Table I. Positional Parameters of Norrufescine Non-H Atoms ($\times 10^4$)[a]

	x	y	z
C(1)	3971 (6)	5938 (12)	2172 (8)
C(2)	3757 (6)	6939 (13)	2578 (9)
C(3)	3298 (5)	6518 (11)	2669 (8)
C(4)	3037 (5)	5026 (12)	2355 (8)
C(5)	3232 (5)	4021 (10)	1943 (7)
C(6)	3695 (5)	4455 (10)	1843 (7)
C(7)	3805 (5)	3142 (11)	1378 (7)
C(8)	3391 (5)	1965 (10)	1197 (7)
C(9)	3045 (5)	2456 (10)	1528 (6)
C(10)	2500 (5)	90 (12)	949 (7)
C(11)	2854 (6)	−407 (12)	633 (8)
C(12)	3323 (5)	507 (11)	761 (7)
C(13)	3727 (6)	225 (11)	494 (7)
C(14)	4151 (6)	1332 (12)	678 (7)
C(15)	4160 (5)	2851 (11)	1083 (7)
C(16)	4535 (8)	4613 (19)	404 (11)
C(17)	5138 (7)	368 (20)	1317 (10)
C(18)	3617 (7)	−1404 (12)	−839 (8)
N(1)	2598 (4)	1565 (8)	1402 (6)
O(1)	3135 (4)	7558 (8)	3087 (6)
O(2)	3706 (4)	−1244 (7)	131 (6)
O(3)	4551 (4)	1016 (8)	453 (5)
O(4)	4610 (4)	3895 (9)	1283 (5)

[a] The positional parameters are expressed as fractions of a unit cell edge. Standard deviations as determined from the variance-covariance matrix of the final cycle of least-squares refinement are given in parentheses and refer to the least significant digits of their corresponding parameters.

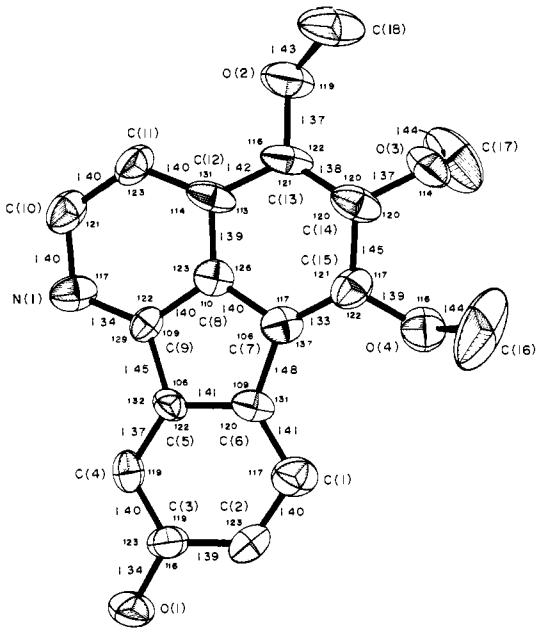

Figure 1. An ORTEP drawing illustrating the molecular structure of norrufescine together with the bond distances (Å) and bond angles (degrees) found in the crystal structure. The average standard deviations of these quantities are 0.01 Å and 0.9°, respectively. Hydrogen atoms have been omitted from the drawing.

verged at a final value of $R = 0.109$ based on the 1175 observed unique reflections. The position of the highest peak in the final difference Fourier map, which had a height of 0.49 e/Å^3, made no chemical sense.

Table I lists the final positional parameters of the non-H atoms. The molecular configuration of norrufescine in the crystal structure is illustrated in Figure 1 together with the atomic numbering scheme used in this report and the covalent bond angles and distances involving non-H atoms found in the structure.

It can be seen in Figure 1 that the phenolic hydroxyl group is substituent to atom C(3). The bond lengths and angles in norrufescine are identical to within experimental error with the corresponding quantities in fluoranthene.[7] There are no unusual bond lengths in the structure. However some angle strain is apparent, especially in the isoquinoline portion of the molecule. Similar angle strain in naphthalene groups attached to five-membered rings has been observed in the crystal structures of acenaphthalene,[8] the cis dimer of acenaphthalene[9] and fluoranthene.[7] Norrufescine, like fluoranthene, is a highly planar molecule. The root-mean-square deviation of the 16 ring atoms of norrufescine from their least-squares plane is 0.03 Å.

An intermolecular O—H···N hydrogen bond of length 2.71 Å is formed between the hydroxyl group and the nitrogen atom of a molecule related to that tabulated in Table I by a twofold rotation axis. There are no other intermolecular contacts in the structure that are less than their minimal van der Waals contact distances.

Acknowledgment. This study was supported, in part, by the National Science Foundation, MRL program, under Grant No. DMR76-00678.

Supplementary Material Available: Listings for norrufescine of the anisotropic thermal parameters for non-H atoms and the positional and thermal parameters for H atoms (2 pages). Ordering information is given on any current masthead.

References and Notes

(1) M. P. Cava, K. T. Buck, I. Noguchi, M. Srinivasan, M. G. Rao, and A. I. Da Rocha, *Tetrahedron*, **31**, 1667 (1975).
(2) M. P. Cava, K. T. Buck, and A. I. DaRocha, *J. Am. Chem. Soc.*, **94**, 5931 (1972).
(3) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination", Macmillan, New York, N.Y., 1968, pp 456–458.
(4) P. Main, M. M. Woolfson, and G. Germain, "MULTAN, A Computer Program for the Automatic Solution of Crystal Structures", Department of Physics, University of York, York, England, 1971.
(5) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(7) F. H. Herbstein and M. Kaftory, *Acta Crystallogr., Sect. B*, **31**, 60 (1975).
(8) H. W. W. Erlich, *Acta Crystallogr.*, **10**, 699 (1957).
(9) T. R. Welberry, *Acta Crystallogr., Sect. B*, **27**, 360 (1971).

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Megalomicins. 6.[1] Tertiary Glycosidic Macrolide Antibiotics. A Structural Revision by Carbon-13 Nuclear Magnetic Resonance and X-Ray Crystallography

Sir:

Independent studies on the megalomicins[1-3] and on the XK-41 complex[4] have led to the assignment of structures for megalomicin A (XK-41-C) (**1**), megalomicin B (XK-41-B_1) (**2**), megalomicin C_1 (XK-41-A_2) (**3**), megalomicin C_2 (XK-41-A_1) (**4**), and XK-41-B_2 (**5**). The novel amino sugar present in these antibiotics was thought to be D-rhodosamine.[5,6] Subsequently the ^{13}C NMR data for megalomicin A (**1**) were published[7] and several anomalies, namely the chemical shifts of C_{12} (δ_c 80.8) and $C_{1''}$ (δ_c 90.8),[8] as well as $C_{2'''}$ (δ_c 37.6), $C_{5'''}$ (δ_c 67.7), $C_{3'''}$ CH_3 (δ_c 19.2),[9] $C_{3''}$ (δ_c 66.0), and $C_{5''}$ (δ_c 59.9) were apparent to us.

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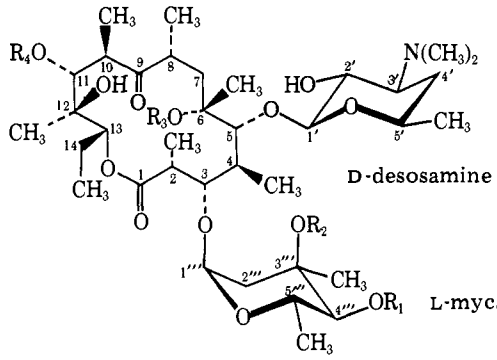
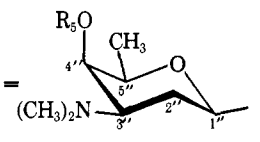


original structure

1, $R_1 = R_2 = R_3 = R_5 = H$
2, $R_1 = COCH_3$; $R_2 = R_3 = R_5 = H$
3, $R_1 = R_2 = COCH_3$; $R_3 = R_5 = H$
4, $R_1 = COCH_2CH_3$; $R_2 = COCH_3$; $R_3 = R_5 = H$
5, $R_1 = COCH_2CH_3$; $R_2 = R_3 = R_5 = H$

$R_4 =$

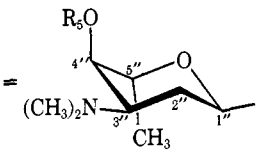


D-rhodosamine

revised structure

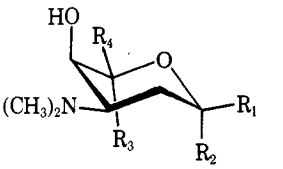
1, $R_1 = R_2 = R_4 = R_5 = H$
2, $R_1 = COCH_3$; $R_2 = R_4 = R_5 = H$
3, $R_1 = R_2 = COCH_3$; $R_4 = R_5 = H$
4, $R_1 = COCH_2CH_3$; $R_2 = COCH_3$; $R_4 = R_5 = H$
5, $R_1 = COCH_2CH_3$; $R_2 = R_4 = R_5 = H$
10, $R_1 = R_2 = R_4 = H$; $R_5 = COC_6H_4I$

$R_3 =$



L-megosamine

A tertiary glycosidic linkage of rhodosamine appeared reasonable in megalomicin A (**1**) in view of the shielding of $C_{1''}$[10,11] and of the 6-methyl group,[7,12,13] but could not be accommodated at C_6 if the original mass spectral data[1] and hydrogen bonding proposals involving the 6-hydroxy and 9-carbonyl groups[7] were correct. An axial linkage for the glycoside was also impossible from rotational considerations[2,3] and was in disagreement with the $J_{^{13}C\text{-}^{1}H}$ coupling constant (158 Hz) that we measured for $C_{1''}$ of **2**.[14-16] It was also biogenetically unacceptable for a D sugar.[17]



6, $R_1 = R_3 = H$; $R_2 = OCH_3$; $R_4 = CH_3$
7, $R_1 = OCH_3$; $R_2 = R_3 = H$; $R_4 = CH_3$
8, $R_1 = OCH_3$; $R_2 = R_4 = H$; $R_3 = CH_3$
9, $R_1 = R_4 = H$; $R_2 = OCH_3$; $R_3 = CH_3$

Spectral data for methyl α- (**6**) and β-D-rhodosaminide (**7**), synthesized by unambiguous routes from 2-deoxy-D-glucose,[18] failed to suggest a satisfactory alternative structure for **1**. Direct comparison of the ^1H and ^{13}C NMR spectral data for **6** and **7** with sugars **8** and **9** isolated from megalomicin A showed that they were not identical. An x-ray study was therefore undertaken on 4″-*O*-(4-iodobenzoyl)megalomicin A (**10**), synthesized from megalomicin A (**1**) by controlled acylation.[18] Acceptable crystals of a dihydrate of **10** were obtained from aqueous acetone. A crystal approximately 0.15 × 0.08 × 0.09 mm was mounted in a glass capillary tube with epoxy resin. The space group was found to be $P2_12_12_1$ by a combination of film and counter methods. The cell constants were found using 16 reflections on a Syntex $P2_1$, four-circle diffractometer (Cu Kα, λ = 1.54178 Å, and Ni filter) to be a = 12.699 (2), b = 19.501 (6), and c = 25.741 (9) Å. The crystal density was measured by flotation in KI as 1.181 (4) mg/mL in excellent agreement with a calculated density of 1.179 mg/mL assuming four molecules in the unit cell. Intensity data were collected using a scintillation counter with pulse-height discrimination, a θ-2θ scan technique, 1°/min scan rate, and four reflections measured every 100 to monitor the extent of crystal decomposition and movement. The extent of decomposition after 8 days of data collection was 35%. Of 3762 reflections gathered, with $\theta \leq 50°$, 1812 (with $I \geq 2.5\sigma$) were considered significantly greater than background. All data were corrected for Lorentz, polarization, decomposition, and absorption. The structure was solved by the heavy-atom technique. A Patterson calculation revealed the position of 12 atoms of the remaining molecule. Inclusion of these additional atoms in a second Fourier calculation led to the position of all

Table I. ^{13}C Chemical Shifts[a]

Carbon	1	Carbon	1	6	7	8	9
C_1	175.5 (s)	$C_{1'}$	104.5 (d)				
C_2	44.8 (d)	$C_{2'}$	71.2 (d)				
C_3	85.1 (d)	$C_{3'}$	65.4 (d)				
C_4	37.2 (d)	$C_{4'}$	28.6 (t)				
C_5	82.9 (d)	$C_{5'}$	69.2 (d)				
C_6	80.4 (s)	$C_{6'}$	21.5 (q)				
C_7	38.8 (t)	3′-$N(CH_3)_2$	40.2 (q)				
C_8	45.8 (d)	$C_{1''}$	90.4 (d)	98.1	101.6	98.2	99.3
C_9	221.3 (s)	$C_{2''}$	27.9 (t)	28.5	30.7	28.8	28.9
C_{10}	37.7 (d)	$C_{3''}$	59.5 (d)	59.8	64.3	60.0	56.0
C_{11}	68.8 (d)	$C_{4''}$	73.5 (d)	66.1	65.8	70.8	67.6
C_{12}	74.4 (s)	$C_{5''}$	67.3 (d)	65.2	71.5	68.6	72.9
C_{13}	76.6 (d)	$C_{6''}$	18.4 (q)	17.1	17.0	18.6	19.7
C_{14}	21.2 (t)	3″-$N(CH_3)_2$	42.5 (q)	42.1	42.4	42.9	42.4
2-CH_3	18.8 (q)	OCH_3		54.7	56.2	55.2	55.2
4-CH_3	9.5 (q)	$C_{1'''}$	98.5 (d)				
6-CH_3	16.5 (q)	$C_{2'''}$	41.0 (t)				
8-CH_3	15.1 (q)	$C_{3'''}$	69.7 (s)				
10-CH_3	12.3 (q)	$C_{4'''}$	77.0 (d)				
12-CH_3	16.3 (q)	$C_{5'''}$	65.5 (d)				
14-CH_3	10.4 (q)	$C_{6'''}$	18.6 (q)				
		3‴-CH_3	25.7 (q)				

[a] Parts per million downfield from $(CH_3)_4Si$ in $CDCl_3$. The symbols in parentheses represent the multiplicities of the signals obtained in the single-frequency off-resonance decoupled spectrum.

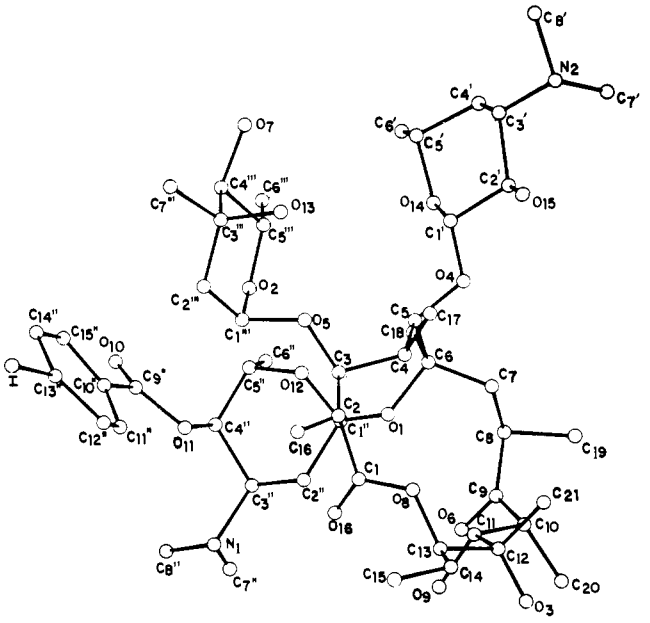


Figure 1. X-ray crystal structure of **10**. The hydrogen atoms are omitted.

but two of the remaining atoms. A difference Fourier revealed the positions of these two carbon atoms. Block-diagonal least-squares refinements with first isotropic and unit weights then anisotropic refinement $w = 1/\sigma^2$ were used. The final discrepancy factors are $R = 0.0949$ and $R_w = 0.1029$ where $R = \Sigma||F_o| - |F_c||/\Sigma F_o$ and $R_w = [(\Sigma w||F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ and where

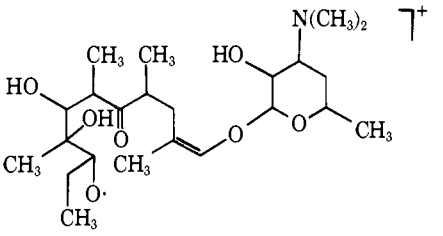
$$w = 1/\sigma^2$$

The x-ray crystal structure of **10** (Figure 1) indicated that the absolute stereochemistry at $C_{5''}$ was L and not D as originally deduced. It is therefore proposed that this sugar be renamed L-megosamine (2,3,6-trideoxy-3-(dimethylamino)-L-*ribo*-hexose). The x-ray study also revealed that the L-megosamine was glycosidically attached to the tertiary 6-hydroxyl group. With these important data it was possible to clarify the ^{13}C NMR anomalies and to explain why the original conclusions had led to the incorrect structure.

The original ^1H NMR assignments (60 MHz)[5,6] for **8** and **9** were confirmed by double resonance experiments at 100 MHz. The small $J_{4,5}$ coupling was consistent with both the original and the revised structures. The observed coupling constants and CD data in TACu ((tetraamino)copper sulfate) solution, clearly supported a $^4C_1$ conformation for **8** and possibly a somewhat flattened $^4C_1$ conformation for **9**, owing to steric repulsion between the axial 5-methyl and 1-methoxy groups in the latter. The chemical shifts (Table I) of C_1 and C_3 in both anomers **8** and **9** indicate that the C_5 axial substituents shielding effect is similar to that of an axially oriented substituent at C_1 or at C_3. In megalomicin A (**1**) the anomeric carbon of L-megosamine is further shielded to δ_c 90.4 owing to the glycosidic attachment to the tertiary 6-hydroxyl group.

In **1** the 6-methyl group is shielded to δ_c 16.5. This upfield shift ($\Delta\delta_c$ − 10.3), relative to erythromycin A, is greater than would be expected simply from glycosylation of the tertiary 6-hydroxyl group. The x-ray study indicates that the 6-*O*-glycoside assumes a more quasi-equatorial orientation thus forcing the 6-methyl group to assume a quasi-axial orientation which would help to account for the additional upfield shift of this methyl group. Owing to the presence of the glycoside, C_6 occurs at δ_c 80.4 in **1** relative to δ_c 74.9 in erythromycin A. The unusual downfield shift of the 9-ketone carbon in erythromycin A (δ_c 221.3) has been attributed specifically to hydrogen bonding between the 6-hydroxyl group and the ketone.[7] In **1** where the 6-hydroxyl group is glycosylated the 9-ketone carbon still appears at δ_c 221.3, clearly indicating that the 9-ketone is still hydrogen bonded. The x-ray data revealed that this hydrogen bond was formed from the 11-hydroxyl group.

The failure of the secondary 11-hydroxyl group to undergo acylation under forcing conditions was originally viewed as evidence for the location of the L-megosamine at that position.[2,3] It is now apparent from models of the revised structure that the 11-hydroxyl group is extremely hindered and would not be readily acylated. The only significant mass spectral fragment affected by the revised structure is hh. However, by



hh

invoking an initial loss of L-megosamine accompanied by cleavage of C_4–C_5 and the lactone group, a reasonable alternative structure may be written for the ion hh which has the correct composition.[1]

The absolute stereochemistry at C_5 of megosamine was originally deduced as D from the sign of the CD extremum of a 4-ketopyranoside degradation product.[5,6] This was obviously incorrect based on the x-ray study and consequently a series of model 4-ketopyrans and 4-ketopyranosides were synthesized by unambiguous routes and their CD spectra were recorded.[18] The data indicated that these 4-ketones do not obey the octant rule, presumably owing to the presence of the pyran oxygen, but instead constitute further examples of a small group of ketones that exhibit anti-octant behavior.[19] Chemical proof of the structure of L-megosamine was obtained by synthesis of both anomers.[18] Full details of this work will be described.[18]

References and Notes

(1) Part 5: R. S. Jaret, A. K. Mallams, and H. F. Vernay, *J. Chem. Soc., Perkin Trans. 1*, 1389 (1973).
(2) A. K. Mallams, R. S. Jaret, and H. Reimann, *J. Am. Chem. Soc.*, **91**, 7506 (1969).
(3) R. S. Jaret, A. K. Mallams, and H. Reimann, *J. Chem. Soc., Perkin Trans. 1*, 1374 (1973).
(4) R. S. Egan, S. L. Mueller, L. A. Mitscher, I. Kawamoto, R. Okachi, H. Kato, S. Yamamoto, S. Takasawa, and T. Nara, *J. Antibiot.*, **27**, 544 (1974).
(5) A. K. Mallams, *J. Am. Chem. Soc.*, **91**, 7505 (1969).
(6) A. K. Mallams, *J. Chem. Soc., Perkin Trans. 1*, 1369 (1973).
(7) J. G. Nourse and J. D. Roberts, *J. Am. Chem. Soc.*, **97**, 4584 (1975). It should be noted that these assignments were made without access to any of the megalomicin degradation products and were interpreted with reference to an erroneous structure.
(8) To conform with current macrolide antibiotic nomenclature practices, (*R*)-*O*-glycosides are given precedence over (*S*)-*O*-glycosides, thus establishing the precedent desosamine (′), megosamine (″), and mycarose (‴).
(9) S. Omura, A. Nakagawa, A. Neszmelyi, S. D. Gero, A.-M. Sepulchre, F. Piriou, and G. Lukacs, *J. Am. Chem. Soc.*, **97**, 4001 (1975).
(10) A. Allerhand and D. Doddrell, *J. Am. Chem. Soc.*, **93**, 2777 (1971).
(11) W. W. Binkley, D. Horton, N. S. Bhacca, and J. D. Wander, *Carbohydr. Res.*, **23**, 301 (1972).
(12) Y. Terui, K. Tori, K. Nagashima, and N. Tsuji, *Tetrahedron Lett.*, 2583 (1975).
(13) S. Omura, A. Neszmelyi, M. Sangare, and G. Lukacs, *Tetrahedron Lett.*, 2939 (1975).
(14) K. Bock, I. Lundt, and C. Pedersen, *Tetrahedron Lett.*, 1037 (1973).
(15) K. Bock and C. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, 293 (1974).
(16) Kindly supplied to one of us (G.L.) by Dr. T. Nara, Kyowa Hakko Kogyo Co., Ltd.
(17) H. Grisebach, "Biosynthetic Patterns in Microorganisms and Higher Plants", Wiley, New York, N.Y., 1967.

(18) Full details will be described in G. Lukacs et al., *J. Chem. Soc., Perkin Trans. 1*, in press.
(19) L. Bartlett, D. N. Kirk, W. Klyne, R. S. Wallis, H. Erdtman, and S. Thoren, *J. Chem. Soc. C*, 2678 (1970).

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Molecular Structure of Diaquo-α,β,γ,δ-tetraphenylporphinatoiron(III) Perchlorate and Perchlorato-α,β,γ,δ-tetraphenylporphinatoiron(III). Two New Structural Types for Iron(III) Porphyrins

Sir:

The stereochemistry of heme centers is justly deemed significant in understanding the function and mechanism of heme proteins.[1] We wish to report the molecular structures of two new iron(III) porphyrins with weak-field axial ligands which demonstrate that iron(III) prophyrins display greater structural diversity than has generally been recognized and point out that there are potential difficulties in assigning stereochemistry from magnetic properties. The two iron(III) porphyrins are a five-coordinate derivative, perchlorato-α,β,γ,δ-tetraphenylporphinatoiron(III), FeTPP($OClO_3$), and a six-coordinate derivative, diaquo-α,β,γ,δ-tetraphenylporphinatoiron(III) perchlorate, $[FeTPP(OH_2)_2]^+ClO_4^-$.

FeTPP($OClO_3$) is conveniently prepared by the reaction of FeTPPCl with $AgClO_4$ in dry THF.[2,3] $[FeTPP(OH_2)_2]^+$ was obtained by recrystallization of FeTPP($OClO_3$) from THF in the presence of aqueous perchloric acid.

FeTPP($OClO_3$) has an unusual effective magnetic moment of 5.0 μ_B at room temperature, decreasing linearly with temperature (to 4.1 μ_B at 40 K). Its Curie-Weiss behavior to 4.2 K (Weiss constant = −5 K), together with the Mössbauer observation[4] of a single compound over the range of 4.2–298 K, rules out the existence of a spin state equilibrium. The similarity of the Mossbauer spectrum[4] to its reported OEP analogue[5,6] suggests that FeTPP($OClO_3$) has either an S = ⅜ ground state with a large orbital contribution to its magnetic moment[7] or a quantum mechanically mixed spin state arising from S = ⅜ and S = ⅝ spin states.[9] $[FeTPP(OH_2)_2]^+$ has a magnetic susceptibility of 5.5 μ_B which is independent of temperature over the range of 77–297 K.[10] Although the magnetic moment is apparently too low for a high-spin complex, electron spin resonance measurements (powder sample from crushed single crystals, 77 K) show an axial spectrum with a strong feature at g = 6, which is typical of high-spin iron(III) porphyrins. Remaining ambiguities in the spin state assignment of these complexes are expected to be resolved by detailed Mossbauer, ESR, and magnetic susceptibility measurements in progress.

Crystal data and refinement results are as follows: $Fe(N_4C_{44}H_{28})(ClO_4)\cdot\frac{1}{2}C_8H_{10}$; monoclinic, a = 14.705 (2), b = 15.487 (3), c = 17.470 (3) Å; β = 95.17 (1)°; space group $P2_1/n$; Z = 4; ρ_{calcd} = 1.37, ρ_{obsd} = 1.37 g/cm³; R_1 = 0.074, R_2 = 0.077;[11] 5124 unique observed data ($F_o > 3\sigma(F_o)$, $2\theta <$ 55°). $Fe(N_4C_{44}H_{28})(OH_2)_2ClO_4\cdot 2C_4H_8O$: orthorhombic, a = 16.772 (2), b = 12.823 (2), and c = 21.301 (2) Å; space group $Pbcn$; Z = 4; ρ_{calcd} = 1.38, ρ_{obsd} = 1.39 g/cm³; R_1 = 0.063, R_2 = 0.062; 3730 unique observed data ($F_o > 3\sigma(F_o)$, $2\theta < 63.7°$). Intensity data were collected on a Syntex $P\bar{1}$ diffractometer with graphite-monochromated Mo Kα radiation using θ–2θ scanning.

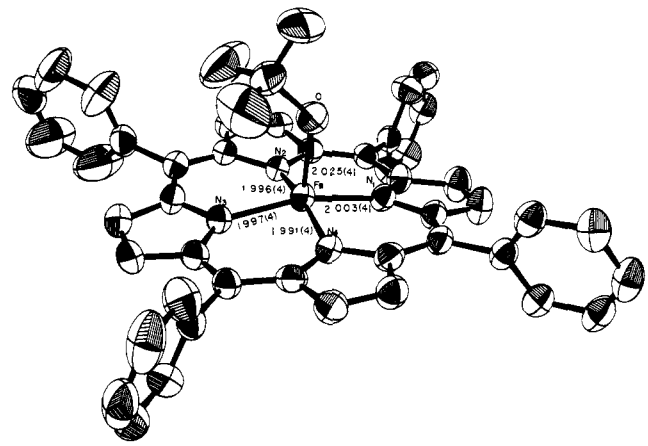

Figure 1. A perspective view of the FeTPP($OClO_3$) molecule. The individual values of the bond distances in the coordination group are displayed.

The molecular stereochemistry and bond parameters of the coordination group of FeTPP($OClO_3$) are displayed in Figure 1. Although the complex is clearly five coordinate, the parameters of the coordination group do not conform to those expected[12,13] for high-spin five-coordinate iron(III) porphyrins. Thus the average Fe–N bond distance (1.997 (5) Å) is considerably shorter than the 2.065-Å value typical of high-spin derivatives, such as chlorohemin[14] and the methoxyiron(III) derivative of mesoporphyrin IX dimethyl ester.[15] Rather, the Fe–N bond distance is only slightly longer than the 1.990-Å value typical of *low-spin* six-coordinate iron(III) porphyrins.[16] A second important distinction is found in the displacement of the iron(III) atom. In FeTPP($OClO_3$), the iron(III) atom is displaced by only 0.27 Å out of the plane defined by the four porphinato nitrogen atoms and 0.30 Å out of the mean plane of the 24-atom core. The usual displacement is ~0.5 Å in the five-coordinate high-spin iron(III) derivatives.[12,13] Since the large displacement of the iron(III) atom and the long Fe–N bonds in the high-spin iron(III) porphyrins are generally associated with the occupancy of the $3d_{x^2-y^2}$ orbital, the structural parameters of FeTPP($OClO_3$) are consistent with an iron(III) atom in which the $3d_{x^2-y^2}$ orbital is either unoccupied or partially occupied; namely an intermediate spin (S = ⅜) or a quantum mechanically mixed (S = ⅜, ⅝) spin state. Indeed, the similarity of the porphinato coordination parameters with those of five-coordinate high-spin d^4 manganese(III) porphyrins,[17] in which the $3d_{x^2-y^2}$ orbital is safely presumed to be unoccupied,[18] is noteworthy. The short Fe–N bond distances in FeTPP($OClO_3$) are achieved by a quasi-D_{2d} ruffling of the porphinato core. The axial Fe–O distance of 2.025 (4) Å is the shortest known metal to perchlorate oxygen distance,[19] but short axial bond distances appear to be a usual feature of five-coordinate iron(III) porphyrins.[12,13]

An overall view of the $[FeTPP(OH_2)_2]ClO_4\cdot 2THF$ molecule is given in Figure 2. The iron(III) atom is located at a crystallographic inversion center and thus the $[FeTPP(OH_2)_2]^+$ ion has required C_i–$\bar{1}$ symmetry with the iron(III) atom precisely centered in the plane of the porphinato ligand. An in-plane position of the iron(III) atom in porphinato complexes has been demonstrated previously only for *low-spin*

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