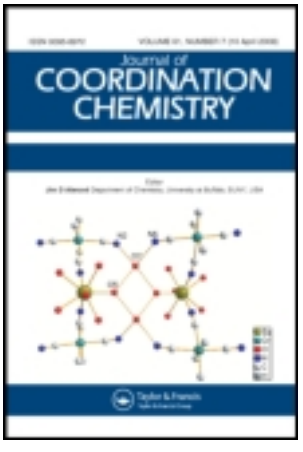

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Synthesis, characterization, and crystal structure of Ni(II) and Cu(II) complexes with *N*-furoyl-*N*′,*N*′-diethylthiourea: antifungal activity

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The complexes *cis-bis*(*N*-furoyl-*N*′,*N*′-diethylthioureato-k^2O,S)nickel(II) and *cis-bis*(*N*-furoyl-*N*′,*N*′-diethylthioureato-k^2O,S)copper(II) were prepared by the reaction of metal acetate with the corresponding acylthiourea derivative. The complexes were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and single-crystal X-ray diffraction. Both complexes show two furoylthiourea ligands bonded to metal to form a four-coordinate complex with square-planar geometry. The antifungal activity of the prepared complexes was studied against the phytopathogenic fungi *Botrytis cinerea* and *Colletotrichum gloeosporioides*, responsible for important plant diseases.

Keywords: Nickel(II) complex; Copper(II) complex; Acylthiourea; Crystal structure; Antifungal activity

1. Introduction

N-acyl-*N*′,*N*′-disubstituted thioureas are bidentate chelating ligands with S and O as donors, forming stable metal complexes with transition and noble metal ions. During complex formation, the ligand is deprotonated, resulting in a neutral complex.

Many transition metal complexes with thiourea derivatives have been reported [1–3]. *N*-benzoyl and *N*-furoyl thioureas have received more attention because this kind of ligand displays rich coordination chemistry and shows varied coordination behavior [4–6]. *N*-acylthioureas form very stable bidentate complexes (*cis* conformation preferred) with a six-membered ring chelate structure and stoichiometry generally being 1 : 2 (M : L, with M = metal ion and L = ligand).

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The biological activities of complexes with thiourea derivatives have been successfully screened for various actions [7–9]. We have recently begun to examine the coordination behavior of a series of substituted furoylthiourea derivatives [10]. In this article, the binding of *N*-furoyl-*N*′,*N*′-diethylthiourea to Ni(II) and Cu(II) is studied as such compounds could be used as antimicrobial agents in agriculture. We report herein IR, ^{1}H-NMR, ^{13}C-NMR spectra, and X-ray structural analysis of the complexes, as well as their antifungal activity against two phytopathogenic fungi: *Botrytis cinerea* and *Collctotrichum gloeosporioides*. These pathogens are widely distributed and cause gray mold on many economically important crops and anthracnose disease on fruits, respectively.

2. Experimental

2.1. *Chemicals and instrumentation*

All reagents and solvents were purchased from commercial sources of analytical grade. Elemental analyses (C, H, N, and S) were performed on a Perkin-Elmer 2400 CHN instrument. IR spectra were recorded on a Nicolet NEXUS 670 IR spectrophotometer using KBr discs. ^{1}H- and ^{13}C-NMR spectra were recorded on an Advance 300 Bruker spectrometer with $CDCl_3$ as solvent, and the assignment of the signals in the ^{13}C-NMR spectra was supported by DEPT-135° spectrum.

Single-crystal X-ray data were collected on a Bruker Smart Apex CCD diffractometer up to $2\theta_{max}$ of 50.7° with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ϕ–ω scan technique. The structures were solved by direct and conventional Fourier methods using SHELXS [11]. Full-matrix least-squares refinements were based on F^2. All non-hydrogen atoms were refined anisotropically; geometrically placed hydrogens were refined with a "riding model" using SHELXL [11]. Further details concerning data collection and refinement are given in table 1.

2.2. *Synthesis of the ligand and complexes*

N-furoyl-*N*′,*N*′-diethylthiourea, HL, was prepared by a procedure similar to that reported in [12]. To 30 cm^3 of ethanol containing HL (2 mmol), an ethanol solution of metal acetate (1 mmol) was added at room temperature for 2 h, and the resulting mixture was stirred for 30 min. The solid complexes were filtered off and recrystallized from ethanol. Single crystals were obtained after 1 week by slow evaporation of a chloroform solution of the complexes.

2.2.1. cis-bis(N-furoyl-*N*′,*N*′-diethylthioureato-k^2O,S)nickel(II) [NiL_2]. Brown. Yield, 74.0%. Anal. Calcd for $C_{20}H_{26}NiN_4O_4S_2$ (%): C, 47.17; H, 5.15; N, 11.00; S, 12.59. Found: C, 47.05; H, 5.22; N, 11.05; S, 12.64. IR (KBr): $\nu = 3050$ (CH), 3018 (CH), 1580 (C=C), 1514, 1409 (CN), 1072 (CS) cm^{-1}. ^{1}H-NMR ($CDCl_3$), ppm: $\delta = 1.20$ (t, $J = 7.05$ Hz, 3H, CH_3); 1.24 (t, $J = 7.10$ Hz, 3H, CH_3); 3.72 (q, $J = 6.97$ Hz, $J = 6.95$ Hz, 1H, CH_2); 6.41 (dd, $J = 3.13$, $J = 1.61$ Hz, 1H, Fr); 7.03 (d, $J = 3.16$ Hz, 1H, Fr), 7.52 (s, 1H, Fr); ^{13}C-NMR ($CDCl_3$), ppm: 171.0 (CS), 163.1 (CO), 150.68, 145.16

Table 1. Summary of crystal data and refinement parameters for the complexes.

Compound	$[NiL_2]$	$[CuL_2]$
Empirical formula	$C_{20}H_{26}NiN_4O_4S_2$	$C_{20}H_{26}CuN_4O_4S_2$
Formula weight	509.28	514.11
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	8.095(1)	8.876(3)
b	8.885(1)	12.371(4)
c	16.421(2)	12.654(4)
α		66.296(4)
β	92.830(2)	71.309(4)
γ		75.176(4)
Volume (Å^3), Z	1179.8(2), 2	1192.2(7), 2
Calculated density (Mg m^{-3})	1.434	1.432
Absorption coefficient (mm^{-1})	1.032	1.124
$F(0\,0\,0)$	532	534
Crystal size (mm^3)	$0.172 \times 0.154 \times 0.126$	$0.40 \times 0.08 \times 0.08$
θ range for data collection (°)	2.48–25.36	1.81–25.38
Limiting indices	$-9 \le h \le 9$	$-10 \le h \le 10$
	$-10 \le k \le 10$	$-14 \le k \le 14$
	$-19 \le l \le 19$	$-15 \le l \le 15$
Reflections collected	9834	12,890
Independent reflections (R_{int})	4322 (0.0298)	4365 (0.0531)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Goodness-of-fit on F^2	1.007	1.025
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0423$; $wR_2 = 0.0932$	$R_1 = 0.0501$; $wR_2 = 0.1103$
Largest difference peak and hole (e Å)$^{-3}$	0.429 and −0.178	0.463 and −0.294
Absolute structure parameter[a]	0.014(15)	

[a]H.D. Flack. *Acta Cryst.*, **A39**, 876 (1983).

(C-arom), 111.43 (C-arom), 115.23 (C-arom), 45.79 (CH_2), 45.27 (CH_2), 12.98 (CH_3), 12.38 (CH_3).

2.2.2. cis-bis(N-furoyl-*N′*,*N′*-diethylthioureato-k^2O,S)copper(II) $[CuL_2]$. Green. Yield, 74.0%. Anal. Calcd for $C_{20}H_{26}CuN_4O_4S_2$ (%): C, 46.72; H, 5.10; N, 10.90; S, 12.47. Found: C, 47.03; H, 5.19; N, 11.05; S, 12.64. IR (KBr): $\nu = 3058$ (CH), 3030 (CH), 1583 (C=C), 1520, 1412 (CN), 1090 (CS) cm^{-1}.

2.3. *Antifungal activity of complexes*

The cultures of fungi employed in this study, *C. gloeosporioides* 20122 and *B. cinerea* 2100, were obtained from the "Colección Española de Cultivos Tipos," Facultad de Biología, Universidad de Valencia, Spain, where a culture of this strain is deposited. Bioassays were performed by measuring inhibition of radial growth on an agar medium in a Petri dish. The test compound was dissolved in DMSO and added to a glucose–malt–peptone–agar medium (61 g of glucose–malt–peptone–agar per liter, pH 6.5–7.0) to give final compound concentrations of 1 and 0.5 mmol L^{-1}. The final DMSO concentration was identical in both control and treated cultures. The medium was

poured into sterile plastic Petri dishes (6 cm diameter for the treated cultures and 15 cm diameter for the control) and, after solidification, a 6 mm diameter mycelial disc of fungus cut from a 24 h old culture was placed in the center of the agar plate. All inoculated plates were incubated at 25°C and the inhibition of radial growth was measured for 5 days. Growth inhibition was calculated as the percentage of radial growth inhibition (RI) relative to the control using the modified Vincent formula [13]: $RI = 100(C - T)/(C - 6)$, where C is the colony diameter in the control and T is the colony diameter in the treatment. Results are the means of at least three independent experiments.

3. Results and discussion

3.1. *IR spectra*

The main vibrational bands of the investigated complexes are given in Section 2. IR spectra of the complexes show significant changes when compared with IR spectra of the corresponding ligand [14]. The most striking change is the N–H stretching frequency at 3300 cm^{-1} in the free ligand, which disappears completely in the complexes, in agreement with the molecular structures in figures 1 and 2. Another striking change is observed for the carbonyl stretching vibration. A strong absorption at 1683 cm^{-1} for HL is ascribed to the stretching of the carbonyl group, which shifts to lower frequencies upon complexation of thiourea because deprotonation induces a large degree of electron delocalization within the chelate rings. The same trend is observed for thiocarbonyl stretching vibration frequency, at 1267 cm^{-1} in the free ligand, and shifts to lower frequencies after complexation; unfortunately, this vibration could not be assigned unambiguously. This is also in agreement with the crystal structures determined for the complexes and suggests that the oxygen of carbonyl and the sulfur of thiocarbonyl are coordinated.

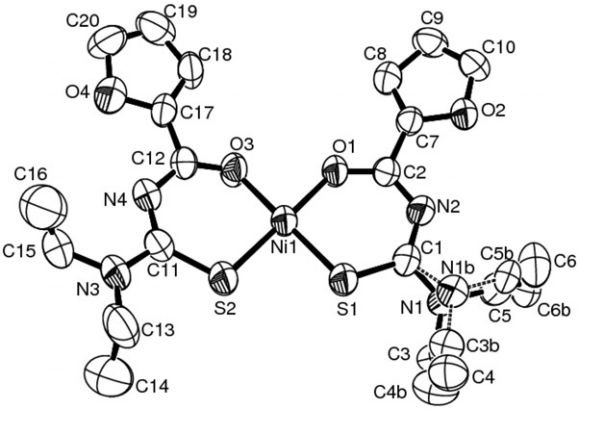

Figure 1. ORTEP drawing of $[NiL_2]$ with hydrogens omitted for clarity. Disorder of one amide group is shown. Thermal ellipsoids are drawn at the 30% probability level.

3.2. *NMR spectra*

Characteristic ^{1}H-NMR and ^{13}C-NMR signals for nickel complex are given in section 2. The N–H signal at 8.35 ppm in HL is not present in the corresponding complex as a consequence of coordination, in agreement with IR results [15]. In ^{13}C-NMR spectra, the signals at 178.3 (C=S) and 153.8 ppm (C=O), typical of the free ligand, disappear. Two new signals, assigned to quaternary carbons, were at 171.0 and 163.1 ppm instead, in accord with the proposed structure for the complex. The effects of circulating π electrons of the chelate rings could account for the opposite displacements that have been found with respect to the free ligand, especially in carbons corresponding to thiocarbonyl and carbonyl groups, with shifts to lower and higher frequencies, respectively.

3.3. *Single-crystal X-ray study*

The molecular structures of complexes are shown in figures 1 and 2. Selected bond lengths and angles are listed in table 2. In the structures, the two furoylthiourea molecules adopt a *cis* conformation, bounded to the central ion by two S and two O atoms. The coordination geometry of both complexes is a distorted square-plane as reflected by O–M–S (M = Ni, Cu) angles. The angles are significantly shorter for [CuL_2]. In the [NiL_2] complex, the Ni–O bond distances [1.862(2) and 1.870(3) Å] are very similar to related structures [16, 17]. As expected, Ni–O bond distance is shorter than Ni–S bond distances [2.137(1) and 2.144(1) Å]. The distances of nickel, sulfur, and oxygen from the best plane through the coordination sphere are −0.015(8), −0.008(0), and −0.0095(0) Å, respectively. The chelate ring systems, Ni1–O1–C2–N2–C1–S1 and Ni1–O3–C12–N4–C11–S2, are nearly planar as well with the largest deviations from the best plane being 0.116(2) Å for O1 and 0.115(1) Å for Ni1. The dihedral angle between these chelate planes is 6.70(6)°. The furan oxygens occupy distal positions, unlike the diphenyl analog [18] which shows proximal positions. In these structures, the furan rings can freely rotate around the C–N single bond because they do not encounter

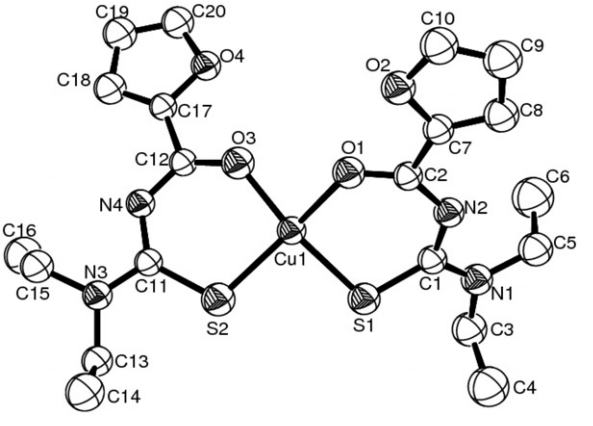

Figure 2. ORTEP drawing of [CuL_2] with hydrogens omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for the complexes.

[NiL_2]		[CuL_2]	
Ni1–O1	1.862(2)	Cu1–O1	1.921(2)
Ni1–O3	1.870(3)	Cu1–O3	1.917(2)
Ni1–S1	2.137(1)	Cu1–S1	2.238(1)
Ni1–S2	2.144(1)	Cu1–S2	2.226(1)
C1–N2	1.335(5)	C1–N2	1.339(4)
C2–N2	1.306(5)	C2–N2	1.319(4)
C1–S1	1.722(4)	C1–S1	1.729(4)
C11–S2	1.733(4)	C11–S2	1.728(4)
C2–O1	1.274(4)	C2–O1	1.258(4)
C12–O3	1.254(4)	C12–O3	1.257(4)
O3–Ni1–S1	178.6(1)	O3–Cu1–S1	160.1(1)
O1–Ni1–S2	178.9(1)	O1–Cu1–S2	161.6(1)
O1–Ni1–O3	84.5(1)	O1–Cu1–O3	85.7(1)
S1–Ni1–S2	85.0(1)	S1–Cu1–S2	90.83(4)
O3–Ni1–S2	94.9(1)	O3–Cu1–S2	95.1(1)
O1–Ni1–S1	95.6(1)	O1–Cu1–S1	94.60(8)
C11–S2–Ni1	108.7(1)	C11–S2–Cu1	107.6(1)
C1–S1–Ni1	108.2(2)	C1–S1–Cu1	104.6(1)
C12–O3–Ni1	130.9(2)	C12–O3–Cu1	129.6(2)
C2–O1–Ni1	131.3(3)	C2–O1–Cu1	130.2(2)
O1–C2–C7	113.2(3)	O1–C2–C7	116.5(3)
O1–C2–N2	130.5(3)	O1–C2–N2	130.3(3)
N2–C1–N1	115.2(4)	N2–C1–N1	114.8(3)
N1–C1–S1	116.8(4)	N1–C1–S1	117.7(3)
C1–N1–C3	120.7(6)	C1–N1–C3	123.5(3)
C2–N2–C1	124.0(3)	C2–N2–C1	124.5(3)

serious steric hindrance. One ethylamine group is disordered over two sites, common for Ni(II) complexes with *N*-acyl-*N′*,*N′*-dialkylthioureas [19]. The unit cell diagram of the nickel complex is shown in figure 3. In the crystal structure, the molecules are linked by weak C–H $\cdots$ O intermolecular contacts forming infinite chains expanding along the *b*-axis, in which furan atom C8 at (x, y, z) acts as a hydrogen-bond donor, *via* H8, to furan atom O2 at $(-x, \frac{1}{2}+y, -z)$.

In [CuL_2] the distances of copper, sulfur, and oxygen from the best plane through the coordination sphere are −0.000(1), −0.069(3), and 0.577(8) Å, respectively. The chelate ring systems, Cu1–O1–C2–N2–C1–S1 and Cu1–O3–C12–N4–C11–S2, deviate significantly from planarity with the largest deviations from the best plane being 0.197(3) Å for O1 and 0.104(10) Å for C11. The dihedral angle between these chelate planes is 33.1(3)°. Compared to [NiL_2] complex, the copper complex shows a more accented distortion from square-planar toward tetrahedral geometry [20–22]. Also, the furan oxygens occupy proximal positions. The unit cell diagram of the copper complex is shown in figure 4. In the crystal structure there are weak C–H $\cdots$ O and C–H $\cdots$ S intermolecular contacts forming hydrogen-bonded $R_2^2(16)$ and $R_2^2(14)$ centrosymmetric rings [23], respectively, as well as weak C–H $\cdots$ C intermolecular interactions forming hydrogen-bonded $R_1^2(7)$, which join the complex molecules into ribbons expanding along the [1 1 0] direction.

The lengths of the C–N bonds in the chelate rings are all shorter than the average C–N single bond distance of about 1.48 Å. In addition, the bond distances of the C–S and C–O in the chelate ring are longer than average C=S and C=O double bond

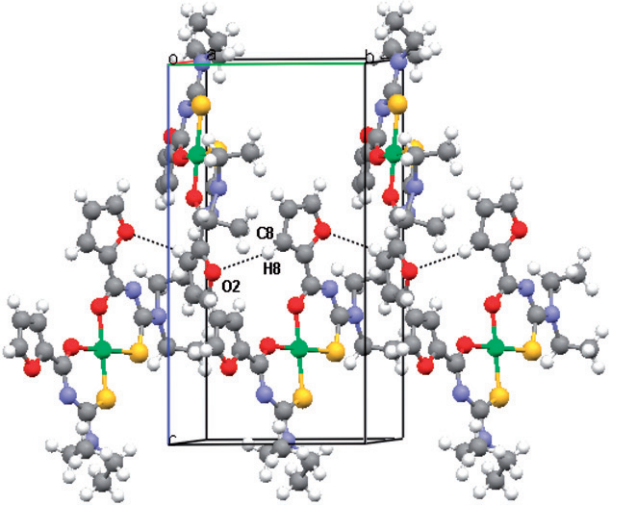

Figure 3. Unit cell diagram of the hydrogen-bonded [NiL_2]. Only the major component of disorder is shown. C–H···O hydrogen bonds are shown as dashed lines.

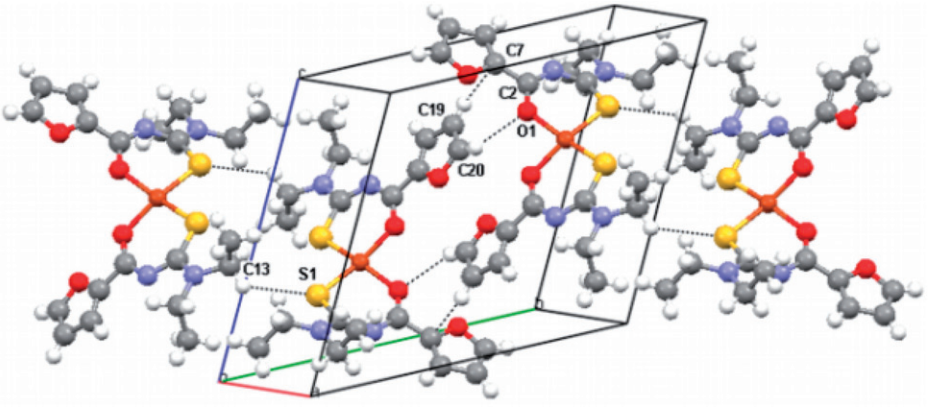

Figure 4. Unit cell diagram of the hydrogen-bonded [CuL_2]. C–H···O, C–H···S, and C–H···C hydrogen bonds are shown as dashed lines.

distances of thiourea derivatives [24–26]. These results can be explained by the delocalization in the chelate rings, which is also supported by IR and NMR data. The C–S bond distances in the complexes are longer than the average C–S bond length in the free ligand (CCDC No. 689278), indicating that the C–S bond distance is sensitive to coordination.

3.4. *Antifungal activity*

The antifungal properties of the Ni(II) and Cu(II) complexes and the furoylthiourea ligand described herein were determined against the growth of the plant pathogenic

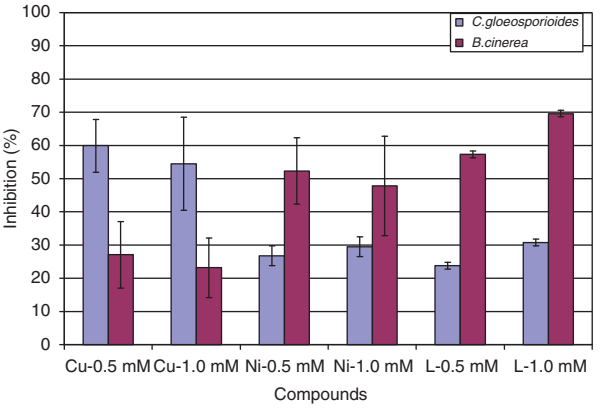

Figure 5. Antifungal activity of complexes, expressed as RI on PDA at 25°C and an incubation of 6 days. The high standard deviations in some data are due to the low solubility of the complexes in the culture medium.

fungi *B cinerea* and *C. gloeosporioides* by the "poisoned food" technique [27, 28] (section 2). Figure 5 shows the antifungal effect displayed by the complexes and the ligand at 0.5 and 1.0 mmol L^{-1}. Curiously, the sensitivity of both microorganisms to the tested complexes was found to be opposite. So, the inhibition of mycelial development of *C. gloeosporioides* by the $[CuL_2]$ complex was higher than that of the $[NiL_2]$ complex, while the inhibition rate of $[CuL_2]$ complex was lower than that of the $[NiL_2]$ complex when *B. cinerea* was treated with these compounds.

Both complexes showed a similar antifungal activity, with a mean value of 40% for the $[NiL_2]$ complex and 44% for the $[CuL_2]$ complex at the concentration of 0.5 mmol L^{-1}. The percentage of inhibition observed for $[NiL_2]$ complex against *B. cinerea* at the concentration of 0.5 mmol L^{-1} was 52%. In spite of being lower than that of the commercial fungicide dichofluanid (>95% at 0.3 mmol L^{-1}) [29], it was higher than those reported using Ni(II) complexes with thiourea linked to benzoyl (about 35% at 0.9 mmol L^{-1}) or morpholine groups (0% at 0.9 mmol L^{-1}) [30]. Thus, furoyl radicals are a good alternative to increase the antifungal activity of this kind of complexes.

The furoylthiourea ligand showed a similar antifungal activity to that of the $[NiL_2]$ complex but lower than that of the $[CuL_2]$ complex against *C. gloeosporioides*. The inhibition rate of *B. cinerea* by this ligand was also similar to that of the $[NiL_2]$ complex but higher than that of the $[CuL_2]$ complex. These results seem to indicate that the biological activity against *B. cinerea* could be correlated with the ligand activity while the presence of the metal could be necessary for the enhancement of the activity against *C. gloeosporioides*.

According to the data obtained, the antifungal effect of both complexes could be considered for integrated pest management strategies in the agricultural setting against *B. cinerea* or *C. gloeosporioides* since the cost of these compounds suggests their use in combination with less expensive synergic methods for controlling plant pathogenic fungi. Nevertheless, studies about the toxicity of these complexes are needed before being used as protective agents against plant diseases caused by fungi.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 689278 for ligand, CCDC No. 689279 for the Ni(II) complex, and CCDC No. 689280 for the Cu(II) complex. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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