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Interaction of a trinuclear copper(I) pyrazolate with alkynes and carbon–carbon triple bond activation[†]

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The trinuclear copper(i) pyrazolate $\{[3,5-(CF_3)_2Pz]Cu\}_3$ forms η^2 -copper/alkyne triple bond coordinated structures in the presence of acetylenes. There is no coordination of copper atoms to the phenyl ring of phenylacetylene and copper(i) acetylide formation during the interaction. It was observed that the complexes formed are the active catalytic species in click reactions.

In the last decade, copper(1) pyrazolate complexes have attracted wide attention due to their diverse structures,¹⁻³ rich supramolecular chemistry,^{2,4-13} and many potential applications in the areas of luminescence,¹⁴⁻²³ catalysis,²⁴⁻²⁸ and adsorption.²⁹ Being Lewis acids, trinuclear copper(1) pyrazolates have shown interesting structural features forming infinite stacks by metallophilic bonding^{16,17} or by complexation with bases such as π -electron systems of arenes^{3,10} or sandwich compounds,^{5,9} ketones^{6,21} and halogens.^{11,19} However, no data on the complexation of copper(I) pyrazolate macrocycles with compounds containing triple bonds have been reported so far. Furthermore, despite the fact that many copper(1) complexes are active catalysts in certain types of reactions, e.g., the dimerization of acetylenes³⁰ and alkyne-azide cycloaddition,^{31,32} a vast majority of the works on macrocyclic copper(1) pyrazolates has been devoted towards the investigation of supramolecular aggregation and its influence on the properties of the macrocycles, but without considering possible activation of the coordinated bonds of bases.

Herein we report our results on the complexation of the trinuclear copper(1) *bis*-(trifluoromethyl)pyrazolate ($\{[3,5-(CF_3)_2Pz]Cu\}_3$ ([CuL]₃); Fig. 1) with 1-octyne **1** and phenylacetylene **2** and

‡ Both authors contributed equally to this work.

 $F_{3}C \rightarrow CF_{3}$ $F_{3}C \rightarrow CF_{3}$ $F_{3}C \rightarrow Cu \rightarrow CF_{3}$ $F_{3}C \rightarrow CF_{3}$ $F_{3}C \rightarrow CF_{3}$

Fig. 1 Structure of complex {[3,5-(CF₃)₂Pz]Cu}₃.

demonstrate the application of the complex as an efficient catalyst for alkyne–azide cycloaddition under mild conditions. 30,31

The titration of 1-octyne or phenylacetylene solutions in CH_2Cl_2 with $[CuL]_3$ showed that the intensities of their $\nu(CH)^{init}$ bands (3304 cm^{-1} for 1 and 3307 and 3294 cm^{-1} for 2) decrease, while new low-frequency ν (CH)^{in compl} bands (3222 cm⁻¹ for **1** and 3217 cm⁻¹ for 2) appear in the IR spectra (Fig. 2 and see Fig. S1 in the ESI⁺). Simultaneously, similar changes are observed in the region of $C \equiv C$ stretching vibrations: the intensities of the initial ν (C \equiv C)^{init} bands (2115 cm⁻¹ for 1 and 2110 cm⁻¹ for 2) decrease and new low-frequency ν (C \equiv C)^{bonded} bands (1945 cm⁻¹ for 1 and 1910 cm^{-1} for 2) appear (see Fig. S2 in the ESI[†]). The coordination of the copper(1) salts to the carbon-carbon triple bond is known to entail the appearance of new low-frequency bands in the ν (CH) and $\nu(C \equiv C)$ regions.^{33,34} Therefore, this spectral behavior evidences the coordination of macrocycle $[CuL]_3$ to the π -electron system of the triple bond but not the formation of the copper(1) acetylide complex via proton elimination. Moreover, the absence of the high frequency bands in both the regions of ν (CH) and $\nu(C \equiv C)$ stretching vibrations in the case of the complexation of phenylacetylene with [CuL]₃ suggests the absence of coordination of copper atoms to the phenyl ring that could be expected based on the well-known affinity of trinuclear group 11 metal pyrazolates to aromatic hydrocarbons.^{3,10} The Job plot for the complexation of [CuL]₃ with 1-octyne (obtained at a total concentration of 0.05 M) has a maximum at 0.66 mole fraction

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Fig. 2 IR spectra of 1-octyne $\mathbf{1}$ (c = 0.05 M, black) and $\mathbf{1}$ in the presence of increasing amounts of [CuL]₃ (0.5 equiv.: red, 1 equiv.: blue) in CH₂Cl₂, d = 2 mm, T = 298 K.

of 1-octyne (see Fig. S3 and S4 in the ESI[†]), suggesting that two acetylene molecules and one macrocycle molecule take part in the complex formation.

The titration of 1-octyne or phenylacetylene solutions in CD₂Cl₂ with complex [CuL]₃ shifts the ¹H NMR resonances of the acetylene group in 1 and 2 to a significantly low field, while other proton resonances (except for the CH₂ group protons close to the $C \equiv C$ of 1-octyne, *vide infra*) shift to a high field. Thus, the addition of one equivalent of the macrocycle $[CuL]_3$ to a solution of phenylacetylene leads to a non-significant high field shift of aromatic proton resonances ($\Delta \delta$ = -0.06 to -0.12 ppm) and a considerable low field shift of an acetylene proton ($\Delta \delta$ = +0.54 ppm) (see Fig. S5 and S6 in the ESI⁺). The integration shows that the ratio of phenyl protons to a proton at the triple bond of 2 does not change upon macrocycle addition (remaining 5:1), which evidences the absence of the proton elimination and formation of a copper(1) acetylide complex (see Fig. S6 in the ESI $^+$). The ¹³C NMR resonances of the carbons at the triple bond broaden and undergo significant low field shifts in the presence of an equimolar amount of the macrocycle ($\Delta \delta$ = +0.85 to +3.31 ppm; Fig. 3). At the same time, the resonances of quaternary (C3) and orthocarbon atoms (C4) drift to a high field ($\Delta \delta$ = -0.18 to -0.27 ppm), while the resonances of meta- and para-carbons undergo comparable low field shifts ($\Delta \delta$ = +0.14 to +0.34 ppm; Fig. 3). The ¹H and ¹³C NMR signals of 1-octyne show similar behavior in the presence of the macrocycle (see Fig. S7 and S8 in the ESI[†]). The ¹³C NMR



Fig. 3 13 C NMR spectra of phenylacetylene 2 (c = 0.05 M, blue) and 2 in the presence of different amounts of **[CuL]**₃ (0.25 equiv.: green, 0.5 equiv.: grey, 0.75 equiv.: magenta, 1 equiv.: olive) in CD₂Cl₂, T = 298 K.

resonance of the quaternary carbon atom of the triple bond (C2) broadens into a base line and it is impossible to establish its position. The carbon resonance of the CH₂ group of **1** close to the C \equiv C bond also undergoes low field shifting and broadening, which confirms the complex formation. All the above mentioned observations prove unequivocally that the interaction of the copper(1) macrocycle with both acetylenes **1** and **2** in solution yields intermolecular complexes, in which the π electron system of the carbon–carbon triple bond is bound to copper *via* η^2 -type coordination. Furthermore, despite the well-known high affinity of trinuclear copper pyrazolates to arenes,^{3,10} there is no interaction with the phenyl ring of phenylacetylene **2** in the solution.

The structures of the complexes were unveiled by single crystal X-ray diffraction analysis. Brownish crystals of both complexes $[CuL]_3$ /phenylacetylene 3 and $[CuL]_3$ /1-octyne 4 were obtained by slow solvent evaporation from equimolar reagent mixtures in CH₂Cl₂/hexane (1:1) solutions in air. Surprisingly, both complexes appeared to contain two copper(1) atoms and one copper(1) atom linked by four pyrazolate ligands. The oxidation of copper(1) to copper(1) corresponds to the presence of oxygen/moisture in the reaction vessel. Copper(1) atoms are located on the inversion centers and in the plane of four neighboring nitrogen atoms (Fig. 4).

In both complexes each copper(1) atom is coordinated to an acetylene fragment *via* $M \cdots \pi$ interaction (the distances between Cu and the C=C bond centroid are 1.879 Å for 3 and 1.890 Å for 4). Also, the C-C bond lengths are in the range typical for triple bonds, being 1.218 and 1.224 Å for 3 and 4, respectively.³⁵ Furthermore, the solid state IR spectra of crystals 3 and 4 are similar to the IR spectra in solution, meaning that the structures of 3 and 4 are the same in the solid state and in solution (see Fig. S9 and S10 in the ESI†). As the trinuclear macrocycles dissociate into mononuclear (MPz) and dinuclear (M₂Pz₂) species at low concentrations, this could be the driving force for their reorganization in the presence of alkynes, yielding the Cu₃Pz₄(η^2 -alkyne)₂ complexes 3 and 4. Unfortunately, the complexity of the equilibria in solution prevents the reliable estimation of the formation constants for 3 and 4.



Fig. 4 Crystal structures of **3** (left) and **4** (right). Copper and nitrogen atoms are ellipsoids (50% probability level), and other atoms are sticks. Fluorine atoms are omitted for clarity.



Scheme 1 Alkyne-azide cycloaddition catalyzed by trinuclear copper(i) pyrazolate complex [CuL]₃.

Next, we tested the ability of the trinuclear copper(1)pyrazolate complex to catalyze the alkyne-azide cycloaddition through the activation of the triple bond of acetylenes. After addition of one equivalent of ortho-fluorobenzyl azide 5 to a 1:1 mixture of $[CuL]_3$ and phenylacetylene 2 in CD_2Cl_2 at room temperature in air, we observed the formation of 1,4-substituted 1,2,3-triazole in a quantitative yield by NMR spectroscopy (Scheme 1a) (see Fig. S11 in the ESI⁺). The click reaction between 1-octyne 1 or phenylacetylene 2 and azide 5 takes place also in the presence of only 1 mol% of [CuL]₃, yielding triazoles 6 and 7 in quantitative yields (Scheme 1b). Noteworthy are the especially mild conditions under which the reaction proceeds: no inert gas atmosphere, base, or heating is required. In addition, we investigated the cycloaddition of phenylacetylene 2 with azide 5 in the presence of 1 mol% of crystals of complex 3 (the structure was proved by XRD and solid state IR spectroscopy). The obtained results are in a good agreement with the reaction shown in Scheme 1b. This experiment, most likely, proves the nature of the key catalytic particle. This feature shows the potential of the trinuclear copper(I) pyrazolate complex as an efficient catalyst not only for alkyne-azide cycloaddition but also for other copper(I) catalyzed transformations.

In summary, we demonstrated for the first time the ability of the trinuclear copper(1) pyrazolate complex to coordinate the carbon–carbon triple bond of acetylenes *via* π -electron bonding. Interestingly, there is no interaction with the phenyl ring of phenylacetylene in solution despite the well-known affinity of trinuclear copper pyrazolates to arenes. No elimination of the acidic proton occurs during the interaction of the copper(1) pyrazolate with 1-octyne and phenylacetylene, but the macrocycle rearranges into bicyclic "spiro" Cu₃Pz₄(η^2 -alkyne)₂ complexes (3 and 4). Moreover, the trinuclear copper(1) pyrazolate complex appeared to catalyze the alkyne–azide cycloaddition

through the activation of the carbon–carbon triple bond. The detailed study of this catalytic reaction is now ongoing in our laboratory and will be reported elsewhere.

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Conflicts of interest

There are no conflicts to declare.

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