Isolation of a singly oxo-bridged Fe(III) dinuclear complex: Synthesis, crystal structure, spectroscopic and magnetic studies

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Abstract

The µ-oxo dinuclear complex \(\text{[Fe}_2\text{O(tptz)}_2\text{[N(CN)}_2\text{]}_2\text{[NO}_3\text{]}_2\text{]}(\text{I})\) (where tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine) has been synthesised and characterised by elemental analysis, FT-IR, UV–vis, cyclic voltammetry, Mössbauer spectroscopy, and variable-temperature magnetic susceptibility measurements and single crystal X-ray diffraction. The iron centres have a pentagonal-bipyramidal geometry. The dimeric neutral complex exhibits typical Fe–µ-O bond lengths of 1.763(1) Å and a bridge angle of 180.00°/C176. The Fe–C1/C1/C1/Fe separation is 3.526(3) Å. The Mössbauer spectrum at room temperature consists of one quadrupole doublet with an isomer shift of 0.41 mm/s and a quadrupole splitting of 1.12 mm/s. Variable-temperature magnetic susceptibility measurements have been measured in the temperature range 300–2 K, revealing an intramolecular antiferromagnetic coupling (\(J = -211.6 \text{ cm}^{-1}\)).

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1. Introduction

The (µ-oxo)diiron(III) unit has been the subject of interest among inorganic chemists for many years [1], which has been further intensified by the occurrence of such traits as synthetic models of the active site from a large class of non-heme diiron enzymes including the invertebrate dioxygen carrier hemerythrin (Hr), ruberythrin, ribonucleotide reductase (RNR), methane monooxygenase (MMOH) and fatty acid desaturases [1,2] and are proposed as nucleation sites for the evolution of the ferritin core [3]. A large body of data exists that define the intrinsic properties of this dinuclear unit. The µ-oxo bridge gives rise to short (≈1.8 Å) Fe–O bonds, strong antiferromagnetic coupling (\(J \approx -100 \text{ cm}^{-1}\) for \(H = 2JS_1\cdot S_2\)) and large Mössbauer quadrupole splittings (\(\Delta E_Q = 1.5 \text{ mm s}^{-1}\)). There are many examples of complexes with the (µ-oxo)diiron(III) unit unsupported by any other bridging ligand as well as those that are supported by one or two additional oxoanionic bridges such as carboxylate or phosphate [4]. Their structures, magnetic, spectroscopic and redox properties, and also chemical reactivities have been intensely investigated and are summarised in several good reviews [5]. In this paper, we have described the synthesis and structure of a singly µ-oxo-bridged compound, \(\text{[Fe}_2\text{O(tptz)}_2\text{[N(CN)}_2\text{]}_2\text{[NO}_3\text{]}_2\text{]}(\text{I})\). To the best of our knowledge, (I) is the first example of a structurally characterised singly oxo-bridged heptacoordinated Fe III dimer with the planar tridentate tptz and the terminal dca ligand.

2. Experimental

2.1. Materials

All the chemicals and solvents used for the synthesis were of reagent grade. Fe(NO3)3⋅9H2O (Merck), 2,4,6-
tris(2-pyridyl)-1,3,5-triazine (Aldrich) and sodium dicyanamide (NaN(CN)₂) (Fluka) were used as received.

2.2. Synthesis of \( \{Fe_2O(tptz)_2[N(CN)_2]_2(NO_3)_2\} \) (I)

Complex I was obtained readily by refluxing a reaction mixture of tptz (2 mmol, 0.624 g) and dca (2 mmol, 0.178 g) with Fe(NO₃)₃·9H₂O (2 mmol, 0.807 g), in methanol-water solution as brown single crystals. The yield of the title compound was approximately 81%, 0.81 g. Anal. Calc. for C₄₀H₂₄Fe₂N₂O₇: C, 47.56; H, 2.31; N, 27.76; Fe, 10.98%.

2.3. Physical techniques

Elemental analysis was carried out using a Perkin–Elmer 2400 II elemental analyser. The infrared spectrum was recorded on a Perkin–Elmer FT-IR spectrophotometer with KBr disc. Perkin–Elmer Lambda 40 (UV–Vis) spectrophotometer was used for the electronic absorption. The solution of the complex was prepared in N,N-dimethylformamide and the OD for of the solution was kept below 0.3. Magnetic susceptibility measurements were carried out on polycrystalline sample, with a Quantum Design SQUID MPMS-XL susceptor apparatus working in the range 300–2 K under a magnetic field of 5000 Oe. Diamagnetic corrections were estimated from Pascal Tables.

2.4. Crystallographic data collection and refinement

Experimental details for I are given in Table 1. Once the data processing was performed by the Kappa CCD analysis softwares [6], the lattice constants were refined by least-square refinement. No absorption correction was applied to the data sets. The unit-cell parameters, crystal system, space group and refinement details are summarised in Table 1. The structure has been solved by direct methods (sir97 program [7]) combined with Fourier difference syntheses and refined against \( F \) using reflections with \( |I/\sigma(I)| > 3 \) CRYSTALS program [8]. All atoms were successfully refined anisotropically.

3. Results and discussion

3.1. Description of the crystal structure

3.1.1. \( \{Fe_2O(tptz)_2[N(CN)_2]_2(NO_3)_2\} \) (I)

A view of the asymmetric unit with atom numbering scheme is shown in Fig. 1. Selected bond lengths and angles are summarised in Table 2. The bridging oxo group O50 lies on the crystallographic center of symmetry that relates both halves of the molecule. Each of the two Fe atoms is heptacoordinated and possesses an N₂O₃ environment by virtue of four nitrogen atoms (N1, N8, N20) from chelating tptz group and terminal dca ligand (N40) and three oxygen atoms from bidentate nitrate moiety (O31 and O33) and a bridging oxygen atom (O50). So the Fe atoms possess distorted-pentagonal bipyramidal geometry.

Fe1 is 0.050(1) Å out of the best equatorial plane which is defined by N1, N8, N20, O31 and O33 (the deviations from the mean plane are 0.011(7), −0.009(8), −0.013(8), −0.001(8) and 0.008(8) Å). The deviation from ideal pentagonal-bipyramidal geometry is indicated by the difference in the basal angles which varies from 55.9(3)° to 91.96(19)° and axial sites are occupied by the oxo group and nitrogen of the dca ligand yielding O50–Fe1–N40 as the trans-axial angle (176.3(3)°). The two axial distances are shorter (Fe1–O50, 1.763(1) Å and Fe1–N8, 2.037(9) Å) than the equatorial bond distances (Fe1–O31, 2.260(8) Å; Fe1–N33, 2.267(7) Å), which are more or less comparable to similar systems [9]. The Fe–O oxo bond length (1.763(1) Å) is in the range found more or less comparable to similar systems [9]. The uncoordinated pyridyl ring makes an angle of 26.4(3)° with the other part of tptz. For singly μ-oxo bridged binuclear iron(III) complexes, the most favourable arrangement is expected to be linear if there are no crystal-packing forces. In this dimer, the Fe–O–Fe bond angle is 180.00° and the Fe–Fe separation is 3.526(3) Å, slightly shorter than the highest value of 3.596(1) Å [12]. The structural parameters of the metal-oxo core are again entirely typical of high-spin dinuclear