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NOTE

Synthesis and Crystal Structure of a Tetaraazamacrocyclic Compound

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The tetaraazamacrocyclic compound of iron, {L·[Fe(CN)$_5$NO]} (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been synthesized and determined by X-ray diffraction. The crystal is triclinic, space group P-1 with unit cell parameters: a = 8.167(3) Å, b = 9.345(2) Å, c = 9.702(3)A, α = 63.823(12)°, β = 73.863(14)°, γ = 73.877 (14)°, V = 627.9(3)Å^3, Z = 1, Mr = 496.42, Dc = 1.313 Mg/m^3, μ = 0.634 mm^{-1}, F(000) = 262, T = 293(2) K, R = 0.0790, wR = 0.1513 for 4885 reflections with I > 2σ(I).

Key Words: Tetaraazamacrocyclic compound, Crystal structure.

In recent years, the metal-ion coordination compounds formed by polyaza macrocycles has been extensively investigated due to the ability of these systems to interact with different substrates such as metal ions or anionic species[1] to form complexes with applications in catalysis, models for metalloenzymes, mechanism and molecular recognition research[2-3]. Recently, in our laboratory, a series of transition metal compounds have been synthesized and studied[4-7].

In this communication, the synthesis and the structure of the tetaraazamacrocyclic compound {L·[Fe(CN)$_5$NO]} (L = 5,5,7,12,12,14-hexa methyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) are reported.

All the reagents were of AR grade and used without further purification. IR spectra was record on a Nexus-870 spectrophotometer. Elemental analyses for C, H and N were performed on a Elementar Vario EL-III analyzer. The crystal structure was determined by Siemens SMART CCD area-detector diffractometer.

Synthesis: The 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene [L·(ClO$_4$)$_2$] was synthesized according to the literature[8,9]. A mixture of 25 mL methanol solution of L·(ClO$_4$)$_2$ (10 mmol) were respectively added 25 mL water solution of K$_3$Fe(CN)$_5$NO (10 mmol), then refluxed for 1 h. After filtered, the solution was kept at room condition for 6 d and then the brown colour rhombus

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crystals resulted from it. IR (KBr, cm^{-1}): 3150(s), 2130, 1890(s), 1660, 1540(s). Anal. Calcd. for $C_{21}H_{32}N_{10}OFe$: C, 50.76; H, 6.45; N, 28.20 %. Found: C, 50.81; H, 6.44; N, 28.16 %.

Structure determination: A single crystal (0.35 mm × 0.30 mm × 0.10 mm) was selected for crystallographic data collection at 293(2) K and structure determinated with graphite-monochromatic MoK_α radiation (λ = 0.71073 Å). A total of 4885 reflections were collected in the range of $2.67^o \leq \theta \leq 27.48^o$, of which 2833 reflections were unique with R_{int} = 0.0124. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system[10] was used in the solution and refinements of the structure. The final full-matrix least-squares refinement including 151 variable parameters for 2833 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of R = 0.0790 and wR = 0.1513, where $w = 1/[\sigma^2(F_0^2) + (0.0000P)^2 + 0.6705P]$, and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.539 and -1.079e/Å^3 (CCDC No. 646129), respectively.

The atomic coordinates and thermal parameters are given in Table-1 and the selected bond lengths and bond angels are in Table-2. The molecular structure of compound is shown in Fig. 1. Fig. 2 shows the packing diagram in the unit cell, in which there are positive negative charge interactions between L^{2+} cations and $[Fe(CN)_5NO]^{3-}$ anions.

TABLE-1
ATOMIC COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^3 Å^2)

Atom	X	Y	Z	U (eq)
Fe	0	0	0	54(1)
N(1)	4886(4)	5004(4)	-1813(3)	33(1)
C(1)	3458(7)	6508(7)	-4116(6)	68(2)
C(2)	4655(5)	6239(5)	-3073(4)	36(1)
C(11)	2088(5)	578(4)	-1507(4)	39(1)
N(11)	3319(5)	918(5)	-2390(4)	58(1)
O	1992(6)	-1776(5)	2551(5)	70(1)

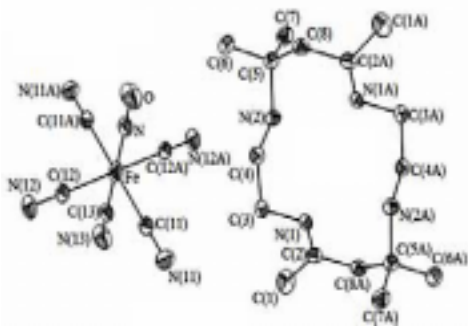

Fig. 1. Structure of the title compound

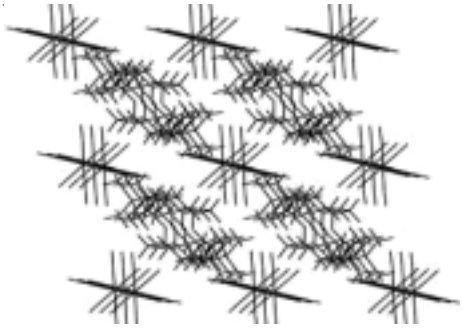

Fig. 2. Molecular packing arrangement

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°) OF {L[Fe(CN)$_5$NO]}

Bond	Dist.	Bond	Dist.	Angles	(°)	Angles	(°)
Fe-N	1.806(3)	C(1)-C(2)	1.493(5)	C(13)#1-Fe-N	180.0(4)	N(1)-C(2)-C(1)	126.1(4)
Fe-C(11)	1.941(4)	N(1)-C(2)	1.274(4)	N#1-Fe-C(11)#1	90.66(17)	C(2)-N(1)-C(3)	119.2(3)
O-N	1.135(4)	N(1)-C(3)	1.473(5)	N-Fe-C(11)#1	89.34(17)	N(1)-C(3)-C(4)	109.9(3)
N(11)-C(11)	1.142(5)	C(3)-C(4)	1.513(5)	O-N-Fe	178.6(4)	C(1)-C(2)-C(8)#2	115.1(3)

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