Preparation and Structure of a Dinuclear Iron(III) Complex with Six Terminally Coordinated Azides: A Precursor for Multidimensional Network

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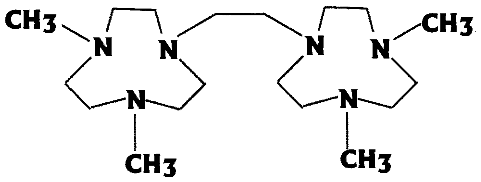
A novel dinuclear hexazido iron(III) complex of a binuclear macrocycle has been synthesized and characterized by its crystal structure determination.

Magneto-structural studies carried out on polynuclear first row transition metal complexes with N_3^-, NCO^-, NCS^- and $NCSe^-$ bridges have received special attention in recent years, in view of their interesting properties.[1-5] In this set the azide group has received major attention owing to its versatility as ligand and the wide variety of magnetic properties of its compounds. Azido compounds have also received attention due to their utility in the synthesis of nitrido complexes of higher valent transition metal ions.[6,7] Synthesis of metal complexes with more than one azide as a terminal ligand is of interest, since they can serve as template for the synthesis of multidimensional network. Extensive work is currently being carried out in the field of molecular magnetism on account of its promising application to diverse areas of technology such as magnetic recording and magnetic optics.[8,9] Currently attempts are being made to synthesize multidimensional networks to achieve this goal.[10] A large number of compounds with diazido grouping have been reported.[11-13] On the other hand not many compounds with three coordinated azides have been structurally characterized. In this communication we describe the synthesis and structural characterization of a diiron(III) complex of a binucleating ligand derived from triazacyclononane, with six coordinated azides.



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The ligand [1,2-di(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane], Me_4dtne, **1**, was prepared from triazacyclononane following a published procedure.[14] The complex $Fe_2Me_4dtne(N_3)_6$, **2**, was prepared by heating 1.090 g (3 mmol) of the ligand Me_4 dtne dissolved in 50 mL of acetonitrile-ethanol (5:1) with 2.1 g (6 mmol) $Fe(ClO_4)_3$. After refluxing the solution for 10 min 1g sodium azide was added to it and refluxing continued for another 2 h. The red solution obtained was rotary evaporated to half its initial volume and left in an open dish for slow evaporation. Within two days crystals suitable for X-ray crystallography were obtained. The electronic spectrum of the compound in methanol shows two intense bands at 336 nm ($4.38x10^3$) and 495 nm ($2.24x10^3$) which arises due to charge transfer interactions. The compound crystallizes in a centrosymmetric space group $p_{\bar{1}}$.[15] The structure of the compound is given in Figure 1. The ORTEP of the molecule shows that both the iron(III) atoms have distorted octahedral geometry with each iron (III) coordinated to three nitrogens of the macrocycle and three azides, all the six azides acting as terminal ligands. The Fe-N bond lengths are typical of high spin Fe(III) compounds. The typical bond lengths and bond angles are given in Table 1. It can be seen from Table 1 that Fe-$N_{macrocycle}$ bond lengths vary only marginally. The Fe-N_{azide} bond lengths on the other hand have different magnitude compared to Fe-$N_{macrocycle}$ bond length. It is of interest to note that all the Fe-$N_{macrocycle}$ bonds are longer compared to Fe-N_{azide} bonds.

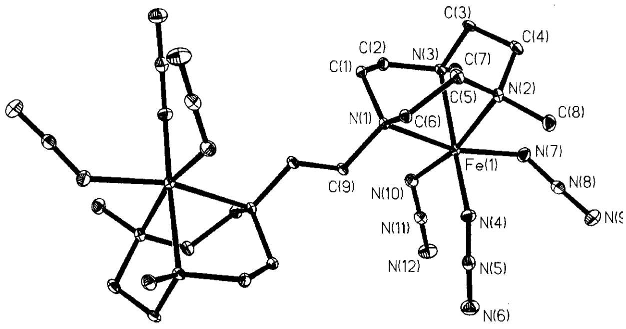

Figure 1. ORTEP view of the crystal structure of **2**

Table 1. Bond Lengths and Bond Angles of **2**

Bond Length /Å		Bond Angle / °	
Fe(1) – N(1)	2.233(2)	N(10) – Fe(1) – N(4)	100.38(9)
Fe(1) – N(2)	2.266(2)	N(4) - Fe(1) – N(7)	96.25(9)
Fe(1) – N(3)	2.224(2)	N(4) – Fe(1) – N(3)	166.62(8)
Fe(1) – N(4)	1.979(2)	N(10) –Fe(1) –N(1)	93.59(8)
Fe(1) – N(7)	2.051(2)	N(7) –Fe(1) – N(1)	165.89(8)
Fe(1) – N(10)	1.973(2)	N(10) – Fe(1) – N(2)	167.56(8)
		N(7) – Fe(1) – N(2)	89.58(8)
		N(1) – Fe(1) – N(2)	78.87(7)
		N(10) – Fe(1) – N(7)	96.30(9)
		N(10) – Fe(1) –N(3)	91.40(8)
		N(7) – Fe(1) – N(3)	90.36(8)
		N(4) – Fe(1) – N(1)	91.83(8)
		N(3) – Fe(1) – N(1)	79.50(7)
		N(4) – Fe(1) – N(2)	89.82(8)
		N(3) – Fe(1) – N(2)	78.57(7)

As seen from Table 1 the three Fe-N$_{macrocycle}$ bond lengths are 2.233(2), 2.266(2) and 2.224(2) Å respectively, whereas the three Fe-N$_{azide}$ bond lengths are 1.973(2), 1.979(2) and 2.051(2) Å respectively. The approximately 0.2 Å lengthening of Fe-N$_{macrocycle}$ bond lengths when compared to Fe-N$_{azide}$ is not surprising, since similar behavior has been observed in the case of triazido Fe(III) complex of the tripodal ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate.[16] The N(10)–Fe–N(4) bond angle is 100.38(9)^o, which is close to the ideal bond angle for an octahedral iron. On the other hand the N(10)–Fe–N(7) bond angle is only 96.30(9)^o. This shortening of bond angle may be due to the steric interaction of N(7) azide ion with the methyl substituent at N(2) atom of the macrocycle. Such a shortening of bond angle is also reflected in the N(4)–Fe–N(7) bond angle which has been found to be 96.25(9)^o. It is surprising that the two iron(III) centres are not bridged by the azide; even though azide is an excellent bridging ligand. Acetate ions on the other hand have been reported to bridge two metal ions coordinated to Me$_4$dtne, **1.**[14] Presence of six terminal azides in **2** can be exploited for the synthesis of three-dimensional clusters.

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15 Crystallographic data: $C_{18}H_{40}Fe_2N_{24}$, triclinic, a = 7.882(1) b = 8.026(1) c = 13.236(2) Å, α = 80.20(2) β = 83.36(2), γ = 65.09(2)°, V = 747.4(2) Å^3 , Z = 1, D_c = 1.565 g cm^{-3} T = 100(2) K, F(000) = 368, λ (MoK$_\alpha$) = 0.71073 Å, μ = 1.028 mm^{-1}. Crystal size 0.35 x 0.25 x 0.18 mm, Siemens SMART diffractometer, θ range 1.56 – 29.99°, 7441 reflections collected, structure solution by direct methods and refinement from 3962 independent reflections. Refinement method was full matrix least-squares on F^2, R1 = 0.0453 [I>2σ (I)] and wR2 = 0.1085 (all data).

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