

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

Planar Neutral Ligand, $C_{26}H_{16}N_8$, and Four Isomorphous Metal Complexes, $[M(C_{26}H_{14}N_8)(H_2O)]$, $M=Mn(II), Co(II), Cu(II), Zn(II)$

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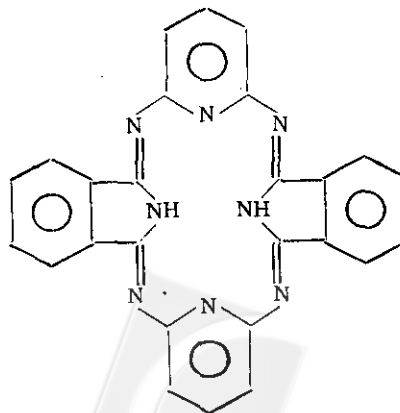
Key Word Index—Crystal structure; hemiporphyrzine; macrocyclic ligand and manganese, cobalt, copper, zinc complexes.

Crystal and molecular structures of the planar neutral ligand, $C_{26}H_{16}N_8$, and the four isomorphous five-coordinated metal complexes, $[M(C_{26}H_{14}N_8)(H_2O)]$, $M=Mn(II), Co(II), Cu(II), Zn(II)$, have been determined from three-dimensional X-ray diffraction data. The free ligand hpH_2 , $C_{26}H_{16}N_8$, belongs to the $P 2_1/c$ space group with $Z=2$, $a=4.142(3)$, $b=23.736(6)$, $c=10.338(3)$ Å, $\beta=94.66(6)^\circ$. The metal complexes monohydrate $Mhp \cdot H_2O$ all belong to the orthorhombic $Pcab$ space group with $Z=8$. The dimensions are roughly $8.8 \times 19.3 \times 23.7$ Å³. In each structure, the macrocyclic ligand has an almost planar conformation which differs from the saddle shaped ligand hydrate ($hpH_2 \cdot H_2O$) and the nickel complex $[Nihp]^{19}$. The distances from the center of the macrocyclic ring to the nitrogen atom of the free ligand are 1.907(6) and 2.245(6) Å. The coordination geometry in these four complexes is square pyramidal with a water molecule as an axial ligand. The bond distances of $M(II)-O(H_2O)$, $M(II)-N1$ (imine), $M(II)-N3$ (pyridine) are: 2.19(1), 2.00(2), 2.27(2) Å respectively for the manganese complex; 2.08(1), 1.97(1), 2.23(1) Å for the cobalt complex; 2.33(1), 1.92(1), 2.18(1) Å for the copper complex; 2.110(5), 1.964(6), 2.252(6) Å for the zinc complex. The variation of metal-ligand distances can be correlated to the metal d orbital occupancy. A comparison with similar ligands will be presented.

The study of the crystal and molecular structures of transition metal complexes, especially those of synthetic and naturally occurring macrocyclic ligands; is necessary in order to fully understand their physical and chemical properties¹⁻³. Several important structural questions are associated with macrocyclic complexes: (1) the sizes and shapes of the cores of the macrocyclic ligands, (2) the extent of the delocalization of the π -electrons in the macrocyclic ligands, (3) the geometric flexibility of the macrocyclic ligand and (4) the electronic configurations of the metal ions.

The free hemiporphorphyrzine hy-

drate, **1**, and its metal derivatives are



1, H_2hp

known to have a saddle shaped geometry, an elliptical core, and a localized double bond arrangement. To complete the structural investigation of this series; structural analyses of the planar neutral hemiporphyrzine ligand, H_2h_p , and the four isomorphous five-coordinated metal complexes, $M(h_p)\cdot H_2O$, $M=Mn(II)$, $Co(II)$, $Cu(II)$, $Zn(II)$ were undertaken.

EXPERIMENTAL

H_2h_p : A sample of the free ligand was prepared according to the method of Honeybourne³. Crystals suitable for X-ray diffraction studies were grown by sublimation at 200°C. A needle crystal about $1.2\times 0.1\times 0.1\text{ mm}^3$ was selected. The

crystal easily breaks into fibers. It crystallized in a monoclinic $P2_1/c$ space group. The cell parameters and the data collection details are given in Table 1. The structure was solved by the direct method using MULTAN. The correct E map reveals all the non-hydrogen atoms. The molecule contains a center of inversion symmetry, only half of the molecule is unique. Least-squares refinement converges to give agreement factors $R=0.11$ and $R_w=0.08$. All the hydrogen atoms were found in the difference Fourier map and refined isotropically with the rest of the parameters. The final difference Fourier map was featureless with residual electron density less than $0.6\text{ e}/\text{\AA}^3$. The final positional and thermal parameters are listed in Table 2.

Table 1. Crystal Data and Data Collection Details for H_2h_p and $Mh_p\cdot H_2O$

Compound	H_2h_p	$Mnh_p\cdot H_2O$	$Co_h_p\cdot H_2O$	$Cu_h_p\cdot H_2O$	$Znh_p\cdot H_2O$
Mol. Wt.	440.44	511.38	515.37	519.99	521.82
Space group	$P 2_1/c$	$P cab$	$P cab$	$P cab$	$P cab$
Cell constants					
$a(\text{\AA})$	4.1416(27)	8.812(7)	8.809(6)	8.795(3)	8.8244(14)
$b(\text{\AA})$	23.7358(57)	19.411(13)	19.322(3)	19.515(5)	19.3761(35)
$c(\text{\AA})$	10.3377(25)	23.634(17)	23.688(4)	23.658(6)	23.6782(56)
$\beta(\text{deg})$	94.66(6)				
Z	2	8	8	8	8
ρ cal. (g/cm^3)	1.44	1.68	1.70	1.71	1.71
ρ exp. (g/cm^3)	1.46(2)	1.67(2)	1.70(2)	1.71(2)	1.71(2)
Radiation (λ , \AA)	$MoK_\alpha(0.7107)$	MoK_α	MoK_α	MoK_α	MoK_α
Crystal Dimension (mm^3)	$1.2\times 0.1\times 0.1$	$0.04\times 0.08\times 0.1$	$0.2\times 0.2\times 0.4$	$0.1\times 0.1\times 0.3$	$0.1\times 0.3\times 0.4$
Diffractometer	CAD4	CAD4	CAD4	CAD4	CAD4
Method	θ - 2θ scan	θ - 2θ scan	θ - 2θ scan	θ - 2θ scan	θ - 2θ scan
Scan speed (primary scan)	20/3	20/6	20/3	20/3	20/3
Scan width	1.8	1.6	1.2	1.2	1.2
2θ limit of data	4-54°	4-46°	4-44°	4-50°	4-50°
No. of unique data collected	2203	2790	2464	3571	4405
No. of data used in refinement	1079	982	1219	2400	2937
No. of variables	155	150	156	325	325
R , (%)	11.5	14.9	8.6	10.5	9.9
R_w , (%)	8.0	8.8	6.1	7.3	6.1
Max. noise in final difference Fourier map ($e/\text{\AA}^3$)	0.5	0.6	0.6	0.6	0.4

Table 2. Fractional Atomic Coordinates and Isotropic Temperature Factors for H_2hp

Atom	X	Y	Z	Biso
N1	0.0032(14)	-0.07161(25)	0.0837(6)	3.7(3)
N2	0.3767(13)	-0.05414(25)	0.2779(6)	3.7(3)
N3	0.3566(12)	0.03264(23)	0.1574(6)	3.2(3)
N4	0.3702(14)	0.1265 (3)	0.0678(6)	3.8(3)
C1	0.1813(17)	-0.0841 (3)	0.2021(7)	3.7(4)
C2	0.4633(16)	0.0015 (3)	0.2583(8)	3.1(4)
C3	0.4566(16)	0.0857 (3)	0.1627(8)	3.4(4)
C4	0.1740(17)	0.1195 (3)	-0.0369(7)	3.7(4)
C9	0.0814(18)	-0.2307 (4)	0.3419(8)	5.1(5)
C10	0.1974(18)	-0.1754 (4)	0.3393(8)	4.5(5)
C11	0.1055(16)	-0.1435 (3)	0.2335(8)	3.4(4)
C12	0.6801(16)	0.0206 (3)	0.3628(7)	3.8(4)
C13	0.7779(16)	0.0758 (3)	0.3613(8)	3.8(4)
C14	0.6723(17)	0.1095 (3)	0.2610(8)	3.8(4)
C15	0.1098(17)	0.1649 (3)	-0.1324(8)	3.5(4)
C16	0.2190(16)	0.2183 (3)	-0.1339(8)	4.2(5)
C17	0.1255(17)	0.2524 (4)	-0.2391(8)	4.7(5)

[$Mhp \cdot H_2O$], for $M=Mn(II)$, $Co(II)$, $Cu(II)$, $Zn(II)$: The samples of the [$Mhp \cdot H_2O$] complexes were also prepared according to reference 7. Crystals suitable for X-ray diffraction studies were prepared by slow cooling of a supersaturated solution obtained by the reaction of $M(OAc)_2$ and H_2hp in hot dmf solution. They all belong to the orthorhombic space group $Pcab$. The refined cell constants, and data collection details for the metal complexes are also given in Table 1. The metal atoms were located in an origin-removed sharpened Patterson map. Subsequent structure factor calculation and Fourier synthesis led to the location of all nonhydrogen atoms. The structures were refined by least-squares techniques. The usual procedures, computer programs, atomic scattering factors, and anomalous terms were employed⁹. The final positional and thermal parameters are listed in Tables 3-6. Although, the results of the refinements are not as good as expected

because of the poor crystal quality, they still supply valid structural information.

RESULTS AND DISCUSSION

A series of crystal structures for free macrocyclic ligands (both the anhydrous ligand H_2hp and the ligand hydrate $H_2hp \cdot H_2O$) and metal complexes ($M=Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$) have been studied in this laboratory. Both the ligand hydrate $H_2hp \cdot H_2O$ and the coordinated $Ni(II)$ complex have a markedly nonplanar saddle shaped geometry³. But the anhydrous ligand form and the metal complex monohydrates ($M=Mn(II)$, $Co(II)$, $Cu(II)$, $Zn(II)$) all have a planar geometry formed by the metal ion and the macrocyclic ring. The structure of [$Mhp \cdot H_2O$] ($M=Mn(II)$, $Co(II)$, $Cu(II)$, $Zn(II)$) reveals a five-coordinate complex with the metals bound to the four nitrogen atoms of the macrocyclic ligand in a planar fashion and a fifth bond⁷ to an oxygen atom of a water molecule in the axial position.

The bond distances of H_2hp and [$Mhp \cdot H_2O$] ($M=Mn(II)$, $Co(II)$, $Cu(II)$, $Zn(II)$) in the plane of the macrocyclic ligand, together with the labeling scheme are shown in Figs. 1 and 2. Figs. 3 and 4.

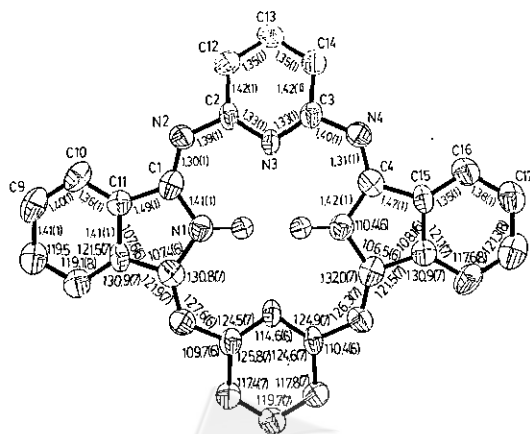


Fig. 1. The molecular structure (ORTEP plot), labeling scheme, and interatomic distances and angles of the free macrocyclic ligand.

Table 3. Fractional Atomic Coordinates and Isotropic Temperature Factors for [Mnhp·H₂O]

Atom	X	Y	Z	Biso
Mn	0.1757(4)	0.08635(16)	0.00603(15)	1.80(18)
O	0.3700(15)	0.1481 (7)	-0.0203 (5)	1.3 (9)
N1	0.2517(21)	0.0276 (8)	0.0723 (7)	1.2 (11)
N2	0.1968(20)	0.1036 (8)	0.1509 (7)	1.1 (11)
N3	0.0580(19)	0.1563 (9)	0.0697 (7)	0.4 (10)
N4	-0.0945(17)	0.2139 (7)	0.0000 (8)	1.5 (10)
N5	0.0209(22)	0.1154 (8)	-0.0474 (6)	1.1 (11)
N6	0.0828(21)	0.0421 (9)	-0.1285 (7)	1.5 (12)
N7	0.2266(20)	-0.0062 (9)	-0.0493 (6)	0.8 (10)
N8	0.3795(21)	-0.0647 (8)	0.0231 (6)	1.8 (13)
C1	0.2637(29)	0.0520 (11)	0.1266 (10)	2.6 (16)
C2	0.0932(27)	0.1502 (12)	0.1253 (10)	2.3 (15)
C3	-0.0459(28)	0.2044 (11)	0.0542 (9)	1.7 (16)
C4	-0.0679(27)	0.1728 (12)	-0.0457 (9)	1.9 (16)
C5	0.0075(27)	0.0962 (11)	-0.1028 (8)	1.0 (13)
C6	0.1716(25)	-0.0081 (10)	-0.1027 (8)	0.9 (12)
C7	0.3209(27)	-0.0598 (10)	-0.0320 (8)	1.5 (12)
C8	0.3423(26)	-0.0287 (11)	0.0654 (9)	1.4 (14)
C9	0.5203(30)	-0.0354 (12)	0.2326 (8)	1.8 (15)
C10	0.4083(25)	0.0121 (11)	0.2147 (9)	1.1 (13)
C11	0.3711(28)	0.0083 (13)	0.1616 (9)	2.9 (18)
C12	0.0341(31)	0.1981 (11)	0.1683 (9)	2.1 (18)
C13	-0.0660(26)	0.2470 (13)	0.1484 (8)	1.8 (13)
C14	-0.1123(23)	0.2492 (13)	0.0909 (7)	1.0 (15)
C15	-0.1480(29)	0.1882 (11)	-0.1002 (9)	1.9 (16)
C16	-0.2424(28)	0.2390 (11)	-0.1176 (8)	1.8 (14)
C17	-0.2866(29)	0.2375 (11)	-0.1771 (10)	3.1 (18)
C18	-0.2336(34)	0.1889 (12)	-0.2127 (9)	3.6 (18)
C19	-0.1370(25)	0.1404 (12)	-0.1945 (8)	1.8 (15)
C20	-0.0902(25)	0.1416 (12)	-0.1392 (9)	1.8 (14)
C21	0.2250(28)	-0.0567 (11)	-0.1438 (9)	2.1 (16)
C22	0.3201(27)	-0.1091 (10)	-0.1228 (8)	1.4 (12)
C23	0.3720(31)	-0.1123 (11)	-0.0679 (9)	3.0 (22)
C24	0.4151(27)	-0.0419 (12)	0.1193 (10)	2.1 (16)
C25	0.5145(26)	-0.0883 (12)	0.1413 (9)	1.5 (12)
C26	0.5704(25)	-0.0872 (13)	0.1980 (8)	2.1 (16)

show side views of the corresponding molecules to illustrate the planar nature of the free ligand and the square pyramidal

coordination sphere of the metal complexes. In order to fully understand the changes which occurred in the geometry of the

Table 4. Fractional Atomic Coordinates and Isotropic Temperature Factors for [Cohp·H₂O]

Atom	X	Y	Z	Biso
Co	0.16169(22)	0.08332(10)	0.00838(8)	1.79(8)
O	0.3494 (10)	0.1410 (4)	-0.0172 (4)	2.0 (5)
N1	0.2481 (14)	0.0308 (6)	0.0714 (5)	1.9 (3)
N2	0.1936 (12)	0.1051 (6)	0.1499 (4)	1.9 (3)
N3	0.0569 (11)	0.1557 (6)	0.0705 (4)	1.04(25)
N4	-0.0980 (11)	0.2157 (5)	-0.0000 (5)	2.2 (3)
N5	0.0124 (12)	0.1177 (5)	-0.0473 (4)	0.92(24)
N6	0.0759 (13)	0.0442 (6)	-0.1277 (5)	2.4 (3)
N7	0.2200 (12)	-0.0040 (6)	-0.0486 (4)	1.3 (3)
N8	0.3763 (11)	-0.0647 (5)	0.0221 (4)	1.5 (3)
C1	0.2581 (17)	0.0542 (7)	0.1265 (6)	1.6 (3)
C2	0.0928 (16)	0.1530 (8)	0.1278 (6)	2.1 (3)
C3	-0.0445 (17)	0.2062 (8)	0.0560 (6)	2.6 (4)
C4	-0.0757 (16)	0.1769 (7)	-0.0440 (6)	1.8 (3)
C5	0.0044 (16)	0.0953 (8)	-0.1035 (6)	2.0 (3)
C6	0.1725 (15)	-0.0049 (7)	-0.1037 (5)	1.4 (3)
C7	0.3112 (15)	-0.0563 (7)	-0.0315 (5)	1.7 (3)
C8	0.3471 (16)	-0.0262 (7)	0.0646 (5)	1.6 (3)
C9	0.5143 (17)	-0.0363 (7)	0.2320 (6)	2.1 (4)
C10	0.4086 (16)	0.0126 (8)	0.2130 (6)	2.2 (4)
C11	0.3614 (16)	0.0092 (7)	0.1583 (5)	1.7 (3)
C12	0.0283 (18)	0.1994 (8)	0.1661 (6)	2.7 (4)
C13	-0.0684 (16)	0.2486 (9)	0.1489 (5)	2.0 (3)
C14	-0.1125 (15)	0.2509 (9)	0.0940 (5)	2.2 (3)
C15	-0.1462 (17)	0.1902 (7)	-0.1005 (5)	1.9 (3)
C16	-0.2465 (19)	0.2429 (8)	-0.1169 (6)	2.9 (4)
C17	-0.2857 (16)	0.2398 (8)	-0.1738 (6)	2.4 (4)
C18	-0.2317 (18)	0.1901 (7)	-0.2110 (6)	2.3 (4)
C19	-0.1367 (17)	0.1392 (8)	-0.1922 (6)	2.6 (4)
C20	-0.0940 (15)	0.1381 (8)	-0.1369 (5)	1.5 (3)
C21	0.2210 (16)	-0.0545 (7)	-0.1415 (6)	1.9 (4)
C22	0.3197 (17)	-0.1069 (7)	-0.1245 (6)	2.7 (4)
C23	0.3614 (15)	-0.1090 (7)	-0.0682 (6)	1.9 (3)
C24	0.4185 (14)	-0.0394 (7)	0.1224 (5)	0.8 (3)
C25	0.5181 (17)	-0.0890 (8)	0.1391 (6)	2.6 (4)
C26	0.5677 (15)	-0.0892 (8)	0.1950 (6)	1.8 (3)

ligand upon coordination, it is necessary to carefully examine the structure of the

macrocyclic ligand both in its free state and in the complex.

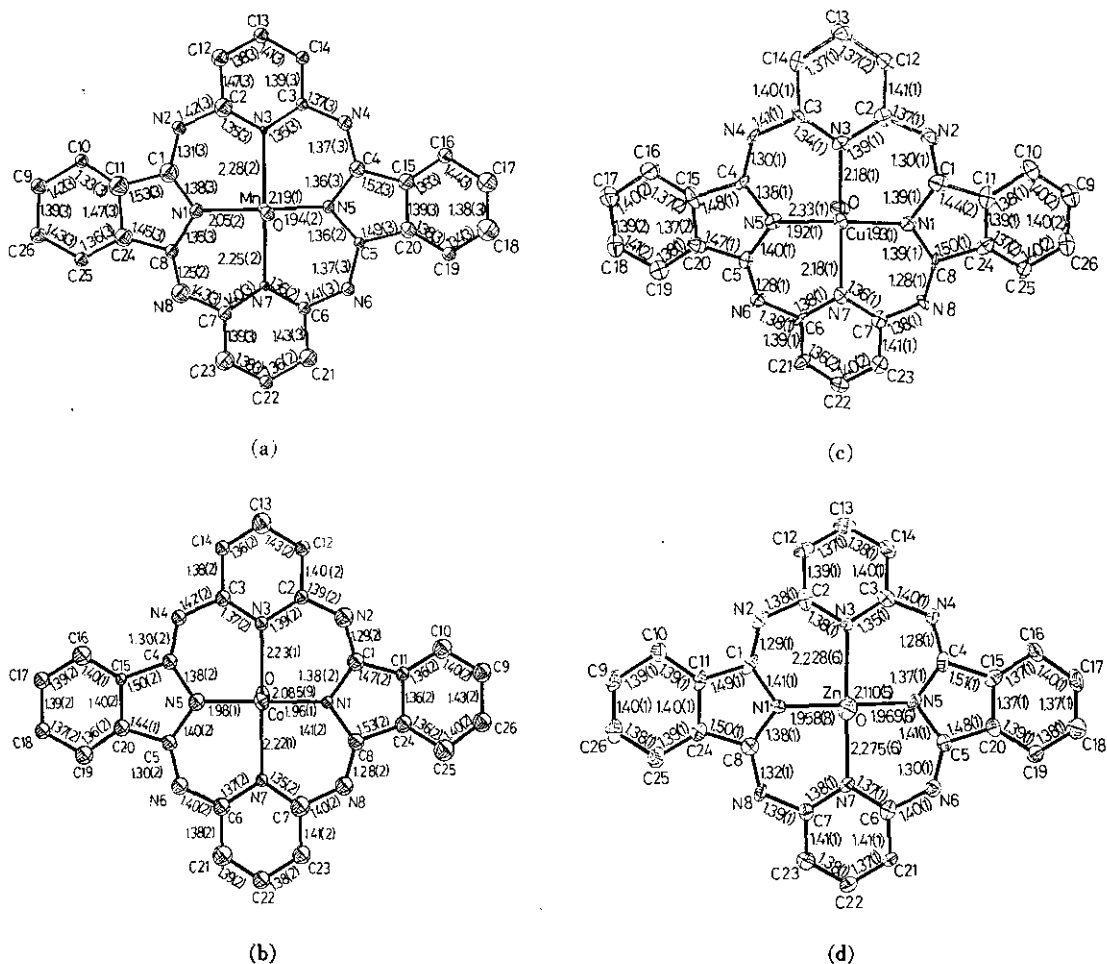


Fig. 2. Drawing of the macrocyclic ligand for the four isomorphous complexes, illustrating the labeling scheme and interatomic distances. The axial ligands are water molecules. (a) $[MnHPH_2O]$, (b) $[CoHPH_2O]$, (c) $[CuHPH_2O]$, (d) $[ZnHPH_2O]$.

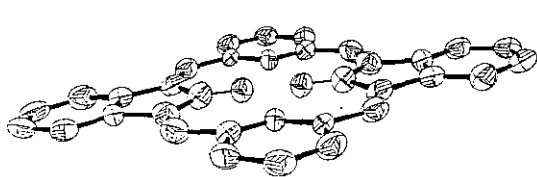


Fig. 3. Side view of the free macrocyclic ligand illustrating the planar conformation.

Structure of the Free Macrocyclic Ligand

The macrocyclic ligand has planar geometry with its center at the crystallographic inversion center. The molecules are stacked along \bar{a} axis with interplanar

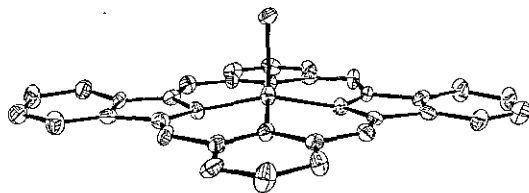


Fig. 4. Side view of the $[MnHPH_2O]$ complexes illustrating the almost planar conformation of the ligand and square pyramidal coordination geometry: $[ZnHPH_2O]$.

spacing 3.36 \AA , comparable to those of graphite (3.35 \AA)⁹, porphine (3.42 \AA)¹⁰ and phthalocyanine (3.38 \AA)¹¹. However, the

Table 5. Fractional Coordinates and Isotropic Temperature Factors for $[\text{Cu}h\text{p}\cdot\text{H}_2\text{O}]$

Atom	X	Y	Z	Biso
Cu	0.1401(2)	0.07697(7)	0.00956(5)	1.68(5)
C1	0.2579(14)	0.0545(5)	0.1295(5)	2.2(5)
C2	0.0885(12)	0.1511(5)	0.1255(4)	1.8(5)
C3	-0.0486(12)	0.2021(5)	0.0541(4)	1.6(5)
C4	-0.0768(12)	0.1734(5)	-0.0456(4)	1.7(5)
C5	0.0048(12)	0.0932(5)	-0.1041(4)	1.5(5)
C6	0.1715(11)	-0.0039(5)	-0.1034(4)	1.4(5)
C7	0.3135(11)	-0.0546(5)	-0.0312(4)	1.6(5)
C8	0.3394(12)	-0.0256(5)	0.0652(4)	1.3(5)
C9	0.5088(13)	-0.0356(6)	0.2323(4)	2.2(6)
C10	0.4050(3)	0.0143(6)	0.2137(4)	2.2(6)
C11	0.3584(13)	0.0115(5)	0.1581(4)	1.8(5)
C12	0.0283(13)	0.1987(6)	0.1646(6)	2.1(6)
C13	-0.0712(13)	0.2485(6)	0.1470(4)	2.2(6)
C14	-0.1100(12)	0.2511(6)	0.0910(4)	1.7(5)
C15	-0.1448(14)	0.1895(6)	-0.1012(4)	2.1(5)
C16	-0.2415(15)	0.2403(6)	-0.1186(5)	2.5(6)
C17	-0.2846(15)	0.2401(6)	-0.1754(5)	3.0(6)
C18	-0.2314(14)	0.1897(6)	0.2121(5)	2.6(6)
C19	-0.1310(14)	0.1381(6)	-0.1937(4)	2.2(5)
C20	-0.0919(13)	0.1398(6)	-0.1373(4)	2.0(6)
C21	0.2240(13)	-0.0530(5)	-0.1415(4)	1.9(5)
C22	0.3163(13)	-0.1052(6)	-0.1249(5)	2.1(6)
C23	0.3610(14)	-0.1069(5)	-0.0683(4)	2.5(4)
C24	0.4129(13)	-0.0386(5)	0.1215(5)	2.0(5)
C25	0.5139(13)	-0.0881(6)	0.1387(4)	2.1(6)
C26	0.5631(13)	-0.0857(6)	0.1950(4)	2.6(6)
N1	0.2461(10)	0.0312(4)	0.0704(3)	1.6(4)
N2	0.1884(10)	0.1059(4)	0.1496(3)	2.2(5)
N3	0.0486(10)	0.1520(4)	0.0688(3)	1.6(4)
N4	-0.1016(9)	0.2117(4)	-0.0018(3)	1.8(4)
N5	0.0118(10)	0.1153(4)	-0.0478(3)	1.4(4)
N6	0.0757(10)	0.0437(4)	-0.1282(3)	1.8(4)
N7	0.2142(10)	-0.0045(4)	-0.0472(3)	1.7(4)
N8	0.3714(9)	-0.0635(4)	0.0227(3)	1.4(4)
O	0.3501(10)	0.1416(4)	-0.0180(3)	3.1(4)

Table 6. Fractional Atomic Coordinates and Isotropic Temperature Factors for $[\text{Zn}h\text{p}\cdot\text{H}_2\text{O}]$

Atom	X	Y	Z	Biso
Zn	0.1646(1)	0.08328(5)	0.00737(4)	1.75(4)
O	0.3524(6)	0.1433(3)	-0.0167(2)	1.9(2)
N1	0.2475(8)	0.0297(3)	0.0703(3)	1.6(3)
N2	0.1906(8)	0.1071(3)	0.1503(3)	1.9(3)
N3	0.0542(7)	0.1561(3)	0.0705(2)	1.2(3)
N4	-0.0954(7)	0.2160(3)	-0.0002(3)	1.7(3)
N5	0.0131(8)	0.1174(3)	-0.0469(2)	1.5(3)
N6	0.0777(8)	0.0433(3)	-0.1278(3)	1.6(3)
N7	0.2208(7)	-0.0050(3)	-0.0492(2)	1.4(3)
N8	0.3754(7)	-0.0648(3)	0.0213(2)	1.6(3)
C1	0.2553(10)	0.0551(4)	0.1263(3)	1.8(3)
C2	0.0886(9)	0.1534(4)	0.1271(3)	1.9(4)
C3	-0.0465(9)	0.2050(4)	0.0552(4)	1.7(4)
C4	-0.0734(9)	0.1756(3)	-0.0423(3)	1.7(4)
C5	0.0093(9)	0.0948(4)	-0.1035(3)	1.4(4)
C6	0.1750(9)	-0.0055(4)	-0.1043(3)	1.7(4)
C7	0.3148(9)	-0.0576(4)	-0.0328(3)	1.6(4)
C8	0.3435(10)	-0.0262(4)	0.0655(3)	1.7(4)
C9	0.5152(10)	-0.0372(4)	0.2315(3)	2.3(4)
C10	0.4086(9)	0.0172(4)	0.2140(3)	1.9(4)
C11	0.3623(9)	0.01101(4)	0.1582(3)	1.7(4)
C12	0.0306(10)	0.1995(4)	0.1667(3)	2.1(4)
C13	-0.0704(11)	0.2488(5)	0.1494(3)	2.3(4)
C14	-0.1097(10)	0.2523(5)	0.0931(3)	2.0(4)
C15	-0.1433(10)	0.1906(4)	-0.0991(3)	1.7(4)
C16	-0.2417(11)	0.2410(5)	-0.1169(3)	2.6(4)
C17	-0.2846(10)	0.2369(5)	-0.1738(4)	2.6(4)
C18	-0.2322(11)	0.1899(5)	-0.2103(4)	2.7(4)
C19	-0.1333(9)	0.1392(4)	-0.1925(3)	1.9(4)
C20	-0.0920(9)	0.1411(4)	-0.1358(3)	1.6(4)
C21	0.2240(10)	-0.0560(4)	-0.0143(3)	1.7(4)
C22	0.3164(11)	-0.1087(4)	-0.1251(3)	2.3(4)
C23	0.3621(9)	-0.1107(4)	-0.0692(3)	1.9(4)
C24	0.4150(10)	-0.0414(4)	0.1214(3)	1.7(4)
C25	0.5173(10)	-0.0915(5)	0.1396(3)	2.4(4)
C26	0.5639(9)	-0.0889(5)	0.1950(3)	2.4(4)

macrocyclic ligand hydrate $h\text{pH}_2\cdot\text{H}_2\text{O}$ has a saddle shaped geometry because of the extended hydrogen bonds between the

water molecules and $h\text{pH}_2$. This is also consistent with the IR spectra which has broad O-H stretching at 3400 cm^{-1} and N-H

stretching at 3220 cm^{-1} .

Both the free ligand, hpH_2 , and its hydrate form, $H_2hp \cdot H_2O$, show a similar double-bond arrangement. They all contain two pyridine rings and two benzenoid rings connected by four imine double bonds (1.30 \AA) as indicated in 1.

The rhombic-planar array of the four nitrogen atoms in the free macrocyclic ligand forms an elliptical core with the "trans" nitrogen atoms separated $3.81(1)$ and $4.49(1)\text{ \AA}$. Thus the nitrogen-to-center distances, N-Ct, of the free ligand, are $1.907(6)$ and $2.245(6)\text{ \AA}$ respectively. The average distance of 2.076 \AA is comparable to that of the ligand hydrate 2.12 \AA^{19} and to that of porphine 2.04 \AA^{20} , but larger

than that of phthalocyanine 1.92 \AA^{21} . The core size of this free ligand is in the optimum range for high-spin divalent metal ions of the first row transition metal series. It is interesting to see how the metal ions fit into the elliptical core. This will be discussed later.

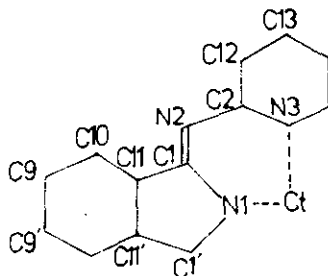
Structures of Four Isomorphous Complexes

The average bond distances and angles of a quarter of the macrocyclic ligand in its free state and of the $[Mhp \cdot H_2O]$ ($M = Mn, Co, Cu, Zn$) complexes, together with the ligand hydrate $hpH_2 \cdot H_2O$ and the $[Nihp]^{22}$ complex are listed in Table 7. The bond parameters and geometry of the

Table 7. Average Chemically Equivalent Intramolecular Bond Distances of Macrocyclic Ligand in H_2hp and Its Metal Complexes.

Bond	H_2hp	$H_2hp \cdot H_2O$	$Mnhp \cdot H_2O$	$Co hp \cdot H_2O$	$Nihp$	$Cu hp \cdot H_2O$	$Zn hp \cdot H_2O$
C(9)—C(9')	1.41(1)	1.413(5)	1.39(3)	1.41(2)	1.391(3)	1.40(2)	1.39(1)
C(9)—C(10)	1.39(1)	1.392(5)	1.41(3)	1.39(2)	1.388(3)	1.40(2)	1.39(1)
C(10)—C(11)	1.36(1)	1.381(5)	1.36(3)	1.37(2)	1.382(3)	1.38(2)	1.38(1)
C(11)—C(11')	1.41(1)	1.401(4)	1.43(3)	1.38(2)	1.387(3)	1.38(2)	1.39(1)
C(11)—C(1)	1.48(1)	1.475(5)	1.50(3)	1.48(2)	1.475(3)	1.47(1)	1.49(1)
C(1)—N(2)	1.30(1)	1.281(4)	1.32(3)	1.28(2)	1.283(3)	1.29(1)	1.30(1)
C(1)—N(1)	1.41(1)	1.399(4)	1.36(3)	1.39(2)	1.383(3)	1.39(1)	1.39(1)
N(2)—C(2)	1.40(1)	1.411(1)	1.41(3)	1.40(2)	1.372(3)	1.38(1)	1.39(1)
C(2)—N(3)	1.33(1)	1.353(4)	1.36(3)	1.37(2)	1.383(3)	1.37(1)	1.37(1)
C(2)—C(12)	1.42(1)	1.394(5)	1.42(3)	1.39(2)	1.397(3)	1.40(1)	1.40(1)
C(12)—C(13)	1.35(1)	1.407(4)	1.38(3)	1.36(2)	1.370(3)	1.37(2)	1.37(1)

a The Quarter of molecule and labeling are drawing below:



macrocyclic ligand in the $[Mhp \cdot H_2O]$ complex are very close to those of the free ligand. A small degree of delocalization in these complexes causes a shortening of

the C1-N1, C2-N2 bonds and a lengthening of the C2-N3 bond. There are small displacements of the metal ions out of the four coordinated nitrogen atoms of the

macrocylic plane, the Cu complex shows the smallest (0.09 Å) and the Mn complex the largest (0.42 Å).

Weak hydrogen bondings in the packing of $[Mhp \cdot H_2O]$, between the water molecules and the neighboring N2, N6 atoms of the macrocylic complex were observed, which are illustrated in Fig. 5.

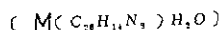
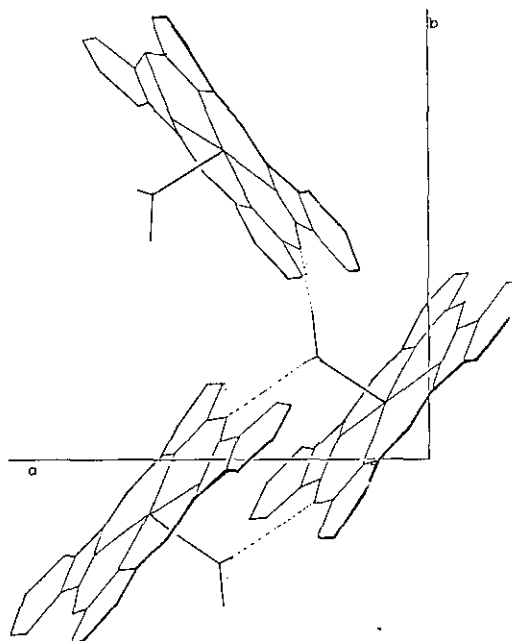


Fig. 5. Packing of $[Mhp \cdot H_2O]$ illustrating the hydrogen bonding between the molecules.

The Inner Coordination Sphere in Four Metal Complexes, $[Mhp \cdot H_2O]$

Table 8 gives a summary of the related parameters for the metal complexes of hemiporphyrzine, and for the porphyrins in five-coordinated geometry. The variations in the bond lengths in the coordination sphere seem to be quite irregular. Here we propose a simple crystal field model to account for the variations of the metal-ligand distances. The principle of the crystal field model is simple: the more electrons in d orbitals

Table 8. Summary of Important Parameters for the Coordination Sphere in the Hemiporphyrzine and Porphyrin Systems

	Distance, (Å)				Ref.
	M-N	Ct-N	M-Ct	M-L	
H_2hp		1.907(6) 2.245(6)			*
$Mnhp \cdot H_2O$	2.20 (2) 2.27 (2)	2.16 2.23	0.42	2.19 (1)	*
$Cuhp \cdot H_2O$	1.925(8) 2.181(8)	1.92 2.18	0.09(5)	2.330(8)	*
$Cohp \cdot H_2O$	1.97 (1) 2.23 (1)	1.94 2.21	0.3 (1)	2.085(9)	*
$Znhp \cdot H_2O$	1.964(6) 2.252(6)	1.93 1.23	0.33(6)	2.110(5)	*
$Nihp$	1.861(2) 1.998(2)				5
Porphyrin		2.04			12
$ZnTPyP(Py)$	2.073(3)	2.047(3)	0.33	2.143(4)	17
$ZnTPP(H_2O)$	2.05 (1)	2.04 (1)	0.19	2.20 (6)	18
$CoTPP$ (1-MeIm)	1.977(6)	1.974	0.13	2.157(3)	19
$CoTPP$ (1, 2-DiMeIm)	1.985(2)	1.9799	0.15	2.216(2)	20
$MnTPP(Cl)$	2.008	1.990	0.27	2.373	21
$CuTPrP$	2.000(5)				22

a. The figure at the right is a diagram of the square-pyramidal coordination group for a five-coordinate metal compound.

b. TPyP: tetrapyrzidineporphyrin.

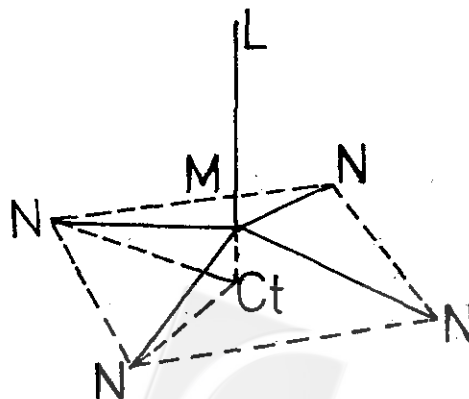
c. TPP: tetraphenylporphyrin.

d. 1-MeIm: 1-methylimidazole.

e. 1,2-DiMeIm: 1,2-dimethylimidazole.

f. TPrP: tetrapropylporphyrin.

* This work.



are directed toward the ligand; the longer

will be the M-L distances because of the electrostatic repulsion. This principle has been successfully applied in several systems¹³⁻¹⁵⁾

There is roughly square pyramidal geometry (C_{4v}) around the metal ions in the $[Mhp \cdot H_2O]$ complexes. The crystal field splitting of the d orbitals should be as follows.

$d_{x^2-y^2}$	9.14 Dq
d_{z^2}	0.86 Dq
d_{xy}	-0.86 Dq
d_{xz} d_{yz}	-4.57 Dq

The high-spin metal ions except the Ni(II) ion will have the following electronic configurations.

\uparrow	\uparrow	—	\uparrow	$\uparrow\downarrow$
\uparrow	\uparrow	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
\uparrow	\uparrow	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
\uparrow	\uparrow	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)

The d orbital in the plane and directed toward the nitrogen atoms is $d_{x^2-y^2}$ and the one directed toward the oxygen atom of the water molecule is d_{z^2} , so M-N distances will be affected by the electron population of the $d_{x^2-y^2}$ orbital and the M-O distances will depend on the number of electrons in the d_{z^2} orbital. On the other hand, there should be a steady contraction of radii from Mn(II) to Zn(II) ions due to the increasing effective nuclear charge of the metal ions. Therefore the variations of the M-L distances shown in Fig. 6. can be rationalized as follows: the Mn(II), Co(II), and Cu(II) ions all have one electron in $d_{x^2-y^2}$ orbital, the M-N distances of those complexes fall on a straight line with a negative slope resulting from the contraction. The Zn(II) ion has two electrons in the $d_{x^2-y^2}$ orbital and has much longer M-N distances. Similarly, the

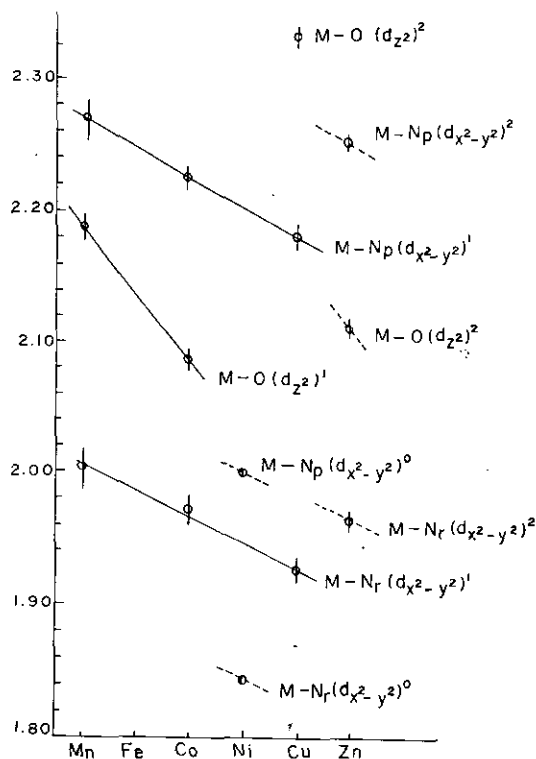


Fig. 6. The variations of bond distances in the coordination sphere of $[MhpH_2O]$ complexes and their rationalization.

Mn(II) and Co(II) ions have one electron in the d_{z^2} orbital, so the M-O distances decrease along the series while the Zn(II) ion has two electrons in d_{z^2} and a much longer M-O distance. However it is noted that $[Cuhp \cdot H_2O]$ has the longest M-O distance, 2.32 Å, which probably results from the strong Jahn-Teller distortion of d^9 complexes. The much shorter M-N distances in $Nihp$ in the diagram is consistent with there being no electron in the $d_{x^2-y^2}$ orbital. The similar porphyrin five-coordinated metal complexes show the same trend in M-L bond distances¹⁷⁻²²⁾.

CONCLUSION

It is fortunate that we could find four isomorphous crystal structures with

different populations in the $3d$ orbitals. Because of the similarity in packing, the M-N bond distances can be correlated directly to the occupancies of certain d -orbitals, namely through the σ -bond. In square pyramid five coordinated metal complexes, they are d_{z^2} and $d_{x^2-y^2}$. The results illustrate that the simple crystal field model works well in these complexes.

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