

# X-ray and Electronic Structure of Tris(benzoylacetonato- $\kappa^2\text{O},\text{O}'$ )iron(III)

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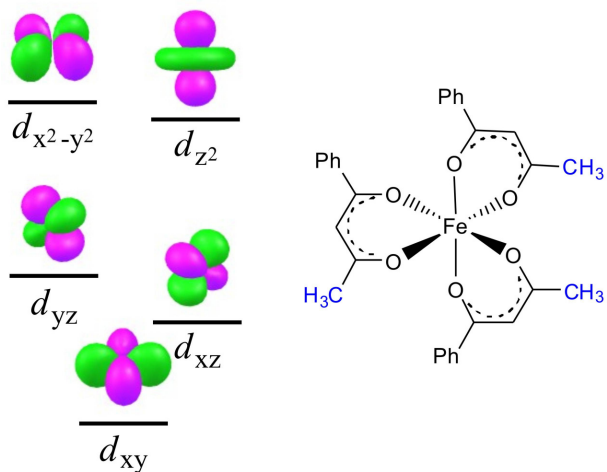
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## Keywords

Iron(III);  $\beta$ -Diketone; Structure; DFT

## Graphical abstract



## Synopsis

Geometry and electronic structure of  $d^5$  Tris( $\beta$ -diketonato)iron(III).

## Highlights

- First crystal structure of tris(benzoylacetato- $\kappa^2\text{O},\text{O}'$ )metal(III)
- Electronic structure of *fac* and *mer*  $[\text{Fe}(\text{CH}_3\text{COCHCOPh})_3]$
- Electronic configuration of  $[\text{Fe}(\beta\text{-diketonato})_3]$   $d_{xy}^1 d_{xz}^1 d_{yz}^1 d_{z^2}^1 d_{x^2-y^2}^1$
- Orbitals ordering in octahedral ligand field  $d_{xy} < d_{yz} \approx d_{xz} < d_{z^2} \approx d_{x^2-y^2}$

## Abstract

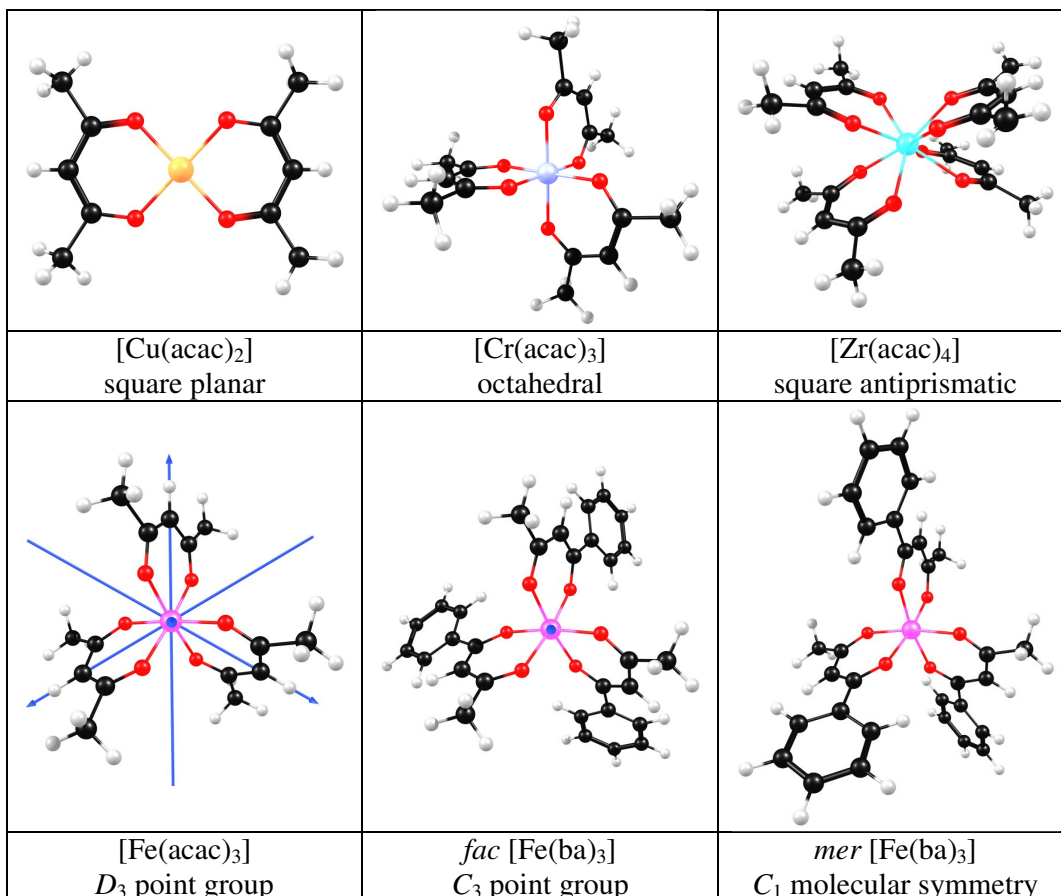
Solid state crystal data of  $d^5$  tris(benzoylacetato- $\kappa^2\text{O},\text{O}'$ )iron(III),  $[\text{Fe}(\text{ba})_3]$ , are presented. The *mer* isomer crystallized in the solid state. Density functional theory calculations show that both *fac* and *mer* isomers of  $[\text{Fe}(\text{ba})_3]$  can exist. Both *fac* and *mer*  $[\text{Fe}(\text{ba})_3]$  are high spin  $d^5$  complexes with the same ordering of the d-based molecular orbitals in order of increasing orbital energy, namely  $d_{xy} < d_{yz} \approx d_{xz} < d_{z^2} \approx d_{x^2-y^2}$ .

## 1 Introduction

$\beta$ -diketones are extensively used as chelating agents in analytical chemistry because of their unique structure [1]. The deprotonated form of the  $\beta$ -diketone acts as ligand to form a metal- $\beta$ -diketonato complex [2]. Typically both oxygen atoms of the  $\beta$ -diketonato ligand bind to the metal to form a six-membered chelate ring. The most common coordination geometries of metal- $\beta$ -diketonato complexes are square planar (groups 10 - 11 with coordination number 4 e.g. Ni(II) [3], Pd(II) [4,5], Pt(II) [6,7] and Cu(II) [8,9,10]), octahedral (groups 5 – 9 coordination number 6: e.g. V(III) [11], Cr(III) [12,13], Mn(III) [14,15], Fe(III) [16,17] and Co(III) [18,19]) or square antiprismatic (group 4 coordination number 6 e.g. Zr(IV) [20] and Hf(IV) [21,22]), as illustrated in Figure 1. Many mixed-ligand metal- $\beta$ -diketonato complexes such as  $[\text{VO}(\text{acac})_2]$  (Hacac = acetylacetonate) [23],  $[\text{Ti}(\beta\text{-diketonato})_2\text{Cl}_2]$  [24,25,26],  $[\text{Ti}(\text{acac})_2(2,2'\text{-Biphenyldiolato})_2]$  [27,28],  $[\text{Cp}_2\text{Ti}(\beta\text{-diketonato})]^+$  with Cp = cyclopentadienyl [29,30],  $[\text{Rh}(\beta\text{-diketonato})(\text{CO})(\text{PPh}_3)]$  [31] and  $[\text{Rh}(\beta\text{-diketonato})(\text{OPPh}_3)_2]$  [32] are also known.

Several  $\beta$ -diketones can be used to extract Fe(III) [33] with the formation of iron- $\beta$ -diketonato complexes [34]. Fe(III) can be extracted completely by benzoylacetone (Hba) under

acidic conditions [35]. Tris( $\beta$ -diketonato)iron(III) complexes also have various application in catalysis such as in cross-coupling reactions [36,37,38,39,40,41,42], during urethane formation [43,44] and transesterification reactions [45].  $[\text{Fe}(\text{acac})_3]$  has been found to catalyze dimerization (isoprene to a mixture of 1,5-dimethyl-1,5-cyclooctadiene and 2,5-dimethyl-1,5-cyclooctadiene [46]) and polymerization (ring-opening polymerization of 1,3-benzoxazine [47]) reactions. It was shown that the catalytic activity of the  $[\text{Fe}(\beta\text{-diketonato})_3]$  catalysts are highly dependent on both the ligand's electronic (i.e. withdrawing or donating) and steric attributes [44,45]. A combined electrochemical and computational chemistry study provided insight into the electronic influence of ligands on the Fe(III)-ion it is coordinated to [48]. An X-ray structural study complemented by a computational chemistry study of the  $[\text{Fe}(\beta\text{-diketonato})_3]$  complex can give a better understanding of the steric arrangement of ligands round the metal. The  $\text{FeO}_6$ -coordination polyhedron of  $[\text{Fe}(\beta\text{-diketonato})_3]$  complexes can be described by an octahedron. The three  $\beta$ -diketonato ligands  $(\text{RCOCHCOR}')^-$  can differently be arranged round the iron(III) ion. When the two groups R and R' on the  $\beta$ -diketonato ligand  $(\text{RCOCHCOR}')^-$  are identical, i.e. when  $\text{R} = \text{R}'$ , the  $\beta$ -diketonato ligand is symmetrical and  $D_3$  molecular symmetry applies to the  $[\text{Fe}(\text{RCOCHCOR}')_3]$  complex.  $[\text{Fe}(\text{acac})_3]$  with  $\text{R} = \text{R}' = \text{CH}_3$  has  $D_3$  molecular symmetry, see Figure 1 (bottom left). However, when the substituents  $\text{R} \neq \text{R}'$ , the molecular symmetry is lowered to either  $C_3$  for *fac*  $[\text{Fe}(\text{RCOCHCOR}')_3]$ , or to  $C_1$  for *mer*  $[\text{Fe}(\text{RCOCHCOR}')_3]$ , see Figure 1 (bottom middle and right) for *fac* and *mer*  $[\text{Fe}(\text{ba})_3]$  ( $\text{R} = \text{Ph}$  and  $\text{R}' = \text{CH}_3$ ). We previously reported the electronic structure of  $[\text{Fe}(\text{acac})_3]$  in  $D_3$  molecular symmetry [48,49] and were curious to see how the ordering and relative energies of the d-based molecular orbitals changed when the molecular symmetry of the Fe(III)( $\beta$ -diketonato) $_3$  complex is lowered to  $C_3$  and  $C_1$ . Here we thus present the a density functional theory (DFT) study on the electronic structure of both the *fac* and a *mer* isomers of a  $[\text{Fe}(\beta\text{-diketonato})_3]$  complex that does not have  $D_3$  molecular symmetry, namely  $[\text{Fe}(\text{ba})_3]$ , as well as the experimental crystal structure of *mer*  $[\text{Fe}(\text{ba})_3]$ .



**Figure 1:** Top: Examples of square planar, octahedral and square antiprismatic metal- $\beta$ -acetylacetonato complexes. Bottom: [Fe(acac)<sub>3</sub>] with *D*<sub>3</sub> point group, *fac* [Fe(ba)<sub>3</sub>] with *C*<sub>3</sub> point group and *mer* [Fe(ba)<sub>3</sub>] with *C*<sub>1</sub> molecular symmetry. The proper rotation axis is around the blue arrows. The *D*<sub>3</sub> point group has the following symmetry operations: E, *C*<sub>3</sub> (perpendicular to the page) and three *C*<sub>2</sub>. Colour code of atoms: Cu (orange), Cr (light blue), Zr (turquoise), Fe (magenta), O (red), C (black) and H (white).

## 2 Experimental

### 2.1 Synthesis

Tris(benzoylacetonato- $\kappa^2$ O,O')iron(III) [Fe(ba)<sub>3</sub>] was synthesized according to literature methods as described previously [44,49,48], using published methods as a guide [50,51,52]. The paramagnetic [Fe(ba)<sub>3</sub>] complex was characterized by MS, elemental analysis and X-ray crystallography.

### *Characterization data for [Fe(CH<sub>3</sub>COCHCOC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>], [Fe(ba)<sub>3</sub>]*

Yield 84%. Colour: red-orange. M.p. 218.5-220.3 °C (reported: 222-224 °C [50]). UV:  $\lambda_{\max}$  298 nm,  $\epsilon_{\max}$  40260 mol<sup>-1</sup>.dm<sup>3</sup>.cm<sup>-1</sup> (CH<sub>3</sub>CN). MS Calcd. ([M], positive mode): *m/z* 539.4. Found: *m/z* 539.1. Anal. Calcd. for FeC<sub>30</sub>H<sub>27</sub>O<sub>6</sub>: C, 66.80; H, 5.05. Found: C, 66.46; H, 5.10

## **2.2 Crystal structure analysis**

Data for the crystals, obtained from solution in diethyl ether, were collected on a Bruker D8 Venture kappa geometry diffractometer, with duo I $\mu$ s sources, a Photon 100 CMOS detector and APEX II [53] 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+ [53] and the intensities were corrected for absorption using SADABS [53]. The structure was solved by intrinsic phasing using SHELXTS and refined by full-matrix least squares, using SHELXTL + [54] and SHELXL-2014+ [54]. 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; all isotropic displacement parameters for hydrogen atoms were calculated as  $X \times U_{eq}$  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 given in the electronic supplementary information.

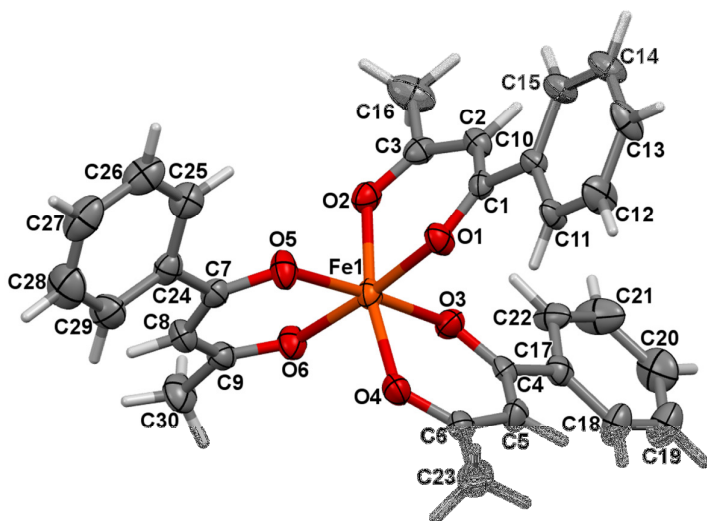
## **2.3 Density functional theory (DFT) calculations**

Density functional theory (DFT) calculations were carried out, using the ADF (Amsterdam Density Functional) 2013 programme [55], with a selection of GGA (Generalized Gradient Approximation) functionals, namely OLYP (Handy-Cohen and Lee-Yang-Parr) [56,57,58,59], S12g [60], OPBE [61], the meta-GGA functionals M06-L [62], TPSS [63,64] as well as the hybrid functionals B3LYP (Becke 1993 and Lee-Yang-Parr) [65] O3LYP [66], B3LYP\* [67] and S12h [60]. The TZP (Triple  $\zeta$  polarized) basis set, with a fine mesh for numerical integration and full geometry optimization, applying tight convergence criteria, was used for minimum energy searches.  $C_3$  symmetry has complex irreducible representations which have not been implemented in ADF [55]; therefore complexes with  $C_3$  input geometry optimize in  $C_1$  symmetry in ADF. Time-dependent density functional theory calculations were carried out with ADF.

### 3 Results and Discussion

#### 3.1 X-ray structure

The [Fe(ba)<sub>3</sub>] existing in the asymmetric unit is disordered over two positions in 0.70 : 0.30 ratio. A depiction [68] of the molecular structure of the main domain of [Fe(ba)<sub>3</sub>] *mer* isomer showing applied numbering scheme, is presented in Figure 2 (see Figure S2 of the Supporting Information for the perspective drawing of the molecular structure of the second domain). Table 1 gives selected geometrical parameters of the main domain of *mer* [Fe(ba)<sub>3</sub>] and Table 2 selected average geometrical parameters of [Fe( $\beta$ -diketonato)<sub>3</sub>] complexes. The relatively symmetrical space fill of the [Fe(ba)<sub>3</sub>] allows alternate packing of the molecules in crystal net, what leads to observed disorder. The three crystallographically independent cyclic benzoylacetato fragments in the main domain of *mer* [Fe(ba)<sub>3</sub>] that include Fe, are ring1 (Fe1-O1-C1-C2-C3-O2), ring4 (Fe1-O3-C4-C5-C6-O4) and ring5 (Fe1-O5-C7-C8-C9-O6). These rings are planar with the largest deviation from planarity of 0.202(1) Å for O2 in ring1, 0.159(1) Å for O4 in ring4 and 0.073 (1) Å for O5 in ring3. The angles between these three rings vary between 68.97(8)° and 78.49(8)°. Two of these three rings are, however, not in the same plane as the phenyl rings attached to them: ring1 is tilted from the plane of its attached phenyl substituent, resulting in a dihedral angle between these planes of 17.6(3)°. The corresponding dihedral angles for ring4 and ring5 with their attached phenyl rings are 5.8(3)° and 33.2(1)°, respectively. Some  $\pi$ -stacking effects [69,70] are observed, with the  $\pi$ ... $\pi$  (parallel) distance of 5.404(5) Å for ring6 (C10-C11-C12-C13-C14-C15) and 5.459(5) Å for ring7 (C17-C18-C19-C20-C21-C22). In addition, another stabilizing interaction with a  $\pi$ -system is observed for the perpendicular C18-H18...ring5 (2.736 Å). Three weak C—H...O hydrogen bonds [71] are present in the crystal structure ( $d(\text{O2}\dots\text{H5}) = 2.56$  Å),  $d(\text{O2}\dots\text{H18}) = 2.60$  Å and  $d(\text{O3}\dots\text{H28}) = 2.58$  Å, see Figure S2) and they create the C(6)DC(8) motifs of the unitary graph set [72].



**Figure 2:** A perspective drawing of the molecular structure of the major isomer of *mer* [Fe(ba)<sub>3</sub>], showing the atom numbering scheme. Atomic displacement parameters (ADPs) are shown at the 50 % probability level.

**Table 1:** Selected experimental (exp) and DFT calculated (calc) geometric parameters for *mer* [Fe(ba)<sub>3</sub>].

	experimental*	calculated				
		B3LYP	B3LYP	OPBE	OLYP	S12g
<b>Bond length (Å)</b>						
Fe(1)-O(1)	2.0007(13)	2.041	2.044	2.049	2.062	2.080
Fe(1)-O(2)	1.9988(14)	2.018	2.018	2.045	2.059	2.086
Fe(1)-O(5)	1.9792(14)	2.030	2.032	2.042	2.050	2.081
Fe(1)-O(6)	2.0016(13)	2.012	2.013	2.041	2.059	2.068
Fe(1)-O(4)	1.9922(14)	2.040	2.044	2.039	2.060	2.081
Fe(1)-O(3)	1.9902 (14)	2.018	2.018	2.050	2.063	2.077
<b>average</b>	<b>1.9937(14)</b>	<b>2.027</b>	<b>2.028</b>	<b>2.044</b>	<b>2.059</b>	<b>2.079</b>
<b>ave calc - ave exp</b>		<b>0.035</b>	<b>0.037</b>	<b>0.053</b>	<b>0.067</b>	<b>0.087</b>
<b>Bond angle (°)</b>						
O(2)-Fe(1)-O(1)	85.84(6)	87.1	87.1	85.7	85.3	81.6
O(5)-Fe(1)-O(6)	86.20(6)	87.2	87.1	85.8	85.7	82.0
O(3)-Fe(1)-O(4)	86.27(6)	86.5	86.4	85.7	85.3	82.0
<b>average</b>	<b>86.10(6)</b>	<b>87</b>	<b>87</b>	<b>86</b>	<b>85</b>	<b>82</b>
<b>ave calc - ave exp</b>		<b>0.8</b>	<b>0.7</b>	<b>-0.5</b>	<b>-0.7</b>	<b>-4.3</b>

\*for the main domain of *mer* [Fe(ba)<sub>3</sub>]

The Fe–O bond lengths for [Fe(RCOCHCOR')<sub>3</sub>] complexes vary between 1.944 and 2.095 Å (see Table 2 and Supporting Information Table S1). In [Fe(RCOCHCOCF<sub>3</sub>)<sub>3</sub>] complexes containing an unsymmetrical β-diketonato ligand where one group substituted on the β-diketonato

is CF<sub>3</sub>, the Fe–O bond near CF<sub>3</sub> (1.944 – 2.001 Å) is generally shorter than the Fe–O near bond near the non–CF<sub>3</sub>, namely group R (1.987 – 2.036 Å). The longest and shortest Fe–O bonds are 2.036 and 1.944 Å respectively, both in the crystal structure of *mer* [Fe(CH<sub>3</sub>COCHCOCF<sub>3</sub>)<sub>3</sub>] [73]. The longest and shortest Fe–O bonds, namely 2.036 Å and 1.944 Å, are near a CH<sub>3</sub> and CF<sub>3</sub> group respectively.

**Table 2:** Selected average geometric parameters for [Fe(RCOCHCOR')<sub>3</sub>] complexes.<sup>a</sup>

R	R'	isomer	O–Fe–O (°)	Fe–O near R (Å)	Fe–O near R' (Å)	CSD ref code
CH <sub>3</sub>	CH <sub>3</sub>	<i>symmetric</i>	87.3(9)	1.99(1)	-	see ref [84]
CF <sub>3</sub>	CF <sub>3</sub>	<i>symmetric</i>	87(1)	2.02(2)	-	BUPTAH
Ph	Ph	<i>symmetric</i>	86.5(7)	2.00(2)	-	DPPDFE, DPPDFE01
<sup>t</sup> Bu	<sup>t</sup> Bu	<i>symmetric</i>	85.4(4)	1.99(1)	-	DUBMES10, DUBMES11
Fu	CF <sub>3</sub>	<i>mer</i>	87.6(4)	2.008(4)	1.986(6)	HILVAB
Th	CF <sub>3</sub>	<i>mer</i>	87(1)	2.01(2)	1.98(2)	TTFBFE01
Th	CF <sub>3</sub>	<i>fac</i>	87.5(0)	1.995(0)	1.974(0)	TTFBFE
CH <sub>3</sub>	CF <sub>3</sub>	<i>mer</i>	87.2(0)	2.02(2)	1.97(3)	DUBMOC10
<sup>t</sup> Bu	CF <sub>3</sub>	<i>fac</i>	86.5(2)	2.01(1)	1.976(7)	SOJXEU01
CH <sub>3</sub>	Ph	<i>mer</i>	86.2(2)	1.996(5)	1.9912(14)	this study

a The Supporting Information Table S1 give a more detailed summary of the geometrical parameters of [Fe(β-diketonato)<sub>3</sub>] complexes.

### 3.2 Computational chemistry study

Neutral [Fe<sup>III</sup>(β-diketonato)<sub>3</sub>] complexes are d<sup>5</sup> complexes with a S = 5/2 (five unpaired electrons) spin state [12,74,75]. It is known that not all functionals correctly predict the spin state of iron complexes [76,77,78,79]. It has previously been shown that the GGA functionals PW91 and BP86 give the wrong spin state for [Fe(acac)<sub>3</sub>], while OLYP and B3LYP correctly give the S = 5/2 high spin state of [Fe(acac)<sub>3</sub>] [49]. In order to identify more functionals that correctly calculate the high spin state of [Fe(acac)<sub>3</sub>], the DFT calculated energies for the possible spin states (S = 1/2, 3/2 and 5/2) of [Fe(acac)<sub>3</sub>] optimized with a selection of different types of DFT functionals, namely the GGA functionals OLYP [49], S12g, OPBE, the meta-GGA functionals M06-L, TPSS, and the hybrid functionals O3LYP, B3LYP [49], B3LYP\*, S12h, are given in Table 3. The hybrid functionals predicted the high spin state as the most stable state by the largest energy difference. The OLYP, S12g, B3LYP, B3LYP\*, S12h and M06-L functionals that correctly calculated the S = 5/2 ground state of [Fe(acac)<sub>3</sub>], should give reliable energies the *fac* or *mer* isomers of [Fe(ba)<sub>3</sub>]. The relative energies of the *fac* and *mer* [Fe(ba)<sub>3</sub>] isomers, obtained by these functionals are



presented in **Table 3**. The insignificant energy difference ( $< 0.03$  eV) obtained between the *fac* and *mer* isomers of  $[\text{Fe}(\text{ba})_3]$ , show that both isomers can exist without any clear preference for the *fac* or the *mer* isomer.

**Table 3:** Relative energies (eV) calculated by a selection of functionals. The lowest energy is indicated in bold as 0.

	meta-GGA TPSS	hybrid O3LYP	GGA S12g	GGA OPBE	GGA OLYP	meta-GGA M06-L	hybrid B3LYP*	hybrid B3LYP	hybrid S12h
Different spin states of $[\text{Fe}(\text{acac})_3]$									
1/2	<b>0.00</b>	<b>0.00</b>	0.35	0.55	0.58 <sup>a</sup>	0.83	0.93	1.35 <sup>a</sup>	2.19
3/2	0.68	0.86	0.65	0.78	0.78 <sup>a</sup>	1.09	1.13	1.45 <sup>a</sup>	1.88
5/2	0.35	0.35	<b>0.00</b>	<b>0.00</b>	<b>0.00<sup>a</sup></b>	<b>0.00</b>	<b>0.00</b>	<b>0.00<sup>a</sup></b>	<b>0.00</b>
$[\text{Fe}(\text{ba})_3]$ isomers									
<i>fac</i> $\text{Fe}(\text{ba})_3$	-	-	<b>0.000</b>	0.004	0.007	<b>0.000<sup>b</sup></b>	0.024	0.027	<b>0.000<sup>b</sup></b>
<i>mer</i> $\text{Fe}(\text{ba})_3$	-	-	0.021	<b>0.000</b>	<b>0.000</b>	0.011 <sup>b</sup>	<b>0.000</b>	<b>0.000</b>	0.011 <sup>b</sup>

a. values from reference 49.

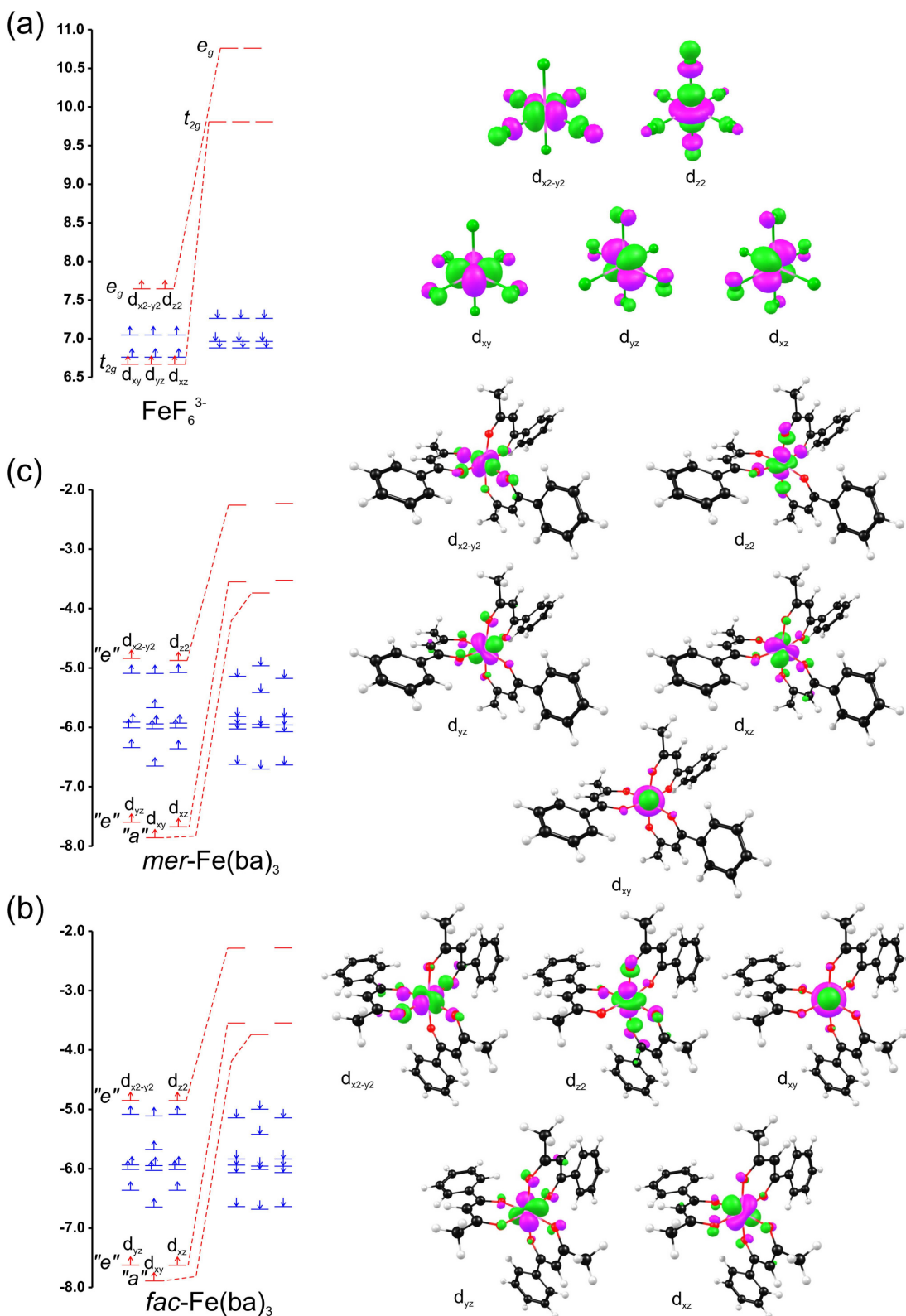
b. single point on OLYP optimized geometry

We previously found that B3LYP is considered to be a good functional to calculate the energy and geometry of the tris( $\beta$ -diketonato)iron(III) complexes with  $\beta$ -diketone = acetylacetonate, 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione and 4,4,4-Trifluoro-1-(2-furyl)-1,3-butanedione [49]. Table 1 compares the calculated and experimental Fe-O bonds and O-Fe-O angles for *mer*  $[\text{Fe}(\text{ba})_3]$  for a selection of functionals. The important geometrical parameters in coordination complexes are the bond lengths and angles involving the metal centre. We will focus on average Fe-O bonds and O-Fe-O angles. All the functionals used gave relatively good geometries, compared to the experimental structure. All functionals over estimated the Fe-O lengths, as generally is the case with gas phase calculations [80]. The hybrid functionals gave closest agreement with experiment, while the GGA density functionals that are known to overestimate bonds lengths [81] performed less accurate.

In an octahedral ( $O_h$ ) environment, the five metal *d*-orbitals of a high spin  $3d^5$  Fe(III)-complex split into two sets, the  $t_{2g}$ -orbitals ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ) with lower energy and the  $e_g$  orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) with higher energy. Figure 3 (left) illustrates this splitting of the *d*-orbitals by a molecular orbital (MO) energy level diagram of the high-spin octahedral  $[\text{FeF}_6]^{3-}$  complex [82]. Distortion from the octahedral symmetry  $O_h$  towards lower  $D_3$  or  $C_3$  symmetry, splits the degenerate  $t_{2g}$ -orbitals into *a* and *e* components. When the *e* is component lower in energy than *a*, it

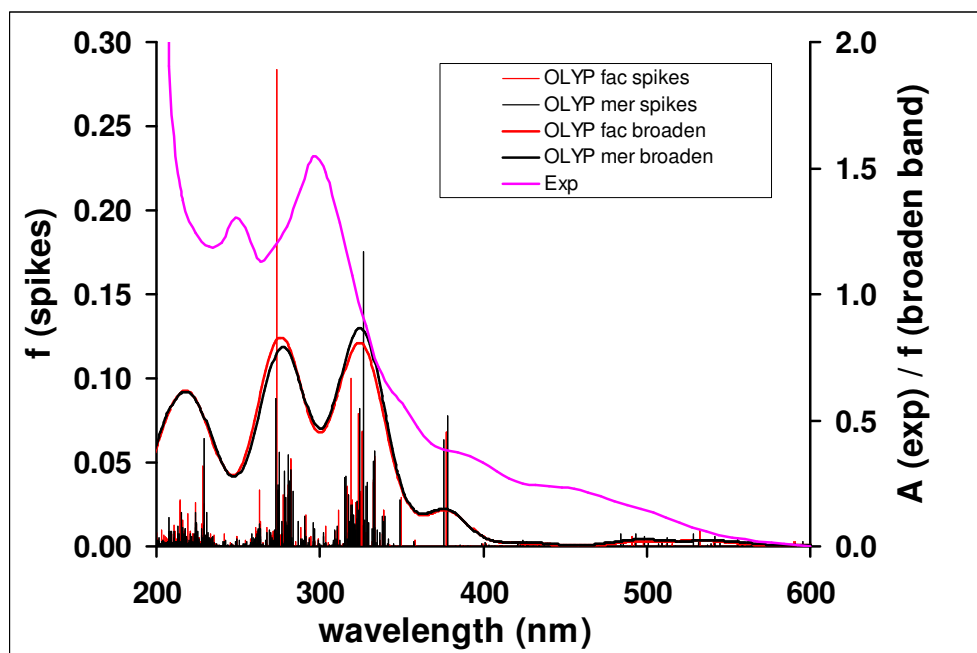
is referred to as a positive distortion and when the  $a$  component is lower in energy than  $e$ , it is referred to as a negative distortion. The high spin  $d^5$   $[\text{Fe}(\text{acac})_3]$  complex containing a symmetrical  $\beta$ -diketonato ligand has  $D_3$  symmetry and exhibits a negative distortion, with the lowest d-orbital having  $a$  symmetry [49]. This distortion affects only the arrangement of the molecular energy levels, and not the physical geometry of  $[\text{Fe}(\text{acac})_3]$ , therefore  $[\text{Fe}(\text{acac})_3]$  thus not exhibit Jahn-Teller distortion like for example  $[\text{Mn}(\beta\text{-diketonato})_3]$  complexes [83]. The  $\text{Fe-O}_{\beta\text{-acac}}$  bond lengths in experimental X-ray structures of  $[\text{Fe}(\text{acac})_3]$  without any crystallographically imposed symmetry, are all similar, ranging from 1.990 – 2.021 Å [84].

Figure 3 shows the DFT calculated molecular energy level diagram of the *fac* and *mer* isomers of  $[\text{Fe}(\text{ba})_3]$ , showing plots of the d-based frontier MOs. Although *mer*  $[\text{Fe}(\text{ba})_3]$  exhibit  $C_1$  molecular symmetry, the arrangement of the d-based MOs are very similar to that of the  $C_3$  *fac*  $[\text{Fe}(\text{ba})_3]$ . The orbital ordering of both *fac*  $[\text{Fe}(\text{ba})_3]$  and *mer*  $[\text{Fe}(\text{ba})_3]$  is thus  $d_{xy} < d_{yz} \approx d_{xz} < d_{z^2} \approx d_{x^2-y^2}$ , as expected for a distorted octahedral ligand field. This is the same orbital ordering that was obtained for the high spin  $D_3$   $[\text{Fe}(\text{acac})_3]$  complex with electronic configuration:  $d_{xy}^1 d_{xz}^1 d_{yz}^1 d_{z^2}^1 d_{x^2-y^2}^1$  [49].



**Figure 3:** OLYP/TZP molecular orbital Kohn-Sham energy levels (eV) for  $[\text{FeF}_6]^{3-}$ , *fac*  $[\text{Fe}(\text{ba})_3]$  and *mer*  $[\text{Fe}(\text{ba})_3]$ , with  $S = 5/2$ . Plots of the d-based MOs are included. The arrows represent spin-up ( $\alpha$  MOs) and spin-down ( $\beta$  MOs) electrons. The d-based orbitals are indicated in red. The y-axis indicates relative energy in eV.

**Figure 4** shows the OLYP/TZP calculated TDDFT spectra for *fac* and *mer* [Fe(ba)<sub>3</sub>], overlaid with the experimental spectrum. The calculated spectrum matches the basic shape of the experimentally observed spectra.



**Figure 4:** Experimental (magenta) and OLYP/TZP calculated TDDFT electronic absorption spectra of *fac* [Fe(ba)<sub>3</sub>] (red) and *mer* [Fe(ba)<sub>3</sub>] (black). The vertical spikes show the calculated oscillators. The broaden line spectrum has been generated by Doppler broadening of spectral lines to enable comparison of calculated spectrum with the experimental spectrum.

#### 4 Conclusions

*Fac* and *mer* tris(benzoylacetonato- $\kappa^2$ O,O')Fe(III) have an electronic configuration of  $d_{xy}^1 d_{xz}^1 d_{yz}^1 d_{z^2}^1 d_{x^2-y^2}^1$  with a similar order of the d-based molecular orbitals namely  $d_{xy} < d_{yz} \approx d_{xz} < d_{z^2} \approx d_{x^2-y^2}$ . This orbital ordering is a negative distortion from octahedral symmetry  $O_h$  towards the lower  $C_3$  symmetry of *fac* [Fe(ba)<sub>3</sub>]. DFT calculated energies of the optimized geometries of *fac* [Fe(ba)<sub>3</sub>] and *mer* [Fe(ba)<sub>3</sub>] show that both the *fac* and *mer* isomers of [Fe(ba)<sub>3</sub>] can exist without any clear preference for the major isomer. *Mer* [Fe(ba)<sub>3</sub>] was isolated and characterized by solid state crystallography.

## Supporting Information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with number: CCDC 1447615. 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/](http://www.ccdc.cam.ac.uk/products/csd/request/)]. Figures S1, S2, Table S1, selected crystallographic data and optimized coordinates of the DFT calculations are given in the Supporting Information.

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## References

---

- [1] R.H. Holm, F.A. Cotton, Spectral Investigations of Metal Complexes of  $\beta$ -Diketones. I. Nuclear Magnetic Resonance and Ultraviolet Spectra of Acetylacetonates, *Journal of the American Chemical Society* 80 (1958) 5658-5663.
- [2] J. Starý, *The Solvent Extraction of Metal Chelates*, MacMillan Company, New York, 1964, pp. 51-79.
- [3] Y. Qu, H.-L. Zhu, Z.-L. You, M.-Y. Tan, Synthesis and Characterization of the Complexes of Pentane-2,4-dione with Nickel(II) and Cobalt(III):  $[\text{Ni}(\text{acac})_2] \cdot 0.5\text{CH}_3\text{OH}$  and  $[\text{Co}(\text{acac})_2\text{NO}_3] \cdot 2\text{H}_2\text{O}$  (acac = Pentane-2,4-dione), *Molecules* 9 (2004) 949-956.
- [4] A.N. Knyazeva, E.A. Shugam, L.M. Shkol'nikova, Crystal chemical data regarding intracomplex compounds of beta diketones VI. Crystal and molecular structure of palladium acetylacetonate, *Journal of Structural Chemistry* 11 (1970) 875-876.
- [5] A.R. Siedle, T.J. Kistenmacher, R.M. Metzger, C.-S. Kuo, R.P. van Duyne, T. Cape, (Tetrathiafulvalene)bis(acetylacetonato)palladium(II),  $(\text{TTF})\text{Pd}(\text{acac})_2$ , a metallotetrathiaethylene containing neutral tetrathiafulvalene, *Inorganic Chemistry* 19 (1980) 2048-2051.
- [6] K. Ha, Crystal structure of bis(pentane-2,4-dionato- $\kappa^2 O, O'$ )platinum(II),  $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ , *Zeitschrift für Kristallographie - New Crystal Structures* 226 (2011) 329-330.
- [7] N. Yu. Kozitsyna, A.E. Gekhman, S.E. Nefedov, M.N. Vargaftik, I.I. Moiseev, *Inorganic Chemistry Communications* 10 (2007) 956-958.

- 
- [8] C.C. Joubert, L. van As, A. Jakob, J.M. Speck, H. Lang, J.C. Swarts, Intramolecular electronic communication in ferrocene-based  $\beta$ -diketonato copper(II) complexes as observed by an electrochemical study, *Polyhedron* 55 (2013) 80-86.
- [9] F.A. Cotton, C.E. Rice, G.W. Rice, The crystal and molecular structures of bis(2,4-pentanedionato)chromium, *Inorganica Chimica Acta* 24 (1977) 231-234.
- [10] V.D. Vreshch, J.-H. Yang, H. Zhang, A.S. Filatov, E.V. Dikarev, Monomeric Square-Planar Cobalt(II) Acetylacetonate: Mystery or Mistake?, *Inorganic Chemistry* 49 (2010) 8430-8434.
- [11] M.N. Sokolov, A.V. Virovets, A.V. Rogachev, P.A. Abramov, V.P. Fedin, Reaction of  $[\text{VO}(\text{OPr})_3]$  with hexamethyldisylthiane in the presence of  $\beta$ -diketones, *Koord. Khim. (Russian Journal of Coordination Chemistry)* 39 (2013) 86-91.
- [12] I. Diaz-Acosta, J. Baker, W. Cordes, P. Pulay, Calculated and Experimental Geometries and Infrared Spectra of Metal Tris-Acetylacetonates: Vibrational Spectroscopy as a Probe of Molecular Structure for Ionic Complexes. Part I, *Journal of Physical Chemistry A* 105 (2001) 238-244.
- [13] R. Liu, J. Conradie, Tris( $\beta$ -diketonato)chromium(III) complexes: Effect of the  $\beta$ -diketonate ligand on the redox properties, *Electrochimica Acta* 185 (2015) 288-296.
- [14] J.P. Fackler Jr., A. Avdeef, Crystal and molecular structure of tris(2,4-pentanedionato)manganese(III),  $\text{Mn}(\text{O}_2\text{C}_5\text{H}_7)_3$ , a distorted complex as predicted by Jahn-Teller arguments, *Inorganic Chemistry* 13 (1974) 1864-1875. (CSD, reference codes: ACACMN02) DOI: 10.1021/ic50138a016
- [15] R. Freitag, J. Conradie, Electrochemical and Computational Chemistry Study of  $\text{Mn}(\beta\text{-diketonato})_3$  complexes, *Electrochimica Acta* 158 (2015) 418-426.
- [16] Sh-Sh. Weng, Ch-Sh. Ke, F-K. Chen, Y-F. Lyu, G-Y. Lin, Transesterification catalyzed by iron(III)  $\beta$ -diketonate species, *Tetrahedron* 67 (2011) 1640-1648.
- [17] M.M. Conradie, J. Conradie, Electrochemical behaviour of Tris( $\beta$ -diketonato)iron(III) complexes: A DFT and experimental study, *Electrochimica Acta* 152 (2015) 512-519.
- [18] V.P. Nikolaev, L.A. Butman, M.A. Porai-Koshits, V.I. Sokol, V.A. Avilov, I.I. Moiseev, *Koord. Khim. (Russian Journal of Coordination Chemistry)* 5 (1979) 882-887.
- [19] R. Liu, P.H. van Rooyen, J. Conradie, Geometrical isomers of Tris(beta-diketonato)metal(III) complexes for  $\text{M} = \text{Cr}$  or  $\text{Co}$ : synthesis, X-ray structures and DFT study, *Inorganica Chimica Acta* 47 (2016) 59-65.
- [20] J.V. Silverton, J.L. Hoard, Stereochemistry of Discrete Eight-Coördination. I. Basic Analysis, *Inorganic Chemistry* 2 (1963) 235-242;

---

F. Hentschel, V.V. Vinogradov, A.V. Vinogradov, A.V. Agafonov, V.V. Guliants, I. Persson, G.A. Seisenbaeva, V.G. Kessler Zirconium(IV) and Hafnium(IV) coordination polymers with a Tetraacetyl-ethane (Bisacac) ligand: synthesis, structure elucidation and gas sorption behaviour, *Polyhedron* 89 (2015) 297-303.

[21] B. Allard, Studies of tetravalent acetylacetonato complexes—I: Coordination and properties in the solid state, *Journal of Inorganic and Nuclear Chemistry* 38 (1976) 2109-2115.

[22] K.V. Zherikova, N.B. Morozova, N.V. Kuratieva, I.A. Baidina, I.K. Igumenov, Synthesis and structural investigation of hafnium(IV) complexes with acetylacetonone and trifluoroacetylacetonone, *Zh. Strukt. Khim. (Russian Journal of Structural Chemistry)* 46 (2005) 1081-1088.

[23] R.P. Dodge, D.H. Templeton, A. Zalkin, Crystal Structure of Vanadyl Bisacetylacetonate. Geometry of Vanadium in Fivefold Coordination, *Journal of Chemical Physics* 35 (1961) 55-67; M. Hoshino, A. Sekine, H. Uekusa, Y. Ohashi, X-ray analysis of bond elongation in VO(acac)<sub>2</sub> at the excited state, *Chemistry Letters* 34 (2005) 1228-1229.

[24] T.A. Tsotetsi, A. Kuhn, A. Muller, J. Conradie, Substitution kinetics of biphenol at dichlorobis(2,4-pentadionato-κ<sup>2</sup>O,O')titanium(IV): Isolation, Characterization, Crystal Structure and Enhanced Hydrolytic Stability of the Product (2,2'-Biphenyldiolato)bis(2,4-pentadionato-κ<sup>2</sup>O,O')titanium(IV), *Polyhedron* 28 (2009) 209-214.

[25] A. Kuhn, J. Conradie, Observed hydrolysis of fluorine substituted bis(β-diketonato)-dichlorotitanium(IV) complexes, *Dalton Transactions* 44 (2015) 5106–5113.

[26] A. Kuhn, J. Conradie, Structural investigation of trifluoromethyl substituted bis(β-diketonato)-dichlorotitanium(IV) complexes displaying a mono-dinuclear equilibrium hydrolysis reaction, *Journal of Molecular Structure* 1089 (2015) 267–276.

[27] A. Kuhn, T.A. Tsotetsi, A. Muller, J. Conradie, Isomer Distribution and Structure of (2,2'-Biphenyldiolato)bis(beta-diketonato)titanium(IV) Complexes: a Single Crystal X-ray, Solution NMR and Computational Study, *Inorganica Chimica Acta* 362 (2009) 3088-3096.

[28] K.H. Hopmann, A. Kuhn, J. Conradie, Substitution reactions of dichlorobis(beta-diketonato-O,O') titanium(IV) complexes with aryl diolato ligands: an experimental and computational study, *Polyhedron* 67 (2014) 231-241.

[29] A. Kuhn, A. Muller, J. Conradie, Syntheses, crystal structure and theoretical modeling of tetrahedral mono-β-diketonato titanocenyl complexes, *Polyhedron* 28 (2009) 966-974.

[30] A. Kuhn, J. Conradie, Electrochemical and Density Functional Theory Study of bis(cyclopentadienyl) mono(β-diketonato) titanium(IV) cationic complexes, *Electrochimica Acta* 56 (2010) 257-264.

- 
- [31] J. Conradie, Density Functional Theory Calculations of Rh- $\beta$ -diketonato complexes, Dalton Transactions 44 (2015) 1503-1515.
- [32] J. Conradie, Oxidation potential of [Rh(beta-diketonato)(P(OPh)<sub>3</sub>)<sub>2</sub>] complexes – relationships with experimental, electronic and calculated parameters, Electrochimica Acta 110 (2013) 718-725.
- [33] K. Inaba, N. Itoh, Y. Matsuno, T. Sekine, Rate of Complex Formation of Iron(III) with Several  $\beta$ -Diketones in Aqueous Perchlorate Solutions Determined by Solvent Extraction Method, Bulletin of the Chemical Society of Japan 58 (1958) 2176-2180.
- [34] S. Katsuta, H. Imura, N. Suzuki, Novel enhancement effect of a proton donor on chelate extraction: extraction of iron(III) with acetylacetone and 3,5-dichlorophenol, Journal of Radioanalytical and Nuclear Chemistry 157 (1992) 255-264.
- [35] J. Starý, E. Hladk, Systematic study of the solvent extraction of metal  $\beta$ -diketonates, Analytica Chimica Acta 28 (1963) 227-235.
- [36] J.C. Lo, J. Gui, Y. Yabe, C.-M. Pan, P.S. Baran, Functionalized olefin cross-coupling to construct carbon–carbon bonds, Nature 516 (2014) 343-348.
- [37] C. Bolm, J. Legros, J. le Paih, L. Zani, Iron-Catalyzed Reactions in Organic Synthesis, Chemical Reviews 104 (2004) 6217-6254.
- [38] J.K. Kochi, Homo coupling, disproportionation and cross coupling of alkyl groups. Role of the transition metal catalyst, Journal of Organometallic Chemistry 653 (2002) 11-19.
- [39] B.D. Sherry, A. Fürstner, The Promise and Challenge of Iron-Catalyzed Cross Coupling, Accounts of Chemical Research 41 (2008) 1500-1511.
- [40] A. Fürstner, A. Leitner, M. Méndez, H. Krause, Iron-Catalyzed Cross-Coupling Reactions, Journal of the American Chemical Society 124 (2002) 13856-13863.
- [41] B. Scheiper, M. Bonnekessel, H. Krause, A. Fürstner, Selective Iron-Catalyzed Cross-Coupling Reactions of Grignard Reagents with Enol Triflates, Acid Chlorides, and Dichloroarenes, Journal of Organic Chemistry 69 (2004) 3943-3949.
- [42] G. Cahiez, H. Avedissian, Highly Stereo- and Chemoselective Iron-Catalyzed Alkenylation of Organomagnesium Compounds, Synthesis 8 (1998) 1199-1205.
- [43] R.A. Ligabue, A.L. Monteiro, R.F. de Souza, M.O. de Souza, Catalytic properties of Fe(acac)<sub>3</sub> and Cu(acac)<sub>2</sub> in the formation of urethane from a diisocyanate derivative and EtOH, Journal of Molecular Catalysis A: Chemical 130 (1998) 101-105.



- 
- [44] M.M. Conradie, J. Conradie, E. Erasmus, Immobilisation of Iron tris( $\beta$ -diketonates) on a two-dimensional flat amine functionalized silicon wafer: A catalytic study of the formation of urethane, from ethanol and a diisocyanate derivative, *Polyhedron* 79 (2014) 52-59.
- [45] S-S. Weng C-S. Ke, F-K. Chen, Y-F. Lyu, G-Y. Lin, Transesterification catalyzed by iron(III)  $\beta$ -diketonate species, *Tetrahedron* 67 (2011) 1640-1648.
- [46] J.A.L. Takacs, G.V. Madhavan, M. Creswell, F. Seely, W. Devroy, Iron-Catalyzed Aminohydroxylation of Olefins, *Organometallics* 5 (1986) 2395-2398.
- [47] A. Misono, Oligomerization of isoprene by cobalt or iron complex catalysts, *Bulletin of the Chemical Society of Japan* 39 (1966) 2425-2429.
- [48] M.M. Conradie, J. Conradie, Electrochemical behaviour of Tris( $\beta$ -diketonato)iron(III) complexes: A DFT and experimental study, *Electrochimica Acta* 152 (2015) 512-519. DOI: 10.1016/j.electacta.2014.11.128
- [49] M.M. Conradie, P.H. van Rooyen, J. Conradie, 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, *Journal of Molecular Structure* 1053 (2013) 134-140.
- [50] E.W. Berg, J.T. Truemper, A Study of the Volatile Characteristics of various metal  $\beta$ -diketone chelates, *Journal of Physical Chemistry* 64 (1960) 487-490.
- [51] K. Endo, M. Furukawa, H. Yamatera, H. Sano, Lifetimes of ortho-Positronium in Benzene Solutions of  $\beta$ -Diketonates of Iron(III) and Cobalt(III), *Bulletin of the Chemical Society of Japan* 53 (1980) 407-410.
- [52] G.S. Hammond, D.C. Nonhebel, C.S. Wu, Chelates of  $\beta$ -Diketones. V. Preparation and Properties of Chelates Containing Sterically Hindered Ligands, *Inorganic Chemistry* 2 (1963) 73-76.
- [53] APEX2 (including SAINT and SADABS); Bruker AXS Inc., Madison, WI, 2012.
- [54] G.M. Sheldrick, *Acta Crystallographica A* 64 (2008) 112-122.
- [55] G. te Velde, F.M Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, Chemistry with ADF, *Journal of Computational Chemistry* 22 (2001) 931-967.
- [56] N.C. Handy, A.J. Cohen, Left-right correlation energy, *Molecular Physics* 99 (2001) 403-412.
- [57] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Physical Review B* 37 (1988) 785-789.

- 
- [58] B.G. Johnson, P.M.W. Gill, J.A. Pople, The performance of a family of density functional methods, *Journal of Chemical Physics* 98 (1993) 5612-5626.
- [59] T.V. Russo, R.L. Martin, P.J. Hay, Density Functional calculations on first-row transition metals, *Journal of Chemical Physics* 101 (1994) 7729-7737.
- [60] M. Swart, A new family of hybrid density functionals, *Chemical Physics Letters* 580 (2013) 166-171.
- [61] M. Swart, A.W. Ehlers, K. Lammertsma, Performance of the OPBE exchange-correlation functional, *Molecular Physics* 102 (2004) 2467-2474.
- [62] Y. Zhao, D.G. Truhlar, A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions, *Journal of Chemical Physics* 125 (2006) 194101/1-18;
- Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theoretical Chemical Accounts* 120 (2008) 215-241.
- [63] J. Tao, J.P. Perdew, V.N. Staroverov, G.E. Scuseria, Climbing the Density Functional Ladder: Nonempirical MetaGeneralized Gradient Approximation Designed for Molecules and Solids *Physical Review Letters* 91 (2003) 146401/1-4.
- [64] V.N. Staroverov, G.E. Scuseria, J. Tao, J.P. Perdew, Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes, *Journal of Chemical Physics* 119 (2003) 12129-12137.
- [65] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, *Journal of Physical Chemistry* 98 (1994) 11623-11627.
- [66] A.J. Cohen, N.C. Handy, Dynamic correlation, *Molecular Physics* 99 (2001) 607-615.
- [67] M. Reiher, O. Salomon, B.A. Hess, Reparameterization of hybrid functionals based on energy differences of states of different multiplicity, *Theoretical Chemistry Accounts* 107 (2001) 48-55.
- [68] L.J. Farrugia, WinGX and ORTEP for Windows : an update, *Journal of Applied Crystallography* 45 (2012) 849-854.
- [69] C.A. Hunter, J.K.M. Sanders, The nature of  $\pi$ - $\pi$  interactions, *Journal of the American Chemical Society* 112 (1990) 5525-5534.
- [70] R. Kruszynski, T. Sieranki, Can Stacking Interactions Exist Beyond the Commonly Accepted Limits?, *Crystal Growth & Design*, 16 (2016) 587-595.

- 
- [71] G.R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999.
- [72] (a) M.C. Etter, Encoding and decoding hydrogen-bond patterns of organic compounds, *Accounts of Chemical Research* 23 (1990) 120-126, (b) J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang, *Patterns in Hydrogen Bonding: Functionality and Graph Set Analysis in Crystals*, *Angewandte Chemie International Edition in English* 34 (1995) 1555-1573.
- [73] I.A. Baidina, P.A. Stabnikov, I.K. Igumenov, S.V. Borisov, *Koord. Khim.* (Russian Journal of Coordination Chemistry) 10 (1986) 404. CSD reference code: DUBMOC10
- [74] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, sixth ed., John Wiley & Sons, New York, 1999, p.790.
- [75] M. Gerloch, J. Lewis, R. C. Slade, Paramagnetic anisotropies and zero-field splitting of some high-spin iron(III) complexes, *Journal of the Chemical Society A* (1969) 1422-1427.
- [76] M. Swart, Accurate Spin-State Energies for Iron Complexes, *Journal of Chemical Theory and Computation* 4 (2008) 2057–2066.
- [77] M. Swart, A.R. Groenhof, A.W. Ehlers, K. Lammertsma, Validation of Exchange–Correlation Functionals for Spin States of Iron Complexes, *Journal of Physical Chemistry A* 108 (2004) 5479-5483.
- [78] J. Conradie, A. Ghosh, DFT Calculations on the Spin-Crossover Complex Fe(salen)(NO): A Quest for the Best Functional, *Journal of Physical Chemistry B* 111 (2007) 12621-12624 .
- [79] J. Conradie, A. Ghosh, Electronic Structure of Trigonal-Planar Transition-Metal–Imido Complexes: Spin-State Energetics, Spin-Density Profiles, and the Remarkable Performance of the OLYP Functional, *Journal of Chemical Theory and Computation* 3 (2007) 689-702.
- [80] W.J. Hehre, *A Guide to Molecular Mechanisms and Quantum Chemical Calculations*, Wavefunction Inc. 153 (2003) 181.
- [81] (a) A.C. Scheiner, J. Baker and J.W. Andzelm, Molecular energies and properties from density functional theory: Exploring basis set dependence of Kohn—Sham equation using several density functionals, *Journal of Computational Chemistry* 18 (1997) 775-795. (b) J.R. Hill, C.M. Freeman and B. Delley, Bridging Hydroxyl Groups in Faujasite: Periodic vs Cluster Density Functional Calculations, *The Journal of Physical Chemistry A*, 103 (1999) 3772-3777. (c) F. Furche and J.P. Perdew, The performance of semilocal and hybrid density functionals in transition-metal chemistry, *The Journal of Chemical Physics* 124 (2006) 044103-044129.

---

[82] H. Levanon, G. Stein, Z. Luz, Electron spin resonance spectrum of the hexafluoroferrate(III) ion in aqueous solutions, *Journal of the American Chemical Society* 90 (1968) 5292–5293.

[83] (a) R. Freitag, J. Conradie, Understanding the Jahn-Teller Effect in octahedral transition metal complexes – a Molecular Orbital view of the Mn( $\beta$ -diketonato)<sub>3</sub> complex, *Journal of Chemical Education* 90 (2013) 1692-1696. (b) R. Gostynski, P.H. van Rooyen, J. Conradie, Jahn-Teller distortion in Tris[4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedionato]manganese(III) isomers: an X-ray and computational study, *Journal of Molecular Structure* 1119 (2016) 48-53 (c) J. Conradie, Bond stretch isomers of d<sup>4</sup> Tris(benzoylacetato-  $\kappa^2$ O,O')Mn(III), *Computational and Theoretical Chemistry* 1087 (2016) 1-5

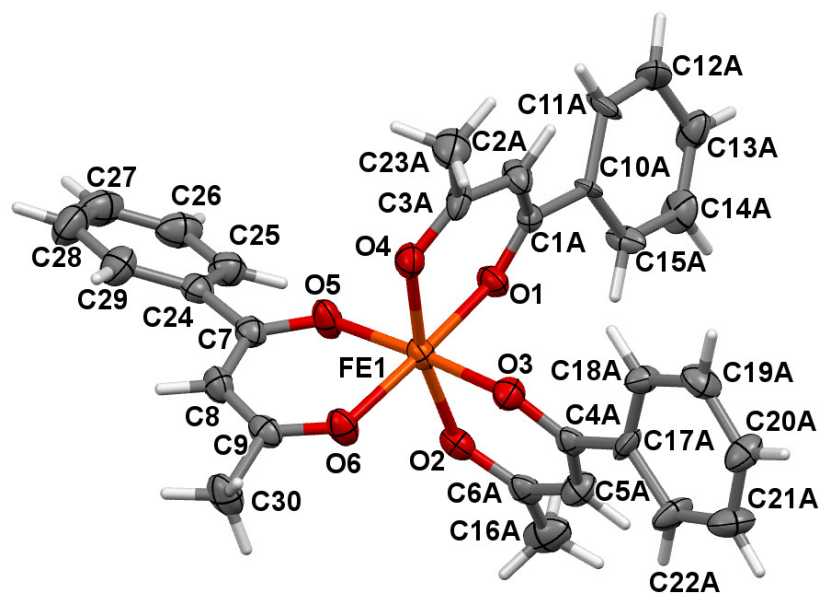
[84] Average value for 10 crystals from CSD, reference codes: FEACAC02, FEACAC02, FEACAC03, FEACAC05, FEACAC07, FEACAC08, FEACAC09, JICMEN, JICMEN01, VUBSOA. Cambridge Structural Database (CSD), Version 5.36, May 2015 update.

## Supporting information

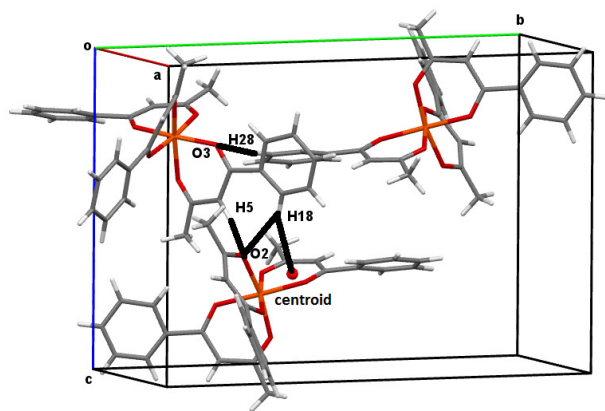
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Figures S1 and S2



**Figure S1.** A perspective drawing of the molecular structure of the second domain of *mer* [Fe(ba)<sub>3</sub>], showing the atom numbering scheme. Atomic displacement parameters (ADPs) are shown at the 50 % probability level.



**Figure S2.** The molecular packing of *mer* [Fe(ba)<sub>3</sub>], showing the intermolecular contacts as solid lines.

TABLE S1.

Crystallographic data for selected published [Fe( $\beta$ -diketonato)<sub>3</sub>] complexes

R	R'	isomer	Symmetrical beta-diketonato ligand										statistics											
			Refcode	O–Fe–O / (°)			Fe–O / (Å)						O–Fe–O / (°)				Fe–O / (Å)							
				ANG1	ANG2	ANG3	DIST1	DIST2	DIST3	DIST4	DIST5	DIST6	ave	max	min	std	ave	max	min	std				
CH <sub>3</sub>	CH <sub>3</sub>	<i>symmetric</i>	FEACAC02	89.2	86.9	89.9	2.018	1.995	2.005	1.994	1.970	1.957	<b>87.3</b>	89.9	84.9	0.9	<b>1.991</b>	2.021	1.957	0.013				
			FEACAC02	84.9	86.2	85.9	2.001	1.976	1.979	2.014	1.983	1.972												
			FEACAC03	87.2	87.6	87.5	1.976	1.994	1.992	1.984	1.996	2.004												
			FEACAC05	87.9	87.6	86.8	1.998	1.976	2.004	2.000	1.983	1.993												
			FEACAC07	87.9	87.3	86.8	1.995	1.977	2.003	1.997	1.981	1.992												
			FEACAC08	88.1	87.5	86.6	1.998	1.982	2.005	2.006	1.985	1.997												
			FEACAC09	87.9	86.7	87.5	2.001	2.006	1.981	2.001	1.995	1.989												
			JICMEN	86.8	86.8	86.8	1.990	2.010	1.990	2.010	1.990	2.010												
			JICMEN01	87.7	87.7	87.7	1.983	1.974	1.983	1.974	1.983	1.974												
			VUBSOA	88.2	86.8	87.4	2.006	1.971	1.981	2.021	1.985	1.998												
CF <sub>3</sub>	CF <sub>3</sub>	<i>symmetric</i>	BUPTAH	86.4	87.6	87.0	2.022	2.001	2.014	2.002	1.986	1.969	<b>87.0</b>	87.6	86.4	0.6	<b>1.999</b>	2.022	1.969	0.019				
Ph	Ph	<i>symmetric</i>	DPPDFE	87.2	86.5	85.5	2.008	1.986	1.997	1.995	1.979	1.963	<b>86.5</b>	87.2	85.5	0.7	<b>1.995</b>	2.018	1.963	0.017				
			DPPDFE01	87.1	86.9	85.7	2.003	2.018	2.008	2.016	1.97	1.993												
<sup>t</sup> Bu	<sup>t</sup> Bu	<i>symmetric</i>	DUBMES10	84.9	84.7	84.9	2.023	2.023	1.984	1.984	1.984	1.984	<b>85.4</b>	86.0	84.7	0.4	<b>1.993</b>	2.023	1.975	0.014				
			DUBMES10	86.0	85.3	85.3	1.983	1.987	1.983	1.987	2.004	2.004												
			DUBMES11	85.2	85.7	85.7	1.988	2.009	1.975	2.009	1.981	1.983												
			DUBMES11	85.6	85.8	85.2	1.991	1.99	1.987	2.011	1.988	1.983												
R	R'	isomer	Unsymmetrical beta-diketonato ligand										statistics											
			Refcode	O–Fe–O / (°)			Fe–O near R / (Å)			Fe–O near R' / (Å)			O–Fe–O / (°)				Fe–O near R / (Å)				Fe–O near R' / (Å)			
				ANG1	ANG2	ANG3	DIST1	DIST2	DIST3	DIST4	DIST5	DIST6	ave	max	min	std	ave	max	min	std	ave	max	min	std
Fu	CF <sub>3</sub>	<i>mer</i>	HILVAB	88.0	87.5	87.3	<b>2.005</b>	<b>2.012</b>	2.009	<b>1.986</b>	<b>1.994</b>	1.978	<b>87.6</b>	88.0	87.3	0.3	<b>2.009</b>	2.012	2.005	0.004	<b>1.986</b>	1.994	1.978	0.008
Th	CF <sub>3</sub>	<i>mer</i>	TTFBFE01	87.9	85.7	85.9	<b>2.015</b>	<b>2.017</b>	1.987	<b>1.998</b>	<b>1.955</b>	1.987	<b>86.5</b>	87.9	85.7	1.2	<b>2.006</b>	2.017	1.987	0.017	<b>1.980</b>	1.998	1.955	0.022
Th	CF <sub>3</sub>	<i>fac</i>	TTFBFE	87.3	87.4	87.3	1.999	1.998	1.999	1.973	1.971	1.971	<b>87.3</b>	87.4	87.3	0.0	<b>1.999</b>	1.999	1.998	0.001	<b>1.972</b>	1.973	1.971	0.001
CH <sub>3</sub>	CF <sub>3</sub>	<i>mer</i>	DUBMOC10	86.4	88.2	87.0	2.002	2.007	2.036	1.977	1.944	2.001	<b>87.2</b>	88.2	86.4	0.9	<b>2.015</b>	2.036	2.002	0.018	<b>1.974</b>	2.001	1.944	0.029
<sup>t</sup> Bu	CF <sub>3</sub>	<i>fac</i>	SOJXEU01	86.6	86.6	86.2	1.995	2.013	2.013	1.981	1.968	1.978	<b>86.5</b>	86.6	86.2	0.2	<b>2.007</b>	2.013	1.995	0.010	<b>1.976</b>	1.981	1.968	0.007
CH <sub>3</sub>	Ph	<i>mer</i>	this study	86.3	86.0	86.2	2.001	1.991	1.996	1.987	1.999	1.976	<b>86.2</b>	86.3	86.0	0.2	<b>1.996</b>	2.001	1.991	0.005	<b>1.987</b>	1.999	1.976	0.012

## Crystallographic supplementary material

### Crystallographic data for *mer*-[Fe(ba)<sub>3</sub>]

Table 1. Crystal data and structure refinement for ml\_ba\_x2\_0m\_delu.

Identification code	shelx	
Empirical formula	C <sub>30</sub> H <sub>27</sub> Fe O <sub>6</sub>	
Formula weight	539.36	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 <sub>1</sub> /c	
Unit cell dimensions	a = 10.2550(8) Å	α = 90°.
	b = 18.7966(15) Å	β = 92.468(3)°.
	c = 13.6343(10) Å	γ = 90°.
Volume	2625.7(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.364 Mg/m <sup>3</sup>	
Absorption coefficient	0.616 mm <sup>-1</sup>	
F(000)	1124	
Crystal size	0.102 x 0.052 x 0.021 mm <sup>3</sup>	
Theta range for data collection	2.633 to 25.348°.	
Index ranges	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -16 ≤ l ≤ 16	
Reflections collected	93261	
Independent reflections	4805 [R(int) = 0.0475]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4805 / 0 / 497	
Goodness-of-fit on F <sup>2</sup>	1.137	
Final R indices [I > 2σ(I)]	R1 = 0.0350, wR2 = 0.0818	
R indices (all data)	R1 = 0.0411, wR2 = 0.0844	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.287 and -0.384 e.Å <sup>-3</sup>	



Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for ml\_ba\_x2\_0m\_delu.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{\text{ij}}$  tensor.

	x	y	z	$U(\text{eq})$
Fe(1)	2360(1)	1474(1)	2684(1)	28(1)
O(1)	778(1)	1150(1)	3367(1)	33(1)
O(2)	1135(1)	1684(1)	1542(1)	32(1)
O(3)	2156(1)	2501(1)	2997(1)	32(1)
O(4)	3332(1)	1396(1)	3977(1)	33(1)
O(5)	2706(1)	473(1)	2326(1)	38(1)
O(6)	3921(1)	1718(1)	1919(1)	34(1)
C(1)	-368(3)	1330(1)	3214(2)	25(1)
C(2)	-792(3)	1729(2)	2400(2)	29(1)
C(3)	-19(3)	1871(2)	1601(2)	29(1)
C(4)	2257(2)	2822(2)	3810(2)	26(1)
C(5)	2674(3)	2488(2)	4682(2)	33(1)
C(6)	3227(3)	1812(2)	4730(2)	31(1)
C(1A)	1293(6)	2961(3)	2683(4)	25(1)
C(2A)	439(7)	2855(4)	1881(5)	36(2)
C(3A)	345(7)	2237(4)	1334(5)	29(2)
C(4A)	480(6)	1114(3)	4225(4)	24(1)
C(5A)	1428(6)	1250(4)	4964(5)	34(2)
C(6A)	2763(7)	1373(4)	4794(5)	32(2)
C(7)	3696(2)	188(1)	1940(1)	29(1)
C(8)	4719(2)	576(1)	1565(2)	34(1)
C(9)	4756(2)	1312(1)	1540(1)	31(1)
C(10)	-1316(8)	1058(3)	3926(7)	25(1)
C(11)	-873(7)	850(4)	4852(7)	29(2)
C(12)	-1714(8)	571(4)	5519(5)	43(2)
C(13)	-3032(8)	497(4)	5246(6)	40(2)
C(14)	-3500(7)	689(4)	4320(7)	40(2)
C(15)	-2632(9)	966(3)	3663(4)	31(1)
C(10A)	-900(14)	944(7)	4443(15)	21(3)
C(11A)	-1173(17)	604(10)	5301(12)	40(3)
C(12A)	-2440(20)	385(9)	5500(14)	52(5)
C(13A)	-3434(17)	583(7)	4838(19)	42(5)
C(14A)	-3174(15)	929(9)	4005(15)	42(4)
C(15A)	-1900(20)	1095(7)	3803(10)	30(3)

C(16)	-619(2)	2214(1)	641(2)	53(1)
C(16A)	-619(2)	2214(1)	641(2)	53(1)
C(17)	1876(6)	3588(3)	3780(6)	29(1)
C(18)	2100(7)	4042(4)	4570(5)	42(1)
C(19)	1757(10)	4753(5)	4510(6)	51(2)
C(20)	1171(9)	5010(4)	3669(9)	54(3)
C(21)	966(8)	4572(5)	2851(7)	55(2)
C(22)	1300(7)	3857(5)	2941(6)	37(2)
C(17A)	1396(17)	3634(9)	3229(14)	32(3)
C(18A)	1748(13)	3672(8)	4195(12)	31(3)
C(19A)	1741(14)	4309(11)	4716(10)	42(3)
C(20A)	1385(14)	4919(10)	4216(15)	39(4)
C(21A)	1050(30)	4939(16)	3238(14)	49(6)
C(22A)	1043(16)	4268(10)	2773(11)	38(3)
C(23)	3706(3)	1513(1)	5687(2)	48(1)
C(23A)	3706(3)	1513(1)	5687(2)	48(1)
C(24)	3666(2)	-602(1)	1871(1)	31(1)
C(25)	2461(2)	-946(1)	1797(2)	39(1)
C(26)	2394(3)	-1675(1)	1716(2)	47(1)
C(27)	3528(3)	-2071(1)	1733(2)	53(1)
C(28)	4716(3)	-1738(1)	1835(2)	56(1)
C(29)	4800(2)	-1003(1)	1888(2)	43(1)
C(30)	5815(2)	1682(1)	1004(2)	45(1)

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Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for ml\_ba\_x2\_0m\_delu.

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Fe(1)-O(5)	1.9792(14)
Fe(1)-O(3)	1.9902(14)
Fe(1)-O(4)	1.9922(14)
Fe(1)-O(2)	1.9988(14)
Fe(1)-O(1)	2.0007(13)
Fe(1)-O(6)	2.0016(13)
O(1)-C(4A)	1.223(6)
O(1)-C(1)	1.232(3)
O(2)-C(3)	1.240(3)
O(2)-C(3A)	1.341(7)
O(3)-C(4)	1.262(3)
O(3)-C(1A)	1.298(6)
O(4)-C(6A)	1.280(8)
O(4)-C(6)	1.299(3)
O(5)-C(7)	1.280(2)
O(6)-C(9)	1.273(2)
C(1)-C(2)	1.393(4)
C(1)-C(10)	1.493(7)
C(2)-C(3)	1.401(4)
C(3)-C(16)	1.561(4)
C(4)-C(5)	1.395(4)
C(4)-C(17)	1.492(7)
C(5)-C(6)	1.392(4)
C(6)-C(23)	1.485(4)
C(1A)-C(2A)	1.385(9)
C(1A)-C(17A)	1.47(2)
C(2A)-C(3A)	1.380(10)
C(4A)-C(5A)	1.393(9)
C(4A)-C(10A)	1.493(17)
C(5A)-C(6A)	1.418(10)
C(7)-C(8)	1.393(3)
C(7)-C(24)	1.488(3)
C(8)-C(9)	1.385(3)
C(9)-C(30)	1.505(3)
C(10)-C(11)	1.380(7)
C(10)-C(15)	1.392(6)
C(11)-C(12)	1.384(7)

C(12)-C(13)	1.393(7)
C(13)-C(14)	1.380(7)
C(14)-C(15)	1.391(6)
C(10A)-C(15A)	1.349(16)
C(10A)-C(11A)	1.373(14)
C(11A)-C(12A)	1.400(18)
C(12A)-C(13A)	1.384(17)
C(13A)-C(14A)	1.345(19)
C(14A)-C(15A)	1.381(14)
C(17)-C(22)	1.362(8)
C(17)-C(18)	1.385(7)
C(18)-C(19)	1.383(9)
C(19)-C(20)	1.360(8)
C(20)-C(21)	1.395(10)
C(21)-C(22)	1.391(7)
C(17A)-C(18A)	1.352(19)
C(17A)-C(22A)	1.385(13)
C(18A)-C(19A)	1.392(17)
C(19A)-C(20A)	1.375(18)
C(20A)-C(21A)	1.362(17)
C(21A)-C(22A)	1.41(3)
C(24)-C(29)	1.385(3)
C(24)-C(25)	1.395(3)
C(25)-C(26)	1.377(3)
C(26)-C(27)	1.379(4)
C(27)-C(28)	1.372(4)
C(28)-C(29)	1.386(3)
O(5)-Fe(1)-O(3)	175.18(6)
O(5)-Fe(1)-O(4)	93.44(6)
O(3)-Fe(1)-O(4)	86.27(6)
O(5)-Fe(1)-O(2)	96.27(6)
O(3)-Fe(1)-O(2)	84.66(6)
O(4)-Fe(1)-O(2)	167.92(6)
O(5)-Fe(1)-O(1)	89.06(6)
O(3)-Fe(1)-O(1)	95.73(6)
O(4)-Fe(1)-O(1)	87.15(6)
O(2)-Fe(1)-O(1)	85.84(6)
O(5)-Fe(1)-O(6)	86.20(6)

O(3)-Fe(1)-O(6)	89.04(6)
O(4)-Fe(1)-O(6)	95.61(6)
O(2)-Fe(1)-O(6)	92.20(6)
O(1)-Fe(1)-O(6)	174.64(6)
C(4A)-O(1)-Fe(1)	134.6(3)
C(1)-O(1)-Fe(1)	128.64(16)
C(3)-O(2)-Fe(1)	125.08(16)
C(3A)-O(2)-Fe(1)	132.2(3)
C(4)-O(3)-Fe(1)	130.30(16)
C(1A)-O(3)-Fe(1)	130.7(3)
C(6A)-O(4)-Fe(1)	122.9(3)
C(6)-O(4)-Fe(1)	126.83(16)
C(7)-O(5)-Fe(1)	130.74(13)
C(9)-O(6)-Fe(1)	129.84(13)
O(1)-C(1)-C(2)	123.1(2)
O(1)-C(1)-C(10)	116.0(4)
C(2)-C(1)-C(10)	120.8(4)
C(1)-C(2)-C(3)	123.7(3)
O(2)-C(3)-C(2)	124.8(3)
O(2)-C(3)-C(16)	113.9(3)
C(2)-C(3)-C(16)	121.0(3)
O(3)-C(4)-C(5)	123.0(3)
O(3)-C(4)-C(17)	115.2(4)
C(5)-C(4)-C(17)	121.8(4)
C(6)-C(5)-C(4)	124.0(3)
O(4)-C(6)-C(5)	124.1(3)
O(4)-C(6)-C(23)	115.6(3)
C(5)-C(6)-C(23)	120.3(3)
O(3)-C(1A)-C(2A)	124.3(5)
O(3)-C(1A)-C(17A)	111.9(9)
C(2A)-C(1A)-C(17A)	123.6(9)
C(3A)-C(2A)-C(1A)	125.1(6)
O(2)-C(3A)-C(2A)	120.7(6)
O(1)-C(4A)-C(5A)	119.1(5)
O(1)-C(4A)-C(10A)	118.7(9)
C(5A)-C(4A)-C(10A)	122.2(9)
C(4A)-C(5A)-C(6A)	124.1(6)
O(4)-C(6A)-C(5A)	128.8(6)
O(5)-C(7)-C(8)	123.71(19)

O(5)-C(7)-C(24)	115.42(17)
C(8)-C(7)-C(24)	120.81(18)
C(9)-C(8)-C(7)	123.62(19)
O(6)-C(9)-C(8)	124.74(18)
O(6)-C(9)-C(30)	115.58(18)
C(8)-C(9)-C(30)	119.64(19)
C(11)-C(10)-C(15)	118.5(7)
C(11)-C(10)-C(1)	119.6(7)
C(15)-C(10)-C(1)	121.8(8)
C(10)-C(11)-C(12)	121.3(7)
C(11)-C(12)-C(13)	119.2(6)
C(14)-C(13)-C(12)	120.9(6)
C(13)-C(14)-C(15)	118.7(7)
C(14)-C(15)-C(10)	121.4(7)
C(15A)-C(10A)-C(11A)	118.1(15)
C(15A)-C(10A)-C(4A)	121.8(19)
C(11A)-C(10A)-C(4A)	120.0(16)
C(10A)-C(11A)-C(12A)	121.8(17)
C(13A)-C(12A)-C(11A)	117.3(19)
C(14A)-C(13A)-C(12A)	120.9(17)
C(13A)-C(14A)-C(15A)	120.1(13)
C(10A)-C(15A)-C(14A)	121.6(12)
C(22)-C(17)-C(18)	118.4(6)
C(22)-C(17)-C(4)	119.0(7)
C(18)-C(17)-C(4)	122.6(7)
C(19)-C(18)-C(17)	121.0(7)
C(20)-C(19)-C(18)	119.7(8)
C(19)-C(20)-C(21)	120.7(8)
C(22)-C(21)-C(20)	118.1(7)
C(17)-C(22)-C(21)	122.0(7)
C(18A)-C(17A)-C(22A)	116.5(16)
C(18A)-C(17A)-C(1A)	123.4(15)
C(22A)-C(17A)-C(1A)	120.1(17)
C(17A)-C(18A)-C(19A)	122.4(13)
C(20A)-C(19A)-C(18A)	118.1(13)
C(21A)-C(20A)-C(19A)	124(2)
C(20A)-C(21A)-C(22A)	114(2)
C(17A)-C(22A)-C(21A)	124.7(17)
C(29)-C(24)-C(25)	119.3(2)

C(29)-C(24)-C(7)	121.8(2)
C(25)-C(24)-C(7)	118.83(18)
C(26)-C(25)-C(24)	120.5(2)
C(25)-C(26)-C(27)	119.8(2)
C(28)-C(27)-C(26)	120.0(2)
C(27)-C(28)-C(29)	120.9(2)
C(24)-C(29)-C(28)	119.4(2)

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for ml\_ba\_x2\_0m\_delu. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Fe(1)	27(1)	30(1)	27(1)	-3(1)	8(1)	-1(1)
O(1)	26(1)	44(1)	29(1)	5(1)	8(1)	1(1)
O(2)	33(1)	38(1)	24(1)	-2(1)	6(1)	-5(1)
O(3)	35(1)	33(1)	28(1)	-4(1)	-2(1)	3(1)
O(4)	27(1)	37(1)	34(1)	-2(1)	3(1)	7(1)
O(5)	36(1)	31(1)	47(1)	-4(1)	19(1)	-3(1)
O(6)	32(1)	32(1)	38(1)	-3(1)	12(1)	-6(1)
C(1)	25(2)	25(1)	25(1)	-4(1)	6(1)	-1(1)
C(2)	23(1)	28(1)	35(2)	2(1)	3(1)	1(1)
C(3)	32(2)	26(2)	29(2)	-1(1)	0(1)	-7(1)
C(4)	16(1)	34(2)	29(2)	-2(1)	7(1)	-1(1)
C(5)	35(2)	38(2)	24(1)	-4(1)	6(1)	5(1)
C(6)	24(2)	40(2)	28(2)	-2(1)	5(1)	1(1)
C(1A)	26(3)	23(3)	25(3)	1(2)	7(2)	-4(3)
C(2A)	31(4)	36(4)	40(4)	3(3)	-5(3)	2(3)
C(3A)	30(4)	28(4)	29(4)	2(3)	9(3)	-8(3)
C(4A)	23(3)	25(3)	24(3)	-1(2)	3(2)	5(2)
C(5A)	28(3)	50(4)	23(3)	-5(3)	1(3)	6(3)
C(6A)	25(4)	34(4)	38(4)	-10(3)	-8(3)	13(3)
C(7)	30(1)	34(1)	24(1)	-2(1)	1(1)	1(1)
C(8)	26(1)	39(1)	36(1)	-2(1)	6(1)	3(1)
C(9)	25(1)	40(1)	27(1)	-2(1)	2(1)	-4(1)
C(10)	20(4)	28(2)	27(3)	1(2)	1(3)	1(2)
C(11)	22(2)	47(3)	20(4)	6(3)	8(4)	3(2)
C(12)	39(5)	66(3)	26(3)	14(2)	11(3)	0(3)
C(13)	28(6)	50(4)	42(5)	22(3)	17(3)	7(3)
C(14)	22(3)	47(4)	51(4)	10(3)	4(4)	-3(3)
C(15)	22(4)	37(2)	35(3)	9(2)	2(3)	0(2)
C(10A)	25(7)	26(5)	12(7)	7(6)	9(9)	0(4)
C(11A)	32(9)	70(7)	19(8)	13(5)	15(5)	6(7)
C(12A)	57(15)	45(7)	56(10)	29(6)	29(10)	16(8)
C(13A)	23(8)	35(7)	69(16)	11(11)	4(11)	3(5)
C(14A)	15(9)	47(7)	64(13)	6(7)	-3(6)	-4(6)
C(15A)	19(8)	50(5)	21(5)	7(4)	-5(8)	-12(8)



C(16)	38(1)	56(2)	65(2)	24(1)	0(1)	-8(1)
C(16A)	38(1)	56(2)	65(2)	24(1)	0(1)	-8(1)
C(17)	25(2)	34(2)	28(3)	2(3)	7(3)	-2(2)
C(18)	61(4)	37(4)	30(3)	-3(2)	11(2)	2(3)
C(19)	74(6)	40(5)	38(4)	-7(4)	11(3)	-1(4)
C(20)	61(5)	27(2)	73(9)	7(8)	-1(8)	7(3)
C(21)	62(3)	26(5)	75(6)	10(5)	-27(3)	0(5)
C(22)	38(2)	20(5)	50(5)	-4(3)	-16(3)	2(3)
C(17A)	28(5)	21(7)	48(11)	13(6)	3(6)	10(5)
C(18A)	43(6)	25(6)	24(7)	4(6)	-3(6)	0(4)
C(19A)	53(8)	47(11)	25(5)	-7(7)	6(5)	-4(7)
C(20A)	41(8)	32(11)	43(13)	1(10)	-14(8)	4(6)
C(21A)	64(8)	46(14)	35(11)	16(10)	-5(10)	-2(8)
C(22A)	58(7)	16(9)	38(5)	1(9)	-13(4)	5(9)
C(23)	52(2)	56(2)	37(1)	-6(1)	-4(1)	10(1)
C(23A)	52(2)	56(2)	37(1)	-6(1)	-4(1)	10(1)
C(24)	40(1)	32(1)	22(1)	0(1)	2(1)	2(1)
C(25)	45(1)	34(1)	37(1)	2(1)	5(1)	-2(1)
C(26)	63(2)	36(1)	40(1)	4(1)	-1(1)	-10(1)
C(27)	87(2)	31(1)	41(1)	2(1)	0(1)	0(1)
C(28)	65(2)	40(1)	62(2)	4(1)	-2(1)	19(1)
C(29)	42(1)	40(1)	46(1)	2(1)	-5(1)	7(1)
C(30)	36(1)	50(1)	51(1)	-1(1)	19(1)	-8(1)

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Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for ml\_ba\_x2\_0m\_delu.

	x	y	z	U(eq)
H(2)	-1654	1915	2386	34
H(5)	2574	2737	5280	39
H(2A)	-125	3236	1693	43
H(5A)	1162	1261	5623	41
H(8)	5430	321	1311	40
H(11)	27	898	5034	35
H(12)	-1397	432	6156	52
H(13)	-3616	312	5705	48
H(14)	-4398	633	4134	48
H(15)	-2944	1094	3021	38
H(11A)	-484	514	5774	48
H(12A)	-2610	111	6065	62
H(13A)	-4313	474	4973	51
H(14A)	-3866	1059	3555	51
H(15A)	-1727	1322	3200	36
H(16A)	-1527	2348	740	79
H(16B)	-117	2638	478	79
H(16C)	-591	1870	102	79
H(16D)	-1071	2673	611	79
H(16E)	-254	2112	3	79
H(16F)	-1239	1838	801	79
H(18)	2496	3862	5162	51
H(19)	1930	5060	5053	61
H(20)	898	5492	3638	64
H(21)	608	4756	2249	66
H(22)	1121	3547	2402	44
H(18A)	2010	3249	4530	37
H(19A)	1975	4321	5397	50
H(20A)	1370	5352	4574	47
H(21A)	846	5368	2898	58
H(22A)	774	4250	2098	45
H(23A)	3586	1865	6206	72
H(23B)	3213	1082	5830	72

H(23C)	4634	1397	5657	72
H(23D)	3223	1490	6291	72
H(23E)	4397	1153	5709	72
H(23F)	4095	1987	5627	72
H(25)	1679	-675	1803	46
H(26)	1570	-1905	1650	56
H(27)	3485	-2574	1672	63
H(28)	5492	-2015	1871	67
H(29)	5628	-776	1935	51
H(30A)	6406	1327	741	67
H(30B)	5422	1963	463	67
H(30C)	6306	1996	1458	67

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Table 6. Torsion angles [°] for ml\_ba\_x2\_0m\_delu.

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C4Ab-O(1)-C1a-C2a	156.1(4)
Fe(1)-O(1)-C(1)-C(2)	10.5(4)
C(4A)-O(1)-C(1)-C(10)	-27.5(4)
Fe(1)-O(1)-C(1)-C(10)	-173.1(3)
O(1)-C(1)-C(2)-C(3)	10.3(4)
C(10)-C(1)-C(2)-C(3)	-165.9(4)
C(3A)-O(2)-C(3)-C(2)	-140.0(6)
Fe(1)-O(2)-C(3)-C(2)	-24.1(4)
C(3A)-O(2)-C(3)-C(16)	46.8(5)
Fe(1)-O(2)-C(3)-C(16)	162.72(16)
C(1)-C(2)-C(3)-O(2)	-2.8(5)
C(1)-C(2)-C(3)-C(16)	169.9(3)
C(1A)-O(3)-C(4)-C(5)	155.1(3)
Fe(1)-O(3)-C(4)-C(5)	6.2(4)
C(1A)-O(3)-C(4)-C(17)	-23.9(4)
Fe(1)-O(3)-C(4)-C(17)	-172.8(2)
O(3)-C(4)-C(5)-C(6)	11.3(4)
C(17)-C(4)-C(5)-C(6)	-169.7(3)
C(6A)-O(4)-C(6)-C(5)	-119.0(6)
Fe(1)-O(4)-C(6)-C(5)	-17.6(4)
C(6A)-O(4)-C(6)-C(23)	59.1(5)
Fe(1)-O(4)-C(6)-C(23)	160.54(17)
C(4)-C(5)-C(6)-O(4)	-5.2(5)
C(4)-C(5)-C(6)-C(23)	176.8(3)
C(4)-O(3)-C(1A)-C(2A)	-162.3(6)
Fe(1)-O(3)-C(1A)-C(2A)	-13.6(8)
C(4)-O(3)-C(1A)-C(17A)	22.3(7)
Fe(1)-O(3)-C(1A)-C(17A)	171.0(6)
O(3)-C(1A)-C(2A)-C(3A)	3.1(11)
C(17A)-C(1A)-C(2A)-C(3A)	178.0(9)
C(3)-O(2)-C(3A)-C(2A)	107.8(8)
Fe(1)-O(2)-C(3A)-C(2A)	11.2(9)
C(1A)-C(2A)-C(3A)-O(2)	-1.7(11)
C(1)-O(1)-C(4A)-C(5A)	-149.7(6)
Fe(1)-O(1)-C(4A)-C(5A)	-8.0(8)
C(1)-O(1)-C(4A)-C(10A)	28.7(7)
Fe(1)-O(1)-C(4A)-C(10A)	170.4(6)

O(1)-C(4A)-C(5A)-C(6A)	-5.4(10)
C(10A)-C(4A)-C(5A)-C(6A)	176.2(8)
C(6)-O(4)-C(6A)-C(5A)	125.1(9)
Fe(1)-O(4)-C(6A)-C(5A)	14.3(10)
C(4A)-C(5A)-C(6A)-O(4)	1.3(12)
Fe(1)-O(5)-C(7)-C(8)	-8.8(3)
Fe(1)-O(5)-C(7)-C(24)	173.90(13)
O(5)-C(7)-C(8)-C(9)	-2.1(3)
C(24)-C(7)-C(8)-C(9)	175.07(19)
Fe(1)-O(6)-C(9)-C(8)	2.1(3)
Fe(1)-O(6)-C(9)-C(30)	179.74(14)
C(7)-C(8)-C(9)-O(6)	5.4(3)
C(7)-C(8)-C(9)-C(30)	-172.1(2)
O(1)-C(1)-C(10)-C(11)	22.1(6)
C(2)-C(1)-C(10)-C(11)	-161.4(4)
O(1)-C(1)-C(10)-C(15)	-153.7(4)
C(2)-C(1)-C(10)-C(15)	22.8(6)
C(15)-C(10)-C(11)-C(12)	-1.7(8)
C(1)-C(10)-C(11)-C(12)	-177.6(5)
C(10)-C(11)-C(12)-C(13)	0.4(9)
C(11)-C(12)-C(13)-C(14)	0.8(10)
C(12)-C(13)-C(14)-C(15)	-0.6(11)
C(13)-C(14)-C(15)-C(10)	-0.7(9)
C(11)-C(10)-C(15)-C(14)	1.8(8)
C(1)-C(10)-C(15)-C(14)	177.7(4)
O(1)-C(4A)-C(10A)-C(15A)	-26.2(14)
C(5A)-C(4A)-C(10A)-C(15A)	152.3(11)
O(1)-C(4A)-C(10A)-C(11A)	151.7(11)
C(5A)-C(4A)-C(10A)-C(11A)	-29.9(15)
C(15A)-C(10A)-C(11A)-C(12A)	3(2)
C(4A)-C(10A)-C(11A)-C(12A)	-174.9(11)
C(10A)-C(11A)-C(12A)-C(13A)	-6(2)
C(11A)-C(12A)-C(13A)-C(14A)	5(2)
C(12A)-C(13A)-C(14A)-C(15A)	0(2)
C(11A)-C(10A)-C(15A)-C(14A)	1(2)
C(4A)-C(10A)-C(15A)-C(14A)	179.2(11)
C(13A)-C(14A)-C(15A)-C(10A)	-3(2)
O(3)-C(4)-C(17)-C(22)	8.5(6)
C(5)-C(4)-C(17)-C(22)	-170.5(4)

O(3)-C(4)-C(17)-C(18)	-170.6(4)
C(5)-C(4)-C(17)-C(18)	10.4(6)
C(22)-C(17)-C(18)-C(19)	-0.4(9)
C(4)-C(17)-C(18)-C(19)	178.7(6)
C(17)-C(18)-C(19)-C(20)	1.1(12)
C(18)-C(19)-C(20)-C(21)	-3.0(13)
C(19)-C(20)-C(21)-C(22)	4.1(12)
C(18)-C(17)-C(22)-C(21)	1.6(9)
C(4)-C(17)-C(22)-C(21)	-177.5(5)
C(20)-C(21)-C(22)-C(17)	-3.4(11)
O(3)-C(1A)-C(17A)-C(18A)	-34.1(16)
C(2A)-C(1A)-C(17A)-C(18A)	150.4(13)
O(3)-C(1A)-C(17A)-C(22A)	150.2(11)
C(2A)-C(1A)-C(17A)-C(22A)	-25.3(16)
C(22A)-C(17A)-C(18A)-C(19A)	1(2)
C(1A)-C(17A)-C(18A)-C(19A)	-174.8(12)
C(17A)-C(18A)-C(19A)-C(20A)	-1(2)
C(18A)-C(19A)-C(20A)-C(21A)	-1(3)
C(19A)-C(20A)-C(21A)-C(22A)	3(4)
C(18A)-C(17A)-C(22A)-C(21A)	1(2)
C(1A)-C(17A)-C(22A)-C(21A)	177.3(17)
C(20A)-C(21A)-C(22A)-C(17A)	-3(3)
O(5)-C(7)-C(24)-C(29)	-151.5(2)
C(8)-C(7)-C(24)-C(29)	31.1(3)
O(5)-C(7)-C(24)-C(25)	27.9(3)
C(8)-C(7)-C(24)-C(25)	-149.5(2)
C(29)-C(24)-C(25)-C(26)	-1.6(3)
C(7)-C(24)-C(25)-C(26)	178.96(19)
C(24)-C(25)-C(26)-C(27)	1.6(3)
C(25)-C(26)-C(27)-C(28)	0.4(4)
C(26)-C(27)-C(28)-C(29)	-2.4(4)
C(25)-C(24)-C(29)-C(28)	-0.3(3)
C(7)-C(24)-C(29)-C(28)	179.1(2)
C(27)-C(28)-C(29)-C(24)	2.3(4)

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Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for ml\_ba\_x2\_0m\_delu [ $\text{\AA}$  and  $^\circ$ ].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
C(5)-H(5)...O(2)#1	0.95	2.56	3.418(3)	150.9

Symmetry transformations used to generate equivalent atoms:

#1  $x, -y+1/2, z+1/2$

## Optimized Cartesian coordinates (Å)

All compounds were optimized with OLYP/TZP

### 1. *fac*-[Fe(ba)<sub>3</sub>] S = 5/2

Fe	-0.001700000	-0.000400000	1.022400000
O	0.894200000	1.432800000	-0.161900000
O	-0.542100000	1.570400000	2.234300000
O	-1.690400000	0.057300000	-0.161500000
O	-1.090900000	-1.255500000	2.233800000
O	0.792000000	-1.491300000	-0.161100000
O	1.628100000	-0.318200000	2.236800000
C	1.733800000	-2.323100000	0.080600000
C	2.552800000	-2.270300000	1.228700000
C	2.465800000	-1.283000000	2.224000000
C	1.148100000	2.662800000	0.082600000
C	0.696500000	3.344100000	1.233200000
C	-0.118700000	2.776100000	2.226000000
C	-2.882400000	-0.338500000	0.082700000
C	-3.246600000	-1.069200000	1.233900000
C	-2.346800000	-1.490800000	2.226600000
C	-0.565100000	3.624200000	3.400900000
H	-0.194600000	4.650000000	3.348800000
H	-1.659800000	3.637100000	3.439000000
H	-0.216300000	3.160900000	4.330200000
C	3.426900000	-1.317800000	3.396300000
H	3.981600000	-0.374000000	3.433700000
H	2.854200000	-1.391600000	4.327200000
H	4.133300000	-2.148600000	3.341200000
C	-2.857700000	-2.300100000	3.402700000
H	-2.632000000	-1.764200000	4.331100000
H	-3.931100000	-2.493500000	3.350600000
H	-2.320200000	-3.253700000	3.442900000
H	1.000100000	4.372200000	1.375800000
H	-4.288700000	-1.321000000	1.376600000
H	3.295500000	-3.044200000	1.367700000
C	-3.923900000	0.031200000	-0.933400000
C	-3.666300000	1.097100000	-1.812300000
C	-5.149400000	-0.648300000	-1.048900000
C	-4.613500000	1.486600000	-2.756900000
C	-6.092100000	-0.264800000	-2.000900000
C	-5.831200000	0.809300000	-2.854200000
H	-2.716000000	1.616700000	-1.738800000
H	-5.367200000	-1.499700000	-0.411100000
H	-4.400800000	2.322000000	-3.420900000
H	-7.030900000	-0.809200000	-2.078800000
H	-6.570600000	1.112000000	-3.593500000
C	1.991400000	3.379600000	-0.931900000
C	2.011600000	4.780500000	-1.050900000
C	2.792300000	2.624100000	-1.805100000
C	2.818100000	5.405400000	-2.000200000
C	3.606500000	3.249900000	-2.746700000
C	3.625200000	4.643000000	-2.847100000
H	1.377300000	5.394000000	-0.418300000



H	2.770000000	1.541300000	-1.729600000
H	2.812700000	6.490500000	-2.081100000
H	4.229000000	2.648400000	-3.406000000
H	4.259900000	5.132200000	-3.583700000
C	1.932800000	-3.410800000	-0.934600000
C	0.873900000	-3.733200000	-1.800300000
C	3.139600000	-4.121000000	-1.061600000
C	1.008800000	-4.750400000	-2.742800000
C	3.277400000	-5.130800000	-2.012000000
C	2.209800000	-5.455400000	-2.851500000
H	-0.055600000	-3.178400000	-1.718000000
H	3.990600000	-3.872900000	-0.434500000
H	0.173600000	-4.994200000	-3.396300000
H	4.222700000	-5.662500000	-2.099700000
H	2.316100000	-6.248800000	-3.589000000

## 2. *mer*-[Fe(ba)<sub>3</sub>] S = 5/2

Fe	-0.055800000	0.064800000	1.198200000
O	0.916100000	1.420600000	-0.014600000
O	-0.380800000	1.669900000	2.445900000
O	-1.752200000	0.252400000	0.061900000
O	-1.214500000	-1.078300000	2.459300000
O	0.538700000	-1.451700000	-0.062900000
O	1.598000000	-0.447900000	2.320700000
C	1.509600000	-2.274600000	0.043500000
C	2.467400000	-2.272400000	1.071700000
C	2.474700000	-1.363000000	2.150300000
C	1.206100000	2.652300000	0.170200000
C	0.824100000	3.387000000	1.312500000
C	0.063700000	2.866000000	2.372400000
C	-2.900300000	-0.301500000	0.170400000
C	-3.281600000	-1.100500000	1.268900000
C	-2.439500000	-1.423700000	2.346600000
C	-0.285600000	3.757300000	3.548600000
H	0.098500000	4.773500000	3.439000000
H	-1.374500000	3.792600000	3.662000000
H	0.119300000	3.316400000	4.466100000
C	-2.984800000	-2.247000000	3.497700000
H	-2.910600000	-1.662100000	4.421200000
H	-4.023300000	-2.549400000	3.348400000
H	-2.362500000	-3.138200000	3.631500000
H	1.158600000	4.411900000	1.402200000
H	-4.299500000	-1.463100000	1.315300000
H	3.220700000	-3.048500000	1.047600000
C	-3.865300000	-0.034900000	-0.948100000
C	-3.625300000	1.052300000	-1.805500000
C	-4.987000000	-0.845400000	-1.195300000
C	-4.489500000	1.332100000	-2.861400000
C	-5.845500000	-0.571100000	-2.258500000
C	-5.603700000	0.522100000	-3.092800000
H	-2.751300000	1.671800000	-1.630500000
H	-5.183800000	-1.715000000	-0.575600000
H	-4.291000000	2.183300000	-3.509600000
H	-6.701800000	-1.217500000	-2.439800000
H	-6.275800000	0.736700000	-3.921600000
C	2.018400000	3.305300000	-0.910200000
C	2.035000000	4.695600000	-1.115500000

C	2.785700000	2.494600000	-1.763500000
C	2.802800000	5.257000000	-2.134600000
C	3.562900000	3.057200000	-2.773200000
C	3.575400000	4.440900000	-2.963300000
H	1.426200000	5.348100000	-0.496600000
H	2.766700000	1.419200000	-1.617600000
H	2.793700000	6.334600000	-2.284800000
H	4.160900000	2.413900000	-3.415800000
H	4.179200000	4.880700000	-3.754900000
C	1.589400000	-3.321600000	-1.050900000
H	2.449800000	-3.985100000	-0.941600000
H	0.671000000	-3.918900000	-1.042400000
H	1.635900000	-2.822500000	-2.024700000
C	3.541700000	-1.453600000	3.202000000
C	4.804400000	-2.018100000	2.954600000
C	3.277600000	-0.938200000	4.481900000
C	5.769000000	-2.074800000	3.959300000
C	4.237100000	-1.007800000	5.489300000
C	5.487000000	-1.576200000	5.232700000
H	5.052100000	-2.391700000	1.965400000
H	2.307700000	-0.489200000	4.673100000
H	6.745600000	-2.504000000	3.745000000
H	4.010600000	-0.615100000	6.478700000
H	6.239100000	-1.625400000	6.017800000