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SYNTHESIS AND ANTIMICROBIAL PROPERTIES OF Zn, Co and Cu COMPLEXES

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ABSTRACT

We have been synthesized hydrogenated Schiff base ligand with Co(II), Cu (II) and Zn(II) complexes. Ligand was synthesized hydrogenation of salicylidene-aniline. Ligand and three metal complexes structure have been proved by spectral analyses. The antimicrobial properties of synthesized compounds have been investigated. Synthesized compounds have shown high antifungal and antibacterial properties. Comparing Schiff bases metal complexes with hydrogenated Schiff base complex compounds hydrogenated complex compounds has shown higher antimicrobial properties, because when azomethines group double bond break down and hydrogen atom enter the structure of ligand it changes complex formation ability of ligand and also influence antimicrobial properties. Other positive side of of our ligand and complex compounds, they have shown antimicrobial properties even 0,25% concentration and they are durable 6 month.

1. Introduction

Microelements are metals which plays important role of life process.In living systems they generally include the structure of enzymes, catalyst different chemical reactions.Zinc is microelement which includes all enzymes structure and plays lifely role in human body [1-5]. Zinc also controls action of immune systems and cell metabolism

Copper after iron and zinc form importance stands in the third stage and protect cell membrane damages [8]. Cobalt includes the structure of B_{12} vitamin and several enzymes. All three microelements in our body form different complex compounds, because they have free d orbital [9].

Schiff Bases are condensation of primary amines with carbonyl compounds and they were first reported by Schiff in 1864 [10-12]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group [16]. Schiff bases are generally excellent chelating agents, especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ions verstality of Schiff base ligands and biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable [17-22]. Nowadays, the research field dealing with Schiff base coordination chemistry has expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry, catalysis and material science, separation

and encapsulation processes, and formation of compounds with unusual properties and structures has been recognized and reviewed [23-28].

Schiff Bases are compounds which form many metal complexes [29]. These compounds have shown large application. Antimicrobial, anticancer, antiallergic antinflammatory properties of compounds give to scientists continue their research in this field [30-34].

After synthesis and successful antitumor investigation of iron (III) N, N^1 bis-(salicyclidene)-1,2(phenylidenediamine (SAP) scientist decided to continue next triad elements Co(II) and Ni(II) SAP complexes. Nowadays many Schiff bases derivatives have been synthesizing. In this work we are going to show synthesis and hydrogenation of Schiff bases ligand and synthesis of metal complexes [35].

2. Experimental part

Synthesis of Schiff base ligand

The ligand was synthesized by the condensation of o-salicyclic aldehyde and aniline in 1:1 molar ratio using absolute alcohol as the reaction medium. The mixture was refluxed on water bath for 1 and a half an hour and then allowed to stand overnight at room temperature. The product was crystallized from the same solvent.

IR spectra (◎, sm-1): 1678 (C=N), 1610 (C=C), 1470, 1180 (C-N (CH3)2. NMR spectra (◎, ppm): 8.146 (C=N), 3.641-3.028 (CH3)2N, 2.050 (4H), 1.205-1.131 (CH2).

The IR spectra of the complexes C=N zone is observed at 1650 sm-1. In comparison with its position in the spectrum of the ligand (1678 sm-1) it is shifted to low-frequency zone. Such a change proves presence of coordination of metal with N atom C=N bond (635-620 sm-1, M=N). On the base of above-mentioned we can conclude that complexes should have such a structure: M(L)2X2, where X-anion. The following is the NMR spectrum.

Synthesis of hydrogenated Schiff Base

Schiff base ligand were added in sodium-borhydride in water solution molar ratio 1:4, solution were filtered out. White crystals separated from solution.

Synthesis of metal complexes

They were prepared by reacting ethanolic solution of metal acetate (Co,Cu, and Zn) in 1:2 molar ratio. The settled down solid coloured complexes were filtered, washed with ethanol, dried in oven.

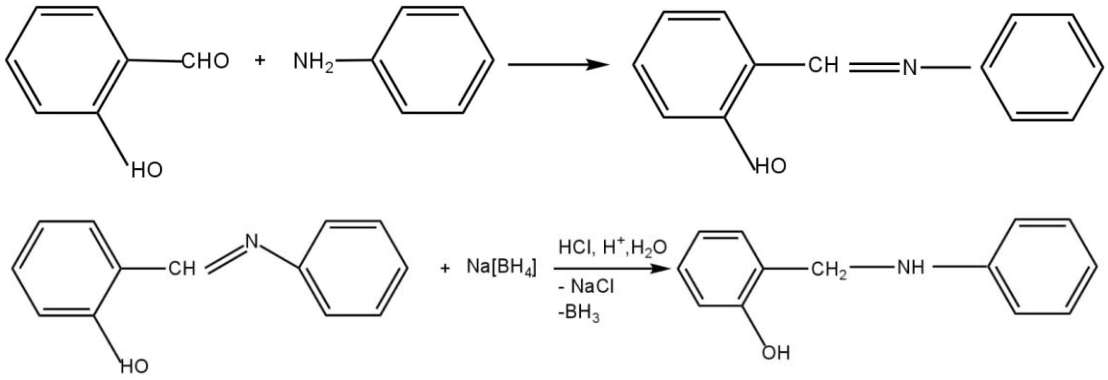
Antimicrobial properties

In literature, it is maintained that ligands and their metal complexes are considerably active against Baccilus megaterium and Candide tropicals, but that the effect of metal complexes is stronger than that of lgands.It was also reported that ligands and their metal complexes are active against Fuherica Coli, Barilum sp and Pseudomanan acurtuginan, while that Cu are more effective.Morever, Cu complexes of ligands were reported to be inhibiting active agents against bacteria and fungus.It was also determined that ligands could produce an inhibiting effect on the development of Aspergillus niger, Penisilum rubium and Augergillus ferreus.Furthermore, it was also established that ligands had an actibacterial effect at 100ppm concentration and they had and antifungisid effect [6].

Antimcrobial activity of the compounds of tested against using Pseudomonas Aeruginosa, Mycobacterium lacticolium, Aspergillus niger, Cladasporium resinale, Penicillium Chrosegenum, Chastomium gloloodium Trichoderma viride. The sterilized (autoclaved 121^0 C for 15 min) medium ($40\text{-}50^0$) was poured into the Petri dishes to give a depth of 3-4 mm and allowed to solidfy. The suspension of the microorganism the steaked on plates.The paper discs impregnated with the test compounds was placed on the solidified medium.The plates were pre-incubated forth at room temperature and incubated at 37^0 C for 24 hour[7].

3. Result and discussion.

We have described the synthesis and antimicrobial properties of Co, Cu and Zn. The structure of ligands and metal complexes were proved IR spectra. First ligand were synthesized by de condensation salicylic aldehyde and aniline. Second ligand were synthesized saliclidene-aniline with sodiumborhydride reaction.



2L+M=L_2M M-Cu(II), Co(II), Zn(II)

The synthesized compounds structure were proved by IR spectra fig.1,2 In the first spectra we can easly observe azomethine fragment in first spectra 1678 sm^{-1}, but when Schiff base hydrogenated the bond between -CH=N- break down and new fragment CH_2-NH formed in 3448 sm^{-1}

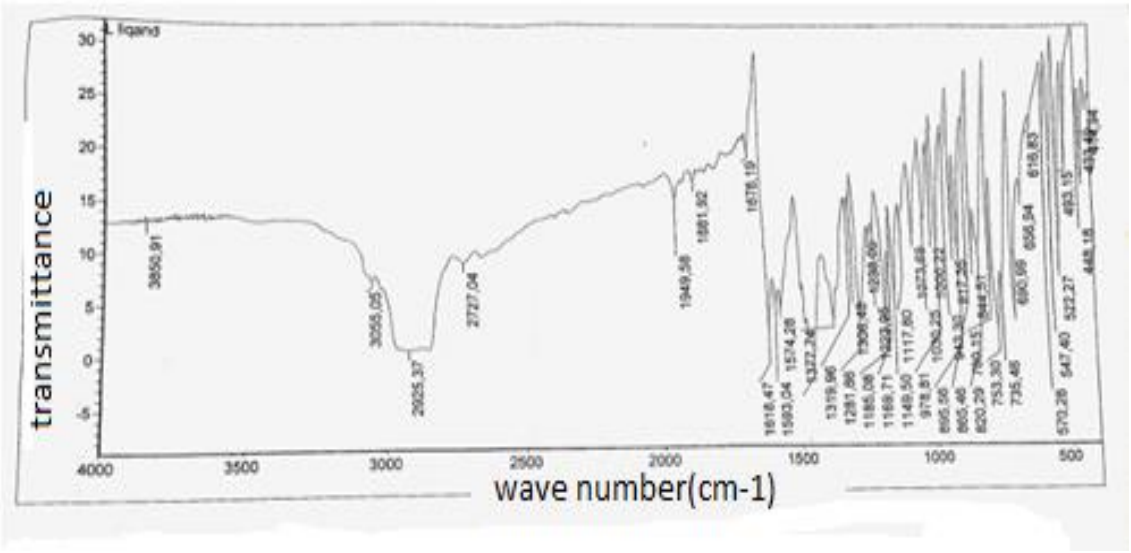


Fig 1. L ligand IR spectra

Fig 2. L₁ligand IR spectra

We have also been synthesized three metal complex of hydrogenated Schiff base. We can also describe structure of three complex, here observable all spectra of complexes fig 3,4..

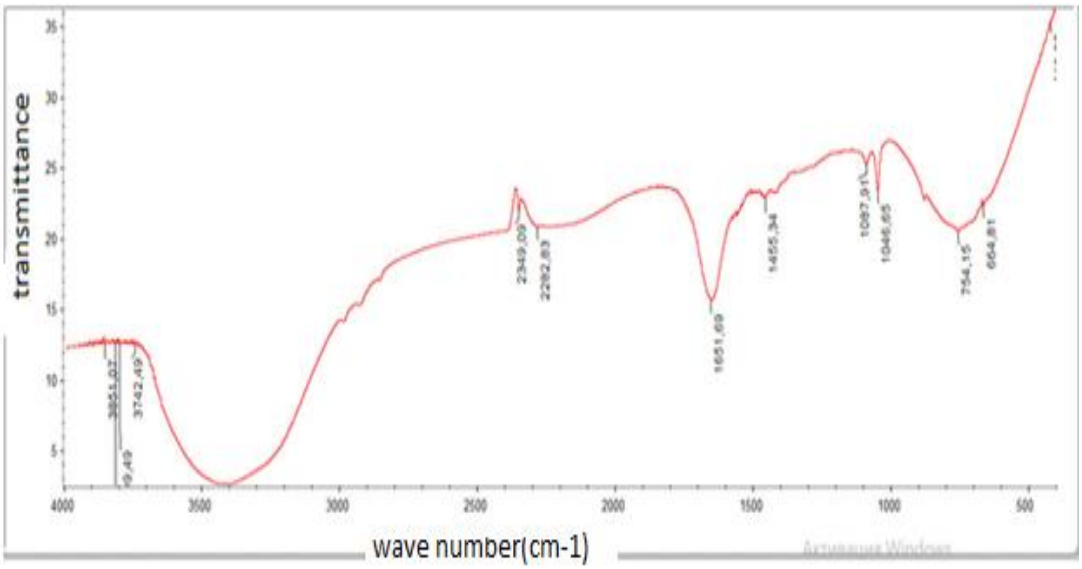


Fig 3. Co complex IR spectra

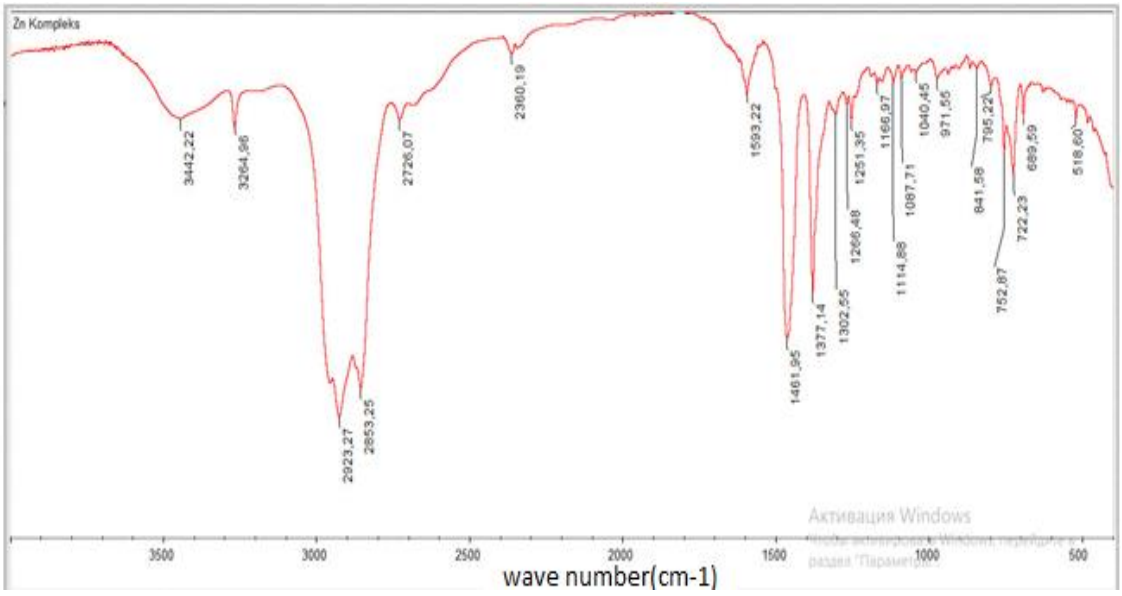


Fig 4. Zn complex IR spectra

If we compare IR Specta of ligands and complexes. By the formation of hydrogenated ligand the azomethine group break down.-CH_2-NH- group appeared higher than 3000 sm^{-1}. In metal complexes appeared 4-5 sm^{-1} differences comparing with ligand.

We firstly have checked by the express method antimicrobial properties of synthesized ligands. When we observed the antimicrobial feature, we checked the antimicrobial properties of the ligand and metal complexes table 1.

From the table, we observed high antimicrobial properties. When we hydrogenated the ligand, we evaluated the antimicrobial properties.

Table 1. Antimicrobial propertiesof synthesized compounds

№	Ligand and complexes	Concentration%	Bactericidial	Fungicidial
1	Ligand	1,0 0,5 0,25	2,8-2,8 2,4-2,4 2,3-2,3	2,80-2,8 2,4-2,4 2,3-2,3
2	hydrogenated ligand	1,0 0,5 0,25	2,9-2,9 2,5-2,5 2,4-2,3	2,9-2,9 2,5-2,6 2,4-2,4
3	Complex of Co	1,0 0,5 0,25	3,0-3,0 2,6-2,6 2,4-2,4	3,3-3,3 2,8-2,8 2,6-2,6
4	Complex of Cu	1,0 0,5 0,25	3,0-3,0 2,5-2,6 2,4-2,4	3,0-3,0 2,5-2,5 2,2-2,2
5	Complex of Zn	1,0 0,5 0,25	3,3-3,4 2.8-2.8 2.7-2.7	3.3-3.3 2,8-2,8 2,7-2,7

If we give attention of above table we have witness high antibacterial and antifungal properties of metal complexes. Comparing with ligands metal complexes have shown high killing effect of microbe. Zinc complexes has shown highest both bacterial and fungi, Co has shown moderate bacteria and highest fungi, copper has shown moderate antimicrobial properties both anti fungi and anti bacterial properties.

Comparing Schiff bases metal complexes with hydrogenated Schiff base complex compounds hydrogenated complex compounds has shown higher antimicrobial properties, because when azomethine group double bond break down and hydrogen atom enter the structure of ligand it changes complex formation ability of ligand and also influence antimicrobial properties. Other positive side of of our ligand and complex compounds, they have shown antimicrobial properties even 0,25% concentration and they are durable 6 month.

4. Conclusion

We have been synthesized hydrogenated Schiff bases metal complexes. We have investigated antimicrobial properties of ligand and Co, Cu, Zn complexes. Comparing with ligand complexes have shown high antimicrobial properties.Zn complex has shown highest antimicrobial properties. Co has shown moderate bacteria and highest fungi, copper has shown moderate antimicrobial properties both anti fungi and anti bacterial properties.

REFERENCES

1. Akriti Goel, Navidha Aggarwal orcid.pngand Sandeep Jain ,2022, Novel Methodology for Synthesis and Computational Analysis of Zinc Complexes of Isatin Derivatives and Screening their Biological Activity, 20, p.10

2. Alessia Catalano, Maria Stefania Sinicropi , Domenico Iacopetta , Jessica Ceramell , Annaluisa Mariconda, Camillo Rosano , Elisabetta Scali, Carmela Saturnino and Pasquale Longo, 2021, A Review on the Advancements in the Field of Metal Complexes with Schiff Bases as Antiproliferative Agents:Aplied sciences:,11: p.18

3. Bin Li, Kevin Huse, Christoph Wölper and Stephan Schulz, 2021 Synthesis and reactivity of heteroleptic zinc(I) complexes toward heteroallenes Royal Society of Chemistry, , 57, p.13692-13695

4. E. B. Dianova, I. G. Pervova, E. A. Dvoskin, and P. A. Slepukhin, 2018, Synthesis and Structure of Zinc(II) Complexes with 2,2'-Bipyridine Russian Journal of General Chemistry, 88, p.843-845.

5. Emad Yousif, Ahmed Majeed , Khulood Al-Sammarrae, Nadia Salih, Jumat Salimon, Bashar Abdullah, 2013 : Metal complexes of Schiff base: Preparation, characterization and antibacterial activity: Arabian Journal of Chemistry, p.6

6. Fadiaa J. Ahmed, Baraa AbdAlqader, Raoah A. Haddad, Rana Ramzi Abed, Mohanad Yakdhan Saleh,2022, Preparation and diagnosis of Zn(II), Cd(II) and Hg(II) complexes with Schiff base ligand derived from trimethoprim Egyptian Journal of Chemistry, 65 , p.359-366 .

7. Gloria V. Seguel, Bernabe L. Rivas, Cesar Paredes,2010, Synthesis and characterization of Zn(2) complex with the acetate and Orotic acid MK ligands, Journal of the Chilean Chemical Society, 55, p.5-7.

8. Han Zhang, Yanhui Zhang,:2015, Zinc(II) and Co(II) Complexes based on Bis(N-allylbenzimidazol-2-ylmethyl) Aniline: Synthesis, Crystal Structures and Antioxidative Activity:Journal of Chemical Research 39(2), p.76-81

9. Hee Sun Park, Ruijing Sun, Eun Joo Lee, Jungho Kim, and Nam Hwi Hur:2022,Triazole-Bridged Zinc Dinuclear Complexes: Mechanochemical Synthesis, Crystal Structure, and Biological Activity; Acs Omega, 7, p. 40860-40868

10. Hijazi Abu Ali, Suhad N. Omar, Mohanad D. Darawsheh & Hadeel Fares: 2016 Synthesis, characterization and antimicrobial activity of zinc(II) ibuprofen complexes with nitrogen-based ligands:Journal of Coordination Chemistry, 69, p.1110-1122

11. I. Waziri, O.O Wahab, G.A.Mala, S.O.Oselusi, S.A.Egieyeh, H.Nasir, 2023, Zinc(2) complex of (Z)-4-(4-Nitrophenyl))Amino)Pent-3-en-2-one, a potential antimicrobial agent; synthesis, characterization, Antimicrobial screening, DFT Calculation and Docking study Chemical Society of Ethiopia and the authors, 37, p.633-651

12. Jean Jacques Anguile,Odette Nana Ngnabeuye,Ndosiri Ndoye Bridget, Tanyi Rogers Fomuta,Alvine Loris Djoumbissie, Alain Charly Kuate Tagne, Jean Ngoune.2018,Synthesis, Characterization and DFT Studies of Two Zinc(II) Complexes Based on 2-Isopropylimidazole Journal of Inorganic Chemistry,p.8

13. Kufre Mabel Udoisang Camillus Uchenna Okonkwo: 2022, Synthesis and Characterisation of Zinc (II) and Nickel (II) Complexes with 3-Hydroxy-4-(2-Hydroxy Phenyl) Amino Cyclobut-3-Ene-1,2-Dione:Research Article,3, p.8

14. K. ÜC. Prousis,G. Athanasellis, V. Stefanou,D. Matiadis,E. Kokalari,O. Igglessi-Markopoulou,V. McKee,and J. Markopoulos Synthesis and Crystal Structure Characterization of Zinc (II) Tetronic Acid Complexes Hindawi Publishing Corporation Bioinorganic Chemistry and Applications, 2010, p.7,

15. Liji John,R. Selwin Joseyphus,I. Hubert Joe: 2020, Biomedical application studies of Schiff base metal complexes containing pyridine moiety: molecular docking and a DFT approach: Research Article, p.14

16. Maldhurew AK and Aswar AS:, 2018, Preparation of Zinc Oxide Nanomaterial using Unsymmetrical Schiff Base Complexes:Journal of Chemistry, 7, p.43-47

17. Marianta Strinoiu, Mihai Răducă & Augustin M. Mădălan , 2020, Zinc(II) mononuclear complexes with Schiff base derivatives of 2-aminofluorene. Synthesis, structural characterization, and optical properties Journal of Cordination Chemistry, 73, p. 2786-2800

18. Michał Abendrot ,Lilianna Chęcińska,Joachim Kusz,Katarzyna Lisowska,Katarzyna Zawadzka, Aleksandra Felczak and Urszula Kalinowska-Lis 2022, Zinc(II) Complexes with Amino Acids for Potential Use in Dermatology: Synthesis, Crystal Structures, and Antibacterial Activityv Molecules, 25, p.951

19. M.Jaya Brabha , M. Anitha Malbi , 2023, Synthesis, characterization and biological activity of zinc complexes of ethylenediamine and its derivatives Chemical Physics Impact, p.6

20. Na Yeon Kim, Jeong Min Hwang, Dr. Seong Ho Han,Ga Yeon Lee, Dr. Bo Keun Park, Dr. Taeyong Eom,Prof. Seung Uk Son, Dr. Taek-Mo Chung, 2021,Synthesis of Heteroleptic Zinc Complexes Containing Aminoalkoxide and β-Diketonate Ligands Chemistry Select, 6, p.5880-5884

21. Patrícia Severino, Juliana C. Cardoso Eliana B. Souto , Wanessa Santana, Erika S. Lisboa, Victoria L. S. dos Santos , Erica T. dos Santos Lima, Ricardo L. C. de Albuquerque-Junior, Beatriz C. Naveros, Antonello Santini, and Sona Jain:2022, Cutaneous/Mucocutaneous Leishmaniasis Treatment for Wound Healing: Classical versus New Treatment Approaches: microbiology research p. 836-852.

22. Pedro H. O. Santiago, Meliza A. S. Bessa, Ralciane P. Menezes, Carlos H. G. Martins & Claudia C. Gatto, 2022, Zn(II) complexes with a new isoniazid ligand: synthesis, structural characterization and antimycobacterial activity Journal ofCordination Chemistry,75, p.347-361

23. Pronoy Ghosh, Shishir K. Dey, Mosummath Hosna Ara, Kaykobad Md. Rezaul Karim, A.B.M. Nazmul Islam:2019, A Review on Synthesis and Versatile Applications of Some Selected Schiff Bases with Their Transition Metal Complexes: Egyptian Journal of Chemistry, 62, p.523-547

24.Ramesh S. Yamgar,' Y. Nivid,² Satish Nalawade, Mustapha Mandewale, R.G. Atram, and Sudhir S. Sawant: 2014, Novel Zinc(II) Complexes of Heterocyclic Ligands as Antimicrobial Agents: Synthesis, Characterisation, and Antimicrobial Studies:Publishing Corparation p.10

25. Rinki Brahma and Jubaraj B. Baruah 2020, Self-Assemblies of Zinc Complexes for Aggregation-Induced Emission Luminogen Precursors ACS PUBLİCATİONS, p.3774-3785

26. Saba H. Mahdi, Enas H. Ali, Dhefaf H. Badri and Lekaa K. Abdul Karem:2021 Schiff Bases and Their Metal Complexes Derived from Ortho-phthalaldehyde: A review: Sys Rev Pharm, 12, p.310-313

27. Sarra Soudani, Melek Hajji, Jin Xiao X Mi, Christian Jelsch, Fréderic Lefebvre, Taha Guerfel, Cherif Ben Nasr,2020, Synthesis, structure and theoretical simulation of a zinc(II) coordination complex with 2,3-pyridinedicarboxylate, Journal of Molecular Structure.

28. Skalickova Sylvie, Kopel Pavel, Cihalova Kristyna, Nejdl Lukas, Melros Rodrigo, Miguel Angel, Sladek Zbysek, Kizek Rene, 2015,preparation and characterization of zinc complexes and evaluation of their antimicrobial activity, p.595-599

29. Lan Hu,Jianjun Fang, Xinyi Zhang, 2020, Synthesis, Crystal Structure of Zinc(II)–Cysteamine Complex and Improvement of Cysteamine Stability Russian Journal of Inorganic Chemistry, 65 ,p.1718-1725.

30. Tadewos Damena, Mamaru Bitew Alem, Zeleke, Tegene Desalegn, *Rajalakshmanan Eswaramoorthy, and Taye B. Demissie, 2022 Synthesis, characterization, and biological activities of zinc(II), copper(II) and nickel(II) complexes of an aminoquinoline derivative:Frontiers Chemistry, 10 , doi: 10.3389/fchem.1053532

31.. Tanmoy Basak,a Antonio Frontera b and Shouvik Chattopadhyay, 2021, Synthesis and characterization of a mononuclear zinc(II) Schiff base complex: on the importance of C–H/p interactions Royal Society of Chemistry, p.8

32. Youssefü Aidibi, Magali Allain, Abdelkrim El-Ghayoury, Philippe Leriche and Lionel Sanguinet, 2021, Elaboration of multimodal ligands based on BOX units: toward full zinc release in Zn(II) complexes by external stimulation, p.30

33. Yue Bing,Xing Li,Mei-Qin Zha, və Dong Jie Wane,2011, Crystal Structures and Luminescent Properties of TwoZinc(II) Complexes with 2-Phenylquinoline-4-carboxylates,Synthesis and Reactivity in Inorganic,Metal-Organic, and Nano-Metal Chemistry, 4 , p.798-804

34. Zahid H.Chohan,Asifa Munawar and Claudiu T.Supuran: 2011, Transition metal ion complexes of schiff-bases. synthesis, characterization and antibacterial properties: Metal Based Drugs, 8, p.137-143

35. Zhi-Qiang Liu,Yoke Mooi Ng,Pei Jen Tiong, Ruwaida Asyikin Abu Talip, Nornadia Jasin,Vivien Yi Mian Jong,and Meng Guan Ta ,2022 Five-Coordinate Zinc(II) Complex: Synthesis, Characterization, Molecular Structure, and Antibacterial Activities of Bis-[(E)-2-hydroxy-N◎-{1-(4-methoxyphenyl)ethylidene}benzohydrazido] dimethyl sulfoxidezinc(II) Complex , International Journal of Inorganic Chemistry , p. 8