Synthesis, Characterization and Study of Amide Ligand Type N₂S₂ and Metal Complexes with Di Valance Manganese, Zinc and tri Valance Iron

Shatha Abd-Alameer Jawad¹, Hussein Ali Ahmed²

¹Department of Chemistry, College of Education and Pure Science, UniversityofKerbala, Karbala, Iraq. ²Department of Chemistry, College of Education and Pure Science, University of Kerbala, Karbala, Iraq.

ABSTRACT

The amideligand type N2S2 have been prepared through one step. Included the reaction between one equivalent of ethylene di amine and one equivalent of mercapto acetic acid compound. the Mn^{+2} , Zn^{+2} , Fe⁺³from there action of the ligand Complexes were prepared with metalions (1:1) ratio, the prepared compounds were characterized by (FT-IR, UV-Vis, ¹HNMR) for the ligand and complexes, (C.H.N)-spectoscopies, as well as the molar conductivity and magnetic success ptibility for prepared complexes. These measurements shows all the complexes have octahedral shape. and make biological study with two types of bacteria (grampositive and gramnegative).

KEYWORDS

Mercepto Acetic Acid, Ethylene Di Amine, Spectra Measurements, Biological Study.

Introduction

complexcompoundschemistry havebig importancein coordinationchemistry. it knownas coordinationcomplexes or complexescompounds, which have central metal atom or ion surrounded by number of molecules or ions could ligands which linked by coordinationwithcentral atom.[1]Thesecompoundshavebig role in menyfildes like industry, agriculture, medicine and engineering [2], N₂S₂ compounds is basicimportance among organic compounds, some of them have biological role as antitumor [3], anti faver, anti fugnal, anti bacterial, anti HIV and as β - lactamase inzyem inhibitors in biological reactions [4-5]. Studys mention that compounds have nitrogen and sulphate as donating atoms used as catalystfor several chemical reactions [6] and used in another applications as photocraphicmaterelase, reagents [7-8], mimics for meny biological systems and used these ligands in Radio pharmaceulrical [9]. In anotherhandamidesare organic compounds containe active group could amideNH₂-C=Osynthysidefromcarbonylgroup-C=Olinkwith amine -NH₂.amides have two types, aliphatic and aromatic and divided to (primary, secondary, tertiary), aromatic amides less active than aliphatic one because of resonance between pair of electrons on nitrogen atom and π - electrons on carbonyl group. Most amides are solid but the simplest one formamide is liquid and have high fusion degrees. these compounds synthesizedby manyprosegers as react alcohol with amines, Easters with amines, but in this studywe react the carboxyl acid with amine with loss aqua molecule [10-13].

Material and Equipment

All chemicals used from Merck andhave enoughpurification. Meltingpointweremeasuredby (electro thermal) melting pointapparatusFT-IR spectrameasuredwith Shimadzu FT-IR-4800Sinfraredspectrophotometer by using KBrdisk,¹H-NMR spectra by used Broker-400 MHz –Germany with DMSO-d⁶solvent. UV-Visible spectrarecorded by UV-Visiblespectrophotometer-1800 Shimadzu, and Digital Conductivity meter–WT-720–in lab(Germany) was used to measure the electrical conductivity.

Synthesis of Ligand

Add $(1.6 \times 10^{-2} \text{ mol}, 1.11 \text{ ml})$ from ethylene di amine to $(3.2 \times 10^{-2} \text{ mol}, 2.2 \text{ ml})$ mercapto acetic acid in ice bath $(0-5)^{\circ}$ C with stirring, a gelatin compound will synthesis, then add30 mlofhotmethanol(30° C), we noticewhiteparticipate, filter and wash twice with coldethanolandether [14], after dry give 1.586 gm, 46.4%, MP: (101-103) °C, formula : $C_6H_{12}N_2S_2O_2$, M.wt :208.29 gm/ mol, C:34.60, H:5.81, N:13.45, found C:34.51, H:5.61, N:13.36.



Fig. 1. Synthesis of ligand

Synthesis of LFeComplex

Add $(0.75 \times 10^{-3}, 0.25 \text{ gm})$ from FeCl₃.6H₂O dissolve in 15ml ofD.W to $(1 \times 10^{-3} \text{ mol}, 0.18 \text{ gm})$ from ligand dissolve in 15ml ofethanol with reflux to $(60-70)^{\circ}$ Cwithstirring, for two hours, we noticeblackparticipate, filter and washtwicewithcoldethanolandether, after dry give 0.31 gm,77.5 %, MP: (299-300) °C, formula : $C_6H_{10}N_2S_2O_2Fe(H_2O)_2Cl,M.wt$:351.62 gm/mol, C:20.50,H:4.59, N:7.97, found C:20.44,H:4.13,N:8.03

Synthesis of LMnComplex

Add $(0.76 \times 10^{-3} \text{ mol}, 0.25 \text{ gm})$ from MnCl₂.2H₂O dissolve in 15ml ofD.W to $(1 \times 10^{-3} \text{ mol}, 0.18 \text{ gm})$ from ligand dissolve in 15ml ofethanol with reflux to $(60-70)^{\circ}$ Candstirring, for two hours, we noticeoff -whiteparticipate, filter and wash twice with coldethanolandether, after dry give 0.34 gm,85 %,MP:dec. (294) °C, formula : $C_6H_{10}N_2S_2O_2Mn(H_2O)_2$,M.wt:330.12 gm/mol: C: 21.70,H:3.04, N:8.44, found C:21.60,H:3.12,N:8.51.

Synthesis of LZnComplex

Add $(0.73 \times 10^{-3} \text{ mol}, 0.25 \text{ gm})$ from ZnCl₂dissolve in 15ml of D.W to $(1 \times 10^{-3} \text{ mol}, 0.18 \text{ gm})$ from ligand with reflux to $(60-70)^{\circ}$ Cand stirring, for two hours, we noticewhiteparticipate, filter and wash twice with coldethanolandether, after dry give 0.34 gm,83 %, MP: (>300) °C, formula : C₆H₁₀N₂S₂O₂Zn(H₂O)₂, M.wt : 342.56 gm/mol, C: 21.04, H:2.94, N:8.18, found C: 21.13, H: 2.83, N: 8.28.



Fig. 2. Synthesis of complexes

FT-IR Spectra

The FT-IR spectra (KBr disk) for ligand H₂L figure (3) show a stretchingvibrationbands thatbelong to v (N-H) in 3362.04cm⁻¹, aliphaticv (-CH₂) in 2914.54cm⁻¹, weak v(S-H) bandin 2760.23 cm⁻¹[15]andstrongbandin1587.47cm⁻¹ belongto amide`scarbonylgroup. while theFT-IR spectrafor complexes figures(4), (5), (6) show disappearv(S-H) anddifferentshift for v (N-H) between (3309-3385) cm⁻¹, v (-CH₂) between (2924-2937) cm⁻¹ and v(-C=O) between(1645-1510)cm⁻¹, in other hand, new bands will appear like v(O-H) for water between(4438- 4470) cm⁻¹. plus v(M-N), v(M-S) between (412-434) cm⁻¹ and (502-553) cm⁻¹ respectivelythatprovecoordination.[16-17] as show in table (1).



Figure 3.IR spectra for liqand



Figure 4.IR spectra for MnL complex



Figure 5.IR spectra for FeL complex



Figure 6.IR spectra for ZnL complex

Compound	v (O-H)	v (N-H)	v(-CH ₂)	υ (S-H)	v(-C=O)	υ (M-S)	v(M-N)
	Water		alfatic				
H_2L		3362 w	2914w	2760 w	1587 s		
MnL	3440 b	3309 w	2924w		1510 s	501w	412 m
FeL	3470 b	3325m	2937w		1645 s	515-553m	432-470 m
ZnL	3438 b	3385 s	2935w		1506 s	507 w	434-468m

Table 1.IR spectra for ligand and it complexes

b = broad, w = weak, m = middle, s = strong

Ultraviolet- Visible

Theelectronicspectraofligandfigure (7) show wideband in ($\lambda = 234-275$)nm belong to $\pi - \pi^*$ and $-\pi^*$,[18-19] when we comparedit with UVspectrumofcomplexes havenoticed the differences, electronic spectraofMn(II) complex figure (8) show three bands at ($\lambda = 300$) nm attributed to charge transition (C.T.) and ($\lambda = 472$)nm, ($\lambda = 577$)nm due to the d-d transitions type ${}^{6}A_{1}g - {}^{4}A_{1}g$, ${}^{6}A_{1}g - {}^{4}Eg$, Fe (III)figure (9)show two bands at ($\lambda = 310$) nm belong to C.T., ($\lambda = 363$) nm due to d-d transition type ${}^{6}A_{1}g - {}^{4}A_{1}g$, while ZnL complex figure (10)show one band at($\lambda = 308$) nm belong to (C.T.), no d-d transition at visible region because Zn(II)has d¹⁰.[20]



¹H-NMR Spectrafor Ligand and Complexes

The ¹H-NMR spectrum in DMSO – d^{10} ($\delta = 2.43-2.57$ ppm) of the ligand Fig (11) displays the chemical shift at ($\delta = 8.1$ ppm, 2H) assigned to protons (N- H), the signals at ($\delta = 4.40$ ppm, 2H) for tutomersum amide bond(

), and ($\delta = 3.40$ ppm, 4H) belong to protons (-CH₂) for ethylene di amine and($\delta = 2.88$ ppm, 4H) for protons (-CH₂) next to (-SH) groupswhichhave($\delta = 1.24$ ppm, 2H) shifting.[21], while the ¹H-NMR spectra in DMSO – d¹⁰ ($\delta = 2.45$ ppm) of the Complexes Figs (12),(13) and (14) show disappear shifting of (-SH) groups because of coordination.[22] and appear chemical shifts at ($\delta = 8.1$ ppm, 2H, $\delta = 8.6$ ppm, 2H, $\delta = 8.5$ ppm, 2H) assigned to protons (N-H) for Mn(II), Fe(III), Zn(II) complexes respectively. And signals for protons (-CH₂) to ethylene di amine at ($\delta = 3.34$ -3.39 ppm, 4H, $\delta = 3.34$ -3.39 ppm, 4H, $\delta = 3.32$ -3.37 ppm, 4H) respectively.finally,displays the chemical shifts at ($\delta = 3.29$ ppm, 4H, $\delta = 3.29$ ppm, 4H, $\delta = 2.38$ ppm, 4H) respectively for protons (-CH₂) next to(S) atoms. and ($\delta = 2.51$ ppm, 4H, $\delta = 2.51$ ppm, 4H, $\delta = 2.38$ ppm, 4H) respectively for (H₂O) protons.



Figure 11.¹H-NMRSpectrafor H₂L Ligand



Figure 12.¹H-NMRSpectrafor MnL complex

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Figure 13.¹H-NMRSpectrafor FeL complex



Figure 14.¹H-NMRSpectrafor ZnL complex

Magnetic Susceptibility and Molar Conductivity

The magnetic properties of the prepared complexes were measured by Faradi methodshowsthe complexes Mn (II) and Fe (III) are paramagnetic with (B.M.) due to existence offive unpaired electrons and dia magnetic ofZn(II) complex[23], and the molar conductivity of the complexes was recorded in DMSO solvent [24] appears the complexes Mn(II) and Zn(II) were non- electrolyte and Fe(III) was electrolyte with 1:1 ratio, supported with octahedral geometry for Mn (II), Fe (III) and Zn (II) complexes. as show in table (2).

compound	Magnetic susceptibility(B.M.)	molar conductivity	hypredization	Proposed structure
MnL	5.81	10.3	$Sp^{3}d^{2}$	Octahedral
FeL	5.83	37.2	$Sp^{3}d^{2}$	Octahedral
ZnL	diamagnatic	5.1	Sp ³ d ²	Octahedral

Table 2. Magnetic susceptibility and molar conductivity forcomplexes

The Antibacterial Activity

Thebacterialstrain Escherichia coli and Staphylococcus aureus were used in this work and then cultured on muller-

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hinton medium and incubated at 37 °C for 24 h the standardized antimicrobial disc, [25] were prepared from (L, MnL, FeLand ZnL) by using sternal filter paper discsaturated with solution for each compoundsFor Staphylococcus aureus the highest inhibitoryeffect was observed n compoundZnL whichshowed low effect from bacteria and followedtheinhibitory effect is low from MnL to FeL andthelowesteffect can sow it in compoundLshowFigure (15). For E. coli the highest inhibitory effectwas observed in compound ZnL followed by FeLand the lowest antibacterialactivity was observed with compound MnL and then was no activity with L compound show Figure (16).



Figure 15. For Staphylococcus zone



	Figure	e 16. For <i>E. coli</i> zon	le						
Table 3.Zone inhibition (Key of symbols: zone inhibition= mm)									
	Compound	Staphylococcus	E. coli						
	$H_{2}L(1)$	10	_						
	MnL(2)	12	9						

15

21

19

21

FeL (3)

ZnL(4)

Conclusion

The molar conductivity and magnetic, as well as the biological activity the success stability. Suggested octahedralgeometry around themanganeseand iron and zincions.

References

- Shriver, D.F., Atkins, P.W., Oveton, T.L., Rourke, J.P., Weller, M.T., Salmon, T.F., Weber J.H., & [1] Armstrong, F.A. (2009). Inorganic chemistry. 6th Ed. New York.
- [2] Dave, V.G., & Vyas, P.J. (2010). Synthesis, structural elucidation and antimicrobial activities of some complexes of Mg(II) having N2S2 potential donors in 18-24 membered macrocyclic rings. International Journal of Chemistry and Applications, 2(2), 88-102.
- [3] Sathisha, M.P., Shetti, U.N., Revankar, V.K., & Pai, K.S.R. (2008). Synthesis and antitumor studies on novel Co (II), Ni (II) and Cu (II) metal complexes of bis (3-acetylcoumarin) thiocarbohydrazone. European

http://annalsofrscb.ro

journal of medicinal chemistry, 43(11), 2338-2346.

- [4] Oliva, C.G., Goya, P., Alkorta, I., Elguero, J., Cuberes, R., &Dordal, A. (2010). N-substitutes-1,2,3-trizole, synthesis, characterization and evaluation ascannabinoidLigands. *ARKIVOC*, 127-147.
- [5] Mohammad, A.A., Aminul, A.M., Ray, J.B., &Karen, A. (2006). The preparatio, characterization and Biological activity of palladium (II) and platinum(II) complexes of tridentate NNS ligand drived from Smethyl and S-benzyldithiocarbazate and the X-crystal structure of the[Pd (mpasme)Cl] complexe. *Transition Metal Chemistry*, 31,79-87.
- [6] Kennedy, A.R., Okoth, M.O., & Walsh, D. (2011). Cantena-poly [(nitrito k 2 O,O') Silver (1)]-μ-1,2 bis[1- (pyridine 4-yl) ethylidene] hydrazine –k2 N:N']. *Metal-organic compounds*, 67(8), 1138.
- [7] Kumar, S., Dhar, D.N., &Saxena, P.N. (2009). ApplicationsofmetalComplexesofSciff-bases– A Review. *Journal of Scientific and Industrial Research*, 68, 181-187.
- [8] Reddy, P.R., & Reddy, A.M. (2002). Synthesis and characterization of Mixed Ligandcomplexes of Cu(II), Ni(II) and Co(II) with cytidine & amino acids. *Indian Journal of Chemistry*, *41*, 2083-2087.
- [9] Dua, R., Shrivastava, S., Sonwane, S.K., & Srivastava, S.K. (2011). Pharmacological significanceof synthetic Hetro cycles Scaffold. *Journal of Advanced biological Research*, 5(3),120-144.
- [10] Gunanathan, C., Ben-David, Y., & Milstein, D. (2007). Direct synthesis of amides from alcohols and amines with liberation of H2. *Science*, 317(5839), 790-792.
- [11] David, K. (2011). Organic chemistry. John wiley& Sons, 1003.
- [12] Kim, B.B., Lee, H.G., Kang, S.B., & Yoon, Y.J. (2012). Effect of substrate Temperature onResidral stress ZnO Thin films prepred by Ion bea Deposition. *Synthesis*,8(1), 27-32.
- [13] Boonen, J., Bronselaer, A., Nielandt, J., Veryser, L., De Tre, G., & De Spiegeleer, B. (2012). Alkamid database: Chemistry, occurrence and functionality of plant N-alkylamides. *Journal of Ethnopharmacology*, 142(3), 563-590.
- [14] Jawad, S.H.A. (2014). Synthesis new macrocyclic ligands type N₂S₂ and theirmetalcomplexes and studying thermodynamic properties of complexes. M.Sc.thesis, Kerbala University.
- [15] Zadeh, A.S., Mansoori, G.A., Hasemian, A.R., Eshghi, H., Sszgarnia, A., &Montazerabadi, A.R. (2010). Dynemic Bio chemistry. *Process Biotechnology and Molecular Biology*, 4(1),6-12.
- [16] Dawood, A.H., Kareem, E.T., &Madlool, A.M. (2012). Binuclear Divalent Complexes of Cobalt, Nickel And Copper with N₂S Ligand Derived from 1,3,4-Thiadiazole 2,5-dithiolate Dipotassium Synthesized via Click Chemistry. *International Journal of Chemical*, 4(6), 64-74.
- [17] Nakamoto, K. (1997). *Infrared and Raman spectra of Inorganic Coordination*.5thEd.Part B,Joh N Wiley & Sons, New York.
- [18] Abass, S.K., Al-Hilfi, J.A., Abbas, S.K., & Ahmed, L.M. (2020). Preparation, characterization and study the photodecolorization of mixed-ligand binuclear Co (II) complex of Schiff base by ZnO. *Indonesian Journal* of Chemistry, 20(2), 404-412.
- [19] Sharma, R.K. (2007). Text Book of Coordination Chemistry. Discovery PublishingHouse.
- [20] Gökce, H., &Bahçeli, S. (2013). Analysis of molecular structure, spectroscopic properties (FT-IR, micro-Raman and UV-vis) and quantum chemical calculations of free and ligand 2-thiopheneglyoxylic acid in metal halides (Cd, Co, Cu, Ni and Zn). Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 116, 242-250.
- [21] Silverstein, R.M., &Webster, F.X. (1998). *Spectrometric identification of organiccompounds*.6th Ed. John wiley and Sons, New York.
- [22] Mir, J.M., Maurya, R.C., Rajak, D.K., Malik, B.A., Jaget, P.S., & Jain, N. (2017). A novel Schiff base complex of brain fuel (sugar) coordinated with intelligence mineral (Zn): synthesis, conjoint DFT-

http://annalsofrscb.ro

experimental evaluation and super oxide dismutation. Karbala International Journal of Modern Science, 3(3), 153-164.

- [23] Dilek, S. (2017). J. Biol. and chem, 45 (1), 67-80.
- [24] Kettle, S.A. (1975). Coordination Compounds Thomas Nelson and Sons. London, 3(186), 212.
- [25] Alnasrawi, T.H., Jawad, S.A., Salman, H.E., & Al-Haideri, M.R. (2020). Synthesis, Characterization and Study of Schiff Base Ligand Type N2 and Metal Complexes with Di Valence Nickel, Copper and Zinc. *International Journal of Pharmaceutical Research*, *1*, 1246-1251.