TABLE VI

NONBONDED ATOM DISTANCES (Å) LESS THAN 4 Å WITH STANDARD DEVIATION OF LAST FIGURE IN PARENTHESES

Cl(1)–Cl(2)	3.34 (2)	Cl(2)–O^c	3.05 (2)
–Cl(3)	3.27 (2)	Cl(3)–N	2.91 (4)
–K^d	3.26 (2)	–N^d	3.55 (3)
–K^b	3.39 (1)	–K^d	3.37 (11)
–O^b	3.56 (2)	–O^d	3.98 (2)
Cl(2)–Cl(3)^e	3.56 (2)	K–O^a	2.76 (2)
–N	3.12 (6)	–O	2.80 (2)
–N^c	3.30 (4)		

[a] Atom at 0, $-y$, $^1/_2 + z$. [b] Atom at $^1/_2$, $^1/_2 + y$, z. [c] Atom at $^1/_2$, $^1/_2 - y$, $^1/_2 + z$. [d] Atom at $^1/_2$, $^1/_2 - y$, $z - {}^1/_2$. [e] Atom at 0, y, $1 + z$.

4.19, $b = 17.6$, $c = 8.84$ Å), and is surrounded by eight chlorine atoms in a distorted cubic coordination. In the monohydrate, the potassium is displaced from the origin to a site which has six chlorine atoms at the corners of a trigonal prism and two water molecules in the centers of two of the rectangular faces. Thus water can be relatively easily lost from the lattice without much disruption of the structure, particularly in the $Cmc2_1$ model where the water molecules all lie above each other along the x axis, but the featureless difference Fourier synthesis and normal thermal parameters for oxygen confirm that the crystal examined here was fully hydrated. The potassium–oxygen distances (2.76 (2) and 2.80 (2) Å) are normal, the three potassium–chlorine distances (3.26 (2), 3.37 (1), 3.39 (1) Å) are somewhat longer than is commonly found (3.20–3.30 Å).[23]

The water molecule has an approximately tetrahedral environment, consisting of two potassium ions and two chlorine atoms [(angle Cl–O–Cl 97°, K–O–K 104°)]. The oxygen–chlorine distance of 3.05 (2) Å is slightly less (0.15 Å) than the sum of the van der Waals radii for oxygen and chlorine, and it is tempting to suggest that the water hydrogen atoms lie on these directions with a weak hydrogen bond between them. This is also a favorable electrostatic configuration of the oxygen atom with respect to the potassium ions.

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The Crystal and Molecular Structure of Bis(3,3′,5,5′-tetramethyldipyrromethenato)nickel(II)[1]

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The crystal and molecular structure of bis(3,3′,5,5′-tetramethyldipyrromethenato)nickel(II), $Ni(C_{13}N_2H_{15})_2$, has been determined by single-crystal X-ray diffraction methods. The crystal data are: space group A2/a (C_{2h}^6, no. 15); cell dimensions $a = 22.352 \pm 0.007$ Å, $b = 7.337 \pm 0.005$ Å, $c = 31.496 \pm 0.008$ Å, $\beta = 114.70 \pm 0.05°$, $V = 4692.7$ Å^3; density 1.29 ± 0.02 g/cm^3 (by flotation), 1.294 g/cm^3 (calcd for $Z = 8$). The intensities of 1616 reflections collected on a manually operated counter diffractometer with Cu Kα radiation were used in solution and refinement. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods to final unweighted and weighted residuals of 0.068 and 0.097, respectively. The molecule possesses distorted D_2 symmetry, and the dihedral angle between the least-squares planes formed by the two ligands (including the nickel atom in each case) is 76.3°. The nickel–nitrogen bond lengths (1.948 (7)–1.957 (8) Å) are identical within experimental error. The bond lengths among the ring atoms indicate that electron delocalization occurs over each planar ring system.

Introduction

Metal complexes of dipyrromethenes are of interest because of their close relation to the biologically important metalloporphyrins. Several papers have appeared in the literature in which the preparation, spectra, magnetic properties, and possible structures of metal complexes of substituted dipyrromethenes are discussed. Much of this work centers on ligands containing methyl substituents in the 5 position of each ring. Porter[3] dealt with bivalent metal complexes (Co, Ni, Cu, Zn, Cd, Pd) and concluded on the basis of models that a planar configuration of the ligands was impossible due to steric repulsions between the 5- and 5′-methyl groups on one ligand and those on the other. Even with hydrogen atoms in the 5,5′ positions, there would probably be sufficient repulsion that true planarity (D_{2h}) could not be achieved.

Recent work by Ferguson and Ramsey[4] and Ferguson and West[5] favors a tetrahedral or distorted tetrahedral arrangement of the ligands. However, their work as well as that of Murakami and Sakata[6] seems to indicate that removal of one or both substituents in the 5 positions on the rings allows a twisting toward planarity, especially in a coordinating solvent.

In view of the uncertainty as to the detailed structure of this type of complex and as a basis for our further

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[1] Research supported by the U. S. Atomic Energy Commission.

[2] NDEA Predoctoral Fellow, 1967–1969.

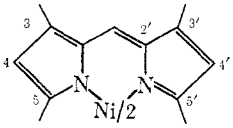
[3] C. R. Porter, *J. Chem. Soc.*, 368 (1938).

[4] J. E. Ferguson and C. A. Ramsey, *ibid.*, 5222 (1965).

[5] J. E. Ferguson and B. O. West, *ibid.*, *A*, 1565 (1966).

[6] Y. Murakami and K. Sakata, *Inorg. Chim. Acta*, **2**, 273 (1968).

investigations of the electronic structures of such molecules, we have undertaken to determine the molecular and crystal structures of several of them by X-ray diffraction. The particular compound chosen first was bis(3,3′,5,5′-tetramethyldipyrromethenato)nickel(II). This compound, I, is easily prepared, forms good crystals, and does not require any special handling.



I

Experimental Section

A sample of bis(3,3′,5,5′-tetramethyldipyrromethenato)nickel(II) was kindly provided by Dr. Stanley Bloom of the Polaroid Corp., Cambridge, Mass. Crystals suitable for X-ray work were obtained by slow diffusion of 1-butanol into a saturated benzene solution of the complex. The crystals, which are dark green and possess a metallic luster, are stable in air.

A single crystal was examined by both Weissenberg (*h0l* and *h1l*) and precession photography (0*kl*, 1*kl*, *hk*0, and *hk*1) and was found to be monoclinic. The systematic absences $k + l = 2n + 1$ for all *hkl* and $h = 2n + 1$ for *h0l* reflections imply that the space group is either A2/a or Aa. These nonstandard choices are equivalent to the standard space groups[7] C2/c (C_{2h}^6, no. 15) or Cc (C_s^4, no. 9), to which they may be converted by interchange of the *a* and *c* axes and reversing the direction of the *b* axis. The space group A2/a with equivalent positions $\pm(x, y, z;\ ^1/_2 - x, y, ^1/_2 - z;\ ^1/_2 + x, ^1/_2 - y, z;\ -x, ^1/_2 - y, ^1/_2 - z)$ was shown to be correct by the successful solution of the structure.

The unit cell dimensions were measured at 22° on a manually operated General Electric XRD-5 diffractometer with Cu Kα radiation [$\lambda(K\alpha_1)$ 1.5404 Å, $\lambda(K\alpha_2)$ 1.5443 Å] and found to be $a = 22.352 \pm 0.007$ Å, $b = 7.337 \pm 0.005$ Å, $c = 31.496 \pm 0.008$ Å, and $\beta = 114.70 \pm 0.05°$, where the error figures quoted are the authors' estimates. Based on the above dimensions and a formula weight of 457.3, the calculated density for $Z = 8$ is 1.289 g/cm^3 which agrees well with the value of 1.29 ± 0.02 g/cm^3 determined by flotation in aqueous $ZnBr_2$ solution. With $Z = 8$ there are no crystallographic symmetry elements imposed on the molecule. The value of μ is 12.9 cm^{-1}.

Intensity data were collected on the manually operated General Electric XRD-5 diffractometer. A monoclinic needle (0.504 mm long) was mounted on a glass fiber with the needle (*b*) axis coincident with the ϕ axis of the eucentric goniometer.[8] The faces corresponded closely to the 001 and 101 faces and had widths of 0.077 and 0.038 mm, respectively. Cu Kα radiation with Ni filtering at the counter was used to collect 2476 independent reflections (*hkl* and $\bar{h}kl$) within the sphere $\theta < 51.0°$. Intensities were measured by a scintillation counter with the pulse height discriminator set to receive 95% of the Cu Kα peak. A coupled θ–2θ moving crystal, moving counter scan technique was employed with a scan range of 2.66° and a scan rate of 4°/min. The takeoff angle was 2°.

Integrated intensities (I) were obtained by subtracting from the total number of counts (P) during the 2.66° scan (40 sec) the total number of counts (B_1, B_2) during 20-sec background measurements at each limit of the scan ($2\theta_{max} - 1.33°$ and $2\theta_{max} + 1.33°$). Assuming the background to vary linearly over the scan range, $I = P - B_1 - B_2$. Several reflections exceeded the linear response range of the counter and were remeasured at a lower tube current. These were scaled to the bulk of the data by measuring several medium-intensity reflections at both tube currents and computing a scaling factor. Six reflections were checked periodically to monitor any decomposition of the crystal. For about the first third of the time of data collection there was no sustained trend, but then a period of slow decline commenced to an average minimum of 96.6% of the original values. This was followed by a sudden increase on the last day of data collection to an average of 101.3% of the original values. It is unlikely that these variations are due to a misaligned or wandering crystal since the alignment was checked frequently. The most probable cause is instability in the instrument electronics, and thus a correction has been applied to the data to account for these changes. Visual examination of the crystal after the data were taken gave no indication of decomposition.

The experimental data were converted to values of $|F_o|^2$ and $|F_o|$ by means of a Fortran IV program PMMO written by M. J. Bennett. Of the 2476 reflections taken, 860 were rejected on the criterion $I/(P + B_1 + B_2)^{1/2} < 3$. The program also calculates an estimated standard deviation for each reflection using the formula.

$$\sigma(F_o) = \text{RLP}\frac{[P + B_1 + B_2 + 0.002(I)^2]^{1/2}}{2.0|F_o|}$$

where RLP is the reciprocal Lorentz–polarization factor. The remaining 1616 reflections were then used for solution and refinement of the structure.

Solution and Refinement

The three-dimensional Patterson function was computed[9] and after some difficulties was successfully interpreted in terms of one nickel atom in a general position of the centric space group A2/a. The nickel atom positional and isotropic thermal parameters were subjected to two cycles of least-squares refinement[10] which gave a conventional (*i.e.*, unit-weighted) residual, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.49. The scattering factors employed were those for neutral Ni (and subsequently for neutral N and C) given by Cromer and Waber.[11] An anomalous dispersion correction was applied to the nickel atom, using the values for $\Delta f'$ and $\Delta f''$ of Cromer.[12] The observed structure factors were now given the same signs as the structure factors calculated from the nickel atoms alone and an electron density map was computed. From it the positions of 13 light atoms, including the four nitrogen atoms, were ascertained. Several more cycles of least-squares refinement, which included anisotropic refinement of the nickel atom, reduced the residual to 0.359. At this point another electron density map was computed, and the approximate coordinates of all the remaining atoms were determined. Three more cycles of least-squares refinement lowered R_1 to 0.086. Another difference Fourier map showed no anomalies indicative of neglected atoms. Up to this point the weighting coefficients employed in all least-squares refinement cycles were given by σ^{-2}, where σ is the esd of the observed structure factor as defined earlier.

An absorption correction[13] was now made (the trans-

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(7) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962.

(8) Diffractometer settings were calculated using D. P. Shoemaker's "MIXG2-A, M.I.T. X-ray Goniometer Package," 1962.

(9) This and other Fourier syntheses were computed using FORDAP II, a version of Zalkin's original program FORDAP, extensively modified and adapted to the IBM 360 computer by B. M. Foxman and L. N. Becka.

(10) Computed using SFLS5, "A Full-Matrix Crystallographic Program for the IBM 360" by C. T. Prewitt (modified by B. M. Foxman), 1966. This program minimizes $\Sigma w||F_o| - |F_c||$, where $w = 1/\sigma^2$.

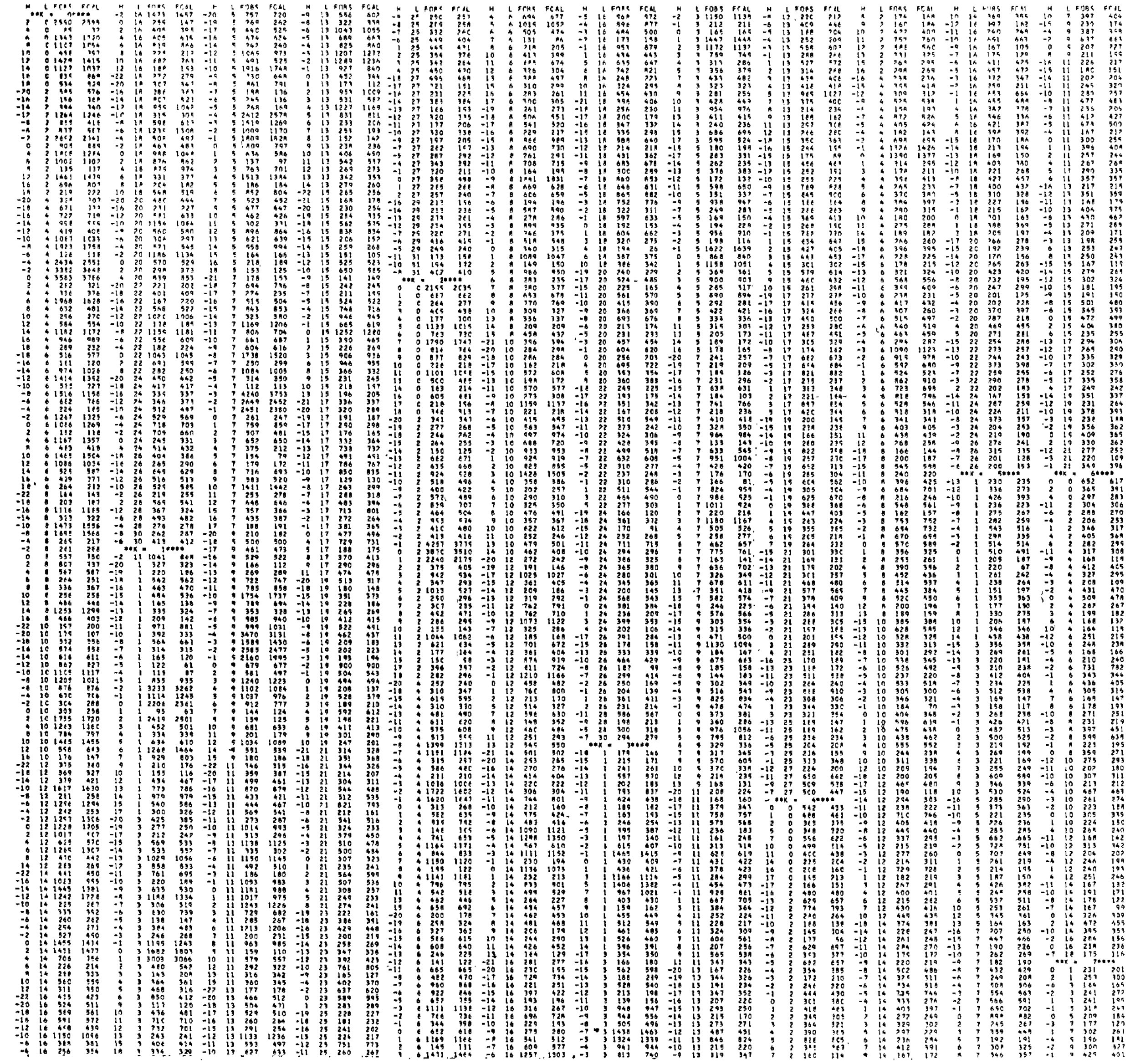
(11) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(12) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(13) W. C. Hamilton, GONO9; extinction and absorption correction for goniostat data on polyhedral crystals.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS IN UNITS OF 0.1 ELECTRON



mission factors varied from 0.92 to 0.97) and the weighting was changed so that $w = (\sigma')^{-2}$ with $\sigma' = (\sigma(F_o))\cdot[A + BF_o + CF_o^2 + DF_o^3]^{1/2}$ and A, B, C, and D were chosen so that $w(|F_o| - |F_c|)^2$ was nearly independent of $|F_o|$ and $(\sin\theta)/\lambda$ in accordance with Cruickshank's criterion.[14] Several more cycles of least squares in which all atoms were eventually refined anisotropically reduced R_1 to 0.068. The weighted residual $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]$ was 0.097. The estimated standard deviation of an observation of unit weight was now 1.064, and all parameter shifts were less than 0.1% of their estimated standard deviations during the last cycle.

A difference Fourier map was calculated when R_1 was 0.079 and from it the approximate locations of 27 of the 30 hydrogen atoms were determined. They were not, however, used in the solution and refinement of the structure. The largest feature in the map had a peak density of 0.63 e$^-$/Å^3 and was at a hydrogen atom position. There was only one nonhydrogen peak (0.38 e$^-$/Å^3) greater than the smallest hydrogen peak. The estimated standard deviation[15] of this electron density map was 0.084 e$^-$/Å^3. No corrections were made for extinction since $|F_c|$ was not consistently larger than $|F_o|$ for the most intense reflections. A list of the observed and calculated structure factors is presented in Table I. All but one F_o value for the rejected weak reflections were found to be acceptably small. The one exception is presumed to be the result of an angle accidentally missed during data collection.

Results

The fractional coordinates and isotropic temperature parameters for all atoms except hydrogen atoms are listed in Table II, and anisotropic temperature param-

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[14] D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press Inc., New York, N. Y., 1965.

[15] D. W. J. Cruickshank, *Acta Cryst.*, **2**, 154 (1949).

Table II

Final Positional and Isotropic Thermal Parameters[a]

Atom	x	y	z	B,[b] Å^2
Ni	0.18594 (6)	0.16092 (23)	0.11692 (5)	4.60
N(11)	0.1047 (3)	0.1284 (10)	0.1248 (3)	4.25
N(12)	0.1406 (3)	0.2374 (10)	0.0518 (2)	4.35
C(11)	0.1585 (5)	0.0530 (16)	0.2098 (3)	6.81
C(12)	0.0971 (5)	0.0887 (12)	0.1640 (4)	4.92
C(13)	0.0404 (4)	0.1570 (12)	0.0900 (3)	4.25
C(14)	0.0273 (4)	0.2076 (11)	0.0451 (3)	3.66
C(15)	0.0713 (4)	0.2442 (12)	0.0257 (3)	3.70
C(16)	0.1674 (4)	0.2889 (13)	0.0221 (3)	4.58
C(17)	0.2402 (4)	0.2967 (14)	0.0380 (3)	5.89
C(18)	0.1172 (4)	0.3306 (13)	−0.0234 (3)	4.78
C(19)	0.0565 (4)	0.2999 (12)	−0.0209 (3)	4.18
C(110)	−0.0109 (4)	0.3221 (14)	−0.0605 (3)	5.74
C(111)	−0.0803 (4)	0.1544 (15)	0.0830 (4)	6.98
C(112)	−0.0045 (4)	0.1345 (13)	0.1107 (4)	5.38
C(113)	0.0317 (5)	0.0924 (13)	0.1578 (4)	5.16
N(21)	0.2568 (3)	−0.0049 (11)	0.1216 (3)	4.31
N(22)	0.2452 (3)	0.3391 (11)	0.1605 (2)	4.59
C(21)	0.1847 (5)	−0.2309 (15)	0.0632 (4)	6.29
C(22)	0.2517 (4)	−0.1575 (15)	0.0976 (3)	5.01
C(23)	0.3252 (4)	0.0317 (14)	0.1488 (3)	4.38
C(24)	0.3497 (4)	0.1797 (14)	0.1758 (3)	4.26
C(25)	0.3157 (5)	0.3226 (15)	0.1823 (3)	4.73
C(26)	0.2300 (5)	0.4956 (15)	0.1756 (3)	5.18
C(27)	0.1599 (5)	0.5569 (15)	0.1598 (3)	6.50
C(28)	0.2878 (5)	0.5916 (15)	0.2081 (3)	6.08
C(29)	0.3413 (4)	0.4769 (16)	0.2117 (3)	5.50
C(210)	0.4141 (4)	0.5095 (18)	0.2430 (4)	8.08
C(211)	0.4353 (4)	−0.1346 (16)	0.1600 (4)	7.08
C(212)	0.3604 (4)	−0.1169 (14)	0.1390 (3)	5.05
C(213)	0.3140 (5)	−0.2350 (14)	0.1069 (4)	5.82

[a] Standard deviations occurring in the last significant figure are given in parentheses. [b] B's are isotropic thermal parameters equivalent to the anisotropic tensors of Table III.

Table III

Anisotropic Temperature Parameters[a] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	18 (0)	300 (5)	12 (0)	6 (1)	4 (0)	−7 (1)
N(11)	24 (2)	229 (21)	12 (1)	3 (5)	7 (1)	−5 (4)
N(12)	22 (2)	231 (19)	13 (1)	1 (5)	6 (1)	−7 (4)
C(11)	37 (3)	408 (35)	13 (2)	13 (9)	4 (2)	11 (7)
C(12)	40 (4)	160 (24)	15 (2)	−5 (7)	11 (2)	−10 (5)
C(13)	23 (3)	180 (22)	14 (2)	5 (6)	7 (2)	−3 (5)
C(14)	22 (3)	155 (23)	11 (2)	−1 (6)	4 (2)	−9 (5)
C(15)	15 (2)	185 (22)	13 (2)	1 (5)	4 (2)	−11 (5)
C(16)	27 (3)	237 (26)	15 (2)	−6 (7)	11 (2)	−10 (5)
C(17)	22 (3)	372 (33)	20 (2)	−15 (7)	12 (2)	−2 (6)
C(18)	26 (3)	218 (24)	15 (2)	2 (7)	6 (2)	−10 (6)
C(19)	26 (3)	188 (25)	11 (2)	12 (6)	5 (2)	−2 (5)
C(110)	27 (3)	342 (30)	12 (2)	14 (7)	1 (2)	3 (6)
C(111)	22 (3)	374 (33)	30 (2)	−4 (8)	14 (2)	−7 (8)
C(112)	23 (3)	248 (28)	25 (2)	−23 (7)	16 (2)	−19 (7)
C(113)	29 (3)	240 (27)	17 (2)	−13 (7)	10 (2)	−7 (6)
N(21)	19 (2)	238 (22)	14 (1)	4 (5)	7 (1)	−7 (4)
N(22)	21 (2)	255 (22)	12 (1)	−6 (6)	3 (1)	−7 (4)
C(21)	30 (3)	345 (31)	20 (2)	−42 (8)	11 (2)	−26 (7)
C(22)	25 (3)	268 (28)	16 (2)	−2 (8)	8 (2)	5 (6)
C(23)	22 (3)	255 (28)	13 (2)	20 (8)	8 (2)	17 (6)
C(24)	27 (3)	205 (26)	12 (2)	0 (7)	7 (2)	−8 (5)
C(25)	28 (3)	251 (28)	11 (2)	−4 (8)	5 (2)	5 (6)
C(26)	38 (4)	258 (29)	11 (2)	9 (8)	8 (2)	0 (6)
C(27)	30 (3)	328 (30)	21 (2)	22 (8)	8 (2)	−17 (7)
C(28)	33 (3)	325 (32)	13 (2)	−15 (9)	3 (2)	−4 (6)
C(29)	32 (3)	347 (33)	10 (2)	−30 (9)	5 (2)	−11 (6)
C(210)	25 (3)	519 (42)	23 (2)	−45 (9)	5 (2)	−39 (8)
C(211)	18 (3)	435 (36)	25 (2)	19 (8)	8 (2)	2 (7)
C(212)	23 (3)	284 (29)	15 (2)	−2 (8)	6 (2)	−1 (6)
C(213)	34 (3)	289 (29)	20 (2)	15 (9)	15 (2)	13 (7)

[a] Anisotropic temperature factors are of the form: exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV

Bond Distances (Å)

Atoms	Distances	Atoms	Distances
Ni–N(11)	1.948 (7)	Ni–N(21)	1.953 (7)
Ni–N(12)	1.953 (7)	Ni–N(22)	1.957 (8)
N(11)–C(12)	1.345 (12)	N(21)–C(22)	1.328 (13)
N(11)–C(13)	1.412 (11)	N(21)–C(23)	1.433 (11)
N(12)–C(15)	1.419 (10)	N(22)–C(25)	1.437 (11)
N(12)–C(16)	1.357 (11)	N(22)–C(26)	1.339 (13)
C(14)–C(13)	1.372 (13)	C(24)–C(23)	1.347 (14)
C(14)–C(15)	1.384 (12)	C(24)–C(25)	1.359 (14)
C(12)–C(113)	1.392 (14)	C(22)–C(213)	1.417 (14)
C(13)–C(112)	1.416 (13)	C(23)–C(212)	1.451 (14)
C(15)–C(19)	1.421 (13)	C(23)–C(29)	1.422 (15)
C(16)–C(18)	1.436 (13)	C(26)–C(28)	1.452 (14)
C(112)–C(113)	1.396 (15)	C(212)–C(213)	1.405 (14)
C(18)–C(19)	1.408 (12)	C(28)–C(29)	1.428 (15)
C(11)–C(12)	1.542 (14)	C(21)–C(22)	1.533 (13)
C(16)–C(17)	1.490 (12)	C(26)–C(27)	1.502 (13)
C(19)–C(110)	1.512 (12)	C(29)–C(210)	1.528 (13)
C(112)–C(111)	1.555 (13)	C(212)–C(21)	11.526 (12)

eters are given in Table III. The structure is depicted in Figure 1 which also presents the atom-numbering scheme. In subsequent discussions ligand 1 and ligand 2 will be those in which the atom numbers all begin with 1 or 2, respectively. Tables IV and V give bond lengths and angles. Two least-squares planes were calculated, one containing ligand 1 plus the nickel atom and the other containing ligand 2 plus the nickel atom. The equations for these planes and distances of atoms from them are given in Table VI. The dihedral angle between the two planes is 76.3°.

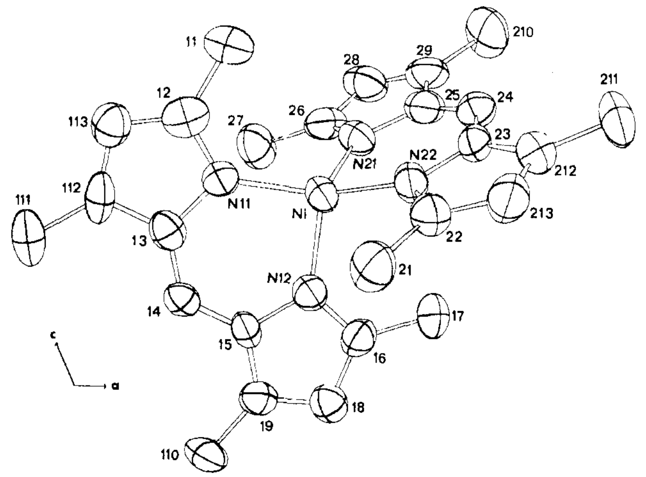


Figure 1.—A perspective drawing of the molecule viewed normal to the (010) plane. The numbering scheme of the atoms is defined.

Discussion

As anticipated, the molecule does not have a planar structure. On the other hand, neither does it have a structure of D_{2d} symmetry with the planes of the two ligands perpendicular to each other. The latter structure is the most symmetrical one possible which avoids —and indeed minimizes—repulsions between the 5-

TABLE V

PRINCIPAL BOND ANGLES (DEG)

Atoms	Angle	Atoms	Angle
N(11)–Ni–N(12)	93.9 (3)	N(21)–Ni–N(22)	94.2 (3)
N(11)–Ni–N(21)	133.1 (3)	N(21)–Ni–N(12)	107.8 (3)
N(11)–Ni–N(22)	112.7 (3)	N(22)–Ni–N(12)	116.5 (3)
Ni–N(11)–C(12)	128.7 (6)	Ni–N(21)–C(22)	127.5 (6)
Ni–N(11)–C(13)	125.7 (6)	Ni–N(21)–C(23)	123.9 (6)
Ni–N(12)–C(15)	125.5 (6)	Ni–N(22)–C(25)	124.4 (6)
Ni–N(12)–C(16)	128.2 (6)	Ni–N(22)–C(26)	128.6 (6)
C(12)–N(11)–C(13)	105 (1)	C(22)–N(21)–C(23)	108 (1)
C(15)–N(12)–C(16)	106 (1)	C(25)–N(22)–C(26)	107 (1)
C(11)–C(12)–N(11)	119 (1)	C(21)–C(22)–N(21)	122 (1)
C(11)–C(12)–C(113)	127 (1)	C(21)–C(22)–C(213)	126 (1)
C(113)–C(12)–N(11)	113 (1)	C(213)–C(22)–N(21)	112 (1)
N(11)–C(13)–C(14)	123 (1)	N(21)–C(23)–C(24)	125 (1)
N(11)–C(13)–C(112)	108 (1)	N(21)–C(23)–C(212)	106 (1)
C(112)–C(13)–C(14)	128 (1)	C(212)–C(23)–C(24)	129 (1)
C(13)–C(14)–C(15)	129 (1)	C(23)–C(24)–C(25)	128 (1)
C(14)–C(15)–C(19)	128 (1)	C(24)–C(25)–C(29)	128 (1)
C(14)–C(15)–N(12)	123 (1)	C(24)–C(25)–N(22)	124 (1)
C(19)–C(15)–N(12)	110 (1)	C(29)–C(25)–N(22)	108 (1)
C(17)–C(16)–N(12)	121 (1)	C(27)–C(26)–N(22)	122 (1)
C(17)–C(16)–C(18)	128 (1)	C(27)–C(26)–C(28)	126 (1)
C(16)–C(18)–C(19)	106 (1)	C(26)–C(28)–C(29)	104 (1)
C(18)–C(19)–C(15)	107 (1)	C(28)–C(29)–C(25)	109 (1)
C(18)–C(19)–C(110)	126 (1)	C(28)–C(29)–C(210)	126 (1)
C(15)–C(19)–C(110)	127 (1)	C(25)–C(29)–C(210)	125 (1)
C(13)–C(112)–C(111)	123 (1)	C(23)–C(212)–C(211)	124 (1)
C(13)–C(112)–C(113)	108 (1)	C(23)–C(212)–C(213)	108 (1)
C(111)–C(112)–C(113)	129 (1)	C(211)–C(212)–C(213)	127 (1)
C(112)–C(113)–C(12)	105 (1)	C(212–)C(213)–C(22)	106 (1)

TABLE VI

Weighted Mean Molecular Planes[a]

Ligand 1: $-0.0652x + 0.9591y + 0.2753z = 1.8990$

Ligand 2: $-0.4160x + -0.4945y + 0.7632z = 0.8798$

Distances of Atoms from Planes, Å

Ligand 1: Ni, −0.016; N(11), −0.057; N(12), 0.019; C(11), 0.075; C(12), 0.016; C(13), −0.066; C(14), −0.084; C(15), −0.061; C(16), 0.084; C(17), 0.171; C(18), 0.053; C(19), −0.053; C(110), −0.145; C(111), 0.029; C(112), 0.021; C(113), 0.084

Ligand 2: Ni, 0.001; N(21), 0.071; N(22), −0.008; C(21), −0.033; C(22), 0.017; C(23), 0.044; C(24), 0.017; C(25), −0.007; C(26), −0.022; C(27), −0.023; C(28), −0.019; C(29), −0.002; C(210), 0.057; C(211), −0.068; C(212), −0.010; C(213), −0.028

[a] The orthogonal coordinates x, y, and z correspond to the crystal axes a, b, and c^*, respectively, and are in ångström units. The weight given to each atom forming the plane is $w_i = [\sqrt[3]{a\sigma_{xi} b\sigma_{yi} c\sigma_{zi}}]^{-2}$.

and 5′-methyl groups of the two ligands. Instead, the molecule has an approximately D_2 structure, where the dihedral angle between the ligand planes is 76.3°. Even this structure is slightly distorted in the sense that the local twofold axes of each of the Ni–ligand groups are not precisely collinear but make an angle of 168.5° with each other. This distortion is presumed to be due to intermolecular forces in the crystal and thus to be without chemical significance. Most of the molecular dimensions may therefore be discussed in terms of the idealized D_2 symmetry, which makes the two ligand groups equivalent and endows each with a twofold axis of rotation, passing through the methene carbon atom, C(14) or C(24), and the nickel atom. For convenience in the following discussion, Figure 2 shows the average lengths and their mean deviations for the nine different bonds, each value being the average over the four crystallographically independent bonds of each type. In seven cases the mean deviation is equal to or less than the average esd of an individual bond in the set, which justifies the use of the average values. The two exceptions have mean deviations of 0.020 and 0.021 Å as compared with average individual esd's of ~0.014 Å. The use of average values is therefore not quite proper here, but they will nevertheless be employed for the sake of simplicity.

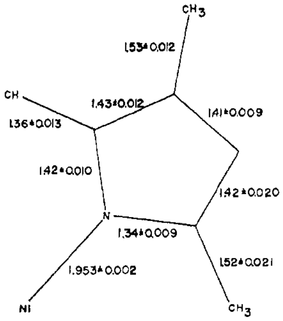


Figure 2.—A diagram showing the average values of bond lengths and their mean deviations.

The four Ni–N distances are equal within the experimental uncertainties as are the two N–Ni–N angles which lie within chelate rings (93.9 and 94.2° with esd's of 0.3°). For full D_2 symmetry the remaining N–Ni–N angles should form two different pairs of equal angles. The distortion mentioned above shows up very clearly in the fact that these equivalencies are not observed. Thus the two large angles are 133.1 and 116.5° while the two small angles are 112.7 and 107.8°.

One of the reasons for carrying out this structure determination was to discover the orientation of the molecules in the crystal for use in future spectroscopic studies. Since the molecule lacks any precise symmetry axis, a statement of orientation can only be made with regard to an arbitrary axis. For this purpose we employ the C(14)–C(24) axis, which would be the unique axis (passing through Ni) in D_{2d} or D_2 symmetry. This axis makes an angle of 1.76° to the crystallographic glide plane and has direction cosines of 0.8258, −0.0308, and 0.5630 with respect to the orthogonal axis set a, b, c^*.

The planarity of the ligands is imperfect and markedly so for ligand 1, as Table VI shows. In ligand 1 the average deviation of the 15 light atoms from the plane is 0.06 Å, while in ligand 2, the average deviation is only 0.027 Å. Since the esd's of light-atom positional parameters are ~0.01 Å, virtually all of the deviations from planarity in ligand 1 are highly significant in a statistical sense. In ligand 2 only five atoms deviate by more than 0.03 Å, and three of these are methyl carbon atoms. Thus, it is uncertain whether there is any meaningful distortion of the tricyclic Ni–ligand 2 skeleton from planarity.

The interatomic distances in the ligands are of considerable interest. It can be seen that the ring carbon to methyl carbon distances average 1.52 Å, which agrees well with the value expected for a C(sp^2)–C(sp^3) distance (1.51 Å). The other six C–C and C–N distances show pronounced variations. It is particu-

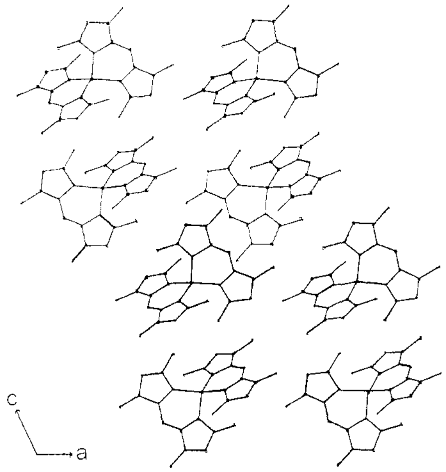
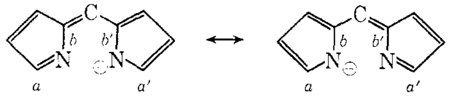


Figure 3.—A diagram of one unit cell projected on the (010) plane.

larly interesting to note that the two N–C distances differ markedly, being 1.42 and 1.34 Å. On the basis of individual esd's and the mean deviations of the averages, this difference is surely real. Qualitatively, this could be accounted for in terms of a resonance description of π-electron delocalization in the ligand, as indicated in formulas IA and IB. By the indicated resonance, the a-type C–N bonds receive a partial π contribution while the b-type C–N bonds receive none. Moreover, both bonds are of approximately the correct length for orders of 1.5 and 1.0, basing estimates on the lengths of C–C bonds of these orders, with the appropriate sp^2 hybridization and subtracting $\sim$0.06 Å to allow for the smaller radius of the N atom. Estimated values of 1.34 and 1.42 Å are thereby obtained. As a direct empirical comparison, the C–N bond of order 1.5 in pyridine[16] has a length of 1.340 ± 0.001Å.



IA IB

The two types of ring C–C bonds have average lengths of 1.41 and 1.43 Å, while the ring C to methene C bonds have an average length of 1.36 Å. The first of these agrees well with the expected bond length of 1.39 Å, while the other two deviate from it by amounts which appear to be significant, though not markedly so. These variations in C–C bond lengths, if real, cannot easily be explained by resonance considerations. However, before undertaking any more detailed analysis, employing MO theory, we will await the results of a study of the homologous cobalt(II) complex whose structure we are now investigating with the expectation of obtaining more precise results.

At this point it might be desirable to compare the observed structure with the ones postulated on the basis of spectroscopic evidence. Ferguson and West[5] examined five different dipyrromethene complexes of nickel. Three of them had methyl substituents in both the 5 and 5′ ring positions along with other substituents in the 3, 3′, 4, and 4′ positions. They obtained the visible spectra in benzene, pyridine, and in the solid state. The spectra changed little with the change in solvent or phase, and all, including the solid-state ones, were considered on the basis of crystal field theory to be indicative of an essentially undistorted tetrahedral configuration. Murakami and Sakata[6] examined the spectra of bis(3,3′,4,4′,5,5′-hexamethyldipyrromethenato)nickel(II) and bis(3,3′,5,5′-tetramethyldipyrromethenato)nickel(II) in chloroform and benzene and likewise interpreted the spectra on the basis of an undistorted tetrahedral configuration. On the other hand, the corresponding copper(II) complexes were considered to show definite signs of "flattening," even in solution, and the cobalt complexes exhibited a fine structure which the authors felt could not be accounted for completely by spin–orbit coupling. The results of this crystal structure investigation suggest that the simple interpretation involving local T_d symmetry that Ferguson and West gave to the solid-state spectra of their nickel complexes may be in error.

There is no simple way to describe the packing that occurs in the crystals of this complex. A packing diagram is given in Figure 3. One could possibly consider it to consist of chains running parallel to the b axis. Each link consists of two complete molecules, and there are four chains passing through each unit cell. The two molecules in each link are related by the twofold axis that passes down the center of the chain.

A question requiring careful consideration is why the dihedral angle between the ligands is not 90°. It this a result of internal electronic stabilization or is it due merely to intermolecular packing forces? A three-dimensional model of one unit cell was constructed and examined carefully to see if the molecules could pack in approximately the same manner with a dihedral angle of 90°. There appeared to be no reason why they could not. There are, however, a few close contacts that could account for the distortion from pure D_2 symmetry. Possibly molecular orbital calculations will show whether the dihedral angle of 76.3° results from a lowering of the electronic energy of the system or merely from packing forces.

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