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Effective Antifungal complexes of mixed lig ands with Calcium and zinc

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Abstract

Two new mixed ligand complexes of transition metals were manufactured by reaction of Zn(II) ion and Ca(II) ion with 2,2′-bipyridine as a primary ligand and L-valine as a secondary ligand. The ligands and their metal complexes were examined utilizing X-ray crystallography, ultravioletvisible spectra and Fourier-transform infrared spectroscopy. The mixed ligand complexes were described with formulae as $Zn(Val)_2$(bipy.) and $Ca(Val)_2$(bipy.). The metal complexes had a pseudo-octahedral structure, and both complexes have the same patterns of structure indicating crystal structure symmetry. However, the yield of Zn complex was at 50% of the basic materials and the yield of Ca complex was 81% of basic materials. Bioactivity showed that Ca chelate could suppressive Phytophthora.

Key words: Zinc complexes, Calcium complexes, 2,2′-bipyridine, bioactivity, Valine

Introduction

L-Valine is one of the 20 proteinogenic amino acids with the chemical formula $HO_2CCH(NH_2)CH(CH_3)$[(1)]. It is classified as a non-polar branched-chain amino acid and is widely present in human food sources such as cottage cheese, fish, poultry, peanuts, sesame seeds, and lentils[(2)]. However, it is seldom present at a ratio exceeding 10 %. It can be obtained from alanine *via* adding two methyls (CH_3) groups to the α-carbon atom[(3)]. The properties and structure of valine are shown in Figure 1 and Table 1, respectively.

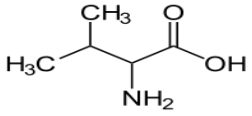

Figure 1 structure of valine

Table 1 the different properties of valine

Compound	molecular formula	Density g/cm^3	Molar mass g mol^{-1}	Solubility	Acidity (pKa)	Physical state	Melting point °C
Valine	$C_5H_{11}NO_2$	1.316	117.15	Soluble in water	2.32 (carboxyl) 9.62 (amino)	White crystalline powder	298 decom.

With regards to the structure of ligand complexes, the insertion of a second competing ligand such as 1,10-phenanthroline, 2,2-bipyridine diminishes the dimensions of the metal complex structure. The 2,2′-bipyridine ligand (Figure 2) has been widely used as a metal

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chelating ligand especially when combined with other transition metals owing to its following properties (1) strong redox stability and ease of functionalization, and (2) neutrality that can constitute charged complexes with metal cations and form symmetrical and asymmetrical isomers[4].

The properties of 2,2′-bipyridine are shown in Table 2.

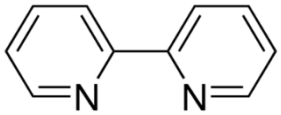

Figure 2 structure of 2,2′-bipyridine

Table 2 the different properties of 2,2'-bipyridine

Compound	molecular formula	Density g/cm^3	Molar mass g mol^{-1}	Solubility	Acidity (pKa)	Physical state	Melting point °C
2,2′-bipyridine	$C_{10}H_8N_2$	1.316	156.18	Slightly Soluble in water	9.67	White crystalline powder	70-73

Another part of complexes (Ca chelate or Zn chelate) represents transition metal ions such as Fe, Co, Ni, Cu, Zn, Ca and Cd that play a vital role in living systems, such as in enzymes or in carriers in a macrocyclic ligand field environment. Bio-coordination chemistry studies into the role of transition metal ions in living systems are now of great interest to chemists[5]. Bio-coordination chemistry can improve our understanding about living systems and the use of these metal ions to create and/or prepare different metal complexes can have a range of applications in our daily life. For many years, the use of bio-coordination chemistry to produce fungicides was surprisingly neglected and currently is still in its early stages. The specific objective of this study was to synthesize new ligand complexes that can potentially use as fungicides against *Phytophthora* species and to investigate of their physical and chemical structural characteristics.

The study of ligand complexes has become increasingly important with respect to their biological activity toward pathogens[6,7]. In general, mixed ligand complexes have been extensively used as antimicrobial[8-10]and anticancer agents[11]. Recently, the importance of bioinorganic chemistryhas grown globally, especially when European Union countries picked "Bio-coordination Chemistry" as one of the seven priority research fields in 1991[12].

The product of potassium phosphite (K_2HPO_3) is used widely against *Phytophthora* species to protect natural ecosystems, urban trees and orchards[13-15]. Phosphite is translocated in both the xylem and the phloem through association with photo-assimilates in a source-sink relationship given that it is trapped inside the phloem[16-18]. Mechanisms of action of phosphite include inciting the plant defence responses and/or act on the pathogen directly by causing inhibition or death[19,18,20,21].

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Phytophthora species cause a variety of diseases in numerous plant species in urban ecosystems[22-25]. In some cities, *Phytophthora* species are commonly associated with declining urban trees[24].

Chemical treatments are considered effective means for control of *Phytophthora* species that attack plants in natural or agricultural environments. Phosphite is a chemical widely used to manage the spread and impact of diseases caused by oomycete plant pathogens, especially *Phytophthora* species[26,14].

Unfortunately, excessive phosphite concentrations can result in phytotoxicity in plants. Also, some *Phytophthora* species have tolerance to phosphite.

Materials and Methods

Preparation of Ca complex

The Ca complex was made using a common method of making mixed ligands metal complexes[27,28]. Briefly, a solution of 2,2′-bipyridine (0.156 g, 1 m.mole) in aqueous ethanol (1:1:5 ml) and solution of L-Valine (0,234, 2 m.mole) in aqueous ethanol (1:1:5 ml) containing sodium hydroxide (0.08, 2mmol) were added simultaneously to a solution of $CaCl_2$.6H2O (1 m.mole) in aqueous ethanol (1:1:10 ml) in the stoichiometric ratio [2Val: Ca: bipy]. The solution was stirred constantly at room temperature for 4 hours then allowed to stand overnight. The crystallized product was filtrated off and washed with aqueous ethanol.

Preparation of Zn complex

The Zn complex was made using the same method of making Ca complex[27,28]. Briefly, a solution of 2,2′-bipyridine (0.156 g, 1 m.mole) in aqueous ethanol (1:1:5 ml) and solution of L-Valine (0,234, 2 m.mole) in aqueous ethanol (1:1:5 ml) containing sodium hydroxide (0.08, 2mmol) were added simultaneously to solution of $ZnCl_2$ (1 m.mole) in aqueous ethanol (1:1:10 ml) in the stoichiometric ratio [2Val: Zn: bipy] (Figure 3). The solution was stirred constantly at room temperature for 4 hours then allowed to stand overnight. The crystallized product was filtrated off and washed with aqueous ethanol.

X-ray crystallography (XRD)

The crystallographic features of the synthesized complexes were studied by X-ray diffraction (XRD) analysis *via* a GBC EMMA diffractometer with CuKα radiation (λ=0.154nm). The diffraction angle value (2θ) in the range (20° - 70°) was scanned at 2°/min with a step size of 0.02°. The analysis was carried out with beam acceleration at operating voltage and current of 35 kV and 28 mA, respectively.

Ultraviolet rays–visible spectra

The absorption spectra of the synthesized complexes were recorded within the wavelength range of 250 – 850 nm using a UV-vis PerkinElmer spectrometer. A halogen lamp was used as a light source coupled with a diffraction grating and photodiode detector. Light intensity calibration was performed by recording a baseline spectrum for a quartz tube filled in water. This calibration process eases the suppression of residual noise.

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Fourier-transform infrared spectroscopy (FTIR)

The infrared reflectance spectra of the synthesized complexes were obtained using a "reflected off" type ofPerkin Elmer Spectrum 100 FTIR spectrometer in a wavenumber range of400 – 4000 cm^{-1}. The samples were placed on a diamond crystal surface area and a pressure the arm was positioned and locked at a force of 100 N in order to confirm the sample was touching evenly onto the crystal surface. Background correction was madebefore the collection of each spectrum.

Bioactivity assay

Calcium and zinc complexes were prepared as described in Chapter 4. Ribeiro's modified medium (RMM)[(29)].with 0.35 mM phosphate and the Zn and Ca chelate were used for liquid media. The pH of the medium was adjusted to 6.4 (using KOH) and autoclaved before addition of phosphite, Zn chelate or Ca chelate. Media were dispensed into 9 cm diameter Petri-dishes (25 ml of liquid Ribeiro's modified medium).

The *P. cinnamomi* isolate MP94-48 was used in this study. Briefly, the isolate was grown on V8 agar plates for 7 days in the dark at 25°C, after which 5 mm diameter plugs were transferred to the RMM plates containing the different phosphite, Zn chelate and Ca chelate treatments. The *P. cinnamomi* isolate was grown in liquid RMM at an initial pH of 6.4 at different concentrations (0, 0.005, 0.40, 0.8 and 0.16, g/l) of phosphite or the chelate complexes. Inoculated plates (3 replications)were sealed with Parafilm® and incubated in the dark at 25°C without shaking. Mycelial growth was assessed by measuring the mycelial biomass dry weight after 7 days. Briefly, the mycelia were lifted out of the liquid, blotted dry with filter paper and dried in an oven at 70°C for one day before weighing. The EC_{50} values were computed from plots of the percent inhibition at different phosphite and Zn chelate or Ca chelateconcentrations compared to growth in the RMM without treatments.

Results and Discussion

Synthesis of Metal Complexes

In aerobic conditions, the complexes were made through interacting the metal salts with the corresponding ligands using a ratio of (1 MCl_2:1 2,2-bipyridine:2 sodium valinate) **(**Fig 3). The mixed ligand metal complexes synthesis can be expressed in the following equations:

1. 2Val H +2NaOH → 2Val- Na+ + H_2O
2. 2Val- Na+ + bipy + MCl_2 → [M (Val)2(bipy)] + 4H_2O + Na Cl

M= Ca (II), Zn (II)

Where bipy is 2,2-bipyridine and Val H is amino acid L-valine

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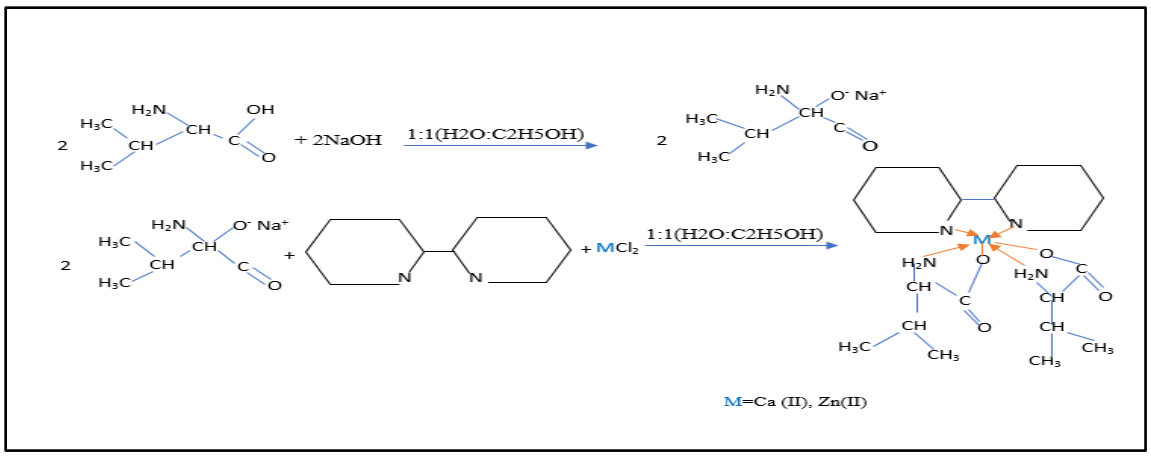

Figure 3 Schematic representation of the preparation of the complexes [M (Val)2(bipy)]

The physicochemical properties, formulae weights and the melting points of the chemicals are listed in Table 3. Both complexes were non-hygroscopic, stable at room temperature and white in color for both solid and liquid states. The results observed in this investigation suggest that the ligands acid L-valine and 2,2-bipyridine coordinate with either Ca (II) or Zn (II) form octahedral geometry. However, the yield of Zn complexwas at 50% of basic materials. Whereas, the yield of Ca chelate was at 81% of the basic materials and is considered a good yield rate.

Table 3 Thephysicochemical properties of the calcium and zinc complexes

Compounds	Molecular Weight	Physical state		% yield
Zn[(Val)2(bipy)]	453.80	White powder	crystalline	81.39
Ca[(Val)2(bipy)]	428.50	White powder	crystalline	55.55

Structural Characterization of Metal Complexes

XRD Analysis

The crystalline structures of the Zn and Ca chelate complexes were determined by X-ray diffraction (XRD) (Fig4). The XRD results reported reflection faces at (77), (72), (89), (123), (143), (75), (100) and (99) nm for the Ca-complex, and (73), (75), (108), (80), (130), (103), (86) and (96) nm for the Zn-complex.

Both samples had the same patterns of structure indicating crystal structure symmetry. For example, the main peak of the Ca-chelate was located at ($2\theta = 32.86$) which is very close to that of the Zn-chelate located at ($2\theta = 32.9$). The principal diffraction peaks of both the Ca-chelate and Zn-chelate were placed in a wide range of temperatures between 25-50 °C. The intense and sharp peaks indicate the improved crystalline quality of the complexes.

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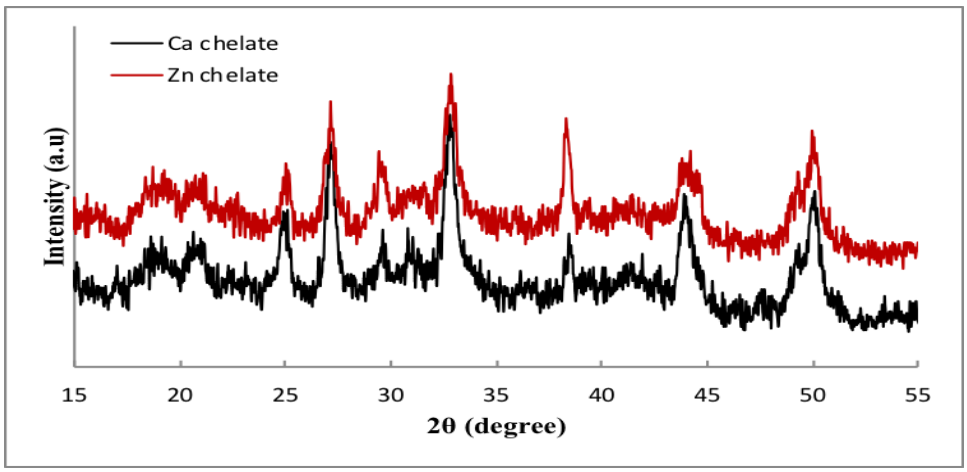

Fig 4 X-ray crystallography data of the calcium and zinc chelate complexes

Ultraviolet rays-visible spectra (UV-Vis)

Recorded absorption spectra of the calcium and zinc chelate complexes can be utilized to confirm their structure and to provide evidence that the electronic transitions occur. In both mixed ligand complexes (Zn complex and Ca complex), the absorption spectra displayed an absorption band around 280 nm (Fig 5) which could be attributed to (n→ π*) transition. Also, both complexes did not show any d-d transitions because of their weakness.

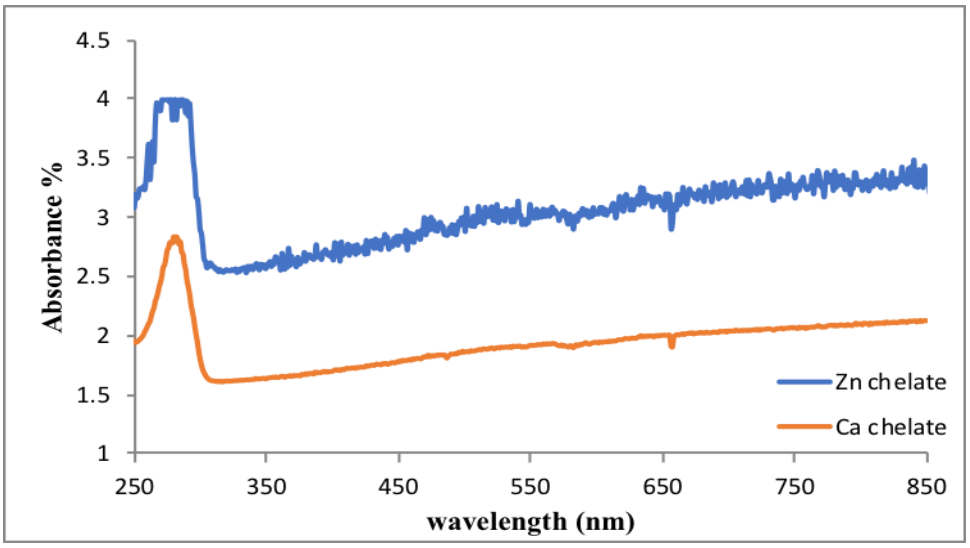

Fig 5 Electronic spectral data of the Zn and Ca chelates

Fourier-transform infrared spectroscopy (FTIR)

The Zn and Ca complexes were also examined by FTIR analysis. This technique can predict the coordination of the complexes to their corresponding ligands. The most important IR band (peak) for both the Zn and Ca chelates was observed at a wavelength of 1565 cm^{-1}(Fig. 6a and b) which reflects a vibrational mode for the υ (C=N) group of 2,2-bipyridine. This vibrational mode suggests that 2,2-bipyridine is similar to 1,10-phenanthroline, and is coordinated to the metal centers[30,31]. Another strong band for both chelates was observed around 3317 cm^{-1} and corresponds to the vibrational mode of (N-H) of the amine group. Two

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bands at 1480 cm^{-1} and 1364 cm^{-1} were related to υ (OCO) symmetry, which indicates the coordination of the carboxylic group to the central metal ion[32-34]. Moreover, other bands with low intensities in the spectra of both complexes were observed in the ranges of 610-542 cm^{-1} and 472-401 cm^{-1} are due to metal-nitrogen υ (M-N) and metal–oxygen υ (M-O) stretching vibrations, respectively[31,32,34].

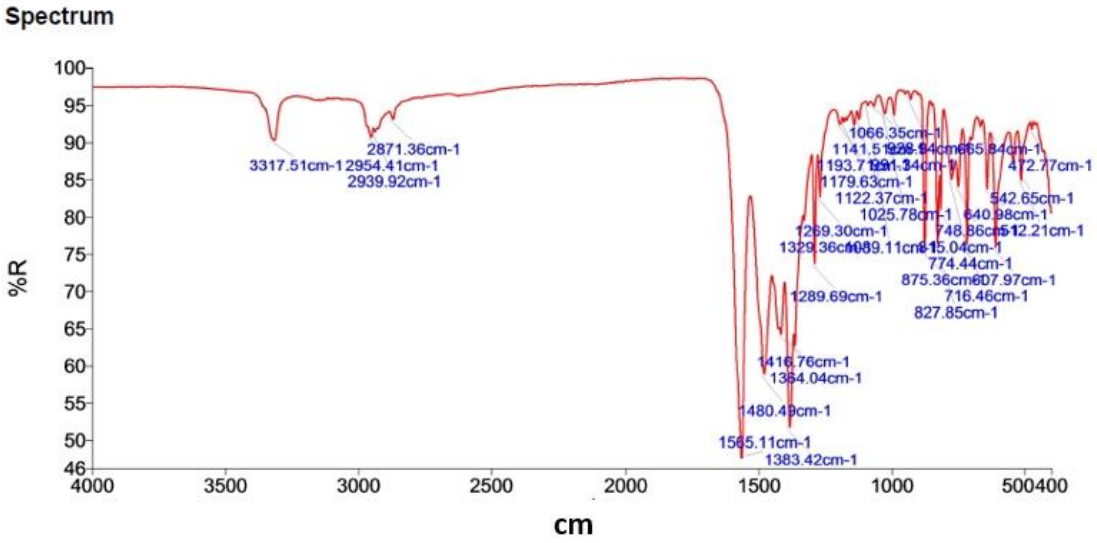

Fig 6a Fourier-transform infrared spectroscopy data of the Ca chelate

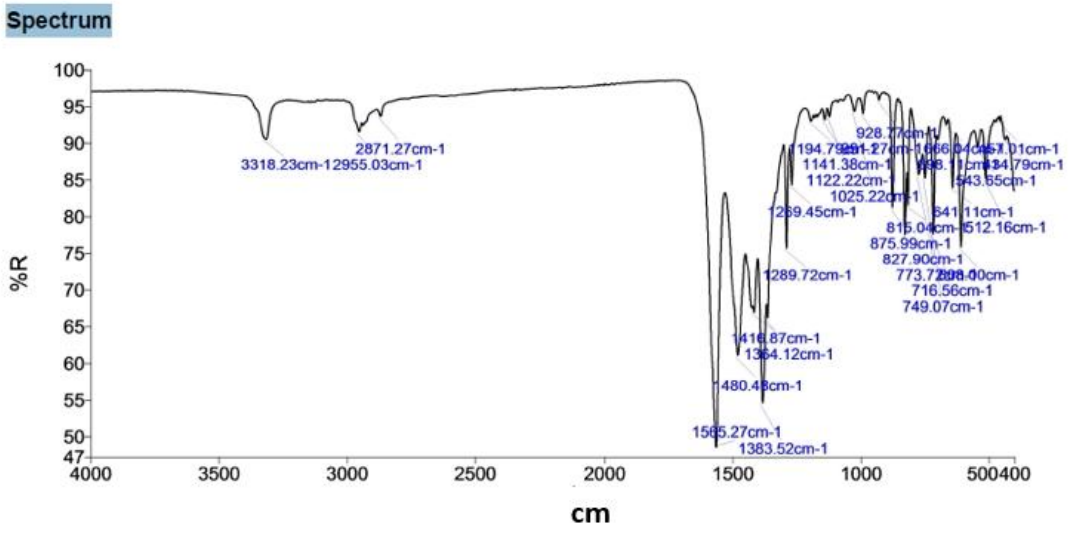

Fig 6b Fourier-transform infrared spectroscopy data of the Zn complex

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Bioactivity assay

At 0.005 g/l of all chemical treatments the mycelial growth did not differ statisticallyfrom the control. For the Ca complextreatments at 0.04, 0.08, and 0.16 g/l as well as phosphite at 0.16 and 0.08 mycelial growth differed statistically to the control. In contrast, mycelial growth in all concentrations of Zn complexdid not differ to the control. The Ca chelate reduced mycelial growth of *P. cinnamomi* more than any of the other treatments tested (table 4 and Fig 7).

Table 4. Dry weights (±SE) and EC_{50} values of* Phytophthora cinnamomi *grown in liquid Ribeiro's modified medium For each column, values with the same letter are not significantly different (P≤ 0.05).

Treatments	**[1]Conc.g/l**	**Dry weight (µg)**	**EC_{50}**
Control	0	2.14+0.21 d	100
Phosphite	0.005	2.14+0.08 d	100
Phosphite	0.04	1.90+0.12 d	87
Phosphite	0.08	1.57+0.21 c	73
Phosphite	0.16	1.38+0.33 b	67
Ca complex	0.005	2.09+0.53 d	100
Ca complex	0.04	1.42+0.33 b	67
Ca complex	0.08	1.28+0.14 b	60
Ca complex	0.16	1.04+0.25 a	47
Zn complex	0.005	2.14+0.08 d	100
Zn complex	0.04	2.00+0.08 d	93
Zn complex	0.08	2.00+0.21 d	93
Zn complex	0.16	1.85+0.16 d	87

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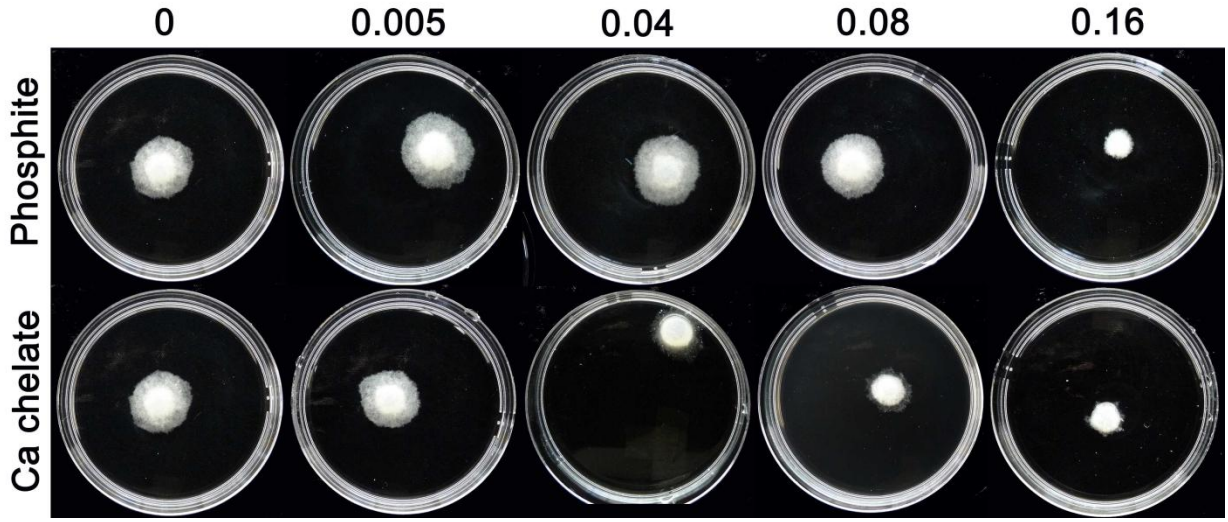

Figure 7.Colony growth of* Phytophthora cinnamomi *grown in liquid Ribeiro's modified medium in the presence of Ca chelate with Phosphite, the concentration of the chemical of g/l

Ligand complexes represent a novel group of candidates with potential as fungicides to control a range of plant pathogens including *Phytophthora* species. The XRD results showed similar patterns for both complexes indicating a similar crystal structure for both of them. This finding is consistent with that of[35]who indicated that similar complex patterns lead to similar crystal structures. The FT-IR results confirmed the presence of carboxylic and amine groups as well as metal-nitrogen υ(M-N) and metal–oxygen υ(M-O) in the metal complexes[31,32,34].Whilst, the UV-Vis results confirmed the presence of an aromatic ring. This result agrees with the findings of[36]Sanap and Patil (2013). The yield of the Zn complex was at 50% of basic materials whilst the yield of the Ca chelate was better at 81% of basic materials. The higher yield of Ca complex makes it more suitable than the Zn complex as a potential fungicide. These results were consistent with numerous studies[37-40]. Good biological activity of mixed ligand complexes against pathogenic microorganisms in both animals and plants.

The results of the present study show that Ca complex effectively inhibit the growthof *Phytophthora cinnamomi.*A possible explanation for the significant effect of Ca chelate might be that calcium ions stimulate may inhibit the growthof *Phytophthora* species by suppression of sporangia formation[41,42].

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