



Jahn-Teller distortion in tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato]manganese(III) isomers: An X-ray and computational study



Roxanne Gostynski^a, Petrus H. van Rooyen^b, Jeanet Conradie^{a,*}

^a Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein, 9300, South Africa

^b Department of Chemistry, University of Pretoria, Private Bag X20, Hatfield, 0028, South Africa

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ABSTRACT

The solid state crystal data of a *mer* isomer of the $[\text{Mn}(\text{CF}_3\text{COCHCOC}_4\text{H}_3\text{S})_3]$ complex, $[\text{Mn}(\text{tfth})_3]$, exhibits elongation Jahn-Teller distortion (elongation of the metal-ligand bonds along the z-axis and shortening of the metal-ligand bonds along both the x and y-axes). Density functional theory calculations (DFT) show that one *fac* and three *mer* isomers of $[\text{Mn}(\text{tfth})_3]$ can exist. The difference between the three *mer* isomers of $[\text{Mn}(\text{tfth})_3]$ is that the Jahn-Teller elongation of the two *trans* axial Mn-O bonds along the z-axis occur along three different $\text{O}_{\text{tfth}}\text{-Mn-O}_{\text{tfth}}$ bonds. DFT calculations further show that the ground state geometry of all the $[\text{Mn}(\text{tfth})_3]$ isomers exhibits elongation Jahn-Teller distortion.

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1. Introduction

Octahedral molecular geometry describes the shape of compounds wherein six atoms, or groups of atoms or ligands, are arranged symmetrically around a central atom. Octahedral complexes of high-spin manganese(III) are subjected to distortions, leading to deviations from the ideal octahedral molecular geometry [1]. Tris(β -diketonato)metal(III) complexes are octahedral complexes with an octahedral coordination polyhedron, MO_6 . Possible distortions from the regular octahedral geometry for tris(β -diketonato)metal(III) complexes, include either elongation or compression along the tetragonal or z-axis, as well as orthorhombic distortion, leading to an asymmetric complex with two long, two medium and two small M-L bonds, see Scheme 1 (a). Crystal structures of different tris(β -diketonato)manganese(III) complexes exhibit elongation Jahn-Teller distortion [2–4] or compression Jahn-Teller distortion [5–7]. Reported structures of $[\text{Mn}(\text{acetylacetonato})_3]$ include three different crystalline forms: namely a β form obtained at room temperature, which exhibited a moderate compression (TC) of the metal-ligand bonds along the z-axis of about 0.05 Å [5]; secondly, a γ form, also obtained at room

temperature (RT), which showed a significant elongation (TE) of the metal-ligand bonds along the z-axis of about 0.18 Å [2]; and thirdly, a δ form, obtained at low temperature (LT) (100 K), exhibiting a Jahn-Teller orthorhombic distortion [8]. This result encouraged us to similarly determine the crystal structure of another $[\text{Mn}(\beta\text{-diketonato})_3]$ complex, at both RT and LT. This study therefore presents the crystal structures of the $[\text{Mn}(\text{tfth})_3]$ complex, where $\text{tfth} = (\text{CF}_3\text{COCHCOC}_4\text{H}_3\text{S})^-$, both at RT and at an LT of 150 K. The experimentally obtained crystal structures are complemented by a density functional theory study, to obtain insight into the electronic structure of this high spin $3d^4$ Mn(III) complex. Since two isomers are possible for tris(β -diketonato)metal(III) complexes containing an unsymmetrical β -diketonato ligand ($\text{RCOCHCOR}'$)⁻ (with different groups substituted on the ligand, $R \neq R'$), namely a facial isomer (*fac*) and a meridional isomer (*mer*) (see Scheme 1 (b)), our aim was also to investigate which isomer would crystallize in the solid state.

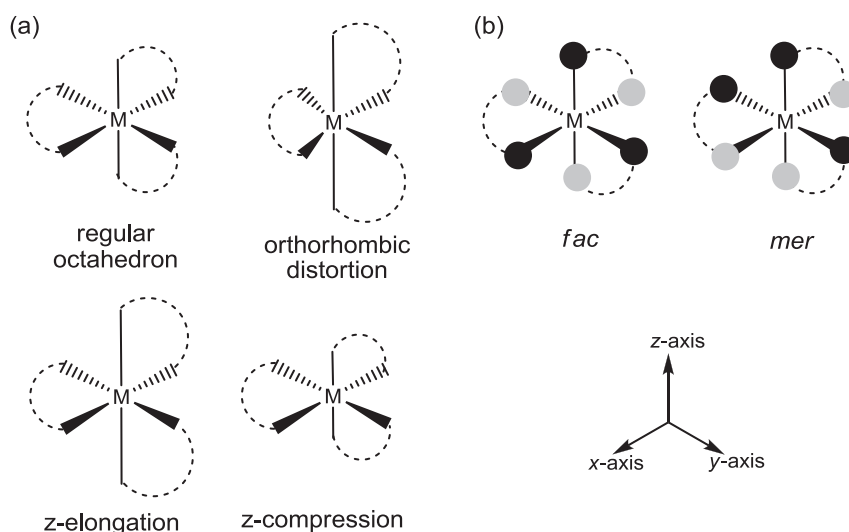
2. Experimental

2.1. Synthesis

Tris(thenoyltrifluoroacetone)manganese(III) was synthesized by a procedure adapted from literature [9], as reported previously

* Corresponding author.

E-mail address: conradj@ufs.ac.za (J. Conradie).



Scheme 1. (a) Possible distortions from the regular octahedral geometry, for tris(β -diketonato)metal(III) complexes. (b) Possible isomers for tris(β -diketonato)metal(III) complexes.

[10]. The paramagnetic $[\text{Mn}(\text{tfth})_3]$ complex was characterized by MS, elemental analysis, UV/vis (supporting information Fig. S2) and X-ray crystallography.

2.1.1. Characterization data for $[\text{Mn}(\text{CF}_3\text{COCHCOCH}_2\text{H}_3\text{S})_3]$, $[\text{Mn}(\text{tfth})_3]$

Yield 97%. Colour: Brown. Melting point 157.5 °C. MS Calculated: $M_r = 718.45$ g/mol, Found: 718.72 g/mol. Elemental analysis, calculated for $\text{MnC}_{24}\text{H}_{12}\text{O}_6\text{F}_6\text{S}_3$: C, 40.1; H, 1.7, Found: C, 40.7; H, 1.99.

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 $\text{I}\mu\text{s}$ sources, a Photon 100 CMOS detector and APEX II [11] control software, using Quazar multi-layer optics, monochromated Mo- $K\alpha$ radiation, by means of a combination of ϕ and ω scans. Data reduction was performed using SAINT+ [11] and the intensities were corrected for absorption using SADABS [11]. The structure was solved by intrinsic phasing using SHELXTS and refined by full-matrix least squares, using SHELXTL + [12] and SHELXL-2015+ [12]. In the structure refinement, all the aromatic 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 $X \times U_{\text{eq}}$ of the atom to which they are attached, where $X = 1.2$. Crystal data and structural refinement parameters are given in the electronic supplementary information. Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre, with numbers: 1449937-1449938.

2.3. Density functional theory (DFT) calculations

Density functional theory (DFT) calculations were carried out, using the ADF (Amsterdam Density Functional) 2013 programme [13], with a selection of GGA (Generalized Gradient Approximation) functionals, namely PW91 (Perdew-Wang 1991) [14], BP86 (Becke-Perdew) [15,16], and OLYP (Handy-Cohen and Lee-Yang-Parr) [17,18], S12g [19], OPBE [20], the meta-GGA functional M06-L [21], as well as the hybrid functionals B3LYP (Becke 1993 and

Lee-Yang-Parr) [22,23], O3LYP [24], B3LYP* [25] and S12h [19]. 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. X-ray structure

The crystal data and structure refinement details of the $[\text{Mn}(\text{tfth})_3]$ crystal in this study, performed at both RT and at a LT of 150 K, are given in the Supporting Information. Fig. 1 and Fig. 2 present perspective drawings [26] of the molecular structure of the mer isomer of $[\text{Mn}(\text{tfth})_3]$, obtained at 296 K (RT) and at 150 K (LT), showing the crystallographic numbering scheme used. Table 1 gives selected geometrical parameters of $[\text{Mn}(\text{tfth})_3]$ and other published $[\text{Mn}(\text{III})(\beta\text{-diketonato})_3]$ complexes. Both the RT and LT $[\text{Mn}(\text{tfth})_3]$ structure crystallize in the $P2_1/n$ space group, with

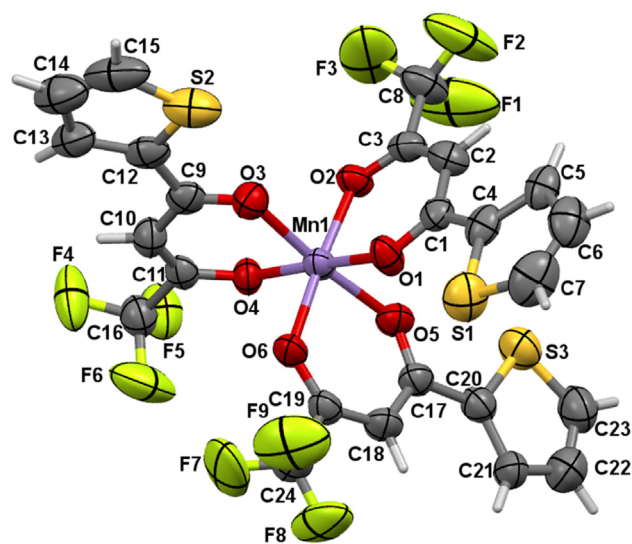


Fig. 1. A perspective drawing of the molecular structure of mer- $[\text{Mn}(\text{tfth})_3]$, obtained at RT of 296 K, showing the atom numbering scheme. Atomic displacement parameters (ADPs) are shown at the 50% probability level.

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