



Fe(III)–azido complex with tetragonally compressed octahedral FeN₆ geometry: synthesis, spectroscopic and X-ray single crystal analysis of [Fe(cyclam)(N₃)₂](ClO₄)

Subratanath Koner^a, Seiichiro Iijima^{a,*}, Fumio Mizutani^a, Kazuaki Harata^a, Masanobu Watanabe^b, Akira Nagasawa^b, Masaru Sato^c

^aNational Institute of Bioscience and Human-Technology, 1-1 Higashi, Tsukuba, Ibaraki 305-8566, Japan

^bDepartment of Chemistry, Faculty of Science, Saitama University, Shimo-Okubo, Urawa, Saitama 338-8570, Japan

^cChemical Analysis Center, Saitama University, Shimo-Okubo, Urawa, Saitama 338-8570, Japan

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Abstract

An Fe(III)–azido complex with the formula [Fe(cyclam)(N₃)₂]ClO₄ (cyclam=1,4,8,11-tetraazacyclotetradecane) has been synthesized from the reaction of *cis*-[Fe(cyclam)Cl₂]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. ⁵⁷Fe 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 CO₂ photoreduction {M=Ni(II) [10]}, and as electrocatalysts in the electrochemical reactions involved in CO₂ and NO₃⁻ reduction {M=Co(III) [11], Ni(II) [11,12]}, and H₂O 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)(N₃)₂]ClO₄, during our efforts to achieve greater insight into the coordinating behavior of azide with Fe(III) ion. The azide (N₃⁻) 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 μ -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)(N₃)₂]ClO₄.

*Corresponding author. Tel.: +81-298-54-6166; fax: +81-298-54-6161.

E-mail address: iijima@nibh.go.jp (S. Iijima)

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)Cl₂]Cl complexes were prepared as previously described [15].

2.2. Preparation of the complex

The complex *trans*-[Fe(cyclam)(N₃)₂](ClO₄) was prepared by mixing the *cis*-[Fe(cyclam)Cl₂]Cl complex (1 mmol) and NaN₃ (2 mmol) dissolved in hot methanol. A methanolic solution of LiClO₄ (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 P₂O₅ in a desiccator. Anal. Found: C, 27.03; H, 5.53; N, 31.75; Fe, 12.9%. Calcd. for C₁₀H₂₄N₁₀FeO₄Cl: C, 27.28; H, 5.46; N, 31.83; Fe, 12.7%. The same product, *trans*-[Fe(cyclam)(N₃)₂](ClO₄), was obtained when *trans*-[Fe(cyclam)Cl₂]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

C₁₀H₂₀N₁₀FeClO₄, orthorhombic, $a=7.8090(4)$, $b=13.137(1)$, $c=17.684(2)$ Å, $V=1814.2(2)$ Å³ (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 α 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)(N₃)₂]ClO₄ was prepared from the reaction of *cis*-[Fe(cyclam)Cl₂]Cl with sodium azide in hot methanol. The same complex was obtained when *trans*-[Fe(cyclam)Cl₂]Cl was used in place of *cis*-[Fe(cyclam)Cl₂]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⁻¹ where the ν_{as} band for coordinated azides generally appears in this type of complex [32,33]. The other bands (e.g. ν_s and δ) of azide were obscured by the presence of ligand bands. The characteristic IR bands at 1092 and 623 cm⁻¹ for perchlorate ion were also found in this complex. Chan and Poon [14] showed that the geometry of the [Fe(cyclam)X₂]Y complexes (where X=Cl, Br, SCN and Y=Cl, ClO₄, etc.) can be determined by inspecting their IR spectral pattern in the region 910–790 cm⁻¹. They observed five prominent bands in the case of *cis*-[Fe(cyclam)Cl₂]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)Cl₂]ClO₄, two bands were observed mainly; one for each kind of vibration appeared in the same region with a separation at least 70 cm⁻¹. The present complex showed two bands in this region that were separated by ca. 74 cm⁻¹. This strongly suggests that the coordination geometry around the metal ion in the complex Fe(cyclam)(N₃)₂(ClO₄) 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)(N₃)₂]⁺ cation

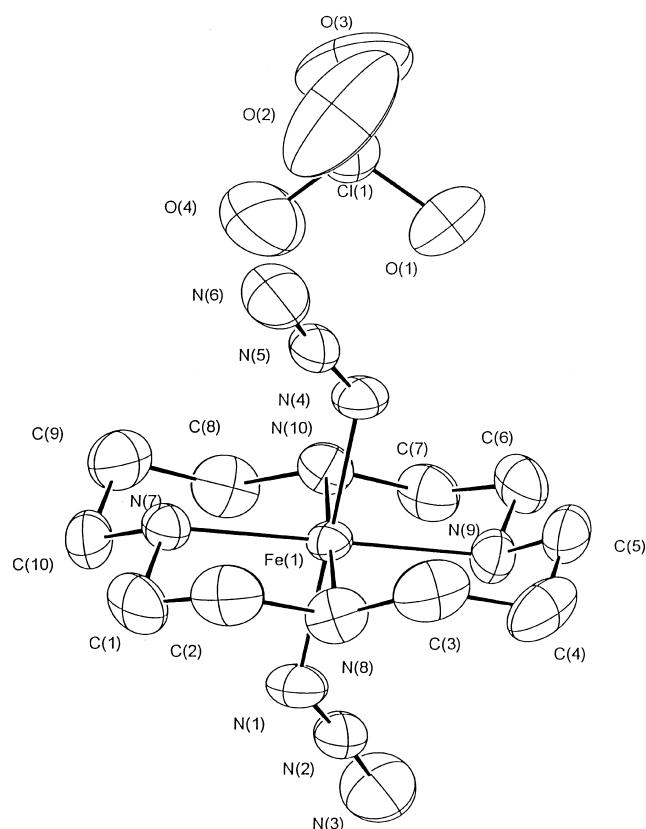


Fig. 1. ORTEP plot of $[\text{Fe}(\text{cyclam})(\text{N}_3)_2]\text{ClO}_4$ with labeling of the non-hydrogen atoms.

and a 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 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 MN_6 geometry is also reported for an 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 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 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 (χ_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 (μ_{eff}) was estimated at room temperature to be 2.17 BM, which is comparable to the reported μ_{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 μ_{eff} in comparison to the expected spin only moment indicates that there is a considerable amount of orbital contribution to its moment. The μ_{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 χ_M with temperature, based on spin-equilibrium between $S = 1/2$ and $S = 5/2$ states, was reported for the related FeN_6 complex

[Na(18-crown-6)(H₂O)₂][Fe(TPP)(N₃)₂]·2C₆H₅Cl [20]. Comparison between the spin states of this complex and *trans*-[Fe(cyclam)(N₃)₂]ClO₄ would indicate that the ligand field of cyclam is stronger than that of TPP²⁻. *trans*-[Fe(cyclam)(N₃)₂]ClO₄ 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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