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THE Fe(III) COMPLEX OF N,N',N''-TRIS(3-HYDROXY-6 METHYL-2-PYRIDYLMETHYL)-1,4,7-TRIAZACYCLONONANE $\text{Fe}(\text{C}_{27}\text{H}_{33}\text{N}_6\text{O}_3 \cdot \text{C}_6\text{H}_6 \cdot 2\text{H}_2\text{O})$

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**THE Fe(III) COMPLEX OF N,N',N''-
TRIS(3-HYDROXY-6 METHYL-2-PYRIDYL-
METHYL)-1,4,7-TRIAZACYCLONONANE
Fe(C₂₇H₃₃N₆O₃·C₆H₆·2H₂O)**

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The crystal structure of FeC₂₇H₃₃N₆O₃·C₆H₆·2H₂O has been determined. This complex is orthorhombic and crystallizes in space group P2₁2₁2₁ with cell parameters $a = 13.226(4)$ Å, $b = 19.410(6)$ Å, $c = 12.779(4)$ Å, $V = 3281(2)$ Å³, $Z = 4$ and $Mr = 659.61$. $R_F = 0.056$ for 1626 observed reflections with $I > 3 \sigma(I)$ and 199 variables. The structure consists of a neutral complex of FeC₂₇H₃₃N₆O₃ with Fe(III) in a slightly distorted octahedral environment coordinated to three tertiary amino nitrogen atoms and three phenolate-like oxygen atoms (FeN₃O₃). The average Fe-N distance = 2.22 Å, Fe-O = 1.91 Å. The twist angle of 54.0° is nearly the value expected for a purely octahedral complex (60°) and a correlation between the twist angle and the stability of the complex in solution is suggested.

KEYWORDS: triazacyclononane, Fe(III), crystal structure, distorted octahedron

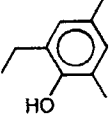
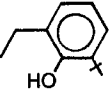
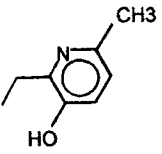
INTRODUCTION

A considerable number of potentially sexadentate ligands containing N-functionalized 1,4-7-triazacyclononane have been synthesized, and their coordination chemistry has been investigated. Some representative examples of these ligands and their metal complexes are listed in Table 1.¹⁻⁸ The crystal structures of the complexes of some of these ligands with trivalent metal ions were also determined (Table 1).

The development of synthetic high-affinity and highly selective chelating agents for Fe(III) has long been an important research project in this group.^{9,10} Potentiometric studies of ligand V in Table 1 showed that this ligand has unusually high affinity for Fe(III) and is more effective for the ferric ion than any other previously reported ligand at physiological pH². Because of its unusually high stability, it would be of interest to determine the structure of the crystalline form of the Fe(III) chelate to see if it differs very much from the crystal structures of other Fe(III) chelates of analogous triazacyclononane ligands such as that of TACN-TA (Table 1).

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Table 1 N-functionalized 1,4,7-triazacyclononane hexadentate ligands for which x-ray structures of trivalent metal complexes have been determined (some formation constants (log K) are also shown)

No.	R	Abbreviation	M(III)	Ref. ^a	log K
I	-CH ₂ COOH	TACN-TA	Fe ³⁺ Cr ³⁺	5	28.3 ^b
II		TACN-TX	Ga ³⁺ Fe ³⁺	4	42.2 ^{c,d} 51.3 ^{c,d}
III		TACN-TB	Fe ³⁺	6	
IV	-CH ₂ CH ₂ SH	TACN-TM	Ga ³⁺	3	
V		TACN-HP	Fe ³⁺	1, this work	49.9 ^c

^aReference for crystal structure determination. ^bRef. 8. ^cIn 75% ethanol 25% water. ^dRef. 7. ^eRef. 2.

EXPERIMENTAL

The ligand *N,N',N''*-tris(3-hydroxy-6-methyl-2-pyridylmethyl)-1,4,7-triazacyclononane (TACN-HP or H₃L, ligand V) was prepared according to the published procedure.¹ All other reagents were of the highest purity available from commercial sources and were used without further purification.

Preparation of Crystals of N,N',N''-tris(3-hydroxy-6-methyl-2-pyridylmethyl)-1,4,7-triazacyclononatoiron(III)

To an aqueous solution of 70 mg (0.14 mm) of TACN-HP, was added 38 mg (0.14 mm) of FeCl₃·6H₂O. The pH of the solution was adjusted to 9.5–10. The Fe(III) complex was extracted with CH₂Cl₂, and the concentrated dark red CH₂Cl₂ solution was loaded on a column of silica gel 60 Å (200–400 mesh, column size dxh = 22×48 mm) and was eluted with CHCl₃ and CHCl₃:MeOH = 9:1, and the eluates were pooled. After the solvent was removed, 0.055 g of a nearly black shining solid residue was obtained, yield 60%. Single crystals suitable for X-ray diffraction were grown from chloroform/benzene solution by the liquid diffusion method.

Crystallographic study of the FeL Complex

A red-brown needle of FeN₆C₃₃O₅H₄₃ having approximate dimensions of 0.060×0.060×0.450 mm was mounted on a glass fiber. Experimental conditions

and crystallographic parameters are reported in Table 2. Cell parameters were obtained from least squares refinement using the setting angles of 24 carefully centered reflections in the range $8.79^\circ < 2\theta < 20.64^\circ$. On the basis of the systematic absences of $h00$ ($h \neq 2n+1$), $0k0$ ($k \neq 2n+1$) and $00l$ ($l \neq n+1$) and the successful solution and refinement of the structure, the space group was determined to be $P2_12_12_1$ (No. 19).

Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.25° with a take-off angle of 6.0° . Scans of $(0.73 + 0.30 \tan P)^\circ$ were made at a speed of $4.0^\circ/\text{min}$ (in omega) The weak reflections ($I < 10.0 \sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

A total of 3276 reflections was collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. No decay correction was applied.

The linear absorption coefficient for Mo $K\alpha$ is 5.1 cm^{-1} . An empirical absorption correction, using the program DIFABS,¹¹ was applied which resulted in transmission factors ranging from 0.84 to 1.10. The data was corrected for Lorentz and polarization effects.

The structure was solved by direct methods.¹² The non-hydrogen atoms were refined either anisotropically or isotropically. The final cycle of full-matrix least-squares refinement¹³ gave unweighted and weighted agreement factors of $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.056$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.059$. The standard deviation of an observation of unit weight¹⁴ was 1.51. The weighting

Table 2 Experimental conditions and crystallographic parameters

Empirical formula	$\text{FeN}_6\text{C}_{33}\text{O}_5\text{H}_{43}$
Formula weight	659.61
Crystal system	orthorhombic
Lattice Parameters	$a = 13.226(4) \text{ \AA}$ $b = 19.410(6) \text{ \AA}$ $c = 12.779(4) \text{ \AA}$ $V = 3281(2) \text{ \AA}^3$
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.341 g/cm^3
F_{000}	1408
Diffractometer	Rigaku AFC5R
Radiation	MoK α ($\gamma = 0.71069 \text{ \AA}$)
Temperature	23°C
$2\theta_{\text{max}}$	50.1°
No. observations ($I > 3.0\sigma(I)$)	1626
No. variables	199
Residuals: R; R_w	0.056; 0.059
Maximum shift/error in final cycle	0.02
Maximum peak in final diff. map	$0.48 \text{ e}^-/\text{\AA}^3$
Minimum peak in final diff. map	$-0.41 \text{ e}^-/\text{\AA}^3$
Scan type	W-2 θ
Crystal to detector distance	285.0 mm
Diam., incident beam collimeter	0.5 mm

scheme was based on counting statistics and included a factor ($p = 0.03$) to down weight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends.

Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ Anomalous dispersion effects¹⁶ were included in Fcalc; the anomalous dispersion terms $\Delta f'$ and $\Delta f''$ were those of Cromer.¹⁷ All calculations were performed with the TEXSAN¹⁸ crystallographic software package. Final positional and equivalent isotropic thermal parameters are presented in Table 3. Selected bond distances are indicated in Table 4 and angles are given in Table 5. Anisotropic thermal parameters and structure amplitudes are provided in Tables S2 and S1 (supplementary material), respectively, available from author.

RESULTS AND DISCUSSION

The ligand H_3L forms a very stable neutral complex with Fe^{3+} at pH 7–10, which is more soluble in organic solvents than in aqueous solution. Therefore it can be purified chromatographically with silica gel. The single crystals were prepared by covering a concentrated chloroform solution of the metal complex with pure benzene which then slowly diffuses into the solution. Crystallographic study showed that during the least squares refinement four benzene rings and eight water molecules were found in the unit cell. The residual electron density peaks from the final differential Fourier analysis distribute along the benzene rings. The thermal factor of the benzene rings is large and the rings were found to rotate or oscillate around the benzene plane. This kind of disorder may cause the R factor to be slightly higher (0.056) than it would otherwise be.

The ORTEP¹⁹ representation of $FeL_3 \cdot C_6H_6 \cdot 2H_2O$ is shown in Figure 1. The ferric ion is in a slightly distorted octahedral environment coordinated to three tertiary amino nitrogen atoms and three hydroxypyridine oxygen atoms (FeN_3O_3). The pendant arms form three six-membered chelate rings. The Fe-N bond lengths are equivalent within experimental uncertainty, and rather long (average 2.223 Å). This is typical for octahedral high-spin ferric ions.⁶ The average Fe-O distance of 1.909 Å is quite short and compares well with six-coordinate Fe(III) phenolate complexes⁶ (with average Fe-O of 1.889 Å). The N-Fe-N bond angles are compressed (average 78.3°) due to steric constraints of the 1,4,7-triazacyclononane backbone of the ligand, whereas the O-Fe-O angles (average 97.7°) are expanded.

The crystalline chelate described above is considerably different from the complex obtained from acid solution and described in a preliminary report¹. The latter compound had a much different empirical formula ($C_{27}H_{58}O_{15}ClFe$), contained HCl (as a hydrochloride), much more water of hydration, had a different crystalline form (rhombohedral) and was assigned to a different space group, R3 (NO. 148).¹ Moreover the acid forms of this complex have been shown to be much less stable,² because of protonation of the pyridine nitrogens.

Tables 4 and 5 show the bond distances and angles of the title compound, while Table 6 shows a comparison of bond lengths and angles of three types of complexes with three different pendant donor groups: hydroxybenzyl, hydroxypyridyl, and acetate. The similarities of the metal-oxygen bond lengths of the hydroxypyridyl (TACN-HP) and the hydroxybenzyl (TACN-TB) ligands indicate similar intrinsic coordinate strengths of the metal-oxygen bonds, and one must look elsewhere for

differences in solution stability. Since TACN-HP has much lower pK's than does TACN-TB, it binds the Fe(III) ion more effectively at physiological pH, where competition with hydrogen ions is important. The longer M-O bond length in the TACN-TA complex indicates a much weaker coordinate bond and lower solution stability. This is partially made up by the shorter M-N bonds, indicating that the Fe(III) ion is closer to the macrocyclic ring in this complex.

Table 3 Positional parameters and B(eq) values for the [N,N',N''-tris(3-hydroxy-6-methyl-2-pyridylmethyl-1,4,7-triazacyclononato)]iron(III) Complex (FeL)

atom	x	y	z	β(eq)
Fe	0.3082(1)	0.24118(9)	0.9892(1)	2.40(7)
O(1)	0.2397(6)	0.2698(5)	0.8666(6)	3.2(4)
O(2)	0.2295(6)	0.2936(5)	1.0885(7)	2.9(4)
O(3)	0.2418(5)	0.1555(4)	1.0120(8)	3.4(4)
O(4)	0.4881(9)	0.0441(6)	0.3826(9)	6.7(3)
O(5)	0.520(1)	0.1275(7)	0.557(1)	8.4(4)
N(1)	0.4278(9)	0.1987(5)	0.8863(8)	2.2(5)
N(2)	0.4168(7)	0.3284(5)	0.9888(8)	2.5(4)
N(3)	0.4234(9)	0.2069(6)	1.1051(8)	2.6(6)
N(4)	0.3412(8)	0.2079(6)	0.6224(9)	3.9(3)
N(5)	0.3456(8)	0.4526(6)	1.1693(9)	3.6(3)
N(6)	0.3651(8)	0.0409(6)	1.1932(9)	3.5(3)
C(1)	0.498(1)	0.2553(7)	0.855(1)	3.1(3)
C(2)	0.461(1)	0.3258(6)	0.879(1)	2.8(3)
C(3)	0.496(1)	0.3213(7)	1.069(1)	2.9(3)
C(4)	0.468(1)	0.2705(6)	1.153(1)	2.8(3)
C(5)	0.510(1)	0.1678(6)	1.052(1)	2.6(3)
C(6)	0.478(1)	0.1439(7)	0.944(1)	2.9(3)
C(7)	0.377(1)	0.1672(7)	0.796(1)	2.8(3)
C(8)	0.322(1)	0.2165(6)	0.2166(1)	2.9(3)
C(9)	0.252(1)	0.2621(7)	0.766(1)	3.3(3)
C(10)	0.194(1)	0.3002(7)	0.689(1)	3.8(3)
C(11)	0.214(1)	0.2902(7)	0.585(1)	4.3(3)
C(12)	0.282(1)	0.2443(8)	0.554(1)	4.0(3)
C(13)	0.314(1)	0.233(1)	0.439(1)	7.3(5)
C(14)	0.3606(8)	0.3939(6)	1.002(1)	2.8(2)
C(15)	0.315(1)	0.3996(6)	1.110(1)	2.8(3)
C(16)	0.249(1)	0.3475(7)	1.146(1)	2.9(3)
C(17)	0.207(1)	0.3561(7)	1.246(1)	3.3(3)
C(18)	0.236(1)	0.4109(7)	1.304(1)	3.8(3)
C(19)	0.308(1)	0.4582(7)	1.266(1)	3.8(3)
C(20)	0.345(1)	0.5184(9)	1.333(1)	6.7(5)
C(21)	0.374(1)	0.1658(8)	1.184(1)	3.4(3)
C(22)	0.3347(9)	0.0991(6)	1.144(1)	2.7(3)
C(23)	0.266(1)	0.0981(7)	1.059(1)	2.6(3)
C(24)	0.227(1)	0.0349(7)	1.032(1)	3.4(3)
C(25)	0.261(1)	-0.0243(7)	1.079(1)	4.3(3)
C(26)	0.331(1)	-0.0199(7)	1.158(1)	4.2(3)
C(27)	0.375(1)	-0.0822(8)	1.211(1)	5.1(4)
C(28)	0.041(1)	0.1251(6)	0.420(1)	9.0(3)
C(29)	0.1106(8)	0.0944(8)	0.353(1)	9.0(3)
C(30)	0.081(1)	0.0401(7)	0.288(1)	9.0(3)
C(31)	-0.019(1)	0.0165(6)	0.290(1)	9.0(3)
C(32)	-0.0886(8)	0.0473(8)	0.357(1)	9.0(3)
C(33)	-0.059(1)	0.1016(8)	0.422(1)	9.0(3)

Table 4 Selected bond distances (Å) for FeL

Fe-O1	1.893(8) ^a	N2-C2	1.52(2)
Fe-O2	1.931(9)	N2-C3	1.47(2)
Fe-O3	1.902(8)	N2-C14	1.48(1)
Fe-N1	2.22(1)	N3-C4	1.50(2)
Fe-N2	2.220(9)	N3-C5	1.53(2)
Fe-N3	2.23(1)	N3-C21	1.44(2)
O1-C9	1.31(1)	N4-C8	1.35(2)
O2-C16	1.30(2)	N4-C12	1.37(2)
O3-C23	1.31(2)	N5-C15	1.34(2)
N1-C1	1.50(2)	N5-C19	1.34(2)
N1-C6	1.45(2)	N6-C22	1.35(2)
N1-C7	1.46(2)	N6-C26	1.34(2)

^aEstimated standard deviations in the last significant figure are in parentheses.

The much lower stability of the N,N',N''-triazacyclononanetriacetate-Fe(III) (TACN-TA)-iron(III) complex relative to the analogous triazacyclononane ligands substituted by hydroxypyridyl and phenolic donors (Table 1) is due in part to the differences in basicity of the oxygen donors, as can be seen from the relative pK's of these functional groups. The lower stability must also be due to the fact that the acetate donors provide five-membered chelate rings with the small Fe(III) ion, rather than the more stable six-membered chelate rings formed by the phenolic and hydroxypyridine donors in the complexes of TACN-TB and TACN-HP, respectively. The greater stabilities of six-membered chelate rings over five-membered chelate rings for small metal ions has been pointed out by Hancock and Martell.²⁰

Wieghardt and coworkers⁵ reported the crystal structures of the Fe(III), Cr(III), Ni(II) and Cu(II) complexes of TACN-TA, and showed that the "twist angle", indicates how the structures vary from the extremes of trigonal prismatic (corresponding to 0° twist angle) to an octahedral structure (which requires a 60° twist angle). They found, for example, that the Fe(III)-TACN-TA structure has a 25.2° twist angle (Table 6), and that it corresponds more closely to a trigonal prismatic than to an octahedral structure. Because the polar groups are farther apart and have lower steric repulsion for each other in the octahedral arrangement than in the

Table 5 Selected bond angles (°) for FeL

O1-Fe-O2	97.5(4) ^a	N1-Fe-N2	79.6(4)
O1-Fe-O3	99.3(4)	N1-Fe-N3	78.2(4)
O1-Fe-N1	87.4(4)	N2-Fe-N3	77.7(4)
O1-Fe-N2	94.8(4)	Fe-O3-C23	134.6(8)
O1-Fe-N3	164.9(4)	Fe-N1-C6	107.6(8)
O2-Fe-O3	96.4(4)	Fe-N2-C2	103.1(7)
O2-Fe-N1	166.1(4)	Fe-N2-C3	112.9(7)
O2-Fe-N2	87.0(4)	Fe-N2-C14	109.2(6)
O2-Fe-N3	95.1(4)	Fe-N3-C21	108.9(8)
O3-Fe-N1	95.5(4)		
O3-Fe-N2	164.9(4)		
O3-Fe-N	87.3(4)		

^aEstimated standard deviations in the least significant figure are given in parentheses.

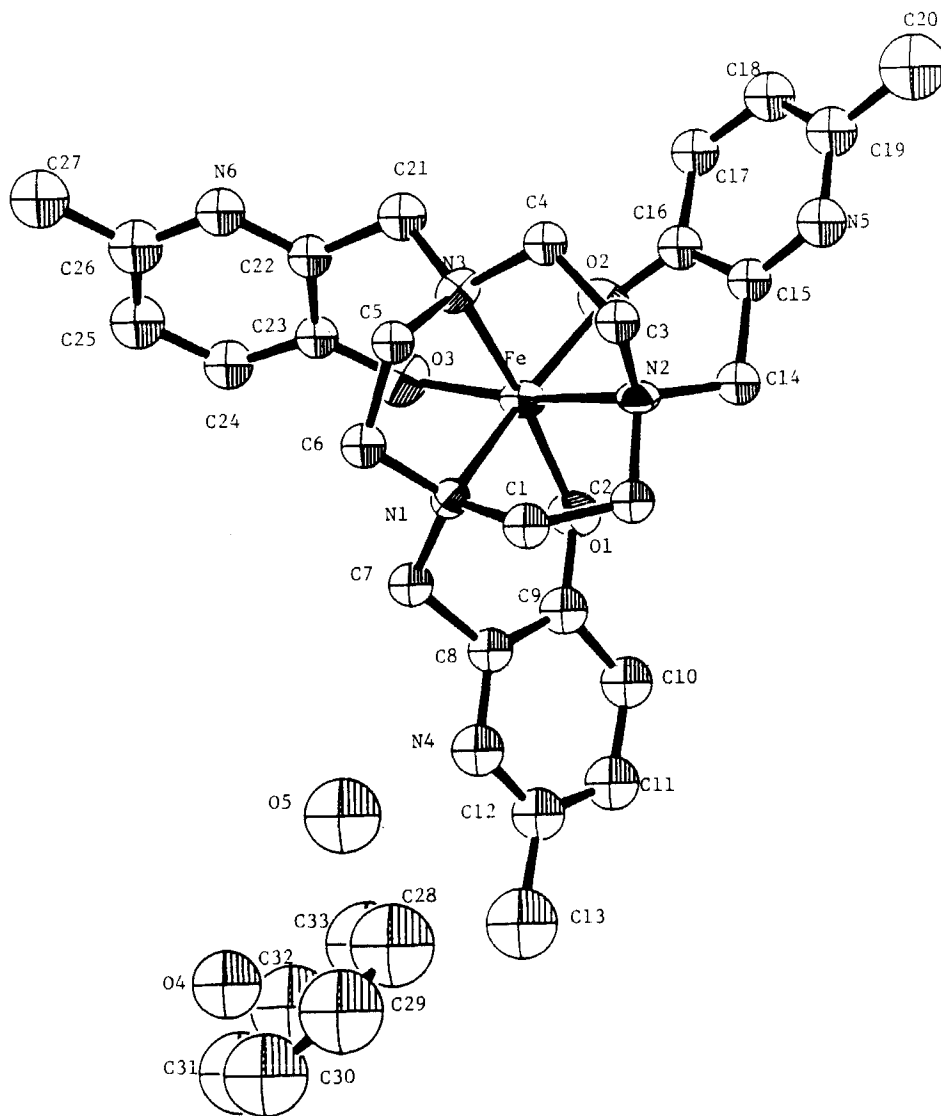
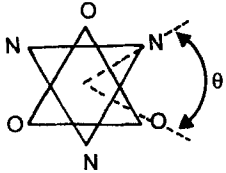


Figure 1 ORTEP¹⁹ representation of FeL structure.

trigonal prismatic structure, a complex containing an octahedral arrangement of donor groups should be more stable. The twist angle of the TACN-HP iron(III) complex of 54.0° corresponds closely to the more stable octahedral structure. Therefore the high stability of this complex is due in part to the octahedral arrangement of its donor groups. Apparently the pendant acetate donor groups in TACN-TA are not long enough to assume the more stable octahedral conformation.

Table 6 Comparison of the X-ray structures of some six-coordinated ferric phenolate complexes

	Fe(TACN-HP)	Fe(TACN-TB) ⁶	Fe(TACN-TA) ⁵
<i>Bond distances (Å)</i>			
Fe-O1	1.893(8)	1.888(4)	1.962(2)
Fe-O2	1.931(9)	1.890(4)	
Fe-O3	1.902(8)	1.890(4)	
Fe-N1	2.22(1)	2.236(5)	
Fe-N2	2.220(9)	2.235(5)	2.181(3)
Fe-N3	2.23(1)	2.250(5)	
<i>Bond Angles (°)</i>			
O2-Fe-O3	96.4(4)	97.7(2)	
O1-Fe-O3	99.3(4)	98.0(2)	94.0(1)
O1-Fe-O2	97.5(4)	96.6(2)	
N1-Fe-N2	79.6	77.7(2)	
N1-Fe-N3	78.2	77.4(2)	79.4(1)
N2-Fe-N3	77.7(4)	77.5(2)	
<i>Twist Angle</i>			
			θ
	Fe(TACN-HP)		54.0°
	Fe(TACN-TA)		25.2° ⁵
	octahedral		60°
	trigonal prismatic		0°

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SUPPLEMENTARY MATERIAL

Tables listing structure amplitudes and anisotropic thermal parameters are available from the authors.

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