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Carboxylic Acid Appended Dipyrrin for the Formation of a Hexanuclear Iridium/Copper Paddlewheel Complex

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Reaction of a heteroleptic cyclometalated iridium complex incorporating a carboxylic acid appended dipyrrin with copper acetate leads to the formation of a hexanuclear species with the paddlewheel structure.

With the advent of coordination polymers, also called metal−organic frameworks (MOFs), the rational construction of inorganic nodes has received a revived interest.[1] Among the many potential nodes described in the literature, the paddlewheel structure[2] is prevalent, in particular, in copper-based MOFs.[3] In these architectures, two possibilities may be used. For the first one, based on the $Cu(OAc)_2$ dimer, the metal center adopts the square-based pyramidal geometry and the two apical positions are bridged by bis-monodentate organic ligands, leading thus to homometallic infinite networks. The second possibility is based on the in situ formation of the paddlewheel node using organic polycarboxylate derivatives.[3] Surprisingly, in spite of the high recurrence of this motif in infinite structures, its translation to the preparation of discrete heterometallic complexes has been almost unexplored. Only a few examples of structurally characterized polynuclear species resulting from the association of metal complexes bearing a peripheral carboxylate unit with copper(II) have been reported.[4] Recently, dipyrrin (dpm) derivatives[5] have been shown to promote the sequential construction of crystalline heterometallic architectures via the introduction, at the meso position, of an additional coordinating group such as pyridine, imidazole, nitrile, and carboxylic acid.[6] The use of heteroleptic complexes incorporating a carboxylic acid appended dpm appeared then as an interesting strategy for the elaboration of heteronuclear species based on the copper paddlewheel motif.

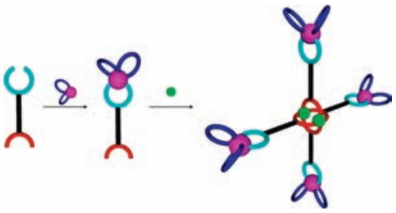

Figure 1. Stepwise approach to the synthesis of a heteronuclear complex based on the paddlewheel core.

For the preparation of such discrete complexes, one may first coordinate the dpm group to a capped metallic fragment and subsequently combine the resulting complex bearing a carboxylate group at its periphery with copper salts to generate the desired heterometallic compound (Figure 1). Surprisingly, only a few heteroleptic complexes featuring a single dpm ligand have been reported.[6,7] In the course of our investigations[7b] of the synthesis of novel luminescent dpm-based complexes,[8] biscyclometalated iridium(III) cores appeared appealing.[9] These moieties, in addition to two free coordinating sites in the cis

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position, also exhibit luminescent properties that can be modulated by the choice of ligands.[9,10]

Complex **3** (Scheme 1), combining the cyclometalated iridium core and a carboxylic acid appended dpm, features, therefore, all of the attributes of an ideal candidate for the formation of paddlewheel-based heterometallic architectures upon reaction with copper(II). Here, we report on the preparation and characterization of a hexanuclear heterometallic Cu_2Ir_4 star-type complex, **4**. For the latter, it is worth mentioning that, because of the chiral nature of the iridium core, five stereoisomers (Λ_4, Δ_4, $\Lambda_3\Delta$, $\Lambda\Delta_3$, and $\Lambda_2\Delta_2$) may be formed. For the $\Lambda_2\Delta_2$ complex, two positional isomers (cis and trans) may exist. Furthermore, because of the square-pyramidal geometry adopted by copper(II), the two apical positions may be occupied by either the same or different auxiliary ligands. This feature further increases the number of possibilities.

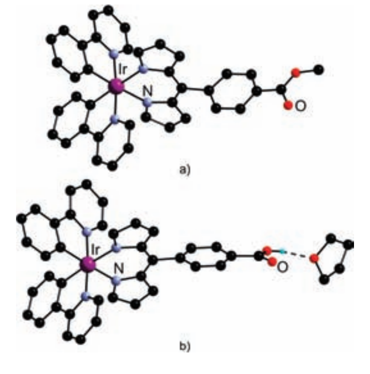
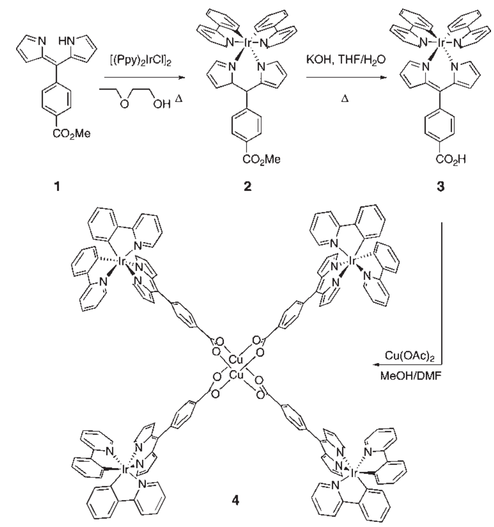


Figure 2. Crystal structures of the mononuclear complexes **2** (a) and **3** (THF) (b). CH hydrogen atoms have been omitted for clarity. Note that only one of the two independent molecules in the structure of **2** is presented here.

Scheme 1. Synthetic Scheme for the Preparation of **4**



Upon reaction of dipyrrin **1**[11] with the tetrakis(2-phenylpyridine-C^2,N')(μ-dichloro)diiridium, $[(Ppy)_2IrCl]_2$ (Ppy = 2-phenylpyridine),[12] the ester-appended complex **2** was obtained in 93% yield.[13a] Subsequent saponification led to complex **3** in 93% yield.[13b] Both complexes, in addition to standard analytical methods, were also characterized by single-crystal X-ray diffraction, which revealed that both compounds crystallize in the triclinic $P\bar{1}$ space group (Figure 2).[14] While for **2** two independent complexes are present, only one is observed in the case of **3**, a tetrahydrofuran (THF) solvate. The iridium cation is in an octahedral coordination environment with the nitrogen atoms of the two Ppy ligands in the trans position. The dpm ligand occupies the equatorial plane, with the two pyrrolic rings being almost coplanar. The average Ir−C and Ir−N bond lengths involving the Ppy ligand are

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(13) (a) **2**: $[(Ppy)_2IrCl]_2$ (149 mg, 1.39×10^{-4} mol) and **1** (101 mg, 3.62×10^{-4} mol) were suspended in dry 2-ethoxyethanol (15 mL) under argon. After the addition of a few drops of NEt_3, the mixture was stirred at reflux (150 °C) for 15 h. Solvents were removed under reduced pressure, and the resulting oil was purified by column chromatography (SiO_2, CH_2Cl_2). **2** (202 mg, 93%) was obtained as a red powder. Single crystalline red rods were grown by the slow diffusion of pentane into a $CHCl_3$ solution. ^1H NMR (300 MHz, $CDCl_3$): δ 3.97 (3H, s), 6.25 (2H, d, J=4.3 Hz), 6.43 (4H, m), 6.82−6.96 (8H, m), 7.58 (6H, m), 7.81 (2H, d, J=8.4 Hz), 7.88 (2H, d, J=5.9 Hz), 8.11 (2H, d, J=8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.3, 117.4, 118.7, 120.9, 121.9, 123.9, 128.4, 129.6, 129.7, 130.5, 130.9, 132.2, 133.7, 136.1, 144.4, 144.6, 146.9, 149.5, 152.8, 156.3, 166.9, 168.7. HRMS (ESI). Calcd for $C_{39}H_{29}N_4O_2Ir$: m/z 778.192 $[M + H^+]$. Found: m/z 778.187 $[M + H^+]$. UV−vis $[CH_2Cl_2, \lambda_{max}/nm (\log \varepsilon)]$: 279 (4.36), 484 (4.36). (b) **3**: A suspension of complex **2** (400 mg, 5.14×10^{-4} mol) in 1:1 THF/H_2O and 4% KOH (2 mL) was stirred at reflux for 4 h. The solution was then cooled in an ice bath, and 1 mL of aqueous HCl (6 N) were slowly added until complete precipitation of the red solid had occurred. The powder was filtered and dried under vacuum. Red-dark crystalline rods of **3** (400 mg, 93%) were grown by the slow diffusion of pentane into a THF solution. ^1H NMR (300 MHz, $CDCl_3$): δ 6.23 (2H, dd, J=4.3 and 1.3 Hz), 6.40 (4H, m), 6.82 (4H, m), 6.93 (4H, m), 7.54−7.66 (6H, m), 7.84 (4H, m), 8.14 (2H, d, J=8.3 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 117.4, 119.0, 120.6, 122.5, 124.0, 128.1, 129.0, 129.9, 130.5, 131.2, 131.8, 132.9, 137.0, 142.7, 144.4, 146.9, 148.5, 151.5, 155.6, 166.8, 167.7. HRMS (ESI). Calcd for $C_{38}H_{27}N_4O_2Ir$: m/z 764.124 $[M + H^+]$. Found: m/z 764.176 $[M + H^+]$. UV−vis $[CH_2Cl_2, \lambda_{max}/nm (\log \varepsilon)]$: 279 (4.45), 484 (4.47). IR (ATR/cm^{-1}): ν_{CO} 1708. (c) **4**: The slow diffusion of a methanolic solution of $Cu(OAc)_2 \cdot H_2O$ (1.3 mg, 6.50×10^{-6} mol) into a DMF solution of **3** (10 mg, 1.31×10^{-5} mol) afforded dark-red single crystals (4 mg, 38%) of **4**. IR (ATR/cm^{-1}): ν_{CO} 1669, 1662, 1654.

(14) (a) Crystal data for **2**: $C_{39}H_{29}IrN_4O_2$, M=777.86, triclinic, space group $P\bar{1}$ (No. 2), a = 11.0105(5) Å, b = 16.6521(7) Å, c = 19.1068(7) Å, α = 72.4530(10)°, β=74.4550(10)°, γ=72.3500(10)°, V=3122.3(2) Å^3, T=173(2) K, Z = 4, D_c = 1.655 g·cm^{-3}, μ = 4.319 mm^{-1}, 47 712 collected reflections, 14 366 independent (R_{int} = 0.0805), GOF = 1.078, R_1= 0.0561, wR_2 = 0.1360 for $I > 2\sigma(I)$ and R_1 = 0.0970, wR_2 = 0.1787 for all data. (b) Crystal data for **3** (THF): $C_{42}H_{35}IrN_4O_3$, M = 835.98, triclinic, space group $P\bar{1}$ (No. 2), a = 11.5527(3) Å, b = 12.4373(3) Å, c = 13.4665(3) Å, α = 77.8200(10)°, β = 69.9860(10)°, γ = 69.9060(10)°, V = 1687.82(7) Å^3, T = 173(2) K, Z = 2, D_c = 1.635 g·cm^{-3}, μ = 3.979 mm^{-1}, 39 253 collected reflections, 7726 independent (R_{int} = 0.0703), GOF = 1.056, R_1 = 0.0443, wR_2 = 0.0748 for $I > 2\sigma(I)$ and R_1 = 0.0697, wR_2 = 0.0876 for all data. (c) Crystal data for **4**: $C_{155}H_{113}Cu_2Ir_4N_{17}O_{10}$, M = 3269.50, triclinic, space group $P\bar{1}$ (No. 2), a = 18.9483(4) Å, b = 20.7016(5) Å, c = 22.6138(5) Å, α = 65.7530(10)°, β = 77.4960(10)°, γ = 75.6160(10)°, V = 7768.3(3) Å^3, T = 173(2) K, Z = 2, D_c = 1.398 g·cm^{-3}, μ = 3.740 mm^{-1}, 168 628 collected reflections, 35 856 independent (R_{int} = 0.0480), GOF = 1.044, R_1 = 0.0725, wR_2 = 0.2108 for $I > 2\sigma(I)$ and R_1 = 0.1108, wR_2 = 0.2320 for all data.

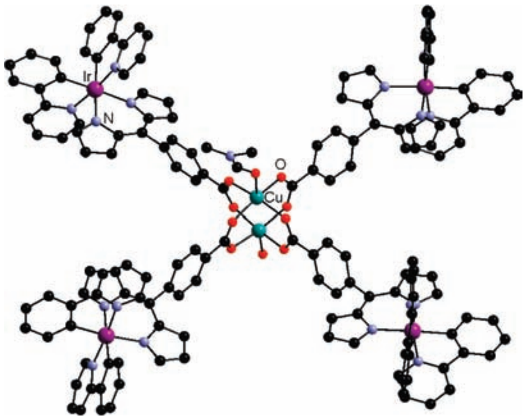

Figure 3. Crystal structure of complex **4**. Hydrogen atoms have been omitted for clarity.

2.019 and 2.046 Å, respectively, while the average distance between nitrogen atoms of the dpm chelate and the metal is 2.139 Å. The latter distance is consistent with the ones reported for other heteroleptic Ir^{III}(dpm) complexes.[7d,10] Note that, unlike other complexes incorporating a carboxylic acid appended dpm,[7a,8e,11] complex **3** does not organize into a hydrogen-bonded dimer but is hydrogen-bonded to the oxygen atom of the THF solvate molecule (d_{O---O} = 2.632 Å and α_{OH---O} = 161.3°; Figure 2).

The redox behavior of **3**, studied by cyclic voltammetry in *N*,*N*-dimethylformamide (DMF), revealed a reversible reduction peak at -1.93 V vs Fc/Fc$^+$ and an irreversible oxidation wave at $+0.51$ V vs Fc/Fc$^+$, as observed for analogous species.[10] The absorption spectra in CH_2Cl_2 for both compounds show an intense band at 484 nm assigned to the $\pi-\pi^*$ ligand-centered transition of the dpm ligand.[7a,b,8,10] Preliminary photophysical investigations in a CH_2Cl_2 solution revealed weak luminescence for both complexes **2** and **3** at 700 and 710 nm, respectively, when excited at 485 nm. This observation is in agreement with other (Ppy)$_2$Ir(dpm) complexes.[10]

Slow diffusion of a MeOH solution of Cu(OAc)$_2$ into a DMF solution of **3** led to the formation of dark-red crystals after 2 weeks. Single-crystal X-ray diffraction revealed that the heterometallic complex [(**3**)$_4$Cu$_2$(DMF)(H$_2$O)] (**4**) crystallizes in the triclinic space group $P\bar{1}$ with one complex in the general position.[14] Additional disordered solvent molecules were also found in the lattice; unfortunately, they could not be refined, and thus the SQUEEZE command was applied. As expected, two copper(II) cations form the paddlewheel motif bridged by the carboxylate groups of four iridium moieties with a Cu−Cu distance of 2.627(3) Å, as usually observed for such species (Figure 3).[15] A DMF molecule and a water molecule occupy the two axial positions. Note that crystallization from a THF/MeOH mixture led to crystals, albeit of lower quality, containing the same type of architecture, however, with two MeOH molecules located at the axial positions. One of the four iridium centers shows a bending around the N−N hinge of the dpm ligand, unlike the other three units and that observed for the precursor complex **3**. As reported for a tripyrrin-based pentanuclear nickel complex,[16] the overall compound is rather flat (Figure 3), with the four iridium cations lying in the same plane. Interestingly, among the many possibilities mentioned above, within the heteronuclear complex, either the $\Lambda_3\Delta$ or $\Lambda\Delta_3$ stereoisomer is obtained.

Powder X-ray diffraction of a batch of **4** demonstrated the presence of a single phase with poor crystallinity owing to partial desolvation.

In attempts to generate infinite one-dimensional networks by the bridging of consecutive units of **4**, analogous reactions in the presence of a ditopic ligand such as 4,4′-bipyridine have only led, so far, to the isolation of crystals of **4**.

Compound **4** was found to be rather insoluble in common organic solvents. Furthermore, attempts to solubilize it in DMF led to its decomposition, as shown by mass spectrometry. This prevented any further solution investigation of this species.

In conclusion, the reaction of a cyclometalated iridium complex bearing a carboxylic acid appended dpm ligand with copper acetate leads to the formation of a heterometallic Cu_2Ir_4 hexanuclear star-type architecture constructed around the Cu_2 paddlewheel motif. With the aim of using this type of core as a node of luminescent-extended MOF-type constructs, functionalization of the cyclometalating ligand is currently under investigation. Extension to Rh$^{II}_2$,[17] Mo$^{II}_2$, and W$^{II}_2$ paddlewheels[18] is also underway.

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Supporting Information Available: X-ray crystallographic data for compounds **2**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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