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

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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: $d_{xy} < d_{xz}$, $d_{yz} < d_{z^2}$, $d_{x^2-y^2}$.

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1. Introduction

β-diketones, RCOCH$_2$COR′, have two carbonyl groups separated by the α-carbon atom; exhibit keto–enol tautomerism, whereas in many cases, the 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.

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 mol) and 10 mmol β-diketone dissolved in 10 mL of ethanol were preheated to 95 °C while stirring. 15 ml 25%

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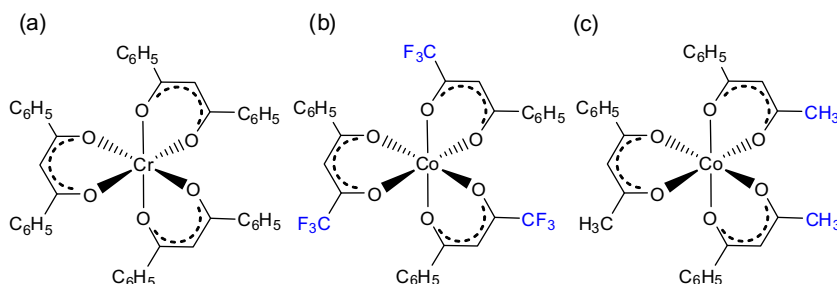
Scheme 1. The tris(β-diketonato)metal(III) complexes of this study: [Cr(dbm)₃] (**1**), the *fac* isomer of [Co(tfba)₃] (**2**) and the *mer* isomer of [Co(ba)₃] (**3**).
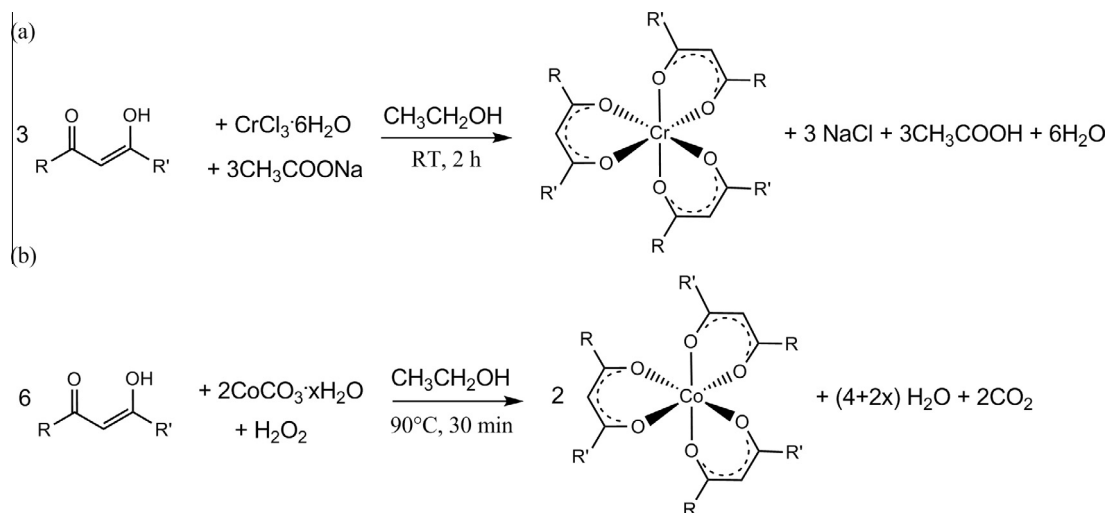
Scheme 2. General synthetic method for the (a) tris(β-diketonato)chromium(III) and (b) the tris(β-diketonato)cobalt(III) complexes.

hydrogen peroxide was added drop-wise to the suspension over 30 min. 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.

2.1.1. Characterization data for [Cr(C₆H₅COCHCOC₆H₅)₃], (**1**) [Cr(dbm)₃]

Yield 90%. Color: Yellow. Melting point 76 °C; MS (*m/z*): Calc. 723.06 [M], Found 722.0 [M−1]⁻. Elemental *Anal.* Calc. for CrC₄₅H₃₃O₆: C, 74.9; H, 4.6. Found: C, 74.8; H, 4.6%.

2.1.2. Characterization data for [Co(C₆H₅COCHCOCF₃)₃], (**2**) [Co(tfba)₃]

Yield 13%. Color: Dark green. M.p. 107.6 °C. ¹H NMR: (300 MHz, δ/ppm, CDCl₃): 6.74 (s, 3H, 3 × H, *fac*), 6.73, 6.75, 6.78 (s, 3H, 3 × H, *mer*), 7.40–7.65 (m, 9H, 3 × Ph, *fac* + *mer*), 7.90–8.05 (m, 6H, 3 × Ph, *fac* + *mer*), MS (*m/z*): Calc. 704.38 [M], Found: [M−1]⁻ 703.98.

2.1.3. Characterization data for [Co(C₆H₅COCHCOCH₃)₃], (**3**) [Co(ba)₃]

Yield 66%. Color: Dark green. M.p. 184.3 °C. ¹H NMR: (300 MHz, δ/ppm, CDCl₃): 2.36 (s, 9H, 3 × CH₃, *fac*), 2.38, 2.40, 2.42 (s, 9H, 3 × CH₃, *mer*), 6.24, 6.26, 6.27 (s, 3H, 3 × H, *fac* + *mer*), 7.28–7.46 (m, 9H, 3 × Ph, *fac* + *mer*), 7.85–7.95 (m, 6H, 3 × Ph, *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 Kα 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 $X \times U_{eq}$ 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 [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.