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ヒノキチオール金属錯体の合成、X線構造解析および抗菌活性

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Synthesis, X-Ray Crystal Structures and Antimicrobial Activities of Transition-Metal Complexes with Hinokitiol Ligand

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Abstract: There exist at least three different polymorphs in the copper(II) complex [Cu(hino)₂] with a hinokitiol ligand (Hhino; 4-isopropyltropolone). In addition to deep-green plate crystals **1a** and deep-green rod crystals **1b**, whose crystal structures have been recently reported, novel green needle crystals **1c** of [Cu(hino)₂] were found, the crystal structure of which was here determined by single-crystal X-ray analysis. Since only one crystal structure has been reported for the copper(II) complex [Cu(trop)₂] with a tropolone ligand (Htrop), the polymorphism found in the crystals of [Cu(hino)₂] would be due to the presence of the isopropyl group on the tropolone ring. The synthetic conditions giving the three polymorphs in good yields were found and the crystals were characterized with elemental analysis, FT-IR, TG/DTA and X-ray powder diffraction (XPD) measurements, as well as solution molecular weight measurements for **1a**. The solid-state magnetic behaviors or the temperature-dependent magnetic susceptibilities were measured with Superconductivity Quantum Interference Devices (SQUID): **1a** showed a weak ferromagnetic interaction, **1b** showed a paramagnetic nature with $S = 1/2$, while **1c** showed a weak antiferromagnetic interaction. The antimicrobial activities for selected bacteria, yeasts and molds were also measured in the water-suspension system: **1a** and **1b** showed no activity, while **1c** showed modest activities, and these activities were compared with those of the neutral Hhino and the anionic hino⁻ ligands.

Keywords: copper(II) complex with hinokitiol, crystal and molecular structures, polymorphism, X-ray powder diffraction, temperature-dependent magnetic susceptibilities, antimicrobial activities

天然系抗菌剤のヒノキチオール (Hhino; 4-イソプロピルトロポロン) を配位子とした銅(II)錯体 [Cu(hino)₂] を合成した。合成条件により、3種類の異なる結晶構造が存在すること(多形現象)を見いだした。Hhino と CuSO₄·5H₂O を 2 : 1 モル比で、水 : エタノール = 1 : 1 の混合溶媒の量を変えて還流した後、室温で slow evaporation して、濃緑色板状結晶 **1a** (収率 70%) および濃緑色柱状結晶 **1b** (収

率 76.5%) を得た。また一度単離したこれらの結晶を水 : エタノール = 1 : 1 の混合溶媒中で再び還流して、冷蔵庫内で slow evaporation して緑色針状結晶 **1c** (収率 65.3%) を得た。それらを元素分析、TG/DTA、FTIR、UV-vis 吸収、ESR、粉末X線回折、SQUID 測定、単結晶X線解析などでキャラクターゼーションした。いずれの分子構造も Cu²⁺ : hino⁻ = 1 : 2 型の平面正方形であるが、柱状結晶お

よび針状結晶にはトロポロン環 4-iPr 基の相対的位置に関する *trans*-型の monomer だけが含まれていたが、板状結晶には *cis*-および *trans*-型異性体の monomer および dimer が含まれていた。板状結晶および柱状結晶サンプルは抗菌性を全く示さなかったが、針状結晶サンプルは広いスペクトルの抗菌活性を示した^{1,2)}。

文献

1) Nomiya K, Yoshizawa A, Kasuga NC, Yokoyama H

and Hirakawa S (2004) Synthesis, solid state characterization and antimicrobial activities of three different polymorphs of a copper(II) complex with 4-isopropyltropolone (hinokitiol). *Inorg. Chim. Acta* **357**: 1168-1176.

2) Nomiya K, Yoshizawa A, Tsukagoshi K, Kasuga NC, Hirakawa S and Watanabe J (2004) Synthesis and structural characterization of silver(I), aluminium(III) and cobalt(II) complexes with 4-isopropyltropolone (hinokitiol) showing noteworthy biological activities. Action of silver (I)-oxygen bonding complexes on the antimicrobial activities. *J. Inorg. Biochem.* **98**: 46-60.