of the Powder (1E, 1'E)-1, 1'-(1, 4-Phenylene) Bis (N-(Adamantan-1-yl) methanimine)," *Iraqi Journal of Science*, vol. 62, No. 4, pp. 1066-1076, 2021.
- [16] N. A.-H. A. Al-Mohammadi, A. S. Al-Fahdawi, and S. S. Al-Janabi, "Design and Characterization of New Dinuclear Macrocyclic Dithiocarbamate Complexes by the Preparation of a Free Ligand Derived from Isopropylamine," *Iraqi Journal of Science*, vol. 62, No. 1, pp. 1-15, 2021.
- [17] K. Buldurun and M. Özdemir, "Ruthenium (II) complexes with pyridine-based Schiff base ligands: Synthesis, structural characterization and catalytic hydrogenation of ketones," *Journal of Molecular Structure*, vol. 1202, p. 127266, 2020.
- [18] Y. K. Abdel-Monem, S. A. Abouel-Enein, and M. Safa, "Synthesis, characterization and molecular modeling of some transition metal complexes of Schiff base derived from 5-aminouracil and 2-benzoyl pyridine," *Journal of Molecular Structure*, vol. 1152, pp. 115-127, 2018.
- [19] T.-J. Khoo, M. K. bin Break, K. Crouse, M. I. M. Tahir, A. M. Ali, A. Cowley, et al., "Synthesis, characterization and biological activity of two Schiff base ligands and their nickel (II), copper (II), zinc (II) and cadmium (II) complexes derived from S-4-picolyl dithiocarbamate and X-ray crystal structure of cadmium (II) complex derived from pyridine-2-carboxaldehyde," *Inorganica Chimica Acta*, vol. 413, pp. 68-76, 2014.
- [20] M. Hong, H. Geng, M. Niu, F. Wang, D. Li, J. Liu, et al., "Organotin (IV) complexes derived from Schiff base N'-[(1E)-(2-hydroxy-3-methoxyphenyl) methylidene] pyridine-4-carbohydrazone: Synthesis, in vitro cytotoxicities and DNA/BSA interaction," *European journal of medicinal chemistry*, vol. 86, pp. 550-561, 2014.
- [21] X. Liu, C. Manzur, N. Novoa, S. Celedón, D. Carrillo, and J.-R. Hamon, "Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis," *Coordination Chemistry Reviews*, vol. 357, pp. 144-172, 2018.
- [22] J. Zhang, L. Xu, and W.-Y. Wong, "Energy materials based on metal Schiff base complexes," *Coordination Chemistry Reviews*, vol. 355, pp. 180-198, 2018.
- [23] D. Ali, N. Khaireldin, M. El-Hashash, M. Elsaidi, A. A. El-Sayed, N. A. Abdelwahed, et al., "Synthesis, characterization and in-vitro antimicrobial evaluation of thermally and photostable Schiff base-modified PVC/nanocomposites," *Egyptian Journal of Chemistry*, vol. 63, pp. 4833-4849, 2020.