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Polyhedron 26 (2007) 1191–1198
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# The case of a $Cd_2Cu_2$ complex containing an apparently $C_3$-symmetric ligand: Erroneous ligand-structure assignment by X-ray diffraction data analysis

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Received 28 August 2006; accepted 10 October 2006
Available online 17 October 2006

## Abstract

A simplified synthesis of a previously reported $Cd_2Cu_2$ complex **4** was developed in order to have a more readily available source of 1,3,5-tris(trifluoromethyl)-cyclohexane-*cis*,*cis*-1,3,5-triol **1**, a unique tridentate ligand, only tentatively identified elsewhere. Attempts to liberate the ligand from **4** resulted in the sole formation of 2,4,6-tris(trifluoromethyl)-tetrahydropyran-*cis*,*cis*-2,4,6-triol (**2**); no traces of **1** were detected. A newly conducted X-ray analysis of complex **4** led to diffraction data that could be explained either by the previously reported structure for **4** or by the statistically disordered structure **5**, containing ligand **2** rather than **1**. Whereas refinement of both models led to equivalent merit factors, mass spectral data and elemental analysis of the crystals revealed unequivocally the sole presence of the tetrahydropyran derivative within the complex and proved thus the erroneous structure assignment **4** previously published for compound **5**.

*Keywords:* Cadmium; Copper; Highly flourinated alkoxy ligand; X-ray structure analysis; Mass spectral analysis

## 1. Introduction

We have been interested in the unique coordinating properties of highly fluorinated alcohols, particularly focusing on the $C_3$-symmetric tridentate ligand 1,3,5-tris(trifluoromethyl)-cyclohexane-*cis*,*cis*-1,3,5-triol [1] ($H_3TTFTCH$, **1**) (Scheme 1). Compound **1** has been claimed to form during polymerisation of trifluoroacetone; however, no firm evidence of its presence was reported [2]. A subsequent NMR investigation concluded that polymerisation of trifluoroacetone in the presence of a secondary amine yields only tetrahydropyran derivatives [3]. The only experimental proof for the existence of **1** is found in the crystal structure of a tetranuclear complex ($[Cu_2(phen)_2(\mu^4\text{-TTFTCH})_2Cd_2(hFacac)_2]$, **4**) [4–6], where **1** coordinates copper and cadmium centers in its trianionic form. This complex has been obtained directly through the reaction of copper-hexafluoroacetylacetonate $[Cu(hFacac)_2]$, with 1,10-phenanthroline-bis(pyrimidine-2-thionato)cadmium(II), ($[Cd(pymt)_2phen]$, **3**), the latter synthesized via an electrolytic procedure using a Cadmium plate electrode [4].

A complex closely resembling **4** has been reported previously [7]. X-ray crystallographic analysis of this compound ($[Cu_4(tfa)_2(\mu^4\text{-TTPT})_2(5\text{-Hmpz})_4]$, **6**) has revealed the presence of the fully coordinated ligand **2** (Scheme 1), a compound that differs from **1** by the sole replacement of a $CH_2$ group by an oxygen atom. Ligand **2** ($H_3TTPT$) thus displays a particular structure comprised of two hemiacetal moieties linked by a common oxygen atom, a structure usually encountered in the chemistry of poly- and perfluorinated diketones [8,9].

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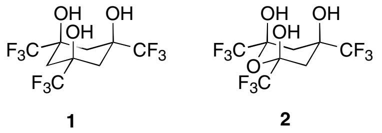
doi:10.1016/j.poly.2006.10.008



Scheme 1. Ligands $H_3$TTFTCH (**1**) and $H_3$TTPT (**2**).

The tetranuclear structure of **6** is largely similar in structure to that observed for the reported structure **4** with the exception that now four copper ions constitute the tetranuclear core. The coordination pattern of the ligand **2** is identical to the one found in **4**. Its formation is accomplished by reaction of copper-hexafluoroacetylacetonate with 3-methyl-1*H*-pyrazole (=3-Hmpz). For both complexes **4** and **6** no attempt as to the isolation of the free ligands **1** and **2**, respectively, has been reported and thus no proof was provided for their stability in their fully protonated forms. While **1** displays a $C_{3v}$ symmetry, **2** belongs to the point group $C_s$.

We present here a greatly simplified synthetic access to **3** avoiding the electrolytic pathway (Scheme 2) [10], full characterisation of the neutral, isolated form of **2**, and unequivocal evidence for the presence of **2**, rather than **1**, in the tetranuclear complex (**4** → **5**), thus in fact contesting the structural interpretation of the diffraction data obtained for this complex, as given in Ref. [4].

## 2. Experimental

### 2.1. General

Reagents were purchased from commercial suppliers and used without further purification. All solvents except tetrahydrofuran (THF) were used without purification. THF was distilled from sodium-benzophenone and, when mentioned, degassed thoroughly by freeze–thaw–vacuum cycles. NMR spectra were recorded on a Bruker Avance 200 (operating at 200.13 MHz for $^1$H, 50.32 MHz for $^{13}$C and 188.31 MHz for $^{19}$F). For $^1$H and $^{13}$C, chemical shifts ($\delta$) are reported in parts per million relative to TMS, using the solvent line as secondary internal reference. For $^{19}$F spectra, chemical shifts are reported in parts per million ($\delta$) relative to $CFCl_3$, using $CFCl_3$ in $CDCl_3$ as external reference. The IR spectra were recorded on a Mattson 3000 FT-IR spectrometer between 3500 and 500 cm$^{-1}$ using KBr disks (w: weak, m: medium, s: strong, vs: very strong, sh: shoulder). The UV–Vis spectra were recorded on a Jasco V-550 spectrometer.

### 2.2. Synthesis

#### 2.2.1. *1,10-Phenanthroline-bis(pyrimidine-2-thionato)-cadmium(II) (3)*

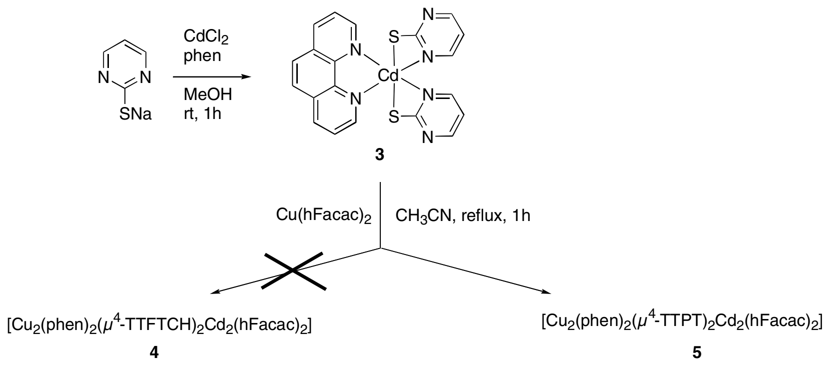
$CdCl_2$ (2.0 g, 10.80 mmol) and 204 mL of methanol were placed into a 500 mL round-bottom flask. The mixture was heated to reflux until all the cadmium chloride was dissolved (*ca.* 2 h). Separately, a freshly prepared MeONa solution (0.24 M, 595 mg Na, 106 mL MeOH) in a 250 mL round-bottom flask was treated with 2-mercaptopyrimidine (2.86 g, 25.0 mmol) and 1,10-phenanthroline monohydrate (0.89 g, 4.48 mmol) was added successively. The resulting yellow thiolate solution was added dropwise to the $CdCl_2$ solution at room temperature. An off-white solid immediately precipitated. After stirring for one additional hour, the reaction mixture was filtered, the precipitate was successively washed with 30 mL of methanol, 30 mL of water and 10 mL of methanol and then dried *in vacuo* to afford 4.78 g of a white powder (9.28 mmol, 85%). The crude material was recrystallised in boiling acetonitrile (*ca.* 2.5 L), and 3.56 g of **3** were isolated as yellow crystals (6.91 mmol, 64%).

*Anal.* Calc. for $C_{20}H_{14}CdN_6S_2$: C, 46.65; H, 2.74; N, 16.32; S, 12.45. Found: C, 46.91; H, 2.94; N, 16.28; S, 12.53%.

$^1$H NMR (DMSO-$d_6$, 200 MHz) $\delta$ 9.26 (1H, d, $^3J = 4.5$ Hz) 8.86 (1H, d, $^3J = 8.0$ Hz); 8.26 (2H, d, $^3J = 5.0$ H) 8.24 (1H, s) 8.11 (1H, dd, $^3J = 8.0$, 4.5 Hz) 6.90 (1H, t, $^3J = 5.0$ Hz); $^{13}$C NMR ($CDCl_3$, 50 MHz) $\delta$ 115.0, 126.5, 128.5, 130.2, 140.4, 142.1, 151.2, 157.8.

#### 2.2.2. *[$Cu_2(phen)_2(\mu^4\text{-}TTPT)_2Cd_2(hFacac)_2$]$CH_3CN$ (5)*

Into a 6 L round-bottom flask were introduced complex **3** (1.49 g, 2.89 mmol), $Cu(hFacac)_2 \cdot xH_2O$ (2.98 g, 6 mmol) and 4.7 L of acetonitrile. The green reaction mixture was



Scheme 2. Synthetic procedure for tetranuclear complex **5**.