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Assembly of a mononuclear ferrous site using a bulky aldehyde-imidazole ligand

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Abstract

A new iron(II) complex has been prepared and characterized. $[\text{Fe}(\text{TrImA})_2(\text{OTf})_2]$ (**1**, TrImA = 1-Tritylimidazole-4-carboxaldehyde). The solid state structure of **1** has been determined by X-ray crystallography. Compound **1** crystallizes in monoclinic space group $P2_1/c$, with $a = 10.8323(18)$ Å, $b = 8.1606(13)$ Å and $c = 24.818(4)$ Å. The iron center is coordinated to two imidazole groups, two pendant aldehyde-derived carbonyl oxygens and two triflate oxygens. The complex is high spin between 300 and 20 K as indicated by variable field variable temperature magnetic measurements. A fit of the magnetic data yielded $g = 2.17$ and $D = 4.05 \text{ cm}^{-1}$. A large HOMO-LUMO gap energy (4.49 eV) exists for **1** indicating high stability.

Keywords

Iron(II); Imidazole; Aldehyde; X-ray crystallography; Magnetic susceptibility; DFT

1. Introduction

Enzymes containing non-heme iron sites are abundant in nature [1–6]. For mononuclear non-heme iron sites, enzymatic functions include a variety of oxygen activating functions [7]. X-ray structures have established examples where mononuclear iron is bound to two, three, or four histidine ligands [2]. 2His enzymes are quite common and comprise the large class of 2His-1-carboxylate oxygenase enzymes along with α -ketoglutarate (α -KG)-dependent halogenase, which activates O_2 to carry out oxidative halogenations of nonactivated and activated carbon centers [8–13]. Several groups have worked on developing ligand systems to mimic these metal binding sites using Histidine mimics such as amine, amide, pyrrole, pyrazole, and pyridine [4,14–16], however, it is anticipated that the imidazolyl group will be the best surrogate for histidine. Incorporation of bulky hydrophobic groups helps to mimic the hydrophobic environment often found at these sites.

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Appendix A. Supplementary data: Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2017.05.028>.

Although the aldehyde functionality is not present in protein-derived ligands, binding of a substrate-derived aldehyde to a non-heme iron center is believed to be present in the enzyme cyanobacterial aldehyde-deformylating oxygenase (cADO) [17] which is part of the fatty alk(a/e)ne biosynthetic pathway so it is important to study these interactions in synthetic model compounds. Ligands containing both imidazole and aldehyde groups can be afforded by utilizing 1-Tritylimidazole-4-carboxaldehyde (TrImA, Scheme 1). The bulky triphenylmethyl group provides hydrophobicity which is often present in metal biosites and may help to direct coordination number and geometry through steric interactions. In this paper, we present the synthesis, structure, and magnetic characterization of TrImA coordinated to iron(II), namely, $[\text{Fe}(\text{TrImA})(\text{OTf})_2]$ (**1**, Scheme 1) as well as theoretical (DFT) studies. Compound **1** is the first example of a structurally characterized complex with iron(II) bonded to an aldehyde oxygen group.

2. Experimental

2.1. Materials

All solvents were purified using an Innovative Technologies Inc. Solvent Purification System. $\text{Fe}(\text{OTf})_2 \cdot 2\text{CH}_3\text{CN}$ was synthesized according to a literature method [18]. 1-Tritylimidazole-4-carbox-aldehyde was purchased from SynChem, Inc. Elemental analysis was performed on pulverized crystalline samples that were heated under vacuum and sealed in a glass ampule prior to submission (Atlantic Microlabs, Inc., Norcross, GA).

2.2. Synthesis

2.2.1. $[\text{Fe}(\text{TrImA})_2(\text{OTf})_2]$ (1**)**—To a stirring suspension of 1-Tritylimidazole-4-carboxaldehyde (176.9 mg, 0.522 mmol) in acetonitrile (2 mL) was added a solution of $\text{Fe}(\text{OTf})_2 \cdot 2\text{CH}_3\text{CN}$ (103.6 mg, 0.237 mmol) in acetonitrile (2 mL) under dry nitrogen atmosphere. The clear orange solution which appeared immediately was stirred for 30 min when an orange precipitate formed. The thus obtained orange solid was collected on a frit, washed with ether and dried under high vacuum. X-ray quality crystals were grown from acetonitrile and ether. Yield: 208.3 mg (85%). Selected IR bands (KBr pellet, cm^{-1}): 3165(w), 1631(s), 1315(s), 1211(s), 1028(s), 807(m), 701(s) and 635 (s). UV-vis (CH_3CN ; λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 213 (115,000, sh), 253 (56,000), 396 (330). Anal. Calcd for $\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_8\text{F}_6\text{S}_2\text{Fe}$: C, 55.93; H, 3.52; N, 5.44. Found: C, 55.72; H, 3.67; N, 5.34.

2.3. Physical characterization

A Cary 50 UV-vis spectrophotometer was used to collect optical spectra. FT-IR spectra were acquired on a Varian 3100 Excalibur Series. Variable temperature magnetic susceptibilities were measured using a Quantum Design MPMS SQUID susceptometer calibrated with a 765-Palladium standard purchased from NIST (formally NSB). A powdered sample of **1** was placed in a plastic bag. The sample was measured in the temperature range 2–300 K with $H = 0.6$ T. The magnetic contribution of the bag was determined between 2–300 K as well and subtracted from the sample. The sample was placed in a plastic drinking straw for measurement. The molar magnetic susceptibility was corrected for the diamagnetism of the complex using tabulated values of Pascal's constants to obtain a corrected molar susceptibility. The program julX written by E. Bill was used for

the simulation and analysis of magnetic susceptibility data [19]. The Hamiltonian operator ($\hat{H}$) was

$$g\beta \widehat{\vec{S}} \cdot \widehat{\vec{B}} + D[\hat{S}_z^2 - 1/3S(S+1)] + E/D(\hat{S}_x^2 - \hat{S}_y^2) \quad (1)$$

where g is the average electronic g value, D the axial zero-field splitting parameter, and E/D is the rhombicity parameter. Magnetic moments were obtained from numerically generated derivatives of the eigenvalues of Eq. (1), and summed up over 16 field orientations along a 16-point Lebedev grid to account for the powder distribution of the sample. Intermolecular interactions were considered by using a Weiss temperature, θ_W , as perturbation of the temperature scale, $kT = k(T - \theta_W)$.

2.4. Computational details

Quantum chemical calculations providing energy minimized molecular geometries, molecular orbitals (HOMO-LUMO), and vibrational spectra for compound **1** were carried out using density functional theory (DFT) as implemented in the GAUSSIAN09 (Rev. C.01) program package [20]. We employed the hybrid functional PBE0 [21] containing 25% of exact exchange. We employed the basis set 6-31G* [22]. Full ground state geometry optimization was carried out without any symmetry constraints. Only the default convergence criteria were used during the geometry optimizations. The initial geometry was taken from the crystal structure coordinates in the quintet state. Optimized structures were confirmed to be local minima (no imaginary frequencies). Experimental and theoretical geometric parameters are summarized in Table 2. Molecular Orbitals were generated using Avogadro [23] (an open-source molecular builder and visualization tool, Version 1.1.0. <http://avogadro.openmolecules.net/>).

2.5. X-ray crystallography

The compound was crystallized by diffusion of ether into an acetonitrile solution of **1**. An orange block from a plate crystal with dimensions $0.624 \times 0.128 \times 0.092$ mm was mounted on a Nylon loop using a very small amount of paratone oil. Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173.15 K. Data were measured using omega and phi scans of 0.5° per frame for 10 s. The total number of images were based on results from the program COSMO [24] where redundancy was expected to be 4.0 and completeness of 100% out to $0.83 \text{ \AA}$. Cell parameters were retrieved using APEX II software [25] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software [26], which corrects for L_p . Scaling and absorption corrections were applied using SADABS [27] multi-scan technique, supplied by George Sheldrick. The structures were solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2 , SHELXL-97 [28], which are incorporated in OLEX2 [29]. All non-hydrogen atoms were refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystals used for the

diffraction study showed no decomposition during data collection. All drawings are done at 50% ellipsoids.

3. Results and discussion

3.1. Synthesis

[Fe(TrImA)₂(OTf)₂] (**1**) was synthesized in good yield at room temperature under dry nitrogen conditions by reacting 2 equiv 1-Tritylimidazole-4-carboxaldehyde (TrImA) with Fe(OTf)₂·2CH₃CN in acetonitrile. Suitable crystals of **1** for X-ray studies were grown from acetonitrile/ether. Our attempts to coordinate three TrImA ligands to iron(II) by adding 3 or 4 equiv of the ligand were unsuccessful and only **1** was produced.

3.2. Crystallography

The crystal structure of **1** was determined. Crystallographic parameters are shown in Table 1 while selected bond distances and angles are given in Table 2. The structure of **1** was solved in the $P2_1/c$ space group which includes a crystallographic C_{2h} and an inversion center. The structure reveals iron(II) in distorted octahedral geometry with ligands derived from two triflate oxygens, two carbonyl oxygens and two 3-imidazole nitrogens all in *trans*-positions (Fig. 1). The Fe-N(Im) distance is 2.134(2) Å which is at the lower end in the range of known high spin iron(II)-N(Im) compounds (2.103–2.272 Å) [30–36]. The short bond is likely due to the participation of the aldehydic oxygen (O1) in the formation of a 5-membered chelate ring. The iron triflate Fe1-O2 distance is 2.101(2) Å which is in the range of other known high spin iron (II)-O(triflate) bond distances (2.025–2.211 Å) [18,37–48]. The Fe1-O1(aldehyde) bond distance is 2.189(2) Å which is quite long for an iron(II)-O(carbonyl) bond (2.009–2.183 Å) [49–55]. The weakness of the bond is highlighted by the fact that it is longer than the iron(II)-O(triflate) bond. The negative charge on the triflate group and the Lewis acidic nature of the iron center combine to make this bond stronger. A search of the CSD yielded no hits for iron(II) bonded to aldehydic oxygen so **1** appears to be the first example of this type of bond. It is possible that chelation may be necessary to stabilize this type of bond. The C=O bond distance in **1** is 1.228(4) Å which is long compared to the same distance in uncoordinated aldehydic carbonyl groups [56,57]. This lengthening is due to donation of electron density by O1 to the Lewis acidic iron center. A triflate oxygen is situated 3.154 Å away from the electrophilic aldehyde carbon constituting a weak interaction. Intramolecular contacts (3.091 Å) are seen between the imidazole C2 and a triflate fluorine (F3). Intermolecular contacts are observed between imidazole C5 and a triflate O3 (3.232 Å) and a phenyl carbon C14 and a triflate fluorine F2 (3.134 Å).

3.3. Magnetic susceptibility

The magnetic properties of **1** were characterized using variable temperature magnetic susceptibility (χ_M) measurements on a powdered sample of **1**. Measurements were taken between 2–300 K with an applied field of 0.6 T. At 300 K $\chi_M T$ has a value of 3.57 cm³ mol⁻¹ K (Fig. 2) consistent with high spin iron(II) ($S = 2$), 3.25–4.06 cm³ mol⁻¹ K [58]. As the temperature is lowered, the $\chi_M T$ value decreases slightly to 3.42 cm³ mol⁻¹ K at 20 K then quickly tends toward 1.63 cm³ mol⁻¹ K at 2 K. The data was simulated using the

program julX [19] which gave a very good fit using $g = 2.17$ and $D = 4.05 \text{ cm}^{-1}$ which is typical for distorted octahedral geometry [59].

3.4. DFT studies

Theoretical calculation (DFT) were performed on **1** in the gas phase using X-ray coordinates as the starting point to optimize the ground state structure. The energies were obtained using PBE0/6-31G*. The calculated metric parameters for the optimized structure were compared to those empirically determined (Table 2). The largest difference between the calculated and experimental bond distances is $0.069 \text{ \AA}$ (Fe1-O1), while the bond angles are in good agreement. Despite slight differences, the calculated structure is very close to the experimental structure and therefore the electronic properties can be confidently surmised. $\langle S^2 \rangle$ before and after annihilation is 6.0050 and 6.0000, respectively and therefore little to no spin contamination is present. The calculated Mulliken charge value on the iron(II) of **1** is +1.22 consistent with high spin iron(II) [60]. Fig. 3 illustrates selected molecular orbitals: HOMO, HOMO-1, LUMO, and LUMO+1 for **1**. It is found that the highest occupied molecular orbital (HOMO, α -266) is largely distributed over the imidazolyl ligand orbitals, triflate oxygens, and d_{xy}^2 orbitals. The lowest unoccupied molecular orbital (LUMO, α -267) is primarily distributed over the imidazole ring and the aldehyde oxygens. The HOMO-LUMO gap for **1** is large (4.49 eV) indicating high stability [61,62].

4. Conclusion

In this study we have utilized 1-Tritylimidazole-4-carboxy-laldehyde (TrImA) to synthesize $[\text{Fe}(\text{TrImA})_2(\text{OTf})_2]$ (**1**) in good yield. Compound **1** possesses the first example of iron(II) bonded to an aldehydic oxygen. Variable temperature magnetic susceptibility measurements revealed **1** to be high spin between 300 K and 20 K. simulations of the data yield $g = 2.17$ and $D = 4.05 \text{ cm}^{-1}$. DFT studies reproduced metric parameters of **1** and indicated a high degree of stability for **1** likely due to the presence of two 5-membered chelate rings derived from TrImA ligands.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
X-ray crystal structure of [Fe(TrImA)₂(OTf)₂] (1) with thermal ellipsoids drawn at the 50% probability level. H atoms are excluded for clarity.

Fig. 2. Temperature-dependent molar magnetic susceptibility ($\chi_M T$) for [Fe (TrImA)₂(OTf)₂] (**1**) at $H = 0.6$ T.

Fig. 3.

Plots of molecular orbitals: HOMO-1, HOMO, LUMO, and LUMO+1 for [Fe(TrImA)₂(OTf)₂] (**1**). Orbital energies (eV) are indicated.

Scheme 1.

(a) Structure of 1-Tritylimidazole-4-carboxylaldehyde (TrImA) and (b) its iron(II) complex [Fe(TrImA)₂(OTf)₂] (1).

Table 1Crystallographic parameters for [Fe(TrImA)₂(OTf)₂] (**1**).

	1
Empirical formula	C ₄₈ H ₃₆ N ₄ O ₈ F ₆ S ₂ Fe
Formula weight	1030.81
Temperature/K	173.15
Wavelength (Å)	0.7103
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.8323(18)
<i>b</i> /Å	8.1606(13)
<i>c</i> /Å	24.818(4)
α /°	90
β /°	90.174(2)
γ /°	90
Volume/Å ³	2193.8(6)
<i>Z</i>	2
<i>D</i> _{calc} /Mg m ⁻³	1.5603
μ /mm ⁻¹	0.527
Goodness-of-fit on <i>F</i> ²	0.911
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0463, <i>wR</i> 2 = 0.1077
Final <i>R</i> indexes [all data]	<i>R</i> 1 = 0.0712, <i>wR</i> 2 = 0.1184

Table 2

Selected bond lengths (Å) and angles (°) for [Fe(TrImA)₂(OTf)₂] (1). Calculated values are in brackets.

<i>Distances</i>	
Fe1-O1 2.189(2) [2.258]	Fe1-N1 2.134(2) [2.140]
Fe1-O2 2.101(2) [2.048]	
<i>Angles</i>	
O1'-Fe1-O1 180.0	N1-Fe1-O1 78.85(9) [76.861]
O2-Fe1-O1 94.35(9) [93.029]	N1-Fe1-O2 95.04(9) [93.784]
O2'-Fe1-O1 85.65(9) [86.971]	N1'-Fe1-O2 84.96(9) [86.216]
O21-Fe1-O2 180.0	N1'-Fe1-N1 180.0
N1'-Fe1-O1 101.15(9) [103.130]	