CRYSTAL AND MOLECULAR STRUCTURE OF THE MACROCYCLIC NICKEL (II) COMPLEX Ni(C₂₂H₂₂H₄): DIBENZO[b, i][5, 7, 12, 14] TETRAMETHYL [1, 4, 8, 11] TETRAAZACYCLOTETRADECA-2, 4, 7, 9, 12, 14-HEXAENEATONICKEL (II)

Yu Wang (王　瑜)*, Shie-Ming Peng (彭旭明)*,

Yu-Lin Lee (李玉麟), Mei-Chen Chuang (莊美琛)

*Department of Chemistry National Taiwan University
Taipei, Taiwan, 107*

Chia-Pin Tang (唐嘉濱) and Chiu-Jane Wang (王瓊珍)

*Department of Chemistry Chun-Shan Institute of Science and Technology
P. O. Box 1-4 Lungtan, Taiwan, 325*

The crystal and molecular structure of the four-coordinate complex Ni(C₂₂H₂₂N₄) containing the tetramethyldibenzotetraaza[14] annulene ligand has been determined from three-dimensional X-ray diffraction data. The complex crystallized in the monoclinic space group C_{2h}^5-P2₁/n with cell dimensions a=14.7967(10), b=11.2169(6), c=11.4510(6) Å, and β=98.467(5)° with Z=4. The final agreement indices from the least-square refinement of 245 variables with 3111 observations F>3σ(F), are R=0.050, R_w=0.037. The structure has a pronounced saddle-shaped conformation with Ni atom at the saddle point coordinated to four nitrogen atoms. The average Ni-N distance is 1.866(3) Å. The delocalized propane-1,3-diiminato chelate rings and the benzene rings are linked by nominally single C-N bonds.

In order to understand the significant role of highly and completely conjugated macrocyclic ligands in biological processes, the importance of the studying of the synthetic macrocyclic ligands has become widely recognized in recent years[1~3]. A large number of macrocyclic complexes which have been synthesized and characterized are based on the dibenzotetraaza[14] annulene frame work[4~10].

Goedken *et al.*[7~9] reported the systematic structural studies of tetramethylated derivatives (i.e. R_i=CH₃, R_2=H). The free ligand (C₂₂H₂₄N₄) and *four-coordinated iron complex* (Fe(C₂₂H₂₂N₄)) were structurally characterized as saddle-like shape conformation[7]. Three

carbon monoxide complexes of [Fe(C₂₂H₂₂N₄)(CO)X], X=none, pyridine, hydrazine, were also characterized by X-ray structural analysis as having a strong CO binding[8]. The structures of three five-coordinated complexes of the type [M(C₂₂H₂₂N₄)X] M=Co(III), Fe(III),
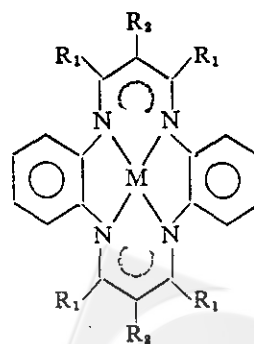
Mn(II); X=I, Cl, N(C₂H₅)₃ were studied to systematize the structural parameters associated with the five-coordinated complexes[9]. Crystallographic studies showed that the complex is essentially planar when $R_1=R_2=H$, $M=Ni$[10], i.e. different from the four-coordinated tetramethylated Ni complex.

The crystal and molecular structure of the title compound was undertaken to extend and elucidate structural tendencies characterized by the various substituted analogues. A structural comparison of the title compound with compounds mentioned above will be discussed.

EXPERIMENTAL

Preparation

The compound was synthesized by refluxing nickel acetate with o-phenylenediamine and acetylacetone in methanol for 24 hours[6]. Crystal of Ni(C₂₂H₂₂N₄), suitable for X-ray study, were grown by slow evaporation of saturated chloroform solution.

Crystallographic data

Preliminary precession photographs of the crystal revealed the systematic absences $h0l$, $h+l=2n+1$, and $0k0$, $k=2n+1$, consistent with the space group $P2_1/n$. The cell parameters obtained by centering 25 reflections with θ range from 34 to 67° are $a=14.7967(10)$, $b=11.2169(6)$, $c=11.4510(6)$ Å, and $\beta=98.467(5)°$. The calculated density, based on four Ni(C₂₂H₂₂N₄) molecules per unit cell is $1.417\,g/cm^3$ which agrees well with the measured one $(1.41(1)g/cm^3)$ by floatation in ZnCl₂ aquo solution.

3567 unique intensity data with 2θ range from 4 to 140° were measured on CAD4 differactometer using Cu K_α radiation with $\theta-2\theta$ scan technique. 3111 reflections were found to be observed. $(F>3\sigma(F))$ The scan parameter is $1.0+0.14(\tan\theta)$ with scan speed $(20/3)\,deg/min$ for majority of the measurements. The back-

grounds were taken at each end of the scan limit with quarter of total scan time.

Solution and Refinement of Structure[11]

The nickel atom was located from the Patterson map, subsequent Fourier syntheses based on this heavy atom revealed the positions of all the nonhydrogen atoms of the macrocyclic ligand. A full matrix isotropic refinement converged to $R=0.10$. The hydrogen atoms of benzene ring were located in the difference Fourier map. The rest of hydrogen atoms were calculated. The methyl groups displayed disorder. The final refinement was completed by two blocked full-matrix refinement including isotropic extinction and anisotropic temperature factors on all the nonhydrogen atoms. It converged to $R=0.050$, $R_w=0.037$ based on 3111 (out of 3567) observed scattering amplitudes(F). The subsequent difference Fourier synthesis showed a max. peak of $0.6\,e/Å^3$ near Ni atom. The isotropic extinction coefficient is $4.06(3)\times 10^{-3}$. The extinction phenomenon is quite serious, the refinement would diverge if the extinction correction is excluded. The final positional and thermal parameters are given in Table I and II. The intramolecular bond angles and the deviation from least-square planes are presented in Table III and IV.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure consists of discrete molecules of Ni(C₂₂H₂₂N₄), shown in Fig. 1. Each Ni atom is coordinated through four nitrogen atoms of the macrocyclic ligand, dibenzotetraaza[14]annulene with average Ni-N distance of 1.866(3) Å. This is comparable to those observed in Ni(dmg)₂[12] and Ni(C₁₈H₁₄N₄)[10], however, it is significantly shorter than those saturated macrocyclic low spin Ni(II) complexes normaly with Ni-N distance of 1.95-2.00 Å[13].

Table I. Positional and Anisotropic Thermal Parameters for the Non-hydrogen Atoms of $Ni(C_{22}H_{22}N_4)$

Atom	X [a]	Y	Z	U_{11} [b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.08810(4)	0.19474(6)	0.31425(6)	3.63(4)	2.82(3)	3.42(4)	-0.07(4)	0.37(3)	-0.17(3)
N1	0.1216(2)	0.1958(3)	0.4772(3)	3.6(2)	3.3(2)	3.4(2)	0.0(2)	0.2(1)	-0.3(2)
N2	0.0494(2)	0.3534(3)	0.3053(3)	3.6(2)	2.6(2)	4.7(2)	-0.1(1)	0.6(2)	-0.3(2)
N3	0.0561(2)	0.1956(3)	0.1501(2)	4.0(2)	3.5(2)	3.1(2)	-0.1(2)	0.5(1)	-0.1(2)
N4	0.1300(2)	0.0374(3)	0.3226(3)	3.4(2)	2.7(2)	4.2(2)	0.0(1)	0.3(1)	-0.1(2)
C1	0.1489(2)	0.2918(4)	0.5408(3)	3.5(2)	4.4(3)	4.0(2)	-0.2(2)	0.5(2)	-0.6(2)
C2	0.1350(3)	0.4059(4)	0.4925(4)	4.9(3)	3.9(3)	4.7(3)	-0.5(2)	0.8(2)	-1.4(2)
C3	0.0851(3)	0.4361(3)	0.3842(4)	4.4(3)	3.2(2)	5.2(3)	-0.1(2)	1.9(2)	-0.7(2)
C4	-0.0106(3)	0.3753(3)	0.2007(3)	3.6(2)	3.4(2)	4.2(2)	-0.2(2)	0.4(2)	0.6(2)
C5	-0.0763(3)	0.4642(4)	0.1836(4)	4.6(3)	3.9(2)	6.4(3)	0.2(2)	0.5(2)	0.3(3)
C6	-0.1369(3)	0.4696(4)	0.0795(4)	4.9(3)	4.7(3)	7.3(4)	0.8(2)	0.2(3)	1.3(3)
C7	-0.1343(3)	0.3839(5)	-0.0056(4)	5.1(3)	6.6(3)	5.6(3)	0.6(3)	-0.5(2)	1.8(3)
C8	-0.0708(3)	0.2906(4)	0.0122(4)	5.3(3)	5.3(3)	4.3(2)	0.2(2)	0.1(2)	0.4(2)
C9	-0.0079(3)	0.2882(4)	0.1144(3)	3.7(2)	3.7(2)	4.0(2)	0.0(2)	0.7(2)	0.7(2)
C10	0.0959(3)	0.1263(4)	0.0775(3)	5.1(3)	4.4(3)	3.3(2)	-0.4(2)	0.7(2)	-0.4(2)
C11	0.1492(3)	0.0286(4)	0.1192(4)	4.6(3)	4.5(3)	3.9(2)	0.5(2)	1.0(2)	-0.6(2)
C12	0.1612(3)	-0.0184(3)	0.2330(4)	3.3(2)	3.1(2)	5.0(3)	-0.2(2)	0.6(2)	-0.8(2)
C13	0.1295(2)	-0.0091(3)	0.4375(3)	2.8(2)	3.4(2)	3.7(2)	-0.1(2)	-0.1(2)	0.3(2)
C14	0.1252(3)	-0.1286(4)	0.4693(4)	4.7(3)	3.6(2)	5.6(3)	-0.3(2)	0.4(2)	0.5(2)
C15	0.1173(3)	-0.1599(4)	0.5853(4)	4.6(3)	5.3(3)	6.9(3)	-0.1(2)	0.3(2)	2.9(3)
C16	0.1095(3)	-0.0741(5)	0.6687(4)	4.2(3)	7.0(3)	5.0(3)	0.3(3)	0.5(2)	2.2(3)
C17	0.1109(3)	0.0450(4)	0.6367(4)	4.1(2)	6.0(3)	3.7(2)	0.5(2)	0.1(2)	0.6(2)
C18	0.1233(2)	0.0782(3)	0.5230(3)	2.8(2)	3.9(2)	3.7(2)	0.0(2)	-0.1(2)	0.4(2)
C19	0.2006(3)	0.2849(4)	0.6654(4)	7.0(3)	7.3(4)	4.2(3)	0.4(3)	-1.5(2)	-1.8(3)
C20	0.0794(3)	0.5679(4)	0.3541(4)	7.0(3)	2.7(2)	8.7(4)	-0.5(2)	1.1(3)	-0.3(2)
C21	0.0887(3)	0.1516(4)	-0.0533(4)	9.1(4)	7.7(4)	3.6(3)	1.7(3)	1.9(3)	0.5(3)
C22	0.2172(3)	-0.1318(4)	0.2519(4)	6.1(3)	3.9(3)	7.4(3)	1.5(2)	1.9(3)	0.0(2)

a. Estimated standard deviations in the least significant figures are given in parenthesis.
b. The form of the anisotropic thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\times10^{-2})$.

Table II. Positional and Thermal Parameters for the Hydrogen Atoms of $Ni(C_{22}H_{22}N_4)$

Atom	ATTACH Atom	X[a]	Y	Z	U[b]
H2	C2	0.1628	0.4679	0.5365	5.06
H5	C5	−0.0788	0.5208	0.2389	5.06
H6	C6	−0.1848	0.5422	0.0681	5.06
H7	C7	−0.1767	0.3861	−0.0723	5.06
H8	C8	−0.0718	0.2327	−0.0424	5.06
H11	C11	0.1907	−0.0046	0.0734	5.06
H14	C14	0.1260	−0.1863	0.4148	5.06
H15	C15	0.1149	−0.2384	0.6057	5.06
H16	C16	0.0995	−0.0933	0.7491	5.06
H17	C17	0.1038	0.1009	0.6909	5.06
H191	C19	0.2100	0.2109	0.6973	10.00
H192	C19	0.2571	0.3174	0.6660	10.00
H193	C19	0.1708	0.3274	0.7145	10.00
H201	C20	0.0450	0.5886	0.2833	10.00
H202	C20	0.0528	0.6068	0.4101	10.00
H203	C20	0.1352	0.5964	0.3530	10.00
H211	C21	0.0539	0.2148	−0.0817	10.00
H212	C21	0.1458	0.1661	−0.0709	10.00
H213	C21	0.0666	0.0871	−0.0944	10.00
H221	C22	0.2261	−0.1632	0.3251	10.00
H222	C22	0.1907	−0.1885	0.2023	10.00
H223	C22	0.2743	−0.1175	0.2326	10.00

a. The position of hydrogen atoms was located in difference Fourier map and was not refined in least-square cycle.
b. The temperature factor assigned as about U_H $=U_{o-attach}+1$. The form of isotropic thermal ellipsoid is $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)\times10^{-2}$.

Table III. Intramolecular Bond Angles in $Ni(C_{22}H_{22}N_4)$

Atoms	Angle, deg	Atoms	Angle, deg
N1-Ni-N2	94.8(1)	C5-C4-C9	119.8(4)
N1-Ni-N4	85.3(1)	C4-C5-C6	120.3(4)
N2-Ni-N3	84.8(1)	C5-C6-C7	119.9(4)
N3-Ni-N4	95.1(1)	C6-C7-C8	120.5(4)
Ni-N1-C1	124.7(3)	C7-C8-C9	119.4(4)
Ni-N1-C18	110.7(2)	N3-C9-C4	113.2(3)
C1-N1-C18	124.3(3)	N3-C9-C8	126.4(4)
Ni-N2-C3	122.1(2)	C4-C9-C8	120.0(4)
Ni-N2-C4	111.3(2)	N3-C10-C11	121.6(4)
C3-N2-C4	126.1(3)	N3-C10-C21	122.3(4)
Ni-N3-C9	110.6(2)	C11-C10-C21	116.1(4)
Ni-N3-C10	123.6(2)	C10-C11-C12	127.3(4)
C9-N3-C10	125.5(3)	N4-C12-C11	121.9(3)
Ni-N4-C12	123.4(3)	N4-C12-C22	121.7(3)
Ni-N4-C13	110.4(2)	C11-C12-C22	116.3(4)
C12-N4-C13	126.1(3)	N4-C13-C14	127.1(3)
N1-C1-C2	120.7(3)	N4-C13-C18	113.8(3)
N1-C1-C19	123.0(4)	C14-C13-C18	118.7(4)
C2-C1-C19	116.2(4)	C13-C14-C15	120.3(4)
C1-C2-C3	127.2(4)	C14-C15-C16	120.9(4)
N2-C3-C2	122.4(4)	C15-C16-C17	119.1(4)
N2-C3-C20	121.0(3)	C16-C17-C18	120.9(4)
C2-C3-C20	116.4(4)	N1-C18-C13	113.1(3)
N2-C4-C5	126.1(4)	N1-C18-C17	126.7(4)
N2-C4-C9	113.7(3)	C13-C18-C17	120.0(4)

Table IV. Deviations from Least-Square Planes

Atom	Planes 1	Planes 2	Planes 3	Planes 4	Planes 5	Planes 6	Planes 7	Planes 8
Ni[a]	−0.2 Å	−0.021 Å	0.53 Å	0.50 Å	−0.78 Å	−0.75 Å	−0.65 Å	−0.65 Å
N1	−0.1(5)	−0.005(6)	0.01(2)					−0.01(3)
N2	−0.1(5)	0.005(6)	0.00(2)				−0.04(4)	
N3	−0.1(5)	−0.005(6)		0.00(3)			−0.03(4)	
N4	−0.1(5)	0.005(6)		0.01(3)				−0.05(3)
C1	0.4(5)		−0.03(2)					
C2	0.7(5)		0.03(2)					
C3	0.4(5)		−0.01(2)					
C4	−0.6(5)				0.01(1)		0.06(4)	
C9	−0.6(5)				0.01(1)		0.06(4)	
C10	0.4(5)			−0.02(3)				
C11	0.7(5)			0.03(3)				
C12	0.4(5)			−0.03(3)				
C13	−0.6(5)					0.00(2)		0.05(3)
C18	−0.6(5)					0.02(2)		0.05(3)
C5					−0.02(1)		0.00(4)	
C6					0.01(1)		−0.02(4)	
C7					0.01(1)		−0.02(4)	
C8					−0.02(1)		−0.01(4)	
C14						−0.02(2)		0.01(3)
C15						0.01(2)		0.00(3)
C16						0.00(2)		−0.02(3)
C17						−0.02(2)		−0.02(3)

Table IV. (continued)

Cofficients of the Plane Equation $PX+QY+RZ=S$[b]

Plane	P	Q	R	S
1	14.032	3.349	−2.818	1.155
2	14.003	3.420	−2.805	1.039
3	13.616	−0.359	−5.969	−1.277
4	11.921	6.305	0.758	2.016
5	10.492	6.293	−6.033	1.031
6	14.314	−0.030	1.240	2.395
7	10.797	6.156	−5.850	0.963
8	14.400	0.096	0.964	2.238

a. Ni atom was not included in the calculation of the plane.
b. The equation of plane is in crystal coordinates.
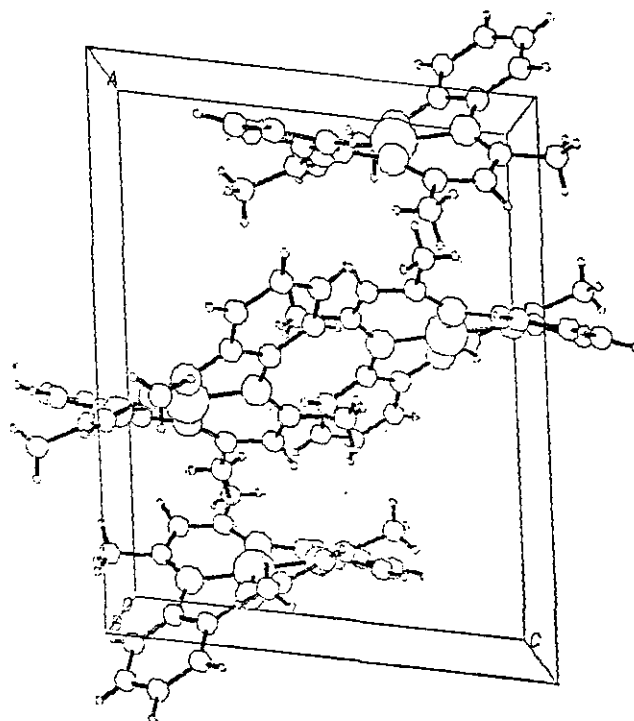
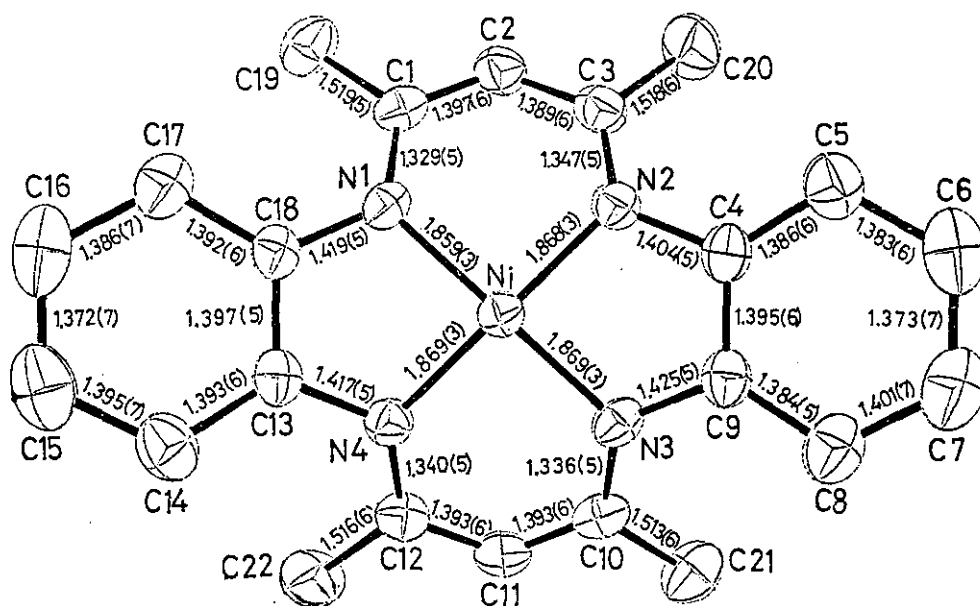Fig. 1. Packing diagram of Ni($C_{22}H_{22}H_4$) in the unit cell.
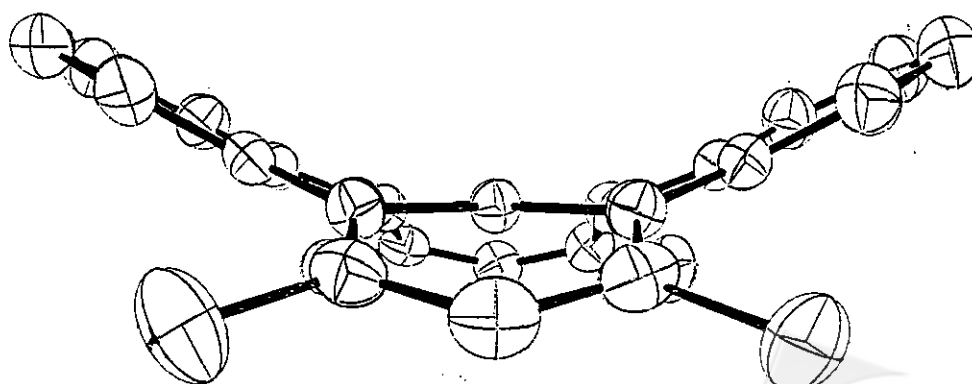
Fig. 2. Saddle-link shape molecular structure of Ni($C_{22}H_{22}N_4$).

Fig. 3. Bond distances of Ni(C₂₂H₂₂N₄).

The ligand is dianionic, thus the 14-membered ring has a 16π-electron system. It forms a saddle-like shape (see Fig. 2) around Ni atom with interplanar angles of benzodiimine/N₄ and pentadiiminato/N₄ 25.8°, 24.7° respectively.

The molecular structures of the free ligand and the Ni complex are compared in Fig. 3 and 4. The bond lengths in the ligand are quite comparable in the benzodiimine moiety. C1-N1, C10-N3, C2-C3 & C11-C12 are somewhat lengthened in the complex than those of free legand, i. e. π-electron in the 2, 4-penta-diiminato part is more delocalized in the complex than that of free ligand. The more obvious
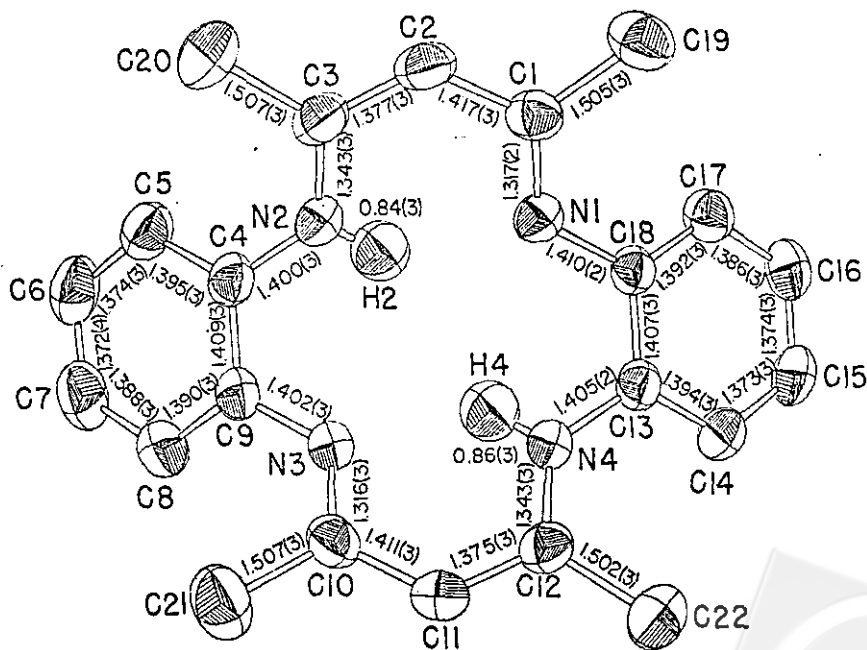

Fig. 4. Bond distances of C₂₂H₂₄N₄.

Table V. Summary of Important Parameters for $M(C_{22}H_{22}N_4)$ Structures

| Compound | Average M-N distance, Å | Metal ion displacement from N_4 plane, Å | Angle between N_4 plane[a] | | Ref |
			Benzene plane[a]	Pentadiiminato plane[b]	
$C_{22}H_{24}N_4$	1.902(Ct-N)	—	24.1, 25.1	32.0, 36.5	7
$Ni(C_{22}H_{22}N_4)$	1.866(3)	0.02	27.4, 27.4	25.5, 24.0	this work
$Co(C_{22}H_{22}N_4)I$	1.901(3)	0.23	21.7, 21.7	19.8, 22.9	9
$Fe(C_{22}H_{22}N_4)$	1.917(3)	0.11	26.2, 21.2	25.2, 23.7	7
$Fe(C_{22}H_{22}N_4)(CO)$	1.927(4)	0.29	22.4, 23.8	24.9, 23.4[c]	8
$Fe(C_{22}H_{22}H_4)(CO)(py)$	1.941(2)	−0.05[d]	22.3, 19.0	19.8, 19.7[c]	8
$Fe(C_{22}H_{22}N_4)(CO)(N_2H_4)$	1.944(4)	0.11	19.5, 26.0	20.6, 22.3	8
$Fe(C_{22}H_{22}N_4)Cl$	2.002(2)	0.60	21.4, 22.2	31.5, 34.2	9
$Mn(C_{22}H_{22}N_4)(NEt_3)$	2.118(3)	0.73	20.6, 20.4	32.8, 37.6	9

a. Benzene planes are defined by C4-C5-C6-C7-C8-C9 and C13-C14-C15-C16-C17-C18 respectively.
b. Pentadiiminato planes are defined by N1-C1-C2-C3-N2 and N3-C10-C11-C12-N4 respectively.
c. Planes were calculated using only four atoms, omitting methine atom C2 C11.
d. Fe is displaced to the opposite of the plane.

change appears in the saddle like conformation; the free ligand gives larger angles (34.2, 36.5°) than those in the complexes (22.2, 25.1°). (see Table V)

Compared with the other seven known structures of the metal complex with this same ligand, the significant differences appear in the metal-nitrogen distance, metal displacement from the N_4 place, and the interplanar angles of pentadiiminato/N_4 plane. The differences are closely correlated in such a way that the longer the M-N distance is, the greater the metal displacement from the N_4 plane is and the larger the tilting (interplanar) angles are, e. g. in $Mn(C_{22}H_{22}N_4)(NEt_3)$ and the title complex, the M-N distances are 2.118, 1.866 Å, the displacements of metal atom from N_4 plane are 0.73, 0.02 Å, and 0.02 Å, and the corresponding tilt angles are 37.6, 24.0 respectively. The angle of benzene/N_4 also implied certain degree of tendency, however it is not as obvious as the ones mentioned above. The detail comparison for the rest of structures are listed in Table V.

REFERENCES

(1) a) N. Herron and D. Busch, *J. Am. Chem. Soc.*, 103, 1236 (1981);
   b) J. Baldwin and J. Huff, *J. Am. Chem. Soc.*, 95, 5757 (1981).
(2) a) S. Peng and V. Goedken, *Adv. Chem. Series*, No. 150 (1976);
   b) S. Peng and V. Goedken, *J. Am. Chem. Soc.*, 98, 8500 (1976).
(3) T. Truex and R. Holm, *J. Am. Chem. Soc.*, 94, 4592 (1972).
(4) F. Hamic, M. Handlovic and O. Lindgren, *Collect Czech. Chem. Comm.*, 37, 2119 (1972).
(5) a) H. Hiller, P. Dimroth, and H. Pfitzner, *Justus Liebigs. Ann. Chem.*, 717, 137 (1968);
   b) P. Chave and C. Honeybourne, *Chem. Comm.*, 279 (1969);
   c) C. Honeybourne, *Inog. Nucl. Chem. Lett.*, 11, 191 (1975).
(6) a) V. Goedken and Y. Park, *Chem. Comm.*, 214 (1975);
   b) V. Goedken, S. Peng, and Y. Park, *J. Am. Chem. Soc.*, 96, 284 (1975).
(7) V. Goedken, J. Pluth, S. Peng, and B. Bursten, *J. Am. Chem. Soc.*, 89, 8014 (1976).
(8) V. Goedken, S. Peng, J. Molin-Norris, and Y. Park, *J. Am. Chem. Soc.*, 98, 8391 (1976).
(9) M. Weiss, B. Bursten, S. Peng, and V. Goedken, *J. Am. Chem. Soc.*, 98, 8021 (1976).
(10) M. Weiss, G. Gordon, and V. Goedken, *Inorg. Chem.*, 16, 305 (1977).
(11) The computation were carried on the local UNIVAC-1106 computer using XRAY/76 system from the university of Maryland. The atomic scattering factors were calculated according to the analytic expression; their coefficients were taken from the International Table Vol. IV based on Hartree-Fock wave function. The anomalous dispersion factors were also taken from Vol. IV.

(12) D. Williams, G. Wohlauer, and R. Rundle, *J. Am. Chem. Soc.*, **81**, 775 (1959).

(13) a) L. Martin, L. DeHayes, L. Zompa, and D. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974);

b) P. Corfield and V. Goedken, private communication.