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New mix-ligand copper(I) and copper(II) pyrazolate complexes with 2,2′-bipyridine

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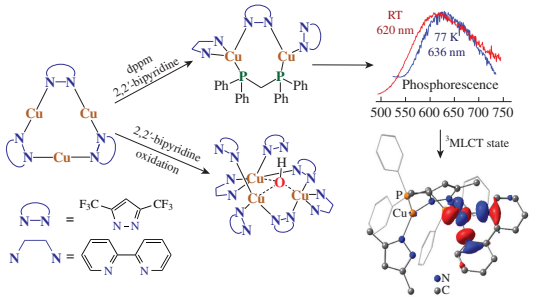
The reaction of the trinuclear copper(I) 3,5-bis(trifluoromethyl)pyrazolate with 2,2′-bipyridine on contact with air leads to the oxidation of Cu centers and affords trinuclear Cu^{II} complex containing bridged pyrazolate OH anions and chelating bipy ligands. Carrying out the reaction in the presence of dppm prevents oxidation and gives dinuclear copper(I) complex with bridging dppm and pyrazolate ligands, and chelating bipy ligand. This complex exhibits red-orange phosphorescence originating from the ^{3}ML^{bipy}CT state.



Keywords: copper complexes, pyrazolates, 2,2′-bipyridine complexes, photoluminescence, phosphorescence, time-dependent density functional theory, crystal structure.

Complexes of copper(I) salts with bipyridine-type ligands are among the well-known and most popular coordination chemistry objects.[1–6] The strong absorption of these complexes corresponding to the MLCT transitions opens the possibility for practical application in photocatalysis or production of light-emitting materials.[7–10] Macrocyclic coinage metal pyrazolates attract an interest of researchers because of their rich coordination chemistry,[11–15] photophysical,[16,17] and catalytic properties.[18–22] We have recently investigated the interaction of silver pyrazolates with bipyridine-type ligands.[23,24] To the best of our knowledge, up to date, there is only one report on the synthesis and structure of copper(I) pyrazolates with bipy, no information on their emission properties being documented.[25]

Herein, we present our results on the complexation of the trinuclear copper(I) 3,5-bis(trifluoromethyl)pyrazolate, $[Cu((CF_3)_2Pz)]_3$, with 2,2′-bipyridine. We have found that these compounds readily reacted even in the solid state: grinding of the colourless solids under argon atmosphere caused immediate colour change to dark red. The new complex appeared to be extremely sensitive to the traces of oxygen and moisture, turning into a blue complex **1** (Scheme 1). Similarly, the dissolution of solid reactants in toluene gives the crimson solution, which becomes blue with time when left on the air. Crystallization from cold solution allowed us to isolate product $Cu_3[(CF_3)_2Pz]_5(bipy)_2(OH)$ **1** being an oxidized Cu^{II} mixed ligand hydroxo complex.†

Recently we have shown that bis(diphenylphosphino)methane (dppm) formed stable complexes with trinuclear coinage metal pyrazolates and affected their photophysical properties.[26] Since it is known that phosphine ligands stabilize metal ions in low oxidation states,[27,28] we attempted to react bipy with $[Cu((CF_3)_2Pz)]_3$(dppm) complex formed *in situ* by mixing equimolar amounts of copper macrocycle and dppm. Crystallization gave yellow air-stable dinuclear Cu^I complex **2** containing all three ligands, $Cu_2[(CF_3)_2Pz](bipy)(dppm)$ (see Scheme 1).‡

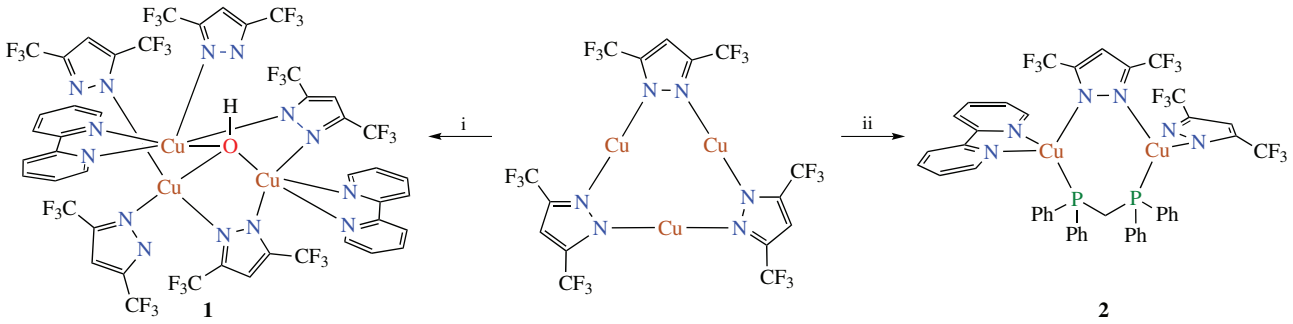
Thus, in the case of the reaction of a free copper macrocycle $[Cu((CF_3)_2Pz)]_3$ with bipy, the oxidation of all copper centers occurred. In contrast, the stabilization with dppm prevents the oxidation of metal centers, with the trinuclear core having rearranged into the dinuclear mix-ligand pyrazolate/dppm cycle. Some byproducts were formed in both cases, however the remaining supernatant solutions left after crystallization of the products were not analyzed.

Compound **1** is a trinuclear complex in which OH^- ligand is centered between three copper(II) ions, and this core is decorated by nitrogen-containing ligands (Figure 1).§ Three copper units are paired by two bridging pyrazolate anions and two of the three

† *Complex* **1**. A mixture of $[Cu((CF_3)_2Pz)]_3$ (50 mg, 0.0625 mmol) and 2,2′-bipyridine (9.8 mg, 0.0625 mmol) was dissolved in toluene (3 ml). The crimson solution was stirred overnight at room temperature in air to become blue. Then, hexane (3 ml) was layered on the surface of the reaction solution. The solution obtained was refrigerated at 5 °C. Within 1 h, the blue crystals have formed, which were isolated by filtration, washed with hexane and Et_2O, and dried under vacuum yielding 21 mg of **1**.

‡ *Complex* **2**. To a solution of $[Cu((CF_3)_2Pz)]_3$ (30 mg, 0.0375 mmol) in toluene (2 ml), dppm (14.4 mg, 0.0375 mmol) was added. The colourless solution was stirred for 1 h, and a solution of 2,2′-bipyridine (5.85 mg, 0.0375 mmol) in toluene (1.5 ml) was added dropwise. The yellow solution was stirred at 60 °C for 3 h. After cooling to room temperature, hexane (3 ml) was added. The product was crystallized at –15 °C, isolated by filtration, washed with cold hexane, and dried under vacuum yielding 27 mg of **2**.

§ *Crystal data for* **1**. $C_{45}H_{22}Cu_3F_{30}N_{14}O$, monoclinic, space group $P2_1/c$, $a = 12.9719(6)$, $b = 12.2711(5)$ and $c = 33.9803(15)$ Å, $\beta = 93.4930(10)°$, $V = 5398.9(4)$ Å^3, $Z = 4$, $d_{calc} = 1.889$ g cm^{-3}, $\mu = 1.328$ mm^{-1}, $R_1 = 0.0358$ [from 12061 unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0899$ (from all 95470 unique reflections).



Scheme 1 *Reagents and conditions*: i, 2,2′-bipyridine, air; ii, dppm, 2,2′-bipyridine.

metal ions are chelated by 2,2′-bipyridine. The other three pyrazolate anions are coordinated to copper centers by deprotonated nitrogen atoms. Two copper atoms chelated by bipy ligands have a distorted triangular bipyramidal environment formed by two nitrogen atoms of bipy ligand, two nitrogen atoms of pyrazolate ligands and oxygen atom. The Cu–N^{Pz} (1.964–2.080 Å) and Cu–N^{bipy} (1.999–2.043 Å) bond lengths are in the range typical of copper(II) pyrazolate-pyridine complexes.[29,30]

Compound **2** is a dinuclear copper(I) complex in which metal atoms are bridged by pyrazolate anion and dppm ligand, forming a [Cu2N2PCP] distorted cycle (Figure 2). The Cu(1) atom is chelated by 2,2′-bipyridine, and Cu(2) is coordinated to the second pyrazolate anion. Angles N(1)–Cu(1)–N(5), N(5)–Cu(1)–P(1), P(1)–Cu(1)–N(1) and N(5)–Cu(1)–N(6) are 109.09(9), 106.36(7), 126.63(7) and 78.69(9)°, respectively. The environment around Cu(1) may be formulated as distorted tetrahedral.[31] In contrast, the Cu(2) atom is in the plane formed by three nearest neighbour atoms (two N^{Pz} and one P^{dppm}). Despite the presence of addition ligands, the Cu–N^{Pz} bond lengths and CuNN^{Pz} angles are in the range typical of trinuclear copper macrocycles.[32]

The electronic spectra of complexes **1** and **2** were measured in CH_2Cl_2 (Figure 3). Complex **1** is blue coloured and complex **2** is yellow, that correlates with the presence of non-intense bands at λ_{max} = 645 ($\varepsilon = 1.7\times10^2$ cm^{-1} mol^{-1}) and 400 nm ($\varepsilon = 7.3\times10^2$ cm^{-1} mol^{-1}), respectively. These bands correspond to the charge-transfer transition from copper ions to bipy ligands. The spectra demonstrate several intense absorptions in the high-energy region (<340 nm) of π → π* character within the bipy and pyrazolate ligands.

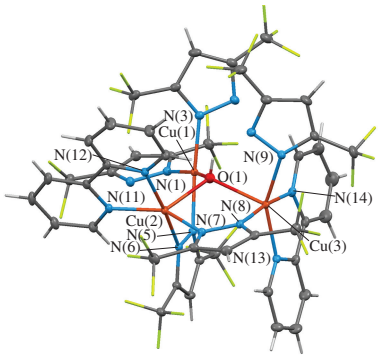


Figure 1 Molecular structure of **1** showing thermal ellipsoids at the 30% probability level. Hydrogen and fluorine atoms are sticks for clarity. Selected bond lengths (Å): Cu(1)–O(1) 1.920(1), Cu(2)–O(1) 2.104(1), Cu(3)–O(1) 2.234(1), Cu(2)–N(11) 2.024(2), Cu(2)–N(12) 1.999(2), Cu(3)–N(13) 2.043(2), Cu(3)–N(14) 1.999(2). Selected angles (deg): N(6)Cu(2)N(12) 173.16(7), N(9)Cu(3)N(13) 152.57(7), N(8)Cu(3)N(14) 172.80(7), N(7)Cu(2)N(11) 143.59(7).

DFT and TD-DFT calculations (CAM-B3LYP/def2-TZVP) of complex **2** predict that the three lowest singlets are ^{1}ML^{bipy}CT transitions involving different d-orbitals of a copper atom Cu(1), which is chelated by bipy (for details, see Online Supplementary Materials, Figure S1 and Table S2). The fourth singlet is a (M+P)L$^{dppm+Pz}$CT transition on the second copper atom [Cu(2)]. Singlets S1–S3 have the same excited electron (LUNTO) localization, on the bipy ligand, with the same orbital symmetry. The two lowest triplet states have rather close vertical energies (3.12, 3.31 eV) but possess different nature. Namely, T_1 is a typical ^{3}LC^{bipy} transition, while T_2 is MLCT being very similar to the S_1 transition (S_H = 0.94, S_E = 0.93).[33] Nevertheless, the excited electron is located on the bipy ligand in both T_1 and T_2. The same is true for HSOMO of the optimized triplet state of complex **2**. The energy difference between the optimized triplet and groung (singlet) states is 1.92 eV that corresponds to the 646 nm emission wavelength (Figure 4), allowing us to suppose that the main photoluminescence channel is a $S_0 \rightarrow S_1$ excitation followed by $T_2 \rightarrow S_0$ MLCT phosphorescence.

The presence of copper(II) ions in complex $[Cu_3((CF_3)_2Pz)_5(bipy)_2(OH)]$ **1** leads to the quenching of light emission, and photoluminescence has been observed only for complex $[Cu_2((CF_3)_2Pz)_2(bipy)(dppm)]$ **2**. Complex **2** in the solid state at room temperature displays a structureless broad band at λ_{max} = 620 nm under UV (370 nm) irradiation with a lifetime τ = 3 μs (see Figure 4). The microsecond domain of lifetime evidences the phosphorescence nature of the emission. The band shape and lifetime demonstrate that emission could be assigned to the charge transfer from copper atom to bipy ligand (^{3}ML^{bipy}CT, *vide infra*). Cooling the sample to 77 K shifts the emission to the lower energy region (λ_{max} = 635 nm) and entails a non-significant

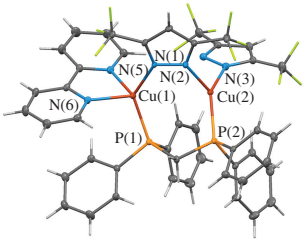


Figure 2 Molecular structure of **2** showing thermal ellipsoids at the 30% probability level. Hydrogen and fluorine atoms are sticks for clarity. Selected bond lengths (Å): Cu(1)–N(1) 2.022(2), Cu(2)–N(2) 2.013(2), Cu(2)–N(3) 1.998(3), Cu(1)–P(1) 2.1967(8), 2.1927(9), Cu(1)–N(5) 2.072(2), Cu(1)–N(6) 2.109(2). Selected angles (deg): N(5)Cu(1)N(6) 78.69(9), P(1)Cu(1)N(1) 126.67(7), N(2)Cu(2)P(2) 118.89(7), N(2)Cu(2)N(3) 107.44(9), P(2)Cu(2)N(3) 133.60(7).

Crystal data for **2**. $C_{45}H_{32}Cu_2F_{12}N_6P_2$, triclinic, space group $P\bar{1}$, a = 10.4244(14), b = 14.4627(19) and c = 15.325(2) Å, α = 87.963(2)°, β = 78.566(2)°, γ = 80.011(2)°, V = 2230.2(5) Å^3, Z = 2, d_{calc} = 1.599 g cm^{-3}, μ = 1.117 mm^{-1}, R_1 = 0.0526 [from 9964 unique reflections with $I > 2\sigma(I)$] and wR_2 = 0.1580 (from all 29778 unique reflections).

CCDC 2046832 and 2046833 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

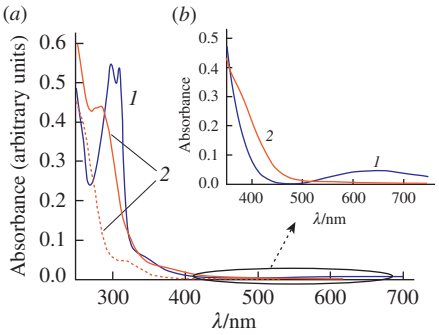


Figure 3 Absorption spectra of **1** (*1*) and **2** (*2*). Experimental in CH_2Cl_2 [solid line, $c = 3 \times 10^{-4}$ mol dm^{-3}, (*a*) $d = 0.1$ cm, (*b*) $d = 1$ cm] and simulated (dotted line, the width at half-height set as 40).

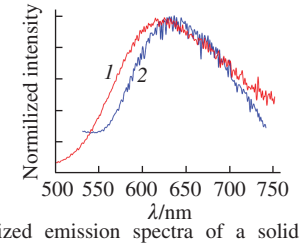


Figure 4 Normalized emission spectra of a solid sample **2** at room temperature (*1*) and 77 K (*2*).

growth of the lifetime ($\tau = 9$ μs) and intensity. This behaviour also supports the charge transfer nature of the emission, not ligand-centered (LC^{bipy}), for which the blue shift of emission at low temperature is typical and corresponds to stabilization of the ground state. These observations indicate that TADF behaviour could occur in the emission observed for this complex.[8]

In conclusion, we have described new types of copper(I) and copper(II) pyrazolates complexes with the 2,2′-bipyridine ligand. In the case of direct interaction of cyclic trinuclear Cu^I bis(trifluoromethyl)pyrazolate with bipy, the oxidation of metal centers occurred to afford a trinuclear complex **1** in which OH^- ligand combines three copper(II) ions. The additional coordination of bis(diphenylphosphino)methane to the starting macrocycle prevents the oxidation processes during the interaction with bipy ligand stabilizing the copper atoms in +1 oxidation state. The thus formed dinuclear copper(I) complex **2** contains metal atoms bridged by pyrazolate anion and dppm ligands with (Cu2N2PCP) distorted cycle. Complex **2** possesses phosphorescence in the solid state. The main luminescence channel is $ML^{bipy}CT$ transition, as is demonstrated by TD-DFT calculations. The experimental (room temperature and 77 K) and calculated emission maxima are in good accordance, being 620, 636, and 646 nm, respectively.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.008.

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