Both trans and cis iron–CTMC complexes, namely, trans-dichlorido[(5SR, 7RS,12RS,14SR)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) tetrachloroferrate, [Fe(C_{14}H_{32}N_{4})Cl_{2}][FeCl_{4}] (1a), the analogous chloride methanol monosolvate, [Fe(C_{14}H_{32}N_{4})Cl_{2}][CH_{2}OH] (1b), and cis-dichlorido[(5SR,7RS,12SR,14RS)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) chloride, [Fe(C_{14}H_{32}N_{4})Cl_{2}]Cl (2), were successfully synthesized and structurally characterized using X-ray diffraction. 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 & Hetterscheid, 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 & Hetterscheid, 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 CrIII–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...
from a cis-Fe\textsuperscript{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.

Although CTMC is known to form as a mixture of stereoisomers, the vast majority of structures contain only isomer A [(5SR,7RS,12SR,14RS)-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 = (5SR,7RS,12SR,14RS)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane] (Tahirov et al., 1995a). Finally, the structure of an Ni\textsuperscript{II}(CTMC) complex has been reported containing a third stereoisomer, C [(5SR,7RS,12SR,14RS)-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[(5SR,7RS,12SR,14SR)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) tetrachloroferrate (1a), the analogous chloride methanol monosolvate (1b), and cis-dichlorido[(5SR,7RS,12SR,14RS)-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–macrocyclic 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 5SR,7RS,12SR,14RS and B is 5SR,7RS,12SR,14RS), confirmed by the structures determined for the resulting Fe\textsuperscript{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)Cl\textsubscript{2}][FeCl\textsubscript{4}]/Cl (1a/1b). CTMC (0.449 g, 1.75 mmol, batch one) was dissolved in a 2:1 (v/v) dimethylformamide–triethyl orthoformate mixture.
Methylformamide–triethyl orthoformate solution and the reaction mixture was warmed and the CTMC solution was transferred to the iron-containing flask. The mixture was then exposed to oxygen and about 2 ml of concentrated hydrochloric acid were added dropwise to the flask while bubbling through oxygen. 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 (35Cl), 384.0 (35Cl, 37Cl). IR (cm⁻¹): N—H 3073 (sh), 3024, 1461, 978 (s), 3024, 1461, 978 (s), 810 (s), 754 (m), 695 (m), 532 (m). 

### Table 1

| Crystal data                                                                 | | | 
| --- | --- | --- |
| Chemical formula               | [Fe(C₁₄H₃₂N₄)Cl₂][FeCl₄] | [Fe(C₁₄H₃₂N₄)Cl₂]Cl·CH₂O | [Fe(C₁₄H₃₂N₄)Cl₂]Cl |
| Mₜ                                | 580.83                       | 450.68                       | 418.63                       |
| Crystal system, space group       | Monoclinic, *C2/c*            | Monoclinic, *P2₁/c*          | Orthorhombic, *Pbcn*         |
| 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 (Å³)                           | 2341.3 (2)                   | 2057.8 (2)                   | 1918.4 (5)                   |
| α, β, γ (°)                      | Mo *Kα*                      | Mo *Kα*                      | Cu *Kα*                      |
| 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           |

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).
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 anion (Cl2). The disordered moieties were restrained to have crystallographic twofold symmetry with half the 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 C1

Table 2

| Bond lengths  | 1a      | 1b      | 2       |
|--------------|---------|---------|---------|
| Fe1—Cl1     | 2.2710 (3) | 2.3084 (3) | 2.3018 (15) |
| Fe1—Cl2     | 2.2710 (3) | 2.3084 (3) | 2.3018 (15) |
| Fe1—N1      | 2.0276 (11) | 2.0787 (9) | 2.154 (4) |
| Fe1—N2      | 2.0276 (11) | 2.0787 (9) | 2.154 (4) |
| Fe1—N3      | 2.0276 (11) | 2.0787 (9) | 2.154 (4) |
| Fe1—N4      | 2.0276 (11) | 2.0787 (9) | 2.154 (4) |

Symmetry code for 2: (i) —x, y, —z + 1/2; for 1a (ii) —x + 1/2, —y + 1/2, —z + 1. † Compound 1b: Cl2.—Fe1.—Cl1.

2.3. Computational details

The cationic portions of 1 and 2 were optimized from the crystallographic coordinates of 1a and 2 (counter-aniions 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 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 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.

Figure 3
Displacement ellipsoid plot of 1b. H atoms (except for those bound to N and methanolic O atoms) have been omitted for clarity.
of the cation in \( \text{lb} \) are very similar to those of \( \text{la} \), 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 \( \text{la} \) and \( \text{lb} \) (Fig. 5) illustrates the general similarity of the cationic moieties. Both \( \text{lb} \) and \( \text{2} \) possess a noncoordinated chloride counter-ion, while \( \text{la} \) contains a tetrachloroferate ion. As noted in the Experimental (Section 2), \( \text{2} \) 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 \( \text{A} \) and \( \text{B} \) (Fig. 1), as noted above. It is clear from the structures of \( \text{la} \), \( \text{lb} \), and \( \text{2} \) that \( \text{A} \) tends to yield an iron complex in the \textit{trans} configuration (\( \text{la}/\text{lb} \)), while \( \text{B} \) tends to yield a complex in the \textit{cis} configuration (\( \text{2} \)). To the best of our knowledge, the structure of \( \text{2} \) is the only example of a CTMC complex of \( \text{B} \), 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 \( \text{2} \) [2.154 (4)—2.213 (4) Å] compared to \( \text{la} \) [2.0203 (11)—2.0276 (11) Å] and \( \text{lb} \) [2.0654 (8)—2.0826 (9) Å]. The N—Fe—N bond angles in \( \text{2} \) also deviate further from the ideal octahedral geometry of 90° than the same bond angles in \( \text{la} \) and \( \text{lb} \). Overall, the data suggest that the folded macrocycle conformation in \( \text{2} \) results in some strain compared to the planar coordination seen in \( \text{la}/\text{lb} \), 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 \( \text{la} \) as a low-spin complex and \( \text{2} \) 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 (\textit{i.e.} \( \text{A} \) into \( \text{B} \) and vice versa).

The DFT calculations indicate that the energy of the \textit{cis} and \textit{trans} configurations are indeed related to the stereoisomer of the macrocycle. A \textit{trans} complex with \( \text{B} \) [Fig. 6(c)] is calculated to have an energy nearly 0.36 eV greater than that of a \textit{trans} complex with \( \text{A} \) [\textit{i.e.} \( \text{la}/\text{lb} \); Fig. 6(a)]. Forcing \( \text{A} \) to assume a 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 \( \text{B} \). The energies of all \textit{trans}-dichloro structures [Figs. 6(a)—(c)] are calculated to be lower than those of all \textit{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 \textit{trans} (\( a-c, S = 1/2 \)) and \textit{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 \( \text{la}/\text{lb} \), \( \text{A} \) clearly prefers a planar coordination geometry. In contrast, a folded macrocycle is most easily obtained with \( \text{B} \), consistent with the structure of \( \text{2} \). 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 \textit{cis} or \textit{trans} metal coordination is observed.
complexes is well established (Clendening et al., 2019; House et al., 1983; Tyler et al., 2016).

The previously reported data for cis/trans-[Fe\textsuperscript{III}(cyclam)Cl\textsubscript{2}]\textsuperscript{+} and cis/trans-[Fe\textsuperscript{III}(HMC)Cl\textsubscript{2}]\textsuperscript{+} 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\textsuperscript{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\textsuperscript{III}(cyclam)Cl\textsubscript{2}]\textsuperscript{+} and cis-[Fe\textsuperscript{III}(HMC)Cl\textsubscript{2}]\textsuperscript{+} are roughly 0.16 and 0.17 Å longer than those of trans-[Fe\textsuperscript{III}(cyclam)Cl\textsubscript{2}]\textsuperscript{+} and trans-[Fe\textsuperscript{III}(HMC)Cl\textsubscript{2}]\textsuperscript{+}, respectively. The N—Fe—N angles of 1a, trans-[Fe\textsuperscript{III}(cyclam)Cl\textsubscript{2}]\textsuperscript{+}, and trans-[Fe\textsuperscript{III}(HMC)-

Cl\textsubscript{2}]\textsuperscript{+} round to 85° between the CH\textsubscript{2}CH\textsubscript{2} linkage and 95° between the CR\textsubscript{2}CH\textsubscript{2}CR\textsubscript{2} linkage. The N—Fe—N bond angles for the complexes with folded macrocycles vary from 79.56 (8) to 81.55 (5)° between the CH\textsubscript{2}CH\textsubscript{2} linkage and from 83.15 (5) to 86.85 (15)° between the CR\textsubscript{2}CH\textsubscript{2}CR\textsubscript{2} 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\textsuperscript{III}(HMC)Cl\textsubscript{2}]Cl (ca 2.21 Å) appears longer than those of 2 and cis-[Fe\textsuperscript{III}(cyclam)Cl\textsubscript{2}]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\textsuperscript{III}(cyclam)Cl\textsubscript{2}]FeCl\textsubscript{4} (2.006 Å) to 1a (2.024 Å) to trans-[Fe\textsuperscript{III}(HMC)Cl\textsubscript{2}]FeCl\textsubscript{4} (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\textsuperscript{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\textsuperscript{III}(HMC)Cl\textsubscript{2}]FeCl\textsubscript{4} (Clendening et al., 2019) and trans-[Fe\textsuperscript{III}(cyclam)Cl\textsubscript{2}]FeCl\textsubscript{4} (Guilard et al., 1997), despite the differences in space group (C2/c, P\textsubscript{2}1/c, and P\textsubscript{2}1/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 7
Illustration of the hydrogen-bonding interactions in 1a.

Figure 8
Illustration of the hydrogen-bonding interactions in 1b.
ammonium position(s) (N2 in 1a) instead participates in hydrogen-bonding interactions with the FeCl₄⁻ units (via Cl3 in 1a), which are also arranged in columns. This similarity suggests that the common tetrachloroferrate 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 FeCl₄⁻ counter-anion, complex 1b (P2₁/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 FeCl₄⁻ 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 (Phen), cis-[Fe⁺⁺⁺(HMC)Cl₂]Cl (Fdd2), and cis-[Fe⁺⁺⁺(cyclam)Cl₂]Cl (P2₁/c) (Clendening et al., 2019; Guilard et al., 1997). As with 1b, neither of the chloride ligands participate 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 FeCl₄⁻ 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 dichloridoiron(III) 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 (Guilard et al., 1997), and compliments the rigid structural preferences ascribed to the stereoisomers of HMC, which
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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References
Becke, A. D. (1993). J. Chem. Phys. 98, 5648–5652.
Bruker (2019). APEX3 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Cao, Z., Forrest, W. P., Gao, Y., Fanwick, P. E. & Ren, T. (2012). Organometallics, 31, 6199–6206.
Clendening, R. A. & Ren, T. (2022). Eur. J. Inorg. Chem. 2022, e202101021.
Clendening, R. A., Zeller, M. & Ren, T. (2019). Acta Cryst. C 75, 1509–1516.
Clendening, R. A., Zeller, M. & Ren, T. (2022). Inorg. Chem. 61, 13442–13452.
Constable, E. C. (1999). In Coordination Chemistry of Macrocyclic Compounds. Oxford University Press.
Dennington, R., Keith, T. A. & Millam, J. M. (2016). GaussView. Version 6. Semichem Inc., Shawnee Mission, KS, USA.
Frisch, M. J., et al. (2016). GAUSSIAN16. Revision A03. Gaussian Inc., Wallingford, CT, USA. https://gaussian.com/.
Guillard, R., Siré, O., Tabard, A., Broeker, G., Richard, P., Nurco, D. J. & Smith, K. M. (1997). J. Chem. Soc. Dalton Trans. pp. 3459–3463.
House, D. A., Hay, R. W. & Akbar Ali, M. (1983). Inorg. Chim. Acta, 72, 239–245.
Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). J. Appl. Cryst. 44, 1281–1284.
Kolinski, R. A. & Korybut-Daszkiewicz, B. (1975). Inorg. Chim. Acta, 14, 237–245.
Kottrup, K. G. & Hetterscheid, D. G. H. (2016). Chem. Commun. 52, 2643–2646.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platnings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.
Mash, B. L., Raghavan, A. & Ren, T. (2019). Eur. J. Inorg. Chem. 2019, 2065–2070.
Meyer, K., Bill, E., Mienert, B., Weyhermüller, T. & Wieghardt, K. (1999). J. Am. Chem. Soc. 121, 4859–4876.
Prakash, J., Rohde, G. T., Meier, K. K., Münck, E. & Que, L. J. (2015). Inorg. Chem. 54, 11055–11057.
Rohde, J.-U., In, J.-H., Lim, M. H., Brennessel, W. W., Bukowski, M. R., Stubna, A., Münck, E., Nam, W. & Que, L. J. (2003). Science, 299, 1037–1039.
Sheldrick, G. M. (2015a). Acta Cryst. A 71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. A 71, 3–8.
Straub, S. & Vöhringer, P. (2021). Angew. Chem. Int. Ed. 60, 2519–2525.
Tahirov, T. H., Lu, T.-H., Liu, G.-S., Chi, T.-Y. & Chung, C.-S. (1995a). Acta Cryst. C51, 1146–1148.
Tahirov, T. H., Lu, T.-H., Liu, G.-S., Chi, T.-Y. & Chung, C.-S. (1995b). Acta Cryst. C51, 2018–2020.
Tyler, S. E., Judkins, E. C., Song, Y., Cao, F., McMillin, D. R., Fanwick, P. E. & Ren, T. (2016). Inorg. Chem. 55, 8736–8743.
Wang, J.-W., Liu, W.-J., Zhong, D.-C. & Lu, T.-B. (2019). Coord. Chem. Rev. 378, 237–261.
Weigend, F. & Ahrlich, R. (2005). Phys. Chem. Chem. Phys. 7, 3297–3305.
Westrip, S. P. (2010). J. Appl. Cryst. 43, 920–925.
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: SAINT (Bruker, 2019); data reduction: SAINT (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[(5SR,7RS,12RS,14SR)-4,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) tetrachloridoferrate (1a)

Crystal data

\[\text{[Fe(C}_{14}\text{H}_{32}\text{N}_{4}\text{)Cl}_{2}]\text{[FeCl}_{4}]\]

\[M_r = 580.83\]

Monoclinic, C\text{2}/c

\[a = 20.3512 (13) \text{ Å}\]
\[b = 6.4815 (4) \text{ Å}\]
\[c = 18.049 (1) \text{ Å}\]
\[\beta = 100.452 (3)^\circ\]
\[V = 2341.3 (2) \text{ Å}^3\]
\[Z = 4\]

Data collection

Bruker AXS D8 Quest

diffraclometer 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\(^{-1}\)

\(\omega\) and phi scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

\(T_{\text{min}} = 0.656, T_{\text{max}} = 0.747\)

71685 measured reflections

4483 independent reflections

3561 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.074\)

\(\theta_{\text{max}} = 33.2^\circ, \theta_{\text{min}} = 3.3^\circ\)

\(h = -31\rightarrow31\)

\(k = -9\rightarrow9\)

\(l = -27\rightarrow27\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.027\)

\(wR(F^2) = 0.067\)

\(S = 1.02\)

4483 reflections

148 parameters

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

\[ w = \frac{1}{\sigma^2(F_0^2) + (0.0297P)^2 + 1.680P} \]
where \( P = (F_0^2 + 2F_c^2)/3 \)

\( \Delta/\sigma_{\text{max}} = 0.001 \)
\( \Delta\rho_{\text{max}} = 0.43 \text{ e Å}^{-3} \)
\( \Delta\rho_{\text{min}} = -0.48 \text{ e Å}^{-3} \)

**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 (Å²)**

| \( x \) | \( y \) | \( z \) | \( U_{iso}/U_{eq} \) | 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) | 0.9803 (7) |
| Cl1 | 0.24845 (2) | 0.46489 (5) | 0.57279 (2) | 0.01997 (7) | 0.9803 (7) |
| N1 | 0.24598 (6) | 0.93617 (17) | 0.58935 (6) | 0.0171 (2) | 0.9803 (7) |
| H1 | 0.2410 (8) | 1.058 (3) | 0.5698 (9) | 0.021 (2) | 0.0197 (7) |
| N2 | 0.35008 (6) | 0.76192 (17) | 0.53443 (6) | 0.0181 (2) | 0.0197 (7) |
| H2 | 0.3592 (8) | 0.642 (3) | 0.5615 (10) | 0.022 (2) | 0.0197 (7) |
| C1 | 0.31267 (7) | 0.9338 (2) | 0.63842 (7) | 0.0220 (3) | 0.0197 (7) |
| H1A | 0.317297 | 0.809713 | 0.670954 | 0.026 (2) | 0.0197 (7) |
| H1B | 0.318213 | 1.057391 | 0.671182 | 0.026 (2) | 0.0197 (7) |
| C2 | 0.36500 (7) | 0.9320 (2) | 0.58942 (8) | 0.0233 (3) | 0.0197 (7) |
| H2A | 0.364878 | 1.065345 | 0.562640 | 0.028 (2) | 0.0197 (7) |
| H2B | 0.409764 | 0.911880 | 0.620775 | 0.028 (2) | 0.0197 (7) |
| C3 | 0.39433 (7) | 0.7600 (2) | 0.47710 (8) | 0.0210 (2) | 0.0197 (7) |
| H3 | 0.386422 | 0.890263 | 0.447113 | 0.025 (2) | 0.0197 (7) |
| C5 | 0.37661 (7) | 0.5783 (2) | 0.42328 (8) | 0.0224 (3) | 0.0197 (7) |
| H5A | 0.412631 | 0.562226 | 0.393511 | 0.027 (2) | 0.0197 (7) |
| H5B | 0.375954 | 0.451418 | 0.453672 | 0.027 (2) | 0.0197 (7) |
| C6 | 0.31013 (7) | 0.5939 (2) | 0.36869 (7) | 0.0196 (2) | 0.0197 (7) |
| H6 | 0.306426 | 0.736177 | 0.346859 | 0.024 (2) | 0.0197 (7) |
| C4 | 0.46790 (7) | 0.7525 (2) | 0.51366 (9) | 0.0259 (3) | 0.0197 (7) |
| H4A | 0.495428 | 0.748858 | 0.474401 | 0.039 (2) | 0.0197 (7) |
| H4B | 0.476420 | 0.628507 | 0.545009 | 0.039 (2) | 0.0197 (7) |
| H4C | 0.479181 | 0.875264 | 0.545082 | 0.039 (2) | 0.0197 (7) |
|    | C7     | H7A    | H7B    | H7C    |
|----|--------|--------|--------|--------|
|    | 0.30763 (8) | 0.345957 | 0.266122 | 0.309221 |
|    | 0.4401 (2)   | 0.462984  | 0.459639  | 0.299169  |
|    | 0.30396 (8)  | 0.279012  | 0.267536  | 0.323860  |
|    | 0.0270 (3)   | 0.041*   | 0.041*   | 0.041*   |

**Atomic displacement parameters (Å²)**

|   | U₁¹ | U₂² | U₃³ | U₁² | U₁³ | U₂³ |
|---|-----|-----|-----|-----|-----|-----|
| 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) | 0.006606 (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, °)**

| Bond | Distance (Å) | Angle (°) |
|------|-------------|-----------|
| Fe2—Cl2 | 2.1931 (5) | C1—C2 1.5028 (19) |
| Fe2—Cl2i | 2.1932 (5) | C1—H1A 0.9900 |
| Fe2—Cl3i | 2.1960 (5) | C1—H1B 0.9900 |
| Fe2—Cl3 | 2.1961 (5) | C2—H2A 0.9900 |
| Fe2B—Cl3Bi | 2.147 (16) | C2—H2B 0.9900 |
| Fe2B—Cl3B | 2.147 (16) | C3—C4 1.523 (2) |
| Fe2B—Cl2B | 2.164 (16) | C3—C5 1.5275 (19) |
| Fe2B—Cl2B | 2.164 (16) | C3—H3 1.0000 |
| Fe1—N2i | 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—N1i | 2.0276 (11) | C6—C7 1.5297 (18) |
| Fe1—Cl1ii | 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—C6i | 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) |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| Cl₂—Fe₂—Cl₂⁺         | 109.32 (3)| N₁—C₁—H₁B           | 110.0     |
| Cl₂—Fe₂—Cl₃⁺         | 108.81 (2)| C₂—C₁—H₁B           | 110.0     |
| Cl₂⁺—Fe₂—Cl₃⁻        | 109.96 (2)| H₁A—C₁—H₁B          | 108.4     |
| Cl₂—Fe₂—Cl₃⁻         | 109.96 (2)| N₂—C₂—C₁            | 108.65 (11)|
| Cl₂⁺—Fe₂—Cl₃⁻        | 108.81 (2)| N₂—C₂—H₂A           | 110.0     |
| Cl₃⁻—Fe₂—Cl₃⁻        | 109.99 (3)| C₁—C₂—H₂A           | 110.0     |
| Cl₃⁻—Fe₂—Cl₃⁻        | 95.0 (17 )| N₂—C₂—H₂B           | 110.0     |
| Cl₃⁻—Fe₂—Cl₃⁻        | 117.8 (12)| C₁—C₂—H₂B           | 110.0     |
| Cl₃⁻—Fe₂—Cl₃⁻        | 117.7 (11)| H₂A—C₂—H₂B          | 108.3     |
| N₂—Fe₁—N₂            | 93 (2)    | N₂—C₃—C₄            | 111.70 (11)|
| N₂—Fe₁—N₂            | 180.0     | N₂—C₃—C₅            | 110.20 (11)|
| N₂—Fe₁—N₁            | 94.79 (4) | C₄—C₃—C₅            | 110.55 (11)|
| N₂—Fe₁—N₁            | 85.21 (4) | N₂—C₃—H₃            | 110.1     |
| N₂—Fe₁—N₁            | 85.21 (4) | C₄—C₃—H₃            | 108.1     |
| N₂—Fe₁—N₁            | 94.79 (4) | C₅—C₃—H₃            | 108.1     |
| N₁—Fe₁—N₁            | 180.0     | C₆—C₅—C₃            | 116.04 (11)|
| N₂—Fe₁—Cl₁⁺          | 88.41 (3) | C₆—C₅—H₅A           | 108.3     |
| N₂—Fe₁—Cl₁⁺          | 91.59 (3) | C₃—C₅—H₅A           | 108.3     |
| N₁—Fe₁—Cl₁⁺          | 89.01 (3) | C₆—C₅—H₅B           | 108.3     |
| N₁—Fe₁—Cl₁⁺          | 90.99 (3) | C₃—C₅—H₅B           | 108.3     |
| N₂—Fe₁—Cl₁⁻          | 91.59 (3) | H₅A—C₅—H₅B          | 107.4     |
| N₂—Fe₁—Cl₁⁻          | 88.41 (3) | N₁⁻⁻—C₆—C₅          | 109.50 (10)|
| N₁—Fe₁—Cl₁⁻          | 90.99 (3) | N₁⁻⁻—C₆—C₇          | 112.31 (11)|
| N₁⁻⁻—Fe₁—Cl₁⁻        | 89.01 (3) | C₅—C₆—C₇            | 110.66 (11)|
| Cl₁⁻⁻—Fe₁—Cl₁⁻       | 180.0     | N₁⁻⁻—C₆—H₆          | 108.1     |
| C₁—N₁—C₆⁺            | 113.43 (10)| C₅—C₆—H₆           | 108.1     |
| C₁—N₁—Fe₁            | 107.75 (8)| C₇—C₆—H₆            | 108.1     |
| C₆⁺—N₁—Fe₁           | 118.07 (8)| C₃—C₄—H₄A           | 109.5     |
| C₁—N₁—H₁             | 106.4 (11)| C₃—C₄—H₄B           | 109.5     |
| C₆⁺—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     |                      |           |

| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| C₆⁺—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⁻⁻       | 72.54 (15) |
### Hydrogen-bond geometry (Å, °)

| D—H···A | D—H     | H···A    | D···A   | D—H···A  |
|---------|---------|---------|---------|----------|
| N2—H2···Cl3\textsuperscript{iii} | 0.917 (18) | 2.704 (18) | 3.5421 (12) | 152.5 (14) |
| N2—H2···Cl3\textsuperscript{b} | 0.917 (18) | 2.66 (3) | 3.43 (3) | 142.1 (14) |
| N1—H1···Cl1\textsuperscript{iv} | 0.862 (18) | 2.643 (18) | 3.4411 (12) | 154.5 (14) |

Symmetry codes: (iii) \(-x+1, -y+1, -z+1\); (iv) \(x, y+1, z\).
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 (Å²)

|       | x      | y      | z      | U_iso*/U_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   | 0.45585(4)  | 0.378135    | 0.385847    | 0.038*      |
| N1    | 0.58062(10) | 0.40542(4)  | 0.67522(7)  | 0.01620(15) |
| N2    | 0.3834(17)  | 0.4855(7)   | 0.8429(12)  | 0.019*      |
| N3    | 0.36207(10) | 0.34494(4)  | 0.95311(7)  | 0.01496(14) |
| N4    | 0.4117(17)  | 0.3639(7)   | 1.0094(12)  | 0.018*      |
| N5    | 0.60971(10) | 0.29159(4)  | 0.83285(7)  | 0.01582(15) |
| N6    | 0.5637(17)  | 0.2639(7)   | 0.7871(11)  | 0.019*      |
| C1    | 0.35940(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   | 0.013350    | 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) |
|     |   U_11  |   U_22  |   U_33  |   U_12  |   U_13  |   U_23  |
|-----|---------|---------|---------|---------|---------|---------|
| Fe1 |  0.0114 |  0.0114 |  0.0130 | −0.0002 |  0.0002 |  0.0001 |
| Cl1 |  0.0181 |  0.0167 |  0.0170 | −0.0015 |  0.0014 | −0.0036 |
| Cl2 |  0.0186 |  0.0175 |  0.0194 | −0.0026 | −0.0019 | −0.0025 |
| Cl3 |  0.0291 |  0.0344 |  0.0220 |  0.0020 | −0.0001 | −0.0046 |
| O1  |  0.0250 |  0.0287 |  0.0214 | −0.0019 | −0.0001 |  0.0001 |
| N1  |  0.0143 |  0.0153 |  0.0189 | −0.0012 |  0.0008 | −0.0002 |
| N2  |  0.0150 |  0.0161 |  0.0163 | −0.0003 | −0.0003 | −0.0003 |
| N3  |  0.0143 |  0.0143 |  0.0162 | −0.0002 |  0.0007 | −0.0007 |
| N4  |  0.0136 |  0.0166 |  0.0170 | −0.0001 | −0.0002 |  0.0016 |
| C1  |  0.0202 |  0.0163 |  0.0219 | −0.0007 |  0.0029 |  0.0049 |
| C2  |  0.0199 |  0.0175 |  0.0209 |  0.0026 |  0.0014 |  0.0045 |
| C3  |  0.0138 |  0.0170 |  0.0194 |  0.0022 | −0.0002 | −0.0013 |
| C4  |  0.0236 |  0.0202 |  0.0271 |  0.0073 |  0.0000 | −0.0005 |
| C5  |  0.0163 |  0.0175 |  0.0191 |  0.0016 |  0.0029 | −0.0026 |
| C6  |  0.0135 |  0.0176 |  0.0171 | −0.0010 |  0.0023 | −0.0011 |
| C7  |  0.0216 |  0.0281 |  0.0229 | −0.0001 |  0.0073 |  0.0035 |
| C8  |  0.0199 |  0.0151 |  0.0200 |  0.0006 |  0.0036 |  0.0034 |
| C9  |  0.0190 |  0.0167 |  0.0185 |  0.0027 |  0.0007 |  0.0041 |
| C10 |  0.0130 |  0.0179 |  0.0214 |  0.0012 |  0.0004 |  0.0003 |
| C11 |  0.0182 |  0.0206 |  0.0375 |  0.0046 | −0.0007 |  0.0013 |
| C12 |  0.0167 |  0.0208 |  0.0212 |  0.0020 |  0.0035 | −0.0014 |
| C13 |  0.0146 |  0.0207 |  0.0204 | −0.0018 |  0.0030 |  0.0008 |
| C14 |  0.0254 |  0.0312 |  0.0263 | −0.0006 |  0.0102 |  0.0049 |
### Geometric parameters (Å, °)

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

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| Bond                  | Distance (Å) | Angle (°) |
|-----------------------|--------------|-----------|
| N2—Fe1—Cl1           | 91.11 (3)    | C6—C7—H7B 109.5 |
| N1—Fe1—Cl1           | 88.53 (2)    | H7A—C7—H7B 109.5 |
| Cl2—Fe1—Cl1          | 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             | 116.3 (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)    | C12—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 |
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\(^i\) | 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\text{SR},7\text{RS},12\text{SR},14\text{RS})-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane]iron(III) chloride (2)

Crystal data

\[\text{[Fe(C_{14}H_{32}N_{4})Cl_{2}]}\text{Cl}\]

\(M_r = 418.63\)

Orthorhombic, \(\text{Pbcn}\)

\(a = 9.2912 (12) \text{ Å}\)
\(b = 11.9579 (19) \text{ Å}\)
\(c = 17.267 (3) \text{ Å}\)

\(V = 1918.4 (5) \text{ Å}^3\)

\(Z = 4\)

\(F(000) = 884\)

\(D_x = 1.449 \text{ Mg m}^{-3}\)

\(\text{Cu K}\alpha \text{ radiation, } \lambda = 1.54178 \text{ Å}\)

\(\theta = 6.6–78.2^\circ\)

\(\mu = 10.15 \text{ mm}^{-1}\)

\(T = 150 \text{ K}\)

Block, yellow

0.12 \times 0.08 \times 0.05 \text{ mm}
**Data collection**

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

Radiation source: I-mu-S microsource X-ray tube
Laterally graded multilayer (Goebel) mirror monochromator

Detector resolution: 7.4074 pixels mm⁻¹

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

| Tmin | Tmax |
|------|------|
| 0.526 | 0.754 |

14150 measured reflections
2055 independent reflections
1324 reflections with \( I > 2\sigma(I) \)

| \( R_{int} \) | \( \theta_{\text{max}} \) | \( \theta_{\text{min}} \) |
|-------|------|------|
| 0.082 | 79.6° | 6.6° |

\( h = -11 \rightarrow 9 \)
\( k = -14 \rightarrow 15 \)
\( l = -21 \rightarrow 15 \)

**Refinement**

Refinement on \( F^2 \)
Least-squares matrix: full

| \( R[F^2 > 2\sigma(F^2)] \) | \( wR(F^2) \) |
|-----------------|---------------|
| 0.066 | 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
H-atom parameters constrained
(\( \Delta/\sigma \))_{\text{max}} < 0.001
\( \Delta \rho_{\text{max}} = 0.58 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.95 \text{ e Å}^{-3} \)

**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 (Å²)**

| x     | y     | z      | \( U_{11} \)/\( U_{22} \)/\( U_{33} \) | Occ. (<1) |
|-------|-------|--------|----------------------------------|-----------|
| C1    | 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) |
### Atomic displacement parameters (Å²)

| Atom   | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|--------|------|------|------|------|------|------|
| Cl₁    | 0.0588 (8) | 0.0373 (7) | 0.0618 (9) | −0.0080 (6) | 0.0109 (7) | −0.0082 (6) |

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| Atom | Upp (Å²) | Upp1 (Å²) | Upp2 (Å²) | Upp3 (Å²) | Upp4 (Å²) | Upp5 (Å²) |
|------|----------|----------|----------|----------|----------|----------|
| 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) |
| C1B  | 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, °)**

| Bond | Distance (Å) | Angle (°) |
|------|--------------|-----------|
| 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'  | 1.495 (7)    | N2B—C1'B 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) |
| Bond                  | Length          | Bond                  | Length          |
|----------------------|-----------------|----------------------|-----------------|
| 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—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—C1i            | 113.8 (4)       | C1B—C2B—H2BB        | 110.0           |
| C6—N2—Fe1            | 118.1 (3)       | H2BA—C2B—H2BB       | 108.3           |
| C1i—N2—Fe1           | 109.4 (3)       | N1B—C3B—C5B         | 111.4 (16)      |
| C6—N2—H2             | 104.7           | N1B—C3B—C4B         | 111.8 (16)      |
| C1i—N2—H2            | 104.7           | C5B—C3B—C4B         | 109.1 (16)      |
| Fe1—N2—H2            | 104.7           | N1B—C3B—H3B         | 108.1           |
| C2—C1—N2i            | 108.7 (4)       | C5B—C3B—H3B         | 108.1           |
| C2—C1—H1A            | 109.9           | C4B—C3B—H3B         | 108.1           |
| N2i—C1—H1A           | 109.9           | C3B—C4B—H4BA        | 109.5           |
| C2—C1—H1AB           | 109.9           | C3B—C4B—H4BB        | 109.5           |
| N2i—C1—H1AB          | 109.9           | H4BA—C4B—H4BB       | 109.5           |
| H1A—C1—C1i           | 108.3           | H4BA—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—C1—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)       | C6B—C5B—H5BB        | 108.0           |
| C5—C3—C4             | 109.3 (5)       | N2B—C6B—C7B         | 113.2 (17)      |
| N1—C3—H3             | 108.0           | N2B—C6B—C7B         | 107.2           |
| C5—C3—H3             | 108.0           | N2B—C6B—C5B         | 112.5 (16)      |
| C4—C3—C4             | 108.0           | C7B—C6B—C5B         | 110.3 (16)      |
| 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—N2i          | 162.2 (2)       |
| C3—C5—H5AB           | 108.0           | N2—Fe1—N1Bi         | 115.1 (9)       |
| C6—C5—H5AB           | 108.0           | N2i—Fe1—N1Bi        | 49.9 (9)        |
| H5A—C5—H5AB          | 117.2           | N2i—Fe1—N2Bi        | 47.4 (10)       |
| N2—C6—C7             | 112.8 (5)       | N2i—Fe1—N2Bi        | 129.5 (9)       |
### Supporting Information

| Bond                  | Distance          | Angle            |
|-----------------------|-------------------|------------------|
| N2—C6—C5             | 112.2 (4)         | N1B—Fe1—N2B     | 86.1 (11) |
| C7—C6—C5             | 110.5 (4)         | N1B—Fe1—N2B     | 83.3 (15) |
| N2—C6—H6             | 107.0             | N2B—Fe1—N2B     | 165 (2)   |
| C7—C6—H6             | 107.0             | N2—Fe1—N1       | 86.85 (15) |
| C5—C6—H6             | 107.0             | N2—Fe1—N1       | 80.87 (16) |
| C6—C7—H7A            | 109.5             | N2—Fe1—N1       | 80.87 (16) |
| C6—C7—H7B            | 109.5             | N2 —Fe1—N1      | 86.85 (15) |
| H7A—C7—H7B           | 109.5             | N1—Fe1—N1       | 92.8 (2)  |
| C6—C7—H7C            | 109.5             | N1B—Fe1—Cl1B    | 88.8 (10) |
| H7A—C7—H7C           | 109.5             | N1B—Fe1—Cl1B    | 176.1 (10) |
| C7—C6—H6             | 107.0             | N2B—Fe1—Cl1B    | 97.3 (10) |
| C5—C6—H6             | 107.0             | N2B—Fe1—Cl1B    | 92.9 (10) |
| N2—C6—H6             | 107.0             | N2B—Fe1—Cl1B    | 127.7 (5) |
| C7—C6—H6             | 107.0             | N2 —Fe1—Cl1B    | 66.5 (6)  |
| C7—C6—H6             | 107.0             | N1—Fe1—Cl1B     | 145.0 (5) |
| C6—C7—H7A            | 109.5             | N1—Fe1—Cl1B     | 97.6 (6)  |
| C6—C7—H7B            | 109.5             | N2—Fe1—Cl1      | 94.16 (12) |
| H7A—C7—H7B           | 109.5             | N2—Fe1—C1       | 87.83 (12) |
| C7—C6—H6             | 107.0             | N1B—Fe1—C1      | 174.94 (11) |
| C6—C7—H7C            | 109.5             | N1B—Fe1—C1      | 98.20 (12) |
| C6—C7—H7C            | 109.5             | N2B—Fe1—C1      | 60.3 (5)  |
| C6—C7—H7C            | 109.5             | N2B—Fe1—C1      | 174.94 (11) |
| C6B—N2B—C1B          | 113.4             | N1B—Fe1—C1      | 87.83 (12) |
| C6B—N2B—Fe1          | 117.5 (16)        | N1B—Fe1—C1      | 87.83 (12) |
| C1B—N2B—Fe1          | 103 (3)           | N1B—Fe1—C1      | 174.94 (11) |
| C6B—N2B—H2B          | 107.6             | N2B—Fe1—C1      | 98.20 (12) |
| C1B—N2B—H2B          | 107.6             | N2B—Fe1—C1      | 94.16 (12) |
| Fe1—N1B—H1B          | 106.4             | N1B—Fe1—C1      | 94.16 (12) |
| Fe1—N1B—H1B          | 106.4             | N1B—Fe1—C1      | 94.16 (12) |
| Fe1—N1B—C1B          | 109.3             | N1B—Fe1—C1      | 87.83 (12) |
| Fe1—N1B—C1B          | 109.3             | N1B—Fe1—C1      | 87.83 (12) |
| Fe1—N1B—C1B          | 109.3             | C1—Fe1—C1       | 91.97 (8)  |
| Fe1—N1B—C1B          | 109.3             | C1—Fe1—C1       | 91.97 (8)  |
| N2—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—C1B—C2B—N1B| −64 (8)   |
| C2—N1—C3—C5          | 177.7 (4)         | N2B—C1B—C2B—N1B| −64 (8)   |
| Fe1—N1—C3—C5         | 56.2 (5)          | N2B—Fe1—C1B     | 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—N2—C6—C7          | −56.8 (6)         | C1B—N2B—C6B—C7B| 67 (5)    |
| Fe1—N2—C6—C7         | 173.0 (4)         | Fe1—N2B—C6B—C7B| −173 (3)  |
| C1—N2—C6—C5          | 68.8 (6)          | C1B—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 (Å, °)

| Bond                  | D—H  | H···A | D···A | D—H···A  |
|-----------------------|------|------|------|----------|
| N1—H1···Cl2          | 1.00 | 2.28 | 3.280 (5) | 176     |

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### supporting information

| Bond        | r (Å) | d (Å) | D (Å)   | Angle (°) |
|-------------|-------|-------|---------|-----------|
| N2—H2···Cl2<sup>ii</sup> | 1.00  | 2.52  | 3.431 (4) | 151       |
| N1B—H1B···Cl2<sup>ii</sup> | 1.00  | 2.23  | 3.23 (3)  | 176       |
| N2B—H2B···Cl2  | 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.