Synthesis and Structure of $[\text{Fe}(\text{TPA})\text{Cl}_2](\text{ClO}_4)$ and $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ Where TPA = Tris-(2-pyridylmethyl)amine

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Abstract

$[\text{Fe}(\text{TPA})\text{Cl}_2](\text{ClO}_4)$, where TPA is tris-(2-pyridylmethyl)amine, crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z=4$, $a=8.6264(10)$ Å, $b=15.459(3)$ Å, and $c=16.008(3)$ Å. The structure was determined at 110 K from 4333 reflections (3520 observed) with $R=0.041$ ($R_w=0.082$). The iron is pseudo-octahedral with the two chloride ions *cis*. The Fe-Cl bond *trans* to the tertiary amine is shorter. $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ exhibits two polymorphic monoclinic forms, and the monohydrate also crystallizes in a monoclinic form. For the $P2_1/c$ polymorph, $Z=2$, $a=10.839(2)$ Å, $b=15.956(3)$ Å, $c=12.416(2)$ Å, $\beta=107.024(10)^\circ$, and the structure was determined at 95 K from 6514 reflections (3974 observed) with $R=0.052$ ($R_w=0.099$). For the $C2/c$ polymorph, $Z=4$, $a=20.5023(17)$ Å, $b=15.2711(13)$ Å, $c=16.1069(11)$ Å, $\beta=124.465(4)^\circ$, and the structure was determined at 161 K from 6250 reflections (3130 observed) with $R=0.0632$ ($R_w=0.1229$). For the hydrate, $P2_1/n$, $Z=4$, $a=16.201(2)$ Å, $b=16.980(3)$ Å, $c=16.451(3)$ Å, $\beta=112.234(5)^\circ$, and the structure was determined at 100 K from 12,745 reflections (6600 observed) with $R=0.097$ ($R_w=0.190$). In each of the $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}]^{2+}$ units, each iron is pseudo-octahedral with the chloride and oxide ions *cis*. The oxide bridge is linear, and the two chlorides are *anti*. The Fe-N distance for the pyridyl ring *trans* to the oxide bridge is quite long due to the *trans* influence of the oxide.

Graphic Abstract

The X-ray structures of $[\text{Fe}(\text{TPA})\text{Cl}_2](\text{ClO}_4)$, where TPA is tris-(2-pyridylmethyl)amine, and three polymorphs of dimeric $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ are presented and discussed.

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Extended author information available on the last page of the article

Keywords Trans influence · Oxido-bridged · Iron(III) · Cis influence · X-ray structure · Tris-(2-pyridylmethyl)amine

Introduction

Tris-(2-pyridylmethyl)amine (TPA), also known as tris-(2-picolyl)amine, is a widely used tripodal ligand [1–25]. It can simultaneously provide four nitrogen donors (three pyridyl nitrogen atoms and a tertiary amine nitrogen) to a single metal center, thus leaving one or two available coordination sites. TPA complexes with most of the 3d metals are known including V(III), V(IV), V(V) [2], Cr(II) [3], Cr(III) [3–5], Mn(II) [6], Mn(III) [7], Mn(IV) [7], Fe(II) [8–10], Fe(III) [11–16], Co(III) [17], Ni(II) [18, 19], Cu(I) [20], Cu(II) [20–23], and Zn(II) [24, 25].

Because of the relative control over the metal site, iron complexes of TPA, and various substituted forms of TPA, have been used to model the metal-binding site of various metalloproteins, and have been extensively explored as catalysts for alkane functionalization [11–13, 26–28]. Given that, for octahedral complexes, one of the additional ligand atoms will be *trans* to a pyridine nitrogen atom and the other will be *trans* to the tertiary amine nitrogen atom, structural investigations are important to fully assess the *trans* influence of these two moieties, and to assess the extent of possible *cis* influences as well.

Herein we report the syntheses and structures of $[\text{Fe}(\text{TPA})\text{Cl}_2](\text{ClO}_4)$ (**1**) and $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ (various forms **2**, **3**, and **4**). These studies originated in the 1990s at Duquesne University, but were only reported in a M.S. thesis at that time [29]. The contact author moved from Duquesne University to the University of Louisiana at Monroe in 1997. While it might have been possible to scan the original data collection paper output and using optical character recognition software, recreate a digital version of the data collection, we decided instead to re-grow the crystals, re-collect the data, re-solve the structures, and re-refine them. This proved to be more involved than anticipated, since $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ presents as various polymorphs and solvates [14, 15, 30–32].

Experimental

All materials were obtained commercially, and used without further purification. $\text{TPA} \cdot 3\text{HClO}_4$ was synthesized according to literature procedures [1, 33], and used without further purification.

Synthesis

$[\text{Fe}(\text{TPA})\text{Cl}_2](\text{ClO}_4)$ (**1**). A mixture of 0.1480 g of $\text{TPA} \cdot 3\text{HClO}_4$ (0.2500 millimole) and 35.0 μL (0.251 millimole) of triethylamine in 20 mL methanol was warmed (to $\sim 60^\circ\text{C}$) and stirred to dissolve all of the ligand. After the solution cooled to room temperature, 0.0292 g of NaCl (0.500 millimole) and 0.1336 g of $\text{Fe}(\text{ClO}_4)_3 \cdot 10\text{H}_2\text{O}$ (0.2500 millimole) were added resulting in a yellow solution. A white powdery precipitate formed in a few minutes. After stirring for 30 min, the mixture was filtered, and the yellow filtrate was allowed to stand at room temperature for 6 days during which time yellow, needle-like crystals formed which were suitable for X-ray crystallography. UV: 300 nm (sh), 384 nm ($\epsilon = 3.3 \text{ mM}^{-1} \text{ cm}^{-1}$) ^1H NMR (ppm) 167, 138, 114, 99.

$[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ (**2,3,4**) is often obtained under a variety of other reaction conditions as a by-product or unanticipated major product. Here is an intentional preparation. A mixture of 0.1480 g of $\text{TPA} \cdot 3\text{HClO}_4$ (0.2500 millimole) and 160.0 μL (1.148 millimole) of triethylamine in 20 mL methanol was warmed (to $\sim 60^\circ\text{C}$) and stirred to dissolve all of the ligand. After the solution cooled to room temperature, 0.0146 g of NaCl (0.250 millimole) and 0.1336 g of $\text{Fe}(\text{ClO}_4)_3 \cdot 10\text{H}_2\text{O}$ (0.2500 millimole) were added resulting in a red-brown solution. A white powdery precipitate formed in a few minutes. After stirring for 30 min, the mixture was filtered, and the red-brown filtrate was allowed to stand at room temperature for 4 h during which time red-brown, plate-like crystals formed which were suitable for X-ray crystallography. UV 332 nm ($\epsilon = 15 \text{ mM}^{-1} \text{ cm}^{-1}$) 382 nm ($\epsilon = 17 \text{ mM}^{-1} \text{ cm}^{-1}$) ^1H NMR (ppm) 34, 29, 20.2, 18, 16, 14, 13, 12, 7, 6.

All the perchlorate salts included in this work proved to be relatively stable for small scale routine synthesis and purification procedures. However, caution should be observed because perchlorate salts of metal complexes with organic ligands are potentially explosive.

X-ray Structure Determinations

Some details of the crystal and data collections are collected in Table 1. X-ray diffraction data were collected primarily at Louisiana State University (but also at the University of Washington) on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) and an Oxford Cryostream cryostat. Data were collected with ω and ϕ scans. Data reduction included corrections for background, Lorentz, polarization and absorption

effects (by the multi-scan method (HKL Scalepack)) [34]. All structures were solved using direct methods [35] and expanded using Fourier techniques [36]. For **1**, **2**, and **4**, all calculations were performed using the teXsan for Windows [37] crystallographic software package. Full-matrix least-squares refinement with anisotropic thermal parameters for all of the non-hydrogen atoms converged. The function minimized in refinement was $\sum w(F_o^2 - F_c^2)^2$ where $w = 1/[\sigma^2(F_o) + (p)^2 F_o^2/4]$. The hydrogen atoms were placed in idealized positions (C–H 0.95 Å), with $U_{iso} = 1.2 U_{eq}$ of the attached atom. Neutral atom scattering factors were taken from Cromer and Waber [38]. Anomalous dispersion effects were included in F_c [39], and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [40]. The values for the mass attenuation coefficients were those of Creagh and Hubbell [41] (Table 2).

For **3**, full-matrix least-squares refinement on F^2 on all reflections used SHELXL97 [42]. All of the H atoms but one were located by difference Fourier synthesis. H atoms were refined with a riding model and U_{iso} values were fixed to be $1.1 U_{eq}$ of the parent atom.

For **2** and **3**, the bridging O atom is located on an inversion center. For **1** and **4**, there is no crystallographically imposed symmetry. The structure of **4** has been previously reported in the literature, [15] and the structure is included here for comparative purposes to give further context to the synthesis and structures of **1–3**.

Spectroscopy

Electronic spectra were recorded either on a HP 8452A (a single beam, diode-array spectrophotometer) at Duquesne University, or a Shimadzu UV1601-PC at the University of Louisiana at Monroe (also a single beam, diode-array spectrophotometer), or a Jasco V-550 (a double-beam spectrophotometer) at Sam Houston State University. HPLC grade acetonitrile (99.9%) and 1 cm path length cuvettes were used.

NMR spectra were recorded at ambient temperature on a Bruker ACP300 at Duquesne University or a JEOL Eclipse +300 FT-NMR at Sam Houston State University. Both were operating at 300 MHz and 5 mm tubes were used. The acquisition conditions were 5.0 μ sec pulses, 8192 data points, a scan width of 100,000 Hz, 0.0 relaxation delay, acquisition time 0.041 s in the former case, and 5.4 μ sec, 8192 data points, 1 s relaxation time, x-offset 100 ppm, and x-sweep 200 ppm in the latter case. The number of scans ranged from 20,000 to 100,000. CD₃CN (99.9%) was used as solvent and the residual proton signal of the solvent was assigned a chemical shift δ value of 1.94 ppm.

Results and Discussion

Synthesis

The units $[\text{Fe}(\text{TPA})\text{Cl}_2]^+$ and $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}]^{2+}$ have proven to be quite stable in a variety of systems. The systems investigated by most workers tend not to be extremely acidic, so the former is less common than the latter. The two units together were first reported [12, 13] when they co-crystallized. The oxido-bridged dimer has proven to be much more common. As mentioned above, it is a common by-product or an unintended product in systems where Fe(III), TPA, chloride and oxide are all present. We have obtained this product in systems while we were attempting to make compounds of the form $[\{\text{Fe}(\text{TPA})\}_2\text{OL}]^{n+}$ where L is relatively poor Lewis base (for example, $\text{L} = \text{O}_2\text{CCH}_2\text{N}(\text{CH}_3)_3$) and in systems while we were attempting to make mononuclear compounds of the form $[\text{Fe}(\text{TPA})\text{L}']^{3+}$ where L' is a neutral bidentate ligand (for example, L' = 2-picolyamine). In this latter case, the source of chloride was apparently reduction of ClO_4^- and in the former case it was chloride contamination.

X-ray Structures

The structure of yellow $[\text{Fe}(\text{TPA})\text{Cl}_2](\text{ClO}_4)$ is shown in Fig. 1. The complex cation has an octahedral Fe(III) center coordinated to four nitrogen atoms of TPA and two *cis* chloride ions. Two of the pyridyls are *trans*. One of the chlorides is *trans* to the tertiary amine and the other is *trans* to pyridine. This latter distance is the longer of the two Fe(III)–Cl distances (2.2900(8) Å vs. 2.2425(8) Å), and the corresponding Fe(III)–N_{py} is longer (2.204(2) Å) than the two Fe(III)–N_{py} distances that are mutually *trans* (2.144(2) and 2.119(2) Å). Coincidentally, the Fe–N_{3°} distance is the same as the Fe–N_{py} *trans* to chloride. TPA isn't able to fully span the *trans* positions, as indicated by the N_{py}–Fe–N_{py} angle of 151.53(9)° which is considerably less than 180°. This same mononuclear cationic unit is also found in $[\text{Fe}(\text{TPA})\text{Cl}_2][\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_4$ [13] and in $[\text{Fe}(\text{TPA})\text{Cl}_2][\text{FeCl}_4]$ [16], and the pattern of distances and angles are the same as found in **1**.

The analogous Fe(II) compound ($[\text{Fe}(\text{TPA})\text{Cl}_2]$) has been structurally characterized twice [9, 10], and the general pattern of distances and angles are observed—the Fe–Cl *trans* to the tertiary amine is shorter as are the mutually *trans* Fe–pyridyl distances, and the N_{py}–Fe–N_{py} angle is significantly less than 180°. What is remarkable is that all of the iron–ligand distances are significantly shorter in **1** compared to the corresponding distances in the Fe(II) compounds. For example the mutually *trans* Fe–pyridyl distances of **1** (2.132 Å) as compared to the Fe(II) compounds (2.190 Å),

Table 1 Crystallographic details

	1	2	3	4
Formula	C ₁₈ H ₁₈ Cl ₃ FeN ₄ O ₄	C ₃₆ H ₃₆ Cl ₄ Fe ₂ N ₈ O ₉	C ₃₆ H ₃₆ Cl ₄ Fe ₂ N ₈ O ₉	C ₃₆ H ₃₆ Cl ₄ Fe ₂ N ₈ O ₉ •H ₂ O
Color	yellow	red-brown	red	red
<i>M</i>	516.57	978.23	978.23	996.25
Crystal class	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁ (#19)	P2 ₁ /c (#14)	C2/c (#15)	P2 ₁ /n (#14)
T (K)	110	95	161	100
<i>a</i> (Å)	8.6264(10)	10.839(2)	20.5023(17)	16.201(2)
<i>b</i> (Å)	15.459(3)	15.956(3)	15.2711(13)	16.980(3)
<i>c</i> (Å)	16.008(3)	12.416(2)	16.1069(11)	16.451(3)
α , (°)	90	90	90	90
β (°)	90	107.024(10)	124.465(4)	112.234(5)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	2134.8(5)	2053.2(6)	4157.8(6)	4189.1(11)
<i>Z</i>	4	2	4	4
<i>D</i> _{calc} , (g/cm ³)	1.607	1.551	1.563	1.580
μ , cm ⁻¹	1.114	1.010	1.018	1.012
<i>F</i> (000)	1052	1000	2000	2040
Crystal size (mm)	0.12×0.15×0.22	0.33×0.27×0.12	0.10×0.05×0.05	0.32×0.30×0.08
θ Range, °	2.63 < θ < 32.56	2.5 < θ < 31.0	2.41 < θ < 30.54	2.5 < θ < 30.5
Reflections measured	7695	11,972	69,944	70,249
Unique reflections	4333	6514	6250	12,745
<i>R</i> _{int}	0.0396	0.038	0.1183	0.050
Observed (criterion)	3520 (<i>I</i> > 3 σ (<i>I</i>))	3974 (<i>I</i> > 3 σ (<i>I</i>))	3130 (<i>I</i> > 2 σ (<i>I</i>))	6600 (<i>I</i> > 3 σ (<i>I</i>))
Parameters	272	268	268	541
<i>S</i> (goodness of fit)	1.00	1.06	0.986	1.03
<i>R</i> indices	<i>R</i> = 0.041	0.052	0.0632	0.097
	<i>R</i> _w = 0.082	0.099	0.1229	0.190
Max. Resid. Peaks (eÅ ⁻³)	0.318 / -0.355	0.76 / -0.59	0.494 / -0.486	2.10 / -1.01

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ and } R_w = \sum [w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

or the shorter iron-Cl distance (2.2425 Å vs 2.339 Å). Of course, as mentioned in various inorganic chemistry textbooks, the effective radius for Fe(II) is typically described as being larger than that for Fe(III) [43]. We will say more about this below.

The structures of **2**, **3** and **4** are naturally all similar consisting of an oxido-bridged diiron(III) core; the asymmetric unit of **2** is shown in Fig. 2, Fig. 3 shows dimeric **2**, the asymmetric unit of **3** is shown in Fig. 4, Fig. 5 shows dimeric

3, and Fig. 6 shows the $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}]^{2+}$ unit of **4**. For both **2** and **3**, the oxide sits on an inversion center, while for **4** there is no crystallographically imposed symmetry. Each iron center in all three structures is roughly octahedral with the oxide and chloride *cis* to one another, the oxide *trans* to a pyridyl group and the chloride *trans* to the tertiary amine. The oxido-bridge is essentially linear (174.0(2)°) for **4** and is required to be linear for **2** and **3**. The oxide exerts a strong *trans* influence—these Fe-N distances are the longest in all

Table 2 Chemical bond distances (Å) and angles (°) for the coordination spheres of (**1–4**)

	1	2	3	4	
Fe-Cl	2.2425(8)	2.3145(7)	2.296(10)	2.302(1)	2.298(1)
Fe-O*	2.2900(8)	1.7947(4)	1.786(5)	1.788(3)	1.785(3)
Fe-N _{3°}	2.204(2)	2.228(2)	2.204(3)	2.218(4)	2.230(4)
Fe-N _{py}	2.144(2)	2.147(2)	2.145(3)	2.166(4)	2.156(4)
	2.119(2)	2.142(2)	2.136(3)	2.138(4)	2.129(4)
Fe-N _{trans}	2.204(2)	2.252(2)	2.286(3)	2.217(4)	2.247(4)
Cl-Fe-O*	97.97(3)	100.56(2)	101.5(3)	98.89(9)	99.2(1)
Cl-Fe-N _{3°}	170.58(6)	165.40(5)	164.9(9)	164.7(1)	165.3(1)
Cl-Fe-N _{py}	103.92(7)	101.47(6)	104.2(9)	107.1(1)	106.1(1)
	102.86(6)	103.51(5)	100.0(9)	99.0(1)	100.1(1)
Cl-Fe-N _{trans}	92.10(6)	88.80(5)	88.86(9)	89.8(1)	90.4(1)
O*-Fe-N _{3°}	91.40(6)	94.00(5)	93.45(8)	95.2(1)	94.7(1)
O*-Fe-N _{py}	93.11(6)	92.89(5)	90.72(9)	93.7(1)	93.1(1)
	92.59(7)	89.30(5)	92.49(9)	92.1(1)	92.0(1)
O*-Fe-N _{trans}	169.47(6)	169.66(5)	167.4(9)	170.9(1)	170.3(1)
N _{3°} -Fe-N _{py}	76.42(8)	76.50(7)	77.71(11)	77.8(1)	77.9(1)
	75.57(8)	76.78(6)	76.70(11)	74.4(1)	74.4(1)
N _{3°} -Fe-N _{trans}	78.60(8)	77.57(7)	76.63(12)	76.5(1)	76.0(1)
N _{py} -Fe-N _{py}	151.53(9)	154.07(7)	154.4(12)	152.0(1)	152.2(1)
N _{py} -Fe-N _{trans}	81.42(8)	89.49(7)	79.65(12)	81.0(1)	82.6(1)
	88.14(9)	84.21(7)	92.77(12)	89.3(1)	87.9(1)
Fe-O-Fe		180	180	174.0(2)	

N_{3°} is the tertiary amine N, N_{trans} is the pyridyl N trans to O (or Cl for **1**), and N_{py} are the pyridyl N which are mutually trans

*Fe–Cl for **1**, which is trans to the pyridyl N

three structures. The Fe–N_{3°} distances are the next longest, suggesting either a relatively strong *trans* influence of chloride, or an inherently poor Lewis basicity of this *tris*-picolyl substituted tertiary amine. One expects a strong bond is needed to produce a strong *trans* influence and the Fe–Cl distances are significantly longer (2.303 Å) than the corresponding Fe–Cl distance in **1** (2.2425(8) Å) which implies that this isn't the *trans* influence of chloride. Indeed, in TPA•3HClO₄ the tertiary amine remains deprotonated in the solid state [44] and in solution [45, 46]. Another possible influence on the Fe–N_{3°} distance is the *cis* influence of the oxido-bridge; that is, the presence of the strong Fe–O bond

may cause a lengthening of all of the other distances around the iron center. This is precisely what is observed with the Fe–N_{py} distances of 2.145 Å for **2,3** and **4** vs 2.132 Å for **1**.

The [{Fe(TPA)Cl}₂O]²⁺ unit has been reported previously in [Fe(TPA)Cl₂]₂[{Fe(TPA)Cl}₂O](ClO₄)₄, and in other polymorphs [13–15]. In all of the reported structures, the details of the oxido-bridged diiron unit are all very similar. In all but **4**, the oxide sits in a special position confirming crystallographic symmetry (twofold symmetry for [14] and inversion symmetry for the others). All of these structures place the chlorides, which are *trans* to the tertiary amine, in *anti* positions. The oxido bridge is essentially linear, with very short iron(III)-oxide bonds and long Fe-pyridine bonds *trans* to the bridge.

The [{Fe(TPA)Cl}₂O]²⁺ unit is similar to [{V(TPA)Cl}₂O]²⁺ [2] with the same relative arrangement of atoms (the oxide sits on an inversion center for the V(III) complex). The M–Cl and M–O distances are shorter for the Fe(III) unit, while the M–N distances are longer. While octahedral high spin Fe(III) has a slightly larger effective ionic radius than octahedral V(III) (0.645 Å vs. 0.640 Å, respectively) [43], the average metal ligand bond distance for all of the [{Fe(TPA)Cl}₂O]²⁺ units (2.142 Å) is significantly longer than the corresponding [{V(TPA)Cl}₂O]²⁺ unit (2.120 Å). The effective ionic radii values of Shannon are based on coordination primarily by oxygen—strictly oxygen for V (six structures) and mostly oxygen for Fe (seven oxygen structures and one fluorine structure) [43], so one might assume that π donation from the ligands is included in the effective ionic radius. This implies that the longer Fe–N distances are σ effects, reflecting the two σ antibonding electrons in Fe(III) as compared to V(III) which is d². For the high spin Fe(III), Fe(II) effective ionic radii comparison (0.645 Å vs. 0.780 Å) [43], the Fe(II) value is based on six structures with mostly oxygen donors (one structure has F/OH disorder), which implies that the difference in size is due to two factors: the increase in π antibonding electron count and the difference in charge on the metal center (the greater the charge, the smaller the radius). However, for the [Fe(TPA)Cl₂]ⁿ⁺ complexes the average Fe(III) ligand bond distance is 2.196 Å and the average Fe(II) ligand bond distance is 2.283 Å or a difference, on average, of 0.087 Å which is considerably smaller than the difference of 0.135 Å in effective ionic radii.

Fig. 1 Thermal ellipsoid plot of $[\text{Fe}(\text{TPA})\text{Cl}_2]\text{ClO}_4$ (**1**) with selected atom labels

Fig. 2 Thermal ellipsoid plot of the asymmetric unit of $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ (**2**) with selected atom labels

Fig. 3 Thermal ellipsoid plot of $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ (**2**)

Fig. 4 Thermal ellipsoid plot of the asymmetric unit of $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ (**3**) with selected atom labels

Fig. 5 Thermal ellipsoid plot of $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2$ (**3**)

Fig. 6 Thermal ellipsoid plot of the $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}]^{2+}$ unit of $[\{\text{Fe}(\text{TPA})\text{Cl}\}_2\text{O}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**4**) with selected atom labels

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Compliance with Ethical Standards

Conflicts of interest/Competing interests None.

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