Halide Influence on Molecular and Supramolecular Arrangements of Iron Complexes with a 3,5-Bis(2-Pyridyl)-1,2,4,6-Thiatriazine Ligand

Katie L. M. Harriman,† Irina A. Kühne,† Alice A. Leitch,† Ilia Korobkov,† Rodolphe Clérac,‡§ Muratee Murugesu,†‡ and Jaclyn L. Brusso*†

†Department of Chemistry and Biomolecular Science, University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6NS, Canada
‡CNRS, CRPP, UPR 8641, F-33600 Pessac, France
§Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

S Supporting Information

ABSTRACT: A series of iron centered complexes, namely, [Fe(Py 2TTA)Cl 2] (1), [Fe(Py 2TTA)Br 2] (2), and [Fe(μ-F)(Py 2TTAO)F] ∞ (3), were isolated via complexation of 3,5-bis(2-pyridyl)-1,2,4,6-thiatriazine (Py 2TTAH) with various ferric halides (e.g., FeF 3, FeCl 3, and FeBr 3). Comparison of the optical and electrochemical spectroscopy, structural analysis, and magnetic studies reveal numerous similarities between the chlorido (1) and bromido (2) derivatives, which crystallize as discrete five-coordinate iron centered complexes with coordination geometries that are intermediate between trigonal bipyramidal and square base pyramid. Conversely, the fluoroido derivative (3) results in a completely different structure due to oxidation of the ligand and the formation of a one-dimensional coordination polymer held together through a bridging fluoride ion. Consequently, the spectroscopic and magnetic behavior of 3 differs significantly compared with 1 and 2. Complexes 1 and 2 exhibit paramagnetic properties typical for a mononuclear S = 1/2 system with weak intermolecular antiferromagnetic interactions at low temperatures, whereas complex 3 demonstrates significant exchange couplings within the chain and weak antiferromagnetic interchain interactions, which stabilize a canted antiferromagnetic state below 4.2 K.

INTRODUCTION

In recent years, the design and development of sulfur and nitrogen containing heterocycles have received a great deal of interest due to their potential role in inorganic, bioinorganic, and supramolecular chemistry. In that regard, heterocycles containing the thiazyl moiety are particularly attractive as the S−N unit not only affords an unpaired electron, but the incorporation of heavy heteroatoms into planar frameworks also provides the potential for structural control through S−N′ and N−HC′ interactions and better opportunities for enhanced magnetic and electronic interactions by virtue of greater orbital overlap.7–9 Thus, targeting such radicals could lead to unique physical properties (e.g., inherent conductivity) along with the potential for strong magnetic interactions between the spin carriers. Recent developments on thiazyl-based radicals provide a glimpse of the aforementioned properties such as magnetization (M) bistability (i.e., M vs H hysteresis associated with a magnet behavior), which can be harnessed through long-range ordering via strong communication between the radical centers.10–13 With that said, relatively little is known about the coordination chemistry of these systems. For example, by coordinating highly delocalized π-conjugated radicals, strong communication between the spin carriers may be induced. In order to achieve such behavior, it is necessary to introduce highly coordinating pockets into the thiazyl-based radical framework. With this in mind, we have focused our attention on the synthesis and coordination chemistry of 3,5-bis(2-pyridyl)-1,2,4,6-thiatriazine (Py 2TTAH; Scheme 1),14 which provides an ideal terpyridine-like stable tridentate coordination pocket while retaining the “active” N=S=N moieties.

Both symmetrically and asymmetrically substituted thiatriazinyl (TTA) radicals have been reported, most of which are partially functionalized by a phenyl group.15–18 With respect to metal coordination, the reactivity of symmetric (Ph 2TTA) and asymmetric (3-phenyl-5-trifluoromethyl-TTA) derivatives with [Cr(Cp)(CO 3) 2] has been explored.19,20 As expected, the TTA substituents played a role in the coordination leading to an η1- adduct bonded through the sulfur atom in Ph 2TTA, whereas the asymmetric ligand resulted in an η1 S=S=N linkage. In both cases, coordination through the central nitrogen of the TTA ring did not occur. By employing heteroaromatic substituents, as in Py 2TTA, coordination through the chelating effect is promoted rendering the N=S=N portion of the heterocyclic ring devoid of substituents. This therefore permits these heteroatoms to engage in supramolecular interactions, which...
has been shown to direct crystal packing in the solid-state and facilitate conductive or magnetic exchange pathways in thiazyl based radical complexes. What is particularly interesting about this ligand system is its ambiguity in regard to oxidation states as both the anionic and neutral states are isolatable, while maintaining the topological of terpy. More specifically, the neutral radical Py2TTA may be prepared from treatment of Py2TTAH with N-chlorosuccinimide in the presence of base (e.g., 4-dimethylaminopyridine: DMAP; Scheme 1). While Py2TTAH is surprisingly robust with a high tolerance toward aqueous, basic, and thermal conditions, once in the radical form (i.e., Py2TTA), it is highly susceptible to oxidation affording the 4-hydro-1-oxo-1,2,4,6-thiatriazine (1-oxo-Py2TTA, see Scheme 1).22

As a first step toward exploring the potentially rich coordination chemistry of Py2TTA, we recently reported the synthesis and detailed study of a mononuclear iron complex ([Fe(Py2TTA)Cl2]; 1). This unique system can be prepared via the reaction between FeIII and Py2TTAH or through the treatment of FeII with the neutral radical Py2TTA.23 Once isolated, [Fe(Py2TTA)Cl2] is quite stable in the solid-state; however, if rigorously degassed solvents were not used, metal-assisted aerial oxidation (Py2TTA to 1-oxo-Py2TTA, see Scheme 1) was observed upon dissolution. While initially this was rather intriguing, such behavior has been reported by Clark et al. where they demonstrated that Lewis-acidic CuII ions catalyze the aerial oxidation of benzothiadiazines to benzothiazyl diazine S-oxides.24 On the basis of this study, it is reasonable to anticipate that other Lewis acids may also catalyze such oxidation. Although FeCl3 salts are also Lewis-acidic, in the case of complex 1 aerial oxidation of the TTA ring occurs following isolation of the coordination complex, not during the synthesis.

As anticipated, in complex 1 coordination to the ligand occurs through the tridentate terpy-like pocket leaving the N=S=N portion of the TTA ligand devoid of substituents permitting these heteroatoms to participate in supramolecular interactions. As a result, within the packing motif of [Fe(Py2TTA)Cl2], there are two dominant structural features, ligand−ligand and halogen−halogen. The latter are non-negligible as the intermolecular Cl−Cl interactions are in good agreement with the sum of the van der Waals radii. In addition to directing packing in the solid state, halide ions are known to play various important roles in coordination chemistry. They can act as noncoordinating counterions for a molecular complex or participate in the coordination environment. Halide ions have also been known to act as monatomic bridges between metal centers in multimetallic complexes and coordination polymers. Notably, due to their relative sizes and charge, halides often dictate the packing arrangement of molecules in the crystal lattice. For example, smaller highly electronegative F− ions can be efficient electron withdrawing groups, whereas the larger and more dispersed negative charge of Cl− and Br− can enhance stability of the resulting complexes. In addition to size and electronegativity, the acidity of different halides can also significantly influence the formation of metal complexes and the overall structural arrangement.27

In order to further investigate the role of the ligand and the halide anion in coordination complex formation, we have focused our attention on synthesizing Fe-Py2TTA complexes with F−, Cl−, Br−, and I− anions. These halide anions were explored to probe their role in the supramolecular packing arrangement and influence on the resulting physical properties. To that end, we herein report the synthesis, optoelectronic, and solid-state properties of a family of Fe complexes with the Py2TTA ligand, which are coordinated to fluoride, chloride, and bromide.

### RESULTS AND DISCUSSION

#### Synthesis

Synthesis of the bromido derivative [Fe-(Py2TTA)Br2] (2) followed a similar route as the preparation of [Fe(Py2TTA)Cl2] (1; Scheme 2). Namely, an acetonitrile

![Scheme 2. Synthesis of Complexes 1, 2, and 3](image-url)

Reagents and conditions: (a) FeCl3, DMF, MeOH, RT; (b) FeBr3, MeCN, CHCl3, RT; (c) FeF3, DMF, MeOH, diethyl ether, RT.

(MeCN) solution of FeBr3 was layered over a chloroform (CHCl3) solution of Py2TTAH affording green-brown block-like crystals of 2 suitable for single crystal X-ray analysis (for experimental details see Supporting Information). In order to isolate the fluorido derivative, a heterogeneous reaction was required due to the limited solubility of FeF3. As such, after a slurry of FeF3 in a DMF/MeOH solution of Py2TTAH was stirred overnight, the mother liquor was separated and placed in a diethyl ether bath at room temperature. After several days, green needle-shaped crystals of [Fe(μ-F)(1-oxo-Py2TTA)F]∞ (3) suitable for single crystal X-ray analysis were obtained. Although the F, Cl, and Br complexes were isolated following

---

DOI: 10.1021/acs.inorgchem.6b00357

Inorg. Chem. 2016, 55, 5375–5383
the aforementioned procedures, the iodo-derivative remains elusive, despite our best efforts. Interestingly, the reactions involving FeCl$_3$ and FeBr$_3$ resulted in mononuclear complexes with very similar structures (\textit{vide infra}), whereas replacing the halide with fluorine (i.e., FeF$_3$) afforded complex 3 in which oxidation of the ligand (Py$_2$TTA to 1-oxo-Py$_2$TTA, see Scheme 1) occurs, and a coordination polymer is formed as a result of a bridging fluoride ion. Initially, oxidation of the ligand was surprising as Py$_2$TTAH is remarkably robust with a high tolerance toward halide exchange leads to an anodic shift in the Fe$^{II}$/Fe$^{III}$ redox potential (by 93 mV),

On the basis of this study, it appears halide exchange leads to an anodic shift in the Fe$^{II}$/Fe$^{III}$ redox potential (by 93 mV),

However, as demonstrated here, the thiatiazine ring is prone to oxidation when coordinated to iron. Such reactivity of the TTA ring has only previously been observed when the brominated derivative (3,5-bis(2-pyridyl)-1-bromo-1,2,4,6-thiatiazine) or radical (3,5-bis(2-pyridyl)-1,2,4,6-thiatriziyl) is exposed to oxygen or moisture affording 3,5-bis(2-pyridyl)-4-hydro-1-oxo-1,2,4,6-thiatiazine. Intriguingly, in the case of complexes 1 and 2, axial oxidation of the TTA ring occurs following isolation of the coordination complex, whereas oxidation occurs during the reaction for 3. The difference between these complexes may be attributed to the relatively high electronegativity of the fluoride ions in comparison to the later halides, enhancing axial oxidation. Furthermore, the relatively small size of the fluoride promotes octahedral coordination. Nonetheless, the susceptibility toward oxidation when coordinated to iron is quite interesting and opens an avenue for metal-non-innocent ligand based catalysis.

Electrochemical Studies. The redox behavior of complexes 1 and 2 were probed by cyclic voltammetry in dichloromethane (DCM). In the case of complex 3, electrochemical studies could not be carried out due to its insoluble nature. As was previously reported, 1 shows two quasi-reversible redox processes at 0.923 V and −0.037 V (vs SCE), which are attributed to the Py$_2$TTA 0/+1 and Fe$^{II}$/Fe$^{III}$ process, respectively. Similar behavior is observed for [Fe(Py$_2$TTA)Br$_2$], with two quasi-reversible redox processes visible within a similar range (0.915 and 0.056 V vs SCE, Figure 1). On the basis of this study, it appears halide exchange leads to an anodic shift in the Fe$^{II}$/Fe$^{III}$ redox potential (by 93 mV), while the Py$_2$TTA 0/+1 process remains relatively constant (i.e., 8 mV cathodic shift). Furthermore, both 1 and 2 are susceptible to metal-assisted ligand oxidation in solution, as observed by the additional redox process occurring at 0.272 V and 0.366 V, respectively. While this could be avoided for 1 by rigorously degassing the solvent (i.e., freeze−pump−thaw) prior to collecting the cyclic voltammogram, for complex 2 oxidation of the TTA ligand in solution is unavoidable, even under those conditions.

Optical Spectroscopy. To probe the effect of halide exchange on the electronic structure, solution absorption and solid state diffuse reflectance spectroscopic studies were carried out on complexes 1, 2, and 3 in the range of 200−1200 nm. Because of the insolubility of complex 3, only solid-state diffuse reflectance was feasible. For comparative purposes, Py$_2$TTAH and 1-oxo-Py$_2$TTAH were investigated, the results of which are presented in Figure 2. As may be expected, the absorption profile of [Fe(Py$_2$TTA)Br$_2$] is quite similar to that of [Fe(Py$_2$TTA)Cl$_2$] with ligand based transitions in the high energy region (273 and 272 nm; cf. 235 and 261 nm for Py$_2$TTAH) as well as a series of less intense bands in the visible region (e.g., 300−400 nm) characteristic of metal centered d−d transitions. Compounds 1 and 2 also exhibit broad and relatively intense low energy transitions observed at 500−1100 nm, which may be indicative of some radical character on the ligand since near-IR bands are often observed in coordination complexes of paramagnetic ligands. The diffuse reflectance measurements are in good agreement with the solution based absorption profiles. While solution measurements could not be performed on [Fe(μ-F)(1-oxo-Py$_2$TTA)]$^+\superscript{\infty}$, the solid state diffuse reflectance spectrum reveals that 3 does not absorb in the NIR region, which is consistent with the lack of potential to form a radical due to oxidation of the ligand. [Fe(μ-F)(1-oxo-Py$_2$TTA)]$^+\superscript{\infty}$ does, however, absorb in the high energy (226 nm) and visible (658 nm) region, which is consistent with ligand based transitions (cf. 224 and 514 nm for 1-oxo-Py$_2$TTAH) and metal centered d−d transitions, respectively.

Structural Studies. While [Fe(Py$_2$TTA)Cl$_2$] (1) crystallizes in the orthorhombic space group Pnma, the bromido derivative [Fe(Py$_2$TTA)Br$_2$] (2) crystallizes in the triclinic space group P1. The variation in the space groups adopted by 1 and 2 has consequences leading to subtle differences in the packing of the molecules (\textit{vide infra}). However, it should be noted that although 1 and 2 crystallize into different space groups, their solid-state structures are remarkably similar as is highlighted in Figures 3, 4, and 5.

In both cases, the metal ion adopts a five-coordinate coordination arrangement with the iron center residing within the plane of the tridentate Py$_2$TTA ligand, coordinated through...
the N1, N4, and N5 atoms. The remaining metal coordination environment is filled by two halide anions above and below the molecular framework. On the basis of the Addison and Reedijk structural parameter ($\tau$), the coordination geometry of 1 is best described as intermediate between trigonal bipyramidal and square base pyramid (0.495), whereas 2 more closely resembles square pyramidal (0.283). Considering the Fe–N bond lengths (Table 1), the two corresponding to the pyridyl rings (N4 and N5) are essentially equivalent and are consistent with what is commonly observed for Fe–N bonds in terpy-based systems. The other, which represents the interaction between iron and the nitrogen on the TTA ring (i.e., N1), is shorter than average indicative of $\pi$-bonding interactions.

Although the bond lengths between the central iron center and the Py$_2$TTA ligand are very similar for both complexes, the Fe–X distances are slightly elongated for the bromido derivative, as expected due to the larger ionic size of the bromide ion in comparison to the chloride. Furthermore, in

**Figure 2.** Solution absorption (top) and solid-state diffuse reflectance (bottom) spectra at room temperature for [Fe(Py$_2$TTA)Cl$_2$] (1; blue line), [Fe(Py$_2$TTA)Br$_2$] (2; red line), [Fe($\mu$-F)(1-oxo-Py$_2$TTA)F]$_\infty$ (3; green line), Py$_2$TTAH (black line), and 1-oxo-Py$_2$TTAH (gray line).

**Figure 3.** Molecular structure of [Fe(Py$_2$TTA)Cl$_2$] (1; left) and [Fe(Py$_2$TTA)Br$_2$] (2; right). H atoms are omitted for clarity.

**Figure 4.** Crystal packing of [Fe(Py$_2$TTA)Cl$_2$] (1) viewed along the $b$-axis (top) and [Fe(Py$_2$TTA)Br$_2$] (2) viewed along the $a$-axis (bottom).

**Figure 5.** Stacking of four molecules of 1 (top) and 2 (bottom) with intermolecular interactions highlighted by dashed lines (Cl–Cl in bright green; N–N in blue; S–S in yellow; Fe–Fe in dark green; Br–Br in olive green). Intermolecular distances are provided.
complex 2 the ligand displays lower planarity than in 1; however, that is likely due to the different crystallographic space groups and the consequence of 1 being situated on a mirror plane.

In the solid-state, complexes 1 and 2 are both highly ordered forming layered structures that are dominated by two structural features, ligand—ligand and halogen—halogen interactions. While these layers are evenly separated in complex 1, this is no longer the case in 2 (Figure 5 and Supporting Information, Figure S1), which may be attributed to the larger size of the bromide ions. Nonetheless, in both complexes the TTA fragment of one molecule overlaps with another one on the next layer (Figure 4), resulting in a number of close intermolecular contacts between neighboring TTA rings (Figure 5).

As well, the pyridyl rings between the ligand of neighboring molecules overlap in a zig-zag fashion for complex 1, whereas in 2 these layers are aligned parallel to the b-axis (Figure 4). Although numerous similarities exist between the solid-state structures of 1 and 2, the subtle discrepancies are likely a result of the difference in anion size and electronegativity. This is perhaps exemplified by considering the halide—halide interactions between molecules of alternating layers. In 1, the chloride—chloride distance of 3.52 Å, resulting from the chloride ion of one molecule interacting with another two layers away, is in good agreement with the sum of the van der Waals radii.40 Conversely, in complex 2 the bromide ions are no longer superposed, resulting in a distance between the bromide ions of 3.81 Å, a value slightly elongated with respect to complex 1 and is nominally larger than the sum of the van der Waals radii.40

While numerous similarities exist between the chlorido and bromido derivatives, replacing the halogen with fluoride ions results in a completely different structure. This is attributed to the reaction between Py2TTAH and FeF3 leading to oxidation of the ligand and the formation of a coordination polymer. Crystals of 3 belong to the monoclinic space group P21/c and consists of Fe chains held together through a single bridging fluoride (Figure 6). The metal ion adopts a distorted octahedral coordination arrangement with the iron center coordinated to the tridentate oxidized Py2TTA ligand (1-oxo-Py2TTA) in the equatorial plane through its three nitrogen atoms (N1, N4, and N5). The remaining equatorial position is occupied by a fluoride ion (F1). The two additional fluoride ions (F2 and F2a), which occupy the axial positions, are μ−bridging to the next iron center in the 1D coordination polymer. In [Fe(μ-F)(1-oxo-Py2TTA)F]∞, the ligand is no longer planar due to oxidation of the sulfur atom (S1) of the TTA ring.22 Considering the Fe−N bond lengths (see Table 1), the two N atoms corresponding to the pyridyl rings (N4 and N5) are in a range similar to those for complexes 1 and 2. The remaining Fe−N bond (Fe1−N1), which represents the interaction between iron and the nitrogen on the TTA ring, is slightly larger in comparison to those in complexes 1 and 2, while still remaining in good agreement to other previously reported iron complexes with terpy-like ligands.41-43 The Fe−F bond lengths fall in the range of 1.80−1.91 Å. This, coupled with the coordination environment and oxidation of the TTA ring leading to an anionic ligand, suggests the presence of FeIII metal ions.

Unlike complexes 1 and 2 in which a number of close ligand−ligand interactions are observed, only one close π−π interaction exists within the polymeric chain of 3 (C12-C2 = 3.37 Å), which is likely due to the bridging fluoride ion. Furthermore, the fluoride bridged Fe chains in 3, which are aligned along the c-axis, are held together through O−H−N−H interactions between the 1-oxo-Py2TTA ligands on neighboring polymers. This leads to interchain Fe−Fe distances of 8.24, 13.83, and 11.49 Å, as highlighted in Figure 7.

**Magnetic Properties.** The dc magnetic susceptibility, χdf, of compounds 1−3 was investigated under 1000 Oe field in the temperature range 1.85−300 K on polycrystalline samples. The corresponding χT vs T plots are presented in Figure 8. At room temperature, the χT values of complexes 1, 2, and 3 are 4.34, 4.36, and 2.73 cm³ K mol⁻¹, respectively. For 1 and 2, the observed χT values are in good agreement with the expected spin only value of 4.375 cm³ K mol⁻¹ for a Fe(III) S = 5/2 center. In the case of 3, the observed low value can be attributed to non-negligible antiferromagnetic interactions between the Fe centers observable even at room temperature (vide infra). The χT curves of 1 and 2 exhibit similar temperature dependent profiles over the entire temperature range, which may be expected due to the similarity between their molecular structures. The decrease of the χT product is gradual with minimal values of 0.18 cm³ K mol⁻¹ for 1 and 2 at 1.9 K. Such temperature decreases can be attributed to intermolecular antiferromagnetic interactions between the spin carriers estimated at zJ/kB = −2.9 K (z and J being the number of next-neighbors and the average exchange interaction between carriers respectively) from the Curie−Weiss fits of the experimental data shown in Figure 8 (note that g values of 2.05(5) and 2.06(5) were obtained from the Curie−Weiss fits for the Fe(III) site in 1 and 2 respectively). For 3, the variable temperature χT curve differs significantly from the other two compounds; upon decrease of the temperature the χT product decreases rapidly to reach a minimum value of 0.19 cm³ K mol⁻¹ at 9.5 K indicating dominant antiferromagnetic interactions.
interactions between the Fe(III) centers through the single fluoride-bridge. On the basis of the 1D structure of 3 (vide supra), the Heisenberg chain model of classical \( S = 5/2 \) spins (\( J \) being the magnetic interaction between the Fe(III) spins), developed by Fisher\textsuperscript{45} in the 1960s, was used to fit the experimental data, considering the following spin Hamiltonian:

\[
\hat{H} = -2J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + g \mu_B H \sum_i \vec{S}_i
\]

As shown in Figure 8, an excellent fit is obtained down to 10 K with \( g = 2.02(5) \) and \( J/k_B = -12.5(1) \) K. The antiferromagnetic interaction in 3 is comparable to fluoride-based systems\textsuperscript{47} and especially the one, \(-8.7 \) K, determined in the (imidH)\textsubscript{2}[Fe\textsubscript{2}oxF\textsubscript{6}] compound (imidH: imidazolium cation, ox: oxalate)\textsuperscript{48} that also displays a single fluoride-bridge between Fe(III) centers. Close inspection of the \( \chi T \) vs \( T \) data below 9 K (Figure 8 inset) reveals a \( \chi T \) product increase with a maximum of 0.39 cm\(^3\) K mol\(^{-1}\) at 3 K and a final decrease to reach 0.28 cm\(^3\) K mol\(^{-1}\) at 1.85 K.

This peculiar thermal behavior is associated with a magnetic susceptibility (Figure 9a) that becomes strongly dependent on the applied dc field below 5 K, suggesting the stabilization of a magnetically ordered ground state. Accordingly, the ac susceptibility exhibits a small but significant out-of-phase signal below 5 K (Figure 9b), consistent with a 3D magnetically ordered phase, which possesses a small spontaneous magnetization as expected for a canted antiferromagnetic state. It is worth noting that ferromagnetic or ferrimagnetic states can be easily ruled out in 3 as the observed \( \chi'' \) signal and the 1.85 K magnetization (that reaches only 0.22 \( \mu_B \) at 7 T; Figure 10a,b) are both small. Below 5 K, a hysteresis effect on the \( M \) vs \( H \) curve is also observed reproducibly in the magnetically ordered phase with a coercive field, \( H_{coerc} \), and remnant magnetization, \( M_{rem} \) which reach 360 Oe and 0.0237 \( \mu_B \) respectively, at 1.85 K (Figures 9c and 10c). From the field dependence of the magnetization shown in Figure 10b,c, the small remnant magnetization (<0.025 \( \mu_B \)) resulting from the noncompensation of the two sublattices in the canted antiferromagnetic phase has been deduced and plotted as a function of the temperature in Figure 11. Remarkably below 4 K, the experimental \( M_{rem} \) vs \( T \) data compare almost perfectly with the temperature variation of the Ising order parameter \( (m) \) in the mean field approximation (that is the solution of the self-consistent equation \( m = \tanh(mT_C/T) \)).\textsuperscript{49,50} This excellent theory/experiment agreement corroborates the direct correlation between the temperature dependence of remnant magnetization and the magnetic phase transition with \( T_C = 4.2 \) K and \( M_{rem} (0 \) K) = 0.0243 \( \mu_B \). Between 4.2 and 8 K above the canted antiferromagnetic phase, fluctuation effects are clearly observed on the \( M_{rem} \) vs \( T \) data (Figure 11). The presence of short-range order between \( T_C \) and about 7 K is also detected by ac susceptibility measurements, which show a broad \( \chi'' \) peak and a nonzero \( \chi'' \) value below 7 K (Figure 9b).

As detailed in the previous paragraphs, combined dc and ac magnetic measurements clearly establish the canted antiferromagnetic ground state of 3 below 4.2 K; therefore it is interesting to schematize the possible spin order in relation to the crystal structure. In 3, the presence of two Fe(III) orientations along the chains is seen in Figures 7 and 12 with a Fe-F-Fe angle of 146.9\(^\circ\) or \( \alpha = 33.1^\circ \). This structural angle is indeed remarkably larger than the magnetic angle, \( \alpha_{magnetic} \), of about 11.1\(^\circ\) between the two uncompensated sublattices of the canted antiferromagnetic phase (Figure 12; note that \( \alpha_{magnetic} \) is estimated from \( M_{rem} (0 \) K) = 0.0243 \( \mu_B \) and the well-established geometrical relation: \( \sin(\alpha_{magnetic}/2) = 2M_{rem}/M_{sat} \) with \( M_{rem} (0 \) K) = 0.0243 \( \mu_B \) and \( M_{sat} = 5\mu_B \) being the magnetization expected at high field after saturation).

Figure 7. Packing arrangement of the fluoride bridged Fe chains in [Fe(μ-F)(1-oxo-Py2TTA)F]\textsubscript{∞} (3) as viewed from the side (along the \( a^* \)-axis; top). Bird’s-eye view of the 1D coordination polymers of 3 along the \( c \)-axis illustrating the separation between chains (bottom). Intermolecular Fe—Fe distances are highlighted by green dashed lines.

Figure 8. Temperature dependence of the \( \chi T \) product at 1000 Oe (\( \chi \) is defined as magnetic susceptibility equal to \( M/H \) per mole of Fe center) for 1 (black), 2 (green), and 3 (blue; Inset: zoom of the data below 20 K). The solid lines indicate the best fit using the magnetic models described in the text.
This result demonstrates that the magnetic exchange along the chain \((J/k_B = -12.5 \text{ K})\) is dominating the spin orientations without overcoming completely the Fe(III) magnetic anisotropy that induces an \(\alpha\) magnetic angle different from zero. It is also interesting to deduce from Figure 12 that the canted antiferromagnetic phase in \(3\) is necessarily the result of interchain antiferromagnetic interactions dominated by those involving different sublattices, which is the only possible situation that induces a noncompensation of the chain magnetization. This spin arrangement is certainly favored by the staggered arrangement of the chains along the \(c\) axis (Figure 12).

**CONCLUSIONS**

In summary, a series of iron complexes, namely, \([\text{Fe(Py}_2\text{TTA})\text{Cl}_2] (1), [\text{Fe(Py}_2\text{TTA})\text{Br}_2] (2),\) and \([\text{Fe}(\mu-\text{F})(1\text{-oxo-Py}_2\text{TTA})\text{F}]_{\infty} (3),\) have been prepared and isolated via complexation of Py$_2$TTAH with various ferric halides (e.g., FeF$_3$, FeCl$_3$, and FeBr$_3$) in order to investigate the role of the ligand and halide anion in coordination complex formation. Furthermore, these Fe-Py$_2$TTA complexes with F$^-$, Cl$^-$, and Br$^-$ anions were explored to probe the effect of halide substitution (i.e., size, electronegativity, etc.) on the supramolecular packing arrangement and to examine their influence on the subsequent physical properties. Comparison of the electrochemical and optical spectroscopy, structural analysis, and magnetic studies reveal numerous similarities between the chlorido (1) and bromido (2) derivatives. More specifically, [Fe(Py$_2$TTA)Cl$_2$] and [Fe(Py$_2$TTA)Br$_2$] crystallize as discrete five-coordinate iron centered complexes with intermediate coordination geometries between trigonal bipyramidal and square base pyramid. As may be expected due to their structural similarities, electrochemical, optical, and magnetic studies reveal the physical properties of 1 and 2 are quite comparable. Conversely, replacing the halogen with fluoride anions results in a completely different structure, which is likely due to
intermolecular antiferromagnetic interactions, whereas complex 3 demonstrates significant exchange couplings within the chain and weak interchain interactions, which stabilize a canted antiferromagnetic ordered state below 4.2 K.

On the basis of the studies described here, it is clear the counterion has a significant impact on the coordination environment and packing arrangement in the solid-state of the resulting coordination complex or polymer. As well, the reactivity of the ligand with respect to metal-assisted aerial oxidation appears to be influenced by the halide. Investigations to further probe and understand the aforementioned metal-assisted aerial oxidation are currently underway.

**ASSOCIATED CONTENT**

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00357.

- Synthetic procedures, electrochemistry, crystallography, and magnetic measurements (PDF)
- Crystallographic information files (CIF1, CIF2)

**AUTHOR INFORMATION**

Corresponding Authors

* (R.C.) E-mail: clerac@crpp-bordeaux.cnrs.fr.
* (M.M.) E-mail: m.murugesu@uottawa.ca.
* (J.L.B.) E-mail: jbrusso@uottawa.ca.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors thank the University of Ottawa, the Canadian Foundation for Innovation (CFI), NSERC (Discovery and RTI grants), the CNRS, the Aquitaine region, the ANR and the University of Bordeaux for their financial support.

**REFERENCES**

Inorganic Chemistry


