Trigonal-prismatic vs. octahedral geometry for MnII complexes with innocent didentate ligands: a subtle difference as shown by XRD and DFT on Mn(acac)2(bpy)
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Trigonal-Prismatic vs. Octahedral Geometry for Mn$^{II}$ Complexes with Innocent Didentate Ligands: A Subtle Difference as Shown by XRD and DFT on [Mn(acac)$_2$(bpy)]


Keywords: Trigonal prism / Distorted octahedron / Density Functional Theory (DFT) / Manganese(II) / Packing effects

In this paper the first example of a mixed-ligand Mn$^{II}$ complex, having a trigonal-prismatic coordination geometry with simple, innocent, didentate ligands is presented. The solution and solid-state structures of [Mn(acac)$_2$(bpy)] as studied by EPR spectroscopy, magnetic susceptibility measurements and XRD are presented: single crystals are hexagonal, space group $P_6_3$ with unit cell dimensions $a = 8.0482(9)$ Å, $c = 51.602(10)$ Å, $V = 2894.6(7)$ Å$^3$ and $Z = 6$. The complex has the trigonal-prismatic geometry only in the solid state. Density functional theory (DFT) calculations were performed to address the question of the preference for a specific coordination geometry in the related Mn$^{II}$ complexes [Mn(acac)$_2$(bpy)] (trigonal prismatic) and [Mn(acac)$_2$(phen)] (distorted octahedral). Based on the very small energy differences for the calculated trigonal-prismatic and octahedral structures it has been concluded that crystal packing effects must contribute largely in determining the trigonal-prismatic structure for [Mn(acac)$_2$(bpy)].

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Introduction

Even though the first observed example of a trigonal-prismatic complex, [Re(1,2-S$_2$C$_2$Ph$_2$)$_3$], dates back from 1965,[1] mixed ligand trigonal-prismatic complexes with simple didentate ligands are still rare. Since 1965 several tris(dithiolene) complexes with trigonal-prismatic or distorted octahedral geometry have been reported.[2] In addition a limited, but growing number of examples of non-dithiolene [M(didentate)$_3$] trigonal-prismatic compounds is known, for instance with buta-1,3-diene, methyl vinyl ketone or acetylacetone as ligands.[3–6] A few mixed ligand trigonal-prismatic complexes of the form [M(didentate)$_1$(didentate2)] are known, for example the complexes with a diimine and two (substituted) catechol semiquinonates as ligands,[7–9] but they are definitely not as common as homoleptic tris(didate) complexes. Most compounds mentioned above have either noninnocent ligands, or ligands that can easily participate in π-(back) bonding. Therefore, it is not unexpected that for these complexes the majority of arguments for favoring trigonal-prismatic over octahedral geometry are electronic in nature, as for example: The overall charge of the complex, ligand-field stabilization energy, matching of ligand and metal orbital energies, bonding between the ligand donor-atoms and π-bonding.[10,11] Even some examples of six-coordinate trigonal-prismatic complexes with monodentate ligands have been reported.[12,13] These complexes all contain d$^0$ metal ions and in these cases the preference for the trigonal-prismatic geometry has been ascribed to the absence of steric or π-bonding effects.

A well-known strategy for obtaining trigonal-prismatic complexes is using rigid, penta- or hexadentate ligands that force the trigonal-prismatic geometry upon a complex by means of steric constraints.[14–16] This successful strategy has resulted in many examples of trigonal-prismatic complexes.

While searching for novel manganese-based catalysts for the oxidative drying of alkyd paints,[17] the X-ray structure of the well-known compound [Mn(acac)$_3$(bpy)] was determined. Although this complex has been claimed to have an octahedral coordination geometry,[18] it appears to be the first example of a mixed-ligand complex with innocent didentate ligands that possesses the trigonal-prismatic coordination geometry. Herein, we describe the crystal structure details and EPR spectra of the complex. DFT calculations have been performed to address the question of the preference for trigonal-prismatic vs. octahedral geometry, comparing this complex with the related octahedral phenanthroline complex, [Mn(acac)$_3$(phen)].
Results

Synthesis and Characterization: The synthesis of [Mn(acac)2(bpy)] is best carried out under argon until the product is isolated and dried, since the complex is very sensitive to air-oxidation when moist or in solution. The dried complex is stable in air. The yield (67%) is satisfactory, as was the elemental analysis.

Spectroscopic Features: The infrared spectrum of [Mn(acac)2(bpy)] is in agreement with literature,[18] with important IR peaks being $\nu$(C–O) 1604, 1578 cm$^{-1}$, $\nu$(C–C) 1516 cm$^{-1}$, $\nu$(M–O) 647, 536, 415 cm$^{-1}$ and $\nu$(M–N) 403, 228 cm$^{-1}$. The electronic spectrum of the solid compound shows an MLCT band at 365 nm (27.4×10$^3$ cm$^{-1}$). The powder spectrum of [Mn(acac)2(bpy)] is in agreement with literature,[18] with impor-

Figure 1. Room temperature powder EPR spectra of [Mn(acac)2(bpy)] and [Mn(acac)2(phen)] (inset). Important EPR parameters for the frozen-solution EPR spectra of [Mn(acac)2(bpy)] and [Mn(acac)2(phen)] (inset). Important EPR parameters for both spectra: frequency 9.434 GHz, power 4 mW.

Figure 2. ORTEP plot of [Mn(acac)2(bpy)], ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] experimentally obtained with XRD compared to values obtained by DFT calculations.

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<th>X-ray</th>
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Torsion angles


The manganese(tii) ion has an almost perfect N2O4 trigonal-prismatic coordination environment, with two acetylacetonate ligands and one bipyridine ligand. The manganese to nitrogen distances are 2.288(3) and 2.283(2) Å. The manganese to oxygen distance for the acetylacetonate li-
Trigonal-Prismatic vs. Octahedral Geometry for Mn$^{II}$ Complexes

The crystal structure has a hexagonal unit cell and space group $P6_1$. Figure 4 and Figure 5 show the packing in the $a$, $b$ and $c$ directions. The structure is composed of right-handed helices along the $c$-axis and therefore is chiral. A single helix consists of six molecules of [Mn(acac)$_2$(bpy)]$^-$ per unit cell, due to the inherent hexagonal symmetry. The helices are tightly packed together in such a way that each molecule in the helix is part of a layer that extends in the $a$ and $b$ direction. Within such a layer, one can observe rows of [Mn(acac)$_2$(bpy)]$^-$ molecules with aligned bipyridine ligands, each bipyridine pointing in-between the acetylacetone. 

The two trigonal-faces of the prism constitute one oxygen atom of each of the acetylacetonate ligands and one nitrogen atom, thus forming O1–O3–N1 and O2–O4–N2. Figure 3 shows the trigonal-prismatic coordination geometry around manganese in more detail, and the dimensions and angles of the prism are tabulated in Table 2. The lengths of the triangular sides are in the range 2.901(2)–3.030(3) Å for the triangle O1–O3–N1 and 2.846(2)–3.007(3) Å for the triangle O2–O4–N2, all angles are in the range 56.88(7)–62.25(7)$^\circ$. The four acetylacetonate oxygen atoms make up an almost exact square, the sides of which are in the range 2.816(2)–2.901(2) Å. The remaining two faces of the prism are trapezoids consisting of two oxygen atoms of one acetylacetonate ligand and are joined by the two nitrogen atoms of bipyrindine. Both faces have an O–O distance of 2.826(2) and 2.816(2) Å, an N–O distance in the range 2.968(3)–3.030(3) Å and a markedly shorter distance of 2.635(3) Å for the N1–N2 side. Since the N1–N2 side is shorter than the O–O sides of the trapezoid faces of the prism, the two triangular faces are not parallel. The planes defined by O1–N1–O3 and O2–N2–O4 make an angle of 4.04(10)$^\circ$. The torsion angles about the centroids of the triangular faces and each of the corners [for example C1–N1–N2–Ct2 are $-2.1(3)^\circ$, $-1.9(3)^\circ$ and $-2.5(3)^\circ$] are faces exactly overlapping. A perfect trigonal prism would have angles of 0$^\circ$, the triangular faces exactly overlapping.

The obtuse angles between the least-squares mean planes of the chelate rings lie in the range 117.67(7)–121.30(6)$^\circ$, in accordance with the trigonal-prismatic coordination geometry.

The crystal structure has a hexagonal unit cell and space group $P6_1$. Figure 4 and Figure 5 show the packing in the $a$, $b$ and $c$ directions. The structure is composed of right-handed helices along the $c$-axis and therefore is chiral. A single helix consists of six molecules of [Mn(acac)$_2$(bpy)]$^-$ per unit cell, due to the inherent hexagonal symmetry. The helices are tightly packed together in such a way that each molecule in the helix is part of a layer that extends in the $a$ and $b$ direction. Within such a layer, one can observe rows of [Mn(acac)$_2$(bpy)]$^-$ molecules with aligned bipyridine ligands, each bipyridine pointing in-between the acetylacetone.

Figure 3. Trigonal-prismatic geometry of [Mn(acac)$_2$(bpy)] in detail.

Figure 4. Crystal packing of [Mn(acac)$_2$(bpy)] in the $a,b$ plane. The acac methyl groups are packed together in rows along $a$.

Table 2. Trigonal prism distances [Å] and angles [$^\circ$] of [Mn-(acac)$_2$(L)], L = bpy (XRD & DFT data) or phen (only DFT).

<table>
<thead>
<tr>
<th>X-ray Calculated</th>
<th>Calulated</th>
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<td>X-ray Calculated</td>
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<tr>
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<td>O3–N1</td>
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<td>O4–N2</td>
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<td>2.635(3)</td>
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<tr>
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</tr>
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<td>O4–N2–N1</td>
<td>92.93(9)</td>
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The crystal structure has a hexagonal unit cell and space group $P6_1$. Figure 4 and Figure 5 show the packing in the $a$, $b$ and $c$ directions. The structure is composed of right-handed helices along the $c$-axis and therefore is chiral. A single helix consists of six molecules of [Mn(acac)$_2$(bpy)]$^-$ per unit cell, due to the inherent hexagonal symmetry. The helices are tightly packed together in such a way that each molecule in the helix is part of a layer that extends in the $a$ and $b$ direction. Within such a layer, one can observe rows of [Mn(acac)$_2$(bpy)]$^-$ molecules with aligned bipyridine ligands, each bipyridine pointing in-between the acetylacetone.
the trigonal-prismatic one, both again favoring the $S = 5/2$ spin state.

Discussion

Structural Features: The manganese to bipyridine distances 2.288(3) and 2.283(2) Å are not extraordinary and comparable to the Mn–N distances reported for the similar compound [Mn(acac)$_2$(phen)], which are 2.307 Å.\textsuperscript{[22]} The bipyridine ligand has a bite angle N1–Mn1–N2 of 70.41°, which is quite small and can be related to the large ionic radius of Mn$^{11}$. Unsubstituted bipyridine ligands in manganese complexes commonly have bite angles varying between 72–80°.\textsuperscript{[23]} Simple donor-atom to donor-atom repulsion energy considerations predict small bite angles for trigonal-prismatic complexes,\textsuperscript{[3]} and indeed the average bite angle for the acetylacetonate ligands (81.81°) is among the lowest found for 2,4-pentanedionato coordinated to manganese(II).\textsuperscript{[23]} The only other case found in literature where the 2,4-pentanedionato ligand coordinated to Mn$^{11}$ has a bite angle smaller than 82°, is in the structure [Mn$^{11}$Mn$^{11}$, (acac)$_2$]$_2$, in which the two peripheral Mn$^{11}$ ions also have a trigonal-prismatic coordination geometry.\textsuperscript{[24]}

Trigonal Prism vs. Octahedron: Why does [Mn(acac)$_2$(bpy)] adopt a trigonal-prismatic coordination geometry in the solid phase, and why does the complex [Mn(acac)$_2$(phen)] not do so? The high-spin d$^5$ Mn$^{11}$ ion has no ligand field stabilization and no large degree of π-bonding is present, since the magnetic data shows both complexes having a spin state of $S = 5/2$. This value would be lower if π-bonding would take place to the extent of that found in rhenium dithiolene complexes for example.\textsuperscript{[25]}

The solid-state EPR spectra for the two complexes are quite different, reflecting the different coordination symmetries and thus the difference in the zero-field splitting parameters. The symmetry of the trigonal-prismatic complex is rhombic, which is the cause of the large EPR signal at $g = 3.25$. Although the exact magnitudes of the zero-field splitting parameters $D$, $E$ and $\lambda$ ($= E/D$) have not been calculated, it is clear from literature that $D$ is likely to be significant ($0.05 < D < 0.15$ cm$^{-1}$) and $\lambda$ will approach its limiting value of 1/3.\textsuperscript{[26]} The complex [Mn(acac)$_2$(phen)] has a fairly regular octahedral coordination environment, which gives very small zero-field splitting values ($D$ in the order of 10$^{-2}$ cm$^{-1}$, $\lambda$ approximately 0) and thus a resonance signal near the free electron value of $g = 2$ is observed.\textsuperscript{[26]}

The similar solution-EPR spectra that are obtained demonstrate that in solution, the geometry around the Mn$^{11}$ ion is comparable for both complexes. The DFT calculations in vacuo show a slight (1.5 kcal/mol) preference for the octahedral geometry for [Mn(acac)$_2$(phen)], although this “octahedral” geometry is significantly trigonally distorted. The complex [Mn(acac)$_2$(bpy)] does not show a preference for either prism or octahedron, but there is some barrier for going from one to the other, since it does not adopt the trigonal-prismatic geometry when starting from the octahedral geometry. The calcu-
Trigonal-Prismatic vs. Octahedral Geometry for MnII Complexes

Contrary to expectation, the difference in rigidity between the bpy and phen ligand does not seem to have a large influence on the coordination geometry. Comparing the torsion angles for the calculated prismatic complexes in Table 2, it can be seen that the phen ligand can be regarded as more rigid than the bpy ligand, judging by the torsion angle N1–C5–C6–N2, which is 0.61° for phen vs. 4.42° for bpy. The same values are found for the calculated octahedral complexes. The deviation from a perfect prism is slightly larger for the phen complex, however, whereas for the calculated octahedral complexes the average trigonal distortion is identical. Furthermore, in the crystal structures the bpy and phen N1–C5–C6–N2 torsion angles are nearly identical, yet the coordination geometry is certainly different.

It thus seems that an important factor for determining the preference for octahedral vs. trigonal-prismatic geometry for the complexes [Mn(acac)2(bpy)] and [Mn(acac)2(phen)] is the crystal structure packing. In the a,b layer of the lattice of [Mn(acac)2(bpy)], the bpy ligand fits precisely in-between the two acac ligands of the next molecule in the row (see Figure 4). The phenanthroline complex has a comparable a,b layer structure where the phenanthroline ligands of the complexes in the layer are aligned in rows and point towards, but do not fit in-between, the acac ligands of the next complex in the row. The tighter packing that results for [Mn(acac)2(phen)] is likely stabilising the trigonal-prismatic geometry.

Conclusions

The trigonal-prismatic and octahedral environments in the compounds [Mn(acac)2(bpy)] and [Mn(acac)2(phen)] are both stable and very similar in energy for the high spin state. However, in the solid state [Mn(acac)2(phen)] favours a (distorted) octahedral geometry whereas [Mn(acac)2(bpy)] adopts a nearly perfect trigonal-prismatic geometry. Since the rigidity of the dinitrogen diimine ligand does not seem to play a role and the energy difference between different ligand environments for the complexes in the vacuum is quite small, packing effects in the crystal lattice must play an important role in determining the final solid-state structure.

Experimental Section

Materials: 2,2’-Bipyridine (bpy) and acetylacetone (Hacac) were purchased from Acros and used as received. [MnII(acac)2(H2O)2] was prepared according to a literature procedure. Methanol was distilled from CaH2 and stored with 3-Å molecular sieves under argon prior to use.

Synthesis of [Mn(acac)2(bpy)]: The title compound was synthesized using a slightly modified procedure from that published. The reaction was performed under argon using standard Schlenk techniques. To a stirred, dark orange solution of [Mn(acac)2(H2O)2] (1 g, 3.46 mmol) in 20 mL of methanol was added a solution of bpy (1.08 g, 6.92 mmol) in 10 mL of methanol. After 1 minute of stirring, [Mn(acac)2(bpy)] precipitated as a bright yellow microcrystalline material. Stirring was continued for an additional 15 minutes and then the product was filtered under argon and dried for 24 hours at room temperature under reduced pressure. Yield: 0.95 g (67%).

Physical Measurements: Elemental analyses on C, H and N was performed with a Perkin–Elmer series II CHNS/O Analyzer 2400. The IR spectrum was recorded with a Perkin–Elmer Lambda 900 spectrophotometer. The diffuse-reflectance technique was used with MgO as a reference for the solid compound. Electron paramagnetic resonance measurements were performed with a JEOL JES-RE2X ESR Spectrometer with a JEOL X-band microwave, a JEOL electromagnet and a JEOL ESPIRIT 330 ESR Datasystem unit. A special quartz Dewar flask was used for measurements at liquid nitrogen temperature (77 K). Magnetic
susceptibility measurements (5–300 K) were carried out using a Quantum Design MPMS-5 ST SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

**DFT Calculations:** Density functional theory (DFT) calculations were performed to address the question of the preference for a specific coordination geometry in the MnII complex [Mn(acac)2(bpy)]. The relative energy of the trigonal-prismatic vs. the octahedral coordination geometry was calculated for the complex [Mn(acac)2(bpy)] in the vacuum. For comparison the same relative energy difference was calculated for the related phanthroline compound [Mn(acac)2(phen)], which is known to have a distorted octahedral environment about the Mn atom in the solid state.[23]

The hybrid B3LYP exchange and correlation functional was used.[23] All self-consistent field (SCF) calculations were done using the 6-31G(d,p) gaussian basis set and were performed with the Gaussian 98 package.[23] The geometries of the various complexes were fully optimised without imposing any symmetry constraint. All calculations were spin unrestricted and the relative stability of the different spin states were checked.

**X-ray Crystallographic Study:** A crystal of dimensions 0.10×0.15×0.35 mm was selected from a batch of yellow prisms, obtained from the filtrate of the reaction mixture overnight at −20 °C. Crystal data and details on data collection are listed in Table 3.

| Table 3. Crystallographic data for [Mn(acac)]2(bpy)]. |
|-----------------|-----------------|
| **Formula**     | C_{20}H_{22}MnN_{2}O_{4} |
| **Fw**          | 409.34           |
| **Crystal system** | hexagonal        |
| **Space group**  | P6_{3}           |
| **a [Å]**       | 8.0482(9)        |
| **c [Å]**       | 51.602(10)       |
| **V [Å^{3}]**   | 2894.6(7)        |
| **Z**           | 6                |
| **δ [Mo-K_{α}]**| 0.71073          |
| **T [K]**       | 150              |
| **δ_{abs} [g cm^{-3}]** | 1.4089(3)    |
| **μ [mm^{-1}]** | 0.712            |
| **R [I > 2σ(I)]^{[1]}** | 0.0291     |
| **wR_{2}^{[2]}** | 0.0584          |
| **GoF**         | 1.035            |

[a] \( R = \Sigma||F_{o}| - |F_{c}||/\Sigma|F_{o}|| \) \( wR_{2} = \{\Sigma|w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma|w(F_{c}^{2})^{2}\}^{1/2} \).

Data were collected with an Enraf–Nonius KappaCCD area detector on a rotating anode. 30196 Reflections were measured (1.0° < θ < 25.37°), 3375 of which were independent (R_{int} = 0.0528). The structure was solved by Patterson methods (DIRDIF[20]) and refined on \( F^2 \) by using SHELXL-97.[21] Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms. Methyl hydrogen atoms were refined as a rigid group, allowing for rotation around the C–C bond. Non-hydrogen atoms were refined with anisotropic displacement parameters Hydrogen atoms were refined with a fixed isotropic displacement parameter linked to the value of the equivalent isotropic displacement parameter of their carrier atoms. A total of 248 parameters were refined. All peaks in the final difference Fourier map were in the range \(-0.19 < \Deltaρ < 0.18 \) e Å\(^{-3}\). The Flack x parameter,[20] derived during the final structure-factor calculation, amounts to \(-0.012(14)\), indicating a correctly assigned absolute structure. Refinement of the inverse absolute structure resulted in an x parameter of 0.97(2) (value derived during the final structure-factor calculation). Figures of merit for this inverted structure are \( R_{1} = 0.0428, wR_{2} = 0.1067 \) and \( S = 1.040 \). CCDC-257462 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see also footnote on the first page of this article): The frozen-solution EPR spectra of [Mn(acac)2(bpy)] and [Mn(acac)2(phen)] are available as supporting information.

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**References**