Structure and Spectroscopic Characterization of Free Base and Metal Complexes of 5,5-Dimethyl-10,15-bis(pentafluorophenyl)isocorrole

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Supporting Information
Experimental

All reagents were purchased from Strem, Acros Organics or Sigma-Aldrich and used as received. UV-visible absorption measurements were carried out with a Hitachi 3100 single monochromator spectrophotometer. Solution NMR spectroscopy was performed with Varian VXR 300 MHz and Varian 500 Mhz NMR instruments. Mass Spectrometric analyses were carried out at the Mass Spectrometry and Proteomics Facility at The Ohio State University in Columbus, OH or at The University of Akron in Akron, OH. 5-Isocorrole 1 was prepared as previously described.1

X-ray intensity data were measured at 100 K (Bruker KYRO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 W power. The crystals were mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystals. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F2 converged.2

Crystallization of 1: X-ray quality crystals of 1 were isolated from a diffusion of methanol into chloroform.

Synthesis of Zn1: A solution containing isocorrole 1 (30 mg, 4.6 x 10^5 moles) and
Zn(OAc)$_2$·2H$_2$O (10 mg, 4.6 x 10$^{-5}$ moles) in chloroform (9 mL) and methanol (1 mL) was heated at reflux in the dark for ~30 min. The solution volume was then reduced to ~1 mL, and the product crystallized upon addition of hexanes affording Zn1 (28 mg, 81%). X-ray quality crystals were grown from a diffusion of methanol into chloroform. High Res. ESI MS (positive ion): 721.0428 M/z (M+H, calcd 721.0406, 3.1 ppm). UV-visible [nm, (M$^{-1}$cm$^{-1}$)]: 851 (9.26 x 10$^3$), 459 (3.16 x 10$^4$), 355 (2.83 x 10$^4$). $^1$H NMR ([D$_4$]MeOD, δ) 1.885 (s, 6H), 6.511 (dd, 4H, J = 4.5 Hz), 6.976 (d, 1H, J = 4.5 Hz), 7.138 (d, 1H, J = 4.5 Hz), 7.179 (d, 1H, J = 4.5 Hz), 7.219 (d, 1H, J = 4.5 Hz) ppm.

Synthesis of Cu1: Cu1 was prepared in an analogous fashion to Zn1 via the addition of Cu(OAc)$_2$·H$_2$O (9.0 mg, 4.6 x 10$^{-5}$ moles). Crystallization of the concentrated reaction mixture upon the addition of hexanes afforded Cu1 (25 mg, 76%). High Res. ESI MS (positive ion): 720.0421 M/z (M+H, calcd 720.0433, 1.7 ppm). UV-visible (nm, (M$^{-1}$cm$^{-1}$)): 847 (1.53 x 10$^4$), 764 (5.74 x 10$^3$), 616 (1.91 x 10$^3$), 572 (3.45 x 10$^3$), 464 (2.45 x 10$^4$), 429 (2.07 x 10$^4$), 356 (1.85 x 10$^4$).

References