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Communication

$Cu(NO_3)_2 \cdot 3H_2O$-Mediated Synthesis of 4′-(2-Pyridyl)-2,2′:6′,2′′-terpyridine (L2) from *N*-(2-Pyridylmethyl)pyridine-2-methylketimine (L1). A C–C Bond-Forming Reaction and the Structure of $\{[Cu(L2)(OH)(NO_3)][Cu(L2)(NO_3)_2]\} \cdot 2H_2O$[†]

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N-(2-Pyridylmethyl)pyridine-2-methylketimine (**L1**) was synthesized from equimolar quantities of (2-pyridyl)methylamine and 2-acetylpyridine. Methanolic solution of **L1** reacted readily with $Cu(NO_3)_2 \cdot 3H_2O$ in air, affording green solid of composition $\{[Cu(\mathbf{L2})(OH)(NO_3)][Cu(\mathbf{L2})(NO_3)_2]\} \cdot 2H_2O$, where **L2** is 4′-(2-pyridyl)-2,2′:6′,2′′-terpyridine. Oxidation of the active methylene group of **L1** to an imide and then condensation with 2-acetylpyridine involving a C–C bond-forming reaction, mediated by a Cu^{2+} ion, are the essential steps involved in the conversion of **L1** to **L2**. **L2** is isolated by extrusion of Cu^{2+} with $EDTA^{2-}$. The copper center in $[Cu(\mathbf{L2})(OH)(NO_3)]$ has a *mer*-N_3O_3 environment, and that in $[Cu(\mathbf{L2})(NO_3)_2]$ has a distorted trigonal-bipyramidal geometry. Two H_2O molecules held by C–H···O interactions are present in the predominantly hydrophobic channels of approximate cavity dimension 7.60 × 6.50 Å created by aromatic rings through π–π interactions.

Terpyridine (tpy) became one of the most important tridentate ligands in coordination chemistry since the report of its synthesis,[1] and subsequently substituted analogues have been reported.[2] Metal complexes of terpyridines have versatile applications, viz., DNA binding ability,[3] cytostatic activity,[4] topoisomerase I inhibitory activity,[5] supramolecular chemistry,[6] enantioselective synthesis,[7] fluorophores,[8] and photoinduced light harvesting.[9] Reviews describing the syntheses of terpyridine, its higher homologues, and its derivatives having aromatic and aliphatic ring substituents have appeared.[10] Recently, structures of mixed-valent Cu^ICu^{II} grid-type coordination polymers based on pyridylterpyridine has been reported.[11] In this Communication, we report a facile formation of 4′-(2-pyridyl)-2,2′:6′,2′′-terpyridine (**L2**) from *N*-(2-pyridylmethyl)pyridine-2-methylketimine (**L1**), plausible intermediates involved, and the molecular structures of $[Cu(\mathbf{L2})(OH)(NO_3)]$ and $[Cu(\mathbf{L2})(NO_3)_2]$.

L1 was synthesized from equimolar quantities of (2-pyridyl)methylamine and 2-acetylpyridine in the presence of anhydrous $MgSO_4$.[12] A methanolic solution of **L1** on reaction with $Cu(NO_3)_2 \cdot 3H_2O$ in air (Scheme 1) afforded a green crystalline solid, which has been structurally characterized as $\{[Cu(\mathbf{L2})(OH)(NO_3)][Cu(\mathbf{L2})(NO_3)_2]\} \cdot 2H_2O$.[13,14]

In this reaction, a Cu^{2+} ion mediates the formation of the central pyridine (Y) ring of **L2** from Schiff base **L1**. Probable intermediates involved in the formation of **L2** are shown in

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[†] Dedicated to Professor Animesh Chakravorty, IACS, Kolkata.

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(12) To 2.5 g of anhydrous $MgSO_4$ suspended in 50 mL of CH_2Cl_2 were added 2-picolylamine (1.08 g, 10 mmol) and 2-acetylpyridine (1.21 g, 10 mmol). The reaction mixture was heated at reflux for 1.5 h, then stirred for another 3 h, and filtered. The filtrate dried over anhydrous Na_2SO_4, after evaporation under vacuum afforded **L1** as a yellowish liquid. Yield: 2.90 g (94%). 400-MHz ^1H NMR (δ (*J*, Hz), $CDCl_3$): 2.49 (3H, s), 4.89 (2H, s), 7.15 (1H, t, 6.0), 7.25 (1H, t, 5.4), 7.61 (1H, d, 7.6), 7.67 (2H, m), 8.20 (1H, d, 8.0), 8.54 (1H, d, 4.8), 8.57 (1H, d, 5.2). IR (KBr, cm^{-1}): 1637, 1590, 1463, 1434.

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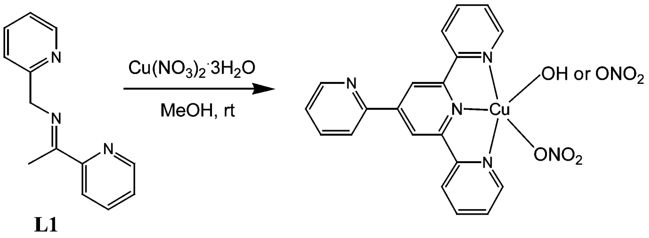
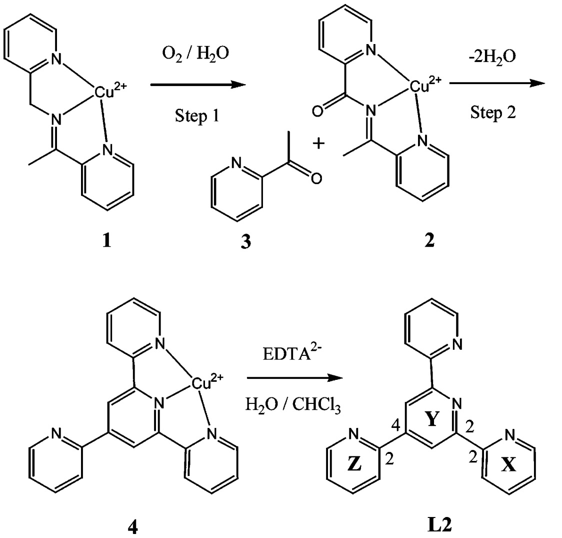
Scheme 1



Scheme 2. Probable Reaction Sequence and Intermediates Involved



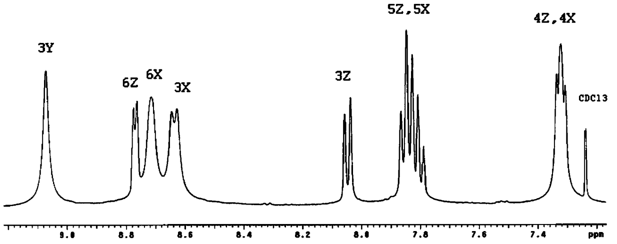


Figure 1. ^{1}H NMR spectrum (400 MHz in $CDCl_3$, at room temperature) of **L2** (labels are in accordance with Scheme 2).

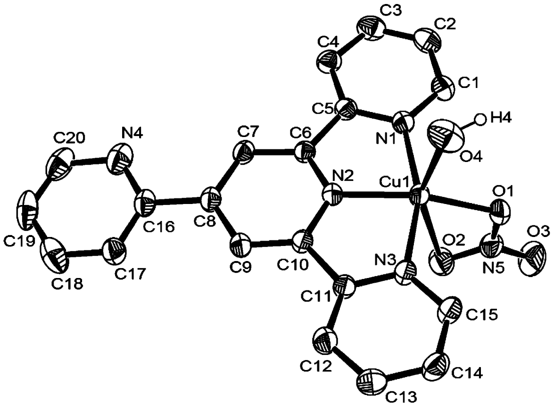


Figure 2. ORTEP (30%) plot for [Cu(**L2**)(OH)(NO_3)]. H atoms except for OH are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu1−O1 1.9707(30), Cu1−O2 2.5674(39), Cu1−O4 2.2510(44), Cu1−N1 2.0097(35), Cu1−N2 1.9285(32), Cu1−N3 2.0216(37); O1−Cu1−O2 55.33(13), O1−Cu1−O4 98.88(15), O1−Cu1−N1 98.28(14), O1−Cu1−N2 159.56(13), O1−Cu1−N3 99.77(14), O2−Cu1−O4 153.80(14), O2−Cu1−N1 97.02(14), O2−Cu1−N2 104.37(13), O2−Cu1−N3 87.81(14), O4−Cu1−N1 90.87(16), O4−Cu1−N2 101.54(16), O4−Cu1−N3 92.91(16), N1−Cu1−N2 80.64(14), N1−Cu1−N3 160.75(15), N2−Cu1−N3 80.11(14).

Scheme 2. Coordination of **L1** to a Cu^{2+} ion (other coligands are omitted) occurs in the generation of **1**. Oxidation of the active methylene group in **1** proceeds in the presence of O_2 and H_2O to produce the metastable imide intermediate (step 1) **2**.[15] In the C−C bond-forming step 2, **2** condenses with 2-acetylpyridine, which could have been released from **L1** in the presence of H^+ (generated in step 1), giving **4** as the stable final product. **L2** is isolated by extraction into the chloroform layer from the aqueous solution of the complex using excess of Na_2EDTA.[17] The ^{1}H NMR spectrum of **L2** is displayed in Figure 1.

The green solid crystallized[18] in triclinic space group $P\bar{1}$, and the unit cell contained an admixture of one molecule each of [Cu(**L2**)(OH)(NO_3)] and [Cu(**L2**)(NO_3)$_2$]. A perspective view of the molecular structures of the two complexes is shown in Figures 2 and 3. In [Cu(**L2**)(OH)(NO_3)], the Cu center is hexacoordinated, having a *mer*-N_3O_3 environment, and the Cu1−O4 distance is 2.2510(44) Å. NO_3^- coordinates in a bidentate fashion with short [Cu1−O1 = 1.9707(30) Å] and long [Cu1−O2 = 2.5674(39) Å] bonds, while in [Cu(**L2**)(NO_3)$_2$], the Cu center is pentacoordinated by the

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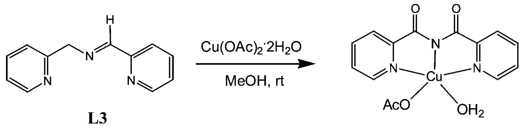
(13) To a methanolic solution (25 mL) of **L1** (180 mg, 0.85 mmol) was added with stirring $Cu(NO_3)_2·3H_2O$ (164 mg, 0.68 mmol) dissolved in methanol (15 mL). An initial violet color that developed upon mixing changed immediately to green; the solution was stirred for 24 h and left undisturbed. Green crystals deposited after 1 week were collected after washing with ice-cold methanol. Yield (based on **L1**): 405 mg (48%). Anal. Calcd for $C_{40}H_{33}N_{11}O_{12}Cu_2$: C, 48.66; H, 3.37; N, 15.61. Found: C, 48.45; H, 3.28; N, 16.02. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1}), CH_3CN solution]: 675 (30); 350 (9830), 335 (11 235), 290 (32 300), 280 (25 560), and 270 (23 875). IR (KBr, cm^{-1}): 1657, 1600, 1473, 1384, 1289. EPR (CH_3CN solution, 77 K): $g_{||} = 2.136$ ($A_{||} = 158$ G); $g_{\perp} = 2.086$ (solid, room temperature); $g_{iso} = 2.013$.

(14) In a thermogram, the loss of two H_2O molecules occurs at the midpoint temperature of 117 °C.

(15) With *N*-(2-pyridylmethyl)pyridine-2-carbaldimine (**L3**), oxidation of both methylene and imine functions occurs upon treatment with Cu(OAc)$_2$·2H_2O under similar conditions, according to the following scheme:



The complex [Cu(bpca)(OAc)(H_2O)]·H_2O [bpca = bis(2-pyridylcarbonyl)amide anion] has been structurally characterized. An ORTEP diagram is given in the Supporting Information. The structure of [Cu(bpca)(OAc)(H_2O)]·H_2O prepared by a different route has been reported.[16]

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(17) To {[Cu(**L2**)(OH)(NO_2)][Cu(**L2**)(NO_3)$_2$]}·2H_2O (150 mg, 0.15 mmol) dissolved in H_2O (30 mL) was added 50 mL of $CHCl_3$ and Na_2EDTA (230 mg, 0.68 mmol), and the resulting mixture was stirred vigorously for 3.5 h. The $CHCl_3$ layer was separated and dried with anhydrous Na_2SO_4. A pale-yellow **L2** (450 mg, yield 96%) was obtained after removal of $CHCl_3$. Mp: 230 °C with sublimation. IR (KBr, cm^{-1}): 1660, 1600, 1583, 1563, 1547, 1465, 1390. 100-MHz ^{13}C NMR (δ, $CDCl_3$): 118.8 (Y3), 121.4 (X3, Z3), 123.8 (Z4), 123.9 (X5), 136.9 (X4, Z5), 148.7 (Y4), 149.2 (X6), 150.1 (Z6), 155.2 (X2), 156.3 (Y2, Z2).

(18) Crystal data: $C_{40}H_{33}N_{11}O_{12}Cu_2$, $M_r = 986.87$, triclinic, space group *P*1, $a = 8.5857(5)$ Å, $b = 14.4378(10)$ Å, $c = 17.1880(11)$ Å, $\alpha = 91.504(4)°$, $\beta = 101.982(4)°$, $\gamma = 91.014(4)°$, $V = 2082.9(2)$ Å^3, $Z = 2$, $D_x = 1.578$ Mg m^{-3}, $\mu = 1.10$ mm^{-1}, $R_{int} = 0.031$, R1 = 0.061, wR2 = 0.212, and $S = 1.11$. Crystal data were collected on a Siemens (Bruker) SMART CCD diffractometer at 296 K.

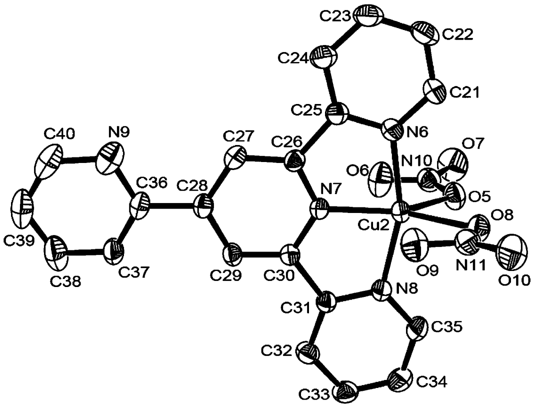

Figure 3. ORTEP (30%) plot for [Cu(**L2**)$(NO_3)_2$]. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu2−O5 2.1190(35), Cu2−O8 2.0902(34), Cu2−N6 2.0042(37), Cu2−N7 1.9328(33), Cu2−N8 2.0014(38), Cu2−O6 2.7942(48), Cu2−O9 2.6646(43); O5−Cu2−O8 82.61(13), O5−Cu2−N6 96.94(15), O5−Cu2−N7 135.20(14), O5−Cu2−N8 96.91(15), O8−Cu2−N6 96.62(15), O8−Cu2−N7 142.18(13), O8−Cu2−N8 98.31(14), N6−Cu2−N7 80.16(15), N6−Cu2−N8 160.79(15), N7−Cu2−N8 80.64(14), O6−Cu2−O9 175.79(15).

three N atoms of **L2** and two monodentate NO_3^- ions and has a distorted trigonal-bipyramidal geometry. In both of the complexes, the average Cu−N distance, in the Y ring [1.931(3) Å], is shorter than that in X rings [2.010(4) Å]. Twisting of the Z ring is −3.23(65)° and −3.42(67)°, respectively, in [Cu(**L2**)(OH)(NO_3)] and [Cu(**L2**)$(NO_3)_2$]. X ring twisting in [Cu(**L2**)(OH)(NO_3)] is +5.55(69)° and −4.53(69)°, while in [Cu(**L2**)$(NO_3)_2$], it is −0.88(72)° and +0.02(69)°.

The aromatic rings of **L2** in both of the complexes are nearly planar. The $\pi-\pi$ interactions having the shortest intermolecular contact of C6···C19, 3.3716(71) Å, and C19···C30, 3.3725(73) Å, are present. Two disordered H_2O molecules present in the lattice were refined with variable site occupancy factors and without added H atoms.[19] These H_2O molecules held by C−H···O interactions are present in the predominantly hydrophobic channels of approximate cavity dimension 7.60 × 6.50 Å created by aromatic rings through $\pi-\pi$ interactions (Figure 4). The channels along the *b* axis are linked by a O4···O7 [2.9111(62) Å] H bond, and a O4···O10 [2.7584(71) Å] H bond interlinks these channels along the *c* axis. The O4−H4···O7 and O4−H4···O10 angles are respectively 73.48(15)° and 162.59(35)°.

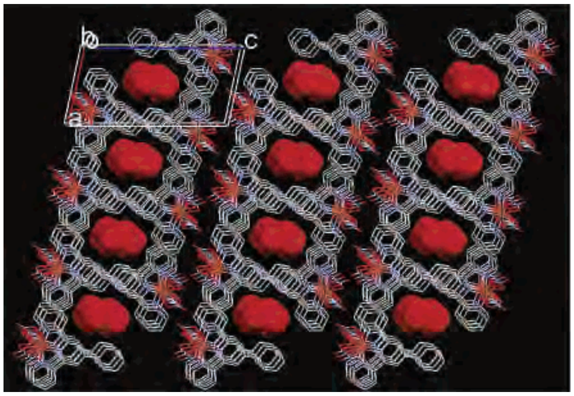

Figure 4. Packing diagram viewed down the *b* axis showing the H_2O molecules inside the channels.

In an acetonitrile solution, {[Cu(**L2**)(OH)(NO_3)][Cu(**L2**)$(NO_3)_2$]}·$2H_2O$ exhibits a broad d−d transition at 675 nm and five sharp intraligand transitions at 350, 335, 290, 280, and 270 nm. The frozen acetonitrile solution shows an electron paramagnetic resonance pattern of $g_{\|} > g_{\perp} > 2$, suggesting that the unpaired electron is in the $d_{x^2-y^2}$ orbital.

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Supporting Information Available: CIF for {[Cu(**L2**)(OH)(NO_3)][Cu(**L2**)$(NO_3)_2$]}·$2H_2O$ and ORTEP diagram and CIF for [Cu(bpca)(OAc)(H_2O)]·H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Site occupancy factors: O11 0.64204, O14 0.35796, O12 0.77456, and O13 0.22544.