CRYSTAL AND MOLECULAR STRUCTURE OF THE MACROCYCLIC 2,11-DIMETHYLDIBENZO[6,7,13,14]-1,5,8,12-TETRAAZA-CYCLOTETRADECA-2,4,6,8,10,13-HEXAENE-NICKEL(II) COMPLEX, $C_{20}H_{18}N_4Ni$

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The crystal and molecular structure of the macrocyclic 2,11-dimethyldibenzo[6,7,13,14]-1,5,8,12-tetraazacyclotetradeca-2,4,6,8,10,13-hexaene-nickel(II) complex, $C_{20}H_{18}N_4Ni$, was elucidated with the aid of three-dimensional X-ray structural analysis. The dark purple crystals are orthorhombic with the space group symmetry $Pca2_1$. The unit cell dimensions are a 18·77(2), b 11·26(1), c 7·81(1) Å. The molecular structure is influenced by the steric effect of the two methyl groups adjacent to the π-electron system. The macrocyclic radical represents a flexible skeleton. The benzene rings of the complex are tilted upwards and the planes of the carbon chains connecting the phenylenediamine groups are tilted downwards from the plane of the four nitrogen atoms co-ordinating the metal atom. The normals of these four planes are placed at the angles +25, +12, −21, and −17°, respectively, to the reference plane NiN_4. The complex is diamagnetic. The average interatomic Ni—N distance is 1·85 Å. The average C—C distance in the benzene rings is 1·39 Å. The standard deviation values are 0·02 Å for the Ni—N bonds, and from 0·01 to 0·04 Å for the C—N and C—C bonds. The resulting R-factor for 1 235 reflections is 9·8%.

The X-ray study of the crystal structures of the dimethyl ester of 2,4-diacetyldeuterioporphyrine-nickel(II) (ref.[1]) and of ethioporphyrine-nickel(II) (ref.[2]) has shown significant deviations from the planarity of the porphyrine skeleton. The skeleton of ethioporphyrine nickel(II) (ref.[2]) is deformed in such a way that two of its pyrrole rings are tilted upwards and the other two downwards, from the plane of the four nitrogen atoms. The deviations from planarity have been explained by an angle strain in the σ-bonds[1] or by the presence of bulky substituents on the porphyrine skeleton, where close packing of molecules is achieved at the expense of losing planarity[3]. For this reason, a study was now carried out of the effect of the delocalized π-bonds and of sterical effects in the fourteen membered macrocyclic complex, 2,11-dimethyldibenzo[6,7,13,14]-1,5,8,12-tetraazacyclotetradeca-2,4,6,8,10,13-hexaene nickel(II), (*I*), on the molecular arrangement, using X-ray structural analysis.

EXPERIMENTAL

Chemical and measurements. The macrocyclic nickel(II) complex (*I*) is a condensation product of the nickel(II) complex of N,N′-*o*-phenylene-bis(1-amino-1-buten-3-one) with *o*-phenylene-

diamine[4]. The melting point of the dark purple crystals is 272—274°C, accompanied by thermal decomposition. The prismatic crystals are elongated in the direction of the *c*-axis. The space group symmetry is $Pca2_1$ or *Pcam*. The dimensions of the unit cell of the orthorhombic crystals were determined by the least squares method from the powder diffraction data, using lead(II) nitrate as an internal standard: *a* 18·77(2), *b* 11·26(1), *c* 7·81(1) Å. The unit cell is formed by 4 $NiC_{20}H_{18}N_4$. The measured value of the density ϱ_0, is 1·49 g cm^{-3}; the calculated value, ϱ_x, is 1·50 g cm^{-3}. In order to perform the structural analysis, the intensities of 1140 independent reflections were measured with the automatic diffractometer, Pailred, using the Mo K_α radiation. Ninety five unobserved reflections were substituted by the statistical values according to Hamilton[5]. All intensities were corrected for the background and recalculated to the structure factors on the relative scale, $|F_0|_{rel}$, using a programme which included corrections for the Lorentz and the polarization factors, and for the absorption. The scale factor and the general temperature factor were calculated with the help of the Wilson statistical relation between the mean intensity and the sum of the squares of all the atomic factors of all the atoms in the unit cell[6].

Determination of the structure. The position of the nickel atom was determined from the three-dimensional Patterson function. With the help of the nickel co-ordinates were determined the probable phases of the structure factors. For the co-ordinate z_{Ni} 0·250, the position of the nickel atom is identical with the position of an atom in the plane of symmetry of the centro-symmetrical space group *Pcam*. Probable phases, calculated only from the contributions of the nickel atom, yield a centro-symmetrical function of the electron density for a structure, consisting of the correct positions of the atoms and their "mirror" images, reflected on a plane of symmetry which is oriented perpendicularly to the *c*-axis. It was possible to carry out the choice of the correct atom positions, corresponding to the space group $Pca2_1$, by means of crystallochemical considerations of the structure of the complex compound. The co-ordinates obtained in this manner were refined by the least squares method. The computations were performed on the IBM 360/65 computer (University of Göteborg), using a system of programs which is at disposal at the Institute of Inorganic Chemistry. First, the co-ordinates and the individual isotropic temperature factors of 25 atoms, together with the scale factors of particular layers, were refined (the intensities around the *c*-axis were obtained). The program for the least squares method employed the block diagonal approximation. After five cycles, the value of *R* decreased to 12·1%. In this phase, corrections for anomalous scattering and anisotropic thermal vibrations were included in the least squares method refinement. After another five cycles, the *R*-factor decreased to the final value 9·8% (9·4% for 1140 observed reflections). Unobserved reflections (95) were not included in the refinement.

The resulting atom co-ordinates and their standard deviations are given in Table I. Table II summarizes the observed and calculated structure factors. The distances and angles are shown in Table III, together with the standard deviations. The intramolecular distances and the bond angles are represented in Fig. 1.

RESULTS AND DISCUSSION

The structure consists of the diamagnetic molecules $NiC_{20}H_{18}N_4$. The macrocyclic ring of 2,11-dimethyldibenzo[6,7,13,14]-1,5,8,12-tetraazacyclotetradeca-2,4,6,8,10,13-hexaene is co-ordinated to the metal atom through four —N= groups (*I*). The heterocyclic radical exhibits significant deviations from planarity. The atoms in the molecule are arranged on the following planes: the reference NiN_4 plane, *A*, the planes of the two benzene rings, *B* and *C*, and the planes of the side chains, *D* and *E*, connecting the phenylenediamine groups.

TABLE I

Resulting Atom Parameters and their Standard Deviations

The positional parameters x, y, z are given as fractions and multiplied by the factor 10^4. The thermal parameters correspond to the expression $\exp(U_{11}h^2 + \ldots + 2U_{12}hk + \ldots)$ and are multiplied by the factor 10^5.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	429 (1)	2 323 (2)	2 500 (0)	283 (0)	232 (1)	244 (6)	− 19 (1)	224 (5)	60 (9)
N(1)	619 (7)	1 271 (11)	4 266 (26)	366 (4)	116 (7)	180 (48)	103 (9)	56 (22)	294 (33)
N(2)	− 451 (7)	2 794 (12)	3 305 (25)	275 (3)	281 (9)	246 (52)	−360 (10)	265 (22)	− 507 (36)
N(3)	1 300 (6)	1 826 (11)	1 617 (24)	256 (3)	208 (8)	− 93 (37)	159 (9)	136 (20)	130 (33)
N(4)	257 (7)	3 374 (12)	706 (31)	152 (3)	244 (9)	526 (56)	294 (9)	− 1 (23)	− 167 (42)
C(1)	1 119 (6)	405 (13)	3 824 (28)	49 (3)	304 (9)	−114 (45)	−308 (9)	− 48 (19)	174 (40)
C(2)	1 517 (8)	711 (10)	2 290 (39)	346 (4)	66 (7)	959 (64)	− 12 (9)	− 858 (39)	1 057 (52)
C(3)	1 976 (9)	− 98 (16)	1 654 (36)	271 (4)	311 (12)	311 (59)	−126 (13)	197 (29)	− 182 (50)
C(4)	2 064 (9)	−1 191 (13)	2 512 (56)	481 (4)	266 (10)	589 (64)	600 (13)	− 525 (50)	− 240 (82)
C(5)	1 698 (9)	−1 486 (14)	3 919 (35)	300 (4)	224 (10)	249 (61)	−139 (11)	352 (30)	− 62 (43)
C(6)	1 219 (9)	− 699 (16)	4 630 (42)	296 (4)	354 (12)	746 (68)	−206 (12)	− 951 (37)	409 (64)
C(7)	− 855 (7)	3 472 (10)	2 113 (34)	179 (3)	73 (7)	612 (69)	− 27 (8)	600 (28)	− 265 (40)
C(8)	− 449 (8)	3 824 (13)	657 (36)	311 (4)	207 (9)	575 (56)	−128 (11)	−1 195 (33)	− 313 (46)
C(9)	− 748 (11)	4 533 (14)	−711 (38)	515 (5)	176 (10)	416 (71)	138 (13)	− 194 (38)	119 (50)
C(10)	−1 481 (11)	4 811 (17)	−448 (41)	590 (5)	448 (14)	556 (65)	683 (16)	− 94 (38)	− 25 (68)
C(11)	−1 882 (10)	4 485 (16)	1 023 (42)	292 (4)	306 (12)	806 (92)	281 (14)	− 94 (36)	− 25 (61)
C(12)	−1 571 (7)	3 821 (12)	2 161 (37)	203 (3)	314 (9)	998 (66)	93 (10)	786 (33)	−1 466 (62)
C(13)	− 650 (11)	2 702 (16)	4 923 (44)	394 (5)	364 (14)	638 (83)	− 92 (14)	329 (35)	286 (65)
C(14)	− 264 (11)	2 107 (18)	6 245 (53)	452 (5)	332 (13)	1 040 (90)	−165 (15)	550 (44)	432 (69)
C(15)	355 (8)	1 417 (14)	5 907 (32)	276 (4)	246 (11)	185 (64)	−180 (11)	− 75 (28)	− 19 (40)
C(16)	645 (11)	800 (17)	7 409 (54)	618 (6)	438 (14)	339 (67)	−294 (16)	− 43 (53)	− 150 (84)
C(17)	749 (10)	3 793 (14)	−253 (37)	504 (5)	233 (10)	363 (62)	−189 (13)	− 43 (35)	770 (52)
C(18)	1 436 (9)	3 408 (17)	−375 (45)	285 (4)	402 (14)	656 (77)	−221 (13)	− 117 (36)	286 (66)
C(19)	1 743 (11)	2 479 (13)	617 (39)	576 (6)	84 (8)	263 (63)	−316 (13)	79 (37)	56 (42)
C(20)	2 477 (8)	2 248 (16)	396 (39)	302 (3)	568 (15)	444 (69)	−102 (14)	1 548 (34)	553 (64)

TABLE II

Absolute Values of the Observed and Calculated Structure Factors

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
		L = 0		3	1	59·6	63·6	5	15	4·7[a]	5·7	8	14	4·6[a]	2·3	12	6	23·6	28·2
0	1	42·1	39·0	3	2	105·7	97·1	6	0	7·0	9·8	8	15	18·4	3·0	12	7	18·1	17·1
0	2	124·1	122·3	3	3	23·5	17·1	6	1	17·2	4·3	9	15	88·5	84·9	12	8	22·9	20·8
0	3	25·8	23·5	3	4	18·6	14·7	6	2	9·7	4·7	9	2	14·4	8·9	12	9	18·7	20·7
0	4	36·2	35·1	3	5	14·4	2·7	6	3	15·7	14·6	9	3	32·8	33·6	12	10	17·1	3·9
0	5	36·0	32·3	3	6	27·0	29·4	6	4	2·5[a]	1·7	9	4	17·3	18·4	12	11	23·3	22·2
0	6	50·2	53·5	3	7	23·3	26·0	6	5	2·7[a]	4·1	9	5	16·0	13·8	13	1	17·6	16·6
0	7	64·3	61·4	3	8	23·9	20·5	6	6	21·1	19·4	9	6	11·3	6·9	13	2	17·8	17·5
0	8	55·6	55·7	3	9	17·4	20·7	6	7	3·1[a]	3·7	9	7	20·9	13·3	13	3	8·3	1·7
0	9	39·3	40·7	3	10	37·8	40·0	6	8	3·3[a]	2·6	9	8	35·2	34·5	13	4	24·0	26·5
0	10	37·6	45·0	3	11	3·8[a]	4·3	6	9	3·5[a]	3·9	9	9	19·5	21·4	13	5	19·6	10·8
0	11	20·6	22·1	3	12	22·5	22·2	6	10	3·7[a]	2·0	9	10	36·9	36·3	13	6	12·0	12·7
0	12	4·0[a]	1·8	3	13	4·2[a]	4·4	6	11	3·9[a]	3·4	9	11	24·1	27·2	13	7	9·1	1·8
0	13	28·4	30·4	3	14	9·7	12·5	6	12	16·5	15·3	10	0	128·8	119·9	13	8	13·0	13·4
0	14	10·5	5·7	4	0	19·1	16·5	7	1	48·4	47·7	10	1	16·8	9·9	13	9	4·0[a]	3·1
1	1	47·9	45·0	4	1	5·1	0·3	7	2	22·2	25·1	10	2	91·2	92·7	13	10	4·1[a]	6·1
1	2	49·4	45·4	4	2	115·6	106·1	7	3	51·8	56·7	10	3	32·8	29·4	13	11	4·3[a]	2·9
1	3	78·6	76·9	4	3	31·3	23·8	7	4	20·3	12·2	10	4	36·3	33·5	13	12	4·6[a]	3·4
1	4	10·7	10·6	4	4	50·9	46·8	7	5	31·8	31·1	10	5	12·9	12·7	14	0	42·9	43·5
1	5	22·0	19·9	4	5	26·9	23·7	7	6	19·0	21·4	10	6	42·9	48·0	14	1	12·5	13·7
1	6	54·5	51·3	4	6	21·9	31·0	7	7	38·8	42·6	10	7	39·0	39·4	14	2	51·3	52·2
1	7	15·7	15·3	4	7	19·4	3·0	7	8	49·3	56·2	10	8	31·1	34·3	14	3	15·3	13·8
1	8	15·0	17·5	4	8	35·6	32·8	7	9	21·6	18·2	10	9	3·7[a]	7·2	14	4	45·5	45·2
1	9	9·2	4·3	4	9	39·7	43·2	7	10	35·6	40·4	10	10	3·9[a]	6·0	14	5	27·5	30·9
1	10	17·2	13·1	4	10	3·6[a]	4·3	7	11	31·1	36·2	10	11	18·6	20·5	14	6	22·8	24·8
1	11	15·7	16·5	4	11	18·3	23·9	7	12	21·5	27·0	10	12	4·3[a]	2·1	14	7	11·6	13·0
1	12	12·2	12·8	4	12	4·0[a]	3·7	7	13	14·9	11·0	10	13	28·9	25·8	14	8	22·9	17·5
1	13	8·7	7·7	4	13	17·0	10·6	7	14	18·7	9·8	11	1	2·8[a]	6·3	14	9	17·5	15·8
2	0	159·4	164·4	5	1	75·1	72·8	8	0	105·4	100·2	11	2	31·2	33·1	14	10	19·4	23·4
2	1	30·4	20·9	5	2	61·6	59·3	8	1	18·9	4·6	11	3	15·5	15·5	14	11	21·6	25·8
2	2	133·7	131·0	5	3	13·0	15·6	8	2	33·8	34·7	11	4	14·5	10·2	15	1	31·2	35·0
2	3	1·9[a]	5·8	5	4	48·5	52·4	8	3	15·1	12·3	11	5	12·4	8·4	15	2	24·2	21·5
2	4	22·7	25·1	5	5	23·4	20·5	8	4	16·7	16·2	11	6	3·3[a]	3·6	15	3	32·1	33·7
2	5	12·6	14·5	5	6	25·1	24·7	8	5	2·8[a]	2·6	11	7	30·4	21·1	15	4	27·1	29·2
2	6	45·4	41·5	5	7	50·4	49·9	8	6	39·7	40·3	11	8	11·8	8·4	15	5	24·3	25·9
2	7	39·3	40·9	5	8	46·0	43·5	8	7	18·7	22·0	11	9	19·6	17·1	15	6	19·2	22·8
2	8	29·8	29·8	5	9	38·4	38·3	8	8	44·8	48·8	12	0	69·4	73·4	15	7	18·4	20·0
2	9	24·1	23·3	5	10	47·3	49·1	8	9	24·1	26·6	12	1	37·6	35·7	15	8	20·8	23·6
2	10	20·7	18·7	5	11	3·9[a]	4·9	8	10	21·4	17·7	12	2	48·2	49·6	15	9	23·1	22·7
2	11	24·6	25·3	5	12	45·8	47·8	8	11	4·0[a]	6·0	12	3	16·5	16·7	15	10	27·1	29·5
2	12	4·0[a]	5·6	5	13	4·3[a]	2·6	8	12	12·4	10·5	12	4	44·7	45·3	16	0	11·8	11·9
2	13	21·1	14·2	5	14	20·7	22·4	8	13	17·5	20·9	12	5	19·9	22·4	16	1	17·5	13·1

TABLE II
(*Continued*)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
16	2	16·6	20·7	21	4	18·9	17·0	3	1	96·3	99·1	5	13	4·8[a]	3·6	8	11	22·5	24·7
16	3	11·9	9·5	21	5	4·3[a]	1·4	3	2	51·1	48·8	5	14	9·4	12·5	8	12	18·5	20·4
16	5	3·6[a]	5·7	21	6	4·4[a]	4·5	3	3	79·9	75·0	6	0	64·8	62·5	8	13	20·6	24·0
16	5	3·7[a]	2·7	21	7	10·0	11·2	3	4	31·3	29·8	6	1	20·3	15·4	9	1	70·0	68·0
16	6	3·8[a]	1·8	22	0	4·4	6·2	3	5	27·4	27·4	6	2	83·5	79·7	9	2	27·8	25·8
16	7	21·0	21·0	22	1	12·2	10·0	3	6	22·3	23·1	6	3	48·0	42·8	9	3	49·7	52·7
16	8	19·7	11·8	22	2	23·4	25·9	3	7	32·9	33·1	6	4	75·0	73·2	9	4	17·2	18·4
17	1	24·0	18·4	22	3	11·3	11·3	3	8	19·3	19·8	6	5	45·5	44·7	9	5	35·6	40·6
17	2	16·3	17·2	22	4	18·5	15·3	3	9	29·0	29·9	6	6	35·7	38·0	9	6	23·3	25·1
17	3	25·9	25·2	22	5	8·8	7·7	3	10	35·8	38·4	6	7	34·8	37·6	9	7	41·9	46·3
17	4	15·9	9·7					3	11	9·1	11·1	6	8	50·2	51·6	9	8	23·2	26·6
17	5	38·0	43·3			L = 1		3	12	16·6	17·4	6	9	56·8	63·1	9	9	15·5	16·0
17	6	10·1	7·1					3	13	5·6	5·0	6	10	16·1	14·5	9	10	15·5	17·7
17	7	9·5	8·4	1	1	139·9	143·8	3	14	9·1	9·9	6	11	33·6	38·1	9	11	3·9[a]	3·9
17	8	18·7	20·3	1	2	106·2	103·5	4	0	5·0	17·8	6	12	11·0	9·7	9	12	19·1	16·7
17	9	15·3	13·0	1	3	120·4	109·0	4	1	75·9	67·3	6	13	22·7	21·4	9	13	20·6	6·7
17	10	23·3	24·3	1	4	13·4	11·3	4	2	86·6	73·6	6	14	5·1[a]	5·2	10	0	59·3	60·0
18	0	11·7	10·2	1	5	54·4	56·7	4	3	43·2	44·7	6	15	18·8	14·8	10	1	15·0	17·1
18	1	17·4	15·7	1	6	58·8	57·2	4	4	70·6	71·4	7	1	42·4	41·3	10	2	25·3	26·4
18	2	3·8[a]	3·5	1	7	40·8	42·0	4	5	59·4	56·2	7	2	39·1	35·6	10	3	17·1	21·3
18	3	3·8[a]	3·5	1	8	41·1	39·8	4	6	43·0	46·7	7	3	56·5	50·7	10	4	18·9	20·1
18	4	6·6	4·1	1	9	25·5	27·1	4	7	39·9	39·3	7	4	26·8	28·0	10	5	17·0	17·4
18	5	11·0	7·3	1	10	27·1	31·6	4	8	21·4	21·7	7	5	12·3	7·7	10	6	23·8	24·6
18	6	21·2	20·6	1	11	18·0	15·5	4	9	41·2	45·1	7	6	13·9	15·4	10	7	35·4	38·0
18	7	8·7	9·1	1	12	17·7	18·9	4	10	18·9	18·0	7	7	8·3	9·5	10	8	15·4	13·9
18	8	4·3[a]	3·7	1	13	10·8	8·9	4	11	35·4	35·5	7	8	15·3	9·7	10	9	23·8	27·4
18	9	19·1	17·6	1	14	19·1	14·3	4	12	4·5[a]	5·1	7	9	17·1	14·8	10	10	4·6[a]	4·6
19	1	23·4	26·4	2	0	91·4	92·9	4	13	20·0	20·7	7	10	17·8	19·6	10	11	7·8	4·9
19	2	15·9	14·4	2	1	92·9	92·4	4	14	10·3	12·2	7	11	15·5	8·0	10	12	5·2	5·0
19	3	26·3	28·6	2	2	107·2	101·1	4	15	23·1	19·1	7	12	7·8	8·1	10	13	6·3	4·7
20	0	14·6	15·5	2	3	101·1	88·9	5	1	12·4	14·0	7	13	8·3	6·7	11	0	69·9	70·2
20	1	4·0[a]	2·0	2	4	70·0	65·2	5	2	42·5	36·6	8	0	69·8	65·9	11	2	22·6	22·1
20	2	8·2	8·8	2	5	33·4	31·9	5	3	22·8	23·2	8	1	13·4	7·7	11	3	58·4	60·4
20	3	4·1[a]	1·9	2	6	22·3	21·6	5	4	14·0	10·8	8	2	78·7	75·3	11	4	27·5	30·1
20	4	18·1	17·2	2	7	16·4	18·0	5	5	38·1	38·6	8	3	42·2	39·3	11	5	42·1	41·9
20	5	4·2[a]	6·4	2	8	8·4	9·2	5	6	15·3	13·5	8	4	55·7	54·3	11	6	36·1	35·3
20	6	17·9	18·1	2	9	20·6	19·7	5	7	16·4	16·5	8	5	25·8	26·2	11	7	28·0	29·0
20	7	9·5	5·8	2	10	10·2	11·0	5	8	14·2	16·2	8	6	29·4	30·1	11	8	11·5	11·3
20	8	13·3	13·1	2	11	22·6	26·5	5	9	9·2	9·6	8	7	52·0	55·4	11	9	17·8	17·3
21	1	13·3	12·6	2	12	18·1	15·4	5	10	19·2	11·4	8	8	22·3	23·9	11	10	19·5	17·3
21	2	4·2[a]	1·3	2	13	12·3	16·6	5	11	11·1	12·1	8	9	31·8	35·5	11	11	6·0	4·8
21	3	22·7	16·8	2	14	6·4	4·6	5	12	8·8	10·8	8	10	21·2	23·6	11	12	17·0	21·1

TABLE II
(*Continued*)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
11	13	4·3	5·4	15	3	17·4	14·9	19	3	8·7	6·0	1	2	55·5	51·4	4	6	27·1	29·4
11	14	19·2	18·0	15	4	14·9	13·1	19	4	4·6[a]	4·6	1	3	40·4	33·2	4	7	16·0	19·5
12	0	9·9	10·1	15	5	25·7	28·1	19	5	17·2	16·5	1	4	14·7	18·8	4	8	16·0	19·5
12	1	6·2	3·4	15	6	18·2	17·7	19	6	21·1	13·5	1	5	55·5	49·9	4	9	18·3	21·3
12	2	2·9[a]	2·9	15	7	16·6	20·8	19	7	11·5	12·2	1	6	11·1	9·6	4	10	16·4	13·3
12	3	23·8	27·3	15	8	17·0	17·4	19	8	17·2	7·8	1	7	13·3	10·8	4	11	16·0	18·7
12	4	3·2[a]	3·2	15	9	17·7	17·3	20	0	9·3	10·6	1	8	15·6	10·9	5	1	63·8	64·1
12	5	6·9	8·7	15	10	10·3	8·7	20	1	17·5	9·9	1	9	14·1	14·4	5	2	51·8	45·7
12	6	9·1	8·6	15	11	4·4	5·9	20	2	20·3	19·6	2	0	57·6	50·7	5	3	81·6	80·8
12	7	7·6	3·4	16	0	32·3	34·5	20	3	8·9	8·2	2	1	7·6	6·7	5	4	41·4	34·1
12	8	13·7	11·3	16	1	9·2	8·2	20	4	19·1	18·3	2	2	99·1	97·1	5	5	60·3	61·2
12	9	14·5	15·5	16	2	32·6	31·8	20	5	18·5	16·1	2	3	29·4	33·3	5	6	47·9	48·2
12	10	8·1	10·1	16	3	11·5	14·5	20	6	17·4	14·6	2	4	120·7	110·9	5	7	50·3	50·8
12	11	6·4	7·0	16	4	28·1	28·9	20	7	17·0	15·0	2	5	29·6	30·3	5	8	27·3	28·7
13	1	46·4	49·8	16	5	23·7	20·9	21	1	19·8	23·7	2	6	54·7	58·7	5	9	25·7	25·8
13	2	6·5	6·8	16	6	18·8	22·4	21	2	8·3	6·3	2	7	50·4	49·4	5	10	26·0	28·6
13	3	51·1	51·7	16	7	22·8	23·7	21	3	20·4	14·1	2	8	15·1	12·8	5	11	10·4	10·3
13	4	18·8	22·4	16	8	13·8	12·2	21	4	11·1	10·1	2	9	34·0	35·9	5	12	17·5	19·4
13	5	43·0	49·4	16	9	19·4	16·5	21	5	19·8	16·8	2	10	18·4	17·3	5	13	7·3	10·0
13	6	18·6	16·5	16	10	18·2	20·6	21	6	4·9[a]	5·4	2	11	27·2	28·8	5	14	27·4	25·4
13	7	13·8	15·6	17	1	7·2	7·0	21	7	10·8	13·8	2	12	13·7	16·7	6	0	42·2	45·0
13	8	14·8	20·2	17	2	17·5	18·1	21	8	17·2	11·6	2	13	24·7	19·4	6	1	9·5	11·4
13	9	18·2	17·8	17	3	4·3[a]	3·9	22	0	6·9	9·7	2	14	2·9	7·4	6	2	12·4	10·0
13	10	16·3	19·5	17	4	13·0	13·9					2	15	19·0	21·4	6	3	9·4	8·3
13	11	10·2	7·8	17	5	7·3	6·8			L = 2		3	1	90·8	75·3	6	4	12·5	14·7
13	12	12·4	11·8	17	6	9·5	9·1					3	2	69·1	65·3	6	5	17·1	18·9
13	13	4·8[a]	4·7	17	7	6·6	7·2	0	1	82·6	76·4	3	3	55·2	57·3	6	6	20·6	21·1
13	14	19·8	16·2	17	8	11·8	12·8	0	2	76·1	74·3	3	4	29·0	32·0	6	7	13·4	6·9
14	0	33·2	40·2	17	9	6·7	6·6	0	3	17·3	13·1	3	5	93·6	95·0	6	8	14·2	8·7
14	1	14·3	10·2	17	10	10·0	9·2	0	4	54·8	56·7	3	6	39·9	40·5	6	9	17·3	15·7
14	2	21·3	22·5	18	0	23·7	24·2	0	5	64·8	65·0	3	7	37·2	37·7	7	1	62·5	63·3
14	3	11·8	7·7	18	1	13·1	13·0	0	6	53·4	52·6	3	8	31·5	34·7	7	2	10·8	11·8
14	4	17·0	17·2	18	2	21·0	22·7	0	7	44·3	47·6	3	9	15·9	14·8	7	3	65·0	60·4
14	5	24·4	27·2	18	3	19·5	11·2	0	8	16·4	17·7	3	10	19·8	20·1	7	4	48·7	52·6
14	6	7·6	9·3	18	4	24·8	29·2	0	9	35·1	37·1	3	11	10·6	10·3	7	5	57·4	56·5
14	7	18·8	20·1	18	5	10·9	10·9	0	10	11·1	6·2	3	12	20·9	23·0	7	6	46·0	44·0
14	8	18·7	22·3	18	6	23·1	27·0	0	11	23·0	21·4	4	0	77·4	64·4	7	7	36·2	35·0
14	9	20·9	19·1	18	7	20·5	22·1	0	12	21·3	16·6	4	1	9·5	11·3	7	8	40·9	43·6
14	10	7·7	7·4	18	8	17·3	12·9	0	13	21·5	20·2	4	2	25·4	23·7	7	9	21·2	21·3
14	11	19·0	14·3	18	9	21·1	22·5	0	14	14·7	11·2	4	3	16·9	16·8	7	10	24·6	23·6
15	1	28·1	27·8	19	1	20·6	18·6	0	15	20·7	21·4	4	4	48·6	48·0	7	11	17·3	15·8
15	2	9·1	7·2	19	2	5·1	3·5	1	1	33·6	31·7	4	5	11·9	8·8	7	12	22·8	23·6

TABLE II
(*Continued*)

H	K	FO	FC
		L = 2	
7	13	3·7[a]	3·8
7	14	20·7	23·3
8	0	47·9	43·9
8	1	24·2	24·0
8	2	50·4	55·0
8	3	35·1	33·6
8	4	38·2	34·1
8	5	5·4[a]	5·7
8	7	34·0	36·7
8	6	17·2	16·4
8	8	6·4[a]	4·3
8	9	24·1	26·3
8	10	6·2[a]	4·7
8	11	5·7[a]	16·5
8	12	20·2	10·9
9	1	45·4	48·0
9	2	26·5	24·7
9	3	21·3	20·5
9	4	14·7	15·9
9	5	27·8	26·1
9	6	27·5	29·3
9	7	28·3	28·2
9	8	17·6	20·0
9	9	11·0	14·9
9	10	6·1[a]	11·7
9	11	17·4	6·8
9	12	18·5	18·9
9	13	2·8[a]	4·5
9	14	22·8	11·8
10	0	38·8	38·9
10	1	13·3	15·1
10	2	43·2	44·6
10	3	11·9	10·2
10	4	46·8	46·2
10	5	27·7	27·0
10	6	47·1	49·7
10	7	33·8	35·2
10	8	6·4[a]	5·8
10	9	20·1	18·3
10	10	5·9[a]	10·4
10	11	19·6	15·3
10	12	7·1	9·2
10	13	25·8	28·0
11	1	15·2	17·7
11	2	16·4	15·7
11	3	19·4	13·9
11	4	16·7	13·1
11	5	30·2	32·5
11	6	22·2	27·3
11	7	18·2	20·0
12	0	65·7	59·4
12	1	13·9	9·7
12	2	61·9	62·2
12	3	36·0	40·0
12	4	61·0	68·3
12	5	28·4	26·5
12	6	41·5	43·3
12	7	16·4	13·3
12	8	25·1	24·1
12	9	32·0	30·8
12	10	5·4[a]	5·3
12	11	19·3	20·7
12	12	3·1[a]	2·4
12	13	19·3	16·7
12	14	20·9	10·1
13	1	33i3	33·6
13	2	5·9[a]	3·0
13	3	24·4	26·6
13	4	6·2[a]	2·9
13	5	21·6	23·8
13	6	23·3	23·4
13	7	16·4	13·2
13	8	19·9	17·5
14	0	26·4	27·2
14	1	20·2	21·5
14	2	34·4	35·5
14	3	12·9	13·5
14	4	35·6	39·6
14	5	11·0	9·9
14	6	13·2	17·9
14	7	12·2	10·2
14	8	17·2	20·8
14	9	16·8	21·6
15	1	37·9	41·0
15	2	14·4	9·7
15	3	21·0	20·2
15	4	6·4[a]	3·4
15	5	6·4[a]	9·9
15	6	24·1	26·3
15	7	17·9	19·7
15	8	22·2	19·4
15	9	12·2	14·1
15	10	20·1	15·8
16	0	27·5	30·2
16	1	9·9	8·2
16	2	19·9	17·3
16	3	11·1	8·0
16	4	18·6	18·0
16	5	6·3[a]	7·9
16	6	23·3	24·8
17	1	31·7	36·1
17	2	6·4[a]	3·1
17	3	26·9	28·7
17	4	16·9	15·5
17	5	17·8	18·0
17	6	27·4	30·7
17	7	20·6	18·1
18	0	25·6	27·3
18	1	16·7	18·1
19	1	16·6	15·7
19	2	10·2	8·6
19	3	20·8	20·6
19	4	18·6	15·1
19	5	16·3	20·0
19	6	11·0	12·4
19	7	18·3	17·0
20	0	21·2	27·0
21	1	21·9	19·2
21	2	10·3	13·6
21	3	18·0	13·0
22	0	21·7	23·0
22	1	4·4[a]	3·0
22	2	23·2	28·0
24	1	18·9	3·5
24	2	20·4	19·6
		L = 3	
1	1	70·0	80·9
1	2	20·2	22·1
1	3	70·8	75·0
1	4	53·7	53·4
1	5	55·2	52·6
1	6	37·0	36·4
1	7	28·0	24·8
1	8	38·2	43·0
1	9	18·9	21·7
1	10	23·7	20·5
1	11	19·6	17·0
1	12	25·8	28·9
1	13	6·7	7·4
2	0	11·5	14·7
2	1	27·9	27·8
2	2	48·3	50·1
2	3	35·8	29·0
2	4	28·7	31·7
2	5	23·9	24·7
2	6	29·2	31·3
2	7	21·2	13·0
2	8	21·1	24·2
2	9	23·3	19·5
2	10	21·4	8·4
2	11	13·4	13·4
2	12	4·0[a]	1·3
2	13	21·4	16·5
3	1	42·6	49·6
3	2	34·1	28·4
3	3	81·7	73·7
3	4	55·6	53·9
3	5	65·9	65·4
3	6	15·1	14·0
3	7	26·7	25·8
3	8	18·6	18·0
3	9	21·4	23·9
3	10	31·6	37·4
3	11	4·5[a]	5·2
3	12	18·4	11·1
4	0	37·0	35·4
4	1	15·6	11·8
4	2	91·8	91·7
4	3	27·2	25·9
4	4	62·1	62·2
4	5	56·9	56·0
4	6	36·3	33·5
4	7	28·2	29·4
4	8	51·1	51·3
4	9	7·6	5·3
4	10	20·4	12·5
4	11	26·4	26·7
4	12	6·0[a]	8·2
4	13	27·7	29·5
4	15	23·6	25·7
5	1	21·7	18·0
5	2	47·4	42·5
5	3	36·6	35·4
5	4	12·8	12·1
5	5	13·7	12·2
5	6	18·7	16·2
6	0	91·2	87·4
6	1	2·9[a]	7·1
6	2	44·2	47·9
6	3	44·0	45·0
6	4	48·4	53·1
6	5	35·1	39·6
6	6	48·7	44·0
6	7	30·2	29·4
6	8	36·2	39·7
6	9	17·7	15·3
6	10	14·9	17·8
6	11	28·7	30·0
6	12	11·9	5·0
6	13	21·4	21·3
7	1	10·2	9·0
7	2	39·3	32·6
7	3	51·4	51·7
7	4	27·2	25·6

TABLE II
(*Continued*)

H	K	FO	FC
		L = 3	
7	5	16·2	18·2
7	6	19·2	20·9
7	7	13·1	11·5
7	8	17·9	16·5
7	9	15·4	14·0
7	10	19·0	15·5
8	0	49·7	50·1
8	1	17·3	16·1
8	2	33·7	36·1
8	4	38·6	41·0
8	5	22·9	22·4
8	6	37·2	37·5
8	7	22·8	24·9
8	8	22·4	21·0
8	10	19·9	20·0
8	11	20·6	20·6
8	12	9·2	15·4
8	13	21·4	23·4
9	1	45·2	46·4
9	2	19·3	18·7
9	3	32·6	37·9
9	4	16·4	16·6
9	5	25·7	24·7
9	6	25·7	23·7
9	7	7·4[a]	7·1
9	8	17·0	20·7
9	9	20·4	17·1
9	10	20·5	18·5
9	12	9·7	19·5
9	14	22·1	17·2
10	0	50·1	53·2
10	1	13·3	13·6
10	2	40·7	38·3
10	3	30·2	26·6
10	5	13·4	12·9
10	6	18·5	20·1
10	7	7·5[a]	3·9
10	8	22·3	25·8
10	9	18·8	22·0
11	1	55·3	58·9
11	2	21·6	25·0
11	3	52·3	52·5
11	4	22·8	24·0
11	5	56·9	57·1
11	6	18·1	23·8
11	7	22·7	23·9
11	8	31·3	27·8
11	10	22·8	23·3
12	2	20·0	22·7
12	3	22·1	23·5
12	4	15·2	10·5
12	5	16·5	16·9
12	7	19·0	18·6
12	8	22·8	16·6
13	1	32·3	27·0
13	2	31·0	33·8
13	3	56·2	55·4
13	4	24·8	25·8
13	5	30·2	31·0
13	6	16·3	9·5
13	7	26·4	29·3
13	8	15·5	18·0
13	9	4·1[a]	2·1
13	10	23·8	25·4
14	0	36·5	36·2
14	1	20·7	20·3
14	2	32·0	29·3
14	3	13·5	8·3
14	4	16·2	14·5
14	5	21·2	18·8
14	6	12·0	9·8
14	7	14·8	13·7
14	8	14·8	17·3
14	9	21·0	15·6
14	10	18·4	15·3
15	1	30·8	34·5
15	2	27·5	28·7
15	3	23·1	24·0
15	4	20·0	21·8
15	5	16·0	9·7
15	6	7·2[a]	7·8
15	7	19·9	18·1
15	8	6·2[a]	6·3
15	9	8·7	8·2
15	10	19·4	20·2
16	0	27·8	34·2
16	1	16·3	19·1
16	2	28·1	29·8
16	3	18·5	15·5
16	4	22·6	28·6
16	5	23·8	24·7
16	6	21·4	15·6
16	7	23·8	23·4
16	8	9·2	12·4
16	9	23·5	20·9
18	1	17·2	19·6
18	0	40·1	47·0
18	2	22·8	24·8
18	3	12·6	11·6
18	4	20·3	17·6
18	5	6·3[a]	3·1
18	6	18·0	20·9
18	7	9·4	8·8
18	8	8·5	11·6
18	9	20·2	18·0
18	10	22·6	11·4
18	11	22·6	16·7
19	1	6·7[a]	5·9
19	2	10·5	10·4
19	3	17·4	17·2
19	4	4·0[a]	4·8
19	5	9·3	8·4
19	6	5·2	4·9
20	0	33·7	34·8
20	1	8·0	2·7
20	2	21·7	16·4
21	1	21·8	23·0
		L = 4	
0	1	18·1	19·7
0	2	77·0	83·8
0	3	16·0	12·3
0	4	46·7	43·0
0	5	14·4	11·8
0	6	67·3	69·5
0	7	60·8	63·4
0	8	35·0	33·3
0	9	27·4	28·9
0	10	13·2	13·2
0	11	21·0	16·8
1	1	18·0	20·8
1	2	3·9[a]	6·9
1	3	19·0	19·1
1	4	12·1	14·0
1	5	24·7	23·4
1	6	12·7	9·1
1	7	18·3	19·8
1	8	17·0	12·7
1	9	17·6	11·1
1	10	8·1	6·9
1	11	17·0	11·7
1	12	10·1	14·8
1	13	19·3	13·8
2	0	60·7	51·4
2	1	6·1	4·4
2	2	41·0	42·1
2	3	20·1	23·5
2	4	54·8	50·2
2	5	29·3	30·3
2	6	37·3	38·2
2	7	18·2	22·8
2	8	20·4	19·2
2	9	23·8	21·6
2	10	16·7	14·0
2	11	21·9	18·6
3	1	47·2	44·8
3	2	19·8	15·7
3	3	37·1	36·3
3	4	15·1	18·3
3	5	31·8	31·7
3	6	21·4	23·4
3	7	52·5	46·3
3	8	32·1	31·6
3	9	6·4	7·1
3	10	14·6	13·8
3	11	11·6	11·1
3	12	22·5	20·3
4	0	74·9	71·5
4	1	20·0	21·2
4	2	30·8	29·7
4	3	24·7	23·6
4	4	36·9	33·3
4	5	19·9	23·5
4	6	18·1	17·5
4	7	17·7	16·3
4	8	11·6	11·1
4	9	17·5	15·7
5	1	64·6	66·9
5	2	5·2[a]	5·5
5	3	61·7	59·7
5	4	34·1	36·2
5	5	56·7	58·4
5	6	48·1	53·3
5	7	36·9	37·3
5	8	32·2	35·7
5	9	18·2	19·4
5	10	19·9	20·6
5	11	21·7	21·6
5	12	22·4	19·9
6	0	31·9	25·1
6	1	13·6	10·5
6	2	19·1	16·7
6	3	13·1	12·0
6	4	15·7	18·5
6	5	11·7	14·7
6	6	7·7[a]	5·7
6	7	16·8	7·5
6	8	8·3[a]	3·0
6	9	15·8	12·9
7	1	70·2	66·7
7	2	24·9	25·2
7	3	44·1	43·5
7	4	14·4	17·8
7	5	52·1	56·7
7	6	32·9	33·8
7	7	15·2	16·9
7	8	24·2	21·9

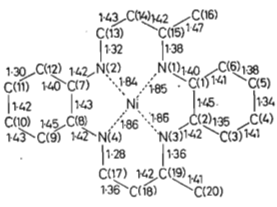
TABLE II
(*Continued*)

H	K	FO	FC
		L = 4	
7	9	16·9	16·1
7	10	21·6	21·4
7	11	18·2	15·6
8	0	39·6	36·8
8	1	15·8	12·5
8	2	37·9	37·9
8	3	6·8[a]	7·3
8	4	28·4	28·8
8	5	16·0	12·4
8	6	20·4	19·1
8	7	24·0	20·7
9	1	45·1	40·0
9	2	9·7	15·4
9	3	47·8	49·8
9	4	4·1[a]	3·3
9	5	30·1	28·9
9	6	15·5	17·5
9	7	24·5	25·3
9	8	27·2	29·7
9	9	7·8	6·8
9	10	18·2	24·3
10	0	64·6	61·3
10	1	7·1[a]	6·4
10	2	33·5	37·0
10	3	15·9	14·8
10	4	46·8	49·0
10	5	28·3	29·9
10	6	32·3	31·4
10	7	32·1	34·2
10	8	14·7	13·1
10	9	19·0	19·7
11	1	5·3[a]	4·1
11	2	17·5	21·1
11	3	31·4	36·6
11	4	22·5	25·3
11	5	23·1	21·8
11	6	6·4[a]	6·4
11	7	6·2[a]	9·0
11	8	17·9	12·4
12	0	29·1	27·7
12	1	19·5	21·4
12	2	37·3	35·8
12	3	23·3	23·3
12	4	36·4	34·3
12	5	8·3[a]	11·3
12	6	29·1	33·3
12	7	22·2	12·7
12	8	21·5	18·7
12	9	21·3	22·1
12	10	5·7[a]	11·1
12	11	29·0	29·0
13	1	24·2	27·9
14	0	38·2	42·1
14	1	8·3[a]	9·1
14	2	31·7	33·0
14	3	16·0	17·6
14	4	31·2	30·2
14	5	21·1	20·0
14	6	19·4	17·6
14	7	13·6	15·1
14	8	11·0	12·2
14	9	21·9	21·7
15	1	28·1	29·5
15	2	16·6	17·7
15	3	29·7	33·2
15	4	20·5	20·5
16	0	16·6	18·2
16	1	13·4	12·6
16	2	4·5[a]	6·4
16	3	4·4[a]	4·0
16	4	15·7	18·0
16	5	19·0	12·1
17	1	23·5	29·9
17	2	6·9[a]	7·0
17	3	34·4	37·8
18	1	9·2	6·0
18	2	8·6	6·1
18	3	11·7	10·3
18	4	15·4	14·6
19	1	21·6	25·7
19	2	11·1	9·2
19	3	24·8	24·6
19	4	6·1[a]	5·6
19	5	26·2	30·6
20	0	23·6	25·7
20	1	5·3[a]	6·9
20	2	19·0	22·1
20	3	19·0	19·3
20	4	6·3[a]	11·4
		L = 5	
1	1	40·0	51·6
1	2	20·2	18·2
1	3	60·4	60·6
1	4	22·2	20·7
1	5	28·1	20·6
1	6	33·5	33·0
1	7	36·9	39·5
1	8	30·5	29·8
1	9	21·1	19·3
1	10	35·3	38·2
1	11	11·8	16·2
1	12	24·8	28·1
2	0	36·9	39·1
2	1	12·7	14·4
2	2	23·8	24·6
2	3	25·6	27·7
2	4	37·5	36·3
2	5	14·0	14·0
2	6	39·5	40·9
2	7	15·5	15·1
2	8	16·9	17·5
2	9	19·8	21·3
2	10	13·5	6·5
2	11	18·9	20·2
3	1	45·0	49·8
3	2	20·5	20·9
3	3	28·5	23·3
3	4	27·8	28·1
3	5	18·5	17·2
3	6	26·6	28·2
3	7	5·2[a]	5·3
3	8	28·5	24·2
3	9	14·5	7·6
3	10	25·5	27·2
4	0	46·2	46·2
4	1	5·0[a]	7·1
4	2	44·6	48·7
4	3	15·6	13·6
4	4	47·7	47·9
4	5	24·1	25·7
4	6	15·5	15·4
4	7	19·5	22·8
4	8	17·7	20·3
4	9	34·1	33·9
4	10	18·0	18·0
5	1	29·5	27·3
5	2	8·6	2·6
5	3	17·0	17·4
5	4	13·2	14·6
5	5	19·1	16·9
5	6	21·6	24·3
6	0	65·1	68·0
6	1	6·7[a]	10·5
6	2	78·4	74·4
6	3	20·5	24·1
6	4	38·1	39·7
6	5	18·9	22·6
6	6	25·7	22·7
6	7	25·1	24·2
6	8	22·8	22·7
6	9	27·7	28·0
6	10	14·5	20·6
6	11	20·7	21·2
7	1	16·5	17·4
7	2	12·7	7·7
7	3	20·3	20·7
7	4	14·8	12·9
7	5	24·7	27·8
7	6	7·5[a]	6·2
7	7	16·3	10·2
8	0	48·4	47·4
8	1	13·1	8·1
8	2	40·3	37·4
8	3	6·8[a]	4·5
8	4	51·3	53·1
8	5	19·2	16·3
8	6	25·6	30·4
8	7	24·1	22·6
8	8	14·8	13·6
8	9	21·6	15·4
9	1	46·2	51·0
9	2	20·0	20·7
9	3	24·4	27·6
9	4	16·6	15·6
9	5	24·6	23·6
9	6	22·3	23·8
9	7	20·7	20·5
9	8	15·6	16·7
9	9	14·8	18·6
9	10	19·6	17·8
10	0	14·8	15·3
11	1	26·2	26·5
11	2	15·4	16·2
11	3	22·8	20·3
11	4	18·8	25·2
11	5	24·8	24·0
11	6	22·7	25·0
11	7	26·3	30·8
11	8	15·1	20·7
11	9	21·6	15·7
11	10	24·7	20·3
12	0	15·6	11·4
12	1	16·2	12·6
12	2	21·4	17·5
12	3	19·7	12·7
12	4	18·0	17·0
13	1	25·4	27·3
13	2	19·5	21·2
13	3	27·5	26·7
13	4	22·5	22·2
13	5	21·9	23·9
13	6	23·9	24·5
13	7	23·6	17·6
13	8	14·5	26·8
13	9	10·8	14·0
13	10	23·8	20·5

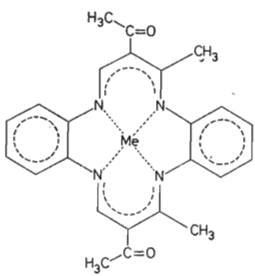
TABLE III
(*Continued*)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
		L = 5		14	3	20·8	18·5	15	1	26·4	33·4	15	6	21·7	19·1	16	4	25·3	27·3
				14	4	19·4	15·5	15	2	5·3[a]	3·8	16	0	25·9	28·7	17	2	4·8[a]	8·1
14	0	19·4	17·6	14	5	5·1[a]	4·9	15	3	18·8	13·3	16	1	10·0	7·1	17	3	4·6[a]	3·9
14	1	24·5	14·2	14	6	20·6	19·3	15	4	20·4	9·1	16	2	35·2	39·4	18	0	25·3	27·9
14	2	26·5	27·3	14	7	22·0	16·3	15	5	19·9	19·6	16	3	5·0[a]	2·6	18	1	10·3	5·7

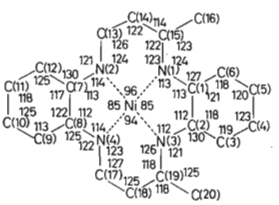
[a] Unobserved reflections.

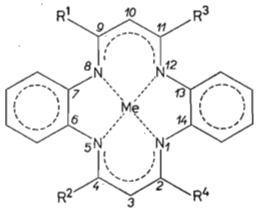


a



IV





b

FIG. 1
Intramolecular Distances (*a*) and Bond Angles (*b*) in the $NiC_{20}H_{18}N_4$ Complex

I; $R^1 = R^2 = H$, $R^3 = R^4 = CH_3$
II; $R^1 = R^2 = H$, $R^3 = R^4 = C_6H_5$
III; $R^1 = R^2 = R^3 = R^4 = CH_3$

TABLE III

Bond Lengths and Angles in $NiC_{20}H_{18}N_4$

Bond	Å	Bond	Å
Ni–N(1)	1·85 (2)	C(3)–C(4)	1·41 (3)
Ni–N(2)	1·84 (1)	C(4)–C(5)	1·34 (4)
Ni–N(3)	1·86 (1)	C(5)–C(6)	1·38 (3)
Ni–N(4)	1·86 (2)	C(7)–C(12)	1·40 (2)
N(1)–C(1)	1·40 (2)	C(7)–C(8)	1·42 (3)
N(1)–C(15)	1·38 (3)	C(8)–C(9)	1·45 (3)
N(2)–C(7)	1·42 (2)	C(9)–C(10)	1·43 (3)
N(2)–C(13)	1·32 (4)	C(10)–C(11)	1·42 (4)
N(3)–C(2)	1·42 (2)	C(11)–C(12)	1·30 (3)
N(3)–C(19)	1·36 (3)	C(13)–C(14)	1·43 (4)
N(4)–C(8)	1·42 (2)	C(14)–C(15)	1·42 (3)
N(4)–C(17)	1·28 (3)	C(15)–C(16)	1·47 (4)
C(1)–C(2)	1·45 (3)	C(17)–C(18)	1·36 (3)
C(1)–C(6)	1·41 (3)	C(18)–C(19)	1·42 (3)
C(2)–C(3)	1·35 (2)	C(19)–C(20)	1·41 (2)
	angle (°)		angle (°)
N(1)–Ni–N(2)	95·9 (0·7)	N(1)–C(1)–C(6)	126·6 (1·8)
N(1)–Ni–N(3)	85·1 (0·7)	C(2)–C(1)–C(6)	120·7 (1·6)
N(1)–Ni–N(4)	178·8 (0·6)	N(3)–C(2)–C(1)	111·5 (1·4)
N(2)–Ni–N(3)	178·0 (0·8)	N(3)–C(2)–C(3)	130·1 (2·4)
N(2)–Ni–N(4)	85·3 (0·7)	C(1)–C(2)–C(3)	118·2 (1·7)
N(3)–Ni–N(4)	93·7 (0·7)	C(2)–C(3)–C(4)	119·3 (2·5)
Ni–N(1)–C(1)	113·1 (1·5)	C(3)–C(4)–C(5)	123·2 (1·9)
Ni–N(1)–C(15)	123·0 (1·0)	C(4)–C(5)–C(6)	120·4 (1·8)
C(1)–N(1)–C(15)	123·6 (1·7)	C(1)–C(6)–C(5)	118·3 (2·4)
Ni–N(2)–C(7)	114·2 (1·4)	N(2)–C(7)–C(8)	112·6 (1·3)
Ni–N(2)–C(13)	123·9 (1·4)	N(2)–C(7)–C(12)	130·2 (2·1)
C(7)–N(2)–C(13)	121·0 (1·6)	C(8)–C(7)–C(12)	117·2 (2·0)
Ni–N(3)–C(2)	112·4 (1·2)	N(4)–C(8)–C(7)	112·3 (1·9)
Ni–N(3)–C(19)	126·1 (1·1)	N(4)–C(8)–C(9)	125·4 (2·1)
C(2)–N(3)–C(19)	121·0 (1·4)	C(7)–C(8)–C(9)	122·3 (1·5)
Ni–N(4)–C(8)	114·2 (1·5)	C(8)–C(9)–C(10)	112·9 (2·2)
Ni–N(4)–C(17)	123·3 (1·3)	C(9)–C(10)–C(11)	124·8 (2·4)
C(8)–N(4)–C(17)	121·8 (1·9)	C(10)–C(11)–C(12)	117·6 (1·8)
N(1)–C(1)–C(2)	112·6 (1·4)	C(7)–C(12)–C(11)	125·1 (2·3)
N(2)–C(13)–C(14)	125·7 (2·1)	N(4)–C(17)–C(18)	127·4 (2·1)
C(13)–C(14)–C(15)	122·4 (3·2)	C(17)–C(18)–C(19)	125·4 (2·4)
N(1)–C(15)–C(14)	122·0 (2·3)	N(3)–C(19)–C(18)	117·5 (1·7)
N(1)–C(15)–C(16)	123·4 (1·7)	N(3)–C(19)–C(20)	124·6 (1·8)
C(14)–C(15)–C(16)	114·4 (1·5)	C(18)–C(19)–C(20)	117·6 (2·1)

Plane *A*, computed by the least squares method for the atoms N(1), N(2), N(3), and N(4), is defined by the equation

$$-0{\cdot}4482x - 0{\cdot}7315y - 0{\cdot}5137z = -3{\cdot}2622 .$$

The deviations of the atoms from the reference plane *A* are as follows: N(1)- −0·02, N(2): 0·02, N(3): 0·02, N(4): −0·02, Ni: −0·01, C(1): 0·45, C(2): 0·48, C(3): 1·02, C(4): 1·50, C(5): 1·49, C(6): 0·96, C(7): 0·28, C(8): 0·23, C(9): 0·44, C(10): 0·73, C(11): 0·74, C(12): 0·57, C(13): −0·39, C(14): −0·75, C(15): −0·57, C(16): −0·91, C(17): −0·39, C(18): −0·60, C(19): −0·49, C(20): −0·83 Å. The benzene ring plane, *B*, computed by the least squares method from the atoms C(1), C(2), C(3), C(4), C(5), and C(6), is represented by the equation:

$$-0{\cdot}7270x - 0{\cdot}3030y - 0{\cdot}5631z = -3{\cdot}3870 .$$

The deviations of the atoms from the mean plane are as follows: C(1): 0·00, C(2): 0·00, C(3): 0·01, C(4): −0·01, C(5): 0·00, C(6): 0·00 Å. The plane of the other benzene ring, *C*, computed by the least squares method from the positions of C(7), C(8), C(9), C(10), C(11), and C(12), is given by the equation

$$-0{\cdot}2741x - 0{\cdot}8344y - 0{\cdot}4782z = -3{\cdot}6044 .$$

The computed distances of the atoms from the central plane are as follows: C(7): 0·00, C(8): 0·00, C(9): 0·00, C(10): 0·01, C(11): −0·02, C(12): 0·02 Å. The side ring plane, *D*, computed by the least squares method from the atoms C(13), C(14), C(15) and C(16), is given by

$$-0{\cdot}5684x - 0{\cdot}8037y - 0{\cdot}1761z = -2{\cdot}4533 .$$

The following deviations of the atoms from the mean plane were calculated: C(13): 0·03, C(14): −0·03, C(15): −0·02, C(16): 0·02, N(1): 0·06, N(2): −0·05 Å. The side ring plane, *E*, computed by the least squares method from the atoms C(17), C(18), C(19), and C(20), is given by

$$-0{\cdot}2383x - 0{\cdot}6584y - 0{\cdot}7173z = -2{\cdot}9679 .$$

The deviations of the atoms from the plane are as follows: C(17): −0·01, C(18): 0·01, C(19): 0·02, C(20): −0·02, N(3): 0·13, N(4): −0·03 Å.

The normals of planes *B*, *C*, *D*, *E* deviate from the normal of the reference plane, *A*, by +25°, +12°, −21°, and −17°, respectively. The two benzene rings are tilted upwards and the planes of the side chains connecting the benzene rings are tilted downwards, from the plane of the nitrogen atoms co-ordinated around the metal atom. The angle between the normals to the benzene rings, *B* and *C*, is 37°, the angle between the normals to the planes superimposed on the side chains, *D* and *E*, is 38°. The macrocyclic radical represents a flexible skeleton. The steric effects of the two methyl groups in positions 2 and 11 on the macrocyclic ring affect the molecular structure and the skeleton deformation. The close approach of the methyl groups and the benzene rings can be alleviated only at the expense of losing planarity. The intramolecular distances C(6)−C(16) and C(3)−C(20) are 2·96 and 2·97 Å, where C(16) and C(20) are the carbon atoms of the methyl groups. The bond angles C(14) to

C(15)–C(16), 114°, and N(1)–C(15)–C(16), 123°, are unsymmetrical. Similar differences are observed between the bond angles C(18)–C(19)–C(20), 118°, and N(3)–C(19)–C(20), 125°.

The average bond length in the benzene ring, *B*, is 1·38 Å, in the benzene ring, *C*, is 1·40 Å. There are significant differences among the C–N bond lengths. The average C–N distances in the phenylenediamine groups are 1·41 and 1·42 Å. The C–N bond lengths between the carbon atoms, C(15) and C(19), which connect the methyl groups with the nitrogen atoms, N(1) and N(3), are 1·38 and 1·36 Å, respectively. Significantly shorter are the N(2)–C(13) and N(4)–C(17) distances: 1·32 and 1·28 Å, respectively. This indicates the partial double character of the bonds, N(2)–C(13) and N(4)–C(17), and a limited delocalization of the π-bond.

The average C–C bond length in the side chain is 1·42 Å. The two methyl groups, adjacent to the π-electron system, partially enter the conjugation present in the macrocyclic ring. This follows also from the short C(15)–C(16) and C(19)–C(20) distances: 1·47 Å and 1·41 Å, respectively. The average Ni–N interatomic distance, 1·85 Å, is short, but typical for diamagnetic nickel complexes. The standard deviations for the Ni–N bonds lie within 0·01 to 0·02 Å, while for the bond angles they have the value 0·7°.

It is interesting to note that the bathochromic shift in the electron absorption spectra of the derivatives, *II* and *III*, can be related to the presence of bulky substituents on the macrocyclic ring, which cause further atomic deviations from planarity[4]. The presence of the —(CO)Me substituent in the *meso* position (*IV*), which affects the charge transfer from the ring, causes a hypsochromic shift in the electron absorption spectra, probably due to a more general π-bond delocalization in the macrocyclic radical, with the more planar arrangement.

The crystals of $NiC_{20}H_{18}N_4$ *were prepared by Dr E. G. Jäger, University of Jena, GDR.*

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