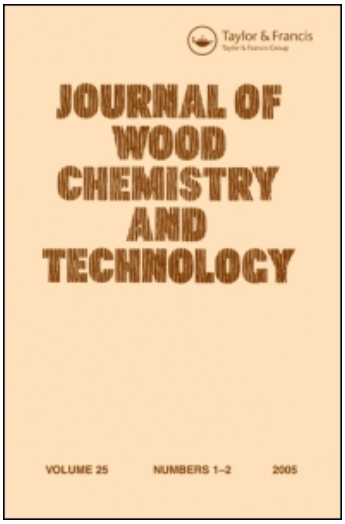

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Formation and Structure of Metal Complexes with the Fungicides Tebuconazole and Propiconazole

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Abstract: Divalent copper and zinc complexes with metal:azole ratio 1:2 were readily formed at room temperature with the fungicides tebuconazole and propiconazole. The structure of copper and zinc tebuconazole acetate and zinc *cis*-propiconazole chloride were examined by X-ray crystallography. In copper tebuconazole acetate, the copper atom lies on a crystallographic inversion center and is coordinated to two triazole and two acetate ligands in a *trans* arrangement. The two binding tebuconazole N atoms and two close binding acetate O atoms form a square plane. The two remaining acetate O atoms have more distant interactions, thus forming an elongated octahedron around the copper atom. The coordination geometry of zinc tebuconazole acetate is tetrahedral and the metal is bound to two triazole and two acetate ligands. The

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geometry is distorted from regular owing to the size of the tebuconazole ligands. The butyl chains are less folded than for the copper tebuconazole complex, resulting in a more extended molecule. The coordination geometry of zinc *cis*-propiconazole chloride is also tetrahedral with the metal atom bonded to two triazole and two chloride ligands.

Keywords: Copper, zinc, tebuconazole, propiconazole, complex, X-ray crystallography, fungicide, wood preservative

INTRODUCTION

Restrictions on the use of chromated-copper-arsenate (CCA) preservatives have led to the development and commercialization of a range of new wood preservatives that do not contain arsenic or chromium.[1,2] The two most widely used preservatives that have replaced CCA are ACQ (ammoniacal copper quaternary) and copper-azole. Both are formulated as water-based alkaline solutions through the use of amine-containing co-solvents, typically ammonia or ethanolamine, and rely on the presence of copper and an organic co-biocide for their effectiveness against microbial pathogens. The organic biocides used in copper-azole may include, but are not restricted to, the azole preservatives known commercially as tebuconazole and propiconazole. Preservatives containing zinc and tebuconazole are described in the patent literature, but they have not been commercialized.[3–6]

FTIR studies have confirmed that the fixation of copper-amine preservatives in wood involves the neutralization of acidic (carboxylic) groups in hemicelluloses and phenolic hydroxyl groups in lignin to form copper-amine-wood complexes.[7] Model studies with vanillin and amine-copper sulphate also suggested that copper-amine wood preservatives may form stable copper-nitrogen-lignin complexes by reaction with guaiacyl units.[8,9] Some wood preservatives fix in wood when their individual components react to form insoluble end products. For example, the fixation of CCA in wood occurs, in part, through the reaction of its individual copper, chromium and arsenic components to form insoluble, amorphous, copper and chromium arsenates as well as other inorganic compounds.[10,11]

There is ample evidence in the literature that triazoles will complex with metals,[12–14] and thus it seems plausible, depending on pH and the nature and ratio of other formulation components, that metal-centered azole complexes are present in copper-azole treatment formulations and in treated wood. This is not only of fundamental interest, but also has practical implications because of suggestions that the formation of metal azole complexes can either enhance[15,16] or reduce[17] the biocidal efficacy of preservative formulations. The other important consideration related to the formation of metal-centered azole complexes is possible active ingredient loss by precipitation or crystallization from wood preserving formulations prior to wood treatment.

This article investigates the formation of metal azole complexes *in vitro*, the structure of the complexes formed and comments on the possibility of their

presence in copper-amine wood preserving formulations and in treated timber. Experiments were conducted with both copper and zinc compounds and two commonly used azole biocides, propiconazole and tebuconazole.

EXPERIMENTAL

Preparation of Metal Complexes

Tebuconazole as used in wood preservation contains a racemic mixture of the two optical isomers shown in Figure 1. Propiconazole is a mixture of *cis* and *trans* isomers, both of which are present as racemic mixtures. *Cis*-propiconazole with the triazolyl group on the same side of the dioxolan ring as the propyl group is shown in Figure 2. The reactions of zinc and copper compounds with tebuconazole and propiconazole were examined in several solvent systems under a range of conditions. Molar ratios of metal salt to triazole used were 1:2 and 1:1. Crystalline complexes yielding single crystals suitable for structural characterization by X-ray crystallography were obtained as described later. The complexes prepared had a metal:triazole ratio of 1:2.

Zinc Tebuconazole Acetate

Ethanol (70 mL) was added to a solution of zinc acetate dihydrate (1.424 g, 6.49 mmol) in water (50 mL). The resulting slightly cloudy solution was filtered through fluted filter paper and became completely clear. Technical tebuconazole (97% pure, 2.0 g, 6.30 mmol) was dissolved in ethanol (70 mL). Water (50 mL) was added to the tebuconazole solution and the resulting solution remained completely clear. The tebuconazole solution was then added to the zinc acetate solution and the product solution, which remained completely clear, was then divided into two equal portions in

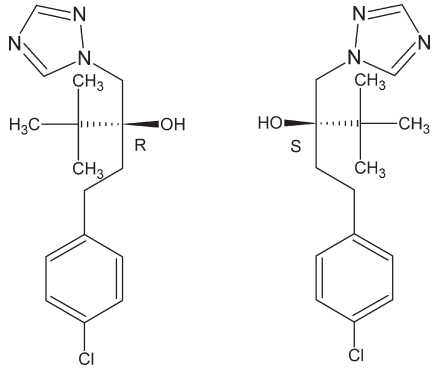

Figure 1. Structure of R and S tebuconazole.

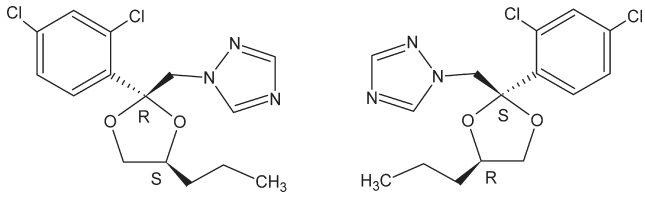

Figure 2. Structure of 2R4S and 2S4R *cis*-propiconazole.

separate 250 mL conical flasks. Traces of crystalline zinc tebuconazole acetate from an earlier preparation were then added to one of the flasks. Noticeable formation of sugar-like crystals took place within two to three hours of seeding and the crystalline deposit was filtered after 2 days, washed with 3×20 mL of ethanol and air dried. Yield 850 mg, 1.064 mmol, 68% allowing for the fact that only one half of the product solution was seeded at this time. A crystal was selected from this batch for X-ray analysis. The solution in the unseeded flask was kept at room temperature and remained completely clear for more than three months. It was then seeded with traces of crystalline zinc tebuconazole acetate from an earlier preparation and, as before, sugar-like crystals were formed within two to three hours. The above preparations were carried out at an approximate 1:1 molar ratio of zinc salt to tebuconazole. In preliminary work with a molar ratio of zinc salt to tebuconazole of 1:2, seeding appeared to be less critical and in one preparation crystals formed in solution after 17 days, even without seeding.

Copper Tebuconazole Acetate

Copper acetate monohydrate (0.648 g, 3.25 mmol) was taken up in ethanol (35 mL) and water (25 mL). The solution was warmed on a hot plate, but a small amount of solid remained undissolved. The solution was filtered slowly through fluted filter paper overnight. Technical tebuconazole (97% pure, 1.0 g, 3.15 mmol) was dissolved in ethanol (35 mL). Water (25 mL) was then added to this solution and the resulting solution remained completely clear. The tebuconazole solution was then added to the filtered copper acetate solution. There was an immediate deepening of the blue color indicating formation of copper triazole complex, but no crystalline deposit was apparent even after standing at room temperature for 2 weeks. The deep blue product solution was then kept at 5°C for 3 days, but there was still no formation of crystalline deposit. The solution was then cooled to -15°C for 2.5 h, and returned to room temperature. Some powdery deposit was now evident, but no crystals had formed yet. The solution was then filtered through fluted filter paper and again set aside at room temperature. Traces of material were scraped from the dried fluted filter paper and sprinkled into

the solution in an attempt to promote crystallization. After a further 3 days violet prisms had begun to form in the solution. They grew steadily and became more numerous in the following two days. They were then filtered, washed with 3 × 10 mL portions of ethanol and air dried. Yield 430 mg, 0.539 mmol, 34%. A crystal was selected for X-ray analysis.

Separation of Propiconazole Isomers

Technical propiconazole is a racemic mixture of *cis* and *trans* isomers, as mentioned earlier. The major *cis* isomer (Figure 2) used to form crystalline zinc *cis*-propiconazole chloride was isolated by column chromatography as follows. A silica chromatography column was prepared by packing Merck silica gel 60, 70–230 mesh (270 g) in ethyl acetate-hexane 1:10. Technical propiconazole (94% pure, 5.0 g) dissolved in ethyl acetate-hexane 1:1 (10 mL) was carefully applied to the top of the column, which was then eluted with ethyl acetate-hexane 1:1. A high flow rate of 8.5 mL per min was found to be quite adequate for good separation of the isomers. The solvent polarity was increased to ethyl acetate-hexane 3:2 during the course of the separation. 40 mL fractions were collected and analyzed by thin layer chromatography on Merck aluminium backed silica gel 60, F254 thin layer plates using ethyl acetate-hexane 1:1 as solvent. Rf of the more mobile less polar *cis* isomer was found to be 0.63 while that of the less mobile more polar *trans* isomer was 0.48. The central fractions of both eluates were combined. Pure *cis*-propiconazole (1.6 g) and pure *trans*-propiconazole (1.2 g) were obtained.

Zinc *cis*-Propiconazole Chloride

Pure *cis*-propiconazole (500 mg, 1.461 mmol) was dissolved in ethanol (5 mL) and the solution was mixed with a solution of anhydrous zinc chloride (100 mg, 0.734 mmol) in ethanol (5 mL). Deposition of the complex commenced within several minutes without seeding. After standing at room temperature for several days, the white crystalline product was filtered by suction, washed with ethanol (10 mL) and air dried. Yield 505 mg, 0.615 mmol, 84%. Colourless needles (m.p. 163–164°C), which tended to form in bunches were obtained after recrystallization from ethanol. One of these was selected for X-ray analysis.

Single Crystal X-Ray Diffraction Studies

Representative crystals for each of the three samples were covered in viscous oil and mounted onto a glass fiber. Low-temperature (≈123 K) data were collected on an Enraf-Nonius CCD area-detector diffractometer (MoKα

radiation, λ 0.71073 Å, frames comprised 1.0° increments in ϕ and ω yielding a sphere of data). Each data set was merged (R_{int} as quoted) to N unique reflections; the structures were solved by conventional methods and refined with anisotropic thermal parameter forms for the non-hydrogen atoms by full-matrix least-squares on all F^2 data using software for crystal structure solution and refinement.[18] Hydrogen atoms were included in calculated positions and allowed to ride on the parent atom with isotropic thermal parameters. Data were corrected for absorption by empirical ([Cu(tebuc)$_2$(OAc)$_2$], [Zn(tebuc)$_2$(OAc)$_2$]) or numerical ([Zn(*cis*-propic)$_2$Cl$_2$]) methods. Crystal data and refinement details for each compound are listed later. CCDC reference numbers are CCDC-656046 to CCDC-656048. See deposit@ccdc.cam.ac.uk for crystallographic data in CIF format.

Crystal and Refinement Data

[Cu(tebuc)$_2$(OAc)$_2$]: $C_{36}H_{50}Cl_2Cu_1N_6O_6$ *FW* 797.26. Monoclinic $P2_1/n$. a 8.575(2), b 21.266(4), c 11.474(2) Å, β 107.26(3)°. V 1998.2(7) Å^3. $Z = 2$. Density (calcd.) 1.325 g/cm^3. μ(MoKα) 0.730 mm^{-1}. Crystal 0.28 × 0.20 × 0.16 mm. 2θmax 55.0°. N_{total} 23830, N 4546 (R_{int} 0.034). T_{min} 0.80, T_{max} 0.94. GoF 1.032, $R1$ 0.034, w$R2$ 0.086 ($I > 2\sigma(I)$), $R1$ 0.043, w$R2$ 0.090 (all data). Max/min residual e$^-$ density 0.455, −0.441 e/Å^3.

[Zn(tebuc)$_2$(OAc)$_2$]: $C_{36}H_{50}Cl_2N_6O_6Zn_1$ *FW* 799.09. Monoclinic $C2/c$. a 17.0570(3), b 32.0630(7), c 29.1412(6) Å, β 104.256(2)°. V 15446.5(5) Å^3. $Z = 16$. Density (calcd.) 1.374 g/cm^3. μ(MoKα) 0.826 mm^{-1}. Crystal 0.30 × 0.25 × 0.13 mm. 2θmax 50.0°. N_{total} 54381, N 13522 (R_{int} 0.104). T_{min} 0.79, T_{max} 0.90. GoF 1.024, $R1$ 0.079, w$R2$ 0.200 ($I > 2\sigma(I)$), $R1$ 0.151, w$R2$ 0.242 (all data). Max/min residual e$^-$ density 3.089, −0.663 e/Å^3. The maximum residual e$^-$ density peak was located 0.28 Å from Zn(I).

[Zn(*cis*-propic)$_2$Cl$_2$]: $C_{30}H_{34}Cl_6N_6O_4Zn_1$ *FW* 820.70. Orthorhombic *Fdd*2. a 23.2071(4), b 56.4622(12), c 5.4583(1) Å, V 7152.1(2) Å^3. $Z = 8$. Density (calcd.) 1.524 g/cm^3. μ(MoKα) 1.179 mm^{-1}. Crystal 0.20 × 0.04 × 0.04 mm. 2θmax 56.6°. N_{total} 18628, N 3997 (R_{int} 0.088). T_{min} 0.87, T_{max} 0.97. GoF 1.009, $R1$ 0.045, w$R2$ 0.065 ($I>2\sigma(I)$), $R1$ 0.094, w$R2$ 0.075 (all data). Absolute structure parameter −0.012(13). Max/min residual e$^-$ density 0.619, −0.532 e/Å^3.

RESULTS AND DISCUSSION

Literature procedures for the preparation of metal azole complexes typically involve mixing and possibly heating solutions of the appropriate reactants in suitable solvents for short time periods, followed by filtration of the

crystalline deposits. For example zinc 4-benzyl-1,2,4-triazole chloride with metal:azole ratio 1:2 was prepared by mixing ethanolic solutions of zinc chloride and 4-benzyl-1,2,4-triazole, followed by filtration of the solid product.[12] Copper propiconazole sulphate and nickel and zinc propiconazole chloride all with metal:propiconazole ratio 1:2, have been reported, but the conditions for their preparation were not specified.[13] Copper $(\text{tebuconazole})_4(\text{chloride})_2$ was prepared by refluxing an ethanolic solution of copper chloride and tebuconazole for 6 h[19] and it appears to be the only metal complex of tebuconazole or propiconazole to have its crystal structure reported in the literature.

The complexes prepared in the present study had a metal:triazole ratio of 1:2 and the preparations were carried out at room temperature. The reasons for using mild conditions were to demonstrate the ease of complex formation and also to more closely approximate the temperatures of a typical wood preserving formulation and of the treated timber. There was great variability in the rate at which complexes crystallized from solution. Zinc *cis*-propiconazole chloride was deposited soon after the solutions were mixed. By comparison, in some instances, both zinc and copper tebuconazole acetate did not crystallize even after several weeks. The introduction of seed crystals soon after the reactant solutions were mixed triggered the deposition of crystalline zinc tebuconazole acetate and would probably also have been effective in the preparation of copper tebuconazole acetate.

The use of propiconazole in these studies was complicated, as mentioned earlier, by the presence of both *cis* and *trans* isomers in the technical active ingredient. Although solids were obtained using technical propiconazole, they were difficult to recrystallize and obviously their purity was suspect. Thus the technical product was purified by column chromatography on silica gel and the major *cis* isomer was used to prepare zinc *cis*-propiconazole chloride. In an analogous preparation, zinc *cis*-propiconazole acetate failed to crystallize and upon concentration of the product solution an oily deposit was obtained which could not be induced to solidify.

Crystals suitable for X-ray diffraction were readily obtained from the initial crystalline deposits of zinc and copper tebuconazole acetate. As both R and S tebuconazole (Figure 1) were employed, three different isomers of the metal complex molecule would be formed, two of which are mirror images of each other. The physical properties of the two mirror image isomers may well be different to those of the other isomer. Complexes prepared in this study are designated in accord with the chirality of the two azole ligands attached to the central metal atom and are thus either R/S, R/R, or S/S. With copper tebuconazole acetate only the R/S isomer was present in the crystal selected. It was probably the only isomer to crystallize from the product solution and this may be reflected in the relatively low product yield of 34%. With zinc tebuconazole acetate, all three isomers R/S, R/R, and S/S were found in the structure of the crystal selected and this may account for the higher (64%) product yield obtained.

The rapidly formed zinc *cis*-propiconazole chloride was recrystallized from ethanol. Again, because two isomers of *cis*-propiconazole 2R4S and 2S4R (Figure 2) were employed, three isomers of the metal complex, two of which are mirror images, would be formed. Their designation would be 2R4S/2S4R, 2R4S/2R4S, and 2S4R/2S4R. After recrystallization from ethanol the metal complex crystal selected was found to contain the 2S4R/2S4R isomer, one of the mirror image pair.

The molecular diagram for copper tebuconazole acetate [$Cu(tebuc)_2(OAc)_2$] is shown in Figure 3, along with selected bond distances and angles. The Cu(II) atom lies on a crystallographic inversion center (relating the two halves of the molecule) and is coordinated to the triazole groups of two tebuconazole ligands and to two acetate ligands in a *trans* arrangement. The N atoms and two acetate O atoms form a square plane, with Cu-N and Cu-O bond distances (Figure 3) comparable to those observed in similar complexes (e.g., Cu-N: 2.006(2), 2.021(2) Å in [$Cu(tebuc)_4Cl_2$] · 4EtOH;[19]

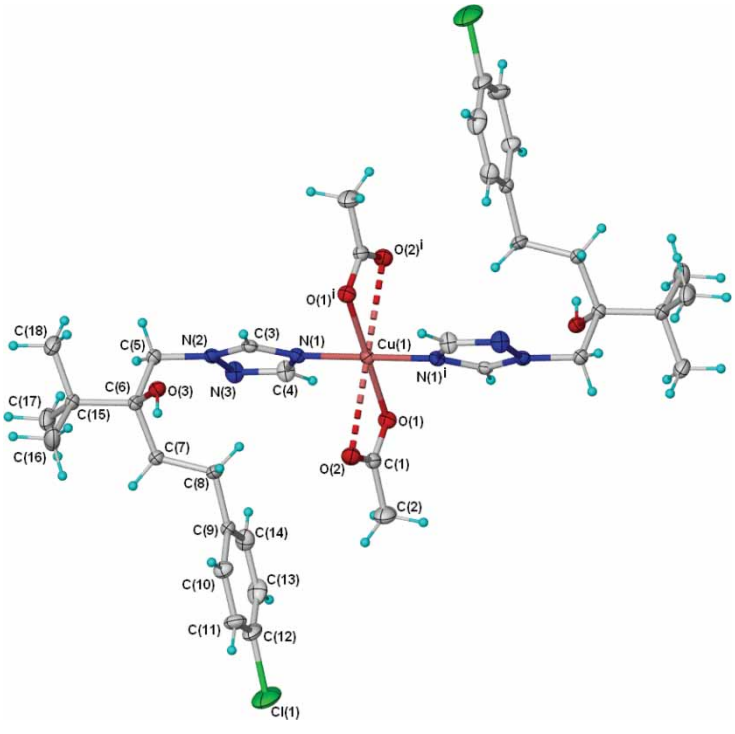

Figure 3. Molecular diagram of R/S-[$Cu(tebuc)_2(OAc)_2$] shown with 50% thermal ellipsoids and hydrogen atoms as spheres of arbitrary size. Atoms denoted^i are generated by symmetry ($^i1 - x, -y, - z$). Selected bond distances (Å) and angles (°): Cu(1)-N(1), 1.971(1), Cu(1)-O(1), 1.963(1), Cu(1)-O(2), 2.625(1), N(1)-Cu(1)-N(1)^i, 180.0, O(1)-Cu(1)-N(1), 89.71(5), O(1)-Cu(1)-N(1)^i, 90.29(5), O(1)-Cu(1)-O(1)^i, 180.0.

Cu-O:1.943(2) Å in $[Cu(L)_2(OAc)_2]$, L = 2,5-bis(1,2,4-triazolyl)pyridine).[20] The remaining two acetate O atoms have more distant interactions with the Cu atom (Figure 3), thus forming an elongated octahedron around the Cu atom, as was also observed in $[Cu(L)_2(OAc)_2]$ above (Cu-O:2.69(5) Å).[20] The *trans* triazole groups in $[Cu(tebuc)_2(OAc)_2]$ are parallel, but not co-planar (with the Cu atom displaced from the ring plane by 0.234(3) Å) and are canted by 36.79(7)° to the coordination plane. The unique tebuconazole ligand has an S configuration about the alcoholic carbon atom C(6), the inversion symmetry generating the R configuration for the second tebuconazole ligand. The pendant p-Cl-phenylbutyl arms are folded (torsion angle N2-C5-C7-C8 18.8(2)°) such that the aryl ring is situated perpendicular to the triazole moiety (dihedral angle 84.06(6)°) and adjacent to the coordinated acetate group, resulting in a relatively compact molecule. The ligand conformation is similar to those in $[Cu(tebuc)_4Cl_2] \cdot 4EtOH$ in which the dihedral angle of the triazole and aryl rings is 87.69(2)°.[19] In the current $[Cu(tebuc)_2(OAc)_2]$ complex, molecules are linked via pairs of hydrogen bonds between the hydroxyl and acetate groups on neighbouring molecules to form chains parallel to the *a* axis.

The zinc tebuconazole acetate complex $[Zn(tebuc)_2(OAc)_2]$ is shown in Figure 4, along with selected bond distances and angles. The crystal structure of the zinc complex has one complete and two half molecules in the asymmetric unit, the latter two with the Zn(II) atom on a crystallographic

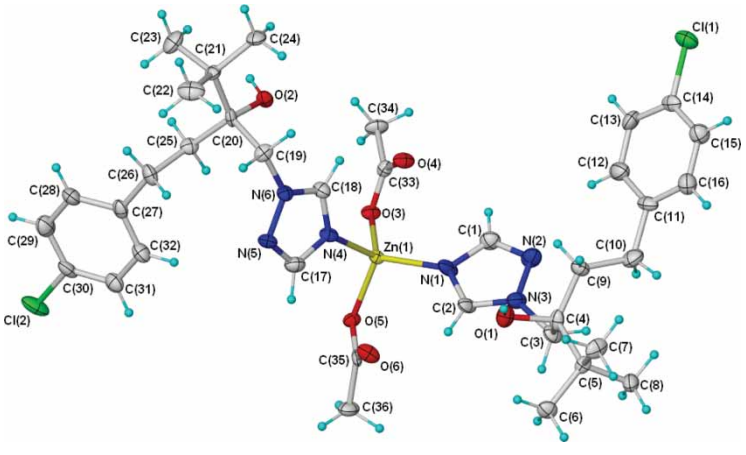

Figure 4. Molecular diagram of R/S-$[Zn(tebuc)_2(OAc)_2]$ shown with 50% thermal ellipsoids and hydrogen atoms as spheres of arbitrary size. The S/S and R/R isomers also present in the crystal structure are not shown. Selected bond distances (Å) and angles (°): Zn(1)-N(1), 2.015(4), Zn(1)-N(4), 2.027(4), Zn(1)-O(3), 1.976(4), Zn(1)-O(5), 1.987(4), N(1)-Zn(1)-N(4), 114.8(2), N(1)-Zn(1)-O(3), 114.4(2), N(1)-Zn(1)-O(5), 108.3(2), O(3)-Zn(1)-N(4), 110.2(2), O(3)-Zn(1)-O(5), 99.1(2), N(4)-Zn(1)-O(5), 108.8(2).

two-fold rotation axis relating the two halves of each of the molecules. The three molecules differ only in the configuration of the tebuconazole ligands (being R/S for Zn(1) and R/R and S/S for Zn(2) and Zn(3), respectively, *cf* solely the R/S diastereomer observed in the Cu complex earlier). The coordination geometry of the Zn centers is tetrahedral and the metal is bound to the triazole groups of two tebuconazole ligands and to two acetate groups. The geometry is distorted from regular by the size of the tebuconazole ligands as shown by the larger N-Zn-N and N-Zn-O angles (Figure 4). The coordinated triazole ring planes are approximately perpendicular to each other (dihedral angle 78.1(2)°). The unidentate acetate groups bisect the N-Zn-N angle, and are possibly held by weak C-H. . .O interactions (2.273–2.581 Å) between the uncoordinated acetate oxygen atom and the C-H of the triazole rings. The Zn-N and Zn-O bond lengths are typical for this type of complex (e.g., Zn-N: 2.010(4), 2.031(5) Å, Zn-O: 1.944(4), 1.976(4) Å in $[Zn(L)_2(OAc)_2]$ L = 2-ethylimidazole).[21] The butyl chains are less folded than for the copper complex earlier (torsion angles, e.g., N3-C3-C9-C10 109.4(5)°, range for all ligands 101.5(5)–108.3(5)°) resulting in a more "stretched out" molecule. Curiously, the dihedral angles between the triazole and aryl rings appear to distinguish between the R and S configurations of the tebuconazole ligands with larger values for the R enantiomer (Zn(1) S 35.9(3), R 66.7(2), Zn(2) R 63.1(2), Zn(3) S 38.6(2)°). As with the copper tebuconazole complex, individual molecules are linked via O-H. . .O (acetate) hydrogen bonds, but in this case forming a 2D sheet parallel to the *ab* face.

The structure of the zinc *cis*-propiconazole chloride complex [Zn(*cis*-propic)$_2$Cl$_2$] is shown in Figure 5, along with selected bond distances and angles. The complex crystallizes in the non-centrosymmetric orthorhombic

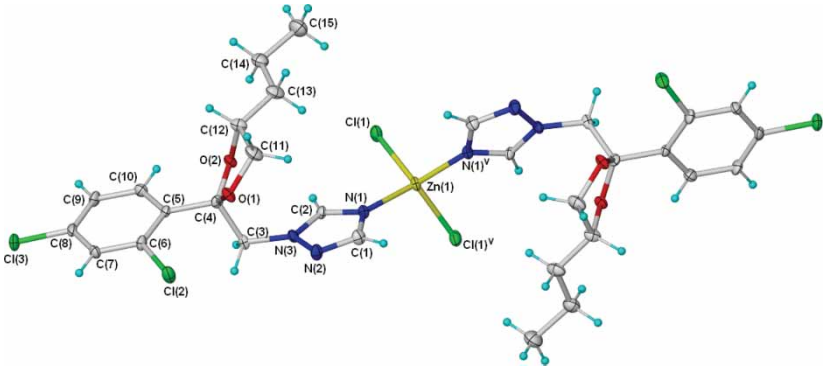

Figure 5. Molecular diagram of 2S4R/2S4R-[Zn(*cis*-propic)$_2$Cl$_2$] shown with 50% thermal ellipsoids and hydrogen atoms as spheres of arbitrary size. Atoms denoted^v are generated by symmetry (^{v}−x, −y, z). Selected bond distances (Å) and angles (°): Zn(1)-N(1), 2.016(3), Zn(1)-Cl(1), 2.254(1), N(1)-Zn(1)-N(1)^v, 119.4(2), N(1)-Zn(1)-Cl(1), 100.15(8), N(1)-Zn(1)-Cl(1)^v, 111.15(8), Cl(1)-Zn(1)-Cl(1)^v, 115.71(5).

space group *Fdd*2, with the Zn atom located on a crystallographic two-fold axis. The coordination of the *cis*-propiconazole ligands to the $ZnCl_2$ moiety is similar to that of the closely related $[Zn(L)_2Cl_2]$ L = 1-{[2-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-triazole—also known as azaconazole,[22] (but which lacks the propyl arm appended to the dioxolan ring), both having two-fold rotation symmetry and similar Zn-N and Zn-Cl distances (e.g., Zn-N: 2.023(4); Zn-Cl: 2.2394(13) Å). In the present complex, the propyl groups occupy space above and below the ZnN_2Cl_2 moiety. The triazole and the aryl rings are almost parallel with a dihedral angle 8.9(2)°, again similar to that of the azaconazole complex above (dihedral angle 14.84(5)°).[22] Only the one stereoisomer of the *cis*-propiconazole is observed in the crystal structure of $[Zn(cis\text{-propic})_2Cl_2]$, the complex being thus 2S4R/2S4R. However, it is possible that crystals of the mirror image complex were present in the bulk sample. There are no significant interactions between molecules of $[Zn(cis\text{-propic})_2Cl_2]$ in this structure.

In summary, it can be seen that divalent copper and zinc complexes can be readily formed from propiconazole and tebuconazole at room temperature, although their deposition or crystallization from solution may take weeks. Seeding is very important to promote rapid crystallization in some instances. Wood preserving formulations, however, usually contain large amounts of other complexing amines such as ammonia and ethanolamine and it becomes important to consider the relative metal binding capacity of these substances in comparison with the triazoles propiconazole and tebuconazole.

There appears to be little published stability constant data for metal complexes of either propiconazole or tebuconazole. The condition stability constant of a monovalent propiconazole copper complex postulated to be $Cu(NH_3)_2(propiconazole)_2^+$ was reported as 5.81×10^{12}.[23] In this polarographic determination the pH of the ammonia-ammonium chloride buffer (0.4 mol/L) was 8.0, but the complex was also present at higher pH. The stability constant for $Cu(NH_3)_4^{2+}$ is 1.00×10^{13} at 25°C and ionic strength 0.5,[24] whereas the stability constant for $Cu(ethanolamine)_4^{2+}$ is much higher at 1.58×10^{15} at 25°C and ionic strength 0.1.[25] The stability constant for $Cu(1\text{-methylimidazole})_4^{2+}$ (1-methylimidazole being the closest structural relative to propiconazole or tebuconazole found in standard literature tables) was 7.24×10^{12} at 25°C and ionic strength 0.1.[26] As can be seen, the values for ammonia and 1-methylimidazole are very similar. A proper comparison of the stability constant for the propiconazole complex from the polarographic study mentioned earlier is not possible, because that complex is with monovalent copper and moreover, the structure of the complex has not been firmly established. Nevertheless, the confirmed existence of a propiconazole copper complex in an ammoniacal environment and the similarity of the stability constants for ammonia and 1-methylimidazole, suggest that in ammonia-based wood preserving formulations, propiconazole and the chemically related triazole, tebuconazole, could exist as metal complexes to a

significant degree. Thus their precipitation from solution may be possible, depending on pH and on the ratio and nature of other formulation components. It follows logically that wood treated with ammonia-based formulations could contain triazoles in the metal complex form to an appreciable extent.

Typical ethanolamine-based copper-azole formulations contain 4 moles of ethanolamine per gram atom of copper. As indicated by a comparison of the respective stability constants earlier, ethanolamine binds copper much more tightly than ammonia or 1-methylimidazole. Ethanolamine probably also binds copper and other metals much more tightly than either propiconazole or tebuconazole, although no precisely relevant literature data has been found. In general, it seems much less likely that metal triazole complexes can exist to a significant extent in ethanolamine-based wood preserving formulations. Wood treated with such formulations may be expected to contain predominantly uncomplexed triazoles.

Another pertinent factor is the greatly increased volatility of ammonia (bp -33.3°C) compared to ethanolamine (bp 170°C). Ammonia is much more readily lost from treated timber and this would tend to shift equilibria in favor of metal triazole complexes during aging of timber following treatment with ammonia-based formulations. Clearly, however, much further work is needed to assess and quantify the extent of triazole metal complex formation in wood preserving formulations and in treated wood.

CONCLUSIONS

Divalent copper and zinc complexes with metal:azole ratio 1:2 were readily formed at room temperature from the fungicides tebuconazole and propiconazole, although their deposition from solution may take many weeks. Seeding of preparative solutions was very useful for the deposition of crystalline zinc tebuconazole acetate. In copper tebuconazole acetate, the copper atom lies on a crystallographic inversion center and is coordinated to two triazole and two acetate ligands in a *trans* arrangement. The two binding tebuconazole N atoms and two close binding acetate O atoms form a square plane. The two remaining acetate O atoms have more distant interactions, thus forming an elongated octahedron around the copper atom. The coordination geometry of zinc tebuconazole acetate is tetrahedral and the metal is bound to two triazole and two acetate ligands. The geometry is distorted from regular by the size of the tebuconazole ligands. The butyl chains are less folded than for the copper tebuconazole complex, resulting in a more extended molecule. The coordination geometry of zinc *cis*-propiconazole chloride is also tetrahedral with the metal atom bonded to two triazole and two chloride ligands. Triazole metal complex formation is believed to be more likely to occur in ammonia-based rather than in ethanolamine-based wood preservative formulations.

REFERENCES

1. Preston, A.F. Wood preservation. Trends of today that will influence the way tomorrow. Forest Prod. J. **2000**, *50* (9), 12–19.
2. Evans, P.D. Emerging technologies in wood protection. Forest Prod. J. **2003**, *53* (1), 14–22.
3. Marx, H.F. Wood preservatives comprising triazole fungicides and metal soaps. German Patent, 4130483, 1993, 6 pp.
4. Egawa, H. Industrial antimicrobial composition containing mixed active agents. Japanese Patent, 2003095829, 2003, 5 pp.
5. Cui, F.; Preston, A.F. Emulsion compositions for wood protection. US Patent Appl., 2006057300 A1 20060316, 2006, 8 pp.
6. Heimdal, S.; Englund, F.; Vigrestad, J.H. A hydrophobic preservative preparation for wood protection. Norwegian Patent, 303724 19965427, 1998.
7. Zhang, J.; Kamden, D.P. FTIR characterization of copper ethanolamine—wood interaction for wood preservation. Holzforschung **2000**, *54* (2), 119–122.
8. Xie, C.; Ruddick, J.N.R.; Rettig, S.J.; Herring, F.G. Fixation of ammoniacal copper preservatives: reaction of vanillin, a lignin model compound, with ammoniacal copper sulfate solution. Holzforschung **1995**, *49* (6), 483–490.
9. Ruddick, J.N.R.; Xie, C.; Herring, F.G. Fixation of amine copper preservatives. Part 1. Reaction of vanillin, a lignin model compound with monoethanolamine copper sulphate solution. Holzforschung **2001**, *55* (6), 585–589.
10. McMahon, W.; Hill, C.M.; Koch, F.C. Greensalt—a new preservative for wood, *Proc. Am. Wood-Preservers' Assoc.*, 1942, 334–348.
11. Dalgren, S.-E.; Hartford, W.H. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part III. Fixation of Tanalith C and comparison of different preservatives. Holzforschung **1972**, *26* (4), 142–149.
12. Bayer, H.O.; Cook, R.S.; von Meyer, W.C. 1,2,4-triazole metal salt complexes. US Patent, 3647810, 1972, 6 pp.
13. Anon. Fungicidally active triazole complexes. Research Disclosure **1979**, *184*, 441.
14. Najer, A.; Parnowska, W.; Lukasiewicz, A. New polymerized complexes of aminotriazole with transition metals as potential fungicidal drugs. Acta Poloniae Pharmaceutica **1997**, *54* (3), 203–205.
15. Heuer, Lutz. Wood preservative containing copper compounds. German Patent 4340853, 1995, 13 pp.
16. Yang, C.; Luo, J.; Xie, X.; Li, Q.; Gu, Y.; Tian, Y.; Zhu, Z. Preparation and application of propiconazole metal complex. Chinese Patent 1923838, 2007, 8 pp.
17. Garavaglia, C.; Mirenna, L.; Filippini, L. Fungicidal compositions comprising triazole derivatives, copper compounds and hydrocarbons. Eur. Pat. Appl., EP 572085 A1 19931201, 1993, 10 pp.
18. Sheldrick, G.M. *SHELX-97, Program for Crystal Structure Solution and Refinement*; Universität Göttingen: Germany, 1997.
19. Zhang, P-Z.; Wu, J. A copper(II) complex of the fungicide tebuconazole. Acta Crystallographica, Section E: Structure Reports Online **2005**, *E61* (3), m560–m562.
20. Yoo, S.-K.; Ryu, J.Y.; Lee, J.Y.; Kim, C.; Kim, S.-J.; Kim, Y. Synthesis, structure and heterogeneous catalytic activity of a coordination polymer containing tetranuclear Cu(II)-btp units connected by nitrates. Dalton Trans. **2003**, *8*, 1454–1456.
21. Horrocks, W.D., Jr.; Ishley, J.N.; Whittle, R.R. Models for cobalt(II)-substituted zinc metalloenzymes. 2. Comparisons of the crystal structures of complexes of the type $[M(RCOO)_2(2\text{-X-Im})_2]$ (Im = imidazole; M = Co, Zn; R = CH_3, C_2H_5,

C_3H_7; X = CH_3, C_2H_5). An unusual type of linkage isomerism. Inorg. Chem. **1982**, *21* (9), 3270–3274.
22. Xie, X.-Q.; Yang, C.-L.; Li, Q.-J.; Luo, J.-X. Dichlorobis(1-{[2-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl]methyl}-1*H*-1,2,4-triazole-κN^4)zinc(II). Acta Crystallographica, Section E: Structure Reports Online **2006**, *E62* (11), m3096–m3097.
23. Luo, J.-X.; Yang, C.-L.; Wu, W.-D.; Yang, M.-M. Studies on polarographic behaviour of propiconazole—copper (I) complex. J. Analy. Sci. **2006**, *22* (4), 458–460.
24. Smith, R.M.; Martell, A.E. *Critical Stability Constants Volume 4: Inorganic Complexes*; Plenum Press: New York, USA, 1976, 41.
25. Smith, R.M.; Martell, A.E. *Critical Stability Constants Volume 2: Amines*; Plenum Press: New York, USA, 1975, 15.
26. Smith, R.M.; Martell, A.E. *Critical Stability Constants Volume 6: Second Supplement*; Plenum Press: New York, USA, 1989, 248.