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Gas phase assembly and X-ray crystal structure of copper(I) 3,5-bis(trifluoromethyl)benzoate network with corannulene

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Dedicated to Robert J. Angelici

Abstract

Gas-phase co-deposition of $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**) with $C_{20}H_{10}$ at 170 °C affords crystals of the first copper(I)–corannulene adduct $[Cu_6(O_2C(3,5\text{-}CF_3)_2C_6H_3)_6](C_{20}H_{10})_2$ (**2**). The X-ray crystallographic characterization of **2** reveals its main structural building blocks: a planar hexanuclear metal core supported by bridging 3,5-bis(trifluoromethyl)benzoate groups and two corannulene molecules. The Cu···Cu distances within the core of 2.6826(8)–2.7607(8) Å fall within the range of cuprophilic interactions. Several intermolecular Cu···C contacts between the cyclic Cu_6-unit and corannulene ranging from 2.799(5) to 3.266(5) Å can be identified. The shortest ones lying within the sum of the van der Waals radii for Cu and C (Σr_{vdW} (Cu, C) = 3.10 Å) are to the rim sites of corannulene. A noticeable flattening of the $C_{20}H_{10}$-bowl in **2** is also observed.

Keywords: Corannulene; Copper(I) carboxylate; Single crystal structure analysis

1. Introduction

From a coordination viewpoint, bowl-shaped polyaromatic hydrocarbons or buckybowls [1] are unique ligands that have multi-site coordination possibilities, namely, convex and concave interior polyaromatic faces, as well as edge or rim carbon atoms capped by hydrogen atoms. They share with fullerenes the convex three-dimensional surface of unsaturated carbon atoms but in contrast have a concave carbon surface that is open and readily accessible. These hydrocarbons constitute a new family of polyarenes that is expected to exhibit system-dependent preferences for metal coordination. Substantial efforts have been directed toward studying the reactivity and ligating properties of buckybowls using various computational techniques [2,3]. However, control of their reactivity in coordination reactions presents a challenge, and experimental evidence [4] regarding preferences for metal binding is still mainly limited to the smallest bowl, corannulene ($C_{20}H_{10}$, Scheme 1) [5].

Ten years ago, the first metal complex of corannulene, $[(C_5Me_5)Ru(\eta^6\text{-}C_{20}H_{10})]^+$, was isolated and spectroscopically characterized [3a]. NMR evidence was subsequently reported for η^6-complexation of corannulene also by $[Ir(C_5Me_5)]^{2+}$ [6], but it was not until 2004 that Angelici and coworkers finally succeeded in structurally characterizing η^6-complexes of corannulene by X-ray crystallography for the first time [7]. From this work, the dramatic impact that transition metals can have on bowl-shaped ligands was brought to light. The X-ray structures of Angelici revealed that the coordination of two ruthenium atoms to corannulene in $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6{:}\eta^6\text{-}C_{20}H_{10})]X_2$ ($X = PF_6^-$ and SbF_6^-) completely flattens the curved polyaromatic surface. This effect is noteworthy, because metal–ion binding may likewise change the shape of other non-planar carbon surfaces, such as the caps or walls of carbon nanotubes, for example. The recently prepared complexes of the type

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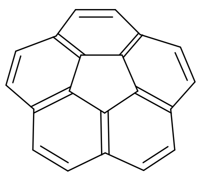

$C_{20}H_{10}$
corannulene

Scheme 1.

$[(\eta^6\text{-arene})M(\eta^6\text{-}C_{20}H_{10})]X_2$ ($M = Ru$, Os; $X = BF_4^-$, PF_6^-, or SbF_6^-) showed [8] an increased stability compared to analogous η^6–corannulene complexes of $[Cp^*Ru]^+$, $[Cp^*Ir]^{2+}$, and $[(COE)_2M]^+$ ($M = Rh$ or Ir) [9]. Three silver(I)-based extended networks built on η^2- and η^1-binding of Ag^+ ions to the rim sites of $C_{20}H_{10}$ were isolated in 2005 [10], but no first row transition metal complexes of corannulene have been reported until now.

To test the reactivity of buckybowls, we rely on the gas-phase co-deposition technique that has been proven successful for coordination of a variety of polyaromatic hydrocarbons [11]. The first crystalline complexes of corannulene were successfully prepared in our laboratory in 2003 using the above solvent-free approach [12] and the $[Rh_2(O_2CCF_3)_4]$ unit as an electrophilic probe. The structural characterization of rhodium(II) complexes with several other bowls revealed their preference for rim coordination by strongly Lewis acidic metal centers [13]. This trend was later extended to the electrophilic diruthenium(I,I) $[Ru_2(O_2CCF_3)_2(CO)_4]$ complex [14]. The use of a soft and single-end Lewis acid, $[Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5]$, recently afforded the first hub-bound corannulene complex [15].

In our laboratory we have recently started testing electrophilic copper(I) carboxylate complexes as probes to study copper(I)–arene substrate interactions. In a course of these studies, we have prepared the first cyclic hexanuclear copper(I) carboxylate, $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]$, and its adduct with planar coronene, $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$ [16]. Importantly, DFT calculations confirmed the latter to be a cocrystallization product held by strong electrostatic ion–dipole interactions without any covalent contribution to bonding. Using bulkier substituents at the benzene groups of carboxylates, we have isolated a new complex, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**), that has a remarkable infinite double-helical structure in the solid state [17]. The latter was shown to produce reactive copper(I) fragments of nuclearities two, four, or six in the gas phase upon sublimation with various planar polyaromatic hydrocarbons. This has prompted us to test the reactivity of copper(I) 3,5-bis(trifluoromethyl)benzoate (**1**) toward the curved polyaromatic surface of corannulene. Herein, we report the synthesis, photoluminescence, and X-ray structural characterization of the first copper(I)–buckybowl adduct, $[Cu_6(O_2C(3,5\text{-}CF_3)_2C_6H_3)_6](C_{20}H_{10})_2$ (**2**).

2. Experimental

2.1. General

All synthetic procedures were carried out under a dry atmosphere of dinitrogen using standard Schlenk and glove-box techniques. Copper(I) 3,5-bis(trifluoromethyl)benzoate, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**), was synthesized using the recently reported procedure [17]. 3,5-Bis(trifluoromethyl)benzoic acid, $(3,5\text{-}CF_3)_2C_6H_3COOH$, was purchased from SynQuest Fluorochemicals and used as received. Corannulene, $C_{20}H_{10}$, was prepared by the known literature procedures [18].

The infrared spectrum of **2** was measured on a Nicolet Magna 550 FTIR spectrometer using a KBr pellet. The photoluminescence spectrum was collected on a Varian Cary Eclipse spectrophotometer, in which the PMT detector was positioned at 90° to the incident beam. Default settings (slit widths of 5 nm and integration time of 0.5 s) were applied. The bulk single crystalline sample was placed in a Varian Cary Sub-micro Fluorometer cell, which was mounted in a standard single cell holder with base. Elemental analysis was performed by Guelph Chemical Laboratories Ltd., Canada.

2.2. Synthesis of $[Cu_6(O_2C(3,5\text{-}CF_3)_2C_6H_3)_6](C_{20}H_{10})_2$ (**2**)

A mixture of crystals of $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**) (0.035 g, 0.109 mmol) with corannulene (0.005 g, 0.020 mmol) was sealed under vacuum (10^{-2} Torr) in a small glass ampule, which was placed in an electric oven at 170 °C. The temperature gradient along the length of the tube was *ca.* 5 °C. Over two weeks, pale yellow plates of **2** had grown at the coldest end of the tube. Yield: 0.030 g (40%). Anal. Calc.: C, 46.50; H, 1.57; O, 7.91. Found: C, 47.00; H, 1.60; O, 8.14%. IR (KBr, cm^{-1}): 3092(w), 3057(w), 3028(w), 1629(m), 1572(m), 1466(w), 1456(m), 1437(m), 1347(s), 1277(s), 1265(sh), 1180(m), 1132(s), 1107(sh), 913(m), 842(m), 820(w), 777(m), 7646(m), 708(m), 699(m), 682(s), 659(m), 547(m). ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 8.11 ($12H_{carb}$), 7.80 ($6H_{carb} + 20H_{cor}$). ^{19}F NMR (282 MHz, $CDCl_3$, 22 °C): δ −63.79. PL (250–750 nm, $\lambda_{ex} = 350$ nm, solid, λ_{max}, nm) 585.

2.3. Crystal structure determination of $[Cu_6(O_2C(3,5\text{-}CF_3)_2C_6H_3)_6](C_{20}H_{10})_2$ (**2**)

The X-ray data were collected with a Bruker SMART APEX CCD-based X-ray diffractometer system using Mo Kα radiation ($\lambda = 0.71073$ Å). A colorless single crystal with dimensions 0.14 × 0.06 × 0.05 mm was mounted on the tip of a glass fiber with silicone grease. A total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame. Data reduction was carried out with the Bruker SAINT program [19], using a