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The Two Faces of Tetramethylcyclam in Iron Chemistry: Distinct Fe–O–M Complexes Derived from $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti/syn}})(\text{TMC})]^{2+}$ Isomers

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Abstract

Tetramethylcyclam (TMC, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) exhibits two faces in supporting an oxoiron(IV) moiety, as exemplified by the prototypical $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{NCCH}_3)](\text{OTf})_2$, where *anti* indicates that the O atom is located on the face opposite all four methyl groups, and the recently reported *syn* isomer $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O}_{\text{syn}})(\text{OTf})](\text{OTf})$. The ability to access two isomers of $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O}_{\text{anti/syn}})]$ raises the fundamental question of how ligand topology can affect the properties of the metal center. Previously, we have reported the formation of $[(\text{CH}_3\text{CN})-(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{anti}}-\text{Cr}^{\text{III}}(\text{OTf})_4(\text{NCCH}_3)]$ (**1**) by inner-sphere electron transfer between $\text{Cr}(\text{OTf})_2$ and $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{NCCH}_3)]-(\text{OTf})_2$. Herein we demonstrate that a new species **2** is generated from the reaction between $\text{Cr}(\text{OTf})_2$ and $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O}_{\text{syn}})(\text{NCCH}_3)]-(\text{OTf})_2$, which is formulated as $[(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{syn}}-\text{Cr}^{\text{III}}(\text{OTf})_4(\text{NCCH}_3)]$ based on its characterization by UV–vis, resonance Raman, Mössbauer, and X-ray absorption spectroscopic methods, as well as electrospray mass spectrometry. Its pre-edge area (30 units) and Fe–O distance (1.77 Å) determined by X-ray absorption spectroscopy are distinctly different from those

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ASSOCIATED CONTENT

Supporting Information

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Crystallographic data (CIF)

Crystallographic and structure refinement data for **4C1** and **5**; select bond lengths and angles for **4C1** and **5**; analysis on the decayed product of **1**; ¹⁹F NMR studies of **4OTf**; DFT calculations and geometric coordinates of **1** and **2** (PDF)

The authors declare no competing financial interest.

of **1** (11-unit pre-edge area and 1.81 Å Fe–O distance) but more closely resemble the values reported for [(TMC)Fe^{III}–O_{syn}–Sc^{III}(OTf)₄(NCCH₃)] (**3**, 32-unit pre-edge area and 1.75 Å Fe–O distance). This comparison suggests that **2** has a square pyramidal iron center like **3**, rather than the six-coordinate center deduced for **1**. Density functional theory calculations further validate the structures for **1** and **2**. The influence of the distinct TMC topologies on the coordination geometries is further confirmed by the crystal structures of [(Cl)(TMC)Fe^{III}–O_{anti}–Fe^{III}Cl₃] (**4**_{Cl}) and [(TMC)Fe^{III}–O_{syn}–Fe^{III}Cl₃](OTf) (**5**). Complexes **1–5** thus constitute a set of complexes that shed light on ligand topology effects on the coordination chemistry of the oxoiron moiety.

Graphical abstract

1. INTRODUCTION

Enzymes with dinuclear metallocofactors perform versatile functions in nature. In their catalytic cycles, the two metal ions are often connected through a bridging ligand with resulting cooperative effects. Oxo-bridged heterobimetallic species stand out as novel examples of this class and act as crucial intermediates in various bimetallic active sites. One example is the Mn–O–Ca unit found in the oxygen-evolving complex (OEC) of photosystem II (PS II) at which the O–O bond is proposed to form.^{1, 2} The other case is the Fe/Mn cofactor in class 1c ribonucleotide reductases from *Chlamydia trachomatis*.^{3, 4} The bimetallic center is proposed to react with O₂ to form an Fe^{III}–O–Mn^{IV} species that serves as the one-electron oxidant of the conserved cysteine residue required to initiate the conversion from ribonucleotides to deoxyribonucleotides.

For decades different strategies have been investigated to prepare synthetic (μ-oxo)–heterobimetallic molecules in order to improve our understanding of the structures and chemical properties of their analogues in nature. For example, Wieghardt reported a series of carboxylate-bridged (TACN)Fe^{III}–O–M(Me₃TACN) complexes (M = Cr^{III} or Mn^{III}, TACN = 1,4,7-triazacyclononane, Me₃TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane) by hydrolysis between FeCl₃(TACN) and MCl₃(Me₃TACN) precursors, where the bridging oxygen atom is derived from H₂O.⁵ In another case, the Que group prepared an [Fe^{II}Mn^{II}BPMP(O₂CCH₂CH₃)₂](BPh₄) compound (BPMP is the anion of 2,6-bis[(bis(2-pyridylmethyl)-amino)methyl]-4-methylphenol) by sequentially adding Fe and Mn salt into the solution with the BPMP ligand, and the Mn–O–Fe core is supported via a phenoxy bridge.⁶

More recently in 2010, Fukuzumi and Nam reported the crystal structure of a novel $[(\text{TMC})\text{Fe}-\text{O}_{\text{syn}}-\text{Sc}^{\text{III}}(\text{OTf})_4(\text{OH}_x)]$ complex (**3**), which was obtained from the reaction of $\text{Sc}(\text{OTf})_3$ with $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCCH}_3)]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).⁷ This structure sparked some controversy with respect to the iron oxidation state,⁸ which was assigned as +4 in the original report but was later revised to +3 after detailed spectroscopic characterization.⁹ Inspired by this result, we reported in 2015 the synthesis of $[(\text{CH}_3\text{CN})(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{anti}}-\text{Cr}^{\text{III}}(\text{OTf})_4(\text{NCCH}_3)]$ (**1**) from the reaction of $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCCH}_3)]^{2+}$ and 1 equiv of $\text{Cr}(\text{OTf})_2$ and were able to assign the Fe oxidation state as +3 unambiguously.¹⁰

The *anti* and *syn* subscripts in **1** and **3** reflect different orientations of the $\text{Fe}=\text{O}$ unit with respect to the methyl groups of the TMC ligand. In **1** the methyl groups of the TMC ligand are presumed to be *anti* to the oxo bridge because the complex was generated from $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCCH}_3)]^{2+}$ in a rapid reaction with $\text{Cr}(\text{OTf})_2$. In contrast, the crystal structure of **3** shows the methyl groups of the TMC ligand to be oriented *syn* to the oxo bridge. The difference in the orientations of the TMC methyl groups in **1** and **3** directly affects the coordination sphere of the Fe center as well as the Fe–O distance. Recently, our group reported $[\text{Fe}^{\text{IV}}(\text{O}_{\text{syn}})(\text{TMC})(\text{OTf})](\text{OTf})$, in which the methyl groups on the ligand are oriented *syn* to the oxo moiety.¹¹ Inspired by the successful generation of **1** from $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCCH}_3)]^{2+}$ and $\text{Cr}(\text{OTf})_2$, we report herein the reaction between $[\text{Fe}^{\text{IV}}(\text{O}_{\text{syn}})(\text{TMC})(\text{NCCH}_3)](\text{OTf})_2$ and $\text{Cr}(\text{OTf})_2$ to form a new species, **2**. UV–vis, resonance Raman, Mössbauer, and X-ray absorption spectroscopic methods, as well as electrospray mass spectrometry, were used to confirm **2** as $[(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{syn}}-\text{Cr}^{\text{III}}(\text{OTf})_4(\text{NCCH}_3)]$, in which the TMC methyl groups are *syn* to the oxo bridge and the Fe center is five-coordinate, while in **1** the TMC methyl groups are *anti* to the oxo bridge and the Fe center is six-coordinate. The correlation between orientation of the TMC methyl groups and the coordination number of the metal center is further clarified with crystallographically characterized complexes $(\text{Cl})(\text{TMC})\text{-Fe}^{\text{III}}\text{-O}_{\text{anti}}\text{-Fe}^{\text{III}}\text{Cl}_3$ (**4_{Cl}**) and $[(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{syn}}\text{-Fe}^{\text{III}}\text{Cl}_3](\text{OTf})$ (**5**). All these results provide insight into how ligand topology can affect the coordination spheres of the metal sites (Figure 1).

2. EXPERIMENTAL SECTION

2.1. Materials

All reagents and solvents were purchased from commercial sources and used as received unless specified. The preparations for $\text{Cr}(\text{OTf})_2 \cdot 2\text{CH}_3\text{CN}$,¹⁰ $\text{Fe}^{\text{II}}(\text{TMC})(\text{OTf})_2$,¹² iodosylbenzene ($\text{C}_6\text{H}_5\text{IO}$),¹³ and 2-(*tert*-butylsulfonyl)iodosylbenzene ($2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_4\text{IO}$)^{14, 15} were carried out following published procedures. (**Caution:** An injury was recently reported while attempting to synthesize $2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_4\text{IO}$,¹⁶ so this synthetic procedure should be carried out with the appropriate safety precautions and protective equipment).¹⁷ The ^{18}O -labeled isotopomer of 2-(*tert*-butylsulfonyl)-iodosylbenzene was synthesized according to the published procedure.¹⁸ All moisture- and oxygen-sensitive compounds were prepared using standard Schlenk-line techniques.

Complexes **4_{Cl}** and **4_{OTf}** were obtained by the following procedures: The oxoiron(IV) species $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCCH}_3)]^{2+}$ was generated by vigorously stirring an acetonitrile solution of $\text{Fe}^{\text{II}}(\text{TMC})-(\text{OTf})_2$ (25 mg in 2 mL, 0.04 mmol) with 2 equiv of solid $\text{C}_6\text{H}_5\text{IO}$ (~17 mg, 0.08 mmol) at room temperature. The unreacted insoluble $\text{C}_6\text{H}_5\text{IO}$ particles were then removed from the solution by filtration using a PTFE syringe filter. One equivalent of $\text{Et}_4\text{NFe}^{\text{III}}\text{Cl}_4$ (13.5 mg, 0.04 mmol, dissolved in acetonitrile) was then added to the solution, and the solution was placed in a diethyl ether bath at $-20\text{ }^\circ\text{C}$ for crystallization. A crystalline solid was obtained within 1 week in 50–60% yield, which was used for NMR and IR analysis. Elemental analysis data obtained from this solid was consistent with its formulation as $(\text{TfO})(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{anti}}-\text{Fe}^{\text{III}}\text{Cl}_3$, so this solid was designated as **4_{OTf}**. Anal. Calcd for $\text{C}_{15}\text{H}_{32}\text{Cl}_3\text{F}_3\text{Fe}_2\text{N}_4\text{OSS}$ (**4_{OTf}**): C, 28.17; H, 5.04; N, 8.76; Cl, 16.63. Found: C, 28.68; H, 5.03; N, 8.74; Cl, 16.15. The ^{18}O -labeled **4_{OTf}** was obtained in an analogous manner using $\text{C}_6\text{H}_5\text{I}^{18}\text{O}$ as an oxidant. However, the single crystal selected for X-ray diffraction analysis was found to possess a composition of $(\text{Cl})(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{anti}}-\text{Fe}^{\text{III}}\text{Cl}_3$ and designated as **4_{Cl}**.

Complex **5** was prepared by following the same procedure except that the oxoiron(IV) species $[\text{Fe}^{\text{IV}}(\text{O}_{\text{syn}})(\text{TMC})(\text{NCCH}_3)]^{2+}$ was generated by adding 1 equiv of $2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_4\text{IO}$ (dissolved in trifluoroethanol) to the acetonitrile solution of $\text{Fe}^{\text{II}}(\text{TMC})(\text{OTf})_2$ at room temperature. Yield = 50–60%. Anal. Calcd for $\text{C}_{15}\text{H}_{32}\text{Cl}_3\text{F}_3\text{Fe}_2\text{N}_4\text{O}_4\text{S}$: C, 28.17; H, 5.04; N, 8.76. Found: C, 27.72; H, 5.16; N, 8.57. ^{18}O -labeled **5** was obtained in an analogous manner using $2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_5\text{I}^{18}\text{O}$ as an oxidant.

2.2. Instrumentation

Elemental analyses were carried out by Atlantic Microlab (Norcross, GA, USA). UV–vis absorption spectra were recorded on an HP 8453A diode array spectrometer. Low-temperature visible spectra were obtained using a cryostat from UNISOKU Scientific Instruments, Japan. Electrospray mass spectrometry was performed on a Finnigan LCQ ion trap mass spectrometer. FTIR measurements were performed using a Thermo Scientific (Nicolet iS5) spectrometer equipped with a diamond ATR module (iD5). Resonance Raman and Raman spectra were collected with an Acton AM-506 monochromator equipped with a Princeton LN/CCD data collection system, with 514.5 nm excitation from a Spectra-Physics model 2060 argon-ion laser or with 515 nm excitation from a 50 mW laser by Cobolt Lasers, Inc. Spectra in acetonitrile were obtained at 77 K using a 135° backscattering geometry. Raman samples were prepared in cuvettes in a $-40\text{ }^\circ\text{C}$ cold bath and quickly transferred to and frozen in EPR tubes. Raman bands were calibrated to indene prior to data collection. The monochromator slit width was set for a band-pass of 4 cm^{-1} for all spectra. Mössbauer spectra were recorded with home-built spectrometers using Janis Research Super-Vartemp dewars. Mössbauer spectral simulations were performed using the WMOSS software package (SEE Co., Edina, MN, USA). Isomer shifts are quoted relative to Fe metal at 298 K. All Mössbauer figures were prepared using SpinCount software.¹⁹

2.3. X-ray Absorption Spectroscopy (XAS)

XAS data were collected at Beamline 7–3 at the Stanford Synchrotron Radiation Lightsource (SSRL) of SLAC National Accelerator Laboratory. Fe K-edge XAS data were collected for frozen solutions maintained at ~10 K over the energy range of 6.9–8.0 keV. An

Fe foil spectrum was measured simultaneously for internal energy calibration using the first inflection point of the K-edge energy (7112.0 eV). Data were obtained as fluorescence excitation spectra using a solid-state germanium detector (Canberra).

Data reduction, averaging, and normalization were performed using the program EXAFSPAK.²⁰ The coordination number of a given shell was a fixed parameter and was varied iteratively in integer steps while the bond lengths (R) and mean-square deviation (σ^2) were allowed to freely float. The amplitude reduction factor was fixed at 0.9 while the edge-shift parameter E_0 was allowed to float as a single value for all shells. The pre-edge features were fitted using the Fityk²¹ program with pseudo-Voigt functions composed of 50:50 Gaussian/Lorentzian functions.

2.4. X-ray Crystallography

Selected single crystals of **4**_{Cl} or **5** were placed onto the top of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX II area detector diffractometer for data collection at 173(2) K.²² The structures were solved and refined using the SHELXL software package and ShelXle graphical user interface.^{23, 24} Additional crystallographic details may be found in the cif files, CCDC numbers 1503819 and 1503820.

2.5. Computational Details

Geometry optimizations were carried out using Turbomole 7.0.1.^{25–27} Starting geometries were based on crystallographic data of complexes **4**_{Cl} and **5**, the previously reported crystal structure of the Fe–O–Sc complex (CCDC 742067),⁷ or combinations thereof. Geometries were optimized using the TPSS²⁸ functional in combination with Grimme's D3²⁹ dispersion correction including Becke–Johnson damping.³⁰ The def2-TZVP³¹ basis set was used for all atoms. Calculations were accelerated using the multipole accelerated resolution of the identity approximation (MARI-J)³² using the appropriate fitting basis set.³³ The conductor-like screening model (COSMO)³⁴ was used with $\epsilon = 35.88$ ³⁵ to mimic CH₃CN solvation. Grid 5 of Turbomole was used in all calculations. For complexes where the two metal centers interact in an antiferromagnetic fashion, a broken symmetry formalism^{36, 37} was used.

Mössbauer parameters were computed using calibration data reported by Römel't et al.³⁸ For this purpose, geometries were optimized using the BP86^{39–41} functional in combination with the def-TZVP⁴² basis set, def-TZVP/J⁴³ fitting basis set, COSMO ($\epsilon = 80$), and grid 5 using Turbomole 7.0.1. Single-point calculations were subsequently carried out in ORCA 3.0.3 using the B3LYP functional in combination with the def-TZVP basis set for all elements except Fe, where the CP(PPP)^{44, 45} basis set was used. In these single-point calculations, grid 7 was used for the Fe atom, grid 5 for all other atoms, and the predefined settings for water were used for COSMO.

For all geometries, numerical second derivatives were computed at the appropriate level of theory and showed no imaginary frequencies. Absolute energies quoted for solvated systems include an outlying charge correction.⁴⁶ Population analyses and structural depictions were made using IboView.^{47–49}

3. RESULTS AND DISCUSSION

3.1. Generation of $[(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_{\text{syn}}-\text{Cr}^{\text{III}}(\text{OTf})_4(\text{NCCH}_3)]$ (**2**)

Following the reported procedure,¹¹ a 0.35 mM solution of $[\text{Fe}^{\text{IV}}(\text{O}_{\text{syn}})(\text{TMC})(\text{NCCH}_3)](\text{OTf})_2$ was first generated by adding 1 equiv of $(2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_4\text{IO})$ (dissolved in trifluoroethanol) to the acetonitrile solution of the iron(II)-precursor complex $\text{Fe}^{\text{II}}(\text{TMC})(\text{OTf})_2$ at $-40\text{ }^\circ\text{C}$. The addition of 1 equiv of $\text{Cr}(\text{OTf})_2$ into the oxoiron(IV) solution resulted in the immediate disappearance of its characteristic 815 nm near-IR band, concomitant with the growth of bands at 395, 446, 515, and 560 nm, indicating the formation of a new species (**2**, Figure 2). The bands at 395, 446, and 560 nm resemble those reported for the closely related complex **1** at 397, 447, and 558 nm, which is generated from the reaction of $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCCH}_3)](\text{OTf})_2$ with $\text{Cr}(\text{OTf})_2$, but the 515 nm band of **2** is unique. The similarity in chromophores reflects the structural similarities between **1** and **2**.

To test our hypothesis that **2** has an Fe–O–Cr core similar to **1**, an aliquot of a solution of **2** was subjected to analysis by electrospray ionization mass spectrometry (ESI-MS). A peak at $m/z + 827.0$ was observed and assigned as $[(\text{TMC})\text{FeO}(\text{Cr}(\text{OTf})_3)]^+$ based on its mass and isotope distribution pattern. This peak was shifted to $m/z + 829.0$ when $2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_4\text{I}^{18}\text{O}$ was used to introduce the ^{18}O isotope (Figure 3). The ESI-MS spectra and the isotope labeling results support the presence of an Fe–O–Cr core in **2**.

While complex **2** is stable at room temperature, complex **1** exhibits a half-life of only 30 min under the same conditions. The latter observation is in agreement with the fact that in the ESI-MS spectrum of **1** only the fragment ion peaks $[\text{Fe}^{\text{II}}(\text{TMC})(\text{OTf})]^+$ and $[\text{Cr}^{\text{IV}}\text{O}(\text{OTf})_3]^-$ were found,¹⁰ while the molecular ion peak $[(\text{TMC})\text{FeO}(\text{Cr}(\text{OTf})_3)]^+$ was detected in the ESI-MS spectrum of **2**. These results suggest that the homolysis of the Fe–O bond in **1** is more facile than for **2**. To test this hypothesis, an excess of PhIO was added into the decay product of **1**, and 90% of $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCCH}_3)](\text{OTf})_2$ was recovered based on the peak growth at 824 nm (Figure S1), confirming that the decay product of **1** is $\text{Fe}^{\text{II}}(\text{TMC})(\text{OTf})_2$ from the homolytic dissociation of its Fe–O bond.

3.2. Resonance Raman Results

Complex **2** was further studied by resonance Raman spectroscopy to gain insight into its Fe–O–Cr core. A resonance-enhanced peak at 877 cm^{-1} was observed upon 514.5 nm excitation (Figure 4). This vibration falls within the $700\text{--}900\text{ cm}^{-1}$ range typically found for the $\nu_{\text{as}}(\text{Fe}=\text{O}-\text{Fe})$ features of other oxo-bridged diiron(III) complexes.⁵⁰ This assignment is corroborated by the observed downshift of the peak from 877 to 832 cm^{-1} upon substitution of ^{18}O into the oxo bridge. The 45 cm^{-1} experimental downshift is slightly larger than the 40 cm^{-1} downshift predicted by Hooke's law based on a diatomic Fe–O model, but similar cases have been reported for the corresponding vibrations in several other oxo-bridged diiron(III) complexes.⁵⁰ The $\nu_{\text{as}}(\text{Fe}=\text{O}-\text{Cr})$ of **2** is over 100 cm^{-1} higher than that of **1** at 770 cm^{-1} ,¹⁰ indicating a stronger bonding interaction in the Fe–O–Cr core of **2**. Complementary to these data is the $\nu_{\text{as}}(\text{Fe}=\text{O}-\text{Sc})$ mode of **3** at 878 cm^{-1} obtained by Raman spectroscopy with 515 nm laser excitation. This frequency is essentially identical to

that of **2**, suggesting that this feature derives from a common (TMC)Fe^{III}-O_{syn}-M unit found in complexes **2** and **3** (Figure 4).

3.3. Mössbauer Spectroscopy of **1** and **2**

In order to confirm the oxidation state of the iron center and the influence of the ligand conformation, we obtained the Mössbauer spectra of **1** and **2** (Figure 5) showing quadrupole doublets at zero applied field for both complexes. Complex **1** has an isomer shift δ of +0.53 mm s⁻¹ and a quadrupole splitting $|E_Q|$ of 0.87 mm s⁻¹, while **2** has a δ of +0.44 mm s⁻¹ and a $|E_Q|$ of 0.89 mm s⁻¹. We found that the Mössbauer spectrum of **2** also contained ca. 20% of **1**, which derives from ~17% [Fe^{IV}(O_{anti})(TMC)-(NCCH₃)](OTf)₂ contaminant present in the generation of [Fe^{IV}(O_{syn})(TMC)(NCCH₃)](OTf)₂.¹¹ Although the isomer shift values of **1** and **2** both fall within the range typical of highspin Fe^{III} species, the observation of quadrupole doublets for **1** and **2** at 4.2 K indicates that they both have an integer spin ground state ($S = 0, 1, 2, \dots$), presumably from coupling to the associated Cr^{III} center. Furthermore, the difference in their isomer shifts of 0.09 mm s⁻¹ suggests that the iron centers in the two complexes differ somewhat in their electronic structures. More interestingly, the isomer shift found for **2** is halfway between the values for **1** and **3**.⁹ However, the magnitude of the coupling constant J cannot be reliably determined, because Mössbauer measurements at higher temperature (up to 180 K) and high applied fields (up to 7 T) show that the electronic systems of these compounds still exhibit intermediate magnetic relaxation.

3.4. XAS Analysis of **2**

Fe K-edge XAS measurements were conducted in order to obtain more structural information on **2**. The Fe K-edge of **2** is observed at 7123.6 eV, which is comparable to the value found for **1** (7124.0 eV)¹⁰ and within the range typical for Fe(III) species.⁵¹ The XAS sample of **2** also exhibits a pre-edge feature at 7113.0 eV (Figure 6), which is fitted with two peaks providing a total area of 26 units, a value that increases to 30 units when the contribution of 20% **1** in the sample is taken into account (Figure 5). These peaks are associated with the 1s-to-3d transitions of the iron(III) center, and the total area reflects the extent to which the iron(III) center is distorted from centrosymmetry.⁵² For comparison, the pre-edge areas reported for **1** and **3** are 11 and 32, respectively.^{9, 10} The much smaller pre-edge area found for **1** is rationalized by the presence of an axial CH₃CN ligand that makes its iron(III) center six-coordinate, while that of **3** has a much higher value because of its square pyramidal iron(III) center. Thus, the comparable pre-edge areas of **2** and **3** strongly suggest that they share a common square pyramidal iron(III) center.

The Fourier-transformed extended X-ray absorption fine structure (EXAFS) region of **2** revealed two prominent features at $r' \approx 1.8$ and 3.2 Å (Figure 7). The best fit of the data consists of one O/N scatterer at 1.77 Å, four O/N scatterers at 2.16 Å, four C scatterers at 2.99 Å, and one Cr scatterer at 3.58 Å (fit #6 in Table 1). In contrast, the best fit for the EXAFS data of **1** shows one O/N scatterer at 1.81 Å, five O/N scatterers at 2.17 Å, four C scatterers at 2.92 Å, and one Cr scatterer at 3.65 Å.¹⁰ The shorter Fe–O distance in **2** (1.77 Å) relative to that in **1** (1.81 Å) is consistent with the absence of an axial ligand *trans* to the oxoiron center in the former. Also, the shorter Fe–O and Fe...Cr distances in **2** than those in

1 indicate a stronger bonding interaction in the Fe–O–Cr core, consistent with the Raman results (Section 3.2). In fact, the dimensions of the Fe–O–Cr core in **2** closely resemble those of the crystallographically characterized Fe–O–Sc core in **3**^{7, 9} (Table 2). As **2** is generated immediately upon reaction of [Fe^{IV}(O_{syn})(TMC)-(NCCH₃)](OTf)₂ with Cr(OTf)₂, it is likely that the TMC methyl groups in **2** remain *syn* to the oxo bridge, like those found in **3** but different from those in **1**, where the TMC methyl groups are *anti* to the oxo bridge (Figure 1). Thus, **2** and **3** would appear to be structurally quite closely related.

3.5. Characterization of (X)(TMC)Fe–O_{anti}–FeCl₃ (**4**_{Cl} and **4**_{OTf}) and [(TMC)Fe–O_{syn}–FeCl₃](OTf) (**5**)

Despite our detailed characterization efforts on **1** and **2**, we were not able to obtain crystals suitable for X-ray crystallography. As an alternative, we have obtained the crystal structures of (Cl)(TMC)Fe–O_{anti}–FeCl₃ (**4**_{Cl}) and [(TMC)Fe–O_{syn}–FeCl₃](OTf) (**5**) (Figure 8), both of which are stable at room temperature. These complexes were obtained from the respective reactions of [Fe^{IV}(O_{anti/syn})(TMC)(NCCH₃)]²⁺ isomers with FeCl₄[–]. Key structural parameters compared in Table 2 show that the structural deductions made for the **1/2** pair are consistent with the crystallographic data obtained for the **4**_{Cl}/**5** pair.

Several points can be made based on structural comparisons among complexes **1–5**. (i) In the crystal structure of **4**_{Cl}, the TMC methyl groups are oriented in an *anti* fashion with respect to the oxo bridge and the Fe center is six-coordinate, while in the crystal structure of **5** the TMC methyl groups are *syn* to the oxo bridge and the Fe center is five-coordinate. These results confirm the correlation between the orientation of the Fe=O unit relative to the TMC methyl groups and the coordination number of the iron center found for (TMC)Fe–O–M complexes **1**, **2**, and **3**. (ii) The Fe_{TMC}–O distance in **4**_{Cl} is significantly longer (~0.1 Å) than that in **5**, which can be attributed to the presence of an axial chloride ligand in **4**_{Cl}. (iii) The Fe(III) ion bound to the TMC ligand in **5** is much farther away from the mean N4 plane of the TMC framework (0.50 Å) than that in **4**_{Cl} (0.044 Å), but comparable to that in **3** (0.53 Å). The longer Fe–N4 plane distance reflects a higher degree of distortion from centrosymmetry resulting from the square pyramidal Fe centers in **3** and **5**.

This structural pattern can also be discerned in the only two other Fe^{III}(TMC) complexes that are crystallographically characterized. The six-coordinate (Me₃cyclam-acetate)Fe–O–FeCl₃ (**6**) reported by Wieghardt and co-workers in 2006⁵³ (Figure 9) exhibits features between those of **4**_{Cl} and **5** but closer to the former (Figure 9). Complex **6** has an Fe_{TMC}–O distance of 1.801 Å and an Fe–N4 plane distance of 0.196 Å. These intermediate values may be rationalized by the fact that **6** has two *syn* methyl groups and two *anti* alkyl groups (Table 2), resulting in effects in between those from a fully *anti* set versus a fully *syn* set of alkyl groups. On the other hand, the Fe–N4 plane distance for [Fe^{III}(η²⁺-O₂)(TMC)]⁺ is 0.644 Å,⁵⁴ so the side-on-bound peroxo ligand pulls the Fe even further away from the mean N4 plane of the TMC macrocycle.

An additional structural feature that divides the above complexes into two subsets is the relative orientation of the two –CH₂–CH₂– units connecting the amine donors in the cyclam rings. The ethylene linkers in **4**_{Cl} are related to each other by a pseudomirror plane, while

those in **3** and **5** are related by a pseudo-2-fold axis (Figure 8, right). Interestingly, the ethylene groups of the cyclam ring in **6** are oriented parallel to each other, like those of **4_{Cl}**, while those of $[\text{Fe}^{\text{III}}(\eta^{2+}\text{-O}_2)(\text{TMC})]^+$ are crossed like those found in **3** and **5**. Furthermore, the ethylene group orientations in $\text{Fe}^{\text{II}}(\text{TMC})(\text{X})$ complexes, which are all five-coordinate, are similar to those of **3** and **5**,^{55–57} while the ethylene group orientations for both *syn* and *anti* isomers of $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{L})]^{2+}$, which are both six-coordinate, are similar to those found in **4_{Cl}**.^{11, 12} So this structural feature likely reflects the Fe–N4 plane distance and the TMC macrocycle conformation required to support this distance.

Therefore, the XRD results of **3**, **4_{Cl}**, and **5** support the proposed structures for **1** and **2** and further illustrate how the orientation of the Fe=O unit relative to the TMC methyl groups affects the parameters of the Fe–O–M core.

As noted in the Experimental Section, a single crystal of **4_{Cl}** was analyzed by X-ray diffraction. However, based on the elemental analysis, the bulk crystalline solid was best characterized as **4_{OTf}**. To assess whether the triflate ion in **4_{OTf}** is bound as a ligand or simply a counterion, ¹⁹F NMR studies were performed on a CD₃CN solution of the bulk crystalline solid. The ¹⁹F NMR spectrum of **4_{OTf}** displays a signal corresponding to the presence of an OTf[–] ion in the solution with a chemical shift close to that observed for free OTf[–] ion in the solution, but its line width was found to be 32 Hz (vs 5 Hz for free OTf[–] ion), suggesting that either this OTf[–] ion is bound to the Fe center in **4_{OTf}** or it is in a rapid exchange equilibrium with CD₃CN solvent. Addition of 10 equiv of triflate ion to this solution led to the sharpening of the peak from 32 to 18 Hz in support of the latter scenario (Figure S2). We have made several attempts to obtain diffraction-quality crystals of **4_{OTf}**, but these efforts have thus far been unsuccessful. Clearly, the crystal of **4_{Cl}** picked out for X-ray diffraction analysis was unrepresentative of the bulk solid. Nevertheless, the obtained crystal structure of **4_{Cl}** provides the information needed for a structural comparison with **5**.

As additional characterization, infrared spectroscopic data were collected on solid samples of **4_{OTf}** and **5**, together with corresponding ¹⁸O isotopomers (Figure 10). Complex **4_{OTf}** exhibits a peak at 800 cm^{–1}, which shifts to 768 cm^{–1} upon ¹⁸O-labeling of the oxo bridge, while **5** shows a peak at 888 cm^{–1}, which shifts to 839 cm^{–1} in its ¹⁸O isotopomer. These features are analogous to those obtained from resonance Raman experiments on **1** and **2** (section 3.2), which reveal respective resonance-enhanced vibrations at 770 and 877 cm^{–1} assigned as $\nu_{\text{as}}(\text{Fe–O–Cr})$ modes. Due to the structural similarities between **1** and **4_{OTf}** and between **2** and **5**, the 800 cm^{–1} peak in **4_{OTf}** and the 888 cm^{–1} peak in **5** are both assigned as $\nu_{\text{as}}(\text{Fe–O–Fe})$ modes. The higher frequency of the $\nu_{\text{as}}(\text{Fe–O–Fe})$ feature in **5** can be rationalized by the shorter (TMC)Fe–O and Fe...Fe distances determined by XRD.

3.6. Computational Studies

To further validate our structural models, as depicted in Figure 1, we carried out density functional theory (DFT) calculations on various structures. At the TPSS-D3(BJ)/def2-TZVP/COSMO ($\epsilon = 35.88$) level of theory, we obtained Fe–O distances of 1.824 Å for **1** and 1.759 Å for **2** and Fe–O–Cr bond angles of 177° for **1** and 173° for **2** (for structural depictions see Figure 11 (A and B)). For complex **2** the Fe–O distance is significantly shorter because of

the five-coordinate nature of the Fe atom in this complex. The structural features of complex **2** are therefore in close agreement with those of the previously reported Fe^{III}–O–Sc^{III} complex **3**, which also shows a nearly linear Fe–O–Sc unit; computed values for **3** at the same level of theory can be found in the Supporting Information and agree well with values predicted by Swart.⁸

Unlike in the Fe–O–Sc complex **3**, the electronic structures of the Fe–O–Cr dimers are substantially different due to the open-shell character of the Cr^{III} unit. Thus, the Fe^{III} and the Cr^{III} atoms constitute an antiferromagnetically coupled $S = 5/2$ high-spin Fe^{III} center and $S = 3/2$ Cr^{III} center, leading to an overall spin state of $S = 1$. This electronic structure is well reflected in the spin density plots shown in Figure 11 (C and D). For comparison we also computed structures with ferromagnetically coupled configurations, but these spin states were found to be higher in energy, and optimized geometries did not agree well with experimentally determined distances (see Supporting Information). In contrast, the structural parameters computed for the antiferromagnetically coupled spin states are in excellent agreement with the bond distances determined from EXAFS, in further support of our structural assignment (see Table 2). The isomer shift values in **1** and **2** both fall in the range of typical high-spin Fe^{III} species and are readily reproduced computationally at the B3LYP/def-TZVP-(Fe:CP(PPP))/BP86/def-TZVP level of theory including COSMO H₂O solvation based on our structural models described before using calibration data by Römelt et al.³⁸ (see Table 2).

4. CONCLUSION

In this study we have compared two pairs of oxo-bridged bimetallic complexes obtained (**1** and **2**, **4**_{Cl}/**4**_{OTf} and **5**) from the reactions of Cr(OTf)₂ or Et₄NFe^{III}Cl₄ with two (TMC)-Fe^{IV}(O_{anti/syn}) isomers. Complex **1** has been assigned in a previous report as [(CH₃CN)(TMC)Fe^{III}–O_{anti}–Cr^{III}–(OTf)₄(NCCH₃)], and **2** is identified in this paper as [(TMC)Fe^{III}–O_{syn}–Cr^{III}(OTf)₄(NCCH₃)] based on UV–vis, resonance Raman, Mössbauer, and X-ray absorption spectroscopic data, as well as electrospray mass spectrometry. In addition, the structures of **4**_{Cl} ((Cl)(TMC)Fe–O_{anti}–FeCl₃) and **5** ((TMC)Fe–O_{syn}–FeCl₃(OTf)) have been determined by X-ray crystallography. On the basis of these studies, the key factor linking the (TMC)Fe–O–M species listed above is the orientation of the methyl groups of the TMC framework relative to the oxo bridge. This characteristic affects three features of the (TMC)Fe–O–M complexes: (i) the coordination number of the Fe site, (ii) the Fe_{TMC}–O distance, (iii) the Fe–N₄ plane distance. When the TMC methyl groups are *syn* to the oxo bridge in the (TMC)Fe–O–M species, the iron center favors a square pyramidal geometry, resulting in a shorter Fe_{TMC}–O distance and a longer distance of the Fe from the mean N₄ plane of the TMC framework. In contrast, when the TMC methyl groups are *anti* to the oxo bridge, the iron center prefers to be six-coordinate, with a longer Fe–O distance and a shorter distance from the mean N₄ plane of the TMC framework. These results emphasize the importance of the ligand topology in determining the coordination sphere of the iron center. Future work will focus on the consequences of replacing the methyl groups of the TMC ligand with other R groups such as the benzyl groups introduced by Nam⁵⁸ on the relative stabilities of the *syn* and *anti* isomers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Structures of complexes 1–5. An asterisk indicates that XRD data have been obtained to determine the structures of these complexes.

Figure 2. UV-vis absorption spectra of (black) 0.35 mM **1** and (red) 0.35 mM **2** in CH₃CN at -40 °C.

Figure 3.

ESI-MS spectral features of **2**. (A) Isotope pattern for the $[(\text{TMC})\text{Fe}^{16}\text{OCr}(\text{OTf})_3]^+$ ion ($m/z + 827$); (B) isotope pattern for the $[(\text{TMC})\text{Fe}^{18}\text{OCr}(\text{OTf})_3]^+$ ion ($m/z + 829$). Based on the intensity ratio between the $m/z + 827$ and $+829$ peaks, the latter sample contains approximately 25% of the $[(\text{TMC})\text{Fe}^{16}\text{OCr}(\text{OTf})_3]^+$ isotopomer, which may arise from incomplete ^{18}O labeling of the $2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_4\text{I}^{18}\text{O}$ oxidant.

Figure 4.

(Top) Resonance Raman spectra of **2** (5 mM) in CH_3CN ($\lambda_{\text{ex}} = 514.5$ nm, 20 mW, 77 K). Black: ^{16}O ; red: ^{18}O . The residual 877 cm^{-1} peak found in ^{18}O -labeled **2** indicates the presence of ^{16}O -labeled **2**, which likely comes from residual $2\text{-}^t\text{BuSO}_2\text{-C}_6\text{H}_4\text{I}^{16}\text{O}$ in the ^{18}O -labeled oxidant used for the preparation of **2**. (Bottom) Raman spectra for **3** (12 mM) in CD_3CN obtained with $\lambda_{\text{ex}} = 515$ nm and 50 mW power at 77 K (black, pure CD_3CN ; red, ^{16}O isotopomer). Asterisks denote solvent peaks.

Figure 5.

(A) Mössbauer spectrum (black) of **1** and the corresponding fitting curve (red) with $\delta = +0.53$ mm/s, $|E_Q| = 0.87$ mm/s. (B) Mössbauer spectrum (black) of **2** and the corresponding fitting curve (red) with $\delta = +0.44$ mm/s, $|E_Q| = 0.89$ mm/s. The fit is improved with the inclusion of a 20% contribution from **1**.

Figure 6.

Pre-edge region of the Fe K-edge XAS spectrum of **2** (black squares): rising-edge fit (red circles), pre-edge peak 1 (blue triangles pointing up, maximum at 7113.7 eV), pre-edge peak 2 (magenta triangles pointing down, maximum at 7113.0 eV), pre-edge fit (green diamonds), residuals (gray triangles pointing left).

Figure 7.

Fourier-transformed Fe K-edge EXAFS data for **2** (dotted black) and the corresponding best fit (solid red, fit #6 in Table 1). Inset: Unfiltered k-space data (dotted black) and its fit (solid red).

Figure 8.

(Left) ORTEP plots for $(\text{Cl})(\text{TMC})\text{Fe}-\text{O}_{\text{anti}}-\text{FeCl}_3$ (**4_{Cl}**) and $[(\text{TMC})\text{Fe}-\text{O}_{\text{syn}}-\text{FeCl}_3](\text{OTf})$ (**5**) at 50% probability. H atoms, solvent molecules, and a counterion (in **5**) have been omitted for clarity. The R_1 values for structures **4_{Cl}** and **5** are 0.023 and 0.048, respectively (CCDC numbers 1503819 and 1503820). The structure of **5** was modeled over two positions with a 90° rotation along the Fe–O–Fe axis. (Right) Conformations of the cyclam rings in **4_{Cl}** and **5**. Red color highlights the different orientations of the two NCH₂–CH₂N bonds relative to each other in each cyclam ring (parallel in **4_{Cl}** and crossed in **5**).

Figure 9.
Structural comparison of complexes 4_{Cl}, 5, and 6.

Figure 10.

(Top) Infrared spectroscopic data for **4**_{OTf} (black, ^{16}O isotopomer; red, ^{18}O isotopomer).
Bottom: Infrared spectroscopic data for **5** (black, ^{16}O isotopomer; red, ^{18}O isotopomer).

Figure 11.

(A and B) Computed geometries for **1** and **2** at the TPSSD3(BJ)/def2-TZVP/COSMO ($\epsilon = 35.88$) level of theory. (C and D) Spin density plots of **1** and **2**. (The purple color depicts positive spin density, and green, negative spin density; isosurface 0.005.) H atoms have been omitted for clarity.

Table 1

Fit Parameters for 2 Based on Unfiltered Data from $k = 2\text{--}15 \text{ \AA}^{-1a}$

fit	Fe-N/O			Fe-N/O			Fe...C			Fe...Cr			E_0	F	F'
	N	R ($\text{\AA}$)	$\sigma^{2+} \times 10^{-3}$	N	R ($\text{\AA}$)	$\sigma^{2+} \times 10^{-3}$	N	R ($\text{\AA}$)	$\sigma^{2+} \times 10^{-3}$	N	R ($\text{\AA}$)	$\sigma^{2+} \times 10^{-3}$			
1	4	2.16	3.14										-10.7	528	644
2	5	2.15	4.27										-10.6	522	640
3	4	2.16	3.16	1	1.77								-6.85	470	608
4	4	2.16	3.19	1	1.77	4.07	4	2.94	8.54				-8.25	423	576
5	4	2.15	3.14	1	1.76	4.83	4	2.94	7.99	1	3.64	-0.2	-9.69	198	394
6	4	2.16	3.28	1	1.77	4.12	4	2.99	9.36	1	3.58	1.33	-6.47	198	394

^aScale factor $S_0^{2+} = 0.9$, GOF = goodness-of-fit calculated as $F = \sqrt{\sum k^6 (\chi_{\text{exp}} - \chi_{\text{calc}})^2} / \sum k^6 \chi_{\text{exp}}^2$. F' indicates the Fe...Cr distance obtained from a double scattering pathway.

Table 2

Spectroscopic and Structural Comparisons of Complexes 1–5

	1	2	3 ^a	4 ^c	5	6 ^b
orientation of the TMC methyl groups to the oxo bridge	<i>anti</i>	<i>syn</i>	<i>syn</i>	<i>anti</i>	<i>syn</i>	
coordination number of the Fe ^{III} (TMC) site	6	5	5	6	5	6
rR or IR peak (¹⁸ O shift) (cm ⁻¹)	773 (-43)	877 (-45)	878	800 (-32) ^a	888 (-49)	N.D.
Mössbauer parameters (δ [E_Q]) of the Fe(TMC) fragment (mm/s)	+0.53	+0.44	+0.36	N.D.	N.D.	
	(+0.50) ^b	(+0.42) ^b	(+0.35) ^b			+0.44 ^f
	[0.87] ^c	[0.89] ^c	[-1.02]			[+1.46] ^f
XANES K-edge energy (eV)	7124.0	7123.6	7122.6	N.D.	N.D.	N.D.
XANES pre-edge area (units)	11	30	32	N.D.	N.D.	N.D.
Fe _{TMC} -N4 plane distance (Å)	N.D.	N.D.	0.53	0.044	0.50 ^e	0.196
Fe–O distance (Å)	(0.192) ^d	(0.554) ^d	(0.550) ^d	(0.061) ^d	(0.515) ^d	1.802
	1.81	1.77	1.748(5)	1.8510(12)	1.742(3) ^e	
Fe...M distances (Å)	(1.824) ^d	(1.759) ^d	(1.759) ^d	(1.826) ^d	(1.745) ^d	
	3.65	3.58	3.64	3.6213(5)	3.4994(14) ^e	3.559
	(3.624) ^d	(3.525) ^d	(3.683) ^d	(3.604) ^d	(3.489) ^d	

^aIR values are determined based on **4OTf**.^bMössbauer parameters were computed at the B3LYP/def-TZVP(Fe:CP(PPP))/BP86/def-TZVP level of theory including COSMO solvation.^cThe sign of E_Q is not determined.^dComputed at the TPSS-D3(BJ)/def2-TZVP/COSMO ($\epsilon = 35.88$) level of theory considering an antiferromagnetically coupled electronic structure.^eDistances and angles are reported for the major position of the disorder modeling (85% occupancy) of **5**. The structure of **5** was modeled over two positions with a 90° rotation along the Fe–O–Fe axis.^fMössbauer data for **6** were collected at 80 K, while Mössbauer data for **1–3** were collected at 4.2 K.