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

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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)Cl]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.

**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 photoinsertion [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 monodenate 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.
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]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)Cl]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 C₁₀H₂₂N₁₈FeClO₄: C, 27.28; H, 5.46; N, 31.83; Fe, 12.7%. The same product, trans-[Fe(cyclam)(N₃)₂](ClO₄)₃, was obtained when trans-[Fe(cyclam)Cl]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

C₁₀H₂₂N₁₈FeClO₄, 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, A = 0.71073 Å), space group P2₁̅2₁̅2₁, Z = 4, red crystals, dimensions 0.35 × 0.2 × 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 MoKα radiation and an 18-kW rotating-anode generator. A total of 2948 reflections were collected using the Weissenberg method in the range 2θ < 2θ < 30° (0 < h < 10, 0 < k < 18, 0 < l < 25). Of 2809 unique reflections measured, only 2158 for which I > 3σ (I) were used in the structure analysis. The structure was solved with the Direid-Patty method in CRYSTAN-3M (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 = ∑|F₀|−|Fᵣ|/∑|F₀| and Rw = ∑w(∥F₀∥−|Fᵣ|)²/∑wF₀|²]¹/² values were 0.050 and 0.052, respectively, using w⁻¹ = a²(F₀) + 0.003(F₀)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)Cl]Cl with sodium azide in hot methanol. The same complex was obtained when trans-[Fe(cyclam)Cl]Cl was used in place of cis-[Fe(cyclam)Cl]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 νₐ band for coordinated azides generally appears in this type of complex [32,33]. The other bands (e.g. νₜ 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)X]₂Y 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)Cl]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]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)₂ClO₄ 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.
The mean Fe–N(cyclam) distance [2.007(6) Å] was almost identical to that in trans-[Fe(cyclam)Cl]Cl [2.006(2) Å] [16], and had an intermediate value between the M–N distances in [Ni(cyclam)Cl]ClO₄ [1.970(4) Å] [36] and [Cr(cyclam)(OCOHNH₂)₃ClO₄·1.5H₂O [2.059(2) Å] [37]. The Fe–N(azido) distances [2.006(2) Å] [16], and had an intermediate value between the M–N distances in [Ni(cyclam)Cl]ClO₄ [1.970(4) Å] [36] and [Cr(cyclam)(OCOHNH₂)₃ClO₄·1.5H₂O [2.059(2) Å] [37]. The Fe–N(azido) distances [1.954(7) and 1.927(6) Å] in this complex were in agreement with the reported values for Fe(TPP)N₂ complexes (TPP = 5,10,15,20-tetraphenylporphinato ion, B = pyridine and methyl-substituted imidazoles) [21,22]. Most trans-[M(cyclam)X₂]Y complexes display a geometry of a tetragonally elongated octahedron around the metal ion [M = Fe(III) [16], Co(II) [38], Ni(II) [39,40], Ni(III) [36], Cu(II) [41,42] and Ag(II) [43]; to our knowledge, a tetragonally compressed octahedron has been reported so far only for [Cr(cyclam)(OCOHNH₂)₃ClO₄·1.5H₂O [37]. In addition, it seems interesting that the related mononuclear Ni(II) complex, [Ni(2,7,9,14-tetramethyl-cyclam)(NCS)]₂, indicates a tetragonally elongated octahedral geometry [44].

Elongated MN₆ geometry is also reported for an Fe₆ complex with bis-pendant amine cyclam ligand, [Fe(trans-diammac)(PF₆)₉] [45]. On the other hand, [Na(18-crown-6)(H₂O)][Fe(TPP)(NCS)]ClO₄ shows a tetragonally compressed FeN₆ 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 Fe–N(azido) and Fe–N(TPP) mean distances is 0.012 Å] [20].

Both cis and trans-[Fe(cyclam)Cl]Cl gave trans-[Fe(cyclam)(NCS)₂]ClO₄ on addition of NaN₃ in hot methanolic medium. In the case of the preparation using cis-[Fe(cyclam)Cl]Cl, it seems reasonable to expect a thermal transformation of cis-[Fe(cyclam)Cl]Cl to the trans form in the hot solution [15]. However, only trans-[Fe(cyclam)(NCS)₂]ClO₄ was obtained even when the reaction was carried out at room temperature in order to prevent the cis→trans transformation.

The molar magnetic susceptibility (χM) of trans-[Fe(cyclam)(NCS)₂]ClO₄ was measured in the temperature range of 4.5–295 K. The effective magnetic moment (μeff) was estimated at room temperature to be 2.17 BM, which is comparable to the reported μeff values for the low spin Fe(III) complexes, trans-[Fe(cyclam)Cl]ClO₄ and trans-[Fe(cyclam)(NCS)₂]ClO₄ [15]. The higher value of μeff in comparison to the expected spin only moment indicates that there is a considerable amount of orbital contribution to its moment. The μeff 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 2T₂g 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 χM with temperature, based on spin-equilibrium between S = 1/2 and S = 5/2 states, was reported for the related FeN₆ 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 TPP⁺. trans-[Fe(cyclam)(N₃)₂]ClO₄ exhibited a Mössbauer spectrum of a single quadrupole doublet, showing an unusual 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.

References


[44] The isomer shifts were 0.31, 0.29 and 0.21 mm/s at 4.2, 78 and 298 K, respectively. The quadrupole splittings were 2.25, 2.25 and 2.15 mm/s at 4.2, 78 and 298 K, respectively.