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Research Article

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Synthesis and fungicidal activity of coordination compounds of nickel (II) and copper(II) carboxylates with urea and thiourea

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ABSTRACT

In this study, twelve new coordination compounds of nickel(II) and copper(II) carboxylates with urea and thiourea have been synthesized and screened for their fungicidal activities against some rotten wood fungi namely streptomyces xantholiticus, four strains of rhizopus oryxae and lactobacillus plantarum; two strains of lactobacillus fermentum, mucor racemosus and aspergillus niger The results showed that the complexes inhibited the growth of streptomyces xantholiticus, rhizopus oryxae, aspergillus niger lactobacillus plantarum, lactobacillus fermentum, and mucor racemosus and aspergillus niger.

INTRODUCTION

The synthesis of coordination compounds of transition metal carboxylates with urea have been of renewed interest in recent years not only as potential binding sites to metals , but also for their found various application in pharmaceuticals, catalysts, in extraction systems water repellents polymer dispersants fertilizer pigments and packing materials[1]. The known influence of urea molecules in biological processes[2] makes the study of coordination compounds vitally interesting. Copper (II) carboxylates have been found to have fungicidal activity and potentially useful in wood protection[3].

In continuation of our studies on metal carboxylates and their derivatives[4,5] we report here our investigations on the physicochemical properties of metal (II) carboxylates and their adducts with urea and thiourea. The fungicidal activities of the compounds are also reported.

The aim of this study is to estimate fungicidal activities of potential new fungicidal agents representing:

$[Cu(C_6H_5COO)NH_2CONH_2]Cl_2$; $[Ni\ (C_6H_5COO^-)NH_2CONH_2]SO_4$; $[Cu\ (C_6H_5COO^-)NH_2CONH_2]SO_4$; $[Cu(C_6H_5COO^-)NH_2CSNH_2]SO_4$ $[Ni(C_6H_5COO^-)\ NH_2CSNH_2]SO_4$; $[Ni(C_6H_5COO^-)NH_2CSNH_2]SO_4$

EXPERIMENTAL SECTION

Commercially available substances such as $CuSO_4.5H_20$, urea and thiourea and all the solvents were used without further purification.

Synthesis

Preparation of $[Cu(C_6H_5COO^-)NH_2CONH_2]SO_4$

Benzoic acid (5g, 0.0206moles) was dissolved in 50ml of 2M NaOH and stirred with a magnetic stirrer. $CuSO_4.5H_2O$ (1.6g, 0.0100moles) dissolved in 10ml of water was added dropwise to the solution and stirred for 30minutes. The resulting solution was filtered through a Buchner funnel using a suction pump and washed with ethanol. The precipitate was light blue in colour (0.32g).

30ml of distilled water was added to the precipitate formed (0.32g) and it was stirred using a magnetic stirrer. Urea (0.0628g, 0.0010moles) was diluted with 10ml of distilled water and added to the solution being stirred dropwisely. The resulting solution was stirred for 30 minutes and filtered to dryness through suction. The precipitate (complex) was weighed and dried over KOH. The colour of the complex is light blue.

Preparation of [Ni $(C_6H_5COO^-)NH_2CONH_2]SO_4$

Benzoic acid (5g, 0.0206moles) was dissolved in 50ml of 2M NaOH and stirred with a magnetic stirrer 2.712g (0.0103moles) of $NiSO_4$ dissolved in 10ml of water was added to the solution while stirring. The solution changed from colourless to light green on addition of the dissolved $NiSO_4$ and the mixture was stirred for the next 30minutes. The precipitate formed was filtered through suction and washed with water and acetone.

Biological Screening

Preparation of potato dextrose agar solution

10g of Potato Dextrose Agar (PDA) was dissolved in 250ml of water and it was homogenized on an hot plate. The solution was prepared in a conical flask and plugged with a cotton wool at the mouth. The solution was sterilized in an autoclave for 15 minutes at 121^0C. The PDA solution was then allowed to cool and paired into petridishes.

Culturing the micro-organisms

Wood of different types were scraped with a blade to the medium and they were incubated for 24hours. The woods were labeled alphabetically and each with its local name (in italics) as follows:

A1	-	*ARA (swietenia mahogani)*
A2	-	*ARA (swietenia mahogani)*
B1	-	*ORIRO(antiaris africana)*
B2	-	*ORIRO (antiaris africana)*
C1	-	*ARABA(ceiba pentandra)*
C2	-	*ARABA (ceiba pentandra)*
D1	-	*GEDU (entandrophragma cylindricum)*

After 24hours, the organisms were sub-cultured using a wire loop into the following categories: A21, A22, A23, B11, B21, C11, C21, C22, D11, D12.

They were incubated for 48 hours after this which the microorganisms were identified to be fungi and were stored in slant bottles to obtain their pure cultures. The fungi were then characterized so as to know their names.

Two types of fungi were identified namely the yeast-like fungi and the mycelial fungi. The yeast-like fungi resemble bacteria in its behavior and was investigated using sensitivity test while the mycelial fungi were investigated using the Minimum Inhibitory Concentration (MIC) test. For the mycelial fungi, the pure cultures in the slant bottles were transferred to the plates using a 5mm cork borer to obtain pure cultures and were incubated for 24hours and 48hours after which the diameter of the growth was measured.

Sensitivity Test

The sensitivity test was used to test the effects of the complexes on the yeast-like fungi using paper discs. The yeast-like fungi were C21, B11, D12 and D11. Four test tubes containing nutrient broth were sterilized in an autoclave and after cooling, the four yeast-like fungi were transferred using wire loop into each test tube. They were labeled and left for 24 hours. Sterilized swabs were dipped into the nutrient broth containing the micro-organism and used to rub the surfaces of the plates. The complexes were dissolved in DMSO and acetone to make a concentration of 0.1g/ml.

Sterilized paper discs (5mm in diameter) were dipped into the complex solution using a forcep and they were placed at equidistance on the plate. The plates were incubated. After 24 hours the zones of inhibition were measured. The result is presented in Table 4.

Minimum Inhibitory Concentration (MIC) test

The mycelial fungi were investigated by the MIC test. The mycelial fungi are C11, A21, A22, C22, B21 and A23. Their pure cultures on the plates were measured after incubation for 24 and 48hours respectively as shown in the Table. The plates were bored in the center using a 5mm cork borer. The cork borer was again used to pick the mycelial fungi from their pure cultures into the bored holes on the plates. The complexes (0.1g / ml in concentration) were then introduced into the plates using syringe and needle. The zones of inhibition of the fungi were measured after 24hours and also after 48hours. The results are shown in Table 4.

Fungicidal activity of the complexes

The fungicidal activity (Table 1) of the yeast like fungi showed overall that the most sensitive fungi to the metal complexes were *Lactobacillus plantarum, Lactobacillus fermentum b* with zones of inhibition ranging from 10mm to 40mm. *Lactobacillus fermentum a* is resistant to three of the five complexes showing 40% inhibition $[Ni(C_6H_5COO^-)NH_2CONH_2]SO_4$ and $[Cu(C_6H_5COO^-)NH_2CSNH_2]SO_4$ has the highest potency for the yeast like fungi i.e 100% inhibition was observed. 75% inhibition was observed in $[Cu(C_6H_5COO^-)NH_2CONH_2]Cl_2$ and $[Cu(C_6H_5COO^-)NH_2CONH_2]SO_4$.

Table 1: Filamentous fungi (control) (mm)

Test organisms	24hours	48hours
Rhizopus oryzae a	60mm	70mm
Rhizopus oryzae b	14mm	43mm
Streptomyces xantholiticus	14mm	63mm
Rhizopus oryzae c	70mm	88mm
Rhizopus oryzae d	75mm	88mm
Mucor racemosus	50mm	88mm

TABLE 2: PERCENTAGE INHIBITION OF THE GROWTH OF THE FILAMENTOUS FUNGI BY THE TESTED COMPLEXES AFTER 24HOURS

TEST ORGANISMS

Complexes	*Rhizopus oryzae a*	*Streptomyces xantholiticus*	*Mucor racemosus*	*Rhizopus oryzae b*	*Rhizopus oryzae c*	*Rhizopus oryzae d*
$[Cu(C_6H_5COO)NH_2CONH_2]Cl_2$	64.29	64.29	90.00	93.33	91.67	92.86
$[Ni(C_6H_5COO^-)NH_2CONH_2]SO_4$	64.29	64.29	90.00	93.33	91.67	92.86
$[Cu(C_6H_5COO)NH_2CONH_2]SO_4$	64.29	64.29	90.00	93.33	91.67	92.86
$[Cu(C_6H_5COO)NH_2CSNH_2]SO_4$	64.29	64.29	90.00	93.33	91.67	92.86
$[Ni(C_6H_5COO)NH_2CSNH_2]SO_4$	-	-	-	-	-	-
$[Cu(C_6H_5COO^-)NH_2CSNH_2]Cl_2$	64.29	64.29	62.00	93.33	91.67	92.86

The percentage inhibition of growth of the filamentous fungi showed that all the complexes has high potency against all the fungi with the exception of $[Cu(C_6H_5COO^-)NH_2CSNH_2]Cl_2$ after 24 hours of incubation (Table 2). The percentage inhibition of growth ranging from 64.29% to 93.33%. The percentage inhibition of growth after 48hours of incubation (Table 3) showed that four of the complexes inhibited the growth of the fungi at a higher percentage.

$[Cu(C_6H_5COO^-)NH_2CSNH_2]Cl_2$ has the lowest potency against the filamentous fungi even after 48hours of incubation. $[Cu(C_6H_5COO^-)NH_2CSNH_2]Cl_2$ is only potent against *Streptomyces xantholiticus*

From the results obtained, there is a conclusive evidence when compared to the work already reported in the literature[6,7,8] that the four metal complexes except $[Cu(C_6H_5COO^-)NH_2CSNH_2]Cl_2$ has fungicidal activity against all the fungi tested.

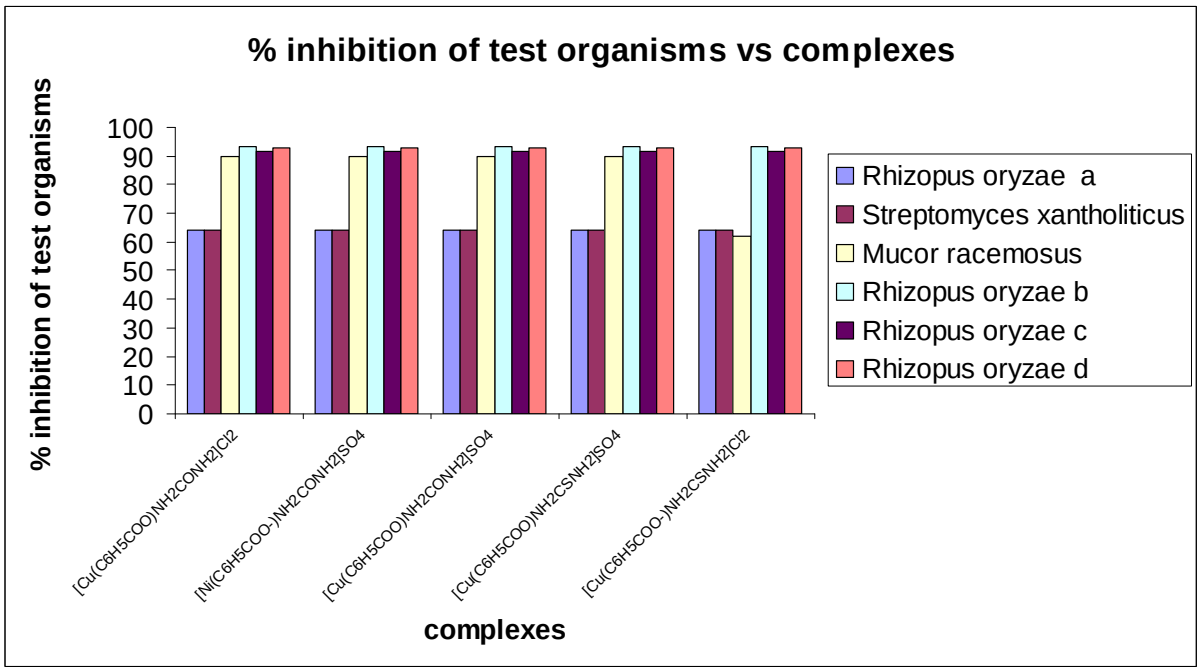

Table 3: Percentage inhibition of the growth of the filamentous fungi by the tested complexes after 48 hours

	TEST ORGANISMS					
Complexes	*Rhizopus oryzae a*	*Streptomyces xantholiticus*	*Mucor racemosus*	*Rhizopus oryzae b*	*Rhizopus oryzae c*	*Rhizopus oryzae d*
$[Cu(C_6H_5COO)NH_2CONH_2]Cl_2$	88.37	92.06	94.32	94.32	92.86	94.32
$[Ni(C_6H_5COO)NH_2CONH_2]SO_4$	88.37	92.06	94.32	94.32	92.86	94.32
$[Cu(C_6H_5COO)NH_2CONH_2]SO_4$	88.37	92.06	94.32	94.32	92.86	94.32
$[Cu(C_6H_5COO)NH_2CSNH_2]SO_4$	88.37	92.06	94.32	94.32	92.86	94.32
$[Ni(C_6H_5COO^-)NH_2CSNH_2]SO_4$	-	-	-	-	-	-
$[Cu(C_6H_5COO^-)NH_2CSNH_2]Cl_2$	25.00	48.81	26.14	94.32	21.43	94.32

TABLE 4 : SENSITIVITY TEST FOR YEAST-LIKE FUNGI (mm)

	TEST ORGANISMS			
Complexes	*Aspergillus niger*	*Lactobacillus fermentum a*	*Lactobacillus fermentum b*	*Lactobacillus plantarum*
$[Cu(C_6H_5COO)NH_2CONH_2]Cl_2$	18	R	27	16
$[Ni(C_6H_5COO)NH_2CONH_2]SO_4$	27	25	35	40
$[Cu(C_6H_5COO)NH_2CONH_2]SO_4$	15	R	27	8
$[Cu(C_6H_5COO)NH_2CSNH_2]SO_4$	18	10	25	14
$[Ni(C_6H_5COO^-)NH_2CSNH_2]SO_4$	-	-	-	-
$[Cu(C_6H_5COO^-)NH_2CSNH_2]Cl_2$	R	R	24	10

R = Resistant

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