# Conformational study of [Cu(CF₃COCHCO(C₄H₃X))₂] (X = O or S), a combined experimental and DFT study

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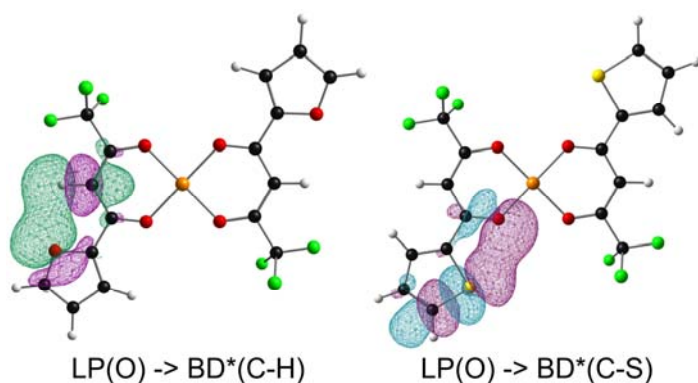
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**Graphical abstract**



LP(O) -> BD*(C-H)          LP(O) -> BD*(C-S)

**Synopsis**

DFT calculations give an electronic understanding of the difference in the experimentally obtained conformers of [Cu(CF₃COCHCO(C₄H₃X))₂] with X = O or S.

**Highlights**

- Combined DFT and experimental structural study of selected bis(β-diketonato)copper(II) complexes

- Crystal structures show *trans* conformational preferences in the crystalline solid state.

- Calculated NBO donor-acceptor interactions show intramolecular bond interactions.

**Keywords**

**Abstract**

To date, only the *trans* isomers of [Cu(β-diketonato)$_2$] complexes are isolated in the solid state. Both experimental solid state structures and density functional theory (DFT) calculations show that for [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$] complexes, the *trans*-2 conformer with X pointing towards the methine H of the β-diketonato ligand is obtained when X = O (complex 1). However, for X = S (complex 2), the *trans*-1 conformer with X pointing away from the methine H of the β-diketonato ligand, as well as the *trans*-2 conformer are possible, with *trans*-1 as the main conformer. A natural bond orbital (NBO) study provided new insights into the preferred orientation of the C$_4$H$_3$X group with respect to both the Cu(II) central atom and the β-diketonato ligand in [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$] complexes.

**1    Introduction**

β-Diketones have been studied for more than a century [1], *inter alia* due to their ability to coordinate to many metals, giving rise to a rich coordination chemistry [2]. Metal-β-diketonato complexes are often studied due to their chemical stability, high molar extinction coefficients and high energy transfer efficiency e.g. in lanthanide complexes [3] with application in disparate fields such as optoelectronic devices [4], telecommunication [5] and bioassays [6]. A rare earth β-diketonato-complex with blue-violet light absorption was synthesized, bearing the 2-thenoyltrifluoroacetonato ligand [7], with application in bioinorganic sensors, organic electroluminescent technology and luminescent materials [8]. These complexes have strong absorption properties, high thermal stability as well as good solubility in many organic solvents [9]. Cu-β-diketonato based gemini-like macro-discotic complexes exhibit liquid crystal properties with

possible application as one-dimensional semiconductors [10]. Furthermore, volatile [Cu($\beta$-diketonato)$_2$] complexes are used in the synthesis of high-temperature superconducting thin films [11]. In this contribution we present the synthesis, structure and properties of two types of copper-$\beta$-diketonato molecules, namely [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$], each with a C$_4$H$_3$X (X = O, complex 1; X = S, complex 2) group (Figure 1). For complexes 1 and 2 containing an unsymmetrical $\beta$-diketone ligand, theoretically two stereo isomers are possible: a *cis* isomer and a *trans* isomer (Figure 1). It would thus be of interest to look at the preferred structural conformations possible for [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$] complexes, namely *cis* or *trans*, as well as to determine the preferred orientation of the 2-furyl or 2-thenoyl group of these complexes.
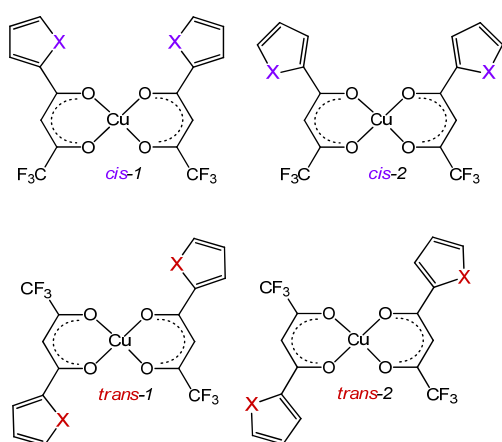


**Figure 1. Different isomers and conformers possible for [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$] molecules with X = O (complex 1) or S (complex 2).**

## 2   Experimental

### 2.1   *Synthesis*

Complexes **1** and **2** were synthesized and purified as described in literature [9,12-16]. The crude product was dissolved in hot toluene and transferred to a flask sealed with parafilm with a few small holes. Slow evaporation of the toluene afforded pure crystalline products.

2.1.1   Characterization data for bis(2-furyltrifluoroacetonato-O,O')-copper(II) (**1**)

Yield: 62%. Colour: Green, M.p. 228 ℃. IR $\bar{\upsilon}$ (cm$^{-1}$): 3163, 3140, 3117, 1700, 1670, 1642, 1620, 1464. UV: $\lambda_{max}$ 335 nm, $\varepsilon_{max}$ 52465 mol$^{-1}$dm$^3$cm$^{-1}$ (CH$_3$CN). MS Calcd. ([M]$^-$, negative mode): *m/z* 473.30. Found: *m/z* 473.77.

### 2.1.2 Characterization data for bis(2-thenoyltrifluoroacetonato-O,O')-copper(II) (2)

Yield: 79%. Colour: Green, M.p. 243 ºC). IR $\bar{\upsilon}$ (cm$^{-1}$): 3086, 1690, 1617, 1604. UV: $\lambda_{max}$ 340 nm, $\varepsilon_{max}$ 47258 mol$^{-1}$dm$^3$cm$^{-1}$ (CH$_3$CN). MS Calcd. ([M]$^-$, negative mode): $m/z$ 505.21. Found: $m/z$ 505.90.

## 2.2 Crystal structure analysis

Diffraction data for complexes **1** and **2** were collected at 150K on a Bruker D8 Venture kappa geometry diffractometer, with duo Iμs sources, a Photon 100 CMOS detector and APEX II [17] control software, using Quazar multi-layer optics, monochromated Mo-$K\alpha$ radiation, by means of a combination of $\phi$ and $\omega$ scans. Data reduction was performed using SAINT+ [17] and the intensities were corrected for absorption, using SADABS [17]. The structure was solved by intrinsic phasing, using SHELXT, and refined by full-matrix least squares, using both SHELXTL+ [18] and SHELXL-2017+ [18]. In the structure refinement, all hydrogen atoms were added in the calculated positions and treated as riding on the atom to which they are attached. All non-hydrogen atoms were refined with anisotropic displacement parameters; all isotropic displacement parameters for hydrogen atoms were calculated as (X × U$_{eq}$) of the atom to which they are attached, where X = 1.2 for all hydrogen atoms. Crystal data, data collection, structure solution and refinement details are available in the CIF (CCDC deposit numbers 1937195 and 1937196.).

## 2.3 Theoretical approach

Density functional theory (DFT) calculations of this study are done with the Gaussian 09 program package [19]. The hybrid functional B3LYP (Becke 1993 and Lee-Yang-Parr) [20,21] with the triple-$\zeta$ basis set 6-311G(d,p) basis set on all atoms, was used. For the d$^9$ Cu-complexes used in this work with S = ½, the open shell unrestricted spin was requested with uB3LYP. Frequency analysis was done on all compounds to confirm that the optimized structures did not exhibit any imaginary frequencies, thus are real minimum energy structures. The optimised structures were used to further conduct a natural bond orbital (NBO) analysis (using the NBO 3.1 module [22] in Gaussian 09. The optimized coordinates of the DFT calculations are provided in the Supporting Information.

## 2.4 Software

Mercury 4.0.0 [23,24] was used to produce Figure 2 and Figure 3. Chemcraft [25] was used to produce Figure 4, Figure 6.

## 3    Results and discussion

According to the Cambridge Structural Database (CSD, May 2019 update), all published crystal structures of [Cu(β-diketonato)$_2$] complexes exhibit the *trans* orientation (Figure 1) [26].   We therefore investigated five different [Cu(β-diketonato)$_2$] complexes to establish the possibility of obtaining *cis*-[Cu(β-diketonato)$_2$] structures: [Cu(CF$_3$COCHCO(C$_4$H$_3$O))$_2$] (complex 1), [Cu(CF$_3$COCHCO(C$_4$H$_3$S))$_2$] (complex 2), [Cu(CF$_3$COCHCOCH$_3$)$_2$], [Cu(CH$_3$COCHCOPh)$_2$] and [Cu(CF$_3$COCHCOPh)$_2$]. Experimental (XRD) analyses suggested the formation of only the *trans* orientation for all five these complexes.   Since the single crystal structures of the latter four complexes are known, we only evaluated the solid state structures of the two [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$] complexes, in order to gain more insight into the preferred orientation of the (C$_4$H$_3$X) group in these molecules.

### *3.1    Crystallography*

A molecular diagram of complexes 1 and 2 is presented in Figure 2, while crystal data and structure refinements are summarised in Table 1.   Additional crystallographic data are provided in the supplementary information. Green plate-like crystals of complexes 1 and 2 crystallize in the *P*-1 and *P*2$_1$/*c* space groups respectively, each with half a molecule in the asymmetric unit cell. For complex 2, five previously reported single crystal structures with unique unit cell parameters (with either *P*-1 or *P*2$_1$/*c* as space groups) are found in the Cambridge Structural Database (CSD). These structures generally consists of two unique polymorphs which exhibit similar geometries for the Cu(II) complexes, as can be seen from the overlay of the structures (Figure 2(c)). The major geometric differences between the two polymorphs are the orientation of the 2-thienyl and fluorine atoms in space (maximum RMS = 0.0111). For additional structure overlays among the various polymorphs of complex 2, see the supplementary information.

Of the previously reported structures of complex 2, only one structure (CSD Refcode TFTBCU01) has been observed to exhibit a minor *trans*-2 component as a positional disorder. Similarly, complex 2 exhibits a 0.85:0.15 disorder of the (C$_4$H$_3$S) group with the major component consistent with the *trans*-2 conformation.    Complex 1, however, exhibits the *trans*-1 conformation only. As is commonly encountered with CF$_3$-containing functional groups, a positional disorder is observed in

the diketonato ligand of complex 1, where two distinct positions for each of the three fluorine atoms were determined and refined.

Table 1 compares selected geometrical data of complexes 1 and 2 from this study, with published structures of [Cu(CF$_3$COCHCO(C$_4$H$_3$S))$_2$] [26]. As is evident from Table 1, [Cu($\beta$-diketonato)$_2$] complexes generally exhibit slightly distorted square planar geometries, where O-Cu-O bond angles do not deviate far from 90° ($\leq$ 3.5°). In general, we observe that the O-Cu-O bite angles of 93.5° (complex 1) and 93.0° (complex 2) compare relatively well with the average O-Cu-O bite angle (93.0(4)°) of six previously published structures of complex 2, as well as with related [Cu($\beta$-diketonato)$_2$] complexes [26]. The Cu-O1 and Cu-O2 bond distances of complex 1 (1.922 and 1.913 Å respectively) and complex 2 (1.909 and 1.908 Å respectively), are within the standard deviation of the average distances of 1.912(4) and 1.915(9) Å of the six previously published structures of complex 2.



(a)                                    (b)                                    (c)
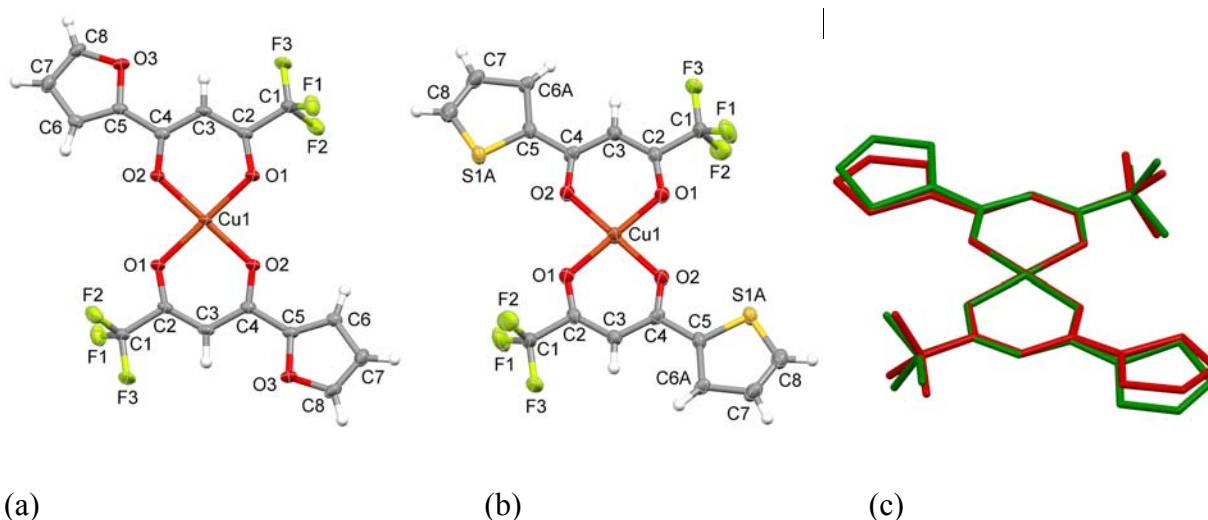
**Figure 2. Perspective drawings, showing the atom numbering scheme, of the molecular structure of complexes (a) [Cu(CF$_3$COCHCO(C$_4$H$_3$O))$_2$] (left, complex 1) and (b) [Cu(CF$_3$COCHCO(C$_4$H$_3$S))$_2$] (middle, main conformer, complex 2). Atomic displacement parameters (ADPs) are shown at the 50 % probability level. Far right (c): Structure overlay of complex 2 (150 K, red) with the same complex from literature, TFTBCU03 (~~Room,~~ green) with each other. The root means square (RMS) overlay value, when using the Cu and two O atoms of the diketonato ligand of the structure in the overlay is 1.11×10$^{-2}$ (2- TFTBCU03).**

**Table 1. Selected experimental and DFT calculated bond lengths (Å) and angles (°) for Complexes 1 and 2.**

CF₃ ... DIST1 ... DIST2 ... C₄H₃X
O1 — O2
ANG  Cu  ANG
O2 — O1
DIST2 ... DIST1
XC₄H₃ ... CF₃
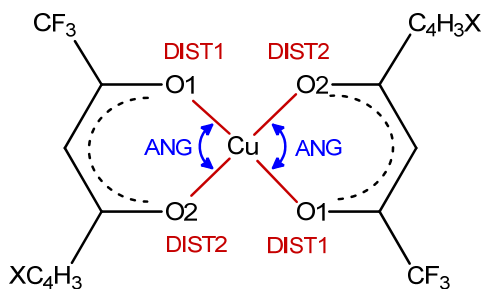
| CSD Refcode / DFT | Temp.[a] (K) | ANG[c] (°) | DIST1[c] Cu-O1 (Å) | DIST2[c] Cu-O2 (Å) | Space group | C₄H₃X group disordered | Main conformation |
|---|---|---|---|---|---|---|---|
| **Complex 1** | | | | | | | |
| this study | 150.0 | 93.5 | 1.922 | 1.913 | $P$-1 | no | *trans*-2 |
| DFT | | 91.9 | 1.926 | 1.923 | | | |
| **Complex 2** | | | | | | | |
| TFTBCU | Room[b] | 92.8 | 1.921 | 1.925 | $P$-1 | no | *trans*-1 |
| TFTBCU01 | Room[b] | 93.3 | 1.904 | 1.912 | $P$-1 | yes | *trans*-1 |
| TFTBCU02 | Room[b] | 92.9 | 1.913 | 1.916 | $P$-1 | no | *trans*-1 |
| TFTBCU03 | Room[b] | 92.1 | 1.914 | 1.929 | $P2_1/c$ | no | *trans*-1 |
| TFTBCU04 | Room[b] | 93.2 | 1.912 | 1.902 | $P2_1/c$ | no | *trans*-1 |
| TFTBCU05 | Room[b] | 93.4 | 1.907 | 1.904 | $P2_1/c$ | no | *trans*-1 |
| **avg published** | | **93.0(4)** | **1.912(4)** | **1.915(9)** | | | |
| this study | 150.0 | 93.0 | 1.909 | 1.918 | $P2_1/c$ | yes | *trans*-1 |
| **avg all** | | **93.0(3)** | **1.911(4)** | **1.915(8)** | | | |
| DFT | | 91.7 | 1.923 | 1.924 | | | |

[a] Temperature at which diffraction data was collected. [b] 283-303 K. [c] Because of the symmetrical nature of each of the structures (half a molecule in the asymmetric unit cell), bond lengths and angles are duplicated and therefore only the unique values (half a molecule) are shown.

Both complexes 1 and 2 exhibit unique packing in three dimensions as can be seen from Figure 3. In both cases, distinct hydrophilic (CF₃-containing) layers among the monomeric [Cu(CF₃COCHCO(C₄H₃X))₂] complexes are observed through the close layer alignment of the CF₃ moieties of the diketonato ligands on each end of the Cu-containing complex (Figure 3(a,b,d,e)). The resultant effect leads to the formation of clear channels in complex 2 (Figure 3(d)), and less so in complex 1 where hydrophilic zig-zag channels could be envisaged. Despite these interesting properties, no solvent inclusion occurs in either complex 1 or 2, or of the other reported structures of complex 2. In addition, no mentionable hydrogen bonds or hydrogen bond interactions (apart from C-H···F interactions) are observed in the molecular and extended short contact structures of complexes 1 and 2. Other notable features include the difference in the intramolecular distances between successive layers of complexes, as packed (Figure 3(c) (complex 1), and Figure 3(f) (complex 2)). Complex 1 forms pairs of Cu sheets with a distance of 1.45 Å, in a ladder-like fashion where each copper atom is separated by *ca.* 10.3 Å. Each of these pairs is then in turn separated by

2.90 Å to form alternating pairs of Cu layers that extend in one direction. Complex 2, however, sees a larger separation between the alternating pairs of Cu layers such that layers of Cu complex sheets are separated by comparative distances (3.83 and 3.04 Å) that extend along the c-direction.
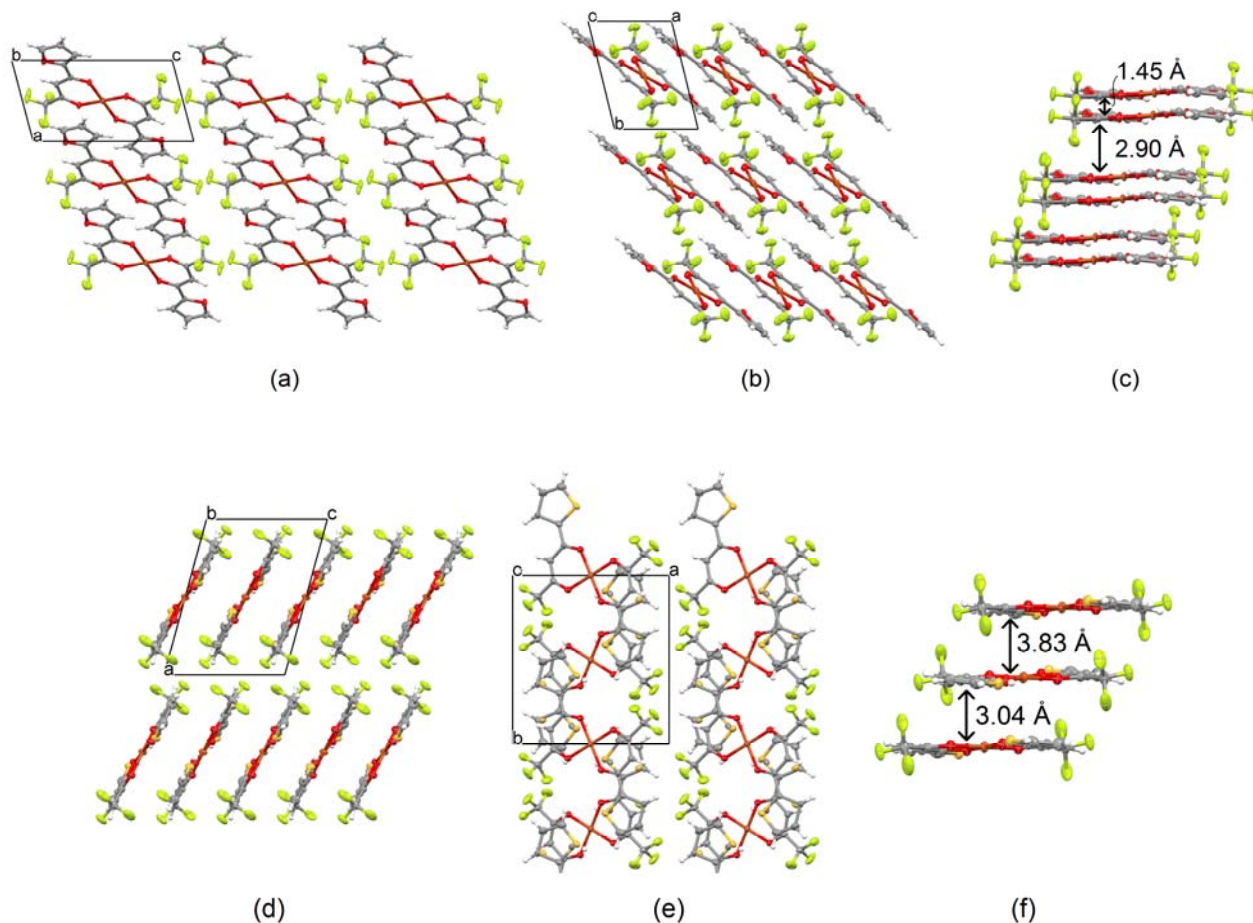


**Figure 3. Packing diagrams of complex 1 as viewed along the b (a) and c (b) axes, and of complex 2 as viewed along the b (d) and c (e) axes. Intramolecular distances between successive layers of complexes as packed are shown in (c) (complex 1), and (f) (complex 2).**

### 3.2 Computational chemistry

To deduce why certain orientations of the $C_4H_3X$ group in $[Cu(CF_3COCHCO(C_4H_3X))_2]$ complexes (Figure 1) are more favourable than others, density functional theory (DFT) calculations were performed on the four possible isomers of each of complexes 1 and 2. The DFT calculated relative gas phase electronic energies of the different isomers and conformers are given in Table 2. Selected structural parameters of importance are summarised in Table 1.

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3.2.1    Geometry and conformational study

The DFT method used here, B3LYP/6-311G(d,p) reproduces the experimental results (Table 1) accurately. For example, the O-C-O angle and C-O distances of $[Cu(CF_3COCHCO(C_4H_3S))_2]$ *trans-*1 are within 1.2° and 1.01 Å of the average experimental data for this complex.  The relative energies obtained for the different isomers and conformers (Table 2) show for both complexes 1 and 2 that a *trans* isomer has the lowest energy, in agreement with experimental observation that no *cis* [Cu(β-diketonato)$_2$] structures have been obtained till date [26]. The results further show that for complex 1 the *trans-*2 geometry is predicted by DFT and that *trans-*1, that lies 0.244 eV higher in energy, is energetically not possible. This agrees with the solid state crystal structure of 1, namely *trans-*2 with the O of the 2-furoyl groups pointing towards the methine hydrogen of the 2-furoyltrifluoroacetonato ligand.

The main conformer of the crystal structure of 2 is *trans-*1, which was found to have the lowest energy in DFT calculations. In solid state, the crystal structure of 2 favours the S atom of the 2-thenoyl groups pointing towards the $O_{β\text{-diketonato}}$ of the 2-thenoyltrifluoroacetonato ligand. However, the DFT calculated energy of *trans-*2 of complex 2 is 0.05 eV above that of *trans-*1, implying that the *trans-*2 conformation is also energetically possible, though less favoured than *trans-*1.  The observed disorder of one of the 2-thenoyl groups in the experimental structure of 2 presented in this study, agrees with this result.  Thus, for each complex, the experimental crystal structure obtained, agrees with the DFT calculated energies obtained.

**Table 2.  DFT calculated relative energies (eV) for the different conformations of complexes 1 and 2.**

| Complex | Conformation | Relative energy/eV | Crystal Structure |
|---|---|---|---|
| **1** | *cis-1* | 0.259 | |
| | *cis-2* | 0.043 | |
| | *trans-1* | 0.244 | |
| | *trans-2* | 0.000 | Crystal structure |
| **2** | *cis-1* | 0.024 | |
| | *cis-2* | 0.099 | |
| | *trans-1* | 0.000 | Crystal structure main 85% |
| | *trans-2* | 0.051 | Crystal structure minor 15% |

### 3.2.2  NBO

A natural bond orbital study (NBO) [27] was conducted to further explore the preferred orientation of the $C_4H_3X$ group in $[Cu(CF_3COCHCO(C_4H_3X))_2]$ complexes (Figure 1). NBO analysis is a computational chemical tool used to analyse intra- and inter-molecular interactions at quantum level to provide information about interactions between filled Lewis type donor NBOs and empty non-Lewis acceptor NBOs. Typical NBO types include: 1-centre core (CR), 1-centre non-bonded (lone pair, LP), 1-centre Rydberg (RY), 2-centre bond (BD) and 3-centre bond (3C) [27, 28]. NBOs as an analysis tool provides us with the ideal Lewis structure of a molecule and provides insights into the interaction between a filled (bonding or lone pair) Lewis type NBO (that act as a donor) and an empty (anti-bonding or Rydberg) non-Lewis NBO (that act as an acceptor). For every donor NBO (i) and acceptor NBO (j), a stabilization energy $E^{(2)}$ associated with electron delocalization between donor and acceptor is calculated by:
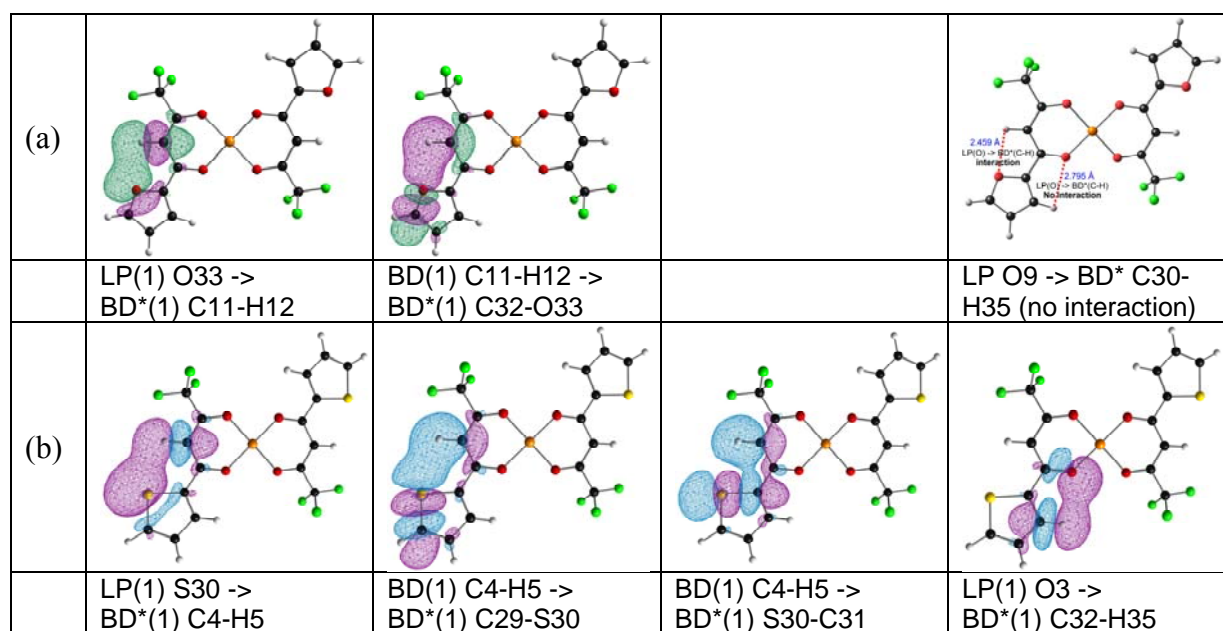
$$E^{(2)} = -q_i \frac{(F_{i,j})^2}{\varepsilon_j - \varepsilon_i}$$

Where $q_i$ is the orbital occupancy, $\varepsilon_i$, $\varepsilon_j$ are diagonal elements and $F_{i,j}$ is the off-diagonal NBO Fock matrix element.

Selected donor-acceptor interactions (namely between filled Lewis type donor and empty non-Lewis acceptor NBOs), which were obtained from an NBO analysis of the intra-molecular interactions within the molecular units of $[Cu(CF_3COCHCO(C_4H_3X))_2]$, are visualised in Table 3, together with values of the calculated second order interaction energy $E^{(2)}$. Due to symmetry, only interactions in one of the $(CF_3COCHCO(C_4H_3X))$ units are listed and discussed. The atom numbering used in the NBO analysis is shown in Figure S1 of the supplementary information. Due to the high energy of complex 1 *trans*-1 (Table 2), no NBO analysis has been performed on this isomer.

The stability of conformer *trans*-2 of complex 1 is ascribed to a weak stabilizing interaction of 0.04 kcal/mol between a lone pair (LP) of oxygen (O33) on the furoyl ring and the C11-H12 anti-bonding orbital (BD*) on the β-diketonato ligand, as well as a weak bonding – anti-bonding interaction of 0.03 kcal/mol between the natural bonding orbital (BD) on C11-H12 and the natural anti-bonding orbital (BD*) on C32-O33, see Figure 4 (a) and Table 3. No interaction is obtained between a lone pair on $O_{\beta\text{-diketonato}}$ LP(O9) and an anti-bonding orbital (BD*)(C30-H35) on the nearby furyl ring with an intra-atomic distance of *ca*. 2.8 Å. However, in conformer *trans*-2 of complex 2 (Figure 4
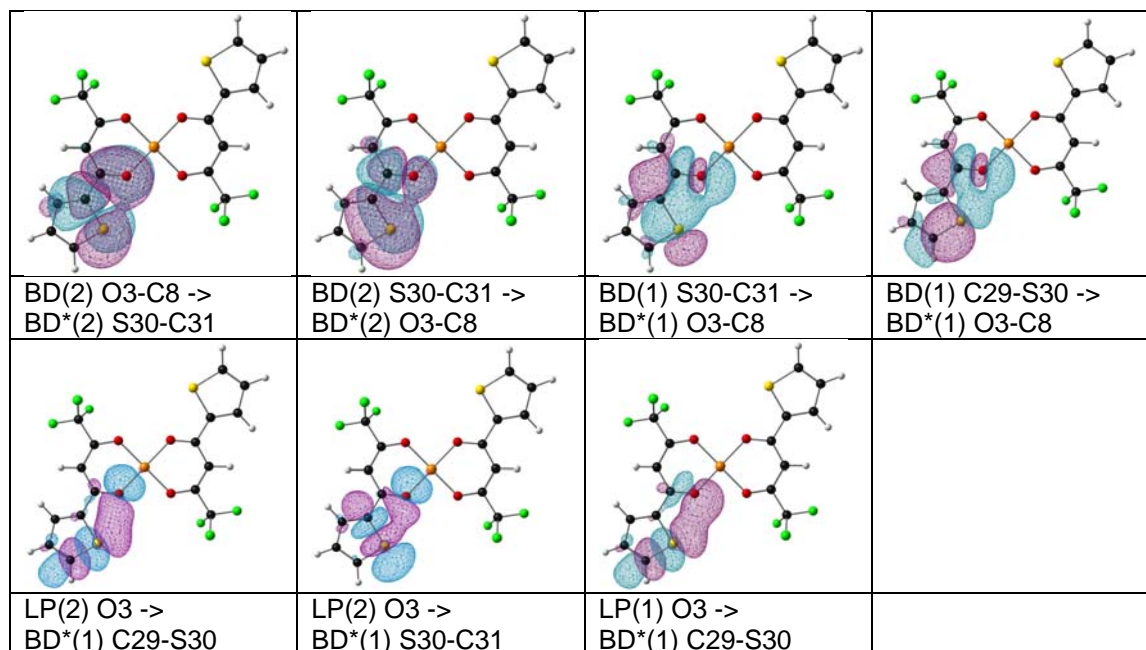
(b)), a weak interaction between LP(1) O3$_{\beta\text{-diketonato}}$ and BD*(1) C32-H35 (0.01 kcal/mol) is observed, since the related intra-atomic distance is shorter, namely *ca*. 2.6 Å. For conformer *trans*-2 of complex 2 (Figure 4 (b)) the a LP(1) S30 - BD*(1) C4-H5 interaction (0.08 kcal/mol), as well as two interactions involving BD(1) C4-H5 and an antibonding C-S NBO, namely BD*(1) C29-S30 and BD*(1) S30-C31 (0.16 and 0.03 kcal/mol, Table 3) is also observed. All these interactions stabilize the minor *trans*-2 conformation of complex 2 that is experimentally related to the disorder of the furyl ring.
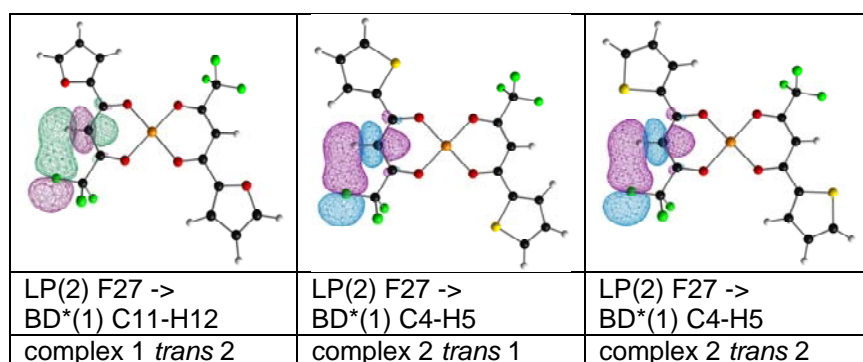


| | | | | |
|---|---|---|---|---|
| (a) | LP(1) O33 -> BD*(1) C11-H12 | BD(1) C11-H12 -> BD*(1) C32-O33 | | LP O9 -> BD* C30-H35 (no interaction) |
| (b) | LP(1) S30 -> BD*(1) C4-H5 | BD(1) C4-H5 -> BD*(1) C29-S30 | BD(1) C4-H5 -> BD*(1) S30-C31 | LP(1) O3 -> BD*(1) C32-H35 |

**Figure 4. Visualisation of the indicated donor – acceptor NBO interactions in [Cu(CF₃COCHCO(C₄H₃X))₂]** *trans* **2 complexes: (a) complex 1 (X = O) and (b) complex 2 (X = S). A contour of 0.03 e/Å³ was used for the NBO plots. Colour code of atoms (online version): Cu (orange), F (green), S (yellow), C (black), O (red) and H (white). Atom numbering is according to Figure S1.**

For the main conformer *trans*-1 of complex 2, several strong stabilizing interaction involving the thienyl S is observed, see Figure 5 and Table 3. The two strongest interactions were found between π-type NBOs, namely between a bonding orbital of sulphur and carbon BD(2) S30-C31 on the thenoyl ring and the anti-bonding orbital BD*(2) O3-C8 on the β-diketonato ligand (5.09 kcal/mol) as well as between the natural bonding orbital BD(2) O3-C8 and the natural anti-bonding orbital BD*(2) S30-C31 (1.96 kcal/mol). Two weaker interactions involves σ-type NBOs, namely between BD(1) S30-C31 and BD*(1) O3-C8 (0.43 kcal/mol) and between BD(1)C29-S30 and BD*(1) O3-C8 (0.04 kcal/mol). The lone pair of oxygen (O3) on the β-diketonato ligand, O$_{\beta\text{-diketonato}}$ LP(O3), further interacts with anti-bonding orbitals on the thenoyl ring namely with BD*(1) C29-S30 (0.23 kcal/mol and 0.11 kcal/mol) and BD*(1) S30-C31 (0.02 kcal/mol).

For all three conformations studied (**1** - *trans* **2**, **2** *trans* **1** and **2** *trans* **2**) there are observed weak interactions between a fluoro lone pair (of CF$_3$) and the adjacent anti-bonding C-H orbital between 0.01 – 0.06 kcal/mol, see Figure 6 and Table 3.



| BD(2) O3-C8 -> BD*(2) S30-C31 | BD(2) S30-C31 -> BD*(2) O3-C8 | BD(1) S30-C31 -> BD*(1) O3-C8 | BD(1) C29-S30 -> BD*(1) O3-C8 |
| LP(2) O3 -> BD*(1) C29-S30 | LP(2) O3 -> BD*(1) S30-C31 | LP(1) O3 -> BD*(1) C29-S30 | |

**Figure 5.  Visualisation of the indicated donor – acceptor NBO interactions in [Cu(CF$_3$COCHCO(C$_4$H$_3$S))$_2$] (complex 2)** *trans* **1 (main conformer).  A contour of 0.02 (top figs) and 0.03 (bottom figs) e/Å$^3$ was used for the NBO plots.  Colour code of atoms (online version):  Cu (orange), S (yellow), F (green), C (black), O (red) and H (white).  Atom numbering is according to Figure S1.**



| LP(2) F27 -> BD*(1) C11-H12 | LP(2) F27 -> BD*(1) C4-H5 | LP(2) F27 -> BD*(1) C4-H5 |
| complex 1 *trans* 2 | complex 2 *trans* 1 | complex 2 *trans* 2 |

**Figure 6.  Visualisation of the indicated donor – acceptor NBO interactions in [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$] (X = O, complex 1)** *trans* **2; X = S complex 2,** *trans* **1 and** *trans* **2.  A contour of 0.03 e/Å$^3$ was used for the NBO plots.  Colour code of atoms (online version):  Cu (orange), S (yellow), F (green), C (black), O (red) and H (white).  Atom numbering is according to Figure S1.**

**Table 3. NBO second order interaction energies, E(2), and calculated NBO occupations, for the indicated donor-acceptor interactions within complexes 1 and 2.**

| Donor NBO type | occupancy | Acceptor NBO type | occupancy | $E^{(2)}$ kcal/mol |
|---|---|---|---|---|
| **1 – trans 2** | | | | |
| LP(1) O33 | 0.98509 | BD*(1) C11-H12 | 0.00598 | 0.04 |
| BD(1) C11-H12 | 0.98643 | BD*(1) C32-O33 | 0.00843 | 0.03 |
| LP(2) F27 | 0.97636 | BD*(1) C11-H12 | 0.00598 | 0.04 |
| **2 – trans 1** | | | | |
| BD(2) O3-C8 | 0.98982 | BD*(2) S30-C31 | 0.43778 | 1.96 |
| BD(1) C29-S30 | 0.99038 | BD*(1) O3-C8 | 0.00971 | 0.04 |
| BD(1) S30-C31 | 0.93053 | BD*(1) O3-C8 | 0.00971 | 0.43 |
| BD(2) S30-C31 | 0.93053 | BD*(2) O3-C8 | 0.22260 | 5.09 |
| LP(1) O3 | 0.97886 | BD*(1) C29-S30 | 0.00961 | 0.23 |
| LP(2) O3 | 0.94646 | BD*(1) C29-S30 | 0.00961 | 0.11 |
| LP(2) O3 | 0.94646 | BD*(1) S30-C31 | 0.01545 | 0.02 |
| LP(1) F27 | 0.99546 | BD*(1) C4-H5 | 0.00625 | 0.01 |
| LP(2) F27 | 0.97660 | BD*(1) C4-H5 | 0.00625 | 0.06 |
| **2 – trans 2** | | | | |
| BD(1) C4-H5 | 0.98597 | BD*(1) C29-S30 | 0.00943 | 0.16 |
| BD(1) C4-H5 | 0.98597 | BD*(1) S30-C31 | 0.01664 | 0.03 |
| LP(1) S30 | 0.99165 | BD*(1) C4-H5 | 0.00636 | 0.08 |
| LP(1) F27 | 0.99544 | BD*(1) C4-H5 | 0.00636 | 0.01 |
| LP(2) F27 | 0.97640 | BD*(1) C4-H5 | 0.00636 | 0.06 |
| LP(1) O3 | 0.98025 | BD*(1) C32-H35 | 0.00792 | 0.01 |

## 4    Conclusion

An experimental X-ray study of [Cu(β-diketonato)$_2$] complexes, in agreement with previously published structures, show that only the *trans* isomers are isolated in the solid state. The solid state structure of [Cu(CF$_3$COCHCO(C$_4$H$_3$X))$_2$] complexes show that when X = O (complex 1) the *trans*-2 conformer with X pointing towards the methine H of the β-diketonato ligand is obtained, while for X = S (complex 2) the main structure is the *trans*-1 conformer with X pointing away from the methine H of the β-diketonato ligand. A DFT study show that for complex 1 with X = O only the *trans*-2 conformer is energetically possible, while for complex 2 with X = S both the *trans*-1 and the *trans*-2 conformers are possible, with the *trans*-1 the main conformer, in agreement with experimental X-ray data. A NBO study identified several strong donor-acceptor interactions that stabilize the C$_4$H$_3$S group of the *trans*-1 conformer of complex 2. Weaker donor-acceptor interactions stabilize the C$_4$H$_3$X group of the *trans*-2 conformers of both complex 1 and 2.

**Supporting Information**

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with numbers 1937195 and 1937196. Copies can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 336033 or ww.ccdc.cam.ac.uk/products/csd/request/]. Selected crystallographic data and optimized coordinates of the DFT calculations are given in the Supporting Information.

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