(21) W. L. Peticolas and B. B. Johnson, *Annu. Rev. Phys. Chem.*, in press.
(22) J. Tang and A. C. Albrecht, "Raman Spectroscopy", Vol. 2, H. A. Szymanski, Ed., Plenum Press, New York, N.Y., 1970, pp 33-68.
(23) M. Garozzo and F. Galluzzi, *J. Chem. Phys.*, **64**, 1720-1723 (1976).
(24) W. L. Peticolas, L. Nafie, P. Stein, and B. Fanconi, *J. Chem. Phys.*, **52**, 1576-1584 (1970).
(25) T. G. Spiro and T. C. Strekas, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2622-2626 (1972).
(26) T. C. Strekas, A. J. Packer, and T. G. Spiro, *J. Raman Spectrosc.*, **1**, 197-206 (1973).
(27) T. B. Freedman and T. M. Loehr, *J. Am. Chem. Soc.*, in press; *Biochem. Biophys. Res. Commun.*, **56**, 510-515 (1974).
(28) G. A. Olah and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3137-3141 (1975).

Structure Relationships between the Four-Coordinate, $S = 1$, Macrocyclic Complex, $[Fe(C_{22}H_{22}N_4)]$, and the Neutral Ligand, $C_{22}H_{24}N_4$

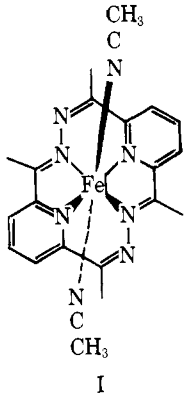
Virgil L. Goedken,*[1] Joseph J. Pluth, Shie-Ming Peng, and Bruce Bursten

Contibution from the Department of Chemistry, The University of Chicago Chicago, Illinois 60637.

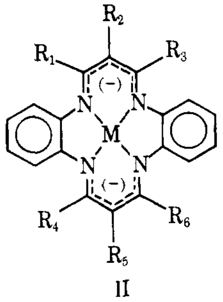
Received March 3, 1976

Abstract: Crystal and molecular structures of the, $S = 1$, four-coordinate iron(II) complex, 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinatoiron(II) and the isomorphous neutral ligand $C_{22}H_{24}N_4$ have been determined by three-dimensional x-ray crystallography. Pertinent crystal data are: space group, $P\bar{1}$; $[Fe(C_{22}H_{22}N_4)]$, $a = 9.429$ (2), $b = 11.401$ (3), and $c = 9.108$ (2) Å, $\alpha = 92.99$ (2), $\beta = 103.01$ (2), and $\gamma = 104.04$ (2)°; $C_{22}H_{24}N_4$, $a = 9.315$ (1), $b = 10.894$ (2), and $c = 9.928$ (1) Å, $\alpha = 96.53$ (1), $\beta = 107.04$ (1), and $\gamma = 101.53$ (1)° with $Z = 2$ for each compound. The ligands have a pronounced saddle-shaped conformation in each structure because of interactions of the methyl groups with the benzene rings. The overall conformations of the neutral ligand and the iron(II) complex are remarkably similar. A detailed structural interpretation of the free ligand is complicated by disorder involving degenerate tautomeric structures in the crystal lattice. The average Fe(II)-N bond distance of 1.918 (3) Å is significantly shorter than observed in $S = 0$ and $S = 1$ iron(II) porphyrin complexes. The donor electron pairs are directed slightly out of the N_4 coordination plane in each structure because of unequal tilting of the 2,4-pentanediiminato and benzenoid planes of the molecule. As a consequence, the Fe(II) atom is displaced 0.114 Å from the coordination plane.

Synthetic macrocyclic ligands have sufficiently diverse characteristics even among the fully conjugated systems to produce profound differences in the physical properties and reactivities of the coordinated metals. These differences are exemplified by the iron(II) complex $[Fe(C_{18}H_{18}N_6)(CH_3CN)_2]^{2+}$ (I), which shows no tendency towards oxidation by molecular oxygen,[2a] and the iron(II) complexes of the dianionic ligands of type II, which are exceedingly reactive toward molecular oxygen.[2b]



I



II

The metal-donor atom distance of a macrocyclic ligand is largely a function of the number of atoms in the macrocyclic ring and the extent of ligand conjugation. For example, the minimum strain M-N distance of 1,4,8,11-tetraazacyclotetradecane (cyclam), a 14-membered ring, and the free-base porphyrins which have 16-membered rings are similar, 2.07[3,4] and 2.04 Å,[5,6] respectively, because the contraction associated with a fully delocalized 16-membered ring compensates for the smaller number of atoms in the 14-membered ring. These values correspond well to commonly observed first-row transition-metal nitrogen distances. The completely conjugated 14-membered ligand, $C_{22}H_{22}N_4{}^{2-}$ (II, R_1, R_3, R_4, R_6 = CH_3; R_2, R_5 = H) is expected to have a much smaller radius than either cyclam or porphyrins because it has the equivalent of seven double bonds in a 14-membered macrocyclic ligand. Crystal structure analyses of three other completely conjugated 14-membered macrocyclic ligand complexes have revealed short metal-nitrogen distances (in the 1.80-1.90 Å range)[1,7-9] and illustrate the effect of extensive bond delocalization in these ligands on metal-nitrogen distances.

Significant departures from ideal metal-ligand bond lengths can considerably alter the properties of the resultant complexes. Small-diameter macrocyclic ligands can lead to unusually short metal-ligand distances, which are reflected in the redox potentials of the metal.[10] If the metal remains in the plane of the ligand, unusual electronic features may be observed. Alternatively, a constricting macrocyclic ligand may result in large displacements of the metal out of the ligand plane and lead to a preference for five-coordination. Large macrocyclic ligands with saturated rings of 16 or more atoms tend to be relatively unstable with respect to ligand dissociation and have weak ligand field strengths.[11] Unusual coordination numbers, for example seven-coordinate Fe(III), have been observed for some larger macrocyclic ligands.[12]

Transition-metal complexes derived from ligands of type II have been prepared and studied by a number of investigators with most of the studies confined to Ni(II),[13-16] although a few studies of complexes with Co(III),[17] Fe(II), Fe(III),[2] and Mo[18] have also been reported. The dianionic tetraaza ligands of II have a number of features in common with porphyrin and phthalocyanine ligands, but also have significant differences. Type II ligands, like the porphyrins and phthalocyanines, have four nitrogen donor atoms confined to a square-planar configuration, a completely conjugated system of double bonds, and two negative charges associated with the complexed form of the ligands. Some important differences are the following: (1) the metal-nitrogen distances of the complexes of II will be shorter than those of porphyrins and phthalocyanines because of decreased ring size, e.g., 14- vs. 16-membered rings; (2) each of the negative charges of II is essentially localized over the six-membered 2,4-pentanediiminato chelate rings, whereas the negative charges of porphyrins and phthalocyanines are delocalized over the entire ligand framework; and (3) type II complexes contain a $4n$ (16π) electron system with ostensibly antiaromatic character, whereas porphyrins and phthalocyanine complexes contain a $4n + 2$ π-electron system for which aromatic character can be ascribed.

Structural analyses of the free ligand, $C_{22}H_{24}N_4$, II, and the four-coordinate iron(II) complex, $[Fe(C_{22}H_{22}N_4)]$, of the dianion of this ligand were undertaken for a number of reasons. The intermediate, $S = 1$ spin state[19] of the iron(II) complex was sufficiently uncommon to warrant a structural investigation for its own sake. A number of other four-coordinate Fe(II), $S = 1$ spin state, complexes have recently been characterized,[20-22] with three four-coordinate Fe(II) complexes of macrocyclic ligands having been subjected to a full x-ray structural investigation. These three structures are the Fe(II) complexes of tetraphenylporphyrin,[22] an octaaza[14]annulene ligand,[9] and phthalocyanine.[23] A comparison of the bond parameters of the metal complex with those of the free ligand should allow some assessment of the flexibility of this macrocyclic ligand. Other aspects of structural interest in these two compounds include: (1) the determination of the metal-free radius of the uncoordinated ligand; (2) the strain arising from the steric interactions in the ligand and the distribution and minimization of this strain energy throughout the structure; (3) the changes which occur in the geometry of the ligand upon coordination; and (4) a comparison of the coordination parameters of the iron complex with related 14- and 16-membered macrocyclic ligands.[24]

Experimental Section

Samples of the neutral ligand, $C_{22}H_{24}N_4$, and the four-coordinate iron(II) complex, $[Fe(C_{22}H_{22}N_4)]$, of the deprotonated ligand were prepared as described elsewhere.[25] Crystals of $C_{22}H_{24}N_4$ suitable for x-ray structure analysis were crystallized from $CHCl_3$ solution by slow evaporation of the solvent. Crystals of $[Fe(C_{22}H_{22}N_4)]$ were grown by slowly cooling a saturated solution of the complex in toluene in a well insulated Dewar flask.

An unsuccessful attempt to solve the structure of $C_{22}H_{24}N_4$ preceded the synthesis and subsequent structural determination and refinement of the iron(II) complex of this ligand. Thus the experimental details as presented here are not in chronological order, but represent the more logical presentation.

X-Ray Analyses. A well-formed crystal of $[Fe(C_{22}H_{22}N_4)]$ with dimensions 0.15 × 0.35 × 0.50 mm was mounted on a glass fiber and covered with three thin coats of epoxy resin to prevent aerial oxidation of this easily oxidized compound. Although the merits of covering an air sensitive compound with epoxy resin, as opposed to mounting a capillary are debatable, the former is simpler and suffices for crystals of moderate air sensitivity and which do not react with the components of the resin.

An examination of this crystal by x-ray precession photography revealed no systematic absences and indicated a triclinic lattice. The crystal was transferred to a Picker FACS-1 automated diffractometer for the accurate determination of lattice constants and diffracted intensities. The angular settings of 30 reflections, paired at $\pm 2\theta$ values in the range of 40–45° using Mo $K\alpha$ radiation, were determined using the automatic centering program developed by Lenhert.[26] Least-squares refinement of the diffraction geometry of these reflections led to the lattice constants given in Table I. The density calculated assuming 2 molecules per unit cell of 1.437 g/cm^3 was in good agreement with the experimental value, 1.42 g/cm^3, determined by flotation in aqueous $ZnCl_2$ solution.

Table I. Crystal Data

	$[Fe(C_{22}H_{22}N_4)]$	$C_{22}H_{24}N_4$
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.429 (2)	9.315 (1)
b, Å	11.401 (3)	10.894 (2)
c, Å	9.108 (2)	9.928 (1)
α, deg	92.99 (2)	96.53 (1)
β, deg	103.01 (2)	107.04 (1)
γ, deg	104.04 (2)	101.53 (1)
Z	2	2
ρ_{expl}, g/cm^3	1.42	1.25
ρ_{calcd}, g/cm^3	1.437	1.233
λ(Mo $K\alpha$), Å	0.71069	0.71069
μ(Mo $K\alpha$), cm^{-1}	8.61	0.808
Minimum; maximum x-ray transmission	0.80; 0.88	0.955; 0.978

Intensity measurements utilized the θ–2θ scanning technique at a rate of 2°/min with a takeoff angle of 3°. The basic symmetrical scan width was 1.6° with an increment of $\Delta(2\theta = 0.692 \tan \theta)$ to allow for spectral dispersion. Stationary crystal-stationary counter backgrounds were measured for 20 s at the 2θ extrema of each scan. A total of 4510 intensities were measured within the limits of $0 < ((\sin \theta)/\lambda) < 0.65$ Å^{-1}. The intensities of three standard reflections were remeasured after every 100 reflections; the intensities decreased smoothly during the data collection to 90% of their original value. The intensities of all reflections were scaled appropriately in blocks of 100 to compensate for the decline of standard intensities.

The raw data were reduced to intensities (I) and estimated errors (σ_I) using $I = S - tb$ and $\sigma_I = [S + t^2B + k^2(S + tB)^2]^{1/2}$ with S = peak scan counts, B = total background costs, t = ratio of peak to background observation times, and k = instability constant = 0.01.[27] These I's and σ_I's were converted to relative structure factors (F) and estimated errors (σ_F) by $F = \sqrt{I/(\mathrm{Lp})}$ and $\sigma_F = [(F^2 + \sigma_{F^2})^{1/2} - F]$ with Lp = Lorentz and polarization factors. A total of 3553 data with $F_o > 3\sigma(F)$ were used in the structural analysis. Corrections were made for absorption of x-rays by the crystal; the minimum and maximum transmission coefficients were between 80 and 88%.

Structure Determination and Refinement of $[Fe(C_{22}H_{22}N_4)]$. A Patterson synthesis was used to determine the coordinates of the Fe atom. An F_o Fourier map using the phases provided from the structure factor calculation based on the coordinates of the iron atom clearly revealed the coordinates of all 26 nonhydrogen atoms.[28] Two cycles of full-matrix least-squares refinement employing isotropic temperature factors for all atoms except Fe, which was treated as anisotropic, converged to $R_1 = 8.7$, $R_2 = 10.9\%$; the function minimized was $\Sigma w[|F_o| - |F_c|]^2$. A difference Fourier synthesis revealed the approximate positions of all 22 hydrogen atoms. The coordinates of hydrogen atoms belonging to the methyl groups were calculated assuming standard tetrahedral geometry and C–H distances of 1.0 Å using the coordinates of the peaks obtained from a difference Fourier map as initial positions; the hydrogen atoms attached to the benzenoid rings were assigned to calculated positions assuming C–H distances of 0.95 Å. The hydrogen atoms were assigned isotropic temperature factors corresponding to those of the attached carbon atoms and included as fixed contributions in the subsequent cycles of refinement. Two final cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms and using statistical weights converged to $R_1 = 5.7$, $R_2 = 6.9$. A final difference Fourier synthesis was virtually featureless. The largest peaks, 0.36 e/Å^3, were located normal to the plane of the ligand and on 0.5 Å either side of the Fe atom. The final atomic coordinates and thermal parameters are listed in Table II.

X-Ray Analysis of $C_{22}H_{24}N_4$. A large well-formed crystal of $C_{22}H_{24}N_4$, 0.27 × 0.32 × 0.57 mm, was examined by precession photography with zero and upper layer photographs and determined to be triclinic. The crystal was transferred to a Picker FACS-1 automated diffractometer for the precise determination of lattice constants. These constants, determined from the angular settings of 26 reflections centered between the 2θ limits of 50 and 59.5° yielded the following initial set of lattice parameters: $a = 9.928$ (1), $b = 10.894$ (2), $c = 9.315$ Å, $\alpha = 101.53$ (1), $\beta = 107.04$ (1), $\alpha = 96.53$ (1)°. Intensity data were then collected with Mo $K\alpha$ radiation using the θ–2θ scan technique between the limits $0 \leq (\sin \theta)/\lambda \leq 0.704$ Å^{-1}. The remaining details of the data collection were identical with those de-

Table II. Final Positional and Thermal[a] Parameters of Nonhydrogen Atoms for $[Fe(C_{22}H_{22}N_4)]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	−0.01995 (6)	−0.17318 (4)	−0.24263 (6)	77.7 (7)	48.8 (4)	103.4 (8)	16.0 (4)	−2.1 (5)	1.9 (4)
N1	−0.0453 (3)	0.0012 (2)	0.2102 (3)	77 (4)	51 (2)	88 (4)	14 (2)	14 (3)	3 (2)
N2	−0.2030 (3)	0.1747 (3)	0.1001 (3)	71 (4)	60 (3)	95 (4)	18 (3)	8 (3)	16 (3)
N3	0.0142 (3)	0.3466 (2)	0.2570 (3)	94 (4)	51 (3)	111 (4)	20 (3)	15 (3)	6 (3)
N4	0.1766 (3)	0.1764 (2)	0.3638 (3)	71 (4)	56 (2)	84 (4)	18 (2)	3 (3)	1 (2)
C1	−0.1404 (4)	−0.0711 (3)	0.0887 (4)	82 (5)	57 (3)	99 (5)	3 (3)	26 (4)	2 (3)
C2	−0.2428 (4)	−0.0271 (3)	−0.0164 (4)	82 (5)	68 (3)	93 (5)	−1 (3)	6 (4)	−6 (3)
C3	−0.2747 (4)	0.0861 (3)	−0.0138 (4)	61 (4)	83 (4)	91 (5)	6 (3)	10 (4)	12 (3)
C4	−0.2434 (4)	0.2846 (3)	0.1236 (4)	93 (5)	70 (3)	108 (5)	32 (3)	26 (4)	35 (3)
C5	−0.3895 (5)	0.3012 (4)	0.0858 (5)	97 (6)	94 (4)	153 (6)	38 (4)	28 (5)	39 (4)
C6	−0.4145 (5)	0.4101 (4)	0.1345 (6)	131 (6)	109 (5)	214 (8)	75 (5)	59 (6)	66 (5)
C7	−0.2978 (6)	0.5015 (4)	0.2221 (6)	181 (8)	79 (4)	236 (9)	75 (5)	87 (7)	49 (5)
C8	−0.1539 (5)	0.4858 (4)	0.2633 (5)	138 (7)	62 (3)	185 (7)	35 (4)	45 (6)	20 (4)
C9	−0.1241 (4)	0.3796 (3)	0.2123 (4)	104 (5)	59 (3)	116 (5)	29 (3)	25 (4)	28 (3)
C10	0.1511 (4)	0.4240 (3)	0.2839 (4)	105 (5)	51 (3)	119 (6)	9 (3)	21 (4)	5 (3)
C11	0.2806 (4)	0.3876 (3)	0.3460 (4)	92 (5)	55 (3)	118 (5)	1 (3)	6 (4)	−8 (3)
C12	0.2955 (4)	0.2774 (3)	0.3893 (4)	79 (5)	75 (3)	88 (5)	17 (3)	4 (4)	−9 (3)
C13	0.1803 (4)	0.0606 (3)	0.4090 (4)	83 (5)	64 (3)	83 (5)	29 (3)	19 (4)	5 (3)
C14	0.2795 (4)	0.0351 (4)	0.5339 (4)	104 (5)	88 (4)	88 (5)	33 (4)	7 (4)	8 (3)
C15	0.2658 (5)	−0.0817 (4)	0.5720 (4)	134 (6)	104 (4)	104 (5)	72 (4)	32 (5)	34 (4)
C16	0.1495 (5)	−0.1750 (4)	0.4913 (4)	156 (7)	73 (4)	120 (6)	57 (4)	45 (5)	26 (4)
C17	0.0436 (4)	−0.1524 (3)	0.3702 (4)	137 (6)	54 (3)	106 (5)	27 (4)	32 (5)	3 (3)
C18	0.0588 (4)	−0.0365 (3)	0.3250 (4)	93 (5)	57 (3)	80 (4)	30 (3)	24 (4)	3 (3)
C19	−0.1394 (5)	−0.2010 (3)	0.0499 (4)	143 (6)	66 (3)	116 (6)	14 (4)	25 (5)	−12 (4)
C20	−0.3877 (5)	0.1057 (4)	−0.1517 (4)	107 (6)	110 (5)	111 (6)	27 (4)	−7 (5)	12 (4)
C21	0.1739 (5)	0.5518 (4)	0.2378 (5)	124 (6)	62 (4)	208 (8)	14 (4)	40 (6)	19 (4)
C22	0.4562 (4)	0.2678 (4)	0.4550 (5)	73 (5)	97 (4)	173 (7)	9 (4)	−7 (4)	15 (4)

[a] The form of anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^{-4}]$.

scribed for the iron complex except that a basic symmetrical scan width of 1.30° was used.

Structure Solution and Refinement. Considerable effort was expended in the application of direct method techniques to the structural solution of this compound. The statistical analysis of the E's derived from the data strongly indicated a centric structure and $P\bar{1}$ as the correct space group. However, application of MULTAN programs[29] failed to reveal the structure or any recognizable fragments in the derived E maps.

Subsequent to these early attempts the structure of the four-coordinate iron(II) complex was solved. Both complexes belonged to the space group $P1$ and had similar cell constants, suggesting the possibility of structural isomorphism. A structure-factor calculation employing the coordinates of the C and N atoms of the ligand derived from the structure of the Fe(II) complex and the initial choice of cell parameters for the free ligand were in poor agreement with the observed structure factors. Examination of the structure factors from this calculation, together with the observation that the "a" and "c" dimensions (and corresponding angles) were similar to one another, suggested that interchanging them would yield much better agreement between the observed and calculated structure factors. The interchange of these axes, giving the cell parameters listed in Table I, then led to moderately good agreement for the observed and calculated structure factors. Two cycles of full-matrix least-squares refinement using isotropic temperature factors and unit weights yielded an $R_1 = 0.13$, $R_2 = 0.14$. Two more cycles of refinement, using statistical weights with anisotropic temperature factors for the C and N atoms and including ten hydrogen atoms at fixed positions converged to $R_1 = 0.08$, $R_2 = 0.119$. A difference Fourier map then revealed the positions of all the remaining hydrogen atoms. The positions of the C-H hydrogen atoms were recalculated assuming standard geometry for the hydrogen atoms attached to the benzenoid rings and a least-squares fit of the hydrogen atoms attached to methyl carbon atoms. The two N-H hydrogen atoms appeared to lie almost in the plane formed by the four nitrogen atoms. The location of these hydrogen atoms was important in drawing conclusions about intramolecular hydrogen bonding, but their coordinates could not be calculated with any degree of reliability due to uncertainty about the hybridization associated with the bonding about the nitrogen atoms. Therefore, the N-H hydrogen atoms were varied in the last cycles of least-squares refinement, while the contributions of the hydrogen atoms attached to carbon atoms were included as fixed contributions. Two cycles of full-matrix least-squares refinement using statistical weights converged to $R_1 = 0.072$, $R_2 = 0.094$. Although the estimated standard deviations of the bond parameters of the resultant structure appeared good and chemically reasonable, the R factor was unusually high considering the crystal quality and the care taken in the data collection and suggested that the model used was inadequate.

A difference Fourier revealed no large peaks, but two small peaks with $\rho = 0.30$ e/Å^3 were located in the vicinity of the two imine nitrogen atoms and in positions consistent with N-H hydrogen atoms. The relatively high R factor thus appeared to be due to the presence of tautomeric disorder in the crystal lattice. A difference Fourier map was calculated through the plane of the four nitrogen atoms based upon a structure factor calculation obtained by omitting the N-H hydrogen atoms. The four highest peaks on this map corresponded to the N-H hydrogen atoms and indicated that the ratio of the tautomers in the lattice was approximately 3:1. The separation between nonhydrogen atoms resulting from the apparent superposition of the tautomeric forms in the crystal lattice would be no more than a few hundredths of an angstrom and completely obscured by thermal motions. Since there appeared to be no completely satisfactory way of refining the structure, the final cycle of refinement included the two N-H hydrogen atoms, but with each occupying two positions, one assigned a multiplicity of 0.75 and the other 0.25. Two final cycles of full-matrix least-squares refinement resulted in $R_1 = 7.1$, $R_2 = 9.1\%$. The final difference Fourier map had a maximum electron density of 0.4 e/Å^3 near one of the methyl groups. The final positional and thermal parameters are listed in Table III. A listing of the observed and calculated structure factor amplitudes for both structures and the calculated hydrogen atom positions for the structures is available. See paragraph at the end of the paper regarding supplementary material.

Results and Discussion

It is a rare event, and also a fortunate one, when the structural details for both a macrocyclic metal complex and its free ligand are presented together to facilitate direct comparison and evaluation of the structural changes which occur within the ligand upon complexation. The crystal structures of the free base, $C_{22}H_{24}N_4$, and the isomorphous Fe(II) complex, $[Fe(C_{22}H_{22}N_4)]$, of the dianionic form of the ligand are closely related and have very similar molecular geometries. Both the free ligand and its four-coordinate Fe(II) complex have a markedly nonplanar saddle shape because of steric interactions of the methyl groups with the benzene rings. The labeling scheme, together with the interatomic distances for the two structures, are presented in Figures 1 and 2. Selected intera-

Table III. Refined Positional and Thermal Parameters for $C_{22}H_{24}N_4$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
N1	−0.0601 (2)	0.0019 (2)	0.2080 (2)	107 (2)	71 (2)	77 (2)	18 (2)	9 (2)	13 (2)
N2	−0.2246 (2)	0.1679 (2)	0.1093 (2)	111 (3)	77 (2)	89 (2)	18 (2)	−1 (2)	18 (2)
N3	0.0117 (2)	0.3578 (2)	0.2858 (2)	105 (2)	64 (2)	115 (2)	19 (2)	15 (2)	23 (2)
N4	0.1797 (2)	0.1937 (2)	0.3800 (2)	98 (2)	68 (2)	108 (2)	22 (2)	9 (2)	20 (2)
C1	−0.1289 (2)	−0.0707 (2)	0.0804 (2)	112 (3)	66 (2)	91 (2)	2 (2)	28 (2)	13 (2)
C2	−0.2367 (2)	−0.0287 (2)	−0.0261 (2)	122 (3)	80 (2)	77 (2)	−3 (2)	1 (2)	5 (2)
C3	−0.2802 (2)	0.0847 (2)	−0.0153 (2)	104 (3)	89 (2)	87 (2)	6 (2)	6 (2)	23 (2)
C4	−0.2575 (2)	0.2852 (2)	0.1434 (2)	111 (3)	81 (2)	96 (3)	24 (2)	25 (2)	36 (2)
C5	−0.4056 (3)	0.3067 (2)	0.0994 (3)	109 (3)	115 (3)	131 (3)	28 (2)	25 (3)	41 (2)
C6	−0.4320 (3)	0.4215 (3)	0.1446 (3)	128 (4)	138 (3)	176 (4)	66 (3)	55 (3)	68 (3)
C7	−0.3131 (3)	0.5163 (2)	0.2388 (3)	191 (5)	103 (3)	207 (5)	76 (3)	83 (4)	51 (3)
C8	−0.1651 (3)	0.4970 (2)	0.2861 (3)	147 (4)	80 (2)	162 (4)	35 (2)	38 (3)	23 (2)
C9	−0.1343 (2)	0.3838 (2)	0.2364 (2)	115 (3)	70 (2)	110 (3)	25 (2)	26 (2)	34 (2)
C10	0.1424 (2)	0.4312 (2)	0.2860 (2)	131 (3)	59 (2)	95 (2)	18 (2)	27 (2)	6 (2)
C11	0.2838 (2)	0.3974 (2)	0.3417 (2)	102 (2)	68 (2)	111 (3)	3 (2)	21 (2)	5 (2)
C12	0.3031 (2)	0.2851 (2)	0.3863 (2)	100 (3)	80 (2)	84 (2)	18 (2)	8 (2)	2 (2)
C13	0.1719 (2)	0.0710 (2)	0.4129 (2)	105 (3)	72 (2)	83 (2)	32 (2)	21 (2)	17 (2)
C14	0.2743 (2)	0.0458 (2)	0.5342 (2)	118 (3)	94 (2)	95 (3)	34 (2)	5 (2)	20 (2)
C15	0.2563 (3)	−0.0739 (2)	0.5678 (2)	132 (3)	109 (2)	103 (3)	59 (2)	25 (2)	42 (2)
C16	0.1337 (3)	−0.1709 (2)	0.4833 (2)	171 (4)	83 (2)	118 (3)	57 (2)	54 (3)	44 (2)
C17	−0.1479 (2)	0.3639 (2)	0.0140 (3)	140 (3)	75 (2)	97 (3)	25 (2)	32 (2)	22 (2)
C18	0.0469 (2)	−0.0285 (2)	0.3247 (2)	106 (3)	66 (2)	77 (2)	29 (2)	23 (2)	14 (2)
C19	−0.0963 (3)	−0.1965 (2)	0.0373 (2)	185 (4)	81 (2)	100 (3)	23 (2)	41 (3)	1 (2)
C20	−0.3845 (3)	0.1162 (2)	−0.1474 (3)	197 (4)	133 (3)	99 (3)	48 (3)	−11 (3)	29 (2)
C21	0.1484 (3)	0.5491 (2)	0.2197 (3)	177 (4)	94 (2)	188 (4)	43 (3)	84 (3)	59 (3)
C22	0.4631 (3)	0.2632 (2)	0.4336 (3)	110 (3)	114 (3)	159 (4)	30 (2)	23 (3)	34 (2)
H1[a]	−0.080 (11)	0.078 (9)	0.247 (10)						
H2[a]	−0.160 (4)	0.146 (3)	0.176 (4)						
H3[a]	0.028 (11)	0.311 (9)	0.309 (10)						
H4[a]	0.089 (4)	0.207 (3)	0.351 (3)						

[a] B fixed at 4.5.

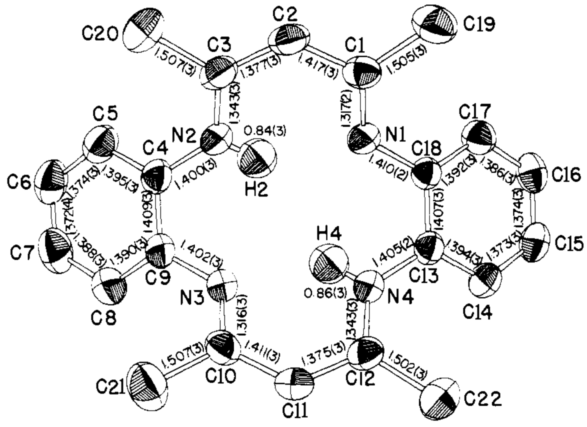


Figure 1. The molecular structure (ORTEP plot, showing 50% probability ellipsoids), labeling scheme, and interatomic distances of the macrocyclic ligand, $C_{22}H_{24}N_4$.

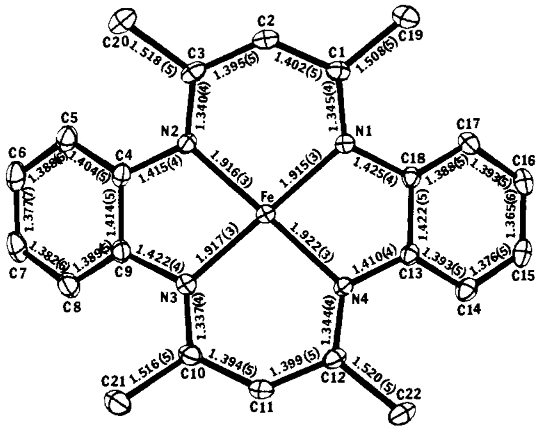


Figure 2. The molecular structure (ORTEP plot showing 20% probability ellipsoids), labeling scheme, and interatomic distances of the four-coordinate iron(II) macrocyclic complex, $Fe(C_{22}H_{22}N_4)$.

tomic angles are listed in Tables IV and V. In both structures the four nitrogen atoms are confined to a good plane with the largest deviations from the plane only 0.015 (3) Å for $[Fe(C_{22}H_{22}N_4)]$ and 0.013 (2) Å for $C_{22}H_{24}N_4$. However, the iron(II) is displaced significantly from the coordination plane, 0.114 Å, and the two amino hydrogen atoms are also directed out of the plane by approximately 0.1 Å.

Structure of the Free Ligand. The free ligand has the conjugated imine-enamine double-bond arrangement for the 2,4-pentanediiminato rings as depicted. Hydrogen bonds bridge the nitrogen atoms of the 2,4-pentanediiminato chelate rings. The hydrogen bond distances for H2-N1 and H4-N3 (Figure 1), 2.00 (3) and 2.01 (3) Å, respectively, are considerably shorter than the nonbonded N-H distances across the *o*-phenylenediamine rings, which average 2.43 (3) Å. The energy barrier of tautomerization to the degenerate form is low, since it merely involves movement of the protons by approximately 1 Å and rearrangement of the double bonds. Both processes are assisted by normal vibrational motions. Thus the observation of disorder involving the degenerate tautomeric forms, although unfortunate from the structural analysis viewpoint, is hardly surprising. The disorder is not present as a 50:50 mixture, however, because the slight rhombic distortion of the ligand, vide infra, probably results in a slightly lower lattice energy for one of the two orientations. This gives rise to one tautomeric form being present in the lattice to a substantially greater extent than the other, 75% vs. 25%, as indicated by the electron density associated with these nitrogen

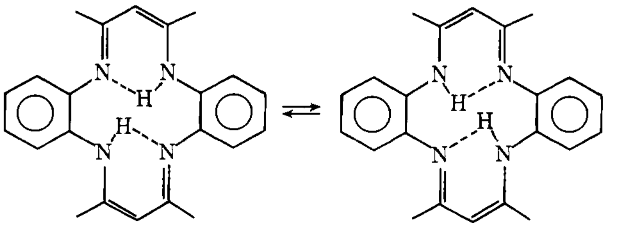


Table IV. Interatomic Angles (deg) for $[Fe(C_{22}H_{22}N_4)]$

Atoms	Angles	Atoms	Angles
N1–Fe–N2	95.9 (1)	C5–C4–N2	126.5 (3)
N1–Fe–N3	174.0 (1)	C9–C4–N2	113.9 (3)
N1–Fe–N4	84.7 (1)	C4–C5–C6	119.8 (4)
N2–Fe–N3	83.5 (1)	C5–C6–C7	120.6 (4)
N2–Fe–N4	172.3 (1)	C6–C7–C8	120.3 (4)
N3–Fe–N4	95.1 (1)	C7–C8–C9	120.5 (4)
C1–N1–C18	125.2 (3)	C8–C9–C4	119.6 (3)
C1–N1–Fe	123.9 (2)	C8–C9–N3	126.3 (3)
C18–N1–Fe	110.7 (2)	C4–C9–N3	113.4 (3)
C3–N2–C4	125.3 (3)	N3–C10–C11	121.2 (3)
C3–N2–Fe	123.2 (2)	N3–C10–C21	121.8 (3)
C4–N2–Fe	111.3 (2)	C11–C10–C21	116.8 (3)
C10–N3–C9	124.8 (3)	C10–C11–C12	129.7 (3)
C10–N3–Fe	123.6 (2)	N4–C12–C11	121.9 (3)
C9–N3–Fe	111.0 (2)	N4–C12–C22	122.5 (3)
C12–N4–C13	125.7 (3)	C11–C12–C22	115.4 (3)
C12–N4–Fe	123.4 (2)	C14–C13–N4	126.8 (3)
C13–N4–Fe	110.7 (2)	C14–C13–C18	118.3 (3)
N1–C1–C2	121.4 (3)	N4–C13–C18	114.6 (3)
N1–C1–C19	123.3 (3)	C13–C14–C15	121.3 (4)
C2–C1–C19	115.2 (3)	C14–C15–C16	120.3 (3)
C1–C2–C3	130.0 (3)	C15–C16–C17	120.1 (3)
N2–C3–C2	121.7 (3)	C16–C17–C18	120.7 (4)
N2–C3–C20	122.0 (3)	C17–C18–C13	119.1 (3)
C2–C3–C20	116.2 (3)	C17–C18–N1	126.7 (3)
C5–C4–C9	119.1 (3)	C13–C18–N1	113.9 (3)

Table V. Interatomic Angles (deg) for $C_{22}H_{24}N_4$

Atoms	Angle	Atoms	Angle
C1–N1–C18	125.7 (2)	C5–C6–C7	120.2 (2)
C1–N1–H1	129.2 (58)	C6–C7–C8	119.9 (2)
C18–N1–H1	104.5 (59)	C7–C8–C9	120.8 (2)
C3–N2–C4	129.1 (2)	N3–C9–C4	117.7 (2)
C3–N2–H2	115.0 (21)	N3–C9–C8	122.9 (2)
C4–N2–H2	115.9 (21)	C4–C9–C8	119.1 (2)
C9–N3–C10	125.1 (2)	N3–C10–C11	120.4 (2)
C9–N3–H3	128.8 (87)	N3–C10–C21	122.6 (2)
C10–N3–H3	106.0 (87)	C11–C10–C21	116.9 (2)
C12–N4–C13	129.8 (2)	C12–C11–C10	126.9 (2)
C12–N4–H4	119.5 (21)	N4–C12–C11	120.3 (2)
C13–N4–H4	110.7 (21)	N4–C12–C22	120.7 (2)
N1–C1–C2	119.5 (2)	C11–C12–C22	118.9 (2)
N1–C1–C19	123.7 (2)	N4–C12–C14	123.1 (2)
C2–C1–C19	116.7 (2)	N4–C12–C18	117.7 (2)
C1–C2–C3	127.7 (2)	C14–C12–C18	119.0 (2)
N2–C3–C2	120.3 (2)	C13–C14–C15	121.3 (2)
N2–C3–C20	120.8 (2)	C14–C15–C16	120.0 (2)
C2–C3–C20	118.8 (2)	C15–C16–C17	119.9 (2)
N2–C4–C5	124.0 (2)	C16–C17–C18	121.0 (2)
N2–C4–C9	117.1 (2)	N1–C18–C13	117.5 (2)
C5–C4–C9	118.7 (2)	N1–C18–C17	123.5 (2)
C4–C5–C6	121.2 (2)	C13–C18–C17	118.7 (2)

hydrogen atoms in the difference Fourier syntheses. This study cannot distinguish between the dynamic tautomeric process described and a static structure in which either long- or short-range order of the two ligand orientations is present.

Similar types of degenerate disorder are possible for the free-base porphyrin and phthalocyanine lattices. Crystal structures of a number of free-base porphyrins and phthalocyanine have been determined, with disorder involving the position of N-H's in some structures.[30] In others, ordered arrangements of the N-H's have been observed.[5,31]

Although this subtle disorder reduces the confidence that may be placed on the derived estimated standard deviations of bond angles and bond lengths, the overall structure appears to be reasonably accurate and may be relied upon to supply some pertinent details for comparison with the complexed form of the ligand. Note the excellent agreement between the chemically equivalent bond lengths in Figure 1.

The extent of delocalization through the 2,4-pentanediiminato linkages (Figure 1) approaches that observed in the dianionic metal complexes of this ligand (Figure 2). For example, there appears to be a genuine lengthening of the N(1)-C(1) and N(3)-C(10) C=N double bonds and shortening of the N(2)-C(3) and N(4)-C(12) amine single bonds. The average of the nominally single N-C bond lengths within the 2,4-pentanediiminato linkages are significantly shorter than the C-N single bonds of the *o*-phenylenediamine moieties, i.e., 1.343 (3) vs. 1.404 (2) Å.

Two facts indirectly lend support to the apparent delocalization, which probably is not as great as that indicated by refinement. First, considering only one 2,4-pentanediiminato fragment, hydrogen bonding of H(2) to N(1) should have the effect of partially equalizing the bond parameters associated with N(1) and N(2). The magnitude of this effect toward lengthening the imine bond and shortening the amine bond is probably small. However, a second effect making a much larger contribution to the delocalization arises from the planarity associated with the bonding of the amine nitrogen atoms. The refined amine hydrogen atom positions lie in the planes defined by C(3)-N(2)-C(4) to within experimental error. Thus the bonding involving the "amine" nitrogen atoms, N(2) and N(4), is not sp^3 but rather sp^2 hybridized with the lone-pair electrons occupying a "p" orbital perpendicular to the bonding plane, permitting extensive delocalization throughout the five-atom N(1)-C(1)-C(2)-C(3)-N(2) ring system.

The square-planar array of the four nitrogen atoms has a slight rhombic distortion with the "trans" nitrogen atoms separated by 3.755 and 3.885 Å for N(1)-N(3) and N(2)-N(4), respectively. Thus the nitrogen-to-center distance, Ct-N, of the neutral ligand is about 1.902 Å. However, the M-N distance expected for the dianionic form of the ligand is less than this value because increased conjugation and contraction is associated with the loss of the two amine protons. This ligand has a significantly smaller core size than the free-base porphyrins, 2.04 Å, and of saturated 14-membered rings, e.g., cyclam, which have ideal metal-nitrogen distances of about 2.07 Å.[3] These latter radii are in the range for unstrained metal-nitrogen distances for divalent first-row transition-metal complexes. Thus, the core size of 1.90 Å for $C_{22}H_{24}N_4$ is considerably less than optimal for high-spin divalent metals of the first transition series.

Structural Details of $[Fe(C_{22}H_{22}N_4)]$ and Comparison Studies. The Fe(II) is clearly four-coordinate; there are no atoms in the vicinity of the vacant axial coordination sites that could serve as axial ligands. The average Fe(II)-N distance, 1.918 Å, is only slightly longer than the N-Ct distance, 1.902 Å, of the neutral free ligand. The low-spin Fe(III)-phenyl complex of the same ligand has average Fe(III)-N distance of 1.908 Å,[17] whereas the average Fe(II)-N distance of six-coordinate, $S = 0$, complexes are longer, 1.937 Å.[32]

The Fe-N distances observed with the $C_{22}H_{22}N_4{}^{2-}$ ligand are significantly shorter than those associated with closely related porphyrin complexes, but interestingly, are comparable to those of phthalocyanine ligands. The average Fe(II)-N distance of the four-coordinate, $S = 1$, complex of tetraphenylporphyrin is 1.972 Å. The Fe-N distances of low-spin, $S = 0$, complexes of porphyrins are slightly longer, about 2.00 Å,[33] whereas high-spin Fe(II) and Fe(III) porphyrin complexes have significantly longer distances, 2.07-2.10 Å,[33-35] because of the substantial displacement (0.5 Å) of the metal from the porphyrin plane. Phthalocyanine ligands have a smaller N-Ct distance than porphyrins due to the substitution of four nitrogen atoms for carbon atoms in the 16-membered ring. The C-N bond lengths are shorter than the comparable C-C bonds in porphyrins and lead to a radial contraction of the ligand. Thus the average Fe-N distance, 1.926 Å, of the $S = 1$ four-coordinate phthalocyanine complex[23] is 0.056 Å shorter than for the analogous porphyrin complex. The shortest Fe-N bond

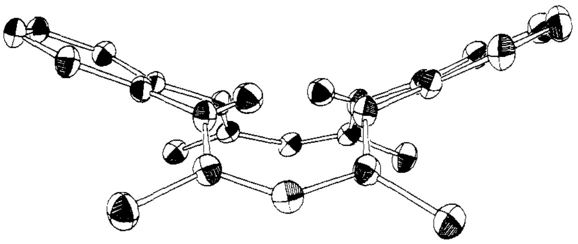


Figure 3. Side view of the free ligand illustrating the double-saddle shape of the ligand and the N-H hydrogen atoms which are directed out of the N_4 plane (ORTEP plot showing 50% probability ellipsoids).

Table VI. Selected Nonbonding Intramolecular Distances in the Two Structures

Atom designation	Distance, Å	
	$C_{22}H_{24}N_4$	$Fe(C_{22}H_{22}N_4)$
N1–N2	2.685 (3)	2.845 (4)
N2–N3	2.699 (3)	2.553 (4)
N3–N4	2.675 (3)	2.833 (4)
N4–N1	2.712 (3)	2.586 (4)
C5–C20	3.105 (3)	3.030 (6)
C8–C21	3.136 (3)	3.064 (6)
C13–C22	3.100 (3)	2.987 (6)
C17–C19	3.049 (3)	2.983 (6)
H2–N1	2.00 (3)	
H2–N3	2.45 (3)	
H4–N1	2.41 (3)	
H4–N3	2.01 (3)	

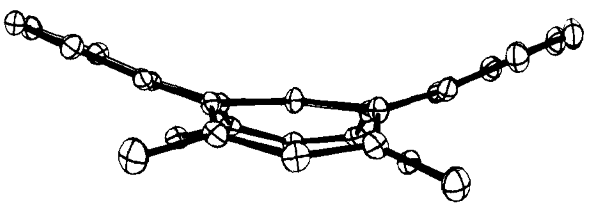


Figure 4. Side view of the four-coordinate iron(II) complex illustrating the slight displacement of the metal from the N_4 donor plane.

Table VII. Selected Dihedral Angles

Atoms defining planes	$[Fe(C_{22}H_{22}N_4)]$ angles, deg	$C_{22}H_{24}N_4$ angles, deg
C20–C3–N2 C3–N2–C4	13.9 (5)	5.1 (4)
C3–N2–C4 N2–C4–C5	31.3 (6)	41.7 (3)
C19–C1–N1 C1–N1–C18	5.9 (5)	3.4 (3)
C1–N1–C18 N1–C18–C17	28.3 (6)	43.4 (3)
C21–C10–N3 C10–N3–C9	13.1 (6)	5.6 (3)
C10–N3–C9 N3–C9–C8	37.7 (6)	54.3 (3)
C22–C12–N4 C12–N4–C13	5.1 (6)	0.4 (3)
C12–N4–C13 N4–C13–C14	28.7 (6)	43.7

lengths of macrocyclic complexes occur in a four-coordinate Fe(II) complex of an octaaza[14]annulene ligand, which has distances of 1.826 (4) and 1.846 (4) Å.[9] These distances are shorter than those of the Fe(II) dibenzo[14]annulene complex for reasons similar to those accounting for the smaller core size of phthalocyanine, e.g., the substitution of four nitrogen atoms for carbon atoms leads to ring contraction of the ligand.

A very noteworthy feature of our structure is the displacement of the iron atom 0.114 Å from the plane of the four nitrogen atoms. There is no evidence from either the anisotropic thermal parameters or the residual electron density on the final difference Fourier map to support a model in which the metal is disordered about either side of the coordination plane as observed for the four-coordinate Mn(II) tetraphenylporphyrin complex[36] and some high-spin iron(III)[35] and zinc(II) complexes[37] of tetraphenylporphyrin. This displacement of the Fe(II) from the N_4 coordination plane contrasts with four-coordinate Fe(II) porphyrins and phthalocyanines for which precise centering of the Fe(II) in the N_4 plane has been predicted[38] and experimentally verified.[22,23] The extent of the displacement of the Fe(II) from the N_4 coordination plane in the title complex is almost identical with that observed for the six-coordinate carbon monoxide complex with the same ligand, $[Fe(C_{22}H_{22}N_4)(CO)(NH_2NH_2)]$,[39] and is slightly less than the displacement of 0.23 Å observed for the five-coordinate iron(III)-phenyl complex.[17] In all cases, the iron atom is displaced to the same side of the ligand, that to which the benzenoid rings are tipped. These observations suggest that some structural features of the ligand itself are responsible for the directed displacement of the metal to one particular side of the plane. The explanation is provided in the analysis of the steric interactions and their influence on the deformations of the macrocyclic ligand (vide infra).

Comparison of the Two Structures. The major structural changes occurring within the ligand framework following complexation with Fe(II) are summarized as follows. First, the loss of the two N-H protons and insertion of the metal is accompanied by delocalization throughout the two six-membered 2,4-pentanediiminato chelate rings. Second, the distance between the N1-N2 and N3-N4 atom pairs increases from the average value of 2.680 Å for the free ligand to 2.839 Å for the Fe(II) complex, while the distance between the N2-N3 and N1-N4 pairs decreases from 2.706 Å for the free ligand to 2.569 Å for the Fe(II) complex. Note that for the free ligand (Table VI), the distances between all N atom pairs are roughly equal as one goes around the ligand and in the absence of any movement of the nitrogen atoms on complex formation, the N-Fe-N angles of the Fe(II) complex would all be approximately 90°. Thus, the structural changes leading to the smaller N-Fe-N angles involving the *o*-phenylenediamine portion of the molecule, 84.1°, as compared to those of the 2,4-pentanediiminato chelate rings, 95.5°, are not due to the smaller bite of the *o*-phenylenediamine ligand, but are necessary to redirect the nitrogen lone pairs toward the Fe(II) atom in the center of the ligand. Third, the average C-N distance of the *o*-phenylenediamine moieties increases on complex formation from a value of 1.404 Å for $C_{22}H_{24}N_4$ to 1.418 Å for the Fe(II) complex. Fourth, changes occur in the dihedral angles about various bonds throughout the structure (Table VII), with the most significant changes occurring in the torsional angles about the C-N bonds of the five-membered chelate rings. Fifth, the strong steric interactions between the methyl groups and the benzenoid rings increase upon complexation to Fe(II) and are accompanied by slight decreases in the average distances between the methyl groups and the benzene rings, from 3.099 Å in the free ligand to 3.016 Å for the metal complex.

Consequences of the Steric Interactions. The strain resulting from the steric interactions of the methyl groups with the benzenoid rings which leads to the saddle shape of the ligands is minimized primarily by angle deformations throughout the structures. However, it is apparent from examination of the dihedral angles in Table VII and Figures 3 and 4 that certain bonds are much more subject to angular distortions than others. The four C-N bonds linking the benzene rings to the 2,4-pentanediiminato chelate rings have the greatest amount of single-bond character. Consequently, the largest dihedral angles are expected to involve these bonds. The dihedral angles about these C-N bonds are significantly larger for the free

Table VIII. Angles between Selected Planes for $[FeC_{22}H_{22}N_4]$ and $C_{22}H_{24}N_4$

Defining planes N(1),N(2),N(3),N(4), and	$FeC_{22}H_{22}N_4$	$C_{22}H_{24}N_4$
N(2),C(4),C(9),N(3)	18.76	19.5
C(4),C(5),C(6),C(7),C(8),C(9)	26.19	24.1
N(1),C(18),C(13),N(4)	16.25	20.6
C(13),C(14),C(15),C(16),C(17),C(18)	21.22	25.1
N(1),C(1),C(3),N(2)	21.3	37.1
N(1),C(1),C(2),C(3),N(2)	25.19	32.0
N(3),C(10),C(12),N(4)	23.1	37.1
N(3),C(10),C(11),C(12),N(4)	23.71	36.5

ligand, 41.7 (3)–54.3 (3)°, than those observed for the iron(II) complex, 28.3 (6)–37.7 (6)°. It is this 10–17° increase in dihedral angles for the free ligand which gives it a much more pronounced saddle shape.

The smaller dihedral angles of the iron complex lead to greater steric compression of the methyl groups and the benzenoid rings. This strain is partially relieved by an increase in the torsional angles about the N–C bonds within the 2,4-pentanediiminato chelate rings. For example, the angle between the planes defined by atoms C20–C3–N2 and C3–N2–C4 is 13.9 (5)° for the iron complex, but only 5.1 (4)° for the free ligand.

The angles formed by the intersection of various least-squares planes of the chelate rings with the N_4 plane also illustrate the consequences of the steric interactions. In general, the intersection angles involving the six-membered 2,4-pentanediiminato chelate rings with the N_4 plane are significantly larger than those of the five-membered rings with the N_4 plane (Table VIII). Consider first the five-membered chelate rings and the attendant benzenoid rings for the Fe(II) complex. The planes defined by the four atoms of these chelate rings and the N_4 plane intersect at angles between 16.3 and 18.8°. The corresponding planes of the free ligand have intersection angles a few degrees larger, 19.5 and 20.6°. The benzene rings are planar, within experimental error, but are tipped upward an additional 5° relative to the attached five-membered chelate rings, yielding intersection angles of 21.2 and 26.2° for the N_4 and benzenoid planes of the Fe(II) complex and 24.1 and 25.1° for the free ligand. Next, consider the angles between planes defined by atoms of the 2,4-pentanediiminato rings and N_4 plane. Planes were calculated for the 2,4-pentanediiminato rings using only four atoms (omitting the methine carbon) and also for all five atoms to determine the effect of the methine carbon on the equation of the plane. The intersection angles of the four-atom chelate planes and the N_4 plane are much larger for the free ligand, 37.1°, than for the iron complex, 21.3 and 23.1°. The analogous angles using the five-atom planes are only slightly larger (Table VIII).

The unequal flexing of the two types of chelate rings, the *o*-phenylenediamine chelate rings and the 2,4-pentanediiminato rings, produces a very significant result. The lone electron pairs of the nitrogen atoms of the dianionic form of the ligand do not point directly toward the center of the plane, but are directed slightly out of the plane, to the side containing the benzenoid rings. Thus to maximize the overlap of ligand and metal orbitals, the metal must be displaced to one side of the N_4 plane.

The preferred diplacement of the metal out of the N_4 plane has important chemical consequences. The axial ligands for complexes of the type MLX_2 will no longer be chemically equivalent. In the extreme cases, this nonequivalence will result in the complete absence of an axial ligand yielding five-coordinate complexes. The formation of unusual five-coordinate Fe(II) and Fe(III) complexes with this ligand, e.g., $[Fe(C_{22}H_{22}N_4)(CO)]$[32] and $[Fe(C_{22}H_{22}N_4)(C_6H_5)]$,[17] may largely be due to the preferred displacement of the iron from the N_4 plane. The relative ease with which the ligand is stripped from the metal complexes (M = Fe(II), Co(II), Ni(II), and Cu(II)) with anhydrous HCl[40] is almost certainly a consequence of this displacement, since analogous complexes devoid of the four methyl groups are planar and much less susceptible to ligand stripping action of HCl.

The crystal structure of a nickel(II) complex of a very similar macrocyclic ligand, differing only in the absence of methyl groups C(20) and C(21), has been reported.[41] The average Ni–N distance in that complex is 1.85 Å, significantly shorter than the Ct–N distance of the free ligand, 1.902 Å. This Ct–N shortening is about that expected because of the increased conjugation accompanying the loss of two N–H protons upon coordination of the ligand.

One final aspect to be noted in both structures is the "locked" saddle-like conformation resulting from the intramolecular steric interactions. These lead to low and uniform thermal motions, at least in the direction perpendicular to the coordination plane, and are largely responsible for the clear resolution of the methyl group hydrogen atoms on the difference Fourier maps. In each structure, a slight oscillatory motion of the entire molecule about the rotation axis passing through the center of the ligand and normal to the N_4 plane is apparent from the increasing root-mean-square displacements observed for the peripherally located atoms (Figures 1 and 2).

Acknowledgment. This research was supported in part by the National Institutes of Health, Grant No. HL14827.

Supplementary Material Available: a listing of hydrogen atom coordinates and the observed and calculated structure factor amplitudes (49 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Address correspondence to this author at the Department of Chemistry, The Florida State University, Tallahassee, Fla. 32306.

(2) (a) V. L. Goedken and Y. A. Park, S. M. Peng, and J. Molin-Norris, *J. Am. Chem. Soc.*, **96**, 7893 (1974); (b) V. L. Goedken and Y. A. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975), and work submitted for publication.

(3) L. M. Martin, L. J. DeHayes, L. V. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974).

(4) V. L. Goedken and S. M. Peng, unpublished x-ray structure analysis of cyclam.

(5) M. L. Chen and A. Tulinsky, *J. Am. Chem. Soc.*, **94**, 4144 (1972).

(6) P. W. Codding and A. Tulinsky, *J. Am. Chem. Soc.*, **94**, 4151 (1972).

(7) V. L. Goedken and S. M. Peng, *J. Am. Chem. Soc.*, **95**, 5774 (1973).

(8) V. L. Goedken and S. M. Peng, *J. Chem. Soc., Chem. Commun.*, 258 (1975).

(9) R. G. Little, J. A. Ibers, and J. E. Baldwin, *J. Am. Chem. Soc.*, **97**, 7049 (1975).

(10) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).

(11) L. F. Lindoy and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4690 (1969).

(12) E. B. Fleischer and S. Hawkinson, *J. Am. Chem. Soc.*, **89**, 720 (1967); S. M. Nelson, P. Bryan, and D. H. Busch, *Chem, Commun.*, 641 (1966).

(13) E.-G. Jäger, *Z. Chem.*, **4**, 437 (1964).

(14) H. Hiller, P. Dimroth, and H. Pfitzner, *Justus Liebigs Ann. Chem.*, 717, 137 (1968).

(15) P. Chave and C. L. Honeybourne, *Chem. Commun.*, 279 (1969).

(16) E.-G. Jäger, *Z. Anorg. Allg. Chem.*, **364**, 177 (1969).

(17) V. L. Goedken, S. M. Peng, and Y. A. Park, *J. Am. Chem. Soc.*, **96**, 284 (1974).

(18) L. G. Bell and J. C. Dabrowiak, *J. Chem. Soc., Chem. Commun.*, 512 (1975).

(19) The room temperature magnetic moment, $\mu = 3.69\ \mu_B$ and its temperature independence down to liquid N_2 temperature is in agreement with an $S = 1$ spin state.

(20) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **94**, 4529 (1972).

(21) J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.*, **95**, 5757 (1973).

(22) J. P. Collman, J. L. Hoard, N. Kim, G. Long, and C. A. Reed, *J. Am. Chem. Soc.*, **97**, 2676 (1975).

(23) J. F. Kirner, W. Dow, and W. R. Scheidt, *Inorg. Chem.*, in press.

(24) S. M. Peng, Y.-A. Park, and V. L. Goedken, Abstracts, 170th Meeting of the American Chemical Society, Chicago, Ill., August, 1975, No. INOR 147.

(25) Y.-A. Park, M. C. Weiss, and V. L. Goedken, submitted for publication.

(26) P. G. Lenhert, *J. Appl. Crystallogr.*, **8**, 568 (1975).

(27) P. Corfield, R. Doedens, and J. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(28) Computations were performed by IBM 370 computer with the aid of the

following programs: Zalkin's FORDAP Fourier program, Busing and Levy's ORFFE function and error program, and Ibers NUCLS least-squares program. Plots of the structures were drawn with the aid of C. K. Johnson's ORTEP. Neutral atom scattering factors were taken from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968). Hydrogen atom scattering factors were taken, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962. Anomalous scattering corrections were applied to heavy atoms and were taken from D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(29) G. Germain and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **24**, 91 (1968).
(30) B. F. Hoskins, S. A. Mason, and J. C. B. White, *Chem. Commun.*, 554 (1969); M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Am. Chem. Soc.*, **86**, 1938 (1964); L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, **43**, 3100 (1965).
(31) S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **86**, 927 (1964).
(32) V. L. Goedken, S. M. Peng, J. Molin-Norris, and Y.-A. Park, *J. Am. Chem. Soc.*, in press.
(33) J. L. Hoard, *Science*, **174**, 1295 (1971).
(34) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2073 (1972).
(35) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967).
(36) B. Gonzalez, J. Kouba, S. Yee, C. Reed, J. Kirner, and W. R. Scheidt, *J. Am. Chem. Soc.*, **97**, 3247 (1975).
(37) M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Am. Chem. Soc.*, **89**, 1996 (1967).
(38) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965).
(39) V. L. Goedken, J. Molin-Case, and Y.-A. Whang, *J. Chem. Soc., Chem. Commun.*, 337 (1973).
(40) V. L. Goedken, Y.-A. Park, and M. Weiss, submitted for publication.
(41) F. Hanic, M. Handlovic, and O. Lindgren, *Collect. Czech. Chem. Commun.*, **37**, 2119 (1972).

Effects of Peripheral Steric Constraints and Metal Ion Size on the Structure of Three Five-Coordinate Macrocyclic Ligand Complexes of the Type $[M(C_{22}H_{22}N_4)X]$, M = Co(III), Fe(III), Mn(II); X = I, Cl, $N(C_2H_5)_3$

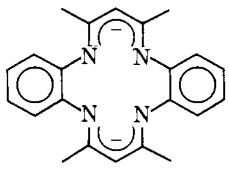
Marvin C. Weiss, Bruce Bursten, Shie-Ming Peng, and Virgil L. Goedken*[1]

Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637. *Received May 19, 1976*

Abstract: The crystal and molecular structures of three five-coordinate complexes of the dianionic macrocyclic ligand $C_{22}H_{22}N_4^{2-}$ have been determined from three-dimensional x-ray diffraction data. The complexes, together with their pertinent crystal data are: $[Co(C_{22}H_{22}N_4)I]\cdot CHCl_3$, space group $D_{2h}{}^{16}$-$Pnma$ with $a = 8.311$ (1), $b = 13.902$ (3), $c = 21.405$ (5) Å, $Z = 4$; $[Fe(C_{22}H_{22}N_4)Cl]\cdot CH_3CN$, space group $C_{2h}{}^5$-$P2_1/c$ with $a = 9.231$ (2), $b = 14.517$ (3), $c = 17.617$ (3) Å, $\beta = 100.10°$, and $Z = 4$; $[Mn(C_{22}H_{22}N_4)(N(C_2H_5)_3)]$, space group $C_{2h}{}^5$-$P2_1/c$ with $a = 11.275$ (8), $b = 17.27$ (13), $c = 14.998$ (10) Å, $\beta = 118.50°$, and $Z = 4$. The structures were refined by full-matrix least-squares techniques to conventional R values of 5.2% (2929 data with $F \geq 3\sigma(F)$), 6.4% (5907 data with $F \geq 3\sigma(F)$), and 5.6% (3883 data with $F \geq 3\sigma(F)$) for the Co, Fe, and Mn compounds, respectively. In each structure, the macrocyclic ligand has a pronounced saddle shape due to the steric interactions of the 2,4-pentanediiminato chelate ring methyl groups with the benzenoid rings. The metal is displaced from the macrocyclic N_4 donor plane; the displacement, a function of the metal–N_4 distance, varies from 0.24 Å for the Co(III) complex to 0.730 Å for the Mn(II) complex. The metal nitrogen distances vary from 1.901 Å for the Co(III) complex to 2.118 Å for the Mn(II) complex. The nature of the ligand distortions resulting from ligand steric interactions and the widely varying metal ion radii are presented along with comparisons drawn from closely related tetraphenylporphyrin structures.

The study of the crystal and molecular structures of transition metal complexes, especially those of synthetic and naturally occurring macrocyclic ligands, is necessary to fully understand their physical and chemical properties. The constraints placed on completely conjugated macrocyclic ring systems with respect to radial expansion and contraction of the N_4 donor core, together with the steric requirements of metal ions with varying radii, may lead to unusual coordination geometries and high reactivity.[2,8] Very flat, highly conjugated, four-coordinate macrocyclic complexes may have solid-state intermolecular interactions similar to those of four-coordinate dimethyl glyoxime complexes of Ni(II) and related complexes that become important in determining their physical and chemical properties.[3]

During a series of studies of the complexes of the 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato ligand (I), the macrocyclic ligand obtained by the nickel(II) template condensation of *o*-phenylenediamine with 2,4-pentanedione first described by Jäger,[4] a number of four-,[5] five-, and six-coordinate[6] complexes of divalent and trivalent transition metals with various ground-state electronic configurations were isolated and characterized.


I

The three complexes chosen for this study, $[Co(C_{22}H_{22}N_4)I]\cdot CHCl_3$, $[Fe(C_{22}H_{22}N_4)Cl]\cdot CH_3CN$, and $[Mn(C_{22}H_{22}N_4)N(C_2H_5)_3]$, are five-coordinate. This is an uncommon coordination number for Fe(III) and Mn(II), and especially rare for Co(III) complexes coordinated to nitrogen and halogen ligands. The Fe(III)[6a] and Mn(II)[7] complexes have normal high-spin, $S = \frac{5}{2}$, configurations, while the Co(III) complex has a rare intermediate $S = 1$ ground state with $\mu_{\mathrm{eff}} = 2.80\ \mu_B$.[8] The normal metal–nitrogen distances for these three metal ions having the ground-state configurations specified span a significant range, from about 1.90 Å for Co(III)[9] to approximately 2.27 Å for Mn(II).[10]

The ideal nitrogen-to-center (N–Ct) distance in the neutral ligand, $C_{22}H_{24}N_4$, is 1.902 Å.[5] The loss of two N–H hydrogens

Goedken et al. / Structure of Ligand Complexes of the Type $[M(C_{22}H_{22}N_4)X]$