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Synthesis and Crystal Structure of Tris[1-(2-azoyl)-2-azabuten-4-yl]amineiron(III), [Fe((pyrol)$_3$tren)]

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The low-spin iron(III) complex with the Schiff base formed from 2,2′,2″-tris(ethylamino)amine (tren) and pyrrole has been synthesized and its crystal and molecular structures have been determined. Although the ligand is potentially a heptadentate, the complex contains six strong iron–nitrogen bonds, while the distance between the metal atom and the apical nitrogen N(10), the potential seventh donor, is 3.304 (1) Å, which approximates the van der Waals contact distance. The crystallographic symmetry imposes a precise threefold axis (C_3) on the molecule through the iron atom and the apical nitrogen N(10). The ligand environment about the metal is a trigonally distorted octahedron, with three upper (pointing toward N(10)) Fe–N bonds of 1.989 (1) Å and three lower Fe–N bonds of 1.936 (1) Å. From comparison with literature data on other ligands, ring substitution at the pyrrole of (pyrol)$_3$tren should lead to neutral high-spin and spin-state crossover complexes; the [Fe((pyrol)$_3$tren)] complex is a good model for the low-spin extreme of such a series. Crystal data: space group $I\bar{4}3d$, $a = 20.058$ (4) Å, $V = 8069$ Å^3, $R = 2.5\%$ for 526 reflections. Full-matrix least-squares refinement converged with a conventional R factor of 2.5%.

Introduction

The magnetic properties and structures of complexes exhibiting spin-state equilibria between high-spin and low-spin forms have recently been extensively studied.[1–15] It is generally observed that a metal–ligand bond length change of about 0.13 Å accompanies the transition from high spin to low spin in a number of d^5 systems.[1] This observation appears to hold true in a series of (electrically neutral) ferric dithiocarbamates, as well as ionic complexes of the form FeL$^+$, where L is a ligand formed from the Schiff base condensation of trien (1,8-diamino-3,6-diazaoctane) and salicylaldehyde, acetylacetone, or 3-chloroacetylacetone.[2] It is clear that in these complexes the anion and water of crystallization exert a strong influence on the position of the spin-state equilibrium and therefore on the magnetic properties. In some cases the presence of a disordered anion has decreased the accuracy of the available crystallographic data, and the influence of the anions on the detailed structure is not known. It is therefore of interest to examine a neutral analogue of such structures.

The complex [Fe((pyrol)$_3$tren)], which consists of neutral low-spin molecules, has been studied crystallographically using counter methods, and its highly accurate structural data are presented here. This complex is a model for a series of substituted complexes which are expected to show spin-state crossover and which will be reported subsequently.

Experimental Section

Preparation of the Complex. tren·3HCl (1.0 g) and NaOCH$_3$ (0.63 g) were suspended in 50 mL of CH$_3$OH and stirred for 20 min. Pyrrole-2-carboxaldehyde (0.29 g) was added and the mixture stirred for a further 20 min. FeCl$_3$·6H$_2$O (1.06 g) was added and the mixture refluxed for 10 min. The solution was then taken to dryness on a rotary evaporator. The resultant black mass was extracted with cold CH$_2$Cl$_2$. Evaporation of solvent left well-formed tetrahedral crystals. A tetrahedral crystal, 0.35 mm on an edge, was chosen for x-ray data collection.

Crystal data for FeN$_7$C$_{21}$H$_{24}$: mol wt 430, space group $I\bar{4}3d$, $Z = 16$, $a = 20.058$ (2) Å, $V = 8069$ Å^3, $\rho_{\text{calcd}} = 1.414$ g cm^{-3}, $\rho_{\text{obsd}} = 1.43$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 7.9$ cm^{-1}, crystal dimensions (distances in mm from centroid): $(1\bar{1}1)$ 0.072, $(\bar{1}11)$ 0.072, $(11\bar{1})$ 0.072, $(\bar{1}\bar{1}\bar{1})$ 0.072.

Collection and Reduction of the Data. The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. The refined cell dimension and its estimated standard deviation were obtained from least-squares refinement of 21 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $0° < 2\theta < 52°$. Scan widths (SW) were calculated from the formula SW $= A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.60 and 0.30°, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan (6°/min), such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100-reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. Of the 817 independent intensities collected, 526 had $F_o^2 > 3\sigma(F_o^2)$ where $\sigma(F_o^2)$ was estimated from counting statistics.[16] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structures. In addition to the systematic absences that determined the space group $I\bar{4}3d$, systematically weaker reflections were observed for even values of the h, k, and l indices when $h + k + l \neq 4n$, suggesting that the iron atom lies on a special position on a threefold rotation axis. This is compatible with the normally observed average volume of approximately 18 Å^3 per nonhydrogen atom and with the threefold chemical symmetry of the three branches of the free ligand. This requires the molecule to possess a threefold rotation axis and reduces the 48 equivalent positions to 16. It is therefore possible to determine the positions of the iron atom and the three independent nitrogen positions from a three-dimensional Patterson function calculated from all intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen and some of the hydrogen atoms.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[17] and those for hydrogen from Stewart et al.[18] The effect of anomalous dispersion for all nonhydrogen atoms was included in F_c using the values Cromer and Ibers[19] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of

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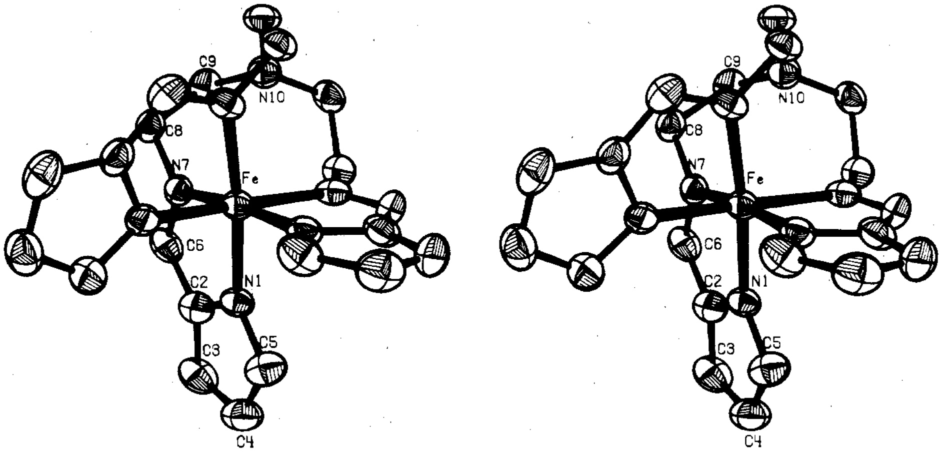

Figure 1. Stereoview of the [Fe((pyrol)$_3$tren)] molecule.

Table I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.16288 (8)	0.1629 (0)	0.1629 (0)	0.00129 (2)	0.0013 (0)	0.0013 (0)	−0.00018 (7)	−0.0002 (0)	−0.0002 (0)
N(1)	0.2593 (1)	0.1590 (2)	0.1613 (2)	0.00145 (7)	0.00180 (8)	0.00139 (8)	−0.0001 (2)	−0.0003 (2)	−0.0003 (2)
N(7)	0.1744 (2)	0.0644 (1)	0.1654 (2)	0.00173 (9)	0.00129 (7)	0.00122 (8)	−0.0003 (1)	−0.0003 (2)	0.0000 (2)
N(10)	0.0678 (5)	0.0678 (0)	0.0678 (0)	0.00175 (22)	0.00175 (0)	0.00175 (0)	0.0000 (5)	0.0000 (0)	0.0000 (0)
C(2)	0.2851 (2)	0.0955 (2)	0.1657 (2)	0.0015 (1)	0.0018 (1)	0.0013 (1)	0.0003 (2)	−0.0005 (2)	−0.0003 (2)
C(3)	0.3542 (2)	0.0991 (2)	0.1661 (2)	0.0016 (1)	0.0030 (1)	0.0022 (1)	0.0012 (2)	−0.0005 (2)	−0.0007 (3)
C(4)	0.3709 (2)	0.1658 (3)	0.1612 (2)	0.0015 (1)	0.0032 (1)	0.0022 (1)	−0.0003 (2)	−0.0004 (2)	−0.0013 (3)
C(5)	0.3115 (2)	0.2011 (2)	0.1581 (2)	0.0018 (1)	0.0021 (1)	0.0019 (1)	−0.0006 (2)	−0.0000 (2)	−0.0011 (2)
C(6)	0.2357 (2)	0.0455 (2)	0.1684 (2)	0.0019 (1)	0.0016 (1)	0.0015 (1)	0.0007 (2)	−0.0006 (2)	0.0001 (2)
C(8)	0.1201 (2)	0.0157 (2)	0.1666 (2)	0.0018 (1)	0.0014 (1)	0.0017 (1)	−0.0003 (2)	−0.0002 (2)	0.0002 (2)
C(9)	0.0903 (2)	0.0066 (2)	0.0974 (2)	0.0021 (1)	0.0014 (1)	0.0018 (1)	−0.0006 (2)	−0.0003 (2)	−0.0003 (2)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.381 (2)	0.066 (2)	0.164 (2)	4.0 (10)	H(81)	0.135 (2)	−0.030 (2)	0.184 (2)	2.3 (8)
H(4)	0.420 (2)	0.187 (2)	0.157 (2)	3.5 (10)	H(82)	0.084 (2)	0.031 (2)	0.193 (2)	1.7 (7)
H(5)	0.301 (2)	0.247 (2)	0.156 (2)	2.3 (9)	H(91)	0.053 (2)	−0.024 (2)	0.102 (2)	2.0 (8)
H(6)	0.245 (2)	0.002 (2)	0.172 (2)	3.0 (9)	H(92)	0.129 (2)	−0.011 (2)	0.068 (2)	3.4 (10)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

Table II. Bond Lengths (Å) for [Fe((pyrol)$_3$tren)]

Fe–N(1)	1.936 (1)	N(10)–C(9)	1.435 (4)
Fe–N(7)	1.989 (1)	C(2)–C(3)	1.389 (8)
Fe–N(10)	3.304 (1)	C(2)–C(6)	1.411 (8)
N(1)–C(2)	1.379 (3)	C(3)–C(4)	1.382 (8)
N(1)–C(5)	1.347 (3)	C(4)–C(5)	1.387 (8)
N(7)–C(6)	1.288 (4)	C(8)–C(9)	1.524 (8)
N(7)–C(8)	1.463 (4)		

Table III. Bond Angles (deg) for [Fe((pyrol)$_3$tren)]

N(1)–Fe–N(7)[a]	81.06 (3)	Fe–N(7)–C(6)	113.9 (1)
N(1)–Fe–N(10)	122.95 (3)	Fe–N(7)–C(8)	125.2 (1)
N(7)–Fe–N(10)	60.55 (3)	C(6)–N(7)–C(8)	120.9 (1)
N(1)–Fe–N(1)	93.22 (3)	N(1)–C(2)–C(3)	109.1 (1)
N(7)–Fe–N(7)	97.89 (3)	N(1)–C(2)–C(6)	113.3 (1)
N(1)–Fe–N(7)[b]	87.87 (3)	C(3)–C(2)–C(6)	137.6 (1)
N(1)–Fe–N(7)[c]	174.23 (3)	C(2)–C(3)–C(4)	107.0 (1)
Fe–N(1)–C(2)	114.27 (4)	C(3)–C(4)–C(5)	106.9 (1)
Fe–N(1)–C(5)	138.85 (4)	N(1)–C(5)–C(4)	110.2 (1)
C(2)–N(1)–C(5)	107.87 (8)	N(7)–C(8)–C(9)	110.9 (1)
C(9)–N(10)–C(9)	119.48 (8)	N(10)–C(9)–C(8)	113.5 (1)

[a] Within the same ligand arm. [b] Adjacent ligand arms. [c] N(1), N(7) opposite.

the remaining hydrogen atoms, which were included for three cycles of refinement and subsequently held fixed. The model converged with $R = 2.5\%$ and $R_w = 2.9\%$. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 3.5\%$; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed structure factors are available.[20] The principal programs used are as described previously.[21]

Results and Discussion

Final positional and thermal parameters for [Fe(pyrol)$_3$tren)] are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 is the stereoscopic pair view of the molecule.

Although the ligand is potentially a heptadentate, the complex contains six strong iron–nitrogen bonds, while the distance between the metal atom and the apical nitrogen N(10), the potential seventh donor, is 3.304 (1) Å, which is greater than the van der Waals contact distance. The crystallographic symmetry imposes a precise threefold axis (C_3) on the molecule through the iron atom and the apical nitrogen N(10). This symmetry essentially reduces the structure determination to an 11-atom problem, not counting hydrogens. The ligand environment about the metal is a trigonally distorted octahedron, with three upper (pointing toward N(10)) Fe–N bonds of 1.989 (1) Å and three lower Fe–N bonds of 1.936 (1) Å.

The nearest related structure is that of the iron(II) complex [Fe((py)$_3$tren)](BF$_4$)$_2$ which has six nearly equal Fe–N distances: Fe–imine nitrogen, all 1.95 Å; Fe–pyridine nitrogen, 1.96, 1.97, 1.98 Å.[22] The distance from the iron atom to the apical tertiary amine nitrogen (3.44 Å) is significantly greater than in [Fe((pyrol)$_3$tren)] (3.304 (1) Å). The pseudooctahedral coordination polyhedron in [Fe((pyrol)$_3$tren)] is twisted 5.6° from a trigonal antiprism (octahedral) toward a trigonal

Table IV. Average Metal–Ligand Distances in Related Hexadentate Complexes

	⟨M–O⟩, Å	⟨M–N⟩, Å	⟨M–lig⟩, Å	Ref
$[Ni(sal)_2trien]\cdot 6H_2O$	2.038	2.094	2.075	24
$[Fe(acacCl)_2trien]PF_6$	1.908	2.135	2.059 (7)	2
$[Fe(acac)_2trien]PF_6$	1.930	2.136	2.068 (3)	2
$[Fe(sal)_2trien]NO_3\cdot H_2O$	1.882	1.966	1.939 (2)	2
$[Fe(sal)_2trien]Cl\cdot 2H_2O$	1.884	1.968	1.940 (2)	2
$[Fe((py)_3tren)](BF_4)_2$		1.96	1.96 (1)	22
$[Fe((pyrol)_3tren)]$		1.963	1.963 (1)	

prism; this compares with a twist of 6° in $[Fe((py)_3tren)](BF_4)_2$.

A further distortion of the complex is a flattening perpendicular to the threefold axis which is more pronounced at the upper end near the apical nitrogen (N(7)–Fe–N(7) = 97.9°) than at the lower end (N(1)–Fe–N(1) = 93.2°). This type of flattening is precisely what would be required if the apical nitrogen, N(10), were coordinated to the iron atom. However, the Fe–N(10) distance is too great to correspond to contact between the atoms. The van der Waals radius is 1.55 Å for N,[23] and the value for Ni of 1.63 Å[23] can be taken as an upper limit for Fe: comparison of metal–ligand bond lengths of nickel and iron complexes with identical ligand environments (Table IV) indicates a shortening of 0.015 and 0.14 Å, respectively, for high- and low-spin iron(III) compared to the nickel(II) values. Thus, the Fe–N(10) distance of 3.304 (1) Å appears to be significantly greater than the sum of the van der Waals radii. The Fe–N(10) interaction is very weak and cannot be called a bond. It is likely that similar reasoning applies to $[Fe((sal)_3tren)]$ (where salicylaldehyde replaces pyrrole-2-carboxaldehyde) in which such seven-coordination had been suggested.[25] At high pressures, seven-coordination may be favored in these complexes and this possibility is being studied via infrared spectroscopy.

The comparison with literature data on ring substitution close to the ligand donor atoms can raise low-spin complexes to high-spin complexes or to intermediate spin-state equilibria;[26–31] for example, tris(phenanthroline)- and bis(terpyridyl)iron(II) and -iron(III) complexes are low spin, but the substituted 5-chlorophenanthroline, 5-methylphenanthroline, 2-(2′-pyridyl)quinoline and dibenzoterpyridyl produce high-spin states. The same effect is produced by steric hindrance adjacent to the imine nitrogen of pyridinedicarboxaldimine complexes. Therefore ring substitution at one, two, or three of the pyrroles adjacent to the pyrrole nitrogen atom would be expected to produce spin-state crossovers in high-spin systems by lengthening the metal–nitrogen bond due to steric hindrance. Weakening of the ligand field by substitutions at other positions of the pyrrole ring may produce similar effects. Complexes of such ligands are currently under investigation, and the present complex will serve as a model for the low-spin extreme.

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Registry No. Fe((pyrol)$_3$tren), 65878-96-8; tren, 4097-89-6; pyrrole-2-carboxaldehyde, 1003-29-8.

Supplementary Material Available: A listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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