

Geometric isomers of dichloridoiron(III) complexes of CTMC (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane)

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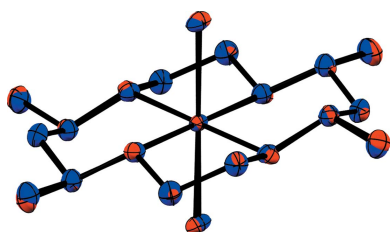
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Both *trans* and *cis* iron–CTMC complexes, namely, *trans*-dichlorido[(5*SR*, 7*RS*, 12*RS*, 14*SR*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) tetrachloridoferrate, $[\text{Fe}(\text{C}_{14}\text{H}_{32}\text{N}_4)\text{Cl}_2][\text{FeCl}_4]$ (**1a**), the analogous chloride methanol monosolvate, $[\text{Fe}(\text{C}_{14}\text{H}_{32}\text{N}_4)\text{Cl}_2]\text{Cl}\cdot\text{CH}_3\text{OH}$ (**1b**), and *cis*-dichlorido[(5*SR*, 7*RS*, 12*SR*, 14*RS*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) chloride, $[\text{Fe}(\text{C}_{14}\text{H}_{32}\text{N}_4)\text{Cl}_2]\text{Cl}$ (**2**), were successfully synthesized and structurally characterized using X-ray diffraction. The coordination geometry of the macrocycle is dependent on the stereoisomerism of CTMC. The packing of these complexes appears to be strongly influenced by extensive hydrogen-bonding interactions, which are in turn determined by the nature of the counter-anions (**1a** versus **1b**) and/or the coordination geometry of the macrocycle (**1a/1b** versus **2**). These observations are extended to related ferric *cis*- and *trans*-dichloro macrocyclic complexes.

1. Introduction

Macrocyclic complexes of transition metals, due to the inherent stability imparted by the macrocyclic effect (Constable, 1999), as well as to the ability to tune the number and position of open coordination sites, have often served as model complexes for the study of a number of chemical phenomena. For example, simple tetraazamacrocycles containing iron have been used to investigate aspects of nitrogen fixation (Meyer *et al.*, 1999), nonheme oxoiron (Prakash *et al.*, 2015; Rohde *et al.*, 2003), CO₂ reduction (Straub & Vöhringer, 2021), and water oxidation catalysis (Kottrup & Hettterscheid, 2016). Importantly, the macrocycle may often adopt either a folded or planar coordination geometry, leaving either *cis*- or *trans*-open coordination sites, respectively. This geometry can dramatically influence the reactivity of the resulting complexes (Kottrup & Hettterscheid, 2016; Meyer *et al.*, 1999).

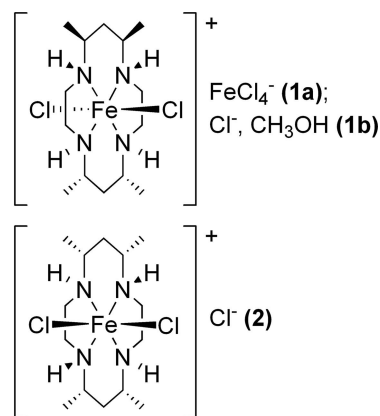
Our group has studied iron–alkynyl complexes supported by cyclam (1,4,8,11-tetraazacyclotetradecane) (Cao *et al.*, 2012), HMC (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) (Clendening *et al.*, 2022), and an HMC-derived tetraimine complex (HMTI = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) (Clendening & Ren, 2022) as models for potential molecular wires. The macrocycle has been shown to strongly affect the properties of these complexes, even tuning the metal–alkynyl bonding. Although Cr^{III}–alkynyl complexes with the macrocycle in both folded and planar conformations have been characterized (Tyler *et al.*, 2016), iron–alkynyl complexes were only isolated with planar macrocycles, even when starting



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from a *cis*-Fe^{III}(cyclam) complex. Seeking to expand our library of compounds, we have recently turned to the investigation of Fe(CTMC) complexes (CTMC = 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane). Nickel complexes of CTMC (and other macrocycles; Wang *et al.*, 2019) have received considerable attention, most recently as efficient carbon dioxide reduction catalysts (Mash *et al.*, 2019), but no iron complexes of CTMC have been reported previously to our knowledge.



Scheme 1

Although CTMC is known to form as a mixture of stereoisomers, the vast majority of structures contain only isomer **A** [(5*SR*,7*RS*,12*SR*,14*RS*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane; Fig. 1]. The structure of the free ligand has been determined, which contained **A** and **B** [Fig. 1; **B** = (5*SR*,7*RS*,12*SR*,14*RS*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane] (Tahirov *et al.*, 1995a). Finally, the structure of an Ni^{II}(CTMC) complex has been reported containing a third stereoisomer, **C** [(5*SR*,7*RS*,12*RS*,14*RS*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane] (Tahirov *et al.*, 1995b). Notably, all the structures of metal-ion complexes of CTMC reported to date contain a planar macrocycle.

Here we report the first examples of iron–CTMC complexes and their crystallographically determined structures, namely, *trans*-dichlorido[(5*SR*,7*RS*,12*RS*,14*SR*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) tetrachloridoferrate (**1a**), the analogous chloride methanol monosolvate (**1b**), and *cis*-dichlorido[(5*SR*,7*RS*,12*SR*,14*RS*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) chloride (**2**). While **1a** and **1b** exhibit the common stereoisomer **A** with a planar macrocyclic conformation, **2** represents the first structurally characterized metal CTMC complex both with stereoisomer **B** and with a folded macrocycle conformation (Fig. 1). Thus, the stereoisomer of the macrocycle appears to control the coordination isomer of the resulting metal complex. Given the importance of macrocycle coordination geometry on the properties of the resultant complex, and the extensive literature on CTMC species, we describe here the structural variations among these species, specifically addressing the differences between the folded (*cis*-dichloro complex) and planar (*trans*-dichloro complexes) coordination motifs. As will be established below, the number and stereochemistry of the macrocyclic substituents can dramatically alter the iron–

macrocycle bonding interactions. This work thus serves as a potential entry point for the development of novel Fe analogues of known complexes while exercising fine-tuned steric and electronic control over the Fe–macrocyclic core.

2. Experimental

The CTMC macrocycle was synthesized as described in the literature (Kolinski & Korybut-Daszkiewicz, 1975; Mash *et al.*, 2019; Tahirov *et al.*, 1995a). Consistent with previous structure determinations of the free ligand (Tahirov *et al.*, 1995a), we found evidence for the presence of at least two stereoisomers of CTMC (**A** is 5*SR*,7*RS*,12*SR*,14*RS* and **B** is 5*SR*,7*RS*,12*SR*,14*RS*), confirmed by the structures determined for the resulting Fe^{III} complexes reported herein. Two batches of CTMC were used to generate the *trans* and *cis* iron CTMC chloride species, with **A** being dominant in batch one (m.p. 178–181 °C) and **B** dominant in batch two (m.p. 70–135 °C). Altering the experimental method did not seem to allow for control over the presence of either stereoisomer of CTMC, and attempts to separate **A** and **B** were unfruitful. This lack of selectivity is consistent with the reported cocrystallization of **A** and **B** from the same synthesis (Tahirov *et al.*, 1995a). All commercially available materials were used as received. The IR spectra (ATR) of **1a**, **1b**, and **2** as powders were collected on a JASCO FT-IR 6300 instrument equipped with a diamond crystal. Magnetic measurements were conducted using a Johnson Matthey Magnetic Susceptibility Balance. Electron-spray ionization mass spectrometry experiments were performed with an Advion Mass Spectrometer.

2.1. Synthesis and crystallization

2.1.1. Synthesis of *trans*-[Fe(CTMC)Cl₂][FeCl₄]/Cl (1a/1b**).** CTMC (0.449 g, 1.75 mmol, batch one) was dissolved in a 2:1 (*v/v*) dimethylformamide–triethyl orthoformate mixture

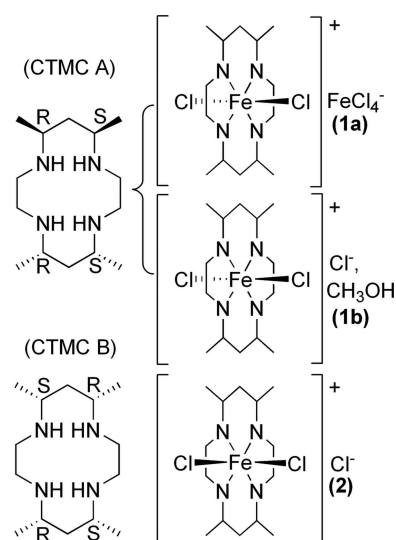


Figure 1 Stereoisomers of CTMC (left) and the resulting iron coordination complexes (right) discussed herein.

Table 1

Experimental details.

For all structures: $Z = 4$. Experiments were carried out at 150 K using a Bruker AXS D8 Quest diffractometer with a PhotonII charge-integrating pixel array detector (CPAD). Absorption was corrected for by multi-scan methods (*SADABS*; Krause *et al.*, 2015).

| | 1a | 1b | 2 |
|--|---|---|---|
| Crystal data | | | |
| Chemical formula | [Fe(C ₁₄ H ₃₂ N ₄)Cl ₂][FeCl ₄] | [Fe(C ₁₄ H ₃₂ N ₄)Cl ₂]Cl·CH ₄ O | [Fe(C ₁₄ H ₃₂ N ₄)Cl ₂]Cl |
| M_r | 580.83 | 450.68 | 418.63 |
| Crystal system, space group | Monoclinic, <i>C2/c</i> | Monoclinic, <i>P2₁/c</i> | Orthorhombic, <i>Pbcn</i> |
| a, b, c (Å) | 20.3512 (13), 6.4815 (4), 18.049 (1) | 8.1632 (4), 20.8470 (12), 12.1387 (7) | 9.2912 (12), 11.9579 (19), 17.267 (3) |
| α, β, γ (°) | 90, 100.452 (3), 90 | 90, 95.024 (2), 90 | 90, 90, 90 |
| V (Å ³) | 2341.3 (2) | 2057.8 (2) | 1918.4 (5) |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Cu $K\alpha$ |
| μ (mm ⁻¹) | 1.93 | 1.13 | 10.15 |
| Crystal size (mm) | 0.20 × 0.20 × 0.20 | 0.34 × 0.10 × 0.09 | 0.12 × 0.08 × 0.05 |
| Data collection | | | |
| T_{\min}, T_{\max} | 0.656, 0.747 | 0.679, 0.747 | 0.526, 0.754 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 71685, 4483, 3561 | 125711, 7859, 6505 | 14150, 2055, 1324 |
| R_{int} | 0.074 | 0.049 | 0.082 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹) | 0.771 | 0.770 | 0.638 |
| Refinement | | | |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.027, 0.067, 1.02 | 0.024, 0.061, 1.04 | 0.066, 0.196, 1.08 |
| No. of reflections | 4483 | 7859 | 2055 |
| No. of parameters | 148 | 235 | 196 |
| No. of restraints | 15 | 0 | 273 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.43, -0.48 | 0.70, -0.58 | 0.58, -0.95 |

Computer programs: *APEX3* (Bruker, 2019), *SAINT* (Bruker, 2019), *SHELXT2014* (Sheldrick, 2015a), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *SHELXL* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

(30 ml) prior to purging with nitrogen. The mixture was stirred and heated while FeCl₂·4H₂O (0.697 g, 3.50 mmol) was dissolved in a 4:3 (v/v) dimethylformamide–triethyl orthoformate mixture (35 ml), previously purged with nitrogen, and was also left to stir and heat. The CTMC solution was transferred to the iron-containing flask *via* a cannula and the reaction was left to stir at 50 °C for 1 h. The reaction mixture was then exposed to oxygen and about 2 ml of concentrated hydrochloric acid were added dropwise to the flask while bubbling through oxygen. An additional 3 ml of concentrated hydrochloric acid were subsequently added, along with excess diethyl ether. A yield of 0.333 g of green powder was recovered *via* filtration and crystals of **1a** (space group *C2/c*; orange blocks) and **1b** (*P2₁/c*; yellow needles) were grown *via* slow diffusion of diethyl ether into a concentrated methanol solution of the product. ESI-MS: $[M]^+$, 381.9 (³⁵Cl₂), 384.0 (³⁵Cl, ³⁷Cl). IR (cm⁻¹): N–H 3174 (*m*), 3116 (*m*). $\mu_{\text{eff}} = 4.6 \mu_{\text{B}}$ for the mixture of **1a/1b**, assuming a molecular weight of 418.63 g for [Fe(CTMC)Cl₂]Cl.

2.1.2. Synthesis of cis-[Fe(CTMC)₂]Cl (2). CTMC (0.199 g, 0.775 mmol, batch two) was dissolved in a 3:1 (v/v) dimethylformamide–triethyl orthoformate solution (16 ml) and then purged with nitrogen. In a second flask, FeCl₂·4H₂O (0.311 g, 1.57 mmol) was dissolved in about 17 ml of a 2:1 (v/v) dimethylformamide–triethyl orthoformate solution and the resulting solution was purged with nitrogen. Both solutions were warmed and the CTMC solution was transferred *via* cannula to the iron material flask and the reaction mixture was

left to stir under nitrogen at 55 °C for 45 min. Oxygen was then bubbled through the solution while 1 ml of concentrated hydrochloric acid was added. The slurry which formed was left to stir at room temperature for 2 h and 0.126 g of orange powder was obtained after filtration and washing with diethyl ether (30.1% yield). Compound **2** crystallized in the space group *Pbcn* from the slow diffusion of acetone into an aqueous solution of the product. ESI-MS: $[M]^+$, 382.0 (³⁵Cl₂), 384.0 (³⁵Cl, ³⁷Cl). IR (cm⁻¹): N–H 3073 (*m*), 3125 (*sh*). $\mu_{\text{eff}} = 5.6 \mu_{\text{B}}$.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were placed in calculated positions, riding on the parent atom, except for the amine H atoms of **1a** (H1 and H2) and **1b** (H1–H4), which were refined. Methyl and hydroxy (methanol) groups were permitted to rotate. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C,N,O})$, with 1.5 for CH₃ and OH, and 1.2 for CH, CH₂, and NH units, respectively. The Fe atom of the FeCl₄⁻ counter-anion in **1a** was modeled with very minor disorder over two positions (both located on twofold rotation axes) with close to identical but slightly shifted positions for the Cl atoms. The anisotropic displacement parameters (ADPs) of the Fe atoms (related by a half unit-cell shift with identical orientations) were constrained to be identical. U^{ij} components

Table 2
 Selected geometric parameters (Å, °) for **1a**, **1b**, and **2**.

| Bond lengths | 1a | 1b | 2 | Bond angles | 1a | 1b | 2 |
|--------------|-------------|------------|-------------|-----------------------------|-----------|--------------|------------|
| Fe1—Cl1 | 2.2710 (3) | 2.3084 (3) | 2.3018 (15) | N1—Fe1—N2 | 85.21 (4) | 85.23 (3) | 86.85 (15) |
| Fe1—Cl2 | — | 2.3047 (3) | — | N1—Fe1—N2 ⁱⁱⁱ | 94.79 (4) | — | 80.87 (16) |
| Fe1—N1 | 2.0276 (11) | 2.0826 (9) | 2.213 (4) | N1—Fe1—N4 | — | 94.13 (3) | — |
| Fe1—N2 | 2.0203 (11) | 2.0787 (9) | 2.154 (4) | N2—Fe1—N3 | — | 94.69 (3) | — |
| Fe1—N3 | — | 2.0654 (8) | — | N3—Fe1—N4 | — | 85.96 (3) | — |
| Fe1—N4 | — | 2.0761 (8) | — | Cl1—Fe1—Cl1 ^{iii†} | 180.0 | 179.012 (11) | 91.97 (8) |

Symmetry code for **2**: (i) $-x, y, -z + \frac{1}{2}$; for **1a**: (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$. † Compound **1b**: Cl2—Fe1—Cl1.

of ADPs for the Cl atoms were pairwise restrained to be similar (using a SIMU restraint with both s.u. values set to 0.01 Å²). The occupancy ratio refined to 0.9803 (7):0.0197 (7). The cationic moiety of **2** exhibits disorder about a *pseudo*-mirror plane through the metal center. Both disordered moieties have crystallographic twofold symmetry with half the cation within the asymmetric unit. Exempt from the disorder are the Fe atom and the noncoordinated chloride counter-anion (Cl2). The disordered moieties were restrained to have similar anisotropic displacement parameters and 1,2 and 1,3 bond distances and angles. The C1—N1 and C1B—N1B bond lengths required additional restraints. The occupancy ratio refined to 0.944 (3):0.056 (3). Notably, the minor disordered moiety maintains the hydrogen-bonding network evident between the major cationic moiety and the chloride counter-anion (*vide infra*), which may facilitate the presence of the minor moiety.

2.3. Computational details

The cationic portions of **1** and **2** were optimized from the crystallographic coordinates of **1a** and **2** (counter-anions were omitted) in the GAUSSIAN16 suite (Frisch *et al.*, 2016) using density functional theory (DFT) under vacuum, with the B3LYP functional (Becke, 1993) and Def2-SVP basis set (Weigend & Ahlrichs, 2005). The experimental magnetic moment of **1a/1b** (*vide supra*) is ambiguous, particularly given the presence of FeCl₄[−]; therefore, both high- and low-spin states were tested: the low-spin state was found to be lowest in

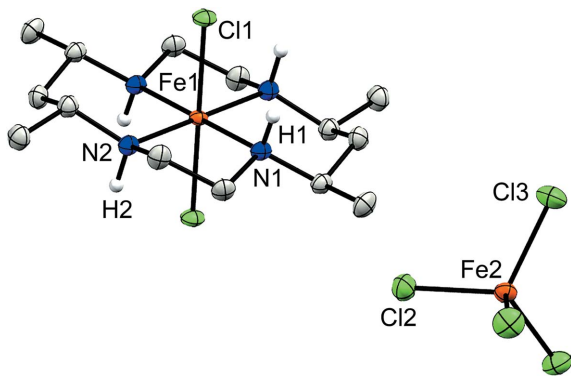


Figure 2
 Displacement ellipsoid plot of **1a**. H atoms (except for those bound to N atoms) and the minor disordered FeCl₄[−] moiety have been omitted for clarity.

energy for **1** and was thus used for all remaining calculations on structures with a planar macrocycle. It was only possible to optimize the high-spin state for **2** (consistent with the experimental magnetic moment); thus, this was the only spin state considered for structures with a folded macrocycle. GaussView6 (Dennington *et al.*, 2016) was used to analyze the data and manipulate the structures to form intermediate stereoisomers, as discussed below (see Fig. 6 for relevant discussion).

3. Results and discussion

Complex **1a** crystallized in the space group *C2/c* with the center of mass of the disordered FeCl₄[−] counter-anion lying on a twofold rotation axis, while the Fe atom of the macrocyclic moiety (Fe1) lies on an inversion center (Fig. 2). In contrast, no atoms lie on special positions in complex **1b**, which crystallized in the space group *P2₁/c* (Fig. 3) with a methanol solvent molecule. Finally, complex **2** crystallized in the space group *Pbcn*, with both the chloride counter-anion and iron center lying on a twofold rotation axis (Fig. 4).

The Fe centers in all three complexes display a pseudo-octahedral geometry with four coordination sites occupied by the N atoms of the CTMC macrocycle and two by the chloride ligands. Additionally, regardless of *cis*- or *trans*-dichloro configuration, **1** and **2** both display similar Fe—Cl bond lengths ranging from 2.2710 (3) Å in **1a** to just greater than 2.30 Å in **1b** and **2** (see Table 2 for selected bond lengths and angles). As expected, each structure exhibits larger N—Fe—N bond angles between amines bridged by the CH(Me)CH₂—CH(Me) linkage and smaller angles between the CH₂CH₂ linkage of the macrocycle. Although the structural parameters

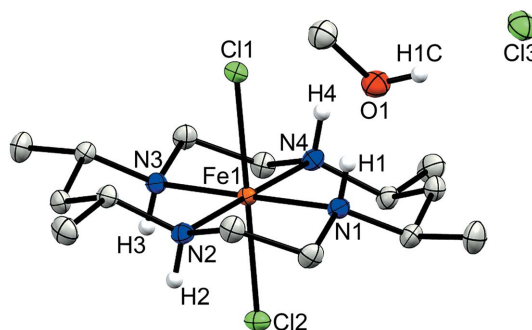


Figure 3
 Displacement ellipsoid plot of **1b**. H atoms (except for those bound to N and methanolic O atoms) have been omitted for clarity.

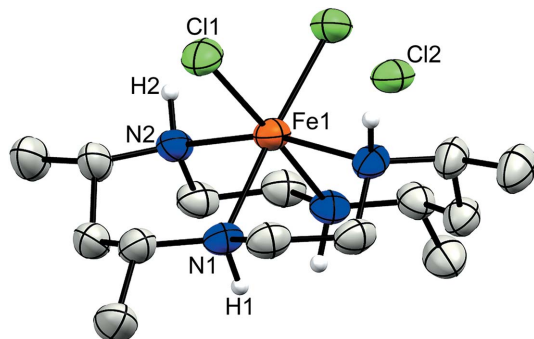


Figure 4
Displacement ellipsoid plot of **2**. H atoms (except for those bound to N atoms) and the minor disordered moiety have been omitted for clarity.

of the cation in **1b** are very similar to those of **1a**, the Fe–N and Fe–Cl bond lengths are slightly elongated in the former, which may be due to the differences in packing (*vide infra*). The least-squares overlay of **1a** and **1b** (Fig. 5) illustrates the general similarity of the cationic moieties. Both **1b** and **2** possess a noncoordinated chloride counter-ion, while **1a** contains a tetrachloridoferrate ion. As noted in the *Experimental* (Section 2), **2** was crystallized with the cationic portion disordered over two positions *via* a *pseudo*-mirror plane. As the second moiety accounts for only 5.6 (3)% of the occupancy and its bond lengths and angles were restrained to match that of the major moiety, it is not considered in the general bond length and angle comparisons.

The CTMC macrocycle appears as stereoisomers **A** and **B** (Fig. 1), as noted above. It is clear from the structures of **1a**, **1b**, and **2** that **A** tends to yield an iron complex in the *trans* configuration (**1a/1b**), while **B** tends to yield a complex in the *cis* configuration (**2**). To the best of our knowledge, the structure of **2** is the only example of a CTMC complex of **B**, and the only structure of a complex with a folded CTMC macrocycle. As seen in Table 2, the Fe–N bond lengths are consistently longer for **2** [2.154 (4)–2.213 (4) Å] compared to **1a** [2.0203 (11)–2.0276 (11) Å] and **1b** [2.0654 (8)–2.0826 (9) Å]. The N–Fe–N bond angles in **2** also deviate further from the ideal octahedral geometry of 90° than the same bond angles in **1a** and **1b**. Overall, the data suggest that the folded macrocycle conformation in **2** results in some strain compared to the planar coordination seen in **1a/1b**, favoring weaker Fe–N bonds.

To rationalize the preferences of a given stereoisomer for planar or folded coordination about the metal center, a series of DFT calculations were completed with **1a** as a low-spin complex and **2** as a high-spin complex in the gas phase. These calculations were completed by rotating one and then two methyl groups on the CTMC macrocycle, effectively reversing the *R* or *S* designation of the methyl groups, until the macrocycle was converted into the other observed stereoisomer (*i.e.* **A** into **B** and *vice versa*).

The DFT calculations indicate that the energy of the *cis* and *trans* configurations are indeed related to the stereoisomer of the macrocycle. A *trans* complex with **B** [Fig. 6(c)] is calculated to have an energy nearly 0.36 eV greater than that of a *trans* complex with **A** [*i.e.* **1a/1b**; Fig. 6(a)]. Forcing **A** to assume a

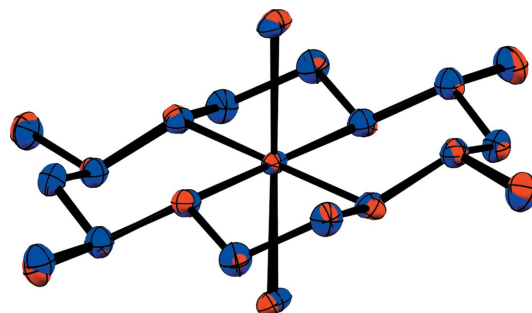


Figure 5
Least-squares overlay of **1a** (blue) and **1b** (red).

folded conformation about the metal center [Fig. 6(f)] results in a calculated energy nearly 0.34 eV higher than that of the folded coordination of stereoisomer **B**. The energies of all *trans*-dichloro structures [Figs. 6(a)–(c)] are calculated to be lower than those of all *cis*-dichloro structures [Figs. 6(d)–(f)]. However, this is likely an artifact due to the different spin states (see *Experimental*, Section 2) assigned for the *trans* (*a–c*, $S = 1/2$) and *cis* (*d–f*, $S = 5/2$) geometries. Moreover, these gas-phase calculations neglect the counter-anions, with which the cations interact substantially in the solid state (*vide infra*). Nevertheless, the stepwise trends within each geometric series (*a–c* and *d–f*) clearly illustrate the dependence of the energy of the planar and folded coordination modes on the stereoisomer of CTMC. Consistent with **1a/1b**, **A** clearly prefers a planar coordination geometry. In contrast, a folded macrocycle is most easily obtained with **B**, consistent with the structure of **2**. These energetic preferences are most reasonably attributed to the effect of the methyl substituents, which lean towards the arrangement of minimal steric interactions. This is consistent with reports on metal complexes of HMC, for which a strong preference of the stereoisomers to form *cis* or *trans* metal

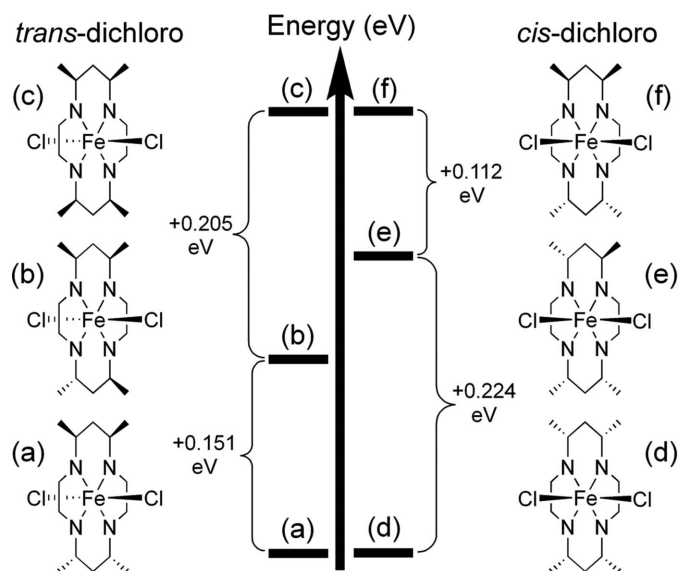


Figure 6
DFT-derived energetic orderings for complexes of various isomers of CTMC in planar (left) or folded (right) conformations.

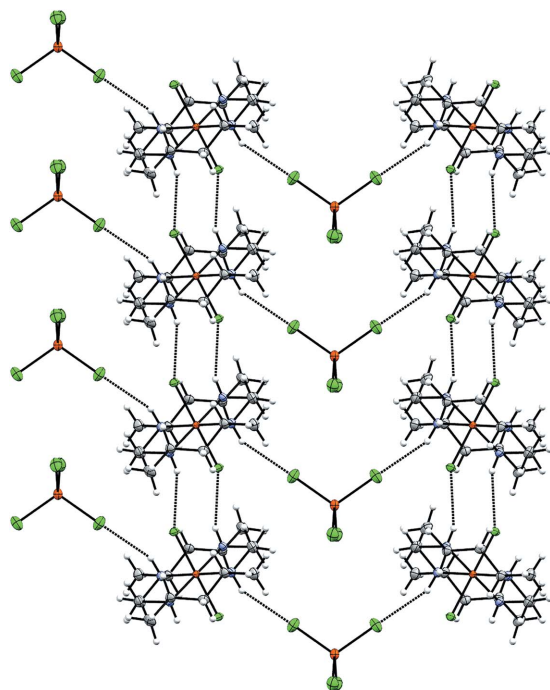


Figure 7
Illustration of the hydrogen-bonding interactions in **1a**.

complexes is well established (Clendening *et al.*, 2019; House *et al.*, 1983; Tyler *et al.*, 2016).

The previously reported data for *cis/trans*-[Fe^{III}(cyclam)-Cl₂]⁺ and *cis/trans*-[Fe^{III}(HMC)Cl₂]⁺ are useful for the discussion pertaining to planar *versus* folded macrocycles (Clendening *et al.*, 2019; Guilard *et al.*, 1997). As with iron-CTMC, the Fe–Cl bond lengths of these Fe^{III} complexes remain similar to one another regardless of a *cis* or *trans* nature. These complexes display Fe–Cl bond lengths ranging from 2.27 to 2.32 Å, with no significant dependence on the coordination geometry of the macrocycle. In contrast, the Fe–N bond lengths for all of the complexes confirm the trends observed for **1a/1b** *versus* **2**. Similar to the difference (0.16 Å) between **1a** and **2**, the averaged Fe–N bond lengths

of *cis*-[Fe^{III}(cyclam)Cl₂]⁺ and *cis*-[Fe^{III}(HMC)Cl₂]⁺ are roughly 0.16 and 0.17 Å longer than those of *trans*-[Fe^{III}(cyclam)Cl₂]⁺ and *trans*-[Fe^{III}(HMC)Cl₂]⁺, respectively. The N–Fe–N angles of **1a**, *trans*-[Fe^{III}(cyclam)Cl₂]⁺, and *trans*-[Fe^{III}(HMC)Cl₂]⁺ round to 85° between the CH₂CH₂ linkage and 95° between the CR₂CH₂CR₂ linkage. The N–Fe–N bond angles for the complexes with folded macrocycles vary from 79.56 (8) to 81.55 (5)° between the CH₂CH₂ linkage and from 83.15 (5) to 86.85 (15)° between the CR₂CH₂CR₂ linkage. In short, each *cis* complex exhibits longer Fe–N bond lengths and N–Fe–N bond angles which deviate further from an ideal octahedral coordination geometry than in the respective *trans* complexes.

It is further possible to compare the structural parameters as the number of methyl groups is systematically varied within either the *cis* or *trans* series. The averaged Fe–N bond lengths of *cis*-[Fe^{III}(HMC)Cl₂]Cl (*ca* 2.21 Å) appears longer than those of **2** and *cis*-[Fe^{III}(cyclam)Cl₂]Cl (both *ca* 2.18 Å) (Clendening *et al.*, 2019; Guilard *et al.*, 1997), which is likely due to the steric bulk of the two methyl groups at the same position of the macrocycle (*e.g.* 5,5 and 12,12), which forces at least one methyl group to be axially oriented. For the *trans* structures, a continuous increase in the averaged Fe–N bond lengths may be observed from *trans*-[Fe^{III}(cyclam)Cl₂]FeCl₄ (2.006 Å) to **1a** (2.024 Å) to *trans*-[Fe^{III}(HMC)Cl₂]FeCl₄ (2.054 Å) (Clendening *et al.*, 2019; Guilard *et al.*, 1997). Although methyl groups are electron rich and would thus be expected to slightly increase the donor strength of the macrocycle towards the electron-poor Fe^{III} center, it appears that steric effects dominate, resulting in a progressively weaker Fe–N bond with increasing number of macrocyclic substituents.

The packing in **1a** is strikingly similar to *trans*-[Fe^{III}(HMC)Cl₂]FeCl₄ (Clendening *et al.*, 2019) and *trans*-[Fe^{III}(cyclam)Cl₂]FeCl₄ (Guilard *et al.*, 1997), despite the differences in space group (*C2/c*, *P2₁/c*, and *P2₁/n*, respectively). The cationic units in all cases pack in a series of columns (see Fig. 7), each linked to the preceding and following unit by two hydrogen bonds between the amine groups and the chloride ligands (N1 and Cl1 in the case of **1a**). The remaining unique

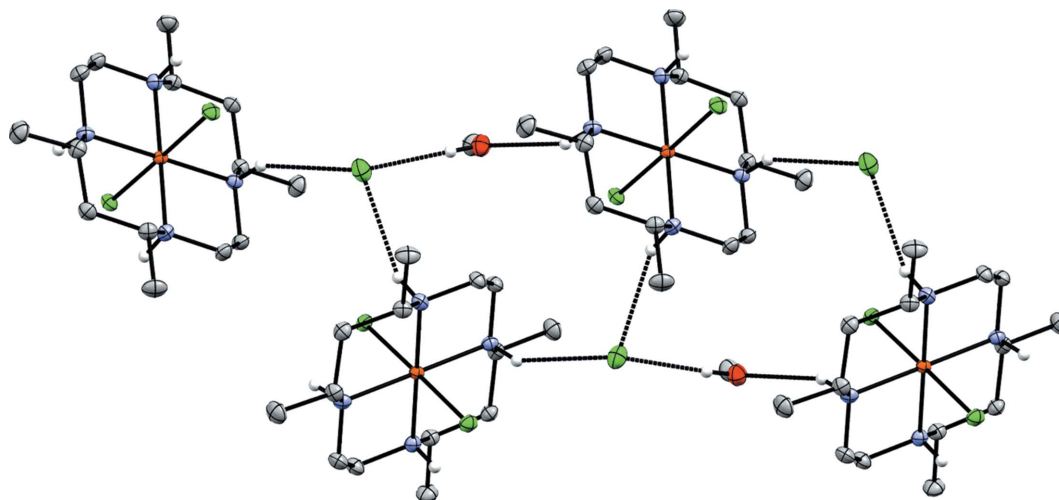


Figure 8
Illustration of the hydrogen-bonding interactions in **1b**.

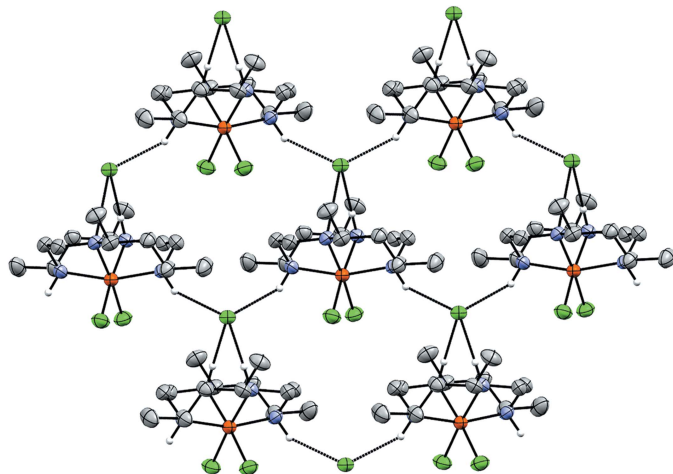


Figure 9
Illustration of the hydrogen-bonding interactions in **2**.

amine position(s) (N2 in **1a**) instead participates in hydrogen-bonding interactions with the FeCl_4^- units (via Cl3 in **1a**), which are also arranged in columns. This similarity suggests that the common tetrachloridoferrate counter-anion may be favored due to this ability to participate in extensive hydrogen-bonding networks with the ferric chloride complexes bearing planar macrocycles. The minor disordered counter-anion of **1a** has the same hydrogen-bonding interactions as its major counterpart.

Lacking the FeCl_4^- counter-anion, complex **1b** ($P2_1/c$) packs differently, forming infinite chains parallel to [001] connected *via* hydrogen bonds with one cation, one chloride counter-anion, and one methanol solvent molecule as the repeat unit that are related to each other *via* one of the glide plane(s) (see Fig. 8). In between the glide planes and between neighboring chains, the molecules are instead related by inversion. Interestingly, and in sharp contrast to the case of **1a** and its structural relatives, there are in **1b** no direct hydrogen bonds between the cationic moieties (N1 is instead hydrogen bonded to the methanol solvent molecule and N3 and N4 to

the chloride counter-anion), and both of the chloride ligands and one of the amine positions (N2) in **1b** do not participate in hydrogen bonding at all.

This illustrates the difficulty of a single chloride counter-anion to effectively facilitate the hydrogen bonding within the *trans* orientation of these complexes, apparently necessitating the solvent inclusion and further supporting the conjecture that the inclusion of FeCl_4^- in the crystal structures is favored by its ability to facilitate ordered packing in the resulting solid. The packing differences may also hint at a supramolecular origin for the elongated Fe—Cl and Fe—N bond lengths of the cationic moieties of **1b** versus **1a**, as the latter engages in more extensive hydrogen bonding (six hydrogen bonds per **1a**⁺ and three per **1b**⁺) which includes the chloride ligands, in contrast to **1b**.

The similarity of the hydrogen-bonding network among structural analogues extends to the cases of **2** ($Pbcn$), *cis*- $[\text{Fe}^{\text{III}}(\text{HMC})\text{Cl}_2]\text{Cl}$ ($Fdd2$), and *cis*- $[\text{Fe}^{\text{III}}(\text{cyclam})\text{Cl}_2]\text{Cl}$ ($P2_1/c$) (Clendening *et al.*, 2019; Guillard *et al.*, 1997). As with **1b**, neither of the chloride ligands participates in hydrogen bonding, nor do any of the cationic moieties hydrogen bond with each other. However, in all three of these structures with a folded macrocycle, a close network of hydrogen bonding is facilitated by the chloride counter-anion, which simultaneously participates in four such interactions with three separate cationic moieties (Fig. 9). Two hydrogen bonds occur with the amines of a single moiety which face into the cavity of the folded macrocycle (N1 and its symmetry equivalent in **2**). The remaining hydrogen bonds are formed from interactions with an outward-facing amine group of two separate moieties. Thus, in the case of the folded macrocycles, the large FeCl_4^- anion is no longer necessary in order to stabilize an extended network of hydrogen bonds. Interestingly, the minor disordered moiety of **2** maintains these strong hydrogen-bonding networks, which perhaps facilitates the disorder about the *pseudo*-mirror plane in **2** (see Fig. 10).

4. Conclusion

This article describes the structural properties of new ferric dichloride complexes of CTMC stereoisomers **A** (**1a/1b** – planar macrocycle) and **B** (**2** – folded macrocycle). DFT calculations are used to support the apparent preferences of **A** and **B** to form planar or folded coordination complexes, respectively. Moreover, comparison to related structures based on cyclam and HMC illustrate a strong dependence of the intermolecular hydrogen-bonding interactions on the macrocyclic coordination geometry [*i.e.* planar (*trans*-dichloro) or folded (*cis*-dichloro)]. Given the known reactivity dependence of a complex on its overall geometry, complexes **1a**, **1b**, and **2** demonstrate how control can be exercised over the geometric coordination isomer by the stereochemistry of as few as four methyl groups on the periphery of the macrocycle. This contrasts with the ability of cyclam (no methyl groups) to assume either folded or planar conformations (Guillard *et al.*, 1997), and complements the rigid structural preferences ascribed to the stereoisomers of HMC, which

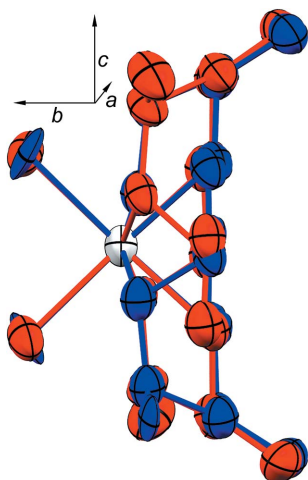


Figure 10
View of the major (red) and minor (blue) disordered moieties of **2** along the *a* axis, with the *b* axis oriented horizontally and the *c* axis vertically.

bears six methyl groups (Clendening *et al.*, 2019; House *et al.*, 1983; Tyler *et al.*, 2016). Work is underway to investigate derivatives of Fe(CTMC) with the goal of studying the charge-transfer excited states of such complexes.

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supporting information

Acta Cryst. (2022). C78, 507-514 [https://doi.org/10.1107/S205322962200849X]

Geometric isomers of dichloridoiron(III) complexes of CTMC (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane)

Stephanie S. DeLancey, Reese A. Clendening, Matthias Zeller and Tong Ren

Computing details

For all structures, data collection: *APEX3* (Bruker, 2019); cell refinement: *SAINTE* (Bruker, 2019); data reduction: *SAINTE* (Bruker, 2019). Program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a) for (1a), (1b); *SHELXT* (Sheldrick, 2015a) for (2). For all structures, program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b) and *SHELXL* (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

trans-Dichlorido[(5*SR*,7*RS*,12*RS*,14*SR*)-4,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) tetrachloridoferrate (1a)

Crystal data

[Fe(C₁₄H₃₂N₄)Cl₂][FeCl₄]

M_r = 580.83

Monoclinic, *C2/c*

a = 20.3512 (13) Å

b = 6.4815 (4) Å

c = 18.049 (1) Å

β = 100.452 (3)°

V = 2341.3 (2) Å³

Z = 4

F(000) = 1192

D_x = 1.648 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9346 reflections

θ = 3.3–33.1°

μ = 1.93 mm⁻¹

T = 150 K

Block, orange

0.20 × 0.20 × 0.20 mm

Data collection

Bruker AXS D8 Quest
diffractometer with PhotonII charge-integrating
pixel array detector (CPAD)

Radiation source: fine focus sealed tube X-ray
source

Triumph curved graphite crystal
monochromator

Detector resolution: 7.4074 pixels mm⁻¹

ω and ϕ scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

T_{min} = 0.656, *T_{max}* = 0.747

71685 measured reflections

4483 independent reflections

3561 reflections with *I* > 2σ(*I*)

R_{int} = 0.074

θ_{\max} = 33.2°, θ_{\min} = 3.3°

h = -31→31

k = -9→9

l = -27→27

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.027

wR(*F*²) = 0.067

S = 1.02

4483 reflections

148 parameters

15 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 1.680P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The iron atom of the FeCl4 counteranion was modelled as having very minor disorder over two positions (both located on two-fold rotation axes) with close to identical but slightly shifted positions for the chlorine atoms. The ADPs of the Fe atoms (related by a half unit cell shift with identical orientations) were constrained to be identical. Uij components of ADPs for the chlorine atoms were pairwise restrained to be similar (using a SIMU restraint with both esds set to 0.01 Angstrom squared). The occupancy ratio refined to 0.9803 (7) to 0.0197 (7).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|-------------|--------------|-------------|----------------------------------|------------|
| Fe2 | 0.500000 | 0.78720 (5) | 0.250000 | 0.02099 (7) | 0.9803 (7) |
| Cl2 | 0.43633 (2) | 0.98293 (8) | 0.30654 (3) | 0.03295 (10) | 0.9803 (7) |
| Cl3 | 0.56398 (3) | 0.59283 (8) | 0.33308 (3) | 0.03643 (12) | 0.9803 (7) |
| Fe2B | 0.500000 | 0.295 (2) | 0.250000 | 0.02099 (7) | 0.0197 (7) |
| Cl2B | 0.4455 (13) | 0.065 (4) | 0.3013 (16) | 0.044 (5) | 0.0197 (7) |
| Cl3B | 0.5568 (16) | 0.519 (4) | 0.3227 (15) | 0.036 (4) | 0.0197 (7) |
| Fe1 | 0.250000 | 0.750000 | 0.500000 | 0.01337 (6) | |
| Cl1 | 0.24845 (2) | 0.46489 (5) | 0.57279 (2) | 0.01997 (7) | |
| N1 | 0.24598 (6) | 0.93617 (17) | 0.58935 (6) | 0.0171 (2) | |
| H1 | 0.2410 (8) | 1.058 (3) | 0.5698 (9) | 0.021* | |
| N2 | 0.35008 (6) | 0.76192 (17) | 0.53443 (6) | 0.0181 (2) | |
| H2 | 0.3592 (8) | 0.642 (3) | 0.5615 (10) | 0.022* | |
| C1 | 0.31267 (7) | 0.9338 (2) | 0.63842 (7) | 0.0220 (3) | |
| H1A | 0.317297 | 0.809713 | 0.670954 | 0.026* | |
| H1B | 0.318213 | 1.057391 | 0.671182 | 0.026* | |
| C2 | 0.36500 (7) | 0.9320 (2) | 0.58942 (8) | 0.0233 (3) | |
| H2A | 0.364878 | 1.065345 | 0.562640 | 0.028* | |
| H2B | 0.409764 | 0.911880 | 0.620775 | 0.028* | |
| C3 | 0.39433 (7) | 0.7600 (2) | 0.47710 (8) | 0.0210 (2) | |
| H3 | 0.386422 | 0.890263 | 0.447113 | 0.025* | |
| C5 | 0.37661 (7) | 0.5783 (2) | 0.42328 (8) | 0.0224 (3) | |
| H5A | 0.412631 | 0.562226 | 0.393511 | 0.027* | |
| H5B | 0.375954 | 0.451418 | 0.453672 | 0.027* | |
| C6 | 0.31013 (7) | 0.5939 (2) | 0.36869 (7) | 0.0196 (2) | |
| H6 | 0.306426 | 0.736177 | 0.346859 | 0.024* | |
| C4 | 0.46790 (7) | 0.7525 (2) | 0.51366 (9) | 0.0259 (3) | |
| H4A | 0.495428 | 0.748858 | 0.474401 | 0.039* | |
| H4B | 0.476420 | 0.628507 | 0.545009 | 0.039* | |
| H4C | 0.479181 | 0.875264 | 0.545082 | 0.039* | |

| | | | | |
|-----|-------------|------------|-------------|------------|
| C7 | 0.30763 (8) | 0.4401 (2) | 0.30396 (8) | 0.0270 (3) |
| H7A | 0.345957 | 0.462984 | 0.279012 | 0.041* |
| H7B | 0.266122 | 0.459639 | 0.267536 | 0.041* |
| H7C | 0.309221 | 0.299169 | 0.323860 | 0.041* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|--------------|--------------|--------------|--------------|---------------|---------------|
| Fe2 | 0.02090 (14) | 0.02448 (15) | 0.01653 (13) | 0.000 | 0.00055 (10) | 0.000 |
| Cl2 | 0.0332 (2) | 0.0394 (3) | 0.02645 (18) | 0.0078 (2) | 0.00606 (16) | -0.00410 (19) |
| Cl3 | 0.0380 (3) | 0.0370 (3) | 0.0316 (2) | 0.0082 (2) | -0.00105 (18) | 0.0104 (2) |
| Fe2B | 0.02090 (14) | 0.02448 (15) | 0.01653 (13) | 0.000 | 0.00055 (10) | 0.000 |
| Cl2B | 0.036 (8) | 0.045 (9) | 0.043 (8) | -0.011 (8) | -0.017 (7) | 0.017 (8) |
| Cl3B | 0.048 (8) | 0.022 (8) | 0.035 (8) | -0.013 (7) | -0.002 (7) | 0.009 (7) |
| Fe1 | 0.01769 (12) | 0.01052 (11) | 0.01146 (10) | 0.00053 (8) | 0.00149 (8) | 0.00009 (8) |
| Cl1 | 0.02917 (16) | 0.01303 (13) | 0.01735 (13) | 0.00079 (11) | 0.00326 (11) | 0.00235 (10) |
| N1 | 0.0219 (5) | 0.0147 (5) | 0.0145 (4) | -0.0005 (4) | 0.0027 (4) | -0.0011 (4) |
| N2 | 0.0198 (5) | 0.0175 (5) | 0.0168 (5) | -0.0004 (4) | 0.0029 (4) | -0.0009 (4) |
| C1 | 0.0241 (6) | 0.0252 (6) | 0.0155 (5) | -0.0013 (5) | 0.0004 (5) | -0.0045 (5) |
| C2 | 0.0222 (6) | 0.0267 (7) | 0.0200 (6) | -0.0033 (5) | 0.0011 (5) | -0.0068 (5) |
| C3 | 0.0212 (6) | 0.0219 (6) | 0.0200 (6) | 0.0005 (5) | 0.0043 (5) | -0.0019 (5) |
| C5 | 0.0238 (6) | 0.0219 (6) | 0.0221 (6) | 0.0032 (5) | 0.0058 (5) | -0.0029 (5) |
| C6 | 0.0242 (6) | 0.0185 (6) | 0.0167 (5) | -0.0002 (5) | 0.0054 (5) | -0.0018 (4) |
| C4 | 0.0202 (6) | 0.0297 (7) | 0.0277 (7) | -0.0008 (5) | 0.0042 (5) | -0.0009 (6) |
| C7 | 0.0333 (8) | 0.0279 (7) | 0.0217 (6) | -0.0021 (6) | 0.0101 (6) | -0.0074 (5) |

Geometric parameters (Å, °)

| | | | |
|------------------------|-------------|--------|-------------|
| Fe2—Cl2 | 2.1931 (5) | C1—C2 | 1.5028 (19) |
| Fe2—Cl2 ⁱ | 2.1932 (5) | C1—H1A | 0.9900 |
| Fe2—Cl3 ⁱ | 2.1960 (5) | C1—H1B | 0.9900 |
| Fe2—Cl3 | 2.1961 (5) | C2—H2A | 0.9900 |
| Fe2B—Cl3B ⁱ | 2.147 (16) | C2—H2B | 0.9900 |
| Fe2B—Cl3B | 2.147 (16) | C3—C4 | 1.523 (2) |
| Fe2B—Cl2B ⁱ | 2.164 (16) | C3—C5 | 1.5275 (19) |
| Fe2B—Cl2B | 2.164 (16) | C3—H3 | 1.0000 |
| Fe1—N2 ⁱⁱ | 2.0203 (11) | C5—C6 | 1.5257 (19) |
| Fe1—N2 | 2.0203 (11) | C5—H5A | 0.9900 |
| Fe1—N1 | 2.0276 (11) | C5—H5B | 0.9900 |
| Fe1—N1 ⁱⁱ | 2.0276 (11) | C6—C7 | 1.5297 (18) |
| Fe1—Cl1 ⁱⁱ | 2.2709 (3) | C6—H6 | 1.0000 |
| Fe1—Cl1 | 2.2710 (3) | C4—H4A | 0.9800 |
| N1—C1 | 1.4802 (17) | C4—H4B | 0.9800 |
| N1—C6 ⁱⁱ | 1.4933 (17) | C4—H4C | 0.9800 |
| N1—H1 | 0.862 (18) | C7—H7A | 0.9800 |
| N2—C2 | 1.4776 (17) | C7—H7B | 0.9800 |
| N2—C3 | 1.4900 (17) | C7—H7C | 0.9800 |
| N2—H2 | 0.917 (18) | | |

| | | | |
|---|-------------|---------------------------|--------------|
| C12—Fe2—C12 ⁱ | 109.32 (3) | N1—C1—H1B | 110.0 |
| C12—Fe2—C13 ⁱ | 108.81 (2) | C2—C1—H1B | 110.0 |
| C12 ⁱ —Fe2—C13 ⁱ | 109.96 (2) | H1A—C1—H1B | 108.4 |
| C12—Fe2—C13 | 109.96 (2) | N2—C2—C1 | 108.65 (11) |
| C12 ⁱ —Fe2—C13 | 108.81 (2) | N2—C2—H2A | 110.0 |
| C13 ⁱ —Fe2—C13 | 109.99 (3) | C1—C2—H2A | 110.0 |
| C13B ⁱ —Fe2B—C13B | 95.0 (17) | N2—C2—H2B | 110.0 |
| C13B ⁱ —Fe2B—C12B | 117.8 (12) | C1—C2—H2B | 110.0 |
| C13B—Fe2B—C12B | 117.7 (11) | H2A—C2—H2B | 108.3 |
| C12B ⁱ —Fe2B—C12B | 93 (2) | N2—C3—C4 | 111.70 (11) |
| N2 ⁱⁱ —Fe1—N2 | 180.0 | N2—C3—C5 | 110.20 (11) |
| N2 ⁱⁱ —Fe1—N1 | 94.79 (4) | C4—C3—C5 | 110.55 (11) |
| N2—Fe1—N1 | 85.21 (4) | N2—C3—H3 | 108.1 |
| N2 ⁱⁱ —Fe1—N1 ⁱⁱ | 85.21 (4) | C4—C3—H3 | 108.1 |
| N2—Fe1—N1 ⁱⁱ | 94.79 (4) | C5—C3—H3 | 108.1 |
| N1—Fe1—N1 ⁱⁱ | 180.0 | C6—C5—C3 | 116.04 (11) |
| N2 ⁱⁱ —Fe1—C11 ⁱⁱ | 88.41 (3) | C6—C5—H5A | 108.3 |
| N2—Fe1—C11 ⁱⁱ | 91.59 (3) | C3—C5—H5A | 108.3 |
| N1—Fe1—C11 ⁱⁱ | 89.01 (3) | C6—C5—H5B | 108.3 |
| N1 ⁱⁱ —Fe1—C11 ⁱⁱ | 90.99 (3) | C3—C5—H5B | 108.3 |
| N2 ⁱⁱ —Fe1—C11 | 91.59 (3) | H5A—C5—H5B | 107.4 |
| N2—Fe1—C11 | 88.41 (3) | N1 ⁱⁱ —C6—C5 | 109.50 (10) |
| N1—Fe1—C11 | 90.99 (3) | N1 ⁱⁱ —C6—C7 | 112.31 (11) |
| N1 ⁱⁱ —Fe1—C11 | 89.01 (3) | C5—C6—C7 | 110.66 (11) |
| C11 ⁱⁱ —Fe1—C11 | 180.0 | N1 ⁱⁱ —C6—H6 | 108.1 |
| C1—N1—C6 ⁱⁱ | 113.43 (10) | C5—C6—H6 | 108.1 |
| C1—N1—Fe1 | 107.75 (8) | C7—C6—H6 | 108.1 |
| C6 ⁱⁱ —N1—Fe1 | 118.07 (8) | C3—C4—H4A | 109.5 |
| C1—N1—H1 | 106.4 (11) | C3—C4—H4B | 109.5 |
| C6 ⁱⁱ —N1—H1 | 106.4 (11) | H4A—C4—H4B | 109.5 |
| Fe1—N1—H1 | 103.7 (11) | C3—C4—H4C | 109.5 |
| C2—N2—C3 | 113.35 (11) | H4A—C4—H4C | 109.5 |
| C2—N2—Fe1 | 107.94 (8) | H4B—C4—H4C | 109.5 |
| C3—N2—Fe1 | 119.26 (8) | C6—C7—H7A | 109.5 |
| C2—N2—H2 | 106.0 (11) | C6—C7—H7B | 109.5 |
| C3—N2—H2 | 105.9 (10) | H7A—C7—H7B | 109.5 |
| Fe1—N2—H2 | 103.1 (11) | C6—C7—H7C | 109.5 |
| N1—C1—C2 | 108.58 (11) | H7A—C7—H7C | 109.5 |
| N1—C1—H1A | 110.0 | H7B—C7—H7C | 109.5 |
| C2—C1—H1A | 110.0 | | |
| C6 ⁱⁱ —N1—C1—C2 | 171.29 (11) | C2—N2—C3—C5 | 179.08 (11) |
| Fe1—N1—C1—C2 | 38.66 (13) | Fe1—N2—C3—C5 | -52.15 (13) |
| C3—N2—C2—C1 | 173.45 (11) | N2—C3—C5—C6 | 70.58 (15) |
| Fe1—N2—C2—C1 | 39.08 (13) | C4—C3—C5—C6 | -165.46 (12) |
| N1—C1—C2—N2 | -52.20 (15) | C3—C5—C6—N1 ⁱⁱ | -72.54 (15) |

| | | | |
|--------------|-------------|-------------|-------------|
| C2—N2—C3—C4 | 55.78 (15) | C3—C5—C6—C7 | 163.13 (12) |
| Fe1—N2—C3—C4 | -175.44 (9) | | |

Symmetry codes: (i) $-x+1, y, -z+1/2$; (ii) $-x+1/2, -y+3/2, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|------------|-------------|-------------|---------------|
| N2—H2 \cdots C13 ^a iii | 0.917 (18) | 2.704 (18) | 3.5421 (12) | 152.5 (14) |
| N2—H2 \cdots C13 ^b iii | 0.917 (18) | 2.66 (3) | 3.43 (3) | 142.1 (14) |
| N1—H1 \cdots C11 ^{iv} | 0.862 (18) | 2.643 (18) | 3.4411 (12) | 154.5 (14) |

Symmetry codes: (iii) $-x+1, -y+1, -z+1$; (iv) $x, y+1, z$.

trans-Dichlorido[(5*SR*,7*RS*,12*RS*,14*SR*)-4,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) chloride methanol monosolvate (1b)

Crystal data

$[\text{Fe}(\text{C}_{14}\text{H}_{32}\text{N}_4)\text{Cl}_2]\text{Cl}\cdot\text{CH}_4\text{O}$

$M_r = 450.68$

Monoclinic, $P2_1/c$

$a = 8.1632$ (4) \AA

$b = 20.8470$ (12) \AA

$c = 12.1387$ (7) \AA

$\beta = 95.024$ (2) $^\circ$

$V = 2057.8$ (2) \AA^3

$Z = 4$

$F(000) = 956$

$D_x = 1.455$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 9046 reflections

$\theta = 2.6\text{--}33.1^\circ$

$\mu = 1.13$ mm^{-1}

$T = 150$ K

Needle, yellow

$0.34 \times 0.10 \times 0.09$ mm

Data collection

Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)

Radiation source: fine focus sealed tube X-ray source

Triumph curved graphite crystal monochromator

Detector resolution: 7.4074 pixels mm^{-1}

ω and phi scans

Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.679, T_{\max} = 0.747$

125711 measured reflections

7859 independent reflections

6505 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 33.2^\circ, \theta_{\min} = 2.7^\circ$

$h = -12 \rightarrow 12$

$k = -32 \rightarrow 32$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.061$

$S = 1.04$

7859 reflections

235 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.6993P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.70$ e \AA^{-3}

$\Delta\rho_{\min} = -0.58$ e \AA^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| Fe1 | 0.47180 (2) | 0.37521 (2) | 0.81519 (2) | 0.01202 (3) |
| Cl1 | 0.27817 (3) | 0.32101 (2) | 0.70046 (2) | 0.01732 (5) |
| Cl2 | 0.66305 (3) | 0.43097 (2) | 0.92874 (2) | 0.01876 (5) |
| Cl3 | 0.52630 (4) | 0.35899 (2) | 0.21489 (2) | 0.02871 (6) |
| O1 | 0.40718 (10) | 0.38361 (4) | 0.44329 (7) | 0.02515 (16) |
| H1C | 0.455854 | 0.378135 | 0.385847 | 0.038* |
| N1 | 0.58062 (10) | 0.40542 (4) | 0.67522 (7) | 0.01620 (15) |
| H1 | 0.5277 (17) | 0.3869 (7) | 0.6179 (12) | 0.019* |
| N2 | 0.33640 (10) | 0.45956 (4) | 0.79670 (7) | 0.01590 (15) |
| H2 | 0.3834 (17) | 0.4855 (7) | 0.8429 (12) | 0.019* |
| N3 | 0.36207 (10) | 0.34494 (4) | 0.95311 (7) | 0.01496 (14) |
| H3 | 0.4117 (17) | 0.3639 (7) | 1.0094 (12) | 0.018* |
| N4 | 0.60971 (10) | 0.29159 (4) | 0.83285 (7) | 0.01582 (15) |
| H4 | 0.5637 (17) | 0.2639 (7) | 0.7871 (11) | 0.019* |
| C1 | 0.53940 (13) | 0.47461 (5) | 0.66291 (9) | 0.01939 (18) |
| H1A | 0.557193 | 0.489153 | 0.587241 | 0.023* |
| H1B | 0.611401 | 0.500151 | 0.716153 | 0.023* |
| C2 | 0.36108 (13) | 0.48431 (5) | 0.68441 (9) | 0.01946 (18) |
| H2A | 0.332969 | 0.530483 | 0.679677 | 0.023* |
| H2B | 0.288599 | 0.461058 | 0.628190 | 0.023* |
| C3 | 0.15991 (12) | 0.45597 (5) | 0.81998 (8) | 0.01685 (17) |
| H3A | 0.102435 | 0.425920 | 0.765204 | 0.020* |
| C4 | 0.07595 (14) | 0.52151 (5) | 0.80674 (10) | 0.0237 (2) |
| H4A | 0.076085 | 0.535789 | 0.729836 | 0.036* |
| H4B | 0.135678 | 0.552648 | 0.855612 | 0.036* |
| H4C | -0.037662 | 0.518041 | 0.826315 | 0.036* |
| C5 | 0.14494 (12) | 0.42890 (5) | 0.93590 (8) | 0.01754 (17) |
| H5A | 0.031619 | 0.437079 | 0.955525 | 0.021* |
| H5B | 0.220314 | 0.453395 | 0.988641 | 0.021* |
| C6 | 0.18158 (11) | 0.35740 (5) | 0.95346 (8) | 0.01603 (17) |
| H6 | 0.123673 | 0.333249 | 0.890369 | 0.019* |
| C7 | 0.11429 (14) | 0.33419 (6) | 1.06051 (9) | 0.0239 (2) |
| H7A | -0.003351 | 0.344022 | 1.058253 | 0.036* |
| H7B | 0.172703 | 0.355944 | 1.123865 | 0.036* |
| H7C | 0.130490 | 0.287752 | 1.067843 | 0.036* |
| C8 | 0.40632 (12) | 0.27600 (5) | 0.96661 (9) | 0.01822 (17) |
| H8A | 0.335978 | 0.249714 | 0.913538 | 0.022* |
| H8B | 0.388881 | 0.261616 | 1.042426 | 0.022* |
| C9 | 0.58568 (12) | 0.26783 (5) | 0.94559 (8) | 0.01813 (18) |

| | | | | |
|------|--------------|-------------|--------------|--------------|
| H9A | 0.656282 | 0.292329 | 1.001177 | 0.022* |
| H9B | 0.616859 | 0.222006 | 0.951977 | 0.022* |
| C10 | 0.78611 (12) | 0.29646 (5) | 0.80966 (8) | 0.01750 (17) |
| H10 | 0.840678 | 0.328751 | 0.861602 | 0.021* |
| C11 | 0.87818 (14) | 0.23277 (5) | 0.82714 (11) | 0.0256 (2) |
| H11A | 0.820901 | 0.199402 | 0.781780 | 0.038* |
| H11B | 0.882138 | 0.220565 | 0.905291 | 0.038* |
| H11C | 0.990414 | 0.237568 | 0.805522 | 0.038* |
| C12 | 0.79645 (13) | 0.32071 (5) | 0.69159 (9) | 0.01947 (18) |
| H12A | 0.718888 | 0.295318 | 0.641738 | 0.023* |
| H12B | 0.908597 | 0.311878 | 0.670309 | 0.023* |
| C13 | 0.75944 (12) | 0.39183 (5) | 0.67087 (9) | 0.01846 (18) |
| H13 | 0.821325 | 0.416959 | 0.731130 | 0.022* |
| C14 | 0.82060 (15) | 0.41270 (6) | 0.56061 (10) | 0.0272 (2) |
| H14A | 0.758797 | 0.389821 | 0.499875 | 0.041* |
| H14B | 0.937854 | 0.402626 | 0.560510 | 0.041* |
| H14C | 0.804288 | 0.458995 | 0.550918 | 0.041* |
| C15 | 0.23468 (15) | 0.38140 (6) | 0.41595 (10) | 0.0275 (2) |
| H15A | 0.211506 | 0.360725 | 0.343752 | 0.041* |
| H15B | 0.190455 | 0.425126 | 0.412864 | 0.041* |
| H15C | 0.182924 | 0.356809 | 0.472335 | 0.041* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|---------------|---------------|
| Fe1 | 0.01143 (6) | 0.01141 (6) | 0.01307 (6) | −0.00026 (4) | 0.00023 (4) | 0.00017 (4) |
| Cl1 | 0.01816 (10) | 0.01672 (10) | 0.01704 (10) | −0.00156 (8) | 0.00141 (8) | −0.00360 (8) |
| Cl2 | 0.01866 (10) | 0.01754 (10) | 0.01942 (11) | −0.00260 (8) | −0.00196 (8) | −0.00258 (8) |
| Cl3 | 0.02918 (13) | 0.03443 (15) | 0.02208 (12) | 0.00209 (11) | −0.00018 (10) | −0.00469 (10) |
| O1 | 0.0250 (4) | 0.0287 (4) | 0.0214 (4) | −0.0019 (3) | −0.0001 (3) | 0.0001 (3) |
| N1 | 0.0143 (3) | 0.0153 (4) | 0.0189 (4) | −0.0012 (3) | 0.0008 (3) | −0.0002 (3) |
| N2 | 0.0150 (3) | 0.0161 (4) | 0.0163 (4) | −0.0003 (3) | −0.0003 (3) | −0.0003 (3) |
| N3 | 0.0143 (3) | 0.0143 (3) | 0.0162 (4) | −0.0002 (3) | 0.0007 (3) | −0.0007 (3) |
| N4 | 0.0136 (3) | 0.0166 (4) | 0.0170 (4) | −0.0001 (3) | −0.0002 (3) | 0.0016 (3) |
| C1 | 0.0202 (4) | 0.0163 (4) | 0.0219 (5) | −0.0007 (3) | 0.0029 (4) | 0.0049 (3) |
| C2 | 0.0199 (4) | 0.0175 (4) | 0.0209 (4) | 0.0026 (3) | 0.0014 (3) | 0.0045 (3) |
| C3 | 0.0138 (4) | 0.0170 (4) | 0.0194 (4) | 0.0022 (3) | −0.0002 (3) | −0.0013 (3) |
| C4 | 0.0236 (5) | 0.0202 (5) | 0.0271 (5) | 0.0073 (4) | 0.0000 (4) | −0.0005 (4) |
| C5 | 0.0163 (4) | 0.0175 (4) | 0.0191 (4) | 0.0016 (3) | 0.0029 (3) | −0.0026 (3) |
| C6 | 0.0135 (4) | 0.0176 (4) | 0.0171 (4) | −0.0010 (3) | 0.0023 (3) | −0.0011 (3) |
| C7 | 0.0216 (5) | 0.0281 (5) | 0.0229 (5) | −0.0001 (4) | 0.0073 (4) | 0.0035 (4) |
| C8 | 0.0199 (4) | 0.0151 (4) | 0.0200 (4) | 0.0006 (3) | 0.0036 (3) | 0.0034 (3) |
| C9 | 0.0190 (4) | 0.0167 (4) | 0.0185 (4) | 0.0027 (3) | 0.0007 (3) | 0.0041 (3) |
| C10 | 0.0130 (4) | 0.0179 (4) | 0.0214 (4) | 0.0012 (3) | 0.0004 (3) | 0.0003 (3) |
| C11 | 0.0182 (5) | 0.0206 (5) | 0.0375 (6) | 0.0046 (4) | −0.0007 (4) | 0.0013 (4) |
| C12 | 0.0167 (4) | 0.0208 (5) | 0.0212 (5) | 0.0020 (3) | 0.0035 (3) | −0.0014 (4) |
| C13 | 0.0146 (4) | 0.0207 (4) | 0.0204 (4) | −0.0018 (3) | 0.0030 (3) | 0.0008 (4) |
| C14 | 0.0254 (5) | 0.0312 (6) | 0.0263 (5) | −0.0006 (4) | 0.0102 (4) | 0.0049 (4) |

| | | | | | | |
|-----|------------|------------|------------|------------|-------------|------------|
| C15 | 0.0257 (5) | 0.0294 (6) | 0.0271 (5) | 0.0009 (4) | -0.0001 (4) | 0.0010 (4) |
|-----|------------|------------|------------|------------|-------------|------------|

Geometric parameters (Å, °)

| | | | |
|------------|-------------|------------|-------------|
| Fe1—N3 | 2.0654 (8) | C5—C6 | 1.5317 (14) |
| Fe1—N4 | 2.0761 (8) | C5—H5A | 0.9900 |
| Fe1—N2 | 2.0787 (9) | C5—H5B | 0.9900 |
| Fe1—N1 | 2.0826 (9) | C6—C7 | 1.5327 (14) |
| Fe1—Cl2 | 2.3047 (3) | C6—H6 | 1.0000 |
| Fe1—Cl1 | 2.3084 (3) | C7—H7A | 0.9800 |
| O1—C15 | 1.4189 (14) | C7—H7B | 0.9800 |
| O1—H1C | 0.8400 | C7—H7C | 0.9800 |
| N1—C1 | 1.4858 (13) | C8—C9 | 1.5176 (14) |
| N1—C13 | 1.4924 (13) | C8—H8A | 0.9900 |
| N1—H1 | 0.876 (14) | C8—H8B | 0.9900 |
| N2—C2 | 1.4875 (13) | C9—H9A | 0.9900 |
| N2—C3 | 1.4941 (13) | C9—H9B | 0.9900 |
| N2—H2 | 0.847 (14) | C10—C12 | 1.5291 (15) |
| N3—C8 | 1.4875 (13) | C10—C11 | 1.5313 (15) |
| N3—C6 | 1.4965 (12) | C10—H10 | 1.0000 |
| N3—H3 | 0.860 (14) | C11—H11A | 0.9800 |
| N4—C9 | 1.4844 (13) | C11—H11B | 0.9800 |
| N4—C10 | 1.4947 (12) | C11—H11C | 0.9800 |
| N4—H4 | 0.864 (14) | C12—C13 | 1.5295 (15) |
| C1—C2 | 1.5148 (15) | C12—H12A | 0.9900 |
| C1—H1A | 0.9900 | C12—H12B | 0.9900 |
| C1—H1B | 0.9900 | C13—C14 | 1.5320 (15) |
| C2—H2A | 0.9900 | C13—H13 | 1.0000 |
| C2—H2B | 0.9900 | C14—H14A | 0.9800 |
| C3—C4 | 1.5306 (14) | C14—H14B | 0.9800 |
| C3—C5 | 1.5309 (14) | C14—H14C | 0.9800 |
| C3—H3A | 1.0000 | C15—H15A | 0.9800 |
| C4—H4A | 0.9800 | C15—H15B | 0.9800 |
| C4—H4B | 0.9800 | C15—H15C | 0.9800 |
| C4—H4C | 0.9800 | | |
| N3—Fe1—N4 | 85.96 (3) | C3—C5—H5A | 108.0 |
| N3—Fe1—N2 | 94.69 (3) | C6—C5—H5A | 108.0 |
| N4—Fe1—N2 | 179.23 (3) | C3—C5—H5B | 108.0 |
| N3—Fe1—N1 | 179.48 (3) | C6—C5—H5B | 108.0 |
| N4—Fe1—N1 | 94.13 (3) | H5A—C5—H5B | 107.3 |
| N2—Fe1—N1 | 85.23 (3) | N3—C6—C5 | 110.41 (8) |
| N3—Fe1—Cl2 | 89.34 (2) | N3—C6—C7 | 111.94 (8) |
| N4—Fe1—Cl2 | 91.66 (3) | C5—C6—C7 | 110.19 (8) |
| N2—Fe1—Cl2 | 87.92 (3) | N3—C6—H6 | 108.1 |
| N1—Fe1—Cl2 | 91.17 (3) | C5—C6—H6 | 108.1 |
| N3—Fe1—Cl1 | 90.97 (2) | C7—C6—H6 | 108.1 |
| N4—Fe1—Cl1 | 89.30 (3) | C6—C7—H7A | 109.5 |

| | | | |
|-------------|--------------|---------------|------------|
| N2—Fe1—C11 | 91.11 (3) | C6—C7—H7B | 109.5 |
| N1—Fe1—C11 | 88.53 (2) | H7A—C7—H7B | 109.5 |
| C12—Fe1—C11 | 179.012 (11) | C6—C7—H7C | 109.5 |
| C15—O1—H1C | 109.5 | H7A—C7—H7C | 109.5 |
| C1—N1—C13 | 113.23 (8) | H7B—C7—H7C | 109.5 |
| C1—N1—Fe1 | 105.46 (6) | N3—C8—C9 | 108.56 (8) |
| C13—N1—Fe1 | 117.38 (6) | N3—C8—H8A | 110.0 |
| C1—N1—H1 | 104.9 (9) | C9—C8—H8A | 110.0 |
| C13—N1—H1 | 107.7 (9) | N3—C8—H8B | 110.0 |
| Fe1—N1—H1 | 107.4 (9) | C9—C8—H8B | 110.0 |
| C2—N2—C3 | 113.63 (8) | H8A—C8—H8B | 108.4 |
| C2—N2—Fe1 | 106.20 (6) | N4—C9—C8 | 108.96 (8) |
| C3—N2—Fe1 | 116.71 (6) | N4—C9—H9A | 109.9 |
| C2—N2—H2 | 107.2 (10) | C8—C9—H9A | 109.9 |
| C3—N2—H2 | 107.2 (9) | N4—C9—H9B | 109.9 |
| Fe1—N2—H2 | 105.3 (9) | C8—C9—H9B | 109.9 |
| C8—N3—C6 | 113.39 (8) | H9A—C9—H9B | 108.3 |
| C8—N3—Fe1 | 105.43 (6) | N4—C10—C12 | 109.40 (8) |
| C6—N3—Fe1 | 116.51 (6) | N4—C10—C11 | 112.60 (8) |
| C8—N3—H3 | 105.4 (9) | C12—C10—C11 | 110.48 (9) |
| C6—N3—H3 | 108.2 (9) | N4—C10—H10 | 108.1 |
| Fe1—N3—H3 | 107.2 (9) | C12—C10—H10 | 108.1 |
| C9—N4—C10 | 113.80 (8) | C11—C10—H10 | 108.1 |
| C9—N4—Fe1 | 105.13 (6) | C10—C11—H11A | 109.5 |
| C10—N4—Fe1 | 116.50 (6) | C10—C11—H11B | 109.5 |
| C9—N4—H4 | 106.5 (9) | H11A—C11—H11B | 109.5 |
| C10—N4—H4 | 107.3 (9) | C10—C11—H11C | 109.5 |
| Fe1—N4—H4 | 107.1 (9) | H11A—C11—H11C | 109.5 |
| N1—C1—C2 | 108.96 (8) | H11B—C11—H11C | 109.5 |
| N1—C1—H1A | 109.9 | C10—C12—C13 | 116.63 (8) |
| C2—C1—H1A | 109.9 | C10—C12—H12A | 108.1 |
| N1—C1—H1B | 109.9 | C13—C12—H12A | 108.1 |
| C2—C1—H1B | 109.9 | C10—C12—H12B | 108.1 |
| H1A—C1—H1B | 108.3 | C13—C12—H12B | 108.1 |
| N2—C2—C1 | 108.71 (8) | H12A—C12—H12B | 107.3 |
| N2—C2—H2A | 109.9 | N1—C13—C12 | 110.98 (8) |
| C1—C2—H2A | 109.9 | N1—C13—C14 | 111.81 (9) |
| N2—C2—H2B | 109.9 | C12—C13—C14 | 110.13 (9) |
| C1—C2—H2B | 109.9 | N1—C13—H13 | 107.9 |
| H2A—C2—H2B | 108.3 | C12—C13—H13 | 107.9 |
| N2—C3—C4 | 111.45 (8) | C14—C13—H13 | 107.9 |
| N2—C3—C5 | 110.38 (8) | C13—C14—H14A | 109.5 |
| C4—C3—C5 | 110.76 (8) | C13—C14—H14B | 109.5 |
| N2—C3—H3A | 108.0 | H14A—C14—H14B | 109.5 |
| C4—C3—H3A | 108.0 | C13—C14—H14C | 109.5 |
| C5—C3—H3A | 108.0 | H14A—C14—H14C | 109.5 |
| C3—C4—H4A | 109.5 | H14B—C14—H14C | 109.5 |
| C3—C4—H4B | 109.5 | O1—C15—H15A | 109.5 |

| | | | |
|--------------|-------------|-----------------|-------------|
| H4A—C4—H4B | 109.5 | O1—C15—H15B | 109.5 |
| C3—C4—H4C | 109.5 | H15A—C15—H15B | 109.5 |
| H4A—C4—H4C | 109.5 | O1—C15—H15C | 109.5 |
| H4B—C4—H4C | 109.5 | H15A—C15—H15C | 109.5 |
| C3—C5—C6 | 117.15 (8) | H15B—C15—H15C | 109.5 |
| C13—N1—C1—C2 | -172.15 (8) | C6—N3—C8—C9 | 170.51 (8) |
| Fe1—N1—C1—C2 | -42.52 (9) | Fe1—N3—C8—C9 | 41.92 (9) |
| C3—N2—C2—C1 | -169.94 (8) | C10—N4—C9—C8 | 170.11 (8) |
| Fe1—N2—C2—C1 | -40.29 (9) | Fe1—N4—C9—C8 | 41.47 (9) |
| N1—C1—C2—N2 | 57.18 (11) | N3—C8—C9—N4 | -57.87 (10) |
| C2—N2—C3—C4 | -57.59 (11) | C9—N4—C10—C12 | 179.51 (8) |
| Fe1—N2—C3—C4 | 178.28 (7) | Fe1—N4—C10—C12 | -57.89 (9) |
| C2—N2—C3—C5 | 178.90 (8) | C9—N4—C10—C11 | 56.26 (11) |
| Fe1—N2—C3—C5 | 54.76 (9) | Fe1—N4—C10—C11 | 178.86 (7) |
| N2—C3—C5—C6 | -71.58 (11) | N4—C10—C12—C13 | 74.04 (11) |
| C4—C3—C5—C6 | 164.50 (9) | C11—C10—C12—C13 | -161.46 (9) |
| C8—N3—C6—C5 | -178.37 (8) | C1—N1—C13—C12 | 176.24 (8) |
| Fe1—N3—C6—C5 | -55.71 (9) | Fe1—N1—C13—C12 | 52.95 (10) |
| C8—N3—C6—C7 | 58.47 (11) | C1—N1—C13—C14 | -60.37 (11) |
| Fe1—N3—C6—C7 | -178.86 (7) | Fe1—N1—C13—C14 | 176.34 (7) |
| C3—C5—C6—N3 | 72.14 (11) | C10—C12—C13—N1 | -71.47 (11) |
| C3—C5—C6—C7 | -163.68 (9) | C10—C12—C13—C14 | 164.17 (9) |

Hydrogen-bond geometry (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|---------------------------|------------|------------|-------------|------------|
| O1—H1C...Cl3 | 0.84 | 2.24 | 3.0607 (9) | 167 |
| N1—H1...O1 | 0.876 (14) | 2.258 (15) | 3.0723 (12) | 154.5 (12) |
| N3—H3...Cl3 ⁱ | 0.860 (14) | 2.588 (14) | 3.3518 (9) | 148.5 (12) |
| N4—H4...Cl3 ⁱⁱ | 0.864 (14) | 2.716 (14) | 3.4925 (9) | 150.2 (12) |

Symmetry codes: (i) $x, y, z+1$; (ii) $x, -y+1/2, z+1/2$.

cis-Dichlorido[(5*SR*,7*RS*,12*SR*,14*RS*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) chloride (2)

Crystal data

[Fe(C₁₄H₃₂N₄)Cl₂]Cl
M_r = 418.63
 Orthorhombic, *Pbcn*
a = 9.2912 (12) Å
b = 11.9579 (19) Å
c = 17.267 (3) Å
V = 1918.4 (5) Å³
Z = 4
F(000) = 884

D_x = 1.449 Mg m⁻³
 Cu *Kα* radiation, λ = 1.54178 Å
 Cell parameters from 2788 reflections
 θ = 6.6–78.2°
 μ = 10.15 mm⁻¹
T = 150 K
 Block, yellow
 0.12 × 0.08 × 0.05 mm

Data collection

Bruker AXS D8 Quest
diffractometer with PhotonII charge-integrating
pixel array detector (CPAD)
Radiation source: I- μ -S microsource X-ray
tube
Laterally graded multilayer (Goebel) mirror
monochromator
Detector resolution: 7.4074 pixels mm⁻¹
 ω and phi scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.526$, $T_{\max} = 0.754$
14150 measured reflections
2055 independent reflections
1324 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.082$
 $\theta_{\max} = 79.6^\circ$, $\theta_{\min} = 6.6^\circ$
 $h = -11 \rightarrow 9$
 $k = -14 \rightarrow 15$
 $l = -21 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.196$
 $S = 1.08$
2055 reflections
196 parameters
273 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0894P)^2 + 2.1112P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.95 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The entire cationic moiety, excluding the central Fe ion, is disordered about a pseudo-mirror plane through the metal center. The two moieties were restrained to have similar anisotropic displacement parameters (SIMU command) and similar 1,2 and 1,3 bond distances (SAME command). Additionally, the distances between C1 and N2, and C1B and N2B were restrained to be similar (SADI command). The two moieties refined to a roughly 0.944 (3) to 0.056 (3) occupancy ratio. Interestingly, analysis of H-bonds revealed extensive hydrogen bonding between both orientations and the chloride counteranion. This high level of hydrogen bonding in the disordered position may facilitate the occupancy of the second position.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|--------------|-------------|----------------------------------|-----------|
| C1I | 0.06475 (16) | 0.14880 (11) | 0.33931 (8) | 0.0527 (4) | 0.944 (3) |
| N1 | 0.0818 (4) | -0.1126 (4) | 0.3317 (2) | 0.0400 (9) | 0.944 (3) |
| H1 | 0.056778 | -0.187227 | 0.309366 | 0.048* | 0.944 (3) |
| N2 | -0.2090 (4) | -0.0128 (3) | 0.3004 (3) | 0.0411 (10) | 0.944 (3) |
| H2 | -0.265622 | 0.055663 | 0.287131 | 0.049* | 0.944 (3) |
| C1 | 0.2829 (6) | -0.1056 (5) | 0.2418 (3) | 0.0476 (15) | 0.944 (3) |
| H1A | 0.254084 | -0.178590 | 0.219657 | 0.057* | 0.944 (3) |
| H1AB | 0.388537 | -0.097899 | 0.236565 | 0.057* | 0.944 (3) |
| C2 | 0.2414 (5) | -0.1003 (5) | 0.3253 (3) | 0.0471 (12) | 0.944 (3) |
| H2A | 0.271799 | -0.027846 | 0.347721 | 0.056* | 0.944 (3) |
| H2AB | 0.289690 | -0.161001 | 0.354366 | 0.056* | 0.944 (3) |

| | | | | | |
|------|-------------|--------------|-------------|-------------|-----------|
| C3 | 0.0315 (6) | -0.1130 (5) | 0.4128 (3) | 0.0452 (12) | 0.944 (3) |
| H3 | 0.061690 | -0.040932 | 0.437252 | 0.054* | 0.944 (3) |
| C4 | 0.0983 (7) | -0.2084 (5) | 0.4591 (3) | 0.0595 (16) | 0.944 (3) |
| H4A | 0.073991 | -0.279922 | 0.434715 | 0.089* | 0.944 (3) |
| H4B | 0.060796 | -0.207092 | 0.512146 | 0.089* | 0.944 (3) |
| H4C | 0.203153 | -0.199423 | 0.460242 | 0.089* | 0.944 (3) |
| C5 | -0.1317 (6) | -0.1208 (5) | 0.4178 (3) | 0.0476 (12) | 0.944 (3) |
| H5A | -0.158073 | -0.131177 | 0.472879 | 0.057* | 0.944 (3) |
| H5AB | -0.162259 | -0.189054 | 0.389749 | 0.057* | 0.944 (3) |
| C6 | -0.2191 (6) | -0.0219 (5) | 0.3860 (3) | 0.0489 (13) | 0.944 (3) |
| H6 | -0.175674 | 0.047726 | 0.408015 | 0.059* | 0.944 (3) |
| C7 | -0.3738 (7) | -0.0272 (5) | 0.4148 (4) | 0.0647 (18) | 0.944 (3) |
| H7A | -0.430007 | 0.032673 | 0.390680 | 0.097* | 0.944 (3) |
| H7B | -0.375245 | -0.018051 | 0.471227 | 0.097* | 0.944 (3) |
| H7C | -0.415638 | -0.099831 | 0.401155 | 0.097* | 0.944 (3) |
| Cl1B | -0.063 (2) | 0.1467 (16) | 0.3395 (14) | 0.050 (6) | 0.056 (3) |
| N1B | -0.073 (3) | -0.115 (2) | 0.331 (2) | 0.044 (2) | 0.056 (3) |
| H1B | -0.045655 | -0.188536 | 0.307266 | 0.053* | 0.056 (3) |
| N2B | 0.216 (3) | -0.009 (3) | 0.301 (2) | 0.045 (3) | 0.056 (3) |
| H2B | 0.276232 | 0.056964 | 0.286463 | 0.054* | 0.056 (3) |
| C1B | -0.274 (6) | -0.109 (6) | 0.241 (4) | 0.042 (5) | 0.056 (3) |
| H1B1 | -0.379699 | -0.109911 | 0.236360 | 0.051* | 0.056 (3) |
| H1B2 | -0.235446 | -0.177516 | 0.216807 | 0.051* | 0.056 (3) |
| C2B | -0.233 (4) | -0.107 (8) | 0.325 (3) | 0.045 (3) | 0.056 (3) |
| H2BA | -0.266504 | -0.036365 | 0.348968 | 0.053* | 0.056 (3) |
| H2BB | -0.278760 | -0.170198 | 0.352068 | 0.053* | 0.056 (3) |
| C3B | -0.022 (4) | -0.119 (4) | 0.412 (2) | 0.045 (3) | 0.056 (3) |
| H3B | -0.054828 | -0.049100 | 0.438483 | 0.054* | 0.056 (3) |
| C4B | -0.085 (6) | -0.219 (6) | 0.456 (3) | 0.051 (6) | 0.056 (3) |
| H4BA | -0.180181 | -0.236572 | 0.434966 | 0.077* | 0.056 (3) |
| H4BB | -0.093223 | -0.199981 | 0.510851 | 0.077* | 0.056 (3) |
| H4BC | -0.021138 | -0.283390 | 0.449623 | 0.077* | 0.056 (3) |
| C5B | 0.141 (4) | -0.124 (4) | 0.416 (3) | 0.045 (3) | 0.056 (3) |
| H5BA | 0.173758 | -0.189970 | 0.386439 | 0.054* | 0.056 (3) |
| H5BB | 0.168807 | -0.136472 | 0.470953 | 0.054* | 0.056 (3) |
| C6B | 0.225 (4) | -0.022 (3) | 0.387 (2) | 0.044 (3) | 0.056 (3) |
| H6B | 0.178104 | 0.045868 | 0.409690 | 0.052* | 0.056 (3) |
| C7B | 0.379 (5) | -0.024 (5) | 0.417 (4) | 0.038 (10) | 0.056 (3) |
| H7BA | 0.429323 | 0.043945 | 0.400233 | 0.057* | 0.056 (3) |
| H7BB | 0.428749 | -0.089744 | 0.395976 | 0.057* | 0.056 (3) |
| H7BC | 0.377971 | -0.027770 | 0.473444 | 0.057* | 0.056 (3) |
| Fe1 | 0.000000 | 0.01505 (8) | 0.250000 | 0.0378 (4) | |
| Cl2 | 0.500000 | 0.14810 (14) | 0.250000 | 0.0466 (5) | |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|-------------|------------|-------------|
| Cl1 | 0.0588 (8) | 0.0373 (7) | 0.0618 (9) | -0.0080 (6) | 0.0109 (7) | -0.0082 (6) |

| | | | | | | |
|------|------------|------------|-------------|-------------|--------------|--------------|
| N1 | 0.037 (2) | 0.033 (2) | 0.049 (2) | 0.0059 (15) | -0.0023 (17) | -0.0005 (17) |
| N2 | 0.037 (2) | 0.033 (2) | 0.053 (2) | 0.0053 (16) | 0.0089 (18) | 0.0072 (18) |
| C1 | 0.038 (3) | 0.039 (3) | 0.065 (4) | 0.006 (2) | 0.004 (2) | -0.003 (3) |
| C2 | 0.038 (2) | 0.041 (3) | 0.062 (3) | 0.004 (2) | -0.004 (2) | -0.002 (2) |
| C3 | 0.050 (3) | 0.040 (3) | 0.046 (3) | 0.008 (2) | 0.001 (2) | -0.002 (2) |
| C4 | 0.075 (4) | 0.053 (4) | 0.051 (3) | 0.017 (3) | -0.003 (3) | 0.006 (3) |
| C5 | 0.049 (3) | 0.044 (3) | 0.049 (3) | 0.005 (2) | 0.007 (2) | 0.008 (2) |
| C6 | 0.047 (3) | 0.049 (3) | 0.050 (3) | 0.006 (2) | 0.016 (2) | 0.011 (2) |
| C7 | 0.056 (3) | 0.065 (4) | 0.074 (4) | 0.012 (3) | 0.025 (3) | 0.017 (3) |
| C11B | 0.039 (9) | 0.033 (9) | 0.079 (13) | 0.021 (7) | -0.030 (9) | -0.038 (9) |
| N1B | 0.044 (4) | 0.039 (4) | 0.049 (4) | 0.005 (4) | 0.007 (4) | 0.005 (4) |
| N2B | 0.039 (6) | 0.037 (6) | 0.058 (6) | 0.004 (5) | -0.004 (5) | 0.000 (6) |
| C1B | 0.039 (8) | 0.035 (8) | 0.053 (8) | 0.008 (8) | 0.009 (8) | 0.006 (8) |
| C2B | 0.043 (5) | 0.039 (5) | 0.051 (5) | 0.005 (5) | 0.010 (5) | 0.007 (5) |
| C3B | 0.046 (5) | 0.039 (5) | 0.049 (5) | 0.006 (5) | 0.002 (5) | 0.002 (5) |
| C4B | 0.058 (10) | 0.046 (10) | 0.050 (10) | 0.007 (10) | 0.001 (10) | 0.007 (10) |
| C5B | 0.044 (5) | 0.039 (5) | 0.052 (5) | 0.007 (5) | -0.002 (5) | 0.001 (5) |
| C6B | 0.039 (6) | 0.037 (6) | 0.055 (6) | 0.004 (6) | -0.005 (6) | 0.000 (6) |
| C7B | 0.037 (19) | 0.015 (18) | 0.06 (2) | -0.013 (17) | -0.018 (19) | 0.004 (18) |
| Fe1 | 0.0342 (5) | 0.0301 (6) | 0.0492 (7) | 0.000 | 0.0037 (4) | 0.000 |
| Cl2 | 0.0444 (9) | 0.0317 (9) | 0.0638 (12) | 0.000 | 0.0015 (8) | 0.000 |

Geometric parameters (Å, °)

| | | | |
|--------------------|-------------|----------------------|------------|
| Cl1—Fe1 | 2.3018 (15) | Cl1B—Fe1 | 2.283 (18) |
| N1—C3 | 1.476 (6) | N1B—C3B | 1.475 (12) |
| N1—C2 | 1.494 (6) | N1B—C2B | 1.494 (12) |
| N1—Fe1 | 2.213 (4) | N1B—Fe1 | 2.20 (3) |
| N1—H1 | 1.0000 | N1B—H1B | 1.0000 |
| N2—C6 | 1.485 (7) | N2B—C6B | 1.484 (13) |
| N2—C1 ⁱ | 1.495 (7) | N2B—C1B ⁱ | 1.50 (2) |
| N2—Fe1 | 2.154 (4) | N2B—Fe1 | 2.21 (3) |
| N2—H2 | 1.0000 | N2B—H2B | 1.0000 |
| C1—C2 | 1.493 (7) | C1B—C2B | 1.495 (13) |
| C1—H1A | 0.9900 | C1B—H1B1 | 0.9900 |
| C1—H1AB | 0.9900 | C1B—H1B2 | 0.9900 |
| C2—H2A | 0.9900 | C2B—H2BA | 0.9900 |
| C2—H2AB | 0.9900 | C2B—H2BB | 0.9900 |
| C3—C5 | 1.522 (7) | C3B—C5B | 1.524 (13) |
| C3—C4 | 1.525 (7) | C3B—C4B | 1.526 (13) |
| C3—H3 | 1.0000 | C3B—H3B | 1.0000 |
| C4—H4A | 0.9800 | C4B—H4BA | 0.9800 |
| C4—H4B | 0.9800 | C4B—H4BB | 0.9800 |
| C4—H4C | 0.9800 | C4B—H4BC | 0.9800 |
| C5—C6 | 1.537 (7) | C5B—C6B | 1.537 (13) |
| C5—H5A | 0.9900 | C5B—H5BA | 0.9900 |
| C5—H5AB | 0.9900 | C5B—H5BB | 0.9900 |
| C6—C7 | 1.522 (8) | C6B—C7B | 1.522 (13) |

| | | | |
|--------------------------|-----------|---------------------------------------|------------|
| C6—H6 | 1.0000 | C6B—H6B | 1.0000 |
| C7—H7A | 0.9800 | C7B—H7BA | 0.9800 |
| C7—H7B | 0.9800 | C7B—H7BB | 0.9800 |
| C7—H7C | 0.9800 | C7B—H7BC | 0.9800 |
| C3—N1—C2 | 112.6 (4) | N2B ⁱ —C1B—H1B2 | 109.3 |
| C3—N1—Fe1 | 119.9 (3) | H1B1—C1B—H1B2 | 107.9 |
| C2—N1—Fe1 | 103.0 (3) | N1B—C2B—C1B | 108.7 (16) |
| C3—N1—H1 | 106.8 | N1B—C2B—H2BA | 110.0 |
| C2—N1—H1 | 106.8 | C1B—C2B—H2BA | 110.0 |
| Fe1—N1—H1 | 106.8 | N1B—C2B—H2BB | 110.0 |
| C6—N2—C1 ⁱ | 113.8 (4) | C1B—C2B—H2BB | 110.0 |
| C6—N2—Fe1 | 118.1 (3) | H2BA—C2B—H2BB | 108.3 |
| C1 ⁱ —N2—Fe1 | 109.4 (3) | N1B—C3B—C5B | 111.4 (16) |
| C6—N2—H2 | 104.7 | N1B—C3B—C4B | 111.8 (16) |
| C1 ⁱ —N2—H2 | 104.7 | C5B—C3B—C4B | 109.1 (16) |
| Fe1—N2—H2 | 104.7 | N1B—C3B—H3B | 108.1 |
| C2—C1—N2 ⁱ | 108.7 (4) | C5B—C3B—H3B | 108.1 |
| C2—C1—H1A | 109.9 | C4B—C3B—H3B | 108.1 |
| N2 ⁱ —C1—H1A | 109.9 | C3B—C4B—H4BA | 109.5 |
| C2—C1—H1AB | 109.9 | C3B—C4B—H4BB | 109.5 |
| N2 ⁱ —C1—H1AB | 109.9 | H4BA—C4B—H4BB | 109.5 |
| H1A—C1—H1AB | 108.3 | C3B—C4B—H4BC | 109.5 |
| C1—C2—N1 | 108.9 (4) | H4BA—C4B—H4BC | 109.5 |
| C1—C2—H2A | 109.9 | H4BB—C4B—H4BC | 109.5 |
| N1—C2—H2A | 109.9 | C3B—C5B—C6B | 117.3 (17) |
| C1—C2—H2AB | 109.9 | C3B—C5B—H5BA | 108.0 |
| N1—C2—H2AB | 109.9 | C6B—C5B—H5BA | 108.0 |
| H2A—C2—H2AB | 108.3 | C3B—C5B—H5BB | 108.0 |
| N1—C3—C5 | 111.7 (4) | C6B—C5B—H5BB | 108.0 |
| N1—C3—C4 | 111.8 (4) | H5BA—C5B—H5BB | 107.2 |
| C5—C3—C4 | 109.3 (5) | N2B—C6B—C7B | 113.2 (17) |
| N1—C3—H3 | 108.0 | N2B—C6B—C5B | 112.5 (16) |
| C5—C3—H3 | 108.0 | C7B—C6B—C5B | 110.3 (16) |
| C4—C3—H3 | 108.0 | N2B—C6B—H6B | 106.8 |
| C3—C4—H4A | 109.5 | C7B—C6B—H6B | 106.8 |
| C3—C4—H4B | 109.5 | C5B—C6B—H6B | 106.8 |
| H4A—C4—H4B | 109.5 | C6B—C7B—H7BA | 109.5 |
| C3—C4—H4C | 109.5 | C6B—C7B—H7BB | 109.5 |
| H4A—C4—H4C | 109.5 | H7BA—C7B—H7BB | 109.5 |
| H4B—C4—H4C | 109.5 | C6B—C7B—H7BC | 109.5 |
| C3—C5—C6 | 117.3 (5) | H7BA—C7B—H7BC | 109.5 |
| C3—C5—H5A | 108.0 | H7BB—C7B—H7BC | 109.5 |
| C6—C5—H5A | 108.0 | N2—Fe1—N2 ⁱ | 162.2 (2) |
| C3—C5—H5AB | 108.0 | N2—Fe1—N1B ⁱ | 115.1 (9) |
| C6—C5—H5AB | 108.0 | N2 ⁱ —Fe1—N1B ⁱ | 49.9 (9) |
| H5A—C5—H5AB | 107.2 | N2—Fe1—N2B ⁱ | 47.4 (10) |
| N2—C6—C7 | 112.8 (5) | N2 ⁱ —Fe1—N2B ⁱ | 129.5 (9) |

| | | | |
|----------------------------|------------|--|-------------|
| N2—C6—C5 | 112.2 (4) | N1B—Fe1—N2B | 86.1 (11) |
| C7—C6—C5 | 110.5 (4) | N1B ⁱ —Fe1—N2B | 83.3 (15) |
| N2—C6—H6 | 107.0 | N2B ⁱ —Fe1—N2B | 165 (2) |
| C7—C6—H6 | 107.0 | N2—Fe1—N1 | 86.85 (15) |
| C5—C6—H6 | 107.0 | N2 ⁱ —Fe1—N1 | 80.87 (16) |
| C6—C7—H7A | 109.5 | N2—Fe1—N1 ⁱ | 80.87 (16) |
| C6—C7—H7B | 109.5 | N2 ⁱ —Fe1—N1 ⁱ | 86.85 (15) |
| H7A—C7—H7B | 109.5 | N1—Fe1—N1 ⁱ | 92.8 (2) |
| C6—C7—H7C | 109.5 | N1B—Fe1—Cl1B | 88.8 (10) |
| H7A—C7—H7C | 109.5 | N1B ⁱ —Fe1—Cl1B | 176.1 (10) |
| H7B—C7—H7C | 109.5 | N2B ⁱ —Fe1—Cl1B | 97.3 (10) |
| C3B—N1B—C2B | 112.8 (16) | N2B—Fe1—Cl1B | 92.9 (10) |
| C3B—N1B—Fe1 | 121.7 (17) | N2—Fe1—Cl1B ⁱ | 127.7 (5) |
| C2B—N1B—Fe1 | 102 (3) | N2 ⁱ —Fe1—Cl1B ⁱ | 66.5 (6) |
| C3B—N1B—H1B | 106.4 | N1—Fe1—Cl1B ⁱ | 145.0 (5) |
| C2B—N1B—H1B | 106.4 | N1 ⁱ —Fe1—Cl1B ⁱ | 97.6 (6) |
| Fe1—N1B—H1B | 106.4 | N2—Fe1—Cl1 | 94.16 (12) |
| C6B—N2B—C1B ⁱ | 113 (4) | N2 ⁱ —Fe1—Cl1 | 98.20 (12) |
| C6B—N2B—Fe1 | 117.5 (16) | N1—Fe1—Cl1 | 87.83 (12) |
| C1B ⁱ —N2B—Fe1 | 103 (3) | N1 ⁱ —Fe1—Cl1 | 174.94 (11) |
| C6B—N2B—H2B | 107.6 | N2—Fe1—Cl1 ⁱ | 98.20 (12) |
| C1B ⁱ —N2B—H2B | 107.6 | N2 ⁱ —Fe1—Cl1 ⁱ | 94.16 (12) |
| Fe1—N2B—H2B | 107.6 | N1—Fe1—Cl1 ⁱ | 174.94 (11) |
| C2B—C1B—H1B1 | 109.3 | N1 ⁱ —Fe1—Cl1 ⁱ | 87.83 (12) |
| N2B ⁱ —C1B—H1B1 | 109.3 | Cl1—Fe1—Cl1 ⁱ | 91.97 (8) |
| C2B—C1B—H1B2 | 109.3 | | |
| | | | |
| N2 ⁱ —C1—C2—N1 | 59.8 (6) | C3B—N1B—C2B—C1B | -178 (5) |
| C3—N1—C2—C1 | 177.6 (4) | Fe1—N1B—C2B—C1B | 50 (6) |
| Fe1—N1—C2—C1 | -51.8 (5) | N2B ⁱ —C1B—C2B—N1B | -64 (8) |
| C2—N1—C3—C5 | 177.7 (4) | C2B—N1B—C3B—C5B | -178 (5) |
| Fe1—N1—C3—C5 | 56.2 (5) | Fe1—N1B—C3B—C5B | -56 (3) |
| C2—N1—C3—C4 | -59.5 (6) | C2B—N1B—C3B—C4B | 60 (5) |
| Fe1—N1—C3—C4 | 179.0 (4) | Fe1—N1B—C3B—C4B | -178 (3) |
| N1—C3—C5—C6 | -65.4 (6) | N1B—C3B—C5B—C6B | 65 (3) |
| C4—C3—C5—C6 | 170.4 (5) | C4B—C3B—C5B—C6B | -171 (3) |
| C1 ⁱ —N2—C6—C7 | -56.8 (6) | C1B ⁱ —N2B—C6B—C7B | 67 (5) |
| Fe1—N2—C6—C7 | 173.0 (4) | Fe1—N2B—C6B—C7B | -173 (3) |
| C1 ⁱ —N2—C6—C5 | 68.8 (6) | C1B ⁱ —N2B—C6B—C5B | -59 (4) |
| Fe1—N2—C6—C5 | -61.4 (5) | Fe1—N2B—C6B—C5B | 61 (3) |
| C3—C5—C6—N2 | 68.8 (7) | C3B—C5B—C6B—N2B | -70 (3) |
| C3—C5—C6—C7 | -164.3 (5) | C3B—C5B—C6B—C7B | 163 (3) |

Symmetry code: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| N1—H1 ⁱⁱⁱ —Cl2 ⁱⁱ | 1.00 | 2.28 | 3.280 (5) | 176 |

| | | | | |
|-----------------------------|------|------|-----------|-----|
| N2—H2...C12 ⁱⁱⁱ | 1.00 | 2.52 | 3.431 (4) | 151 |
| N1B—H1B...C12 ⁱⁱ | 1.00 | 2.23 | 3.23 (3) | 176 |
| N2B—H2B...C12 | 1.00 | 2.43 | 3.36 (3) | 154 |

Symmetry codes: (ii) $x-1/2, y-1/2, -z+1/2$; (iii) $x-1, y, z$.