Supplementary Information for:

Reversible Methanol Addition to Copper Schiff Base Complexes: A Kinetic, Structural, and Spectroscopic Study of Reactions at Azomethine C=N Bonds

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Crystallographic Methods

A blue plate 0.42 x 0.40 x 0.03 mm³ crystal of 1 grown from a solution of dry acetonitrile/ether was mounted on a glass fiber for collection of x-ray data on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer. The CrystAlisPro¹ CCD software package (v 1.171.36.32) was used to acquire a total of 1,521 fifteen-second frame ω-scan exposures of data at 100K to a θ max = 57.40° using monochromated MoKα radiation (0.71073 Å) from a sealed tube. Frame data were processed using CrystAlisPro RED to determine final unit cell parameters: a = 8.7479(8) Å, b = 10.1421(7) Å, c = 12.9690(10) Å, α = 68.941(7)°, β = 75.950(7)°, γ = 88.025(7)°, V = 1039.90(14) Å³, D calc = 1.749 Mg/m³, Z = 2 to produce raw hkl data that were then corrected for absorption (transmission min./max. = 0.627 /1.000; μ = 1.367 mm⁻¹) using SCALE3 ABSPACK². The structure was solved by Direct methods in the space group P1bar using SHELXS-90³ and refined by least squares methods on F² using SHELXL-97³. Non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Methylene, methine and imidazole hydrogen atoms were located by difference maps and refined isotropically. Methyl hydrogen atoms were placed in their geometrically generated positions and refined as a riding model and these atoms were assigned U(H) = 1.5 x Ueq. For all 5,359 unique reflections (R(int) 0.049) the final anisotropic full matrix least-squares refinement on F² for 332 variables converged at R1 = 0.038 and wR2 = 0.089 with a GOF of 1.04.

Crystals of 4 suitable for x-ray analysis were grown from a non-dried acetonitrile/ether solution and mounted on a CryoLoop for collection of x-ray data on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer. X-ray structural analysis for 4 was performed on a 0.28 x 0.21 x 0.02 mm³ blue plate using a 835 frame, forty second frame ω-scan data collection strategy at 100 K to a 2θ max = 55.50°. Complex 4 crystallizes in the triclinic space group P-1 with unit cell parameters: a = 8.227(3) Å, b = 11.003(4) Å, c = 11.441(4) Å, α = 78.99(3)°, β = 70.69(3)°, γ = 88.76(3)°, V = 958.4(6)Å³, Z = 2 and D calc = 1.818 Mg/m³. 4,447 independent data were corrected for absorption (transmission min./max. = 0.038 /1.000; μ = 1.481 mm⁻¹). The structure was solved by Direct methods using SHELX³. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were located and refined as described above for 1. For reflections I >2σ(I) (R(int) 0.043) the final anisotropic full matrix least-squares refinement on F² for 317 variables converged at R1 = 0.054 and wR2 = 0.127 with a GOF of 1.06.

Crystals of 5 were grown from a methanol/ether solution and mounted on a glass fiber for collection of x-ray data on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer. X-ray structural analysis for 5 was performed on a 0.35 x 0.28 x 0.26 mm³ blue prism using a 1,337 frame, twenty second frame ω-scan data collection strategy at 100 K to a 2θ max = 56.3°. Complex 5 crystallizes in the monoclinic space group Pn with unit cell parameters: a = 13.0049(3) Å, b = 11.5913(2) Å, c =
15.1039(4) Å, β = 104.371(3)°, V = 2205.57(9) Å³, Z = 4 and D_{calc} = 1.719 Mg/m³. The 10,813 independent data were corrected for absorption (transmission min./max. = 0.808 /1.000; μ = 1.298 mm⁻¹). The structure was solved by Patterson methods using SHELX³ and contains two molecules in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Amine NH’s and methanol OH’s were located by difference maps and refined isotropically. Methylene, methine, imidazole and methyl hydrogen atoms were placed in their geometrically generated positions, refined as riding models and these atoms were assigned U(H) = 1.2, 1.2, 1.2 and 1.5 x Ueq respectively. For reflections I >2σ(I) (R(int) 0.041) the final anisotropic full matrix least-squares refinement on F² for 616 variables converged at R1 = 0.039 and wR2 = 0.096 with a GOF of 1.09.

Crystals of 6 were grown from vapor diffusion of ether into a methanol solution and mounted on a glass fiber for data collection. X-ray structural analysis for 6 was performed on a 0.47 x 0.43 x 0.21 mm³ blue prism using a 940 frames, twenty second frame o-scan data collection strategy at 100 K to a 2θmax = 58.4°. 6 crystallizes in the triclinic space group P-1 with unit cell parameters: a = 8.30645(16) Å, b = 12.6697(2) Å, c = 13.6657(2) Å, α = 93.3069(14)°, β = 103.0089(16)°, γ = 107.1032(17)°, V = 1327.40(4) Å³, Z = 2 and D_{calc} = 1.707 Mg/m³. The 7,190 independent data were corrected for absorption (transmission min./max. = 0.745 /1.000; μ = 1.078 mm⁻¹). The structure was solved by Patterson methods using SHELX. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Methylene, methine, imidazole, amine, methanol and water hydrogen atoms were located by difference maps and refined isotropically. Methyl hydrogen atoms were placed in their geometrically generated positions and refined as a riding model and these atoms were assigned U(H) = 1.5 x Ueq. For reflections I >2σ(I) (R(int) 0.022) the final anisotropic full matrix least-squares refinement on F² for 418 variables converged at R1 = 0.047 and wR2 = 0.105 with a GOF of 1.05.

Crystals of 7 were grown from vapor diffusion of ether into a methanol solution and mounted on a glass fiber for data collection. X-ray structural analysis for 7 was performed on a 0.42 x 0.22 x 0.21 mm³ blue prism using a 950 frames, twenty second frame o-scan data collection strategy at 100 K to a 2θmax = 57.4°. 7 crystallizes in the triclinic space group P-1 with unit cell parameters: a = 7.83639(13) Å, b = 11.5417(3) Å, c = 12.5358(3) Å, α = 88.3240(19)°, β = 73.9097(18)°, γ = 82.5500(16)°, V = 1080.17(4) Å³, Z = 2 and D_{calc} = 1.677 Mg/m³. 5,581 independent data were corrected for absorption (transmission min./max. = 0.741 /1.000; μ = 1.104 mm⁻¹). The structure was solved by Patterson methods using SHELX. The tetrafluoroborate anion has a tumbling disorder that was modeled with two 50% occupancy groups, (F1a–F6a) and (F1b–F6b) in addition to the full occupancy B atom. To aid in the BF₄ disorder model 42 restraints were used. The ratio for the anion disorder was fixed at 50:50 after being determined from unstable refinement of the F-atom occupancies. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Methylene, methine, imidazole, amine, methanol and
water hydrogen atoms were located by difference maps and refined isotropically. Methyl hydrogen atoms were placed in their geometrically generated positions and refined as a riding model and these atoms were assigned U(H) = 1.5 x Ueq. For reflections I >2σ(I) (R(int) 0.026) the final anisotropic full matrix least-squares refinement on F² for 350 variables converged at R₁ = 0.059 and wR² = 0.126 with a GOF of 1.05.

Crystals of L₁ were grown from aqueous solution at 4° C and mounted on a glass fiber for data collection. X-ray structural analysis for L₁ was performed on a 0.40 x 0.38 x 0.33 mm³ colorless prism using a 900 frames, twenty second frame ω-scan data collection strategy at 100 K to a 2θmax = 59.1°. The ligand L₁ crystallizes in the monoclinic space group C2/c with unit cell parameters: a = 9.37814(17) Å, b = 12.2120(2) Å, c = 11.9164(2) Å, β = 95.9045(16)°, V = 1357.49(4) Å³, Z = 4 and Dcalc = 1.284 Mg/m³. The 1,902 independent data were corrected for absorption (transmission min./max. = 0.976 /1.000; μ = 0.088mm⁻¹). The structure was solved by Direct methods using SHELX. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Methylene, methine, imidazole and water hydrogen atoms were located by difference maps and refined isotropically. Methyl hydrogen atoms were placed in their geometrically generated positions and their thermal parameters were allowed to refine. For reflections I >2σ(I) (R(int) 0.019) the final anisotropic full matrix least-squares refinement on F² for 115 variables converged at R₁ = 0.034 and wR² = 0.082 with a GOF of 1.04.

References

2. SCALE3 ABSPACK included in CrysAlis PRO RED, V 1.171.36.32.
<table>
<thead>
<tr>
<th>Table S1. Crystal Data and Structure Refinement for 1,4 – 7, and L1.</th>
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<td><strong>largest peak and hole (e Å⁻³)</strong></td>
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R1 = Σ||F₁| - |F₂||/Σ|F₁|; wR² = (Σ[w(Fo² - Fc²)]²)/Σ[w(Fo²)]; where w = q/σ²(Fo²) + (aq)² + bσ². 
GOF = S/[Σ(w(Fo² - Fe²))²/(n - p)]¹/².
Figure S1. Electronic spectrum of 2 in acetonitrile.

Figure S2. Electronic spectrum of 3 in acetonitrile.
Figure S3. Electronic spectrum of 6 in acetonitrile.

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Figure S25. Non-covalent interactions in 7. Hydrogen bond D···A acceptor distances are indicated in units of Å.
Figure S26. Plot of $k_{\text{obs}}$ versus [CH$_3$OH] for 1 and 4.

Figure X. Plot of $k_{\text{obs}}$ versus [CH$_3$OH] for 1 and 4.

$k_2 = 0.11 \times 10^{-2}$ M$^{-1}$s$^{-1}$

$k_3 = 1.9 \times 10^{-2}$ M$^{-1}$s$^{-1}$

Figure S27. Plot of $k_{\text{obs}}$ versus [CH$_3$OH] for 2 and 3.