Experimental descriptions

General Method

All chemicals were purchased from Aldrich, Nacalai Tesque and Wako Pure Chemicals. \([\text{Cu(tptm)}(\text{CH}_3\text{CN})]\text{PF}_6\) was prepared according to the previously reported method.\(^1\) All reagents and solvents were used without further purification. IR spectra were recorded on a JASCO FT/IR-420 spectrophotometer in the range of 4000-400 cm\(^{-1}\). Elemental analyses were carried out by the Analytical Centre of the Graduate School of Science in Osaka City University using a Perkin-Elmer 240C elemental analyser.

X-ray Crystallographic analyses

Data were collected on a Rigaku AFC-7/Mercury CCD area-detector diffractometer with graphite monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.7107 \ \text{Å}\)). The CrystalClear software\(^2\) was used for data collections, processing and corrections for Lorentzian and polarization effects. Absorption corrections were applied on comparison of multiple symmetry equivalent measurements. The structures were solved by SIR97\(^3\) direct methods, expanded using Fourier techniques\(^4\) and refined by full matrix least-squares against \(F^2\) using the CRYSTAL software. CrystalStructure was used for a graphical interface.\(^5\) For \(4\{\text{CuF(tptm)}\}\cdot 12(\text{H}_2\text{O})\) (2), sulfur atoms were treated as disordered in positions due to orientations of pyridine rings in the complexes, however, carbon, nitrogen and hydrogen atoms in the pyridine rings were not treated as disordered. All non-hydrogen atoms except for sulfur atoms having smaller site occupancies were refined anisotropically. Hydrogen atoms in the complexes were located on the calculated positions and those in water molecules were found on the difference Fourier maps. They were refined using the riding model. For \(6\{\text{CuF(tptm)}\}\cdot 14.5(\text{H}_2\text{O})\cdot 0.5(\text{toluene})\) (3), one of the water molecules and the methyl carbon atom of toluene were disordered due to crystallographic inversion centre. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the complex molecules were generated according to the stereochemistry and those in the water molecules were found on the difference Fourier maps. All hydrogen atoms were refined using a riding model. Hydrogen atoms on O10, O12 and O15 were missing entirely, one of hydrogen atoms on each O4, O9 and O11 water molecule were missing. The largest residual electron density peak (2.43 eÅ\(^3\)) was found near the sulfur atom.

\(4\{\text{CuF(tptm)}\}\cdot 12(\text{H}_2\text{O})\) (2)

Tetra-\(n\)-butylammonium fluoride (50 \(\mu\)L of 1.0 M solution in THF) was added to a solution of \([\text{Cu(tptm)}(\text{CH}_3\text{CN})]\text{PF}_6\) (0.0312 mmol, 18.5 mg) in acetonitrile (5 mL) and the solvent of the green solution was evaporated to dryness. The resulting green residue was extracted with dichloromethane (5 mL) and cyclohexane was then carefully layered on top of the dichloromethane solution. The mixture was placed in a refrigerator at -20 °C for a week to give green crystals of pure
4[CuF(tptm)]·12(H2O) (7.2 mg, 48%). Anal. Calcd for 4(C16H12CuFN3S3)·12H2O: C, 40.11; H, 3.79; N, 8.77. Found: C, 40.43; H, 3.70; N, 8.78 %%. IR(nujor, cm\(^{-1}\)): 3359, 3255, 1651 (O–H); 1585, 1559, 1420, 1274, 1133, 1045, 1006, 763, 724, 637, 489 (complex).

6[CuF(tptm)]·14.5(H2O)·0.5(toluene) (3)

Tetra-n-butylammonium fluoride (80 \(\mu\)L of 1.0 M solution in THF) was added to [Cu(tptm)(CH3CN)]PF6 (0.076 mmol, 45.1 mg) dissolved in acetonitrile (10 mL). The solvent of the resulting solution was then evaporated to dryness and the residue was extracted with toluene (5 mL) that was saturated with water (0.15 mmol, as estimated by a Karl-Fisher titration). Cyclohexane (20 mL) was then carefully layered on top of the toluene solution and after 3 days the layers diffused together and pure 6[CuF(tptm)]·14.5(H2O)·0.5(toluene) formed as green crystals (25.7 mg, 74%). The crystal used for X-ray analysis was obtained using the same crystallising procedure described above for the bulk material. Anal. Calcd for 6(C16H12CuFN3S3)·14.5H2O·0.5toluene: C, 41.82; H, 3.70; N, 8.82. Found: C, 41.69; H, 4.15; N, 8.36 %%. IR(nujor, cm\(^{-1}\)): 3365, 3253, 1648 (O–H); 1584, 1554, 1419, 1274, 1130, 1044, 1004, 762, 723, 635, 489 (complex).

Reference