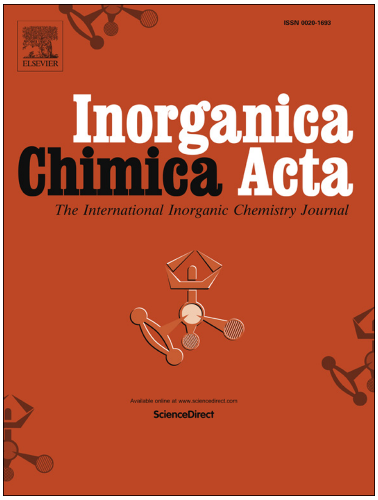


Geometrical isomers of Tris(β-diketonato)metal(III) complexes for M = Cr or Co: synthesis, X-ray structures and DFT study

Renyuan Liu, Petrus H. van Rooyen, Jeanet Conradie

PII: S0020-1693(16)30111-6
DOI: http://dx.doi.org/10.1016/j.ica.2016.03.019
Reference: ICA 16954

To appear in: *Inorganica Chimica Acta*

Received Date: 15 January 2016
Revised Date: 8 March 2016
Accepted Date: 11 March 2016

Please cite this article as: R. Liu, P.H. van Rooyen, J. Conradie, Geometrical isomers of Tris(β-diketonato)metal(III) complexes for M = Cr or Co: synthesis, X-ray structures and DFT study, *Inorganica Chimica Acta* (2016), doi: http://dx.doi.org/10.1016/j.ica.2016.03.019

Geometrical isomers of Tris(β-diketonato)metal(III) complexes for M = Cr or Co: synthesis, X-ray structures and DFT study.

Renyuan Liu,[a] Petrus. H. van Rooyen,[b] Jeanet Conradie[a,*]

[a] Department of Chemistry, PO Box 339, University of the Free State, 9300 Bloemfontein, Republic of South Africa.

[b] Department of Chemistry, University of Pretoria, Private Bag X20, Hatfield, 0028, South Africa.

*Contact author details:

Name: Jeanet Conradie

Tel: +27-51-4012194

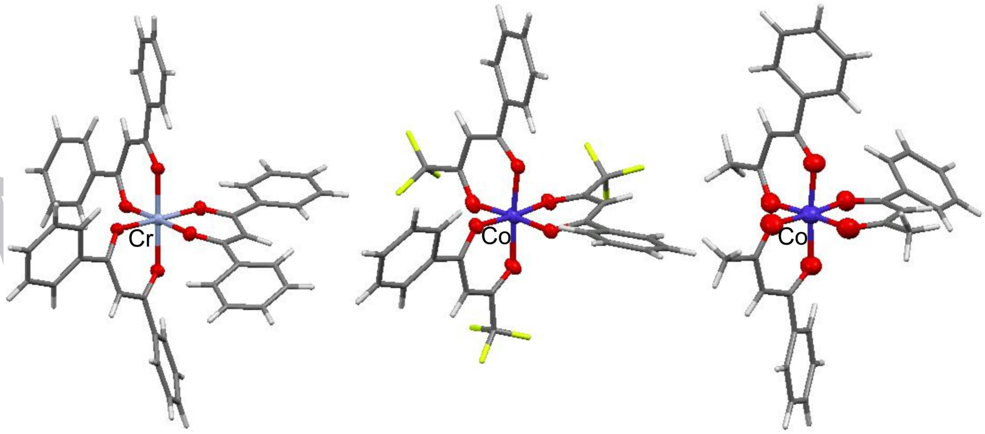
Fax: +27-51-4446384

e-mail: conradj@ufs.ac.za

Keywords

Chromium(III); Cobalt(III); β-Diketone; Structure; DFT

Graphical abstract



Synopsis

Synthesis, crystal and electronic structures of selected symmetrical, *fac* and *mer* isomers of tris(β-diketonato)metal(III) complexes.

Highlights

Crystal structures of *fac* and *mer* isomers of tris(β-diketonato)cobalt(III)

Crystal structure of tris(β-diketonato)chromium(III)

Molecular energy levels and orbitals of [Cr(acac)$_3$] and [Co(acac)$_3$]

Structures with D_3, C_3 and C_1 molecular symmetry

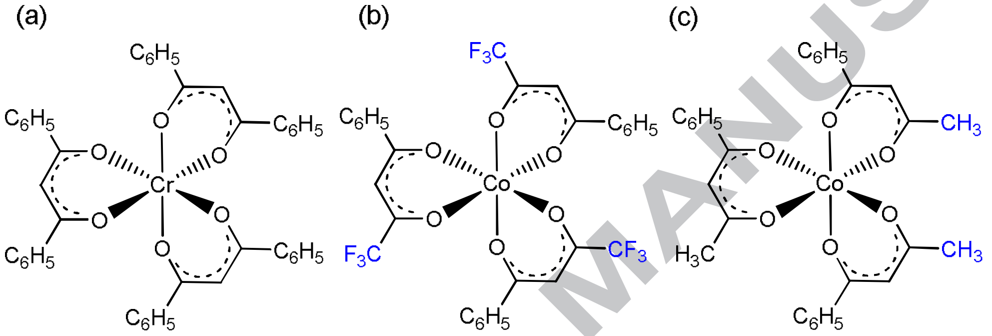
Abstract

Solid state crystal data of three tris(β-diketonato)metal(III) complexes (M = Cr or Co), representative of the three different molecular symmetries that these complexes can obtain, namely D_3, C_3 or C_1 symmetry, are presented and compared with related experimental structures. Density functional theory calculations show that both *fac* and *mer* isomers of tris(β-diketonato)metal(III) complexes containing unsymmetrical β-diketonato ligands can exist, in agreement with experimental NMR data. The orbital ordering for both the $S = 3/2$ [Cr(acac)$_3$] and $S = 0$ [Co(acac)$_3$] (Hacac = acetylacetone) complexes in order of increasing orbital energy is: $d_{xy} < d_{xz}, d_{yz} < d_{z2}, d_{x2-y2}$.

1 Introduction

β-diketones, RCOCH$_2$COR', have two carbonyl groups separated by the α-carbon atom; whereas in many cases, the keto-enol tautomer possesses the highest stability. The most known *β*-diketone is acetylacetone (Hacac), where the substituents R and R' on both carbonyl groups are methyl groups. Due to the keto–enol tautomerism of *β*-diketones, the hydrogen atom of the enolic from of β-diketone ligands can be replaced by a metal to form a metal-*β*-diketonate complex. An important application of β-diketones is thus the solvent extraction of metals [1]. The well-known class of metal *β*-diketonates, the tris(β-diketonato)metal(III) complexes, has various applications in catalysis. For example, [Co(acac)$_3$] has made a significant impact in the oxidation of alkanes [2], alkenes [3] and alcohols [4], and is also used for the hydrogenation of unsaturated organic molecules [5] and cross-coupling of organozinc compounds [6]. Examples of the catalytic use of

[$Cr(acac)_3$] are cross-coupling of organozinc compounds [7] and the polymerization of propylene and ethylene [8]. Factors influencing the catalytic activity of transition metal complexes include the arrangement of the ligands round the metal (steric factors) as well as the electronic properties of the ligands attached to the metal [9]. Tris(β-diketonato)metal(III) complexes have a six-coordinate metal(III) ion and the coordination polyhedron can be described by an octahedron. For octahedral tris(β-diketonato)metal(III) complexes containing β-diketonato ligands ($RCOCHCOR'$)$^-$ with substituents R ≠ R', the stereochemistry is adequately defined using the terms *fac* or *mer*. In this contribution, we present the synthesis, X-ray and electronic structure of three examples of tris(β-diketonato)metal(III) complexes, [$Cr(dbm)_3$] (**1**), the *fac* isomer of [$Co(tfba)_3$] (**2**) and the *mer* isomer of [$Co(ba)_3$] (**3**), see Scheme 1.



Scheme 1: The tris(β-diketonato)metal(III) complexes of this study: [$Cr(dbm)_3$] (**1**), the *fac* isomer of [$Co(tfba)_3$] (**2**) and the *mer* isomer of [$Co(ba)_3$] (**3**).

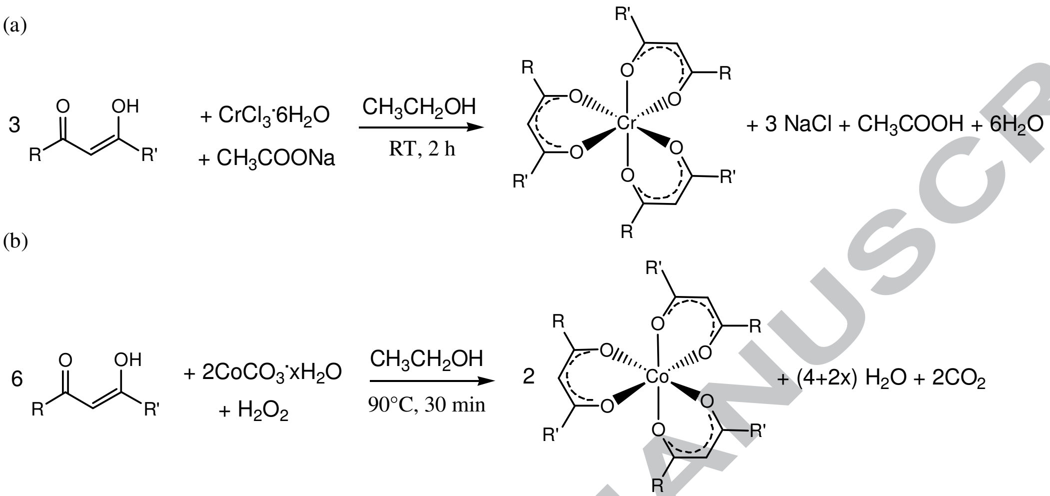
2 Experimental

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 dried and distilled prior to 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. MALDI-TOF spectra were collected by a Bruker Microflex LRF20 in the positive mode with the minimum laser power required to observe signals.

Complexes (**1**) – (**3**) were synthesized as shown in Scheme 2. [$Cr(dbm)_3$] (**1**) was synthesised according to Rahman's method [10] as reported previously [11]. Tris(β-diketonato)cobalt(III) complexes (**2**) and (**3**) were synthesised by the method of Bryant and

Fernelius with minor changes [12]. Cobalt(II) carbonate (1.25 g, 0.0105 mole) and 10 mmole β-diketone dissolved in 10 mL of ethanol were preheated to 95°C while stirring. 15 ml 25 % hydrogen peroxide was added drop-wise to the suspension over 30 minutes. The precipitate was filtered and washed with excess water, and then dried in a desiccator at room temperature. Complexes (**1**) – (**3**) were recrystallized from diethyl ether.



Scheme 2: General synthetic method for the (a) tris(β-diketonato)chromium(III) and (b) the tris(β-diketonato)cobalt(III) complexes.

Characterization data for $Cr(C_6H_5COCHCOC_6H_5)_3$, (**1**) *[Cr(dbm)*$_3$*]*

Yield 90 %. Colour: Yellow. Melting point 76°C; MS (m/z): Calc. 723.06 [M], Found 722.0 $[M-1]^-$. Elemental analysis, Calculated for $CrC_{45}H_{33}O_6$: C, 74.9; H, 4.6 Found: C, 74.8; H, 4.6.

Characterization data for $Co(C_6H_5COCHCOCF_3)_3$, (**2**) *[Co(tfba)*$_3$*]*

Yield 13 %. Colour: Dark green. M.P. 107.6 °C. ^1H NMR: (300 MHz, δ/ppm, $CDCl_3$): 6.74 (s, 3H, 3xH, *fac*), 6.73, 6.75, 6.78 (s, 3H, 3xH, *mer*), 7.40-7.65 (m, 9H, 3xPh, *fac* + *mer*), 7.90-8.05 (m, 6H, 3xPh, *fac* + *mer*), MS (m/z): Calc.704.38 [M], Found: $[M-1]^-$ 703.98.

Characterization data for $Co(C_6H_5COCHCOCH_3)_3$, (**3**) *[Co(ba)*$_3$*]*

Yield 66 %. Colour: Dark green. M.P. 184.3 °C. ^1H NMR: (300 MHz, δ/ppm, $CDCl_3$): 2.36 (s, 9H, $3\times CH_3$, *fac*), 2.38, 2.40, 2.42 (s, 9H, $3xCH_3$, *mer*), 6.24, 6.26, 6.27 (s, 3H, 3xH, *fac* + *mer*), 7.28-7.46 (m, 9H, 3xPh, *fac* + *mer*), 7.85-7.95 (m, 6H, 3xPh, *fac* + *mer*). MS (m/z): Calc. 542.47, Found: 542.11.

2.2 Crystal structure analysis

Data for the crystals, 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 [13] control software using Quazar multi-layer optics monochromated, Mo-*K*α radiation by means of a combination of ϕ and ω scans, at 150(2)K. Data reduction was performed using SAINT+ [13] and the intensities were corrected for absorption using SADABS [13]. The structure was solved by intrinsic phasing using SHELXTS and refined by full-matrix least squares, using SHELXTL + [14] and SHELXL-2013+ [14]. 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 × 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 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 [15], with a selection of GGA (Generalized Gradient Approximation) functionals, namely PW91 (Perdew-Wang 1991) [16], BP86 (Becke-Perdew) [17,18], and OLYP (Handy-Cohen and Lee-Yang-Parr) [19,20], as well as the hybrid functional B3LYP (Becke 1993 and Lee-Yang-Parr) [21,22]. The TZP (Triple ζ polarized) basis set, with a fine mesh for numerical integration and full geometry optimization, applying tight convergence criteria, was used for minimum energy searches.

3 Results and Discussion

3.1 Synthesis

Scheme 2 gives the synthetic approach for complexes (**1**) – (**3**). To obtain the [$\mathrm{Cr^{III}}$(β-diketonato)$_3$] complex, chromium(III) chloride was dissolved in the minimum amount of water and added drop-wise to a solution of the β-diketone in ethanol. A saturated sodium acetate solution was added drop-wise to deprotonate the β-diketone, which completed the coordination with the $\mathrm{Cr^{III}}$ cation. To obtain the [$\mathrm{Co^{III}}$(β-diketonato)$_3$] complexes, cobalt(II) carbonate was oxidized to cobalt(III) oxide by the hydrogen peroxide. In the presence of the β-diketonato ligand in the suspension, the coordination to the freshly oxidized $\mathrm{Co^{III}}$ cation proceeded immediately.

[Co(β-diketonato)$_3$] complexes have a low spin singlet state (S = 0) [23] while [Cr(β-diketonato)$_3$] complexes are paramagnetic with a quartet spin state (S = 3/2) [24]. The three methine hydrogen atoms (and also the hydrogen atoms of the R and R' groups) of *fac* [Co(β-diketonato)$_3$] are NMR equivalent, since they are related by a threefold rotation axis. The ^{1}H NMR spectrum of *fac* [Co(tfba)$_3$] and *fac* [Co(ba)$_3$] thus have one singlet for the three methine hydrogen atoms. However, the three methine hydrogen atoms (and the hydrogen atoms of the R and R' groups) of *mer* [Co(β-diketonato)$_3$] are not related through symmetry. For the three methine hydrogen atoms, the three hydrogen atoms are NMR inequivalent and the ^{1}H NMR spectrum of *mer* [Co(tfba)$_3$] and *mer* [Co(ba)$_3$] each thus have three singlets for the three methine hydrogen atoms. A mixture of *fac* and *mer* [Co(β-diketonato)$_3$] will thus have four singlets for the methine hydrogen atoms and similarly the hydrogen atoms of the R and R' groups. Both the *fac* and *mer* isomers were observed on ^{1}H NMR for [Co(tfba)$_3$] (**2**) and [Co(ba)$_3$] (**3**), with the *mer* isomer the main isomer.

3.2 Molecular structures

Perspective drawings [25] of the molecular structures of [Cr(dbm)$_3$] (**1**), the *fac* isomer of [Co(tfba)$_3$] (**2**) and the *mer* isomer of [Co(ba)$_3$] (**3**), showing the crystallographic numbering scheme used, are presented in Figure 1, Figure 2 and Figure 3 respectively. The central metal atom in each of the three tris(β-diketonato)metal(III) complexes (M = Cr or Co), displays the expected octahedral geometry. The angles between the three planes that include the β-diketonato ligands in each of (**1**), (**2**) and (**3**) (Table 1), vary significantly more in (**1**) and (**2**), when compared to the angles observed for (**3**)**.** This is most likely the result of the increased steric requirements of the substituents on the β-diketonato ligands. This variation is also evidenced by the larger deviations of atoms from least squares planes in each of the three rings (R1, R2 and R3, see Table 1) observed in (**1**) and (**2**). The crystallographic packing observed in (**1**) and (**2**) shows significant π-π interactions which is absent in the packing of (**3**) (Supporting Information Figures S1 – S8, Table S1). There are also stronger intermolecular hydrogen bonds present in complexes (**1**) and (**2**) compared to those observed for (**3**). In addition, one F-atom in each of the three CF$_3$ groups of (**2**) is involved in this hydrogen bonding.

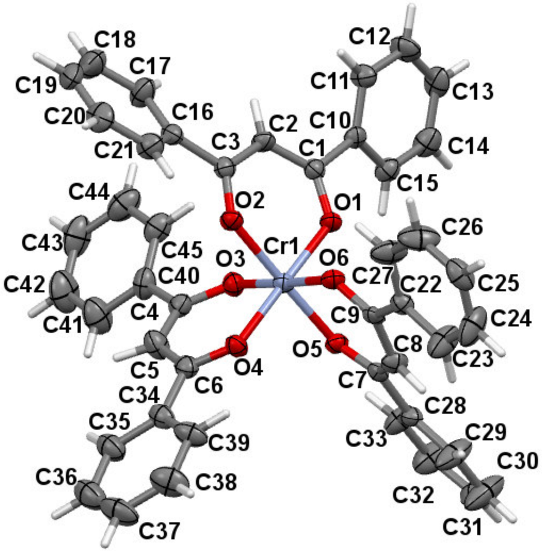


Figure 1: A perspective drawing of the molecular structure of [Cr(dbm)$_3$]**,** (**1**), showing the atom numbering scheme. Atomic displacement parameters (ADPs) are shown at the 50 % probability level.

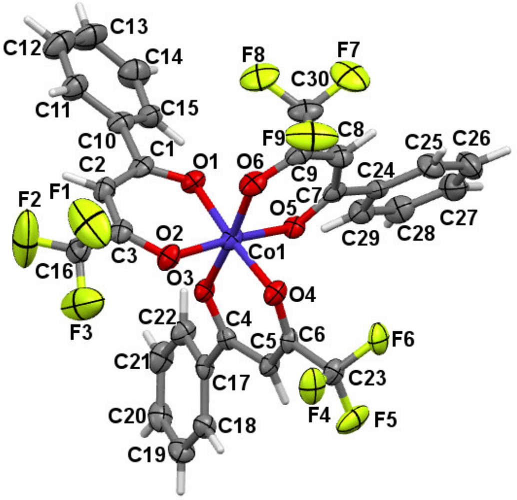


Figure 2: A perspective drawing of the molecular structure of the *fac* isomer of [Co(tfba)$_3$], (**2**), showing the atom numbering scheme. Atomic displacement parameters (ADPs) are shown at the 50 % probability level.

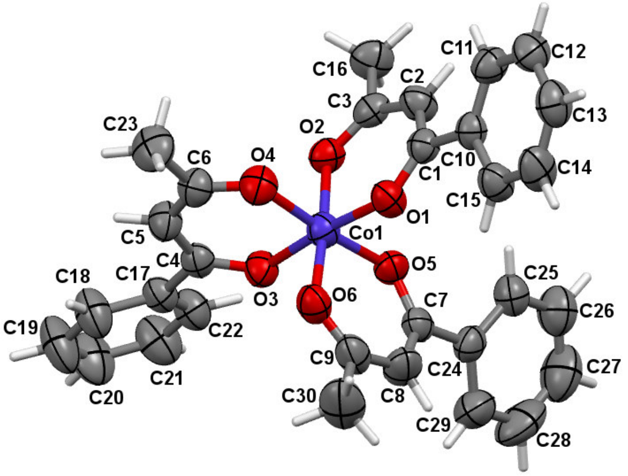


Figure 3: A perspective drawing of the molecular structure of the *mer* isomer of [Co(ba)$_3$], (**3**), showing the atom numbering scheme. Atomic displacement parameters (ADPs) are shown at the 50 % probability level.

Table 1: Selected geometric parameters for [Cr(dbm)$_3$], the *fac* isomer of [Co(tfba)$_3$] and the *mer* isomer of [Co(ba)$_3$].

	[Cr(dbm)$_3$] (**1**)	[Co(tfba)$_3$] (**2**)	[Co(ba)$_3$] (**3**)
M-O(1) / Å	1.945(2)	1.881(3)	1.875(2)
M-O(2) / Å	1.971(2)	1.882(3)	1.883(2)
M-O(3) / Å	1.939(2)	1.875(3)	1.879(2)
M-O(4) / Å	1.949(2)	1.872(3)	1.889(3)
M-O(5) / Å	1.959(2)	1.869(3)	1.874(2)
M-O(6) / Å	1.954(2)	1.885(3)	1.888(3)
M-O (ave) / Å	**1.953(2)**	**1.877(3)**	**1.881(2)**
O(1)-C(1) / Å	1.274(4)	1.265(5)	1.272(4)
O(2)-C(3) / Å	1.279(4)	1.270(5)	1.270(4)
O(3)-C(4) / Å	1.288(4)	1.264(4)	1.278(4)
O(4)-C(6) / Å	1.283(4)	1.275(5)	1.273(4)
O(5)-C(7) / Å	1.274(4)	1.261(5)	1.273(4)
O(6)-C(9) / Å	1.275(4)	1.272(5)	1.264(5)
O-C (ave) / Å	**1.279(4)**	**1.267(5)**	**1.272(4)**
O-M-O / ° (*trans, ave*)	177.71(10)	174.28(13)	175.5(11)
O-M-O / ° (*cis, ave*)	90.00(10)	90.04(13)	90.04(13)

Table 2: Crystallographic and refinement data for [Cr(dbm)$_3$] (**1**), the *fac* [Co(tfba)$_3$] (**2**) and *mer* [Co(ba)$_3$] (**3**).

	[Cr(dbm)$_3$] (**1**)	[Co(tfba)$_3$] (**2**)	[Co(ba)$_3$] (**3**)
Empirical formula	$C_{45} H_{33} Cr O_6$	$C_{30} H_{18} Co F_9 O_6$	$C_{30} H_{27} Co O_6$
Formula weight (g mol^{-1})	721.71	704.37	542.44
Crystal system	Monoclinic	Monoclinic	Triclinic
space group	P 2_1/c	P 2_1/c	P -1
a (Å)	16.9785(6)	9.5067(7)	9.7546(5)
b (Å)	9.7442(3)	31.906(2)	9.8755(6)
c (Å)	21.2271(7)	9.9607(8)	14.2557(8)
α (°)	90	90	83.883(2)
β (°)	92.772(2)	108.122(2)	84.5540(10)
γ (°)	90	90	77.6970(10)
Volume (Å^3)	3507.7(2)	2871.4(4)	1330.41(13)
Z	4	4	2
D_{calc} (Mg/m^3)	1.367	1.629	1.354
Absorption coefficient (mm^{-1})	0.378	0.700	0.687
F(000)	1500	1416	564
Reflections collected	32119	88047	48015
Data used / restraints / parameters	7168 / 0 / 469	5878 / 0 / 415	4879 / 0 / 334
Goodness-of-fit on F^2	1.068	1.219	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0658, wR2 = 0.1356	R1 = 0.0669, wR2 = 0.1532	R1 = 0.0510, wR2 = 0.1214
R indices (all data)	R1 = 0.1114, wR2 = 0.1534	R1 = 0.0782, wR2 = 0.1577	R1 = 0.0809, wR2 = 0.1343
Largest diff. peak and hole (e.Å^{-3})	0.448 and -0.640	0.970 and -0.805	0.469 and -0.229

Selected average structural parameters of [Cr(dbm)$_3$] are compared to the structural parameters of previously published crystal structures of [Cr(acac)$_3$] [26], [Cr(dpm)$_3$] [27] (Hdpm = dipivaloylmethane or 2,2,6,6-tetramethyl-3,5-heptanedione, also abbreviated as Hthd) and [Cr(hfaa)$_3$] [28] (hfaa = 1,1,1,5,5,5-hexafluoroacetylacetonato) in Table 3. Data for [Co(ba)$_3$ and [Co(tfba)$_3$] as well as previously published crystal data of [Co(acac)$_3$] [29], [Co(dbm)$_3$] [30], [Co(dpm)$_3$] [31] and [Co(tfaa)$_3$] [32], are also included in Table 3 (see the electronic supporting information for more detail). The average Cr–O bond lengths and O-Cr-O bond angles are all similar within 0.02 Å and 1.2° except for [Co(hfaa)$_3$]. For the four [Cr(β-diketonato)$_3$] complexes, the average Cr–O bond lengths and O-Cr-O bond angles are all similar within 0.01 Å and 1.1°. Since the difference between Cr–O bond lengths and O-Cr-O bond angles in the same crystal are of a similar order (up to 0.03 Å and 1.2°), temperature has a slight influence on experimental structural parameters [33,34] (published experimental data are obtained at different temperatures, see electronic supporting information), and the differences in the average experimental data in Table 3 are close to the experimental error of the structural data (taken as three times the uncertainty in the bond length/angle), no conclusions or trends can be drawn from the average experimental data in Table 3 for a specific metal. Generally, the average experimental Cr–O bond lengths are slightly larger and the O–Cr–O bond angles thus slightly smaller than the experimental Co–O bond lengths and O–Co–O bond angles, as expected for Cr with a larger atomic radius than Co.

Table 3: Selected average geometric parameters for Co(β-diketonato)$_3$ and Cr(β-diketonato)$_3$ complexes.

	Co(β-diketonato)$_3$			Cr(β-diketonato)$_3$			Reference	
β-diketonato	Co-O / Å	O-Co-O / °	C-C-C / °	Cr-O / Å	O-Co-O / °	C-C-C / °	Co(β-diketonato)$_3$	Cr(β-diketonato)$_3$
hfaa	2.07	87.6	123.0	1.94	90.6	119.9	28	32
dpm	1.87	95.8	125.0	1.95	90.0	124.5	27	31
dbm	1.88	95.5	124.9	1.95	90.2	124.7	this study,	30
acac	1.89	95.0	124.8	1.96	91.1	125.1	26	29
tfaa (*mer*)	1.89	96.1	125.4				32	
tfba (*fac*)	1.88	95.8	122.7				this study	
ba (*mer*)	1.88	96.0	125.1				this study	
average all	**1.90**	**94.9**	**124.8**	**1.95**	**90.8**	**124.3**		

3.3 *Computational chemistry study*

Tris(β-diketonato)metal(III) complexes have an octahedral structure. No crystallographically imposed symmetry was observed in the crystal structures of complexes (**1**) – (**3**), however, depending on the β-diketonato ligand, and the arrangement of the ligands round the metal, the tris(β-diketonato)metal(III) complexes can either have a D_3, C_3 or C_1 molecular symmetry: D_3 symmetry applies to complexes with symmetrical β-diketone ligands, *e.g*. M(acac)$_3$; C_3 rotational symmetry applies to complexes with unsymmetrical β-diketone ligands, arranged in such a way that they have a 3-fold rotational axis (called *fac* isomers); and C_1 symmetry applies to complexes with unsymmetrical β-diketone ligands, arranged in such a way that they have no symmetry elements (called *mer* isomers). Complexes (**1**) – (**2**) are examples of tris(β-diketonato)metal(III) complexes displying molecular symmetry of D_3 ([Cr(dbm)$_3$] (**1**)) or C_3 (*fac* [Co(tfba)$_3$] (**2**)) that were not observed in the solid state.

Neutral Cr^{III}(β-diketonato)$_3$ complexes are d^3 complexes with a spin state of S = 3/2 (three unpaired electrons) [24]. Input geometries in lower symmetries than D_3 (C_1, C_2 and C_3) all converged to the same lowest energy geometry with D_3 symmetry (all Cr–O bonds and O–Cr–O angles converged to the same value as given in **Table 4**). The most important bond lengths and angles in organometallic complexes are those involving the metal centre. The average experimental Cr–O bonds and in [Cr(acac)$_3$] obtained from 18 published X-ray structures are slightly overestimated by 0.02 (PW91, BP86 and B3LYP) – 0.05 (OLYP) Å for the calculated bonds. This is expected, since gas phase calculations as well as GGA density functionals tend to overestimate bonds lengths [35]. Longer calculated bond lengths, compared to crystallographic measured bond lengths, have also been found for [Fe(acac)$_3$] [36] and other metal β-diketonato complexes [37,38]. The calculated O–Cr–O angle of [Cr(acac)$_3$] is within 0.4° of the average experimental value, except for the OLYP calculated value. Generally differences between experimental and calculated bond lengths below the threshold of 0.02 Å, are considered meaningless [39]. Results discussed in the previous section indeed showed that Cr–O bond lengths and O–Cr–O bond angles in the same [Cr(acac)$_3$] crystal differ up to 0.03 Å and 1.2° (also see electronic supporting information). Thus the PW91, BP86 and B3LYP functionals all give a good agreement with experimental geometric parameters.

The d^6 Co^{III}(β-diketonato)$_3$ complexes are low spin with S = 0 [23]. Input geometries in lower symmetries that D_3 (C_1, C_2 and C_3) all converged to the same lowest energy geometry of D_3 symmetry with Cr–O bonds and O–Cr–O angles as given in **Table 4**. The calculated DFT Co–O bonds and O–Cr–O bond angles for [Co(acac)$_3$] are again slightly longer than the average experimental values obtained from 11 published X-ray structures, namely 0.02 (PW91, BP86 and B3LYP) – 0.04 (OLYP) Å for the bonds and up to 2° for the angles (see electronic supporting information). Thus, for [Cr(acac)$_3$], the PW91, BP86 and B3LYP functionals all give structural parameters in good agreement with experimental geometric parameters.

Table 4: DFT-calculated Cr – O bond lengths (Å) and O – Cr – O bond angles (deg) obtained by the indicated functionals, for [Cr(acac)$_3$] and [Co(acac)$_3$] optimized with D_3 symmetry constraint.

	B3LYP	**OLYP**	**BP86**	**PW91**	**Experimental (average)**
[Cr(acac)$_3$]					
d(Cr – O)	1.983	2.008	1.980	1.978	1.96 [29]
O – Cr – O	91.5	89.7	91.4	91.5	91.1 [29]
[Co(acac)$_3$]					
d(Co – O)	1.911	1.925	1.908	1.906	1.89 [26]
O – Co – O	96.7	96.1	97.0	97.1	95.0 [26]

The DFT calculated energies of the *fac* and *mer* isomers of the [Co(ba)$_3$], [Co(tfba)$_3$] and [Co(tfaa)$_3$] are given in **Table 5**. DFT calculated energy differences below 1 kcal mol^{-1} (4.184 kJ mol^{-1}) are within the accuracy of DFT [40]. The small energy differences obtained between the *fac* and *mer* isomers thus indicate that both isomers should be experimentally possible, as was experimentally observed on ^{1}H NMR for [Co(tfba)$_3$] (**2**) (in this study) and [Co(ba)$_3$] (**3**) (in this study) and [Co(tfaa)$_3$] [41]. Experimentally, crystals of *mer* isomers were found for [Co(ba)$_3$] and

[$Co(tfaa)_3$] and crystals of *fac* isomers were found for [$Co(tfba)_3$]. Packing forces in the crystal may favour a specific isomer above another.

Table 5: DFT calculated electronic (E) and Gibbs free (G) energies for the indicated Co(β-diketonato)$_3$ complexes and functionals.

		Relative *E* (kJ mol^{-1})				**Relative *G* (kJ mol^{-1})**				**X-tal structure**
		B3LYP	**OLYP**	**BP86**	**PW91**	**B3LYP**	**OLYP**	**BP86**	**PW91**	
$Co(ba)_3$	*fac*	0.0	0.2	0.0	0.0	2.1	0.3	0.0	0.0	
	mer	0.5	0.0	0.5	0.0	0.0	0.0	5.3	2.4	*mer*
$Co(tfba)_3$	*fac*	7.3	6.3	5.5	3.8	4.7	8.6	2.9	3.8	*fac*
	mer	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
$Co(tfaa)_3$	*fac*	3.1	0.9	1.2	0.7	7.8	0.9	3.5	0.8	
	mer	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	*mer*

Figure 4 and Figure 5 show the molecular energy level diagram of [$Cr(acac)_3$] and [$Co(acac)_3$] optimized under the D_3 symmetry constraint, including plots of the d-based frontier MOs. In an octahedral complex, the presence of ligands leads to the splitting of the five metal-d-orbitals into two different levels, due to the breaking of orbital degeneracy. The bottom three energy levels are collectively referred to as t_{2g} and consist of d_{xy}, d_{xz}, and d_{yz}. The two upper energy levels are collectively referred to as e_g and consist of d_{x2-y2} and d_{z2}. Distortion from the octahedral orbital energies (O_h) towards D_3 ligand symmetry, splits the degenerate t_{2g}-orbitals further into *a* and *e* components. The orbital ordering for both [$Cr(acac)_3$] and [$Co(acac)_3$] complexes in order of increasing orbital energy are: $d_{xy} < d_{xz}$, $d_{yz} < d_{z2}$, d_{x2-y2}. The $S = 3/2$ [$Cr(acac)_3$] and $S = 0$ [$Co(acac)_3$] complexes may be described by the following electronic configurations: $d_{xy}^1 d_{xz}^1 d_{yz}^1 d_{z2}^0 d_{x2-y2}^0$ and $d_{xy}^2 d_{xz}^2 d_{yz}^2 d_{z2}^0 d_{x2-y2}^0$. The same orbital ordering was obtained for the high spin $Fe(acac)_3$ complex with electronic configurations: $d_{xy}^1 d_{xz}^1 d_{yz}^1 d_{z2}^1 d_{x2-y2}^1$ [36].

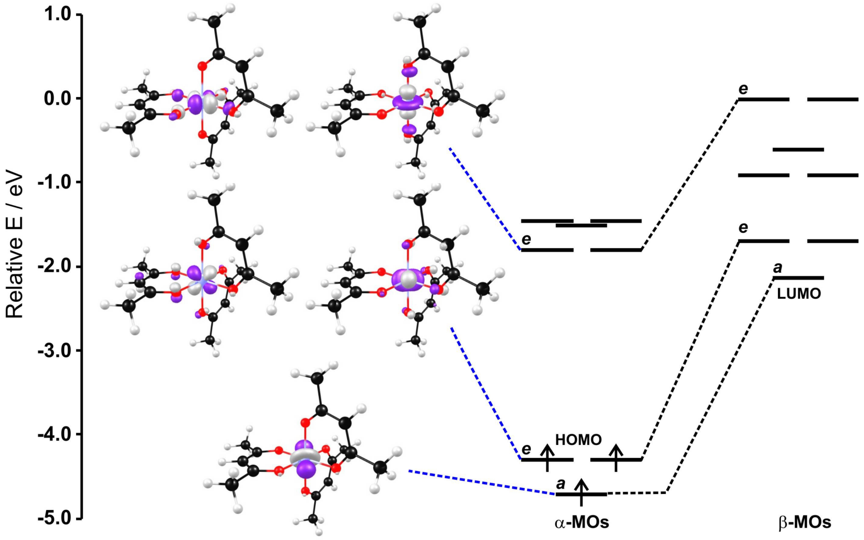


Figure 4: Molecular orbital Kohn-Sham energy levels (eV) for [Cr(acac)$_3$], with S = 3/2, optimized under the D_3 symmetry constraint. Plots of the *d*-based MOs are included. The black arrows represent the three unpaired electrons in the top α HOMOs. The MOs of α *d*-orbitals are illustrated on the left of the figure, and the β *d*-orbitals are illustrated on the right.

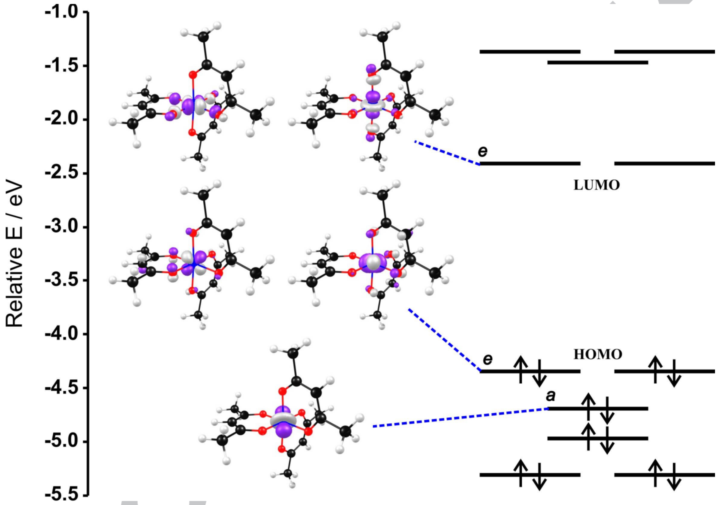


Figure 5: Molecular orbital Kohn-Sham energy levels (eV) for [Co(acac)$_3$], with S = 0, optimized under the D_3 symmetry constraint. Plots of the *d*-based MOs are included. The black arrows represent electrons in the top HOMOs.

4 Conclusions

DFT calculations showed that both *fac* and *mer* isomers of the [Co(ba)$_3$], [Co(tfba)$_3$] and [Co(tfaa)$_3$] can exist. Experimentally in CDCl$_3$ solution, on ^{1}H NMR, both isomers were observed with *mer* as the main isomer. In the solid state, crystals of *mer* isomers for [Co(ba)$_3$] and [Co(tfaa)$_3$] and crystals of *fac* isomer for [Co(tfba)$_3$] were isolated. Packing forces in the crystal may favour a specific isomer above the other.

Supporting Information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with numbers: 1440622-1440624. 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 the optimized coordinates of the DFT calculations are given in the Supporting Information.

Acknowledgements

This work has received support from the South African National Research Foundation and the Central Research Fund of the University of the Free State, Bloemfontein, South Africa. The High Performance Computing facility of the UFS is acknowledged for computer time.

References

---

[1] Starý, J.; The Solvent Extraction of Metal Chelates, MacMillan Company, 1964, p 51-79

[2] A. Pokutsa, J. Le Bras, J. Muzart, Kinet. Catal. 48 (2007) 26.

[3] T. Tokuyasu, S. Kunikawa, A. Masuyama, M. Nojima, Org. Lett. 4 (2002)3595.

[4] M. H. Peyrovi, V. Mahdavi, M. A. Salehi, R. Mahmoodian, Catal. Commun., 6 (2005) 476.

[5] C.S. Consorti, A.P. Umpierre, R.F. de Souza, J. Dupont, P.A.Z. Suarez, J. Braz. Chem. Soc. 14 (2003) 401.

[6] G. Dunet, P. Knochel, Synlett 9 (2007) 1383.

[7] N. Jiang, A. J. Ragauskas, Tetrahedron Lett. 48 (2007) 273.

[8] (a) F.M.B. Coutinho, R.K. Iwamoto, M.A.S. Costa, L.C. de Santa Maria, Polymer Bulletin 40 (1998) 695. DOI: 10.1007/s002890050310; (b) Y-W. Shin, H. Nakatani, T. Uozumi, B. Liu, T. Sano, K. Nitta, M. Terano, Polymer International 52 (2003) 29.

[9] (a) E.A. Shor, A.M. Shor, V.A. Nasluzov, A.I. Rubaylo, J. Struct. Chem. 46 (2005) 220. (b) J. Conradie, Dalton Trans. 44 (2015) 1503.5 (c) M.M. Conradie, J. Conradie, E. Erasmus, Polyhedron 79 (2014) 52.

[10] A.K. Rahman, M.B. Hossain, M.A. Halim, D.A. Chowdhury, M.A. Salam, African Journal of Pure and Applied Chemistry 4 (2010) 216.

[11] R. Liu, J. Conradie, Electrochim. Acta 185 (2015) 288.

[12] Bryant, B. E.; Fernelius, W.C.; Inorg. Syn., 1957, 5, 188.

[13] APEX2 (including SAINT and SADABS); Bruker AXS Inc., Madison, WI, 2012.

[14] G.M. Sheldrick, Acta Cryst. (A64) 2008 112.

[15] G. te Velde, F.M Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, J. Comput. Chem., 22 (2001) 931.

[16] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671. Erratum: J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Perderson, D.J. Singh, C. Fiolhais, Phys. Rev. B 48 (1993) 4978.

[17] A.D. Becke, Phys. Rev., A38 (1988) 3098.

[18] J.P. Perdew, Phys. Rev. B33 (1986) 8822; Erratum: J.P. Perdew, Phys. Rev. B34 (1986) 7406.

[19] N.C. Handy, A.J. Cohen, Mol. Phys., 99 (2001) 403-412.

[20] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B, 37 (1988) 785. (b) B.G. Johnson, P.M.W. Gill, J.A. Pople, J. Chem. Phys. 98 (1993) 5612. (c) T.V. Russo, R.L. Martin, P.J. Hay, J. Chem. Phys. 101 (1994) 7729.

[21] A.D. Becke, J. Chem. Phys., 98 (1993) 5648.

[22] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.

[23] (a) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry. 2nd ed.; John Wiley & Sons: New York, London, Sydney, 1966; p 875. (b) T. L. Poulos, J. Kraut, J. Biol. Chem. 255 (1980) 8199. (c) I. Diaz-Acosta, J. Baker, J.F. Hinton, P. Pulay, Spectrochim. Acta Part A 59 (2003) 363.

[24] H.S. Jarrett, J. Chem. Phys. 27 (1957) 1298.

[25] L. J. Farrugia, WinGX and ORTEP for Windows : an update, J. Appl. Crystallogr. 45 (2012) 849-854.

[26] Cambridge Structural Database (CSD), Version 5.36, May 2015 update, CSD reference codes: ACACCR12, ACACCR, ACACCR02, ACACCR05, ACACCR07, ACACCR08, ACACCR08, ACACCR08, ACACCR08, ACACCR08, ACACCR08, ACACCR10, ACACCT, ACACCT, ACACCZ, ACACCZ01, ACACCZ02, ACRTUR.

[27] Cambridge Structural Database (CSD), Version 5.36, May 2015 update, CSD reference codes: FECWAL01, FECWAL02.

[28] Cambridge Structural Database (CSD), Version 5.36, May 2015 update, CSD reference codes: IGAGEC, IGAGEC01

[29] Cambridge Structural Database (CSD), Version 5.36, May 2015 update, CSD reference codes: ACONPB, ACOSEU, COACAC01, COACAC02, COACAC03, COACAC06, COACAC07, COACAC08, COACAC09, COACAC10, COACAC11

[30] Cambridge Structural Database (CSD), Version 5.36, May 2015 update, CSD reference codes: JINRIH01, JINRIH02.

[31] Cambridge Structural Database (CSD), Version 5.36, May 2015 update, CSD reference codes: FECWEP01, FECWEP02.

[32] Cambridge Structural Database (CSD), Version 5.36, May 2015 update, CSD reference codes: GUCGOA.

[33] M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus, R.K. Birkedal, P. Norby, D.S. Wragg, N.S. Gupta, Z. Anorg. Allg. Chem. 636 (2010) 2422

[34] M.A.K. Ahmed, H. Fjellvag, A. Kjekshus, P.D.C. Dietzel, Z. Anorg. Allg. Chem. 634 (2008) 247.

[35] (a) A.C. Scheiner, J. Baker, J.W. Andzelm, J. Comput. Chem. 18 (1997) 775. (b) J.R. Hill, C.M. Freeman, B. Delley, J. Phys. Chem. A, 103 (1999) 3772. (c) F. Furche, J.P. Perdew, J. Chem Phys. 124 (2006) 044129.

[36] 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, J. Mol. Struct. 1053 (2013) 134.

[37] M.M. Conradie, J. Conradie, Stereochemistry of the Reaction Products of the Oxidative Addition Reaction of Methyl Iodide to [Rh((C_4H_3S)COCHCOR)(CO)(PPh_3)]: a NMR and Computational Study. R = CF_3, C_6H_5, C_4H_3S, Inorg. Chim. Acta 362 (2009) 519-530.

[38] M.M. Conradie, J. Conradie, Methyl Iodide Oxidative Addition to Rhodium(I) Complexes: a DFT and NMR Study of [Rh(FcCOCHCOCF_3)(CO)(PPh_3)] and the Rhodium(III) Reaction Products, S. Afr. J. Chem.61 (2008) 102-111.

[39] W.J. Hehre, A Guide to Molecular Mechanisms and Quantum Chemical Calculations, Wavefunction Inc., (2003) p153.

[40] W. Koch, M.C. Holthausen, A Chemist's Guide to Density Functional Theory, Second Edition, Wiley-VCH Verlag, 2001, p 251

[41] R. Fay, T. S. Piper, J Am. Chem. Soc. 85 (1963) 500.