



# Fe(III)–azido complex with tetragonally compressed octahedral FeN<sub>6</sub> geometry: synthesis, spectroscopic and X-ray single crystal analysis of [Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)

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## Abstract

An Fe(III)–azido complex with the formula [Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>) (cyclam=1,4,8,11-tetraazacyclotetradecane) has been synthesized from the reaction of *cis*-[Fe(cyclam)Cl<sub>2</sub>]Cl with sodium azide in methanol. The X-ray structural analysis reveals that the Fe(III) atom possesses a tetragonally compressed octahedral geometry with a *trans* configuration of two azido ions. Variable-temperature (4.5–295 K) magnetic susceptibility measurements show that the complex is low spin over the whole temperature range. <sup>57</sup>Fe Mössbauer spectral measurements also suggest the same spin state of the Fe(III) ion. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Azido complex; Cyclam; Mössbauer spectroscopy; X-ray diffraction; Iron(III) complex

## 1. Introduction

1,4,7,11-Tetraazacyclotetradecane (cyclam), a macrocyclic tetraamine with a 14-membered cyclic structure, forms stable complexes with many kinds of metal ions [1–3]. Recently, a number of reports have been published regarding the catalytic properties of metal(M)–cyclam complexes, for example, as homogeneous catalysts for olefinic epoxidation/peroxidation {M=Fe(II) [4,5], Fe(III) [6,7], Ni(II) [8,9]} and CO<sub>2</sub> photoreduction {M=Ni(II) [10]}, and as electrocatalysts in the electrochemical reactions involved in CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup> reduction {M=Co(III) [11], Ni(II) [11,12]}, and H<sub>2</sub>O oxidation {M=Mn(III/IV) [13]}. In particular, iron cyclam complexes are of great interest as the models of non-heme iron oxygenases [4–7].

Cyclam, being a strong field ligand, has an affinity to form a complex with iron(III), while this particular metal

ion forms barely any stable complexes with simple or acyclic amine ligands [14]. However, only a few Fe(III)–cyclam complexes have been reported so far [15,16]. In the present study, we prepared the first Fe(III)–cyclam complex with azide groups, *trans*-[Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>), during our efforts to achieve greater insight into the coordinating behavior of azide with Fe(III) ion. The azide (N<sub>3</sub><sup>−</sup>) group being a versatile bridging ligand has aroused immense interest in the preparation of metal–organic molecular assemblies exhibiting three-dimensional magnetic ordering [17–19]. The number of Fe(III) complexes with azide group(s) is also limited to date: several terminal azido complexes [20–25] and, to our knowledge, only two  $\mu$ -azido complexes have been reportedly isolated [26,27]. On the other hand, due to the recent discovery of the *azidomet* form of hemerythrin, the preparation of Fe(III) complexes containing a monodentate azide, which mimics the active site of this non-heme metalloprotein, has received additional impetus and importance [28,29].

In this paper, we report the synthesis and crystal preparation procedures, spectroscopic characterization and crystal structure of *trans*-[Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>).

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## 2. Experimental

### 2.1. Materials

1,4,8,11-Tetraazacyclotetradecane (cyclam) was purchased from Aldrich and was used without further purification. All other chemicals were of analytical reagent (AR) grade. The *trans*- and *cis*-[Fe(cyclam)Cl<sub>2</sub>]Cl complexes were prepared as previously described [15].

### 2.2. Preparation of the complex

The complex *trans*-[Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>) was prepared by mixing the *cis*-[Fe(cyclam)Cl<sub>2</sub>]Cl complex (1 mmol) and NaN<sub>3</sub> (2 mmol) dissolved in hot methanol. A methanolic solution of LiClO<sub>4</sub> (1 mmol) was then added dropwise to the resultant deep red solution. The desired dark-red crystalline product was obtained after ca. 24 h at a yield of 62%. The crystals were collected by filtration and dried over P<sub>2</sub>O<sub>5</sub> in a desiccator. Anal. Found: C, 27.03; H, 5.53; N, 31.75; Fe, 12.9%. Calcd. for C<sub>10</sub>H<sub>24</sub>N<sub>10</sub>FeO<sub>4</sub>Cl: C, 27.28; H, 5.46; N, 31.83; Fe, 12.7%. The same product, *trans*-[Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>), was obtained when *trans*-[Fe(cyclam)Cl<sub>2</sub>]Cl was used as the starting material to prepare the complex. Single crystals suitable for X-ray measurement were obtained by slow evaporation of the mother liquor of the prepared complex.

**Caution!** Azido-perchlorate metal complexes are potentially explosive. Only a small amount of material should be prepared and it should be handled with caution.

### 2.3. Spectral and magnetic measurements

IR spectra (nujol mull) were recorded on a Jasco 7300 FT-IR spectrometer. Carbon, hydrogen and nitrogen analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer, whereas iron content was estimated using an Hitachi Z-8100 atomic absorption spectrophotometer. The Mössbauer spectra were measured using an instrument as described previously [30]. The isomer shifts are reported relative to metallic iron foil. The magnetic susceptibilities under 6.49 kG were measured by a Faraday balance mainly consisting of a Cahn 2000 microbalance in the temperature range of 4.2–295 K [31].

### 2.4. Crystal data

C<sub>10</sub>H<sub>20</sub>N<sub>10</sub>FeClO<sub>4</sub>, orthorhombic,  $a=7.8090(4)$ ,  $b=13.137(1)$ ,  $c=17.684(2)$  Å,  $V=1814.2(2)$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 20 automatically centered reflections,  $\lambda=0.71073$  Å), space group  $P2_12_12_1$ ,  $Z=4$ , red crystals, dimensions  $0.35\times 0.2\times 0.2$  mm,  $T=298$ .

### 2.5. Data collection, structure solution and refinement

X-ray intensities were recorded on a MAX Science DIP-3000 image processor with graphite-monochromated MoK $\alpha$  radiation and an 18-kW rotating-anode generator. A total of 2948 reflections were collected using the Weissenberg method in the range  $2^\circ < 2\theta < 30^\circ$  ( $0 < h < 10$ ,  $0 < k < 18$ ,  $0 < l < 25$ ). Of 2809 unique reflections measured, only 2158 for which  $I > 3\sigma(I)$  were used in the structure analysis. The structure was solved with the Dirdif-Patty method in CRYSTAN-GM (software package for structure determination, MAC Science) and refined finally through full-matrix least squares calculations. Anisotropic refinements were carried out for the non-hydrogen atoms. All of the hydrogen atoms, partially located in difference Fourier maps, were refined isotropically. The final  $R[\sum ||F_o| - |F_c|| / \sum |F_o|]$  and  $R_w\{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\}$  values were 0.050 and 0.052, respectively, using  $w^{-1} = \sigma^2(F_o) + 0.003(F_o)^2$ .

## 3. Results and discussion

An Fe(III)-azido complex with the formula of [Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> was prepared from the reaction of *cis*-[Fe(cyclam)Cl<sub>2</sub>]Cl with sodium azide in hot methanol. The same complex was obtained when *trans*-[Fe(cyclam)Cl<sub>2</sub>]Cl was used in place of *cis*-[Fe(cyclam)Cl<sub>2</sub>]Cl; the identity of the two products was confirmed by comparison of their infrared spectra. The complex showed a strong band in the IR spectra at 2047 cm<sup>-1</sup> where the  $\nu_{as}$  band for coordinated azides generally appears in this type of complex [32,33]. The other bands (e.g.  $\nu_s$  and  $\delta$ ) of azide were obscured by the presence of ligand bands. The characteristic IR bands at 1092 and 623 cm<sup>-1</sup> for perchlorate ion were also found in this complex. Chan and Poon [14] showed that the geometry of the [Fe(cyclam)X<sub>2</sub>]Y complexes (where X=Cl, Br, SCN and Y=Cl, ClO<sub>4</sub>, etc.) can be determined by inspecting their IR spectral pattern in the region 910–790 cm<sup>-1</sup>. They observed five prominent bands in the case of *cis*-[Fe(cyclam)Cl<sub>2</sub>]Cl, which appeared in this region; three of which were for N–H vibrations and the other two for C–H vibrations, whereas in the case of *trans*-[Fe(cyclam)Cl<sub>2</sub>]ClO<sub>4</sub>, two bands were observed mainly; one for each kind of vibration appeared in the same region with a separation at least 70 cm<sup>-1</sup>. The present complex showed two bands in this region that were separated by ca. 74 cm<sup>-1</sup>. This strongly suggests that the coordination geometry around the metal ion in the complex [Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>) is *trans*.

An ORTEP view of the title complex with the atom-labeling scheme is shown in Fig 1. The selected bond distances and angles are listed in Table 1. The asymmetric unit of the complex contains a [Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation

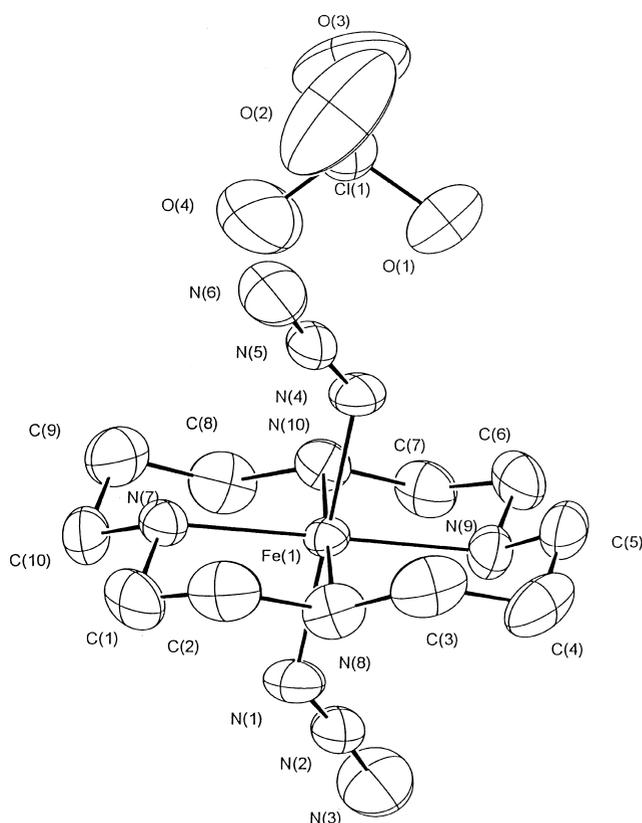


Fig. 1. ORTEP plot of  $[\text{Fe}(\text{cyclam})(\text{N}_3)_2]\text{ClO}_4$  with labeling of the non-hydrogen atoms.

and a  $\text{ClO}_4^-$  anion. The results of X-ray structural analysis revealed that the coordination polyhedra around the metal is a tetragonally compressed octahedron with a  $\text{FeN}_6$  chromophore. The four equatorial positions of the octahedron are occupied by the four nitrogen atoms of cyclam, while the two axial azides that bonded to the  $\text{Fe}(\text{III})$  atom lead to a *trans* configuration of the complex. It is well understood that macrocyclic tetraamines can possess one of five distinct conformations, four *trans* forms and one *cis* form, in their metal complexes [34,35]. In this complex, cyclam possesses the *trans*-III conformation [34,35], which is usual for octahedral complexes containing this structure of cyclotetraamine.

Table 1  
Selected bond distances (Å) and angles ( $^\circ$ ) of  $[\text{Fe}(\text{cyclam})(\text{N}_3)_2]\text{ClO}_4$

Fe(1)–N(1)	1.954(7)	N(1)–Fe(1)–N(4)	179.4(3)
Fe(1)–N(4)	1.927(6)	N(1)–Fe(1)–N(8)	86.0(3)
Fe(1)–N(7)	2.007(6)	N(1)–Fe(1)–N(10)	93.4(3)
Fe(1)–N(9)	2.006(6)	N(1)–Fe(1)–N(7)	91.6(3)
Fe(1)–N(8)	2.008(6)	N(7)–Fe(1)–N(9)	179.7(3)
Fe(1)–N(10)	2.006(5)	N(8)–Fe(1)–N(10)	178.6(3)
N(1)–N(2)	1.157(9)	N(7)–Fe(1)–N(4)	91.6(3)
C(1)–C(2)	1.484(13)	N(1)–N(2)–N(3)	176.2(9)
Cl(1)–O(1)	1.431(6)	O(1)–Cl(1)–O(2)	109.5(5)
Fe(1)–N(1)–N(2)	130.9(6)	Fe(1)–N(4)–N(5)	130.6(5)

The mean  $\text{Fe}–\text{N}(\text{cyclam})$  distance [2.007(6) Å] was almost identical to that in *trans*- $[\text{Fe}(\text{cyclam})\text{Cl}_2]\text{Cl}$  [2.006(2) Å] [16], and had an intermediate value between the  $\text{M}–\text{N}$  distances in  $[\text{Ni}(\text{cyclam})\text{Cl}_2]\text{ClO}_4$  [1.970(4) Å] [36] and  $[\text{Cr}(\text{cyclam})(\text{OCONH}_2)_2]\text{ClO}_4 \cdot 1.5\text{H}_2\text{O}$  [2.059(2) Å] [37]. The  $\text{Fe}–\text{N}(\text{azido})$  distances [1.954(7) and 1.927(6) Å] in this complex were in agreement with the reported values for  $\text{Fe}(\text{TPP})\text{N}_3\text{B}$  complexes (TPP $^{2-}$  = 5,10,15,20-tetraphenylporphinato ion, B = pyridine and methyl-substituted imidazoles) [21,22]. Most *trans*- $[\text{M}(\text{cyclam})\text{X}_2]\text{Y}$  complexes display a geometry of a tetragonally elongated octahedron around the metal ion  $\{\text{M} = \text{Fe}(\text{III})$  [16],  $\text{Co}(\text{II})$  [38],  $\text{Ni}(\text{II})$  [39,40],  $\text{Ni}(\text{III})$  [36],  $\text{Cu}(\text{II})$  [41,42] and  $\text{Ag}(\text{II})$  [43]}; to our knowledge, a tetragonally compressed octahedron has been reported so far only for  $[\text{Cr}(\text{cyclam})(\text{OCONH}_2)_2]\text{ClO}_4 \cdot 1.5\text{H}_2\text{O}$  [37]. In addition, it seems interesting that the related mononuclear  $\text{Ni}(\text{II})$  complex,  $[\text{Ni}(2,7,9,14\text{-tetramethyl-cyclam})(\text{N}_3)_2]$ , indicates a tetragonally elongated octahedral geometry [44]. Elongated  $\text{MN}_6$  geometry is also reported for an  $\text{Fe}^{2+}$  complex with bis-pendant amine cyclam ligand,  $[\text{Fe}(\text{trans-diammac})](\text{PF}_6)_2$  (diammac = 6,13-diamino-6,13-dimethyl-cyclam) [45]. On the other hand,  $[\text{Na}(18\text{-crown-6})(\text{H}_2\text{O})_2][[\text{Fe}(\text{TPP})(\text{N}_3)_2] \cdot 2\text{C}_6\text{H}_5\text{Cl}]$  shows a tetragonally compressed  $\text{FeN}_6$  geometry (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane). However, the extent of the distortion is very small in this case [the difference between the  $\text{Fe}–\text{N}(\text{azido})$  and  $\text{Fe}–\text{N}(\text{TPP})$  mean distances = 0.012 Å] [20].

Both *cis* and *trans*- $[\text{Fe}(\text{cyclam})\text{Cl}_2]\text{Cl}$  gave *trans*- $[\text{Fe}(\text{cyclam})(\text{N}_3)_2]\text{ClO}_4$ , on addition of  $\text{NaN}_3$  in hot methanolic medium. In the case of the preparation using *cis*- $[\text{Fe}(\text{cyclam})\text{Cl}_2]$ , it seems reasonable to expect a thermal transformation of *cis*- $[\text{Fe}(\text{cyclam})\text{Cl}_2]$  to the *trans* form in the hot solution [15]. However, only *trans*- $[\text{Fe}(\text{cyclam})(\text{N}_3)_2]\text{ClO}_4$  was obtained even when the reaction was carried out at room temperature in order to prevent the *cis*–*trans* transformation.

The molar magnetic susceptibility ( $\chi_M$ ) of *trans*- $[\text{Fe}(\text{cyclam})(\text{N}_3)_2]\text{ClO}_4$  was measured in the temperature range of 4.5–295 K. The effective magnetic moment ( $\mu_{\text{eff}}$ ) was estimated at room temperature to be 2.17 BM, which is comparable to the reported  $\mu_{\text{eff}}$  values for the low spin  $\text{Fe}(\text{III})$  complexes, *trans*- $[\text{Fe}(\text{cyclam})\text{Cl}_2]\text{ClO}_4$  and *trans*- $[\text{Fe}(\text{cyclam})(\text{NCS})_2]\text{NCS}$  [15]. The higher value of  $\mu_{\text{eff}}$  in comparison to the expected spin only moment indicates that there is a considerable amount of orbital contribution to its moment. The  $\mu_{\text{eff}}$  value gradually decreased with decreasing temperature and, at 4.5 K, it was 1.72 BM. This is not unexpected for a low spin complex with a  $^2T_{2g}$  ground state where the temperature dependence of the magnetic moment is a function of the spin–orbit coupling parameter [47]. A fairly large increase in  $\chi_M$  with temperature, based on spin-equilibrium between  $S = 1/2$  and  $S = 5/2$  states, was reported for the related  $\text{FeN}_6$  complex

[Na(18-crown-6)(H<sub>2</sub>O)<sub>2</sub>][Fe(TPP)(N<sub>3</sub>)<sub>2</sub>]·2C<sub>6</sub>H<sub>5</sub>Cl [20]. Comparison between the spin states of this complex and *trans*-[Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> would indicate that the ligand field of cyclam is stronger than that of TPP<sup>2-</sup>. *trans*-[Fe(cyclam)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> exhibited a Mössbauer spectrum of a single quadrupole doublet, showing an usual paramagnetic state at 4.2, 78 and 298 K [46], and the isomer shift values were of a typical low-spin Fe(III) state [48]. This study shows that these Mössbauer results are essentially consistent with the above cryomagnetic data.

### Supplementary data

Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available upon request, quoting the deposition number CCDC 113938.

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