STRUCTURAL RELATIONSHIPS BETWEEN THE HEMIPORPHYRAZINE MACROCYCLIC LIGAND AND ITS METAL COMPLEXES. I.

Saddle Shaped Neutral Ligand Hydrate, $C_{26}H_{16}N_8 \cdot H_2O$, and Nickel Complex, $[Ni(C_{26}H_{14}N_8)]$

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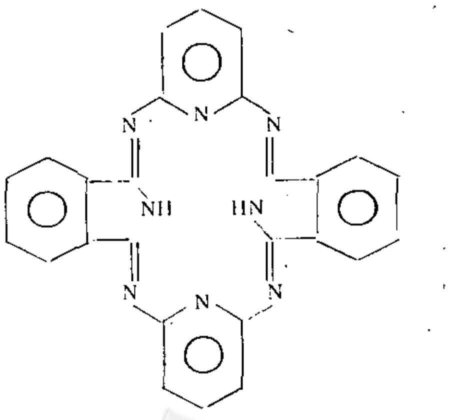
Key Word Index—Crystal structure; hemiporhyrazine; macrocyclic ligand and nickel complex.

Crystal and molecular structures of the neutral ligand hydrate, $C_{26}H_{16}N_8 \cdot H_2O$, and the diamagnetic nickel(II) complex, $[Ni(C_{26}H_{14}N_8)]$, have been determined by three-dimensional X-ray crystallography. Pertinent data are: $C_{26}H_{16}N_8 \cdot H_2O$, Pnmm with $Z=2$, $a=4.6142(3)$, $b=14.7687(7)$, $c=15.0650(5)$ Å, $R=0.068$; $R_w=0.038$; $[Ni(C_{26}H_{14}N_8)]$, $I2/c$ with $Z=4$, $a=22.0437(11)$, $b=3.7637(4)$, $c=23.4742(11)$ Å, $\beta=92.7(1)°$, $R=0.039$, $R_w=0.025$. The overall conformations of the neutral ligand and the Ni(II) complex are similar, both have a pronounced saddle shape. The Ni(II)-N bond distances in the Ni-complex are 1.861(2) and 1.998(2) Å. The distances from nitrogen atoms to the center of the ring in free ligand are 2.020(3) and 2.220(3) Å, which are significantly longer than those of Ni(II) complex. A detailed comparison about the core size with similar ligand is presented.

Conjugated macrocyclic compounds play significant roles in a number of important biological processes[1], and there has been a resurgence of interest in electrical properties of such compounds[2]. The macrocyclic ligand I, 5,25:12,18-diimino-7,11:20,24-dinitrilo dibenzo [*c*, *n*] [1,6,12,17]-tetrazadocosine (abbreviated as Hemiporphyrazine hpH_2), is obtained by the nontemplate condensation of *o*-phthalonitrile and 2,6-diaminopyridine.



I, hpH_2

It is believed to be a suitable parent system for biochemical and electrical studies[3,4]. Like the azaporphins, it contains a crossconjugate macrocyclic system and consists of four donor nitrogen atoms confined to a square-planar configuration, a completely conjugated system of double bonds, and inner 16-membered ring, two negative charges associated with the complex form of the

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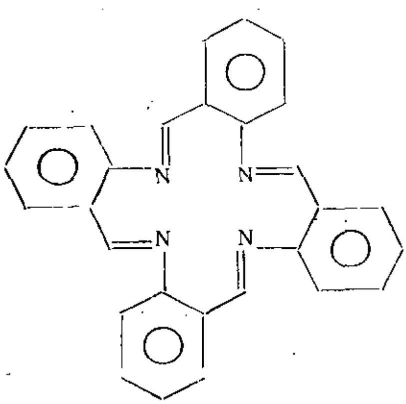
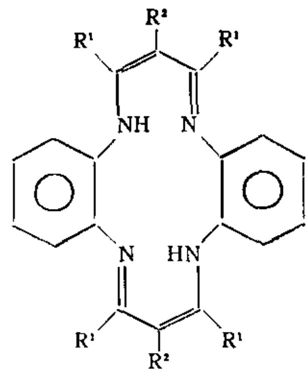
ligand. The only difference is its two pyridine rings instead of the pyrrole rings found in azaporphin.

The free ligand I and its metal complexes were first synthesized by Elvidge and Linstead[5]. Smirnov[6] reported the thermodynamic and kinetic stabilities of these complexes. Honeybourne[7] did some molecular orbital calculations hpH_2 ligand. The crystal and molecular structures of the free ligand[8] and its Ni(II) (Ni*hp*[9] and Ni*hp*$(py)_2$)[10], Ge(IV) (Ge*hp*F_2)[11], Fe(IV) $(FeOhp)_x$[12] derivatives have been reported.

The Ni*hp* were reinvestigated because the previous structure[9] was solved in projection using two-dimensional film data. The limited number of upper level data prevented conclusive results regarding the extent of non-planar distortion and comparison of certain bond lengths which are important in deducing the extent of aromaticity of *hp* ligand in the complex. Structural analysis of the free ligand hydrate, $hpH_2 \cdot H_2O$, was also undertaken to facilitate the direct comparison and evaluation of the structural changes which occur within the ligand upon complexation. A detailed comparison of the structural parameters with those of fully conjugated macrocyclic system such as 16-membered porphyrins[13], phthalocyanines[14], TAAB[15], and 14-membered TADA *etc.*[16,17] will be presented.



II, TAAB



III, TADA

EXPERIMENTAL

$hpH_2 \cdot H_2O$ was prepared according to the method of Honeybourne[18]. Yellow crystals suitable for X-ray diffraction studies were grown by slow cooling of their saturated nitrobenzene solution for three days. It crystallized in space group Pnmm. The refined cell constants, other crystal data and data collection details for the ligand hydrate together with Ni complex are in Table 1. The structure was solved by the direct method using MULTAN. The correct E map reveals all the non-hydrogen atoms with the molecular symmetry C_{2v} coincide with the *mm* symmetry at $y=1/4$, $z=1/4$. The oxygen atom at the intersection of the two planes was first ignored for the pile up density at the symmetry site. It was then found to be crucial for the convergence of the least-squares process. All the hydrogen atoms were found in the difference Fourier map after the isotropic refinement. The final agreement indices are 6.8% and 3.8% for R and R_w respectively with 908 observations and 101 variables. The final difference Fourier map was featureless with residual electron density less than $0.3\,e/\text{Å}^3$. The positional and thermal parameters are listed in Table 2.

Ni*hp* complex was also prepared according to the ref. 18. Crystals suitable for X-ray diffraction studies were grown by slow cooling of their saturated nitrobenzene solution for two days. It

Table 1. Crystal Data and Data Collection Details

Compound	$hpH_2 \cdot H_2O$	Ni*hp*
Mol. wt.	458.46	497.13
Space group	Pnmm	I2/*c*
Cell constants a (Å)	4.6142(3)	22.0437(11)
b	14.7687(7)	3.7637(4)
c	15.0650(5)	23.4742(11)
β (deg)		92.7(1)
No of reflections used to determine cell constants	25	23
Z	2	4
Crystal dimension (mm^3)	.6x.1x.1	.7x.1x.05
ρ calcd. (g/cm^3)	1.48	1.70
ρ exptl.	1.46(2)	1.68(2)
Diffractometer	CAD4	CAD4
Radiation (λ, Å)	Cu K_α (1.5418)	Cu K_α (1.5418)
Method for data collection	θ-2θ scan	θ-2θ scan
Scan speed	6.67-1 deg/*min*	6.67-1 deg/*min*
2θ limit	4-140°	4-140°
No of unique data collected	1055	1854
No of data used in refinement ($I>2\sigma(I)$)	908	1566
No of variables	101	188
Final *R*	6.8	3.9
R_w	3.8	2.5
Max. residual electron density (e/A^3)	0.3	0.4

crystallized in a monoclinic space group I2/*c*. The refined cell constants, other crystal data for the Ni*hp* complex are in Table 1. The atoms of the inner sixteen-membered ring were located in an origin-removed, sharpened Patterson synthesis with the knowledge of the location of Ni atom being at the two fold. Subsequent refinements and the difference Fourier syntheses led to the location of all non-hydrogen atoms. The struture was refined by least-squares techniques. The usual procedures, computer programs, atomic scattering factors, and anomalous terms were employed[19]. The final three least-square cycles varied positional and anisotropic thermal parameters of all nonhydrogen atoms and positional and isotropic thermal parameters of hydrogen atoms. At convergence, the conventional and weighted *R* valuse were 3.9% and 2.5% for 1566 observations and 188 variables. The final difference Fourier map was featureless with residual electron density around nickel atom. The final positional and thermal parameters are listed in Table 3.

RESULTS AND DISCUSSION

It is very fortunate that both macrocyclic metal complex and its free ligand can be studied to facilitate direct comparison and evaluation of the structural changes which occur within the ligand upon coordination. The crystal structures of the free ligand hydrate, $hpH_2 \cdot H_2O$, and the pseudo isomorphous Ni(II) complex, Ni*hp*, of the dianionic form of the ligand

Table 2. Atomic Positional and Thermal Parameters of $(C_{26}H_{18}N_8) \cdot H_2O$

Atom	X^a	Y	Z	$U_{11}^{a,b}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	0.6976(11)	0.2500	0.2500	2.6(3)	4.9(3)	4.8(4)	0.0	0.0	0.0
C1	0.2843(7)	0.4285(2)	0.1736(2)	3.2(2)	3.0(2)	3.4(2)	0.6(2)	−0.2(2)	0.3(2)
C2	0.0921(7)	0.3277(2)	0.0694(2)	3.3(2)	3.9(2)	2.3(2)	−0.7(2)	0.3(2)	−0.1(2)
C9	0.8136(9)	0.6232(2)	0.2031(2)	5.5(3)	3.3(2)	4.5(2)	−0.7(2)	0.5(2)	0.5(2)
C10	0.6439(9)	0.5621(3)	0.1555(2)	4.5(2)	3.3(2)	3.4(2)	0.3(2)	0.0(2)	0.6(2)
C11	0.4733(7)	0.5030(2)	0.2036(2)	3.0(2)	3.0(2)	3.1(2)	0.1(2)	−0.3(2)	0.0(2)
C12	−0.1332(8)	0.3330(2)	0.0076(2)	3.3(2)	4.9(2)	2.7(2)	−0.1(2)	−0.3(2)	0.1(2)
C13	−0.2489(12)	0.2500	−0.0214(3)	3.4(4)	6.6(4)	2.6(3)	0.0	0.2(3)	0.0
N1	0.1750(9)	0.3868(3)	0.2500	3.7(3)	3.4(3)	2.4(2)	−0.4(2)	0.0	0.0
N2	0.2376(7)	0.4085(2)	0.0921(2)	4.1(2)	3.4(2)	2.6(2)	0.2(2)	−0.2(2)	0.3(1)
N3	0.2040(9)	0.2500	0.1026(2)	3.0(2)	3.2(2)	2.4(2)	0.0	−0.3(2)	0.0
H1	0.023 (11)	0.335 (3)	0.250	4.0					
H2	0.551 (10)	0.250	0.286 (3)	4.5					
H9	0.935 (8)	0.667 (2)	0.179 (2)	5.0					
H10	0.630 (8)	0.559 (3)	0.092 (2)	4.5					
H12	−0.218 (9)	0.401 (2)	−0.012 (2)	4.5					
H13	−0.450(11)	0.250	−0.062 (3)	4.5					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\times 10^{-2}]$.

[b] The form of isotropic thermal ellipsoid is $\exp[-8\pi^2U\sin^2\theta/\lambda^2)\times 10^{-2}]$.
$U_H=U_{Attack}+1$ and are fixed in the refinement.

are closely related and have similar packings and molecular geometries. Both the free ligand hydrate and its four coordinated Ni(II) complex have column-like packing and markedly nonplanar saddle shape molecules which are shown in Figs. 1 to 6. The hydrogen bonding in the $hpH_2 \cdot H_2O$ plays an important role in packing the molecules in a column as shown in Fig. 7. The water molecule is located between the centers of two neighboring macrocyclic ligands with its two hydrogen atoms hydrogen-bonded to two pyridine nitrogen atoms of the lower *hp* molecule and its oxygen lone pairs toward the two N-H of the upper *hp* molecule. Thus the hydrogen bonds are, through the entire column, along $\vec{a}$ axis in $hpH_2 \cdot H_2O$.

The ligand hpH_2 has the structure of a fully conjugated double bond arrangement which contains two pyridine rings and two benzenoid rings connected by four imine double bonds as depicted in I. The

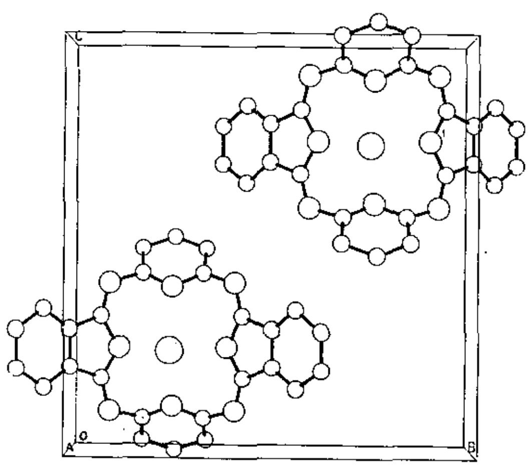


Fig. 1. View down the $\vec{a}$ crystal axis illustrating the arrangement of the $hpH_2 \cdot H_2O$ molecules in the unit cell.

Table 3. Atomic Positional and Thermal Parameters of Ni*hp*

Atom	X	Y	Z	Biso	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.0	0.08068(19)	0.2500	2.19(3)	2.39(3)	3.47(4)	2.44(3)	0.00	0.02(2)	0.00
N1	0.05217(7)	0.1209 (6)	0.31439(7)	2.08(11)	2.24(10)	3.76(14)	1.92(9)	0.03(11)	−0.16(8)	−0.07(11)
N2	0.15027(8)	0.0476 (6)	0.27594(7)	2.41(12)	2.27(10)	4.24(15)	2.63(10)	0.09(12)	−0.12(8)	−0.08(12)
N3	0.07088(8)	0.0297 (6)	0.20063(7)	2.09(11)	2.27(10)	3.34(14)	2.34(10)	−0.03(10)	0.15(8)	0.02(10)
N4	-0.01693(8)	0.1654 (6)	0.38953(7)	2.49(12)	2.72(11)	4.33(16)	2.41(10)	0.17(11)	0.07(8)	−0.19(11)
C1	0.11467(10)	0.1512 (7)	0.31446(9)	2.22(13)	2.34(12)	3.43(17)	2.67(12)	0.02(13)	−0.32(10)	0.59(13)
C2	0.12843(9)	-0.0575 (7)	0.22305(9)	2.15(11)	2.50(12)	2.77(14)	2.90(13)	−0.30(13)	−0.00(10)	0.37(13)
C3	0.06412(10)	0.0122 (7)	0.14209(9)	2.20(14)	2.61(12)	3.34(18)	2.39(12)	−0.67(13)	0.11(9)	0.11(13)
C8	0.03458(10)	0.2191 (7)	0.36796(9)	2.15(12)	3.12(13)	3.05(16)	2.00(12)	0.39(13)	−0.25(10)	−0.03(12)
C9	0.20196(10)	0.5403 (8)	0.44304(10)	2.89(14)	3.45(14)	3.93(18)	3.59(14)	−0.82(15)	−1.04(11)	0.29(15)
C10	0.19566(10)	0.3976 (8)	0.38877(9)	2.66(13)	3.02(13)	3.77(17)	3.32(14)	−0.15(15)	−0.63(11)	0.26(15)
C11	0.13745(10)	0.5032 (7)	0.36897(9)	2.22(13)	2.93(13)	3.23(16)	2.28(12)	0.01(13)	−0.42(10)	0.35(12)
C12	0.17082(10)	-0.2344 (8)	0.19088(10)	2.56(14)	2.46(13)	3.73(17)	3.52(14)	0.28(13)	0.41(11)	0.02(14)
C13	0.15904(11)	-0.2925 (8)	0.13389(10)	2.77(14)	3.05(14)	3.66(17)	3.83(15)	−0.10(14)	0.95(12)	−0.34(14)
C14	0.10677(10)	-0.1536 (8)	0.10895(9)	2.61(15)	3.15(14)	4.09(19)	2.69(13)	−0.57(14)	0.44(10)	−0.46(14)
C24	0.08763(10)	0.3574 (7)	0.40195(9)	2.27(13)	3.07(13)	3.15(17)	2.42(12)	0.04(13)	−0.47(10)	0.07(13)
C25	0.09369(11)	0.5003 (8)	0.45596(9)	2.76(16)	3.89(14)	4.18(20)	2.43(12)	−0.02(14)	−0.24(11)	−0.24(14)
C26	0.15202(11)	0.5922 (8)	0.47613(9)	2.93(13)	4.77(16)	3.74(17)	2.61(13)	−0.28(17)	−0.93(11)	−0.27(15)
H9	0.2417 (8)	0.611 (7)	0.4585 (8)	3.4 (6)	4.3 (7)					
H10	0.2308 (9)	0.366 (7)	0.3637 (8)	3.5 (6)	4.4 (7)					
H12	0.2084 (9)	-0.304 (6)	0.2114 (8)	3.6 (6)	4.6 (8)					
H13	0.1871 (8)	-0.432 (7)	0.1117 (8)	3.3 (6)	4.1 (7)					
H14	0.0972 (8)	-0.167 (6)	0.0674 (8)	2.6 (5)	3.3 (7)					
H25	0.0572 (9)	0.539 (7)	0.4789 (8)	3.6 (6)	4.5 (7)					
H26	0.1584 (9)	0.695 (6)	0.5143 (8)	3.4 (6)	4.3 (8)					

* The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\times10^{-2}]$.

* The form of isotropic thermal ellipsoid is $\exp[-8\pi^2U\sin^2\theta/\lambda)\times10^{-2}]$.

average bond distances of a quarter of the molecules for free ligand hydrate and the ligand of Ni*hp* complex are listed in Table 4. The benzene ring formed by C11-C10-C9-C26-C25-C24 six atoms are aromatic in both free ligand hydrate and Ni*hp* complex. The bonds C11-C1 (1.475(5) in $hpH_2\cdot H_2O$, 1.475(3) in Ni*hp*) which connect the benzene ring and the inner macrocyclic ring have a single bond character. The bonds C1-N2, 1.281(4) in $hpH_2\cdot H_2O$ and 1.283(3) in Ni*hp*, are also equal and have a double bond character. Small differences in two structures are shown in C1-N1 (1.399(4) in $hpH_2\cdot H_2O$, 1.383(3) in Ni*hp*), N2-C2 (1.411(4) in $hpH_2\cdot H_2O$ and 1.372(3) in Ni*hp*), C2-N3 (1.353(4) in $hpH_2\cdot H_2O$ and 1.383(3) in Ni*hp*), C12-C13 (1.407(5) in $hpH_2\cdot H_2O$ and 1.370(3) in Ni*hp*). These differences may be rationalized by the small contribution of the resonance form, **IV**, in Ni*hp* complex.

This is also the case in other four metal complexes, [M*hp*H_2O], M=Mn(II), Co(II), Cu(II), Zn(II)[20].

Other interesting differences in two structures and anhydrous free ligand[20] are the tilt angles between various least-squares planes (*e.g.* benzene, pyridine planes) and the plane formed by four nitrogen atoms in the coordination sphere (Table 5). Anhydrous free ligand is planar it is easily understood that the fully conjugated

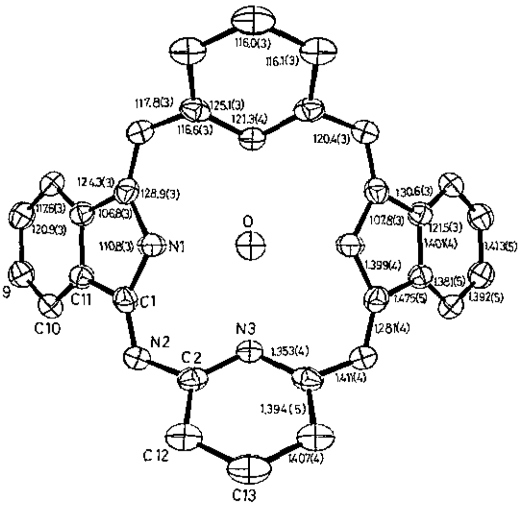


Fig. 2. Molecular structure (ORTEP plot), labeling scheme, and selected interatomic distances and angles of the $hpH_2 \cdot H_2O$ molecule.

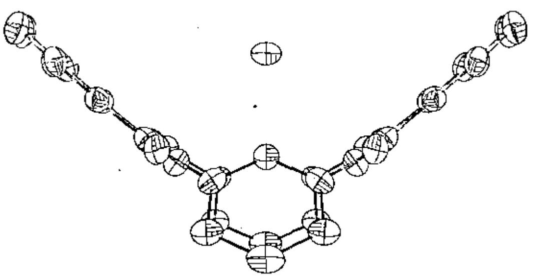


Fig. 3. Side view of the ligand hydrate illustrating the saddle shape of the ligand.

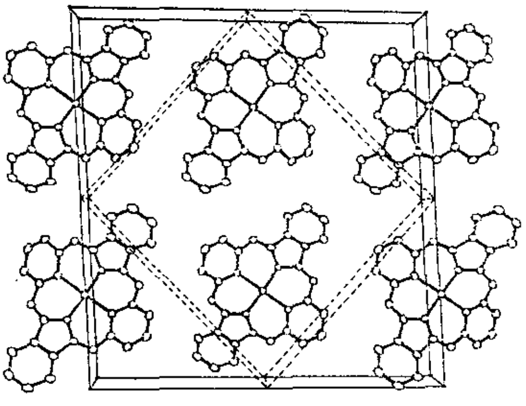


Fig. 4. View down the $\vec{b}$ crystal axis illustrating the arrangement of the Ni*hp* molecules in the unit cell, the dash line illustrating the pseudo-isomophous cell with $hpH_2 \cdot H_2O$.

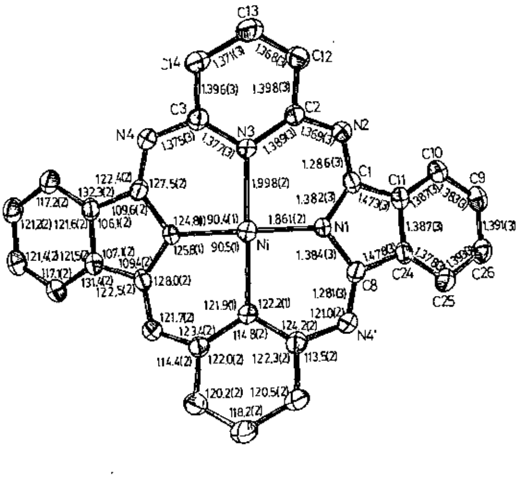


Fig. 5. Molecule structure (ORTEP plot), labeling scheme, and selected interatomic distances and angles of the Ni*hp* molecule.

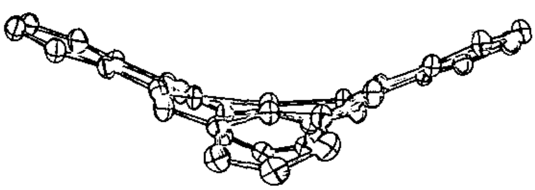


Fig. 6. Side view of the four coordinate nickel (II) complex illustrating the saddle shape of the molecule.

Table 4. Average Bond Distances of $[Ni(C_{26}H_{14}N_6)]$ and $(C_{26}H_{16}N_6) \cdot H_2O$

Atoms	Type of bond	$[Ni(C_{26}H_{14}N_6)]$ (Å)	$(C_{26}H_{16}N_6) \cdot H_2O$ (Å)
C(9)-C(9′)	C-C bonds in benzene ring	1.391(3)	1.413(5)
C(9)-C(10)		1.388(3)	1.392(5)
C(10)-C(11)		1.382(3)	1.381(5)
C(11)-C(11′)		1.387(3)	1.401(4)
C(11)-C(1)	C-C single bond	1.475(3)	1.475(5)
C(1)-N(2)	imine double bond	1.283(3)	1.281(4)
C(1)-N(1)	C-N single bond	1.383(3)	1.399(4)
N(2)-C(2)	C-N single bond	1.372(3)	1.411(4)
C(2)-N(3)	C-C and C-N bonds in pyridine ring	1.383(3)	1.353(4)
C(2)-C(12)		1.397(3)	1.394(5)
C(12)-C(13)		1.370(3)	1.407(4)

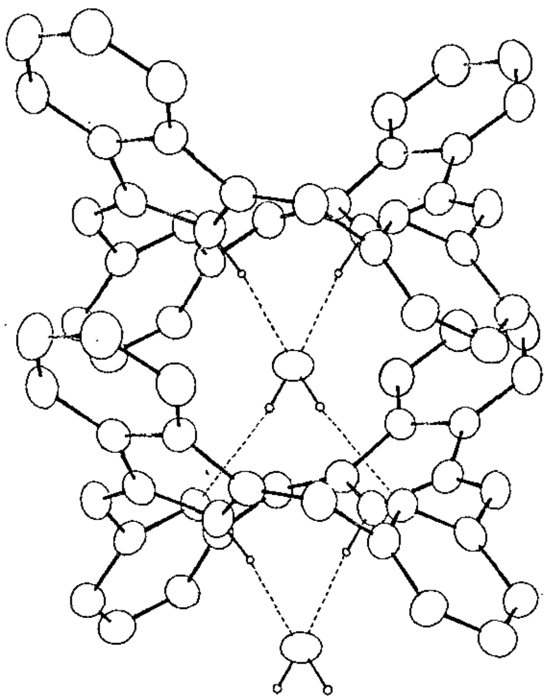
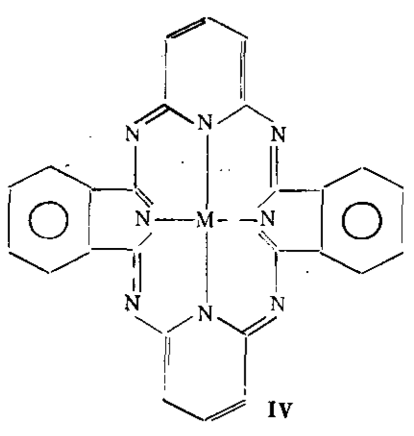


Fig. 7. View between the crystal $\vec{b}$, $\vec{c}$ axes illustrating the hydrogen bonds between the water molecules and macrocyclic ligands.



IV

macrocycle will favor the planar conformation. In the case of $hpH_2\cdot H_2O$, the saddle shape of macrocycle comes mainly from the hydrogen bonding between the water molecule and the macrocyclic ligand as described above. But Ni*hp* complex maintains the saddle shape conformation as the consequence of "core contraction" due to the low-spin Ni (II) complex. The

Table 5. Selected Dihedral Angles Between the Least-Squares Planes* in $H_2hp\cdot H_2O$ and Ni*hp*

Planes	Dihedral Angle	
	$H_2ph\cdot H_2O$	Ni*hp*
Plane 1-Plane 2	48.2°	14.0°
Plane 1-Plane 3	38.7°	25.2°
Plane 1-Plane 4	41.5°	25.5°
Plane 3-Plane 4	2.8°	1.1°

* Plane 1 is defined by the four coordinated nitrogen atoms.
Plane 2 is defined as the six membered pyridine ring.
Plane 3 is defined as the five membered pyrole ring.
Plane 4 is defined as the six membered benzene ring.

average core sizes for the *hp* ligand are 2.12 Å for ligand hydrate and 2.08 Å for anhydrous ligand. However, the ideal low-spin Ni-N distances are about 1.93 Å which is 0.15 to 0.19 Å shorter than those in free ligand. The shortening of Ni-N distances in the Ni*hp* complex causes the deformation of planar ligand to saddle shape conformation. On the contrary, for some high-spin metal complexes (M=Mn (II), Co(II), Cu(II), Zn(II)), the average M-N distances are about the same as the core size and they all form planar complexes[20].

Considering the four nitrogen atoms in the free macrocyclic ligand hydrate as in a plane, they form an elliptical core with the "trans" nitrogen atoms separation of 4.040(10) and 4.448(10) Å for N1-N1′ and N3-N3′ respectively. Thus the average nitrogen atom to the center of the ring distance, Ct-N, is 2.120 Å. This average core size for $hpH_2\cdot H_2O$ is larger than for those in porphyrin (2.04)[13] and phthalocyanine (1.91)[13,14]. It is even slightly larger than the size of high-spin divalent ions of the first row transition metals. But hpH_2 forms diamagnetic complex with Ni(II) with Ni-N distances 1.861(2) and 1.998(2) Å. It has about 0.2 Å "core contraction" from ligand hydrate to its Ni-complex.

The average Ni-N distance 1.930 Å in the Ni*hp* complex is comparable to those in other low-spin macrocyclic Ni complexes (Table 6)[13~17,21]. In general, the Ni-N

Table 6. Comparison of Coordination Parameters for Completely Conjugated Macrocyclic Ligand and Their Ni Complexes

Compound	$hpH_2 \cdot H_2O$	hpH_2	Nihp	NiTAAB[a]	H_2Por[b]	Ni(Por)[b]
Ni-N distances or Ct-N distances	2.020(3) 2.220(3)	1.907(6) 2.245(6)	1.861(2) 1.998(2)	1.90(2)	2.04	1.95
Average	2.120(3)	2.076(6)	1.930(2)	1.90(2)	2.04(2.01)	1.95(1.93)
$N-N_{cis}$ distances	3.003(3)	2.944(6) 2.947(6)	2.740(2) 2.743(2)	2.69 2.69	2.88	2.76
Average	3.003	2.945	2.741		2.88(2.84)	2.76(2.73)
Size of inner membered ring	16	16	16	16	16	16
No. of Nitrogen atoms in inner ring	8	8	8	4	4	4
Overall conformation of Macrocylic ligand	Saddlelike	Planar	Saddlelike	Saddlelike	Planar	Planar
Angles between plane and N_4 plane	40° 48°	—	14° 25°	24°	—	—
Reference	This work	next paper	This work	15	13	13

Compound	H_2Pc[c]	Ni(Pc)[c]	H_2Me_4TADA[d]	Ni(Me_4TADA)	Ni(OADA I)[e]	Ni(OADA II)[e]
Ni-N distances or Ct-N distances	1.92	1.83	1.878(3) 1.942(3)	1.866(3)	1.832(5)	1.784(1) 1.820(1)
Average	1.92	1.83	1.910(3)	1.866(3)	1.832(5)	1.802(1)
$N-N_{cis}$ distances	2.65 2.76	2.56 2.60	2.680 2.706	2.521 2.752	2.475 2.693	2.428 2.644
Average	2.70	2.58	2.693	2.634	2.584	2.536
Size of inner membered ring	16	16	14	14	14	14
No. of Nitrogen atoms in inner ring	8	8	4	4	8	8
Overall conformation of Macrocylic ligand	Planar	Planar	Saddlelike	Saddlelike	Planar	Planar
Angles between plane and N_4 plane	—	—	25° 34°	25° 27°	—	—
Reference	13,14	13,14	16	17	21	21

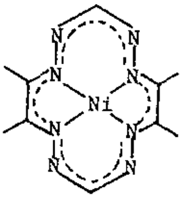
a. The ligand is II

b. Por=Porphyrin, average of various Por; ( ) is OEP.

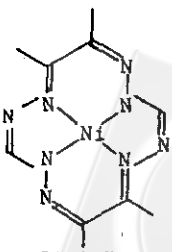
c. Pc=Phthalocyanine

d. The ligand is III and $R_1=R_3=CH_3$, $R_2=H$.

e. NiOADA I and NiOADA II are isomer and have formula $Ni(C_{10}H_{14}N_8)$, their structure are following:



OADA I



OADA II

distances (or core size of marocycle) of 14-membered ring complexes are shorter than those of 16-membered ring complexes. The more nitrogen atoms the macrocycles have, the shorter the Ni-N distances (or core size) are. A similar trend is also observed in the $N-N_{cis}$ distances (Table 6) of the five- and six-membered chelate rings. Neverthless, the hpH_2 (16-membered ring with eight nitrogen atoms) has a larger core size than that of porphyrins (16-membered ring with four notrogen atoms) which is probably attributable to the localized electronic structure and unsymmetrical geometry of the hpH_2 macrocycle.

CONCLUSION

The molecular and crystal structure of $hpH_2 \cdot H_2O$ manifest the localized electronic structure of $hpH_2 \cdot H_2O$ and the saddle shape conformation of ligand hydrate as a result of the hydrogen bonding between the water molecules and the macrocyclic ligand. Upon complexation of Ni(II) ion, the hydrogen atoms of the pyrole nitrogen atoms were removed and the ligand became of dianion form hp^{2-}. The bond pattern and conformation of ligand in the complex show no significant changes from those in free ligand hydrate. This indicates that other resonance forms of the ligand anion may make only small contributions to the electronic structure. The tilt angles of the saddle shape of the ligand anion were smaller in the complex than in free ligand hydrates (see Table 6). These two structures are also comparable with other macrocycles and their Ni(II) complexes as shown in Table 6.

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