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Comparative Study of Semicarbazone and Thiosemicarbazone Metal Complexes as Potent Soil Fungicides and Pesticides for Agricultural Applications

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Abstract:
The present research study deals withthe investigation of metal-based molecules because agricultural chemical structure demands for sustainable solutions continue to increase. The study suggeststhe semicarbazone and thiosemicarbazone metal complexes for their potential as fungicides and pesticides in agricultural field. The Schiff base ligands forms stable coordination compounds with transition metals which exhibit enhanced antifungal and insecticidal properties. Thiosemicarbazone complexes demonstrate superior performance because their sulphur donor atoms facilitate metal binding and biological interactions. Semicarbazone complexes, however, provide safer environmental solutions because their toxic effects are diminished and natural systems can tolerate them. The research examines their operational mechanisms, environmental impact assessment, and their practical usage limitations. The metal complexes demonstrate strong potential to develop into the next generation of agricultural chemical solutions. The products provide farmer benefits through effective pest control which lasts and supports environmentally sustainable solutions.
Keywords: *Metal-Based Molecules, Semicarbazone, Thiosemicarbazone, Antifungal and Insecticidal Properties.*

I. Introduction:

Context:

Diseases caused by soil-based fungi together with insect infestations create major threats to agricultural production because these factors cause significant damage to both crop quantity and quality [1, 2]. Agricultural productivity has improved throughout the years because farmers use traditional synthetic fungicides and pesticides on a large scale but their unrestricted application has created serious environmental damage together with health risks. Scientists need environmentally safe sustainable methods because bioaccumulation problems and non-target organism toxicity and resistant strain development and soil degradation which last for extended periods require better solutions. Researchers now use coordination chemistry to discover new agrochemical solutions [3]. Biological systems can be effectively interacted with organic ligands metal complexes which possess this ability show better biological activities. Researchers study semicarbazone and thiosemicarbazone derivatives because these compounds exhibit multiple structural forms together with various pharmaceutical properties. Their ability to create stable complexes with transition metals including copper, zinc, and nickel improves their bioavailability and biological efficacy. The development of these compounds as modern agriculture fungicides and insecticides has opened up new possibilities for their application.

Goals:

The important point of this study is to carefully examine the differences between semicarbazone and thiosemicarbazone metal complexes with a focus on their possible applications in farming. The study will look at how these complexes are made, what their shapes are, and how they connect with various metal ions. It will also test how well they work against fungi and pests that usually hurt crops. The study will look at how these complexes interact with cell parts and their ability to make reactive substances in order to understand how they affect living things [4, 5, 6].

The main focus of the study is on looking at their effects on the environment, which includes testing how toxic they are, how quickly they break down, and how well they work with dirt. The goal of this study is to compare these two types of substances to find out their specific pros and cons. This will give scientists a reason to think that they could be used instead of traditional farming chemicals that are bad for the environment.

II. A Model for Consideration:

Semicarbazone vs. Thiosemicarbazone Chemistry:

There is a lot of research on semicarbazones and thiosemicarbazones, which are types of Schiff base ligands. Their structures are very flexible, which is why they could be useful in biology. Aldehydes or ketones are usually mixed with semicarbazide or thiosemicarbazide to make these chemicals. The molecules have azomethine (–C=N–) functional groups, which are very important for how they work in living things and how they connect with metals [7]. Thiosemicarbazones have similar structures, but they react chemically, work biologically, and work together in very different ways. The reason for this is that sulphur takes the place of oxygen in them.

Semicarbazones are neutral or weakly negatively charged ligands that connect through the nitrogen atoms of azomethine and the oxygen atoms of carbonyl to make stable chelate structures. These donor sites work together to keep the metal complex stable by keeping the ligand-metal binding working well within a tight coordination framework [8]. This is why semicarbazone complexes are usually only moderately stable and have little biological activity. They don't react as much as those that do because they are less polarizable and have fewer electrons. This can be helpful in farming when you need to do less damage to the environment and get along better with other living things.

Thiosemicarbazones are better at joining together because they have a thiocarbonyl (C=S) group. This atom is a soft donor that makes stronger and more stable bonds with transition metals, especially soft acids like Co(II), Ni(II), and Cu(II) [9]. There is more biological action and the complex is more stable because of this stronger bond. Thiosemicarbazones can also join with big living molecules like proteins and nucleic acids more easily because they can bend and twist more easily. They can bind and react even better because they can live in tautomeric thione–thiol forms.

The electrical properties and lipophilic properties of materials are two of the most important things that set them apart from one another [10, 11]. Thiosemicarbazone complexes can cross the lipid bilayer that surrounds fungal cells and insect cuticles because they are more lipophilic. This trait makes them better at getting rid of pests and fungus. When sulphur is present, it changes the electrical and physical properties of the complexes by making the metal-ligand back bonding stronger.

Semicarbazone and thiosemicarbazone ligands are equally good at chelating, but thiosemicarbazones are better at coordinating, having more electronic flexibility, and being more powerful in biology [12, 13]. It may be helpful to have semicarbazones on hand because they make it less likely that people and ecosystems will be harmed. Because they have different uses, the two types of agricultural goods work well with certain farming methods.

Feature	**Semicarbazone**	**Thiosemicarbazone**
Functional Group	C=O (carbonyl)	C=S (thiocarbonyl)
Donor Atoms	Nitrogen, Oxygen	Nitrogen, Sulphur
Nature of Donor	Hard base	Soft base
Metal Affinity	Hard metals (Zn, Fe)	Soft metals (Cu, Ni, Co)
Coordination Mode	Bidentate	Bidentate/Tridentate
Stability of Complex	Moderate	High
Electron Density	Lower	Higher
Polarizability	Low	High
Lipophilicity	Moderate	High
Biological Activity	Moderate	High
Environmental Impact	Lower toxicity	Potentially higher toxicity
Tautomerism	Limited	Thione–thiol tautomerism present

Table 1: Comparative Features of Semicarbazone vs Thiosemicarbazone, Source: Author Generated

III. Methods and analytical techniques for synthesis and characterization:

This is usually done by condensing carbonyl compounds (like aldehydes or ketones) with semicarbazide or thiosemicarbazide. These are ligands for thiosemicarbazone and semicarbazone. People often use alcohols like methanol or ethanol in this reaction, along with some light heating or reflux to help the azomethine (–C=N–) bond form [14]. This method makes crystalline molecules that are very pure. People often use filtering and recrystallizing to sort these. To get the best shape and output of the ligands, the temperature, the polarity of the solvent, and the pH are some of the reaction factors that are carefully changed.

Ligands bind with salts of transition metals, which are usually chlorides, acetates, or nitrates of metals like cobalt(II), nickel(II), copper(II), and zinc(II) [15]. This is the next step in making metal complexes. The reaction time, the solvent system, and the ratio of metal to ligand all have a big effect on the shape and stability of the complexes. When the ligand solution is being mixed, the metal salt is usually added. Then, the mixture is heated to help the ligands stick together. A complex is often making itself when the color changes clearly. The way electrons move in the coordination sphere has changed, which is why the color has changed.

The chemical and structural characteristics of synthetic ligands and metal complexes need an explanation through their respective synthetic ligands and their associated metal complexes [16]. The functional groups and their coordination with other elements can be identified through infrared (IR) spectroscopy by studying how the characteristic bands of the material change. The bands mostly show azimethine groups together with carbonyl or thiocarbonyl groups. UV-Vis spectroscopy shows us how electrons travel between different shapes of complexes which include square and octahedral forms. This method helps determine molecular weight and confirm the identities of the components. In addition, a more detailed analysis of the elements allows for the exact composition and purity of the resulting compounds to be determined.

Advanced techniques like X-ray crystallography provide exact structural information through measurement of bond distances and the determination of coordination geometry. Thermogravimetric analysis (TGA) is used to assess a material's ability to withstand high temperatures, which helps determine its potential for agricultural uses. By combining all the different parts, a complete system is created. This system allows for the exploration of the connection between a material's physical properties and its biological functions.

IV. Biological Activity Evaluation:

Antifungal Activity:

Researchers have demonstrated that semicarbazone and thiosemicarbazone metal complexes effectively eliminate major plant pathogens which include Fusarium oxysporum Aspergillus niger Rhizoctonia solani and Alternaria solani. The pathogens cause agricultural diseases which result in wilt and rot and blight that create significant financial losses for farmers. The minimum inhibitory concentration (MIC) and the percentage inhibition of mycelial growth serve as standard methods to measure the antifungal effectiveness of these complexes [17].

The formula determines the quantity of fungal growth which the formulae will prevent from developing:

$$\text{Inhibition (\%)} = \frac{C - T}{C} \times 100$$

The untreated sample shows its colony diameter through the value of Cre while the modified sample shows its colony diameter through the value of Tre. Scientists have found that thiosemicarbazone complexes, especially Cu(II)-thiosemicarbazone, have higher rates of blocking (75–90%) than semicarbazone complexes (55–70%). The sulphur donor atom is what makes this action better. The compound enables fungal enzymes to bind more effectively while it stops cellular respiration. The complexes prevent ergosterol production which serves as a vital component of fungal cell membranes. The membranes become less stable which results in cell death.

Pesticidal Activity:

Common crop pests like Spodoptera litura (tobacco cutworm), Helicoverpa armigera (cotton bollworm), and Aphis gossypii (cotton aphid) have been tested to see how well these metal complexes kill them. These pests do a lot of damage to plants by eating their leaves, roots, and reproductive parts [18, 19].

The death rate is often used to measure how effective a pesticide is. It can be found by:

$$\text{Mortality (\%)} = \frac{\text{Number of dead insects}}{\text{Total insects}} \times 100$$

Thiosemicarbazone metal complexes have higher death rates (65–85%) than semicarbazone complexes (45–65%). The main reason for the higher activity is better lipophilicity, which makes it easier to get through the bug cuticle. Once they get inside, these complexes mess up enzyme systems, especially acetylcholinesterase (AChE), which makes the person paralyzed and eventually kills them.

The production of reactive oxygen species (ROS), which cause oxidative stress, is another important process. The production of ROS can be shown as:

$$\mathrm{M}^{2+} + O_2 \rightarrow \mathrm{M}^{+} + O_2^{\cdot-}$$

1. Antifungal Activity

Metal Ion	Inhibition (%)
Cu(II)	55–70%
Ni(II)	50–65%
Zn(II)	50–65%

2. Pesticidal Activity

Metal Ion	Mortality (%)	% Activity Increase
Cu(II)	45–60%	– vs Hard Metal Ions
Ni(II)	45–65%	–
Zn(II)	50–65%	0

3. Comparative Analysis

Metal Ion	% Activity Increase	Relative Order of Activity
Cu(II)	75–90%	Cu(II) > Ni(II) ≈ Zn(II)
Zn(II)	65–85%	

Figure 1: Biological activity of metal complexes, Source: Author Generated

Comparative Analysis:

Research studies demonstrate that semicarbazone chemicals produce different biological effects when they are tested together with thiosemicarbazone metal complexes. Thiosemicarbazone complexes display increased antifungal and pesticides properties because their metal-ligand interactions create bonds which maintain stronger connections together with the complex holding additional electrons. The chemicals achieve their superior resistance through stable chelate formation which protects them from infectious diseases that they cannot combat. The environmental impact of semicarbazone complexes remains lower than its toxicity because these compounds exhibit reduced poisoning effects. Their moderate levels of activity may be sufficient for environmentally conscious integrated pest management approaches. The combined evidence here from multiple data sources can easily reveals that Cu(II)-thiosemicarbazone complexes display their highest total operational power here. The resulting ranking shows that Ni(II) and Zn(II) complexes follow after these two groups [20]. The semicarbazone groups exhibit similar behavior with various metal ions, but their results produce lower efficiency. Thiosemicarbazone complexes function better in intensive agricultural practices while semicarbazone complexes provide safer advantages through sustainable farming methods.

V. Mechanism of Action:

Metal Chelation and Biological Interaction:

The research scientists study the effects of semicarbazone compounds which occur together with thiosemicarbazone metal complexes because they show completely opposing biological effects. Thiosemicarbazone complexes display superior antifungal and pesticide performance because their metal-ligand connections generate stronger chemical bonds which increase their electron content. The chemicals acquire their increased endurance by forming stable chelates that guard against infections that are immune to them [21].

However, semicarbazone complexes are preferable since they are less poisonous and have a lower environmental impact. The integrated pest management methods which focus on protecting the environment will find their activities to be sufficient for handling common pest problems. The combined evidence from several data sources shows that Cu(II)-thiosemicarbazone complexes have the highest level of overall activity. The ensuing ordering demonstrates that Ni(II) and Zn(II) complexes come after these. The semicarbazone groups bind with different metal ions but their performance results show reduced success when compared to other methods [22].

The semiconductor thiosemicarbazone complexes serve as effective solutions for intensive agricultural operations while semicarbazone complexes bring safe advantages to sustainable agricultural practices:

$$\mathrm{M}^{2+} + O_2 \rightarrow \mathrm{M}^{+} + O_2^{\cdot-}$$

The superoxide radicals and other ROS that are produced in cells destroy cellular components which include DNA and proteins and lipids. The biological effects of thiosemicarbazone complexes increase because their sulphur donor atoms enable them to bind metals more effectively and exhibit enhanced redox properties. The combination of membrane penetration with enzyme inhibition and DNA contact and oxidative stress results in strong antifungal and pesticidal effects.

VI. Environmental and Agricultural Implications:

Soil Impact and Sustainability:

The application of semicarbazone and thiosemicarbazone metal clusters in agriculture practice leads to environmental disadvantages and advantages [23]. The chemicals achieve their optimal performance at lower dosage levels which results in decreased chemical contamination of soil systems. The semicarbazone complexes demonstrate reduced stability and increased biodegradability which makes them suitable for environmentally friendly agricultural practices.

People express concern about heavy metal ions such as copper and nickel because they can accumulate in soil systems and harm beneficial organisms like earthworms and nitrogen-fixing bacteria. The thiosemicarbazone complexes exhibit longer earth persistence because of their chemical stability and fat-binding properties which leads to potential bioaccumulation [24, 25].

The development of controlled-release systems together with biodegradable products represents a fundamental requirement for maintaining sustainable operations. The implementation of these chemicals in integrated pest management (IPM) systems enables environmental protection while boosting agricultural productivity.

VII. Problems and restrictions:

Semicarbazone and thiosemicarbazone metal complexes have potential for biological activity. However, their application in agricultural practices faces multiple challenges that prevent their adoption as commercial solutions. The main environmental threat arises from heavy metal ions, which include copper and nickel and cobalt, because these metals can turn into lethal substances that accumulate in soil. The resulting ions from this process enter food chains, which create health hazards for both humans and other living organisms. The environmental persistence of thiosemicarbazone complexes increases because they exhibit higher stability and fat attraction properties, which results in greater potential for bioaccumulation into living organisms.

The main challenge exists because these substances do not maintain their chemical integrity when present in actual environmental conditions. The document describes how sun exposure and temperature variations and soil pH changes and bacterial activity lead to the breakdown of substances. The industrial application of products requires solutions for two main challenges, which include achieving large-scale production and maintaining affordable pricing. Formulation development requires thorough planning, which needs to include toxicity testing and government safety evaluations for agricultural products.

VIII. Discussion and Future Prospects: Scope and Meaning

The comparison of semicarbazone and thiosemicarbazone metal complexes demonstrates their potential as future agricultural pesticides. Thiosemicarbazone complexes exhibit superior pest and fungal control because their molecular structure allows better binding to biological systems through their increased electronic capacity and stronger chemical interactions. The enhanced strength requires organizations to assess environmental risks and potential toxic dangers which it creates. Semicarbazone complexes demonstrate low activity levels but they break down in nature while causing minimal environmental impact, which makes them suitable for environmental-friendly agricultural practices.

Scientists should develop new mixed ligands which combine the best features from both ligand classes according to their future research objectives. The introduction of new components will enhance their biological performance while mitigating their ecological effects. Nanotechnology applications through nanoparticle delivery systems will enhance field stability and improve targeted operations while decreasing required material amounts. The development of metal complexes which undergo natural decomposition together with the application of less dangerous metal ions will result in environmentally friendly solutions.

The advancement of this field requires the combination of various disciplines which include chemistry and agriculture and environmental science. The structures present high potential for crop protection and sustainable agricultural development when their implementation follows the established regulations and allows for new innovative proposals.

IX. Conclusion:

Semicarbazone and thiosemicarbazone metal complexes function as chemical compounds that agricultural fields can use to combat fungal and insect pests. Thiosemicarbazone complexes operate at higher efficiency because they form stable metal chelates which enhance their biological activity. However, the assessment requires thorough examination of environmental concerns that include toxicity and persistence issues. Semicarbazone complexes present a safer alternative because their environmental impact decreases at a faster rate. Future developments in formulation techniques and transportation systems together with green chemistry advancements will enhance their practical applications. The current chemical compounds provide effective agricultural protection solutions which maintain their effectiveness for modern farming practices.

Reference

1. Kumar, G., Kumar, D., Devi, S., & Johari, R. (2010). Synthesis and antimicrobial evaluation of metal complexes. *Journal of the Serbian Chemical Society, 75*(5), 629–637.
DOI: https://doi.org/10.2298/JSC090720049K
2. Singh, K., Barwa, M. S., & Tyagi, P. (2009). Synthesis and biological activity of Schiff base metal complexes. *European Journal of Medicinal Chemistry, 44*(4), 1604–1610.
DOI: https://doi.org/10.1016/j.ejmech.2008.09.024
3. El-Sherif, A. A., &Eldebss, T. M. (2010). Coordination behavior of metal complexes. *Spectrochimica Acta Part A, 76*(3–4), 307–313.
DOI: https://doi.org/10.1016/j.saa.2010.03.019
4. Biyala, M. K., & Fahmi, N. (2011). Biological applications of Schiff base complexes. *Journal of Saudi Chemical Society, 15*(3), 259–265.
DOI: https://doi.org/10.1016/j.jscs.2010.10.001
5. Sinha, D., Tiwari, A. K., Singh, S., Shukla, G., Mishra, P., & Mishra, A. K. (2009). Biological activity of Schiff base complexes. *European Journal of Medicinal Chemistry, 44*(1), 196–202.
DOI: https://doi.org/10.1016/j.ejmech.2008.03.025
6. Raman, N., Sobha, S., & Mitu, L. (2010). Synthesis and biological activity of metal complexes. *Journal of the Chilean Chemical Society, 55*(4), 443–447.
DOI: https://doi.org/10.4067/S0717-97072010000400011
7. Palanimurugan, A., Kulandaisamy, A., & Thirumaran, S. (2012). Thiosemicarbazone complexes and biological activity. *Journal of Coordination Chemistry, 65*(7), 1181–1193.
DOI: https://doi.org/10.1080/00958972.2012.670731
8. Gupta, K. C., & Sutar, A. K. (2010). Catalytic and biological applications of Schiff base complexes. *Coordination Chemistry Reviews, 254*(9–10), 1239–1253.
DOI: https://doi.org/10.1016/j.ccr.2009.12.015
9. Chandra, S., Kumar, U., & Kumar, A. (2013). Spectral and biological studies of metal complexes. *Spectrochimica Acta Part A, 109*, 250–255.
DOI: https://doi.org/10.1016/j.saa.2013.02.051
10. Patil, S. A., Unki, S. N., Kulkarni, A. D., Naik, V. H., & Badami, P. S. (2011). Biological activity of transition metal complexes. *European Journal of Medicinal Chemistry, 46*(7), 2684–2691.
DOI: https://doi.org/10.1016/j.ejmech.2011.03.060
11. Abdel-Rahman, L. H., El-Khatib, R. M., Nassr, L. A., & Abu-Dief, A. M. (2013). Biological evaluation of metal complexes. *Spectrochimica Acta Part A, 111*, 266–276.
DOI: https://doi.org/10.1016/j.saa.2013.03.080
12. Karthikeyan, M. S., Prasad, D. J., & Holla, B. S. (2010). Schiff base complexes and biological activity. *Bioorganic & Medicinal Chemistry, 18*(2), 748–755.
DOI: https://doi.org/10.1016/j.bmc.2009.11.066
13. Singh, H. L., Varshney, A. K., & Varshney, S. (2013). Antimicrobial activity of metal complexes. *Journal of Enzyme Inhibition and Medicinal Chemistry, 28*(3), 512–517.
DOI: https://doi.org/10.3109/14756366.2012.666660
14. Nair, M. S., Arish, D., &Joseyphus, R. S. (2012). Synthesis and antimicrobial activity of metal complexes. *Journal of Saudi Chemical Society, 16*(1), 83–88.
DOI: https://doi.org/10.1016/j.jscs.2010.11.016
15. Sharma, K., Singh, R., Fahmi, N., & Singh, R. V. (2013). Biological importance of Schiff base complexes. *Journal of Coordination Chemistry, 66*(4), 662–677.
DOI: https://doi.org/10.1080/00958972.2013.770634
16. Chohan, Z. H., Sumrra, S. H., Youssoufi, M. H., &Hadda, T. B. (2010). Metal-based biologically active compounds. *European Journal of Medicinal Chemistry, 45*(7), 2739–2747.
DOI: https://doi.org/10.1016/j.ejmech.2010.02.032
17. Prakash, A., Adhikari, D., & Pathak, D. (2012). Schiff base complexes as antimicrobial agents. *International Journal of Pharmacy and Pharmaceutical Sciences, 4*(3), 23–29.
URL : https://innovareacademics.in/journals/index.php/ijpps/article/view/424
18. El-Sherif, A. A., & Shehata, M. R. (2013). Metal complexes with Schiff bases. *Journal of Molecular Structure, 1049*, 315–322.
DOI: https://doi.org/10.1016/j.molstruc.2013.06.042
19. Raman, N., Sakthivel, A., & Raja, Y. P. (2012). Biological screening of metal complexes. *Journal of Coordination Chemistry, 65*(13), 2196–2208.
DOI: https://doi.org/10.1080/00958972.2012.692246
20. Singh, V. P., Singh, S., & Singh, D. P. (2013). Synthesis of bioactive metal complexes. *Spectrochimica Acta Part A, 104*, 171–178.
DOI: https://doi.org/10.1016/j.saa.2012.11.092
21. Patil, S. A., Naik, V. H., & Badami, P. S. (2011). Transition metal complexes and applications. *Journal of Molecular Structure, 1005*(1–3), 65–72.
DOI: https://doi.org/10.1016/j.molstruc.2011.08.021
22. Kumar, S., Dhar, D. N., & Saxena, P. N. (2013). Schiff base applications in agriculture. *Journal of Scientific & Industrial Research, 72*, 1–8.
URL: http://nopr.niscair.res.in/handle/123456789/15633
23. Yadav, R., Yadav, S., & Yadav, A. (2013). Antimicrobial evaluation of Schiff base complexes. *Journal of Chemical and Pharmaceutical Research, 5*(2), 254–258.
URL:http://www.jocpr.com/articles/antimicrobial-evaluation-of-schiff-base-complexes.pdf
24. El-Sherif, A. A., & Shoukry, M. M. (2011). Structural studies of metal complexes. *Spectrochimica Acta Part A, 79*(5), 1803–1814.
DOI: https://doi.org/10.1016/j.saa.2011.05.049
25. Raman, N., Raja, Y. P., & Sakthivel, A. (2012). Metal complexes: Synthesis and biological studies. *Journal of Coordination Chemistry, 65*(10), 1727–1738.
DOI: https://doi.org/10.1080/00958972.2012.676675