Synthesis and X-ray Crystal Structure of a Triple-Stranded Helical Supramolecular Complex Formed between Tris(3-(pyridin-2-yl)pyrazole)ruthenium(II) and Copper(I)

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Self-assembly of supramolecules with helical structures has been one of the focuses in supramolecular chemistry.[1] The general synthetic strategy involves the use of multidentate ligands to wrap around one or more metal centers to produce single-,[2−4] double-,[5−8] and triple-stranded[9−15] metal helicates. We have tried a different approach in which smaller building blocks of metal complexes containing only bidentate ligands are linked together to form the desired supramolecular structure. In this work, the synthesis of a triple-stranded ruthenium helicate, $\{[Ru(py\text{-}pz)_3]_2Cu_3\}(ClO_4)$ (**2**), from $[Ru(py\text{-}pzH)_3](ClO_4)_2$ (**1**) (where py-pzH = 3-(pyridin-2-yl)pyrazole) and $Cu(ClO_4)_2$ is reported.

The coordination chemistry of the 3-(pyridin-2-yl)pyrazole (py-pzH) ligand and its analog has been studied by a number of researchers.[16] Complex **1** was synthesized from py-pzH[17] and $RuCl_3{\cdot}3H_2O$.[18] An acetonitrile solution of **1** shows three absorption bands at 400 nm ($\epsilon = 1.74 \times 10^4$ M^{-1} cm^{-1}), 279 nm ($\epsilon = 5.05 \times 10^4$ M^{-1} cm^{-1}), and 243 nm ($\epsilon = 5.00 \times 10^4$ M^{-1} cm^{-1}), in the UV−vis spectrum. The first absorption is the MLCT transition, while the last two are intraligand in origin. The MLCT band is red-shifted to 430 nm ($\epsilon = 1.08 \times 10^4$ M^{-1} cm^{-1}) upon deprotonation of the pyrazole by the addition of 3 equiv of triethylamine. Such lowering in MLCT energies has also been reported by Meyer *et al.* in their studies of pyrazole/pyrazolyl complexes of ruthenium(II).[19] It was concluded that the pyrazolyl moiety possessed much better π-donating ability comparing to that of the pyrazole ligand.

Complex **1**, after deprotonation by the addition of excess NEt_3, reacts with Cu(I) or Cu(II) ions in methanol to give a supramolecular structure containing two tris(3-(pyridin-2-yl)pyrazolyl)ruthenium(II) units linked together by three Cu(I) ions:[20]

$$\underset{\mathbf{1}}{Ru(py\text{-}pzH)_3^{\,2+}} \xrightarrow[NEt_3]{-3H^+} [Ru(py\text{-}pz)_3^{\,-}] \xrightarrow[NEt_3]{3Cu(II)\text{ or }3Cu(I)} \underset{\mathbf{2}}{[Ru(py\text{-}pz\text{-}Cu^{I}\text{-}pz\text{-}py)_3Ru]^+}$$

The structure of **2** is shown in Figure 1.[21] **2** possesses a C_3 rotation axis. Each Ru center is coordinated to three 3-(pyridin-

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(18) 3-(Pyridin-2-yl)pyrazole (0.28 g) and $RuCl_3{\cdot}3H_2O$ (0.10 g) were refluxed in ethanol for 3 days. $NaClO_4$ (0.1 g) was then added, and the mixture was refluxed for a further 30 min. The resultant greenish brown solution was evaporated to dryness under reduced pressure. The residual was dissolved in methanol, and the solution was filtered. Greenish yellow **1** was obtained by slow diffusion of diethyl ether into the methanol solution. Yield: 87%. ^{1}H NMR (300 MHz, CD_3CN), δ: 7.21 (m, 6H, pyrazole H), 7.51−7.63 (m, 3H, pyridine H), 7.82−7.99 (m, 6H, pyridine H), 8.13 (m, 3H, pyridine H), 11.88 (s, 3H, pyrazolyl NH).

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(20) A 0.1 g amount of trimethylamine was slowly added to a stirring methanol solution of **1** (0.20 g). The color of the solution turned rapidly from bright yellow to deep red. $Cu(ClO_4){\cdot}6H_2O$ (0.30 g) in 10 mL of methanol was then added. The resultant mixture was refluxed for 8 h. The mixture was cooled, and the orange precipitate was collected by filtration. The crude **2** obtained was washed with diethyl ether and recrystallized over dichloromethane/diethyl ether as long orange-red needles. Yield: 57%. ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 6.91 (d, 12H, pyrazole H), 6.96 (d, 6H, pyridine H), 7.13 (d, 6H, pyridine H), 7.72 (t, 6H, pyridine H), 7.89 (d, 6H, pyridine H). Anal. Calcd for $C_{48}H_{36}N_{18}ClO_4Ru_2Cu_3{\cdot}CH_2Cl_2$: C, 40.6; H, 3.0; N, 17.4. Found: C, 40.4; H, 3.0; N, 17.4. X-ray-quality crystals of **2** were obtained by slow diffusion of diethyl ether into an acetone solution of **2**.

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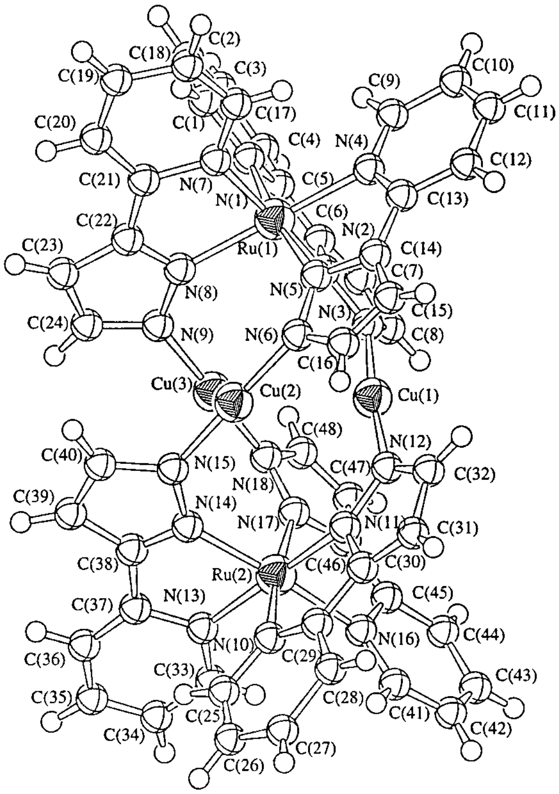

Figure 1. Perspective view of $\{[Ru(py\text{-}pz)_3]_2Cu_3\}(ClO_4)$ (**2**). Selected bond lengths (Å) and angles (deg): Ru(1)−N(1) 2.04(3), Ru(1)−N(2) 2.10(2), Ru(1)−N(4) 2.10(2), Ru(1)−N(5) 2.04(3), Ru(1)−N(7) 2.09(3), Ru(1)−N(8) 2.07(2), Ru(2)−N(10) 2.03(3), Ru(2)−N(11) 2.07(3), Ru(2)−N(13) 2.04(3), Ru(2)−N(14) 2.04(3), Ru(2)−N(16) 2.14(2), Ru(2)−N(17) 2.11(3), Cu(1)−N(3) 1.91(3), Cu(1)−N(12) 1.78(3), Cu(2)−N(6) 1.89(3), Cu(2)−N(15) 1.82(3), Cu(3)−N(9) 1.82(2), Cu(3)−N(18) 1.86(2); N(3)−Cu(1)−N(12) 173(1), N(6)−Cu(2)−N(15) 177(1), N(9)−Cu(3)−N(18) 175(1).

2-yl)pyrazolyl ligands. The geometry around Ru(1) is distorted octahedral with an average bond distance of 2.09 Å (2.07(2)−2.10(2) Å) for Ru(1)−N(7), Ru(1)−N(8), Ru(1)−N(4), and Ru(1)−N(5) and a bond distance of 2.04(3) Å for both Ru(1)−N(1) and Ru(1)−N(5). The octahedral Ru(2) center is more distorted. The three shorter ruthenium−nitrogen bonds are Ru(2)−N(10), Ru(2)−N(13), and Ru(2)−N(14) in the range 2.03(3)−2.04(3) Å. The three longer Ru−N bonds are Ru(2)−N(11), Ru(2)−N(16), and Ru(2)−N(17) in the range 2.07(3)−2.14(2) Å. Each pyrazolyl moiety is coordinated to a Cu(I) center with bond distances ranging from 1.78(3) to 1.91(3) Å. The arrangement of the two pyrazolyl rings and the Cu center is essentially linear (173(1)−177(1)°). Three [py-pz-Cu^I-pz-py] chains interweave the two Ru centers in the form of a triple-stranded helix.

The ^1H NMR spectrum of **2** is simple and consistent with the crystal structure in that all 3-(pyridin-2-yl)pyrazolyl ligands are equivalent. This indicates that the triple-stranded helical structure of **2** is intact in solution. The UV−vis spectrum of **2** in acetonitrile shows that the $Ru^{II}(d\pi) \rightarrow$ py-pz(π^*) MLCT band is further red-shifted to 437 nm ($\epsilon = 3.44 \times 10^4$ M^{-1} cm^{-1}). A new band at 306 nm ($\epsilon = 8.81 \times 10^4$ M^{-1} cm^{-1}) is observed and is attributable to the $Cu^I(d\pi) \rightarrow$ pyrazolyl(π^*) MLCT transition.[24]

The assembling of simple metal complexes into supramolecules has proved feasible, and we will continue our efforts to explore such supramolecular synthetic strategies.

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Supporting Information Available: Text and a table giving experimental crystallographic details and tables listing atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and nonbonded contacts (22 pages). Ordering information is given on any current masthead page.

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(21) Crystal data for complex **2**, $[C_{48}H_{36}N_{18}Cu_3Ru_2][ClO_4]\cdot{}^1/_3H_2O$: $M =$ 1363.11, trigonal, space group $R3c$ (No. 161), $a = 30.123(2)$ Å, $c = 29.767(2)$ Å, $V = 23391(2)$ $Å^3$, $Z = 18$, $D_c = 1.742$ g cm^{-3}, $F(000) = 12\,191.52$, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $T = 295$ K, μ(Mo Kα) = 18.91 cm^{-1}, red block 0.12 × 0.12 × 0.19 mm, 4003 unique data measured on a HAR research image plate scanner, 65 3° frames with exposure time of 5 min per frame, 2406 observed reflections [$F_o > 3\sigma(F_o)$]. The structure was solved by direct-method[22] and Fourier-difference techniques. Full-matrix least-squares refinement on F was employed, and Cu and Ru atoms were refined anisotropically: $R =$ 0.076 and $R' = 0.080$, $w = [\sigma^2(F_o)]^{-1}$. Positional disorder of the oxygen atoms associated with the ClO_4^- anion was encountered. Refinement of these parameters led to an unreasonable geometry of the ClO_4^- group even when constraints were applied. All hydrogen atoms were generated in their ideal positions except those associated with the water solvate. Calculations were performed on a Silicon-Graphics computer using the program package TeXsan.[23] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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