

SYNTHESIS CITRIC ACID SUBSTITUTED CO, NI AND ZN COMPLEXES AND ANTIMICROBIAL PROPERTIES

SÍNTESE DE COMPLEXOS DE CO, NI E ZN SUBSTITUÍDOS POR ÁCIDO CÍTRICO E PROPRIEDADES ANTIMICROBIANAS

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Abstract

This scientific research aims the synthesis and antimicrobial investigations of citric acid substituted metal complexes. Ligand and all synthesized compounds were evaluated high antibacterial and antifungal properties. Sustainable Development Goals (SDGs), particularly SDG 3 (Good Health and Well-being) and SDG 12 (Responsible consumption and production). Coordination chemistry is a modern branch of chemistry. Synthesis of new complex compounds has increased because of different application of these compounds. Coordination compounds have shown high antimicrobial properties. Nowadays scientist have been working in the different class of complex compounds, but they prefer synthesis of natural ligand substituted metal complexes. IR spectra were investigated by use of UR-20 spectrometer. Elemental analyses were carried out in Horiba Spectrometer. Antimicrobial activity of the compounds of tested against using *Pseudomonas Aeruginosa*, *Mycobacterium lacticolium*, *Aspergillus niger*, *Cladasporium resinale*, *Penicillium Chrosegenum*, *Chastomium gloloodium* *Trichoderma viride*. Synthesized all complex compounds have shown high antibacterial and high antifungal properties. The complex compounds even a very low concentrations have shown high antimicrobial properties. We have investigated antimicrobial properties and when we observe high results, we have continued study of duration of complex compounds. In the result of our investigation our compounds have been showed 8 month duration of bacteria and fungi. The first time we have synthesized nickel perchlorate containing citric acid complexes. We have also been investigated mix bacteria and fungi cultures.

Keyword: Citric Acid. Metal Complex. Antimicrobial Properties. SDG 3. SDG 12. IR Spectra. Elemental Analyses.

Resumo

*Esta pesquisa científica visa a síntese e a investigação antimicrobiana de complexos metálicos substituídos por ácido cítrico. O ligante e todos os compostos sintetizados foram avaliados quanto às suas elevadas propriedades antibacterianas e antifúngicas. Os Objetivos de Desenvolvimento Sustentável (ODS), em particular o ODS 3 (Saúde e Bem-Estar) e o ODS 12 (Consumo e Produção Responsáveis), são relevantes para este estudo. A química de coordenação é um ramo moderno da química. A síntese de novos compostos complexos tem aumentado devido às suas diversas aplicações. Os compostos de coordenação têm demonstrado elevadas propriedades antimicrobianas. Atualmente, os cientistas têm trabalhado em diferentes classes de compostos complexos, mas preferem a síntese de complexos metálicos substituídos por ligantes naturais. Os espectros de infravermelho foram investigados utilizando um espectrômetro UR-20. As análises elementares foram realizadas no espectrômetro Horiba. A atividade antimicrobiana dos compostos foi testada contra *Pseudomonas aeruginosa*, *Mycobacterium lacticolium*, *Aspergillus niger*, *Cladasporium resinale*, *Penicillium chrosegenum*, *Chastomium gloloodium* e *Trichoderma viride*. Todos os compostos complexos sintetizados apresentaram altas propriedades antibacterianas e antifúngicas. Os compostos complexos, mesmo em concentrações muito baixas, demonstraram altas propriedades antimicrobianas. Investigamos as propriedades antimicrobianas e, ao observarmos resultados promissores, prosseguimos com o estudo da duração da atividade dos compostos complexos. Como resultado de nossa investigação, nossos compostos apresentaram uma duração de 8 meses contra bactérias e fungos. Sintetizamos, pela primeira vez, complexos de ácido cítrico contendo perclorato de níquel. Também investigamos culturas mistas de bactérias e fungos.*

Palavras-chave: Ácido Cítrico. Complexo Metálico. Propriedades Antimicrobianas. SDG 3. SDG 12. Espectros de IR. Análises Elementares.

1 INTRODUCTION

Coordination chemistry is a modern branch of chemistry. Synthesis of new complex compounds has increased because of different application of these compounds (Gavin. H.Hedwig *et al.*,1980). Coordination compounds have shown high antimicrobial properties (Oleg Zelenin, *et al.*, 2007). Nowadays scientist have been working in the different class of complex compounds, but they prefer synthesis of natural ligand substituted metal complexes (Natalie Byrd, *et al.*,2023)

Citric acid naturally occurs in citrus fruits. Synthetic versions are produced from a type of mold and are often used as an additive (Rosaria Ciriminna, *et al.*, 2017). They can cause adverse reactions in some conditions (Papadopoulou Olga, *et al.*, 2023). Citric acid is found naturally in citrus fruits, especially lemons and limes. It is what given them their tart, sour taste. A manufactured form of citric acid is commonly used as an additive in food cleaning agents and nutritional supplements (Kariyappa Agay, *et al.*, 2021). However, this manufactured form differs what's found naturally in citrus fruits. Citric acid first was first derived from lemon juice by a Swedish researcher in 1784. The odorless and colorless compounds was produced from lemon juice until the early 1900 when researchers discovered it could also be made from the black mold *Aspergillus niger*, which creates citric acid when it feeds on sugar. Because of its acidic, sour –tasting nature, citric acid is predominantly used as flavouring and preserving agent, especially in soft drinks and candies. It is also used to stabilize or preserve medicines and as disinfectant. This study has demonstrated that at pH 9–10 under sulfate-reducing conditions bacteria can ferment citrate, a widely used decontaminant in the nuclear industry (Adedibu C.Tella, *et al.*, 2010). The citrate fermentation products can then support sulfidation in low Ni systems to partially precipitate nickel sulfides and bioreduce U(VI) to form poorly soluble non-crystalline U(IV)–phosphates (Adedibu C.Tella, *et al.*, 2010) Removal of citrate by biodegradation in wastes at high pH will eliminate the potential for radionuclide-citrate complexation, and the implied elevated solubility of radionuclides, notably Ni^{2+} , in radioactive waste disposal scenarios where citrate is present (Domenico Iacopetta, *et al.*, 2023)

2 THEORETICAL FRAMEWORK

The investigation has shown significant progress in utilization of transition metals complexes as drugs to treat several human diseases (Suman Kumari, Seema, *et al.*, 2022). The advances in inorganic chemistry provide better opportunities to use metal complexes as therapeutic agents. Medicinal inorganic chemistry can exploit the unique properties of metal ions for the design of new drugs. The use of transition metal complexes as therapeutic compounds has become more and more pronounced (Pooja Sethi, *et al.*, 2020). The complexes offer a great diversity in their action, they do not only have anticancer properties but have also been used as anti-inflammatory, anti-infective and antidiabetic compounds.

3 METHODOLOGY

IR spectra were investigated by use of UR-20 spectrometer. Elemental analyses were carried out in Horiba spectrometer. Antimicrobial activity of the compounds was tested against using *Pseudomonas Aeruginosa*, *Mycobacterium lacticolium*, *Aspergillus niger*, *Cladasporium resinale*, *Penicillium Chrosegenum*, *Chastomium gloloodium*, *Trichoderma viride*. The sterilized (autoclaved 121⁰ C for 15 min) medium (40-50⁰) was poured into the Petri dishes to give a depth of 3-4 mm and allowed to solidify. The suspension of the microorganism was streaked on plates. The paper discs impregnated with the test compounds were placed on the solidified medium. The plates were pre-incubated for 24 hours at room temperature and incubated at 37⁰ C for 24 hours.

3.1 Citric acid substituted nickel complexes

Citric acid and Ni(ClO₄)₂ were taken in a 1:1 molar ratio and added to a flask with the presence of 25 ml water. The reaction was carried out for three hours at a temperature of 70⁰C. After the chemical reaction, the hot solution was filtered out. Green crystals were formed upon cooling of the solution.

IR: OH-3463,41, CH-2933,26;1633,00;1445,98;1120,93, CH₂-2341,66, C=O-2027,18, Ni-O-625,93

Calculated: C-29,14%, O-43,36 %, H-1,62%, Ni-23,76%.

Found: C-29,10 %, O-43,34%, H-1,63%, Ni-23,74%

3.2 Citric acid substituted cobalt complexes

Citric acid and $\text{Co}(\text{NO}_3)_2$ were taken 1:1 molar ratio adding in flask with presence of 25 ml water reaction was carried out three hours at temperature 70°C . After chemical reaction hot solution was filter out. Purple crystals were formed cooling of solution.

IR: OH-3447,46, CH-3360,15;3337,10;3173,50, Co-O-619,74

Calculated: C-29,14%, O-43,34 %, H-1,61%, Co-23,88%.

Found: C-29,09 %, O-43,32%, H-1,60%, Co-23,86%.

3.3 Citric acid substituted zinc complexes

Citric acid and $\text{Zn}(\text{OH})_2$ were taken 1:1 molar ratio adding in flask with presence of 25 ml water reaction was carried out three hours at temperature 70°C . After chemical reaction hot solution was filter out. Yellow crystals were formed cooling of solution.

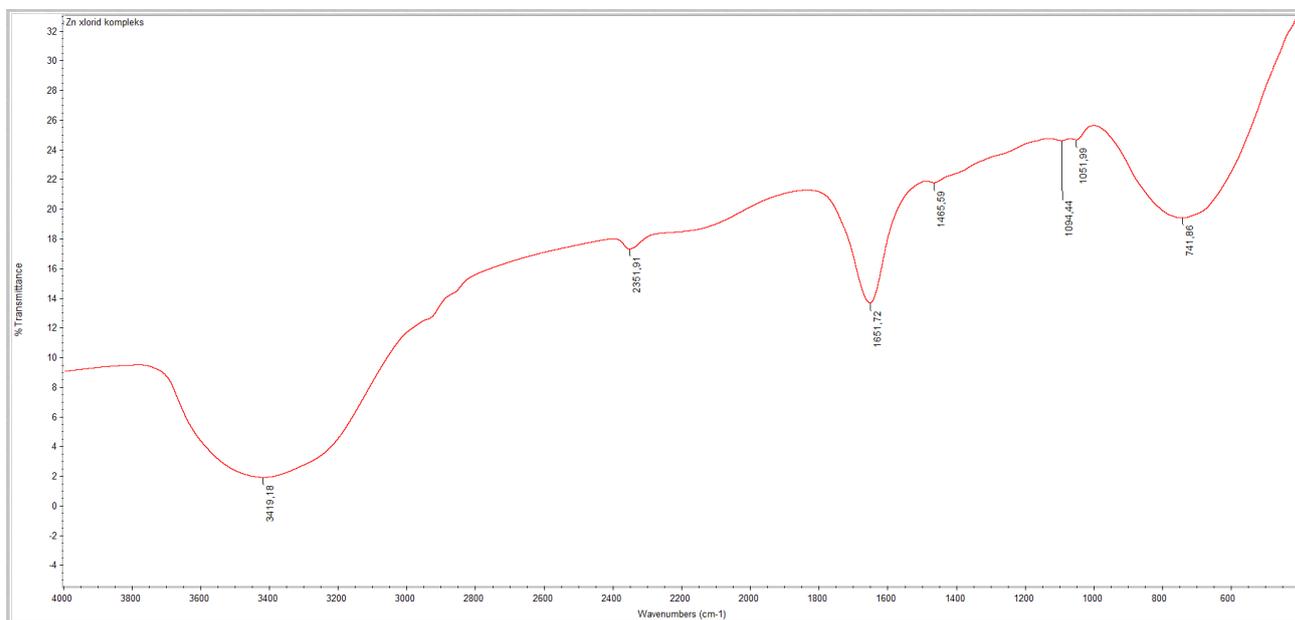
IR: OH-3419,18, CH-2351,91;1651,72; H_2O -1465,59, Zn-Cl-741,86.

Calculated: C-28,45%, O-44,26%, H-1,58%, Zn—25,69

Found: C-28,43 %, O-44,27%, H-1,56 %, Zn-25,68%

4 RESULT AND DISCUSSION

We have been synthesized citric acid substituted Co, Ni and Zn complexes. We have proved structure of synthesized compounds by IR spectroscopy.

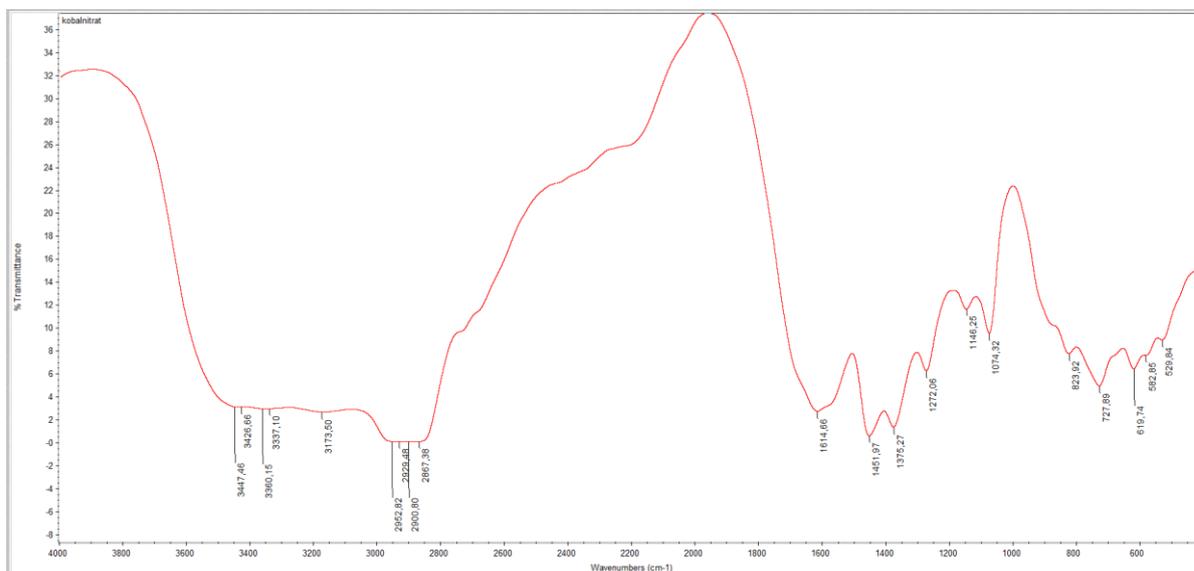
Figure 1*Complex compounds of Zinc chloride with citric acid*

IR: OH-3419,18, CH-2351,91;1651,72; H₂O-1465,59, Zn-C -741,86

We have been synthesized citric acid substituted Zn, Co, and nichel complexes. Structure of all complexes were proved by IR spectra. Spectra of zinc complex Zn-O realition was shown at 741,86 sm^{-1} wavelength. C=O relation was observed at 1651,72 sm^{-1} and 3419,18 sm^{-1} wavelength. 2351,91 wavelength was shown CH₂. Fragment.

Figure 2

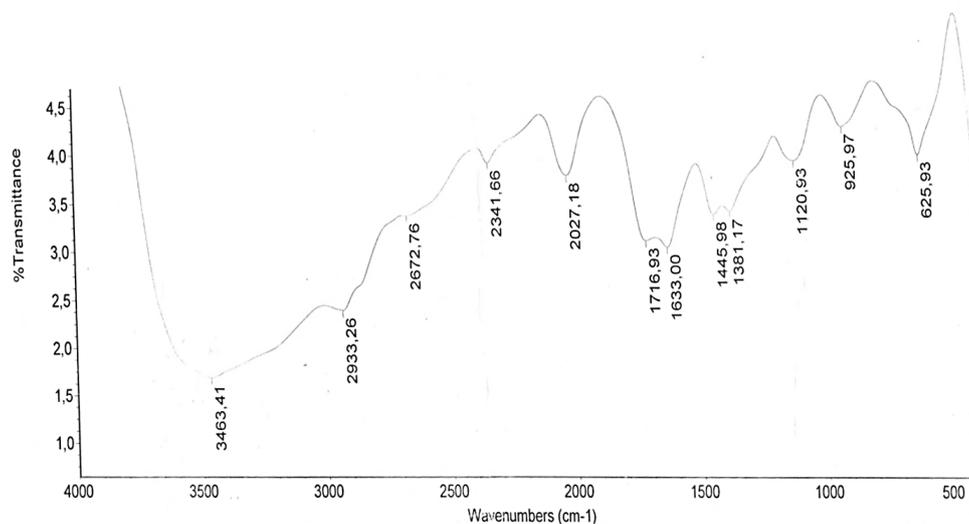
IR spectra of citric acid with cobalt nitrate



IR spectra of citric acid substituted Cobalt2-nitrate complexes C=O group was observed at $3447,46\text{ cm}^{-1}$ wavelength. $2929,48$ and $2867,38\text{ cm}^{-1}$ wavelengths were shown CH_2 absorption spectra. $619,74\text{ cm}^{-1}$ wavelength was shown Co-O absorption spectra.

Figure 3

IR spectra of nickel perchorate with citric acid



IR:OH-3463,41,CH-2933,26;1633,00;1445,98;1120,93,CH₂-2341,66,C=O-2027,18, Ni-O-625,93

Calculated: C-29,14%,O-43,36 %, H-1,62%, Ni-23,76%.

Found: C-29,10 %, O-43,34%, H-1,63%, Co-23,74%

5 RESEARCH IMPLICATIONS

We have been synthesized citric acid substituted Co, Ni and Zn complexes. The structure of synthesized compound was determined different analyses methods. We have revealed that synthesized complexes are chelate complexes. In IR spectra metal bonded with oxygen atom and ring closed. We have been investigated antimicrobial properties of synthesized metal complexes. Antimicrobial properties were carried out by diffusion method. All synthesized compounds have shown high antimicrobial properties.

Table №1

Antimicrobial properties of complexes

Compound	Concentration %	Antibacterial	antifungal
Co complex	1	3,0-2,9	3,0-3,1
	0,5	2,7-2,7	2,8-2,8
	0,25	2,4-2,5	2,6-2,6
Ni complex	1	2,9-3,0	3,2-3,3
	0,5	2,8-2,7	2,8-2,9
	0,25	2,6-2,5	2,7-2,7
Zn complex	1	3,3-3,4	3,0-3,0
	0,5	2,9-2,9	2,8-2,8
	0,25	2,8-2,8	2,6-2,6

We have shown the antimicrobial properties of all three complexes in the table. Zinc complex have shown highest antibacterial properties, even when we decreased concentration of complex it is maintained their antibacterial properties. Ni complex has shown high antifungal properties, but it has shown moderate antibacterial properties. Cobalt complex has shown moderate antimicrobial properties against both bacteria and fungi.

Table № 2

The study investigated the duration of antimicrobial activity of zinc substituted citric acid complex

Number of Weeks 1	Concentration %	Inhibition zone diametr, sm	
		Bacteria(MPA)	Fungi (SA)
1	1,0	3,0-3,1	3,2-3,1
	0,5	2,8-2,8	3,0-3,0
2	1,0	2,7-2,8	3,3-3,3
	0,5	2,6-2,6	3,3-3,2
3	1,0	2,6-2,8	3,5-3,5
	0,5	2,4-2,4	3,1-3,1
4	1,0	2,5-2,6	3,0-3,1
	0,5	2,2-2,2	2,7-2,6
5	1,0	2,2-2,2	2,9-3,0
	0,5	1,9-2,0	2,4-2,4
6	1,0	2,1-2,1	2,5-2,5
	0,5	1,9-1,8	2,1-2,2
7	1,0	1,9-2,0	2,1-2,2
	0,5	1,6-1,7	1,8-1,8
8	1,0	2,0-2,0	1,6-1,6

6 ORIGINALITY/VALUE

We have been studied stability of complexes and determining the duration of the antimicrobial effect of the test compounds belonging to various classes of chemical compounds in experimental conditions behave differently; Zinc exhibited antimicrobial properties for a long time, cobalt slowly inactivated, nickel lose their antimicrobial activity immediately after their introduction into the additives. The antimicrobial properties all compounds exhibited strong bacteria and fungi effects. Metal complex have been found to be more effective than their ligand as the process of complexation dominantly affects the overall biological behavior of. The compound also the zone of inhibition increases with the concentration.

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Authors' Contribution

Both authors contributed equally to the development of this article.

Data availability

All datasets relevant to this study's findings are fully available within the article.

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