Porphyrins. XXIX. The Crystal and Molecular Structure and Luminescence of Bis(dimethylamine)etio(I)porphinatorhodium(III) Chloride Dihydrate[1]

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Abstract: A luminescing rhodium(III) etioporphyrin has been synthesized. Single crystal X-ray diffraction identified the compound as bis(dimethylamine)etio(I)porphinatorhodium(III) chloride dihydrate, $RhC_{36}N_6H_{50}Cl \cdot 2H_2O$. The compound crystallizes in the monoclinic space group $P2/n$ with unit cell dimensions $a = 14.446$ (6) Å, $b = 10.943$ (7) Å, $c = 12.319$ (6) Å, and $\beta = 105.68$ (1)°; the density is 1.32 g/cm³ for $Z = 2$. The structure was solved from 2158 observed reflections using conventional heavy-atom Patterson techniques; the light atoms were located from Fourier and ΔF syntheses; the final $R = 0.068$. The octahedrally coordinated rhodium atom is in the plane of a planar porphyrin ring. The average Rh–ring nitrogen distance is 2.038 (6) Å and the Rh–amine nitrogen distance is 2.090 (8) Å. The crystal packing, unique for porphyrins, is dominated by hydrogen-bonded chains between the amine hydrogen and the chloride ion. The luminescence in solution is characterized by a room temperature fluorescence quantum yield, $\phi_f \sim 2 \times 10^{-4}$, and a liquid nitrogen temperature phosphorescence quantum yield, $\phi_p = 0.23$, and lifetime, $\tau_p = 0.73$ (2) msec.

The study of bis(dimethylamine)etio(I)porphinatorhodium(III) chloride dihydrate was undertaken as part of a larger effort to understand the electronic structure of heme. Iron porphyrin in the form of heme plays key enzymatic roles during which the metal electronic configuration changes from d^6 to d^5 and possibly even to d^4. The way such changes occur is determined by the energy of the low lying electronic states and their modification by various local environments created by the protein in which the heme is embedded. We have approached this problem through the study of the luminescence of related metal porphyrins[3] and through the study by the extended Hückel model of iron porphyrin itself.[4] A major theoretical question is the relation of the metal d and porphyrin π electrons: in particular what are the relative energies of dd, $d\pi^*$, πd, and $\pi\pi^*$ excited states. To answer this question it is helpful to identify these states in porphyrins containing other central metals.

In the course of our general studies in this area the following contradiction came to light. It was established that Co(III), Co(II), and Ni(II) (d^6, d^7, d^8, respectively) show no luminescence,[5a] and it was postulated that this is due to the presence of dd transitions lying between the porphyrin $\pi\pi^*$ triplet and the ground state. Surprisingly, Pd(II) and Pt(II) porphyrins, which are d^8, phosphoresce strongly suggesting a far larger dd energy gap. The question arose whether a similarly large gap would occur in Rh(III) porphyrin, which is d^6. To answer this question the synthesis reported here was undertaken. It was indeed found that the molecule does phosphoresce and, like Pd(II) porphyrin,[5b] even shows a weak fluorescence. In the course of the chemical preparation it was found that the molecule forms crystals suitable for X-ray study. In view of the fact that the detailed geometry around the metal must be known if the dd energy gap is to be theoretically calculated accurately, the X-ray structure reported below was undertaken.

Synthesis of the Rhodium Etioporphyrin. The synthesis essentially follows Adler's general method for the preparation of metalloporphyrins in dimethylformamide[6a] (DMF). Free base etioporphyrin(I) was added to a heated solution of $RhCl_3$ (hydrated) in DMF. (Our first run was successful using a rhodium salt of indeterminable age from a vial labeled $RhCl_3$ (anhydrous). Later attempts to repeat the synthesis using fresh $RhCl_3$ (anhydrous) failed.) The reaction mixture was refluxed until no further conversion of the free base to the metalloporphyrin could be detected (~18 hr). Reaction progress was monitored by visible absorption spectra of aliquots extracted from the reaction pot at periodic intervals. Conversion to the rhodium porphyrin was ~80%. The product proved to be water soluble; thus addition of water to the reaction mixture did not induce the expected precipitation of the metalloporphyrin. The DMF–H_2O solution was filtered (removal of unreacted H_2Etio) and the solvent removed by rotary evaporation. The dark brown residue was dried, added to a dry silica gel chromatographic column, and eluted with chloroform until the bands were well resolved. The dark orange rhodium porphyrin layer was cut out of the column and eluted from the silica gel with methanol.

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[1] (a) Presented in part at the IXth International Congress of Crystallography, Kyoto, Japan, 1972. (b) Paper XXVIII: A. M. Schaffer, M. Gouterman, and E. R. Davidson, *Theor. Chim. Acta*, in press.

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[3] M. Gouterman, "Symposium on Excited States of Matter," Lubbock, Texas, April 1971, C. W. Shoppee, Ed., Texas Technical University Press, Lubbock, Texas, 1972.

[4] Paper VIII: M. Zerner, M. Gouterman, and H. Kobayshi, *Theor. Chim. Acta*, **6**, 363 (1966).

[5] (a) Paper XVIII: D. Eastwood and M. Gouterman, *J. Mol. Spectrosc.*, **35**, 359 (1970). (b) Paper XXII: J. B. Callis, M. Gouterman, Y. M. Jones, and B. H. Henderson, *J. Mol. Spectrosc.*, **39**, 410 (1971).

[6] (a) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, 32, 2443 (1970). (b) Chemical analyses on metalloporphyrins are often quite inaccurate: D. Dolphin, private communication.

The purified porphyrin was crystallized from a methanol–chloroform solution. No free base or metalloporphyrin impurities could be detected in the electronic absorption, luminescence, and excitation spectra. The mass spectrum confirmed the compound as a rhodium porphyrin. Complete identification of the compound was elucidated from the crystal structure analysis. *Anal.* Calcd $C_{36}H_{50}N_6RhCl \cdot 2H_2O$: C, 58.5; N, 11.4; H, 7.1; Cl, 4.8. Found:[6b] C, 54.6; N, 11.8; H, 6.3; Cl, 7.2.

Crystallographic Data. Crystals of the rhodium porphyrin were grown by evaporation from a 1:1 chloroform–methanol solution. The material crystallized readily into dark brown platelets (red in transmitted light if thin enough). The high absorption coefficient of the material precluded the search for an optical extinction axis. Since the larger crystals tended to have broad, slightly split reflections, the intensity data were collected on a needle-shaped fragment with the approximate dimensions 0.10 × 0.25 × 0.60 mm. The crystal was mounted with the needle axis (($h0\bar{h}$ axis) along the spindle. The crystal form is monoclinic, with b along the shortest dimension for this particular crystal. The unit cell parameters (obtained from the least-squares refinement of the parameters derived from measurements with Mo Kα (λ 0.71069 Å) radiation of the 2θ values of 7 reflections) are a = 14.446 (6) Å, b = 10.943 (7) Å, c = 12.319 (6) Å, and β = 105.68 (1)°. These values along with ρ_m = 1.30 g cm^{-3} (ρ_c = 1.320 g cm^{-3}) give two molecules in the unit cell. The only systematic absences occurred in the $h0l$ net for $h + l = 2n + 1$. Thus the space group could be either Pn or $P2/n$. (The choice of a c glide would have required that β = 146°.)

Intensity data were collected to a 2θ limit of 50° with Mo Kα radiation on a four-circle automatic diffractometer using an $\omega - 2\theta$ scan with a constant scan rate of 2°/min and variable scan ranges.[7] The take-off angle of the X-ray tube was 3°. Backgrounds were measured by stationary counting at each limit of the scan: 4 sec for $2\theta < 20°$ and 10 sec for $2\theta \geq 20°$. Three standards were measured every 100 reflections throughout the period of data collection and they gave no indication of crystal deterioration. Of the 3465 reflections collected, 2158 were greater than $2\sigma_I$ and coded as observed. ($\sigma_I = [\sigma_c^2 + (0.01 \cdot \sigma_I^2)^2]^{1/2}$ where σ_c is determined from counting statistics and 0.01 is the instability factor.) Intensities were converted to structure factors in the usual way, including an analytically calculated absorption correction[8] (μ = 5.6 cm^{-1}).

Structure Solution and Refinement. The position of the rhodium atom was readily determined from an ordinary Patterson synthesis. Calculation of the structure factors with this one position using a B of 2 Å^2 for the rhodium and a scale of 1.0 for the F's gave 0.51 for the discrepancy index, $R = \Sigma_{hkl}||F_o| - |F_c||/\Sigma_{hkl}|F_o|$. Since all structural details except the porphinato core were unknown, the space group was initially taken to be Pn. Subsequent F_o syntheses located all the nonhydrogen atoms and permitted identification of the unknown portions of the structure. The R before refinement (omitting the waters) was 0.194.

Full matrix least-squares refinement[9] on scale, positional, and anisotropic thermal parameters in space group Pn converged to R = 0.100 and R_w = 0.091 ($R_w = \Sigma_{hkl}w(|F_o| - |F_c|)^2/\Sigma_{hkl}w|F_o|^2$, where $w = 1/\sigma_F^2$). Clearly, something was wrong. Calculated molecular parameters were disturbing if not impossible, especially the Rh–N bond lengths. The four Rh–N$_p$ (porphine) bonds varied from 1.88 (3) to 2.07 (3) Å; the two Rh–N$_a$ (amine) bonds were 1.80 (3) and 2.21 (2) Å, respectively. At this point we decided to change the space group to $P2/n$ for the following reasons: the correlation matrix terms representing the interaction between parameters which would be centrosymmetrically related in a centric cell were large; the rhodium atom was within 0.03 Å of a center of symmetry; the chloride ion was within 0.17 Å of a twofold axis; the light atom contents of the cell could readily assume the additional symmetry. As a starting set for further refinement, an idealized set of porphinato core coordinates[10] was used. All of the nonporphinato core light atoms were relocated by a ΔF synthesis calculated from the model coordinates. Refinement, again on all positional and isotropic thermal parameters, in $P2/n$, led to R = 0.088, R_w = 0.098, and significantly, but not sufficiently, improved the structure. The Rh–N$_p$ bond lengths still differed from one another by 7σ.

We decided to undertake further refinement using unit weights under the rationale that the contribution of the light atoms to the total structure would be enhanced relative to the rhodium contribution, thereby improving the light atom positions. Due to its special position in the unit cell, the Rh does not contribute to reflections with $h + l = 2n + 1$. Since these reflections are relatively weak, they contribute more to the least-squares residuals when unit weights are used. Indeed, more chemically reasonable light atom bond parameters were obtained with the use of unit weights. The final refinement cycle, in $P2/n$ using unit weights with the calculated positions of all hydrogen atoms added as fixed parameters, gave R = 0.068. The Rh–N$_p$ bond lengths were now within 3σ. The atomic thermal and positional parameters resulting from this refinement are listed in Table I. Table II lists the calculated hydrogen positions used in the refinement.

As an indication of the overall correctness of the structure, ΔF syntheses calculated before the final refinement cycles revealed all the hydrogens except those bonded to the amine nitrogen and to the terminal methyl carbons on the ring periphery. However, every ΔF synthesis calculated at each state of refine-

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[7] L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **17**, 1195 (1964).

[8] As described by N. W. Alcock in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 271.

[9] The following atomic form factors were used in the refinements: Rh(I) extrapolated from Rh(0) and Rh(III), and nitrogen from D. T. Cromer and J. T. Weber, *Acta Crystallogr.*, **18**, 104 (1965); chloride ion from H. Viervoll and O. Ogrim, *ibid.*, **2**, 277 (1949); carbon and oxygen from J. Berhuis, L. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veerendaal, *ibid.*, **8**, 478 (1955); hydrogen from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[10] The model coordinates used were those of the porphinato core of Sn^{IV}TPPCl$_2$: D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 6689 (1972). Sn^{IV}TPPCl$_2$ is the only porphyrin crystal study to date in which the molecule assumes D_{4h} symmetry. The model coordinates were oriented relative to the existing rhodium porphyrin core by least squares.

Table I. Positional and Thermal Parameters for $(DMA)_2Rh^{III}EtioCl \cdot 2H_2O$

Atom	Fractional coordinates[a]			Thermal parameters[b]					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0[c]	0[c]	0[c]	251 (4)[d]	618 (8)	708 (8)	−18 (8)	168 (4)	−146 (12)
N(1)	−1368 (5)	−291 (7)	131 (7)	29 (4)	75 (10)	86 (7)	−2 (4)	18 (4)	−10 (6)
N(2)	−8 (5)	1715 (7)	616 (7)	25 (4)	64 (7)	86 (7)	−0 (4)	22 (4)	−13 (6)
N(3)	624 (5)	−711 (8)	1606 (7)	31 (4)	81 (8)	84 (7)	3 (5)	22 (4)	−16 (6)
C(1)	−1888 (6)	−1340 (10)	−134 (10)	30 (5)	76 (10)	110 (11)	−7 (6)	29 (6)	−12 (9)
C(2)	−2808 (7)	−1166 (10)	129 (10)	29 (5)	85 (11)	114 (11)	−20 (6)	28 (6)	−18 (9)
C(3)	−2808 (6)	−58 (13)	542 (8)	30 (4)	104 (10)	92 (8)	−14 (9)	30 (5)	−34 (12)
C(4)	−1900 (6)	532 (9)	567 (9)	26 (5)	81 (9)	84 (9)	4 (5)	25 (5)	−6 (8)
C(5)	−1628 (7)	1690 (9)	905 (9)	30 (5)	77 (10)	96 (10)	7 (6)	27 (6)	−11 (8)
C(6)	−758 (7)	2275 (9)	934 (9)	44 (6)	69 (9)	78 (9)	1 (6)	28 (6)	−19 (8)
C(7)	−487 (8)	3488 (10)	1339 (10)	52 (6)	66 (10)	118 (12)	−1 (7)	29 (7)	−20 (9)
C(8)	420 (8)	3673 (11)	1244 (11)	51 (7)	77 (11)	138 (14)	−13 (7)	40 (8)	−27 (10)
C(9)	691 (7)	2573 (9)	782 (9)	39 (5)	67 (10)	94 (10)	−6 (6)	20 (6)	−19 (8)
C(10)	1602 (7)	2396 (10)	569 (11)	37 (5)	73 (10)	128 (12)	−19 (6)	27 (7)	−24 (10)
C(11)	−3608 (8)	−2118 (12)	−112 (16)	40 (6)	106 (14)	212 (23)	−8 (8)	54 (10)	8 (15)
C(12)	−3505 (12)	−2914 (17)	852 (18)	84 (12)	192 (24)	286 (27)	−17 (14)	72 (15)	53 (21)
C(13)	−3604 (8)	608 (12)	915 (12)	36 (6)	147 (15)	153 (15)	3 (8)	55 (8)	−28 (13)
C(14)	−1104 (10)	4376 (12)	1783 (16)	74 (9)	97 (13)	214 (22)	−12 (9)	82 (12)	−68 (14)
C(15)	−1000 (15)	4132 (18)	2996 (17)	154 (19)	184 (27)	240 (22)	16 (18)	119 (18)	−66 (20)
C(16)	1014 (9)	4802 (12)	1544 (13)	72 (8)	72 (14)	179 (16)	−6 (8)	50 (9)	−34 (12)
C(17)	1054 (9)	159 (15)	2496 (11)	76 (8)	115 (16)	106 (11)	3 (11)	18 (8)	−17 (14)
C(18)	35 (9)	−1577 (13)	2064 (11)	57 (8)	155 (17)	103 (12)	11 (10)	28 (8)	49 (12)
Cl	2500[c]	−2474 (4)	2500[c]	38 (2)	84 (4)	186 (7)	0[c]	6 (3)	0[c]
O	−3333 (12)	3741 (18)	−669 (13)	169 (14)	370 (33)	188 (18)	72 (18)	54 (13)	16 (20)

[a] The values of the fractional coordinates and thermal parameters are multiplied by 10^4 except for rhodium, whose thermal parameters are multiplied by 10^5. [b] Thermal parameters are in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Parameter held constant during refinement. [d] Numbers in parentheses are estimated standard deviations.

Table II. Calculated Hydrogen Positions Used in the Final Refinement Cycle of $(DMA)_2Rh^{III}EtioCl \cdot 2H_2O$

Atom[b]	Fractional coordinates[a]			Atom[b]	Fractional coordinates[a]		
	x	y	z		x	y	z
H(5)	−2155	2231	1193	H(151)	−224	4196	3543
H(10)	2119	3159	7600	H(152)	−1417	4770	3396
H(111)	−4304	−1692	−298	H(153)	−1235	3175	3169
H(112)	−3555	−2710	−800	H(161)	973	5156	2370
H(121)	−3538	−2356	1656	H(162)	1773	4613	1586
H(122)	−4082	−3604	762	H(163)	747	5527	901
H(123)	−2800	−3401	1135	H(3)	1094	−1143	1402
H(131)	−3961	−81	1383	H(171)	1509	−362	3207
H(132)	−3294	1381	1484	H(172)	472	606	2749
H(133)	−4149	972	180	H(173)	1482	807	2176
H(141)	−880	5309	1736	H(181)	492	−2043	2795
H(142)	−1853	4272	1366	H(182)	−504	−1008	2354
				H(183)	−338	−2205	1424

[a] The values of the fractional coordinates are multiplied by 10^4. [b] Isotropic thermal parameters were set at $B = 8.0$ for all hydrogen atoms except H(3), H(5), and H(10), whose $B = 5.0$. H(3) is bound to N(3).

ment consistently revealed troughs and peaks of 1 to 1.5 electrons/Å^3 in the immediate vicinity of the rhodium.[11] The nonequivalence of the Rh–N_p bond lengths can be attributed to this dominant feature, as the N_p furthest from the rhodium lay within a trough and the N_p closest to the rhodium approached a positive peak. Most probably, this difficulty was caused by a systematic error in the data, such as an incomplete absorption correction, although it could be argued that bonding density was partially responsible. A high order data refinement using the 1327 observed reflections for which $\sin \theta/\lambda \geq 0.4$ gave $R = 0.063$ and an essentially flat ΔF synthesis, if contoured at the previous levels. If the high order refinement ΔF synthesis is contoured at a smaller interval, consistent with the reduction in structure factor intensity at this $\sin \theta/\lambda$, the same features as noted above are present. The light atom positions obtained from the high order data refinement varied somewhat from those of the full data refinement; however, a comparison of the averages of chemically equivalent interatomic distances and angles for the two refinements reveal no differences greater than 1σ. The two Rh–N_p bond lengths remained as nonequivalent as before. These results strengthen the suspicion that the problem is a systematic error. Again, considering the entire data set, removal of the 11 most intense structure factors ($|F| > 150$) did not change the ΔF synthesis. Perusal of the structure factor table[12] reveals that ΔF =

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(11) F. A. Cotton and J. G. Norman, *J. Amer. Chem. Soc.*, **93**, 80 (1971), in their determination of chlorobis(dimethylglyoximato)triphenylphosphinerhodium(III), report finding a peak with a density of 1.34 electrons/Å in the vicinity of the rhodium atom. Also their final Rh–N distances varied 6σ.

(12) A compilation of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4822. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

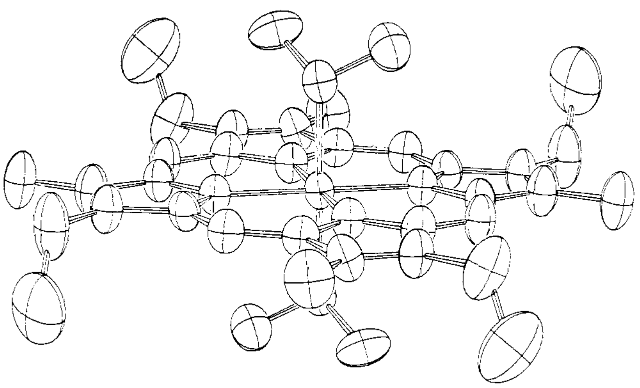

Figure 1. A plot of atom positions of the rhodium porphyrin cation with thermal ellipsoids at the 50% probability level.

$F_{\text{calcd}} - F_{\text{obsd}} > 0$ for reflections whose l index is negative and that $\Delta F < 0$ where l is positive. This occurs for 21 of the 25 reflections with $F_c > 100$. This trend had been evident since the early stages of refinement. Although it is the only systematic trend in the intensity data we have found, we are unable to relate it to the lack of agreement between "equivalent" Rh–N bond distances.

X-Ray Results and Discussion. The crystallographic study has shown the porphyrin moiety to be a cationic complex of rhodium(III) with a formal charge of (+)1. The monovalent counterion is a chloride ion. The rhodium atom is octahedrally coordinated and centered within the plane of the porphyrin with two dimethylamines as axial ligands.[13] The compound will hereafter be abbreviated as $(DMA)_2Rh^{III}EtioCl$. Two waters of hydration occur with each porphyrin moiety. A plot of the atom positions of the porphyrin cation including the calculated thermal ellipsoids is illustrated in Figure 1.

Figure 2 gives the pertinent interatomic distances and angles for the porphyrin entity. The agreement between portions of the molecule which are expected to be chemically equivalent is generally 3σ[14] or better. Figure 3 gives the averaged values for the equivalent parameters. That the porphinato skeletal parameters vary systematically as a function of the central radius has been demonstrated by Collins and Hoard.[15] Thus two different porphyrin moieties with the same inner ring radii ought to have the same porphine ring parameters. In Table III we compare $(DMA)_2Rh^{III}EtioCl$ and $\alpha,\beta,\lambda,\delta$-tetra(4-pyridyl)porphinatomonopyridinezinc(II) (PyZnTPyP). Their central core radii differ by less than 0.01 Å. The overall agreement between the two compounds is quite remarkable in view of the different ring substituents and the metal nonplanarity in the Zn case.

The porphyrin skeleton, including the methyl and methylene carbons bonded to the C_b's, is planar, with 0.04 Å the maximum deviation and 0.02 Å the root mean square of the deviations from the least-squares plane. This degree of ring planarity is quite unusual; in fact, only two other reported porphyrin structures, $Sn^{IV}TPPCl_2$[10] and $Sn^{IV}OEPCl_2$,[16] are unambiguously

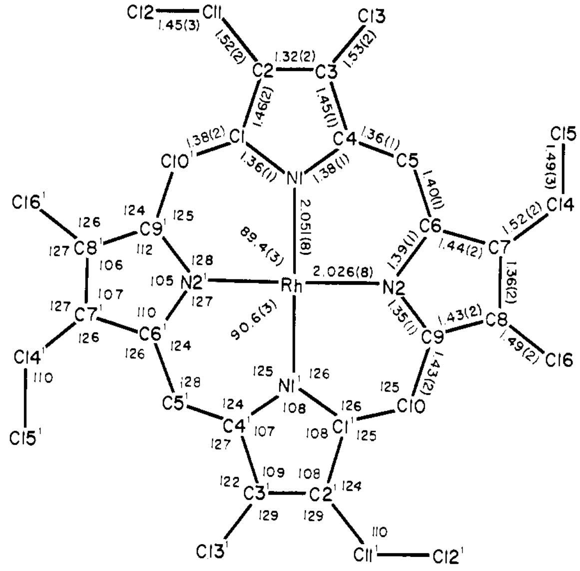

Figure 2. Bond distances, in Å, and angles, in degrees, of the porphyrin skeleton. All angles have esd of 1° except those involving the rhodium.

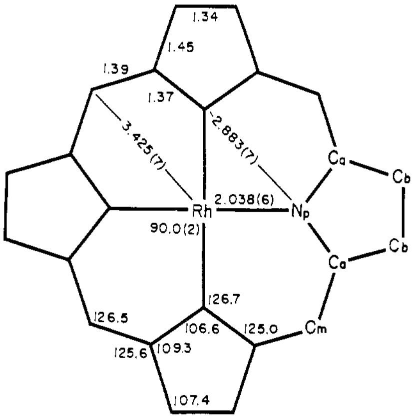

Figure 3. Averaged bond distances, in Å, and angles, in degrees, for chemically equivalent positions of the porphyrin skeleton. Standard deviations in bond lengths and bond angles not involving rhodium are 0.01 Å and 0.5–0.7°, respectively.

Table III. Comparison of Averaged Bond Distances and Angles of the Porphine Skeleton between This Structure and PyZnTPyP[15]

Type of distance	Length, Å RhEtio	Length, Å ZnTPyP	Type of angle	Angles, deg RhEtio	Angles, deg ZnTPyP[a]
C_t–N[b]	2.038 (6)	2.047 (3)	C_a–N–C_a	106.6 (6)	106.6
N–C_a	1.37 (1)	1.369 (2)	C_t–N–C_a	126.7 (4)	126.3
C_a–C_m	1.39 (1)	1.406 (2)	C_a–C_m–C_a	126.5 (7)	125.2[c]
C_t–C_m	3.425 (7)	3.448 (2)	N–C_a–C_m	125.0 (5)	125.7[c]
C_a–C_b	1.45 (1)	1.447 (2)	C_b–C_a–C_m	125.6 (5)	124.5[c]
C_b–C_b	1.34 (1)	1.355 (3)	N–C_a–C_b	109.3 (5)	109.8
			C_a–C_b–C_b	107.4 (5)	106.9

[a] σ's *ca.* 0.2°. [b] C_t = ring center. This is equivalent to the Rh position, but not to the Zn position. For other nomenclature, refer to Figure 3. [c] Angles affected by the nonplanarity of the porphine ring of PyZnTPyP.

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(13) The two axial dimethylamine ligands have been subsequently detected by nmr. A doublet corresponding to the six amine-methyl hydrogens is centered at τ 13.93. The proton bound to the amine nitrogen was not located. The rest of the nmr spectrum was as expected for an etioporphyrin.

(14) The σ's were calculated using the atomic position variences obtained from the least-squares refinement. Because unit weights were used in this refinement, the σ's can only be regarded as best estimates.

(15) D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970).

(16) D. L. Cullen and E. F. Meyer, Jr., *J. Chem. Soc. D*, 629 (1971).

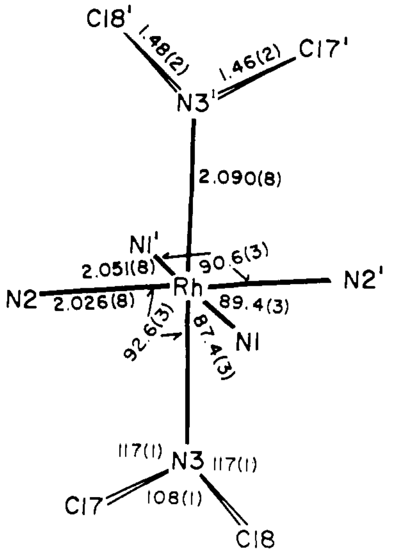

Figure 4. Interatomic distances, in Å, and angles, in degrees, for the coordination sphere of the rhodium, including the dimethylamine parameters.

planar. All other porphyrin structures have statistically significant deformations normal to the mean plane of the ring although local planarity in the pyrrole groups is always preserved. The only evidence for porphyrin ring deformations in the $(DMA)_2Rh^{III}$-EtioCl is the observation that the largest components of the thermal parameters are normal to the ring. In the structures reported so far, ring nonplanarity appears to depend either on the metal being out of the plane of the central nitrogens or on intermolecular packing forces. $(DMA)_2Rh^{III}$EtioCl is loosely packed, so the latter are not effective. Examination of a variety of porphyrin structures shows that the metal atom is out of the central nitrogen plane only in cases of five coordination or in cases of large metal atoms, *e.g.*, Sn(II). However, in this case the Rh atom is not large and is six coordinate.

Six coordination is the favored geometry in all d^6 rhodium complexes. Figure 4 presents the nearly octahedral bond lengths and angles for the rhodium coordination sphere. The $Rh-N_a$ bonds are only 0.05 Å longer than the $Rh-N_p$ bonds, a difference which can largely be ascribed to the known 0.03 Å difference in radii for sp^2 and sp^3 nitrogen atoms. None of the bond angles deviate significantly from 90°. The $Rh-N_p$ distance is the same as the 2.04 Å reported for phenylrhodium tetraphenylporphine (C_6H_5-Rh^{IV}TPPCl).[17] The $Rh-N_p$ and $Rh-N_p$ distances occur within the range of recently reported Rh(III)-N values, wherein 1.99 Å for glyoxime[11] is a lower limit and 2.09 Å for amines[18] or pyridine[19] is a common value. Since there may be some inclination to take the difference of ~0.025 Å between calculated $Rh-N_p$ distances as real, let us summarize our reasons for believing it probably is an artifact: (i) the deviation lies within 3σ; (ii) there are unexplained residual densities in the ΔF syntheses; (iii) the loose packing of the molecules provides no obvious external steric factors for distortion; (iv) there is no internal electronic reason for distortion in view of the pseudo-closed shell d^6 electronic configuration of the Rh.

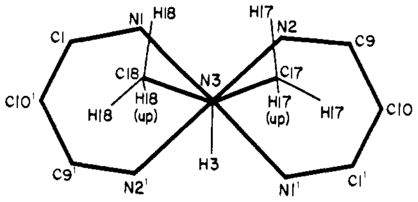

Figure 5. A schematic drawing of the orientation of the dimethylamine above the porphyrin plane.

As can be seen from Figure 5, the orientation of the DMA above the porphyrin plane closely approximates that of piperidine in Pip_2Fe^{II}TPP.[20] In both cases the hydrogen bound to the amine nitrogen is calculated to be equidistant between adjacent pyrrole nitrogens. In light of the differing charge densities on pyrrole nitrogen and amine nitrogen (negative and positive, respectively) and the short distance between the calculated hydrogen position and the N_p, some hydrogen bonding to N_p may occur in addition to hydrogen bonding to the chloride. This hydrogen was not found. The hydrogens bound to the DMA carbons were located, indicating that rotation of these methyls is completely hindered. The contacts of two hydrogens on each amine carbon with the ring are very short, up to 0.3 Å less than the van der Waals contact distance of 2.9 Å. These contacts are listed in Table IV.

Table IV. Close Contacts between DMA Hydrogens and the Porphine Skeleton

Contact	Dist, Å	Contact	Dist, Å
H(3)-N(1)'	2.57	H(172)-N(2)	2.80
H(3)-N(2)'	2.63	H(182)-N(1)	2.80
H(173)-N(2)	2.66	H(183)-N(1)	2.80
H(173)-C(9)	2.63	H(183)-C(1)	2.70
H(173)-C(10)	2.68	H(183)-C(10)'	2.64
H(173)-C(1)'	2.80	H(183)-C(9)'	2.66
H(173)-N(1)'	2.86	H(183)-N(2)'	2.74

Nonetheless, these short interactions result in no noticeable lengthening of the $Rh-N_a$ bond nor deformations of the ring. Only a distortion of the $C-N_a-Rh$ bond angle from tetrahedral (to 117°) is observed.

The $(DMA)_2Rh^{III}EtioCl \cdot 2H_2O$ has a packing scheme which differs from all other porphyrins reported thus far. The major intermolecular forces are hydrogen bonds between the DMA hydrogens and the chloride ions, as illustrated in Figure 6. Thus the crystal contains infinite hydrogen-bonded chains of alternating cation and anion up the *n* glide. The chloride ion lies in a roughly tetrahedral environment, hydrogen bonded to two water molecules and to two DMA's. The two water molecules appear to fill holes in the lattice and do not form any sort of cross network of hydrogen bonds. They have moderate positional freedom, as shown by their large thermal parameters. The $N_a \cdots Cl$ distance of 3.27 Å and the $O \cdots Cl$ distance of 3.15 Å lie comfortably within the range

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reported for similar hydrogen bonds.[21] The pertinent angles about the chloride ion are $\angle$O–Cl–O′ = 127.8 (5)°, $\angle N_{DMA}$–Cl–N'_{DMA} = 107.6 (2)°, $\angle N_{DMA}$–Cl–O = 117.5 (3)°, and $\angle N_{DMA}$–Cl–O′ = 93.3 (4)°.

Two other features of the packing might be noted. In contrast to the two previously determined etioporphyrins,[22,23] the molecule packed in an ordered fashion with respect to the methyl and ethyl substituents on the pyrrole rings. The only intermolecular C···C distances less than 3.60 are 3.40 Å for C(2)···C(17) and 3.57 Å for C(11)···C(17). However, no unusually short contact distances are observed if the calculated positions of the hydrogens bonded to these atoms are considered.

Porphyrin Ligand Field Geometries. It is of considerable interest to establish metal–nitrogen distances as these critically affect theoretical calculations through the overlap of metal–nitrogen orbitals. Therefore, regularities deducible from X-ray studies are important, as it may not be possible to carry out structural determinations for each metal that would be studied theoretically.

We might venture the following generalizations.

(i) The porphyrin central core radius has been found to vary from a minimum of 1.929 Å[24] for the highly ruffled tetragonal form of NiOEP to a maximum of 2.098 Å[10] for $Sn^{IV}TPPCl_2$. Comparison of isovalent structures in which the metal has the same spin state between first and second transition rows suggests a ring increase of 0.05 Å. This can be seen in comparison between Fe(II) (2.004 Å)[20] and Ru(II) (2.045 Å),[25] Co(III) (1.98 Å)[26] and Rh(III) (2.04 Å), Ni(II) (1.96 Å)[27] and Pd(II) (2.01 Å),[28] and stretching a point, Zn(II) (2.047 Å)[15,29] and Sn(IV) (2.10 Å).[10,16]

(ii) As pointed out by Hoard,[30] for structures of the same metal in different spin states, the high-spin structure has a larger metal–nitrogen distance and is nonplanar in all structures done so far. Consistent with this view, theoretical calculations have shown that for iron porphyrins nonplanarity is necessary for high-spin electronic configurations.[4]

(iii) The nitrogen to center distance for first row transition elements with partly filled d shells is smaller than that found for elements such as Mg,[31] Zn, and Sn. It is the largest for VO,[32] at the beginning of the series, which is in line with the trend in atomic radii.

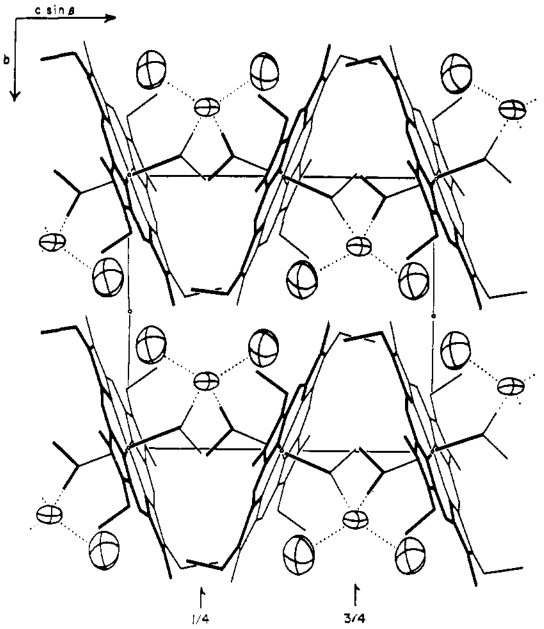

Figure 6. Packing of the contents of the unit cell in an *a* axis projection. Hydrogen bonds are indicated by dotted lines. Thermal ellipsoids at the 50% probability level are drawn for the chloride ions and the water oxygens (larger ellipsoids) only.

We might note that our generalizations are by no means intended to cover the subtleties of porphyrin conformation such as the variation of ring structural parameters with central core radius, the nonplanarity of closed shell metals such as Zn and Mg, unusual axial ligand properties, or the detailed changes in the Fe structures with spin and oxidation state that are under continuing investigation by Hoard and coworkers.[33]

Knowledge about the axial ligands of porphyrins, both their identity and structural parameters, is also necessary for detailed understanding of porphyrin luminescence behavior. The strength of the ligand field about the central metal is strongly affected by the axial ligand. In addition, the axial ligands can actively influence the phosphorescence lifetimes of the metalloporphyrins by contributing to the spin–orbit coupling term between the singlet and triplet states.[34]

Results and Discussion

Electronic Spectra. Figure 7 gives the absorption and emission spectra and Table V summarizes the spectroscopic data. The experimental procedures used for the collection of the luminescence data have been described elsewhere.[34] A PDP-8E computer was placed on line to provide preliminary processing of the output data. Instrument response corrections could be applied and signal/noise ratios enhanced by means of signal averaging (each output was the aver-

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(21) A careful recent structure determination, that of arginiric hydrochloride monohydrate, J. Dow, L. H. Jensen, S. K. Mazumdar, R. Srinivasan, and G. N. Ramachandran, *Acta Crystallogr., Sect. B*, **26**, 1662 (1970), reports six N–H···Cl bonds, which vary over 3.20–3.37 Å, and two O–H···Cl bonds, 3.11 and 3.20 Å.

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(26) W. R. Scheidt, personal communication.

(27) Only the essentially planar Ni structures have been considered for this value, *i.e.*, 1.96 (1) Å for NiEtioP by E. B. Fleischer, *J. Amer. Chem. Soc.*, **85**, 146 (1963); 1.960 (4) Å for NiDeuteroP by T. A. Hamor, W. S. Caughey, and J. L. Hoard, *ibid.*, **87**, 2305 (1965); and 1.963 Å in the triclinic form of NiOEP by D. L. Cullen and E. F. Meyer, Jr., American Crystallographic Association, Winter Meeting, 1973, p 21.

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(29) Also 2.04 (1) Å in $H_2OZn^{II}TPP$ by M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Amer. Chem. Soc.*, **89**, 1996 (1967); and 2.05 (1) Å in $pyZn^{II}OEP$, D. L. Cullen and E. F. Meyer, Jr., American Crystallographic Association, Summer Meeting, 1971, p 82.

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Table V. Spectroscopic Data for $(DMA)_2Rh^{III}EtioCl$

Absorption[a,b]				Emission[d]				
	Wavelength				Wavelength			
Band	nm	cm^{-1} ($\times 10^3$)	ϵ, m*M*	Band	nm	cm^{-1} ($\times 10^3$)	Relative no. of photons	Yields and lifetimes
N(0,0)	342	29.2	19	Q(0,0)[b,c]	552	18.1	10.0	$\phi_f = 2 \times 10^{-4}$ [b,c]
B(0,0)[e]	397	25.2	157	Q(0,1)[b,c]	600	16.7	7.4	
Q(1,0)	514	19.5	15	T(0,0)[c]	657	15.2	10.9×10^3	$\phi_p = 0.23$[c]
Q(0,0)	546	18.3	33	T(0,1)[c]	733	13.6	1.3×10^3	$\tau_p = 0.73$ (2) msec[c]

[a] In CH_2Cl_2. [b] Room temperature. [c] Liquid N_2 temperature. [d] In 2-methyltetrahydrofuran. [e] $\Delta_{1/2}$ Soret = 22 nm, which is anomalously broad.

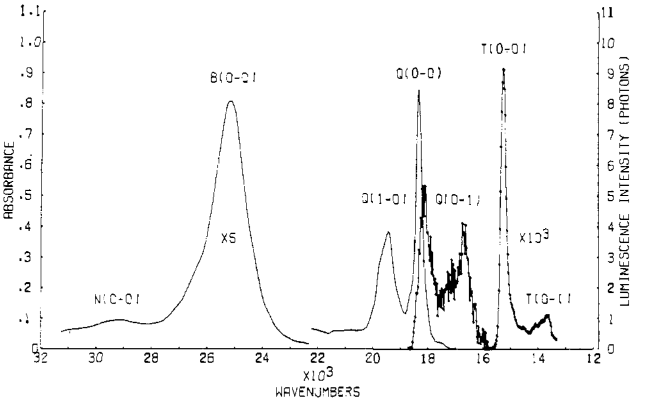

Figure 7. The electronic spectra of $(DMA)_2Rh^{III}EtioCl$. The absorption spectrum (smooth line) was obtained at room temperature in dichloromethane. The Soret (B(0–0)) band has been reduced by a factor of five. The emission spectrum was obtained in 2-methyltetrahydrofuran: the fluorescence at room temperature, the phosphorescence in a 77°K glass. The phosphorescence has been reduced by a factor of 10^3. Each stipple on the emission spectrum represents a data point.

age of 4096 readings). The latter feature was of great importance in the detection of the extremely weak $(DMA)_2Rh^{III}EtioCl$ fluorescence. The yields were measured relative to zinc etioporphyrin(I) whose fluorescence yield is $\phi_f = 0.04$.[35]

The luminescence of $(DMA)_2Rh^{III}EtioCl$ reported here is very similar to $Pd^{II}Etio$ reported earlier.[5b] There is a very weak fluorescence and a strong phosphorescence. Both luminescences have been unambiguously identified with the rhodium porphyrin by excitation spectra. We presume that the fluorescence yields reported in Table V represent prompt fluorescence only. At room temperature the triplet was undoubtedly quenched too quickly for delayed fluorescence to occur, although a miniscule amount of RT phosphorescence was observed in undegassed samples; at liquid nitrogen temperature little thermal repopulation is expected. We unsuccessfully attempted to observe phosphorescence from a solid polycrystalline sample.

It is interesting to compare the luminescence of Rh(III) with other metal porphyrins. While Becker and Allison[36] reported luminescence of Co(III) and Fe(II), which are d^6 like Rh(III), our laboratory was unable to verify the report on Co(III).[5a] We believe that the Fe(II) emission is doubtful until substantiated by excitation spectra. The d^6 configuration in an octahedral field is a pseudo-closed shell and might be expected to show moderate fluorescence yields and phosphorescence lifetimes of 10 to 100 msec as do d^0 and d^{10} metalloporphyrins such as Mg, Zn, and Sn(IV).[28–30] On the contrary, Rh(III) resembles Pd(II) with a very weak fluorescence yield and a short triplet lifetime, although Pd(III) is d^8. Recently we discussed the phosphorescence properties of group IVa porphyrins[34] and how these properties were determined by a spin–orbital integral $iZ = \langle e_{gx}|b_z|e_{gy}\rangle$, where b_z is the spin–orbit interaction. Tentatively, we would explain luminescence results as follows. Due to greater delocalization of the $e_g(\pi^*)$ into d_π, the integral Z is far bigger for metalloporphyrins with configurations d^6 and d^8 than for d^{10}. Moreover the ligand field splittings for second transition row metals are far bigger than for first row metals, so that the dd transitions are at higher energy than the lowest $\pi\pi^*$ transitions for Pd(II) and Rh(III) but at lower energy than the lowest $\pi\pi^*$ transitions for Fe(II) and Co(III). Consistent with this view, we are tempted to ascribe the anomalous broadness of the Soret band to the presence of underlying transitions of either dd, $d\pi^*$, or πd character.

These hypotheses then account for three types of luminescence behavior exhibited by diamagnetic metal porphyrins. (i) In d^6 Fe(II) or Co(III) complexes, low energy dd transitions deactivate $\pi\pi^*$ luminescence. (ii) In d^6 Rh(III) and d^8 Pd(II) complexes, the dd transitions are at too high energy to provide pathways for radiationless decay, but delocalization of the $e_g(\pi^*)$ orbitals into d_π gives rise to a large spin–orbit coupling that produces low fluorescence yields and short triplet lifetimes. (iii) In d^0 and d^{10} metal complexes, neither effect is operating so that moderate fluorescence yields and longer triplet lifetimes are observed.

To verify this picture good electronic MO calculations on accurate molecular geometries will be necessary. Another point of interest is whether axial ligands can affect dd transition energies. The dimethylamine present in this case certainly must play a role in the ligand field responsible for the large dd energy gap. We are currently further investigating rhodium porphyrins in order to study the effect of varying the axial ligand. Preliminary results on a phenyl rhodium octaethylporphyrin indicate that in solution it exhibits a phosphorescence with a lifetime $\tau_p \sim 1.1$ msec (77°K).

Acknowledgments. We thank Professor L. H. Jensen for the use of his facilities and for encouragement and

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advice. Crystallographic programs used were those of XRAY70.[37] The crystallographic figures were drawn with the aid of the ORTEP[38] program. We also thank Miss Jo Anne Backstrom for programming the PDP-8E. This work was supported by U. S. Public Health Grants GM-14292 and GM-10828 from the National Institutes of Health.

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The Structure of Histamine

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Received February 28, 1973

Abstract: The structure of histamine free base has been determined from three-dimensional X-ray data, collected by counter methods. The tautomer obtained in the solid state by recrystallization from benzene is 5-(2-aminoethyl)imidazole, with no evidence for the coexistence of 4-(2-aminoethyl)imidazole. The imidazole and NH_2 groups are trans to one another across the C–C bond of the ethyl group. The nitrogen and carbon atoms of the imidazole ring are coplanar. The dihedral angle between this plane and the plane of the carbon and nitrogen atoms of the aminoethyl side chain is 66.3°. Distances within the molecule are in good agreement with recent X-ray and neutron diffraction results on the orthorhombic form of L-histidine, despite the fact that orthorhombic L-histidine is a derivative of 4-ethylimidiazole, rather than 5-ethylimidazole. In histamine free base there is an N–H$\cdots$N hydrogen bond involving the N–H function of the imidazole ring with the NH_2 group on the side chain of an adjacent molecule. In this way infinite zig-zag chains of imidazole molecules are formed in the crystal. Histamine free base crystallizes in space group $C_2{}^2$-$P2_1$ of the monoclinic system, in a cell of dimensions $a = 7.249$ (2), $b = 7.634$ (3), $c = 5.698$ (2) Å, and $\beta = 104.96$ (2)°. A density of 1.218 g/cm^3 calculated for two molecules in the unit cell agrees with that of 1.20 (1) g/cm^3 observed by flotation in an ethyl benzoate–iodobenzene medium. A total of 548 unique reflections was collected using Cu Kα X-radiation, prefiltered with Ni foil. The structure was solved by direct methods and refined by least-squares methods to a final agreement index on F of 3.1%.

The cooperation of endopeptidases, which break the proteins at certain places into large fragments, and of exopeptidases, which hydrolyze these fragments, results in a mixture of amino acids. Some of these amino acids are used to build new endogenous proteins. Most, however, are degraded further and included in these degradations is the well known enzymic decarboxylation of the amino acids which gives rise to primary amines. Many amines of this type possess a strong pharmacological activity. This is true for histamine, the product of the decarboxylation of histidine.[2]

For histamine, which is present in mammal tissue (lung, muscle, etc.) and blood, ponderous volumes have been written. Its primordial activity at the central nervous system level and in regulation of insomia[3–5] led many authors to consider histamine as the third chemical mediator, following adrenaline and acetylcholine. Furthermore, histamine is a powerful vasodilator and a stimulator of gastric secretion in higher animals.[6–10]

Free histamine, obtained by the enzymic decarboxylation of histidine, forms complexes with metals of biological interest and it is well known that the majority of active compounds are those capable of forming a a six-membered ring between a 2-amino side chain nitrogen, a tertiary nitrogen of an aromatic nucleus, and some polar center. Indeed, in order to be involved in the binding between small molecules and proteins, a metal must be capable of forming an independent complex with the small molecule.[11] The crystal structures of some metal complex of histamine are already known,[12–15] but surprisingly the crystal structure of histamine free base was unknown until the present work. Niemann and Hays[16] considered three possible tautomeric structures (Figure 1) and, from a consideration of the possible resonance forms of each tautomer and from bond energies, concluded that only structures I and II are possible. They further concluded that tautomer I is the structure responsible for the histamine-like activity of histamine. Although structure I, 4-(2-aminoethyl)imidazole, may exist in solution and, in fact, has the same tautomeric form as

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