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Crystal and electronic structures of tris[4,4,4-Trifluoro-1-(2-X)-1,3-butanedionato]iron(III) isomers (X = thienyl or furyl): An X-ray and computational study

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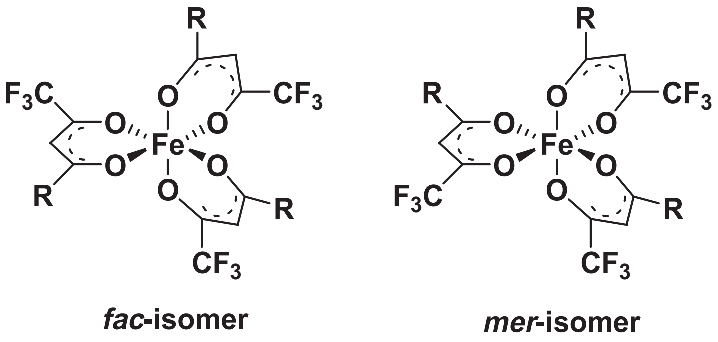
HIGHLIGHTS

- Crystal structures of *fac* and *mer* isomers of tris(beta-diketonato)$_3$ complexes.
- DFT calculations showed that the *mer* isomers are energetically favoured for both complexes.
- Molecular energy levels and orbitals of [Fe(acac)$_3$].
- DFT calculations showed that complex [Fe(acac)$_3$] is high-spin.

GRAPHICAL ABSTRACT

Electronic and crystal structures of selected *fac* and *mer* isomers of tris(beta-diketonato)$_3$ complexes.



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ABSTRACT

DFT calculations showed that [Fe(acac)$_3$] (where acac = acetylacetonato) is high-spin, with a negative D_3 distortion from the octahedral ligand field. Calculations further showed that, although both the *fac* and *mer* isomers of complexes [Fe(CF$_3$COCHCOR)$_3$], where R = C_4H_3S or C_4H_3O, can exist, the *mer* isomers are energetically favoured in both complexes. The structure of the major *mer* isomer of [Fe(CF$_3$COCHCOC$_4$H$_3$S)$_3$] has been published previously, while the crystal structure of the minor *fac* isomer of [Fe(CF$_3$COCHCOC$_4$H$_3$S)$_3$] is presented in this study. The structure of the *mer* isomer of [Fe(CF$_3$COCHCOC$_4$H$_3$O)$_3$], in agreement with DFT calculations, showed that the furyl substituent pointed towards the CF$_3$ group in a *syn* orientation.

1. Introduction

In organic chemistry, complex tris(acetylacetonato)iron(III) or [Fe(acac)$_3$], has been explored as a catalyst and reagent in many reactions. For example, [Fe(β-diketonato)$_3$] has been found to catalyze the reaction of N-sulfonyl oxaziridines with olefins to form 1,3-oxazolidine products [1]; to catalyze the dimerization of isoprene to a mixture of 1,5-dimethyl-1,5-cyclooctadiene and 2,5-dimethyl-1,5-cyclooctadiene [2]; to catalyze the cross-coupling reaction of Grignard reagents with alkyl halides [3]; to catalyze the acylation of Grignard reagents [4]; and to catalyze the ring-opening polymerization of 1,3-benzoxazine [5]. In the latter case, it has been found that by replacing the acetylacetonato ligand by hexafluoroacetylacetonato, the activity of the iron complex was remarkably enhanced [5]. From the various iron(III) complexes

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examined in the cross-coupling reaction of Grignard reagents with alkyl halides, [Fe(dibenzoylmethanato)$_3$] was found to be the most effective, as far as rates and deactivation [6] are concerned. Effective catalyst design should focus on factors such as catalyst efficiency, costs, toxicological benignity, environmental friendliness and long-term stability. It therefore is necessary to continuously study the basic structure and properties of complexes related to known catalysts.

In this contribution we present the synthesis, structure and properties of two [Fe(β-diketonato)$_3$] complexes: where β-diketonato = 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione, abbreviated as tta (**1**); and 4,4,4-Trifluoro-1-(2-furyl)-1,3-butanedione, abbreviated as tffu (**2**). For these β-diketonato-iron(III) complexes, with a unsymmetrical β-diketone ligand, two stereo isomers are possible: a facial isomer (*fac*) and a meridional isomer (*mer*); see Scheme 1. The ligands in the facial isomer are arranged symmetrically around the metal, while the ligands in the meridional isomer are arranged in such a way that one ligand is unsymmetrical.

2. Experimental

2.1. Materials and methods

Reagents were obtained from Merck and Sigma–Aldrich. Solid reagents employed in preparations were used directly, without further purification. Liquid reactants and solvents were distilled prior to use. Doubly distilled H_2O was used. Organic solvents were dried and distilled before use. Melting points (m.p.) were determined by an Olympus BX51 system microscope, assembled on top of a Linkam THMS600 stage, and connected to a Linkam TMS94 temperature programmer. Elemental analysis was performed by Canadian Microanalytical Service Ltd., Canada. MALDI-TOF-MS (matrix assisted laser desorption/ionization time-of-flight mass spectrometry) spectra were collected by a Bruker Microflex LRF20, in the negative and positive reflection mode (independently), using the minimum laser power required to observe signals.

The β-diketones used in this study were obtained from Merck and Sigma–Aldrich. Both [Fe(β-diketonato)$_3$] complexes were prepared by an adapted procedure [7,8].

[Fe(tta)$_3$] (**1**): A metal solution of 0.15 mmol $Fe(NO_3)_3 \cdot 9H_2O$ (dissolved in 10 ml H_2O) was buffered with 0.45 mmol $CH_3COONa \cdot 3H_2O$ (dissolved in 10 ml H_2O). To this buffered metal solution, a 0.53 mmol β-diketone (Htta) solution was added (solid Htta dissolved in 10 ml EtOH). The resulting solution was stirred well for 30 min and left overnight in a fume hood. The precipitate was collected by filtration and washed with H_2O. Yield 78%. Color: dark red. M.p. 158.0–161.0 °C (reported: 159–160 °C [7], 162.5 °C [9]). UV: λ_{max} 333 nm, ε_{max} 48,461 mol^{-1} dm^3 cm^{-1} (CH_3CN). MS Calcd. ([M], negative mode): *m*/*z* 719.4. Found: *m*/*z* 718.9. Anal. Calcd. for $FeC_{24}H_{12}S_3O_6F_9$: C, 40.07; H, 1.68. Found: C, 39.51; H, 1.70.

[Fe(tffu)$_3$] (**2**): A metal solution of 0.15 mmol $Fe(NO_3)_3 \cdot 9H_2O$ was buffered with 0.45 mmol $CH_3COONa \cdot 3H_2O$ (dissolved in minimal H_2O). To this, EtOH was added to produce a 1:1 H_2O:EtOH solution. With the aid of a syringe, liquid 0.53 mmol β-diketone (Htffu) was added. The resulting solution was stirred well (with a lid on) for 30 min and left overnight in a fume hood (without lid). The precipitate was collected by filtration and washed with H_2O. Yield 92%. Color: dark red. M.p. 205.0–208.0 °C (reported: 201–208 °C [7]). UV: λ_{max} 333 nm, ε_{max} 53,476 mol^{-1} dm^3 cm^{-1} (CH_3CN). MS Calcd. ([M], positive mode): *m*/*z* 671.2. Found: *m*/*z* 671.1. Anal. Calcd. for $FeC_{24}H_{12}O_9F_9$: C, 42.95; H, 1.80. Found: C, 42.91; H, 1.83.

Density functional theory (DFT) calculations were carried out, using the ADF (Amsterdam Density Functional) 2012 programme [10], with a selection of GGA (Generalized Gradient Approximation) functionals, namely PW91 (Perdew–Wang 1991) [11], BP86 (Becke–Perdew) [12,13], and OLYP (Handy–Cohen and Lee–Yang–Parr) [14,15], as well as the hybrid functional B3LYP (Becke 1993 and Lee–Yang–Parr) [16,17]. The TZP (Triple ζ polarized) basis set, with a fine mesh for numerical integration, a spin-unrestricted formalism and full geometry optimization, applying tight convergence criteria, was used for minimum energy searches. Scalar relativistic effects, with the ZORA (Zero Order Regular Approximation) formalism [18–22], were included for all optimizations.

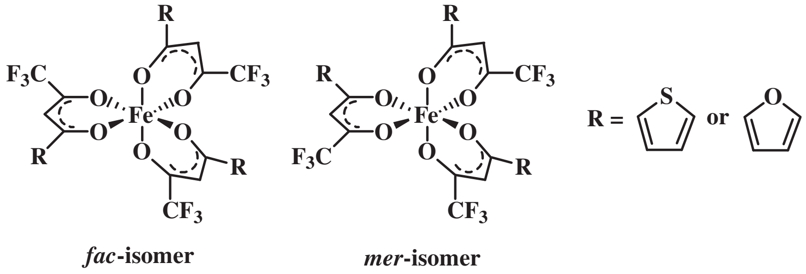
2.2. Crystal structure analysis

Data for red crystals of [Fe(tta)$_3$] (**1**, isomer *fac*) and [Fe(tffu)$_3$] (**2**, isomer *mer*), obtained from solutions in diethyl ether, were collected on a Bruker D8 Venture kappa geometry diffractometer, with duo Iμs sources, a Photon 100 CMOS detector and APEX II [23] control software using Quazar multi-layer optics monochromated, Mo Kα radiation by means of a combination of ϕ and ω scans. Data reduction was performed using SAINT+ [23] and the intensities were corrected for absorption using SADABS [23]. The structure was solved by intrinsic phasing using SHELXTS and refined by full-matrix least squares, using SHELXTL+ [24] and SHELXL-2013+ [24]. In the structure refinement, all hydrogen atoms were added in calculated positions and treated as riding on the atom to which they are attached. All non-hydrogen atoms were refined with anisotropic displacement parameters, except C5 in [Fe(tta)$_3$] (**1**), all isotropic displacement parameters for hydrogen atoms were calculated as $X \times$ Ueq of the atom to which they are attached, where $X = 1.5$ for the methyl hydrogens and 1.2 for all other hydrogens. Crystal data and structural refinement parameters are summarized in Table 1.

3. Results and discussion

3.1. Molecular structures of [Fe(tta)$_3$] (1, isomer fac) and [Fe(tffu)$_3$] (2, isomer mer)

Perspective drawings [25] of the molecular structures of [Fe(tta)$_3$] (**1**, isomer *fac*) and [Fe(tffu)$_3$] (**2**, isomer *mer*), showing the crystallographic numbering scheme used, are presented in Figs. 1 and 2. Diffraction quality crystals of [Fe(tta)$_3$] and [Fe(tffu)$_3$]



Scheme 1. The facial (*fac*) and meridional (*mer*) isomers of [Fe(β-diketonato)$_3$] complexes, with unsymmetrical β-diketonato ligands, where R = C_4H_3S (1) or C_4H_3O (2).