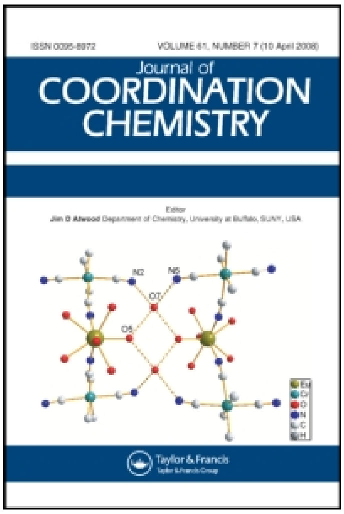

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# Synthesis and crystal structures of the chelating ligand 3-[(2,6-dimethylphenyl)hydrazono]-1,1,1-trifluoropentane-2,4-dione and its complex with copper(II)

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The new aryl hydrazone ligand, **1**, featuring an acetyl group of a previous compound of reference replaced by a trifluoroacetyl moiety and a corresponding Cu(II) complex, **2**, have been synthesized and studied by X-ray crystallography. A distinct influence of the fluorine substitution relative to the nonfluorinated parent compound is manifested both in the free ligands and Cu(II) complexes, and in particular has an effect on the packing structures mainly due to C–H $\cdots$ F contacts.

*Keywords*: 3-(Arylhydrazono)-1,1,1-trifluoropentane-2,4-dione; Copper(II) complex; Synthesis; Crystal structure; Supramolecular interactions

## 1. Introduction

Coupling of a 1,3-dicarbonyl compound with an aromatic diazonium salt to yield an arylhydrazone is a synthetic process commonly known as the Japp–Klingemann reaction [1]. This method has given rise to a variety of hydrazones derived from different arylamines and 1,3-dicarbonyls [1–4]. They are described as antineoplastic components [5] and systems showing particular conformational and hydrogen bond behavior [6–8], with the latter property being connected to keto–enol and $\pi$-electron delocalization connected to the current discussion [9] about the so-called "resonance assisted hydrogen bond" (RAHB) [10]. But certainly the most interesting property of these hydrazones is their high ability to form complexes with transition metal ions [3, 11–13]. In the case of Cu(II) and Ni(II), mononuclear six-membered 2 : 1 chelate complexes, involving $N_2O_2$ binding sites that are quasi quadratic, are found [3].

A gradual replacement of hydrogen for fluorine in a hydrazone was shown to markedly affect the crystal packing structure [14], stimulating a further question regarding the consequence of fluorine substitution on transition metal complexes connected with the property of crystal-engineering [15, 16]. Hence, a trifluoromethyl

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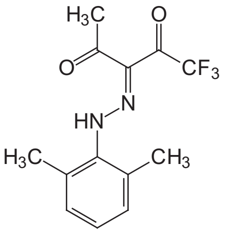

**1** (LH)
**2** ($CuL_2$)

Figure 1. Compounds studied in this article.

containing hydrazone **1** (figure 1) was studied. Here we report details on the synthesis and crystal structures of the particular hydrazone and its complex with Cu(II), embedded in a comparative discussion involving the fluorine-free compounds.

## 2. Experimental

### 2.1. *General*

Melting points were determined with a hot-stage microscope (VEB Dresden Analytik) and are uncorrected. Elemental analyses were determined on a Heraeus CHN rapid analyzer. The IR spectra were obtained with a Nicolet 510 FT-IR spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded using a Bruker Avance DPX 400 (400 MHz) instrument. The chemical shifts ($\delta$) are reported as ppm relative to $SiMe_4$. The mass spectra (ESI) were recorded with a Bruker Daltonik ESQUIRE-LC iontrap (solvent: acetonitrile/water/5% formic acid). Organic solvents were purified by standard procedures. Starting compounds 2,6-dimethylaniline, 1,1,1-trifluoropentane-2,4-dione, and copper(II) acetate were purchased from Fluka.

### 2.2. *Synthesis of 3-[(2,6-dimethylphenyl)hydrazono]-1,1,1-trifluoropentane-2,4-dione, LH (1)*

A cold solution of the diazonium salt, prepared from 2,6-dimethylaniline (2.42 g, 20 mmol) in hydrochloric acid (3 N, 40 mmol) and $H_2O$ (5 $cm^3$) [17], was added under cool conditions (0°C) and under stirring to a mixture composed of 1,1,1-trifluoropentane-2,4-dione (3.07 g, 20 mmol), NaOH (1.0 g, 25 mmol), sodium acetate (8.2 g, 100 mmol), methanol (160 $cm^3$), and water (160 $cm^3$). The mixture was allowed to warm to room temperature and stirred for 1 h. Extraction with toluene ($3 \times 50\,cm^3$), evaporation of the solvent, and recrystallization from ethanol yielded 72% of **1** as yellow crystals; m.p. 187–188°C. Anal. Calcd for $C_{13}H_{13}F_3N_2O_2$ (%): C, 54.55; H, 4.58; N, 9.79. Found: C, 54.82; H, 4.52; N, 9.79. IR (KBr): $\nu_{max}$ 3315 (N–H), 1624 (C=O), 1593 (C=N), 1530 (C=C), 755 (Ar–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta_H$ 2.68 (s, 3 H, $CH_3CO$), 7.16 (d, 2 H, *m*-Ar–H), 7.28 (t, 1 H, *p*-Ar–H), 15.61 (s, 1 H, NH). $^{13}C$ NMR

(100 MHz, $CDCl_3$): $\delta_C$ 30.51 ($CH_3CO$), 112.31, 115.84, 118.12, 121.02 ($CF_3$, $^1J_{C-F} = -292$ Hz), 127.90 (*o*-Ar–C), 129.77 (*m*-Ar–C), 129.17 (C=N), 130.94 (*p*-Ar–C), 137.31 (C–N), 176.64 ($CF_3$–CO), 197.86 ($CH_3$–CO). MS(ESI): *m*/*z* 284.8 $[M-H]^-$.

### 2.3. *Preparation of $CuL_2$ (2)*

Saturated ethanolic solutions of **1** and copper(II) acetate monohydrate in molar ratio 2 : 1 were combined. The mixture was heated to 60°C and stirred for 1 h. After cooling to room temperature, the precipitate, which had formed, was collected, washed with small amount of cold ethanol, and dried to yield 30% of **2** as red powder; m.p. 241–243°C. Anal. Calcd for $C_{26}H_{24}CuF_6N_4O_4$ (%): C, 49.25; H, 3.80; N, 8.84. Found: C, 49.82; H, 3.53; N, 8.82. IR (KBr): $\nu_{max}$ 1693, 1634 (C=O), 1542 (C=N), 1499 (C=C), 778 (Ar–H). MS (ESI): *m*/*z* 631.8 $[M-H]^-$.

### 2.4. *Crystal structure determination*

Intensity data were collected on a Bruker APEX II diffractometer with graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega$- and $\varphi$-scans. Reflections were corrected for background, Lorentz and polarization effects. Preliminary structure models were derived by the application of direct methods [18] and refined by full-matrix least squares calculation based on $F^2$ for all reflections [19]. For the metal complex, an empirical absorption correction based on multi-scans was applied using SADABS [20]. All non-hydrogen atoms were refined anisotropically. With the exception of H(2) in structure **1**, all hydrogen atoms were included in the models in calculated positions and constrained to bonding atoms.

## 3. Results and discussion

The hydrazone LH, **1** (figure 1), was synthesized by diazotation of 2,6-dimethylaniline and reaction of the corresponding diazonium salt with 1,1,1-trifluoropentane-2,4-dione, following the Japp–Klingemann procedure [1]. The copper(II) complex $CuL_2$, **2**, was prepared by co-crystallization of stoichiometric amounts of **1** and Cu(II) acetate from ethanolic solution. Single crystals of **1** and **2** suitable for X-ray investigations were obtained by slow evaporation of solutions of **1** in ethanol or **2** in *n*-butanol as yellow and red crystals, respectively. Relevant crystallographic data are summarized in table 1. Structural parameters of selected interactions are listed in tables 2 and 3, respectively. Molecular structures are depicted in figures 2 and 4, and packing illustrations are presented in figures 3 and 5.

### 3.1. *Crystal structure of LH (1)*

In conformity with previous findings [3, 4, 14], the molecular structure of LH (**1**) shows the presence of an intramolecular six-membered hydrogen-bonded ring formed between the NH-moiety and one of the carbonyl groups containing a strong hydrogen bond

Table 1. Crystal data and structure refinement details for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{13}H_{13}N_2O_2F_3$ | $C_{26}H_{24}N_4O_4F_6Cu$ |
| Formula weight | 286.25 | 634.03 |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P*-1 | $P2_1/n$ |
| Unit cell dimensions (Å, °) | | |
| *a* | 7.2685(8) | 10.4658(2) |
| *b* | 8.5145(10) | 11.9742(2) |
| *c* | 11.6822(14) | 10.8708(3) |
| $\alpha$ | 79.683(7) | 90.0 |
| $\beta$ | 86.327(7) | 90.018(1) |
| $\gamma$ | 65.888(6) | 90.0 |
| Volume ($Å^3$), *Z* | 649.20(13), 2 | 1362.32(5), 2 |
| *F*(000) | 296 | 646 |
| Calculated density ($mg\,m^{-3}$) | 1.464 | 1.546 |
| Absorption coefficient ($mm^{-1}$) | 0.128 | 0.883 |
| Data collection | | |
| Temperature (K) | 153(2) | 298(2) |
| Reflections collected | 18,158 | 8413 |
| $\theta$ range for data collection (°) | 2.9–30.8 | 3.2–26.5 |
| Index ranges $\pm h$, $\pm k$, $\pm l$ | $-10 \le h \le 10$; $-12 \le k \le 12$; $-16 \le l \le 16$ | $-11 \le h \le 13$; $-15 \le k \le 13$; $-13 \le l$ d 13 |
| No. of unique reflections | 4069 | 2804 |
| Independent reflection | [*R*(int) = 0.0274] | [*R*(int) = 0.0294] |
| Refinement method | Full-matrix least-squares on all $F^2$ | Full-matrix least-squares on all $F^2$ |
| Weighting expression $w^a$ | $[\sigma^2(F_o^2) + (0.1000P)^2 + 0.7272P]^{-1}$ | $[\sigma^2(F_o^2)+(0.0114P)^2 + 0.2733P]^{-1}$ |
| No. of refined parameters | 188 | 190 |
| No. of *F* values used $[I > 2\sigma(I)]$ | 2833 | 2078 |
| Final *R* indices | – | – |
| $R(=\Sigma\vert\triangle F\vert/\Sigma\vert F_o\vert)$ | 0.0518 | 0.0389 |
| *wR* on $F^2$ | 0.1629 | 0.1029 |
| Goodness-of-fit on $F^2$ | 0.914 | 1.039 |
| Largest difference peak and hole ($e\,Å^{-3}$) | 0.36/−0.23 | 0.33/−0.35 |

$^aP = (F_o^2 + 2F_c^2)/3$.

[N(2)–H(2)···O(1)] (figure 2a), as suggested by the geometric parameters (table 3) [21]. The fact that the oxygen of the $COCF_3$ fragment does not participate in this hydrogen-bonded ring formation, but is only involved in weak intermolecular hydrogen bonding [C(10)–H(10)···O(2), 2.71 Å, 139.3°] [22], indicates diminished H acceptor ability caused by the negative inductive effect of the fluorines. Two fluorines of each molecule take part in intermolecular cross-linkage by forming relatively short C–H···F hydrogen bonds (H···F 2.51, 2.59 Å) [15, 23]. This may explain the distortion of the pentane-2,4-dione unit which is reflected by bond and torsion angles that deviate from ideal values. In contrast to the planar geometry of the analogous non-fluorinated parent compound [4], in the present case the *ortho*-disubstituted aromatic unit is inclined at an angle of 17.9° with respect to the mean plane of the hydrogen-bonded ring (figure 2b). A comparative examination of the crystal structures of both compounds reveals the tendency of the molecules to form infinite hydrogen-bonded strands, which in turn are organized into 2-D sheets. Nevertheless, structural differences worthy of note exist, which can be attributed to the presence of fluorine in **1**. They induce additional intermolecular contacts as well as conformational changes, giving rise to altered

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Bond lengths | | |
| C(1)–C(2) | 1.498(3) | 1.491(3) |
| C(2)–C(3) | 1.473(2) | 1.425(3) |
| C(3)–C(4) | 1.448(2) | 1.458(3) |
| C(4)–C(5) | 1.550(3) | 1.556(4) |
| C(3)–N(1) | 1.339(2) | 1.355(3) |
| C(6)–N(2) | 1.407(2) | 1.453(3) |
| N(1)–N(2) | 1.287(2) | 1.281(2) |
| C(2)–O(1) | 1.227(2) | 1.255(3) |
| C(4)–O(2) | 1.208(3) | 1.207(3) |
| Cu(1)–O(1) | | 1.888(2) |
| Cu(1)–N(2) | | 1.965(2) |
| Bond angles | | |
| C(3)–N(1)–N(2) | 119.1(1) | 123.0(2) |
| C(1)–C(2)–O(1) | 118.8(2) | 115.1(2) |
| C(5)–C(4)–O(2) | 116.0(2) | 115.9(2) |
| N(2)–Cu(1)–O(1) | | 88.9(1) |
| Torsion angles | | |
| C(1)–C(2)–C(3)–C(4) | −3.8(3) | −0.9(4) |
| C(2)–C(3)–C(4)–C(5) | −178.2(2) | 168.3(2) |
| C(2)–C(3)–C(4)–O(2) | 1.9(4) | −10.2(4) |
| C(4)–C(3)–C(2)–O(1) | 176.5(2) | 179.2(2) |
| C(3)–N(1)–N(2)–C(6) | −178.2(1) | 179.8(2) |
| Interplanar angles | | |
| mpla(1)[a] ··· mpla(2)[b] | 17.9 | 83.5 |

[a] Best plane through atoms C(1)–C(2)–C(3)–C(4)–C(5)–N(1)–N(2).

[b] Best plane through atoms C(6)–C(7)–C(8)–C(9)–C(10)–C(11).

Table 3. Selected hydrogen bond interactions in **1** and **2**.

| | | Distances (Å) | | | Angles (°) |
|---|---|---|---|---|---|
| D–H ··· A | Symmetry | D–H | D ··· A | H ··· A | D–H ··· A |
| **1** | | | | | |
| N(2)–H(2) ··· O(1) | *x*, *y*, *z* | 0.85 | 2.535(3) | 1.83 | 138.5 |
| C(10)–H(10) ··· O(2) | *x*, *y*, −1+*z* | 0.95 | 3.489(3) | 2.71 | 139.3 |
| C(1)–H(1C) ··· F(1) | 1−*x*, −*y*, 1−*z* | 0.98 | 3.474(3) | 2.51 | 169.7 |
| C(1)–H(1B) ··· F(3) | 2−*x*, −*y*, 1−*z* | 0.98 | 3.515(3) | 2.59 | 156.5 |
| **2** | | | | | |
| C(10)–H(10) ··· O(2) | *x*, *y*, 1+*z* | 0.93 | 3.498(4) | 2.77 | 135.9 |
| C(13)–H(13A) ··· F(3) | −0.5+*x*, 0.5−*y*, 0.5+*z* | 0.96 | 3.285(3) | 2.42 | 149.1 |

relationships between the molecules of consecutive sheets. In the non-fluorinated parent compound, inter-sheet interactions are restricted only to weak $\pi \cdots \pi$ contacts between the unequal molecular parts, as shown in the crystal structure of **1** (figure 3). The arene–arene interactions with a closest distance of 3.5 Å [24] and C–H ··· F hydrogen bonds stabilize the crystal structure in the stacking direction of the molecular sheets.

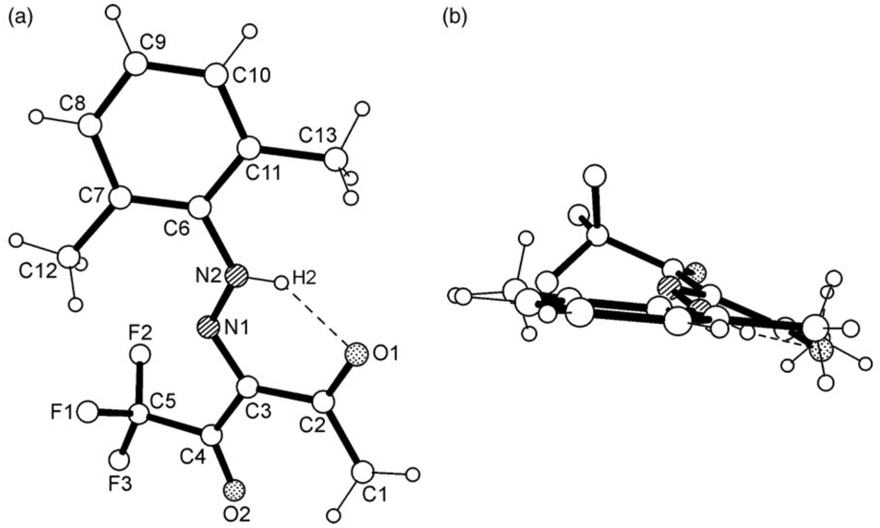

Figure 2. Molecular structure of LH (**1**): (a) top view showing the hydrogen bonded ring and indicating the atom numbering scheme; (b) side view. The broken lines represent the hydrogen bonds.

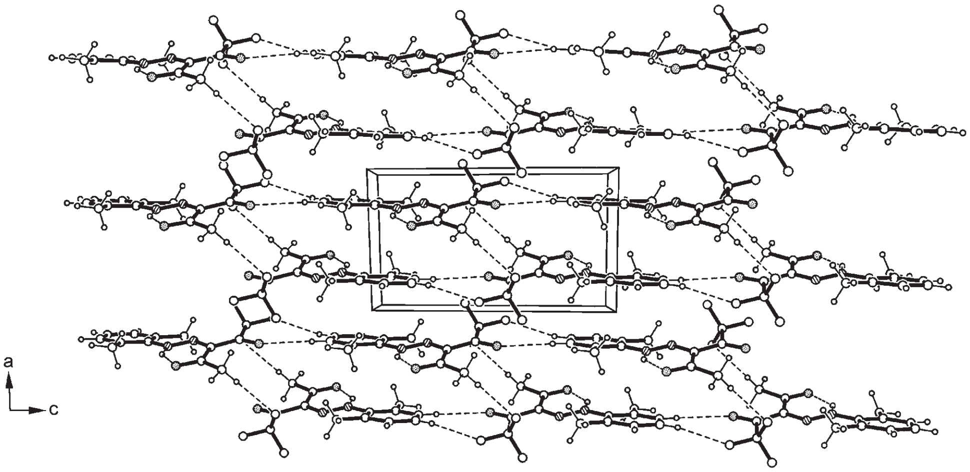

Figure 3. Packing structure of LH (**1**) showing the mode of intermolecular interactions (broken lines). The heteroatoms are shaded.

### 3.2. *Crystal structure of CuL$_2$ (2)*

Complex **2** crystallizes in the monoclinic space group $P2_1/n$ comprising one half of the complex molecule in the asymmetric entity of the unit cell, i.e., the molecule has a center of symmetry at copper(II). The coordination environment of the copper ion shows a nearly regular square planar geometry of $N_2O_2$ with Cu–O and Cu–N distances being 1.888(2) and 1.965(2) Å, respectively. In order to prevent intramolecular strain,

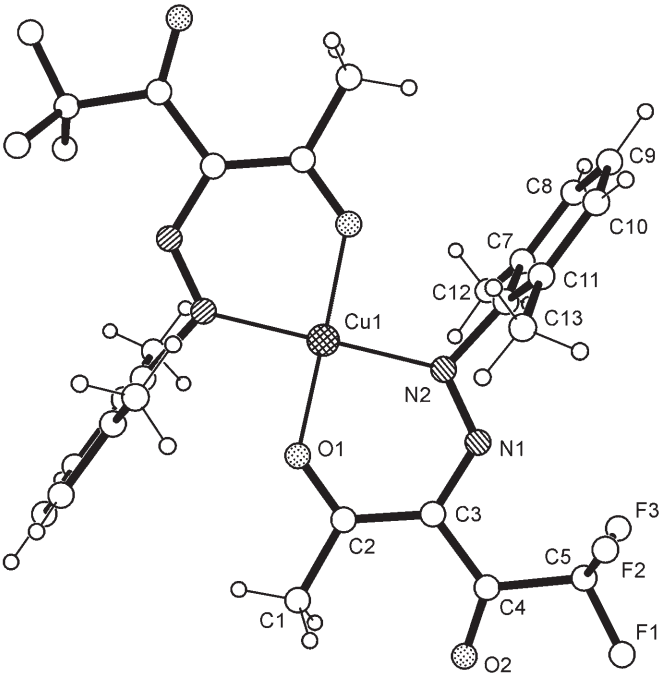

Figure 4. Perspective view of **2** showing the atom numbering scheme.

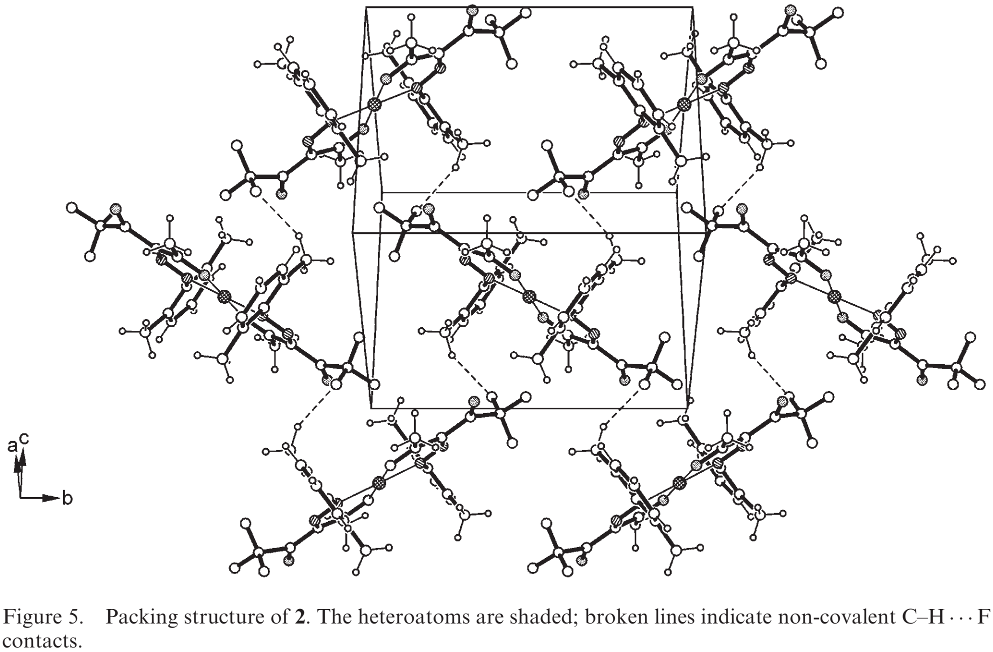

Figure 5. Packing structure of **2**. The heteroatoms are shaded; broken lines indicate non-covalent C–H ··· F contacts.

the 2,6-dimethylphenyl rings are arranged approximately perpendicular (83.5°) with respect to the $CuN_2O_2$ plane (figure 4). Complex formation causes an increase in the C(2)–O(1) bond length [1.255(3) Å] whereas the C(2)–C(3) bond [1.425(3) Å] is significantly shortened, indicating a change of $\pi$-electron distribution within the pentane-2,4-dione fragment. In the crystal structure of **1**, these bond lengths are 1.227(2) and 1.473(2), respectively. Similar to **1**, also in the structure of **2** the oxygen of the $CF_3CO$ unit is an acceptor site for a weak intermolecular C–H $\cdots$ O hydrogen bond (H $\cdots$ O 2.77 Å). In addition, one fluorine is associated with the methyl hydrogen of an adjacent molecule (H $\cdots$ F 2.42 Å). In the packing structure of **2** (figure 5), the observed mode of molecular cross-linking is favored by an inclination of neighboring molecules which, however, prevent aromatic interactions. A different structural situation is found in the Cu(II) complex of the non-fluorinated parent compound [3], which crystallizes from the same solvent as a monohydrate with the water molecule located on the vertex of the quadratic-pyramidal coordination sphere of the metal ion. In this latter case, the packing structure is determined by coordination behavior of the water, leading to O–H $\cdots$ O bonded molecular zigzag strands which are further associated by edge-to-face aromatic interactions [24].

## 4. Comparative reflection and conclusions

The aryl hydrazone ligand **1** and its complex with copper(II) were studied by X-ray crystal structure technique in order to expose the effect of a methyl for trifluoromethyl exchange in the pentane-2,4-dione fragment of a corresponding fluorine-free parent compound. The following findings emerge from the comparative examination.

Regarding the molecular geometries of **1** and the fluorine-free compound [4], an intramolecular six-membered, hydrogen-bonded ring is formed in both cases, as is usual for this class of compounds [3, 4]. In **1**, the oxygen of the acetyl unit is involved in hydrogen-bonded ring formation, in agreement with the higher H acceptability of the respective carbonyl group compared to the trifluoroacetyl moiety being diminished in its H acceptability due to the strong electron-withdrawing fluorine. Analogous behavior has been found with a related fluorine-substituted hydrazone [14]. However, a clear difference between **1** and the fluorine-free parent compound is revealed by the intermolecular cross-linkage of **1** with two fluorines of each molecule included into relatively short C–H $\cdots$ F contacts [15, 23]. As a consequence, the overall planar geometry of the parent compound is impaired in **1**, giving rise to a distortion of the pentane-2,4-dione moiety and a bend of the aromatic unit with respect to the plane of the hydrogen-bonded ring. Although hydrogen-bonded strand formation is characteristic of the packing structures both in the absence or presence of fluorine, the fluorine containing **1** features a network of interactions to a much greater extent, contributing to stabilization of the crystal structure.

A comparison of the copper(II) complexes of **1** and the fluorine-free compound [3] shows a distinct difference in the chemical composition of the complexes since the parent complex is a monohydrate while **2** crystallized free of water. That this different behavior may only be attributed to the hydrophobic nature of the organic fluorine is possibly a too simple view. Intermolecular interactions created by the fluorines should assist in stabilizing the packing structure of **2** and thus provide some compensation for the hydrogen-bonded water molecule. The complex molecules, however, are rather similar in the structure, including the square planar geometry of the $N_2O_2$ coordination sites.

In summary, replacement of a methyl for trifluoromethyl group in an aryl hydrazone of the present type makes an obvious impact on the crystalline packing structures of the free ligand as well as the corresponding complexes with copper(II), while the changes of the molecular geometries caused by the fluorines are secondary. Hence, fluorine substitution of a given ligand, such as presented here, may open an interesting possibility for the crystal-engineering of coordination compounds of which the metal–organic framework structures (MOFs) are cases in point [25, 26].

## Supplementary material

Supplementary material for the crystal structure determinations has been deposited at the Cambridge Crystallographic Data Centre and can be ordered under CCDC Nos. 716,026 (**1**) and 716,027 (**2**).

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