and 2 that in the present compound hydrogen bonding also plays a role and is responsible for some interesting structural features. (1) There is a movement of the imino nitrogen toward the Br^- ion, as reflected by the Mn–N–N angles of 123° and the Mn–N–C angles of 133°. (2) There is a movement of the Br^- ion from the perpendicular position toward the N–H groups. (3) There are short Br–N distances of 3.34 and 3.37 Å for Br–N(3) and Br–N(4′), respectively, compared with Br–C distances of 3.71 and 3.68 Å for Br–C(1) and Br–C(2′) (see Figure 2 for indicated distances). This feature is of course related to (1) and (2). (4) The orientation of the five-membered rings is nearly perpendicular. A more flattened orientation would be expected on the basis of ligand–ligand repulsions. (5) The rather long Mn–Br bond is 2.727 Å. Comparable literature values for Mn–Br bond lengths are 2.52 Å (in the rather covalent $Mn(CO)_5Br$),[17] 2.49 Å (in five-coordinate $Mn(Me_6tren)Br_2$),[18] 2.68 and 2.72 Å (in one-dimensional polymeric $MnBr_2 \cdot 2H_2O$),[19] and 2.72 Å (in the layer structure of $MnBr_2$).[20] (6) The angles of hydrogen bonding N–H · · · Br are 126 (3)° which seem to be acceptable values.[21]

Finally, we compared the N · · · Br distances found in the present study with those predicted with the relation of Bellamy and Owen:[22] $\Delta\nu = 50(x^2 - x)$, in which $\Delta\nu$ is the difference in infrared maxima between the gaseous ligand (3540 cm^{-1})[4] and the complexed ligand (3310 cm^{-1})[2] and $x = (d/R)^6$ with $d = 3.95$ Å.[14] This formula predicts $R = 3.35$ Å, whereas values of 3.34 and 3.37 Å are found (Table V).

Acknowledgments.—The authors are indebted to Drs. W. L. Groeneveld and C. Romers for their interest in this study. Mr. R. A. G. de Graaff is thanked for many valuable discussions and for help with the computer programs. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

(17) L. F. Dahl and C. H. Wei, *Acta Crystallogr.*, **16**, 611 (1963).

(18) M. DiVaira and P. L. Orioli, *ibid., Sect. B*, **24**, 1269 (1968).

(19) B. Morosin, *J. Chem. Phys.*, **47**, 417 (1967).

(20) E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, *Phys. Rev.*, **110**, 638 (1958).

(21) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

(22) L. J. Bellamy and A. J. Owen, *Spectrochim. Acta, Part A*, **25**, 329 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE-MELLON UNIVERSITY, PITTSBURGH, PENNSYLVANIA 15213

The Crystal Structure and Properties of π-Triphenylcyclopropenylchlorodipyridinenickel(0)–Pyridine, a π Complex of a Three-Membered Aromatic Ring

BY R. M. TUGGLE AND D. L. WEAVER*

Received January 14, 1971

The crystal and molecular structure of π-triphenylcyclopropenylchlorodipyridinenickel(0)–pyridine, $[(\pi\text{-}C_3(C_6H_5)_3)NiCl(C_5H_5N)_2] \cdot C_5H_5N$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as well-separated molecular units in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 16.570$ (3), $b = 10.538$ (1), $c = 22.483$ (5) Å, and $\beta = 129.14$ (1)°. The structure has been refined by full-matrix least-squares methods to a conventional R factor of 0.081 for the 2361 reflections with $I > 2.0\sigma(I)$. When the triphenylcyclopropenyl group is assumed to occupy one coordination position, the coordination geometry about the nickel atom is a distorted tetrahedron. The triphenylcyclopropenyl group is complexed in true π fashion, the three nickel–cyclopropenyl carbon distances being 1.896 (8), 1.958 (8), and 1.968 (8) Å. Carbon–carbon distances in the cyclopropenyl ring are equal within experimental error to an average value of 1.421 (7) Å and are lengthened significantly in this complex compared with the free ligand in $(C_3(C_6H_5)_3)(ClO_4)$. The nickel–chlorine and average nickel–nitrogen (pyridine) distances are 2.322 (3) and 2.024 (5) Å, respectively.

Introduction

The stability of the cyclopropenium cation as implied by the simple Hückel $4n + 2$ rule ($n = 0$) was confirmed by the synthesis of the triphenylcyclopropenium cation[1] and more recently the parent[2] ion, $C_3H_3^+$. However, the first attempts to obtain transition metal π complexes of this aromatic species were unsuccessful.[3,4] In 1964 Gowling and Kettle[5] presented evidence that the reaction of $(C_3(C_6H_5)_3)Br$ with $Ni(CO)_4$ gave a dimer complex of the formulation $[(\pi\text{-}C_3(C_6H_5)_3)NiBr(CO)]_2$ which contained this carbocyclic ring π bonded to the nickel atom. In order to determine whether this was the mode of bonding and to gain a better understanding of the bonding of small aromatic ring systems to transition metals, an X-ray structural determination of a closely related monomeric derivative,[6] $[(\pi\text{-}C_3(C_6H_5)_3)NiCl(C_5H_5N)_2] \cdot C_5H_5N$, was undertaken.

Experimental Section

Preparation.[7]—Reaction of the dimeric complex $[(\pi\text{-}C_3(C_6H_5)_3)$-

---

(1) (a) R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958); (b) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).

(2) R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970).

(3) C. E. Coffey, *ibid.*, **84**, 118 (1962).

(4) J. Chatt and R. G. Guy, *Chem. Ind.* (*London*), 212 (1963).

(5) E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **3**, 604 (1964).

(6) A preliminary account of this work has been given: D. L. Weaver and R. M. Tuggle, *J. Amer. Chem. Soc.*, **91**, 6506 (1969).

(7) E. W. Gowling, Ph.D. Thesis, Sheffield University, 1965.

$NiCl(CO)]_2$ with excess pyridine gave air-stable red crystals of the pyridine adduct $[\pi\text{-}C_3(C_6H_5)_3Ni(Cl)(py)_2]\cdot py$. *Anal.* Calcd for $NiC_{36}H_{30}N_3Cl$: Ni, 9.81; C, 72.21; H, 5.05; N, 7.02; Cl, 5.92. Found: Ni, 10.24; C, 71.40; H, 4.80; N, 7.35; Cl, 6.24. Single crystals suitable for X-ray examination were obtained from pyridine–hexane mixtures.

Magnetic Susceptibility Measurement.—The susceptibility was measured by the Faraday method using Pt as a calibrant and the complex was found to be diamagnetic.

Infrared Spectrum.—The infrared spectrum was recorded on a Perkin-Elmer Infracord spectrometer using a KBr pellet. Major absorptions in cm^{-1} are 3100 (s), 1680 (m), 1600 (s), 1555 (m), 1495 (s), 1455 (s), 1370 (m), 1350 (m), 1220 (m), 1155 (m), 1070 (s), 1040 (s), 760 (s), and 695 (s).

Electronic Spectrum.—The electronic spectrum was obtained on a Cary Model 14 recording spectrophotometer.

Collection and Reduction of the X-ray Data

Crystals of $[(\pi\text{-}C_3(C_6H_5)_3)NiCl(py)_2]\cdot py$, prepared as described above, were shown to be in the monoclinic system from precession and Weissenberg photographs. The observed systematic absences $h0l$, l odd, and $0k0$, k odd, are consistent with the uniquely determined space group $P2_1/c$ (C^5_{2h}). Unit cell parameters were determined on a GE XRD-5 diffractometer using Cu K$\bar{\alpha}$ radiation (λ 1.5418 Å) by least-squares treatment of the 2θ values for 21 reflections ($34 < 2\theta < 74°$). The values thus obtained were a = 16.570 (3), b = 10.538 (1), c = 22.483 (5) Å, and β = 129.14 (1)°. For four formula units of the monopyridine solvate the calculated density is 1.31 g/cm^3 which compares well with the observed density of 1.30 g/cm^3 determined by the flotation method.

A single crystal of approximate dimensions 0.1 × 0.3 × 0.05 mm along the a, b, and c^* directions was mounted on a glass fiber with its b^* axis coincident with the φ axis of a GE XRD-5 diffractometer. Measurement of the kinematic intensity profile[8] (takeoff angle 4°) by the ω-scan method showed a peak width of 0.38° at half-maximum intensity for several reflections.

Intensity data were collected by the θ–2θ scan technique using a symmetric 2θ scan range of 3° and a rate of 2°/min. Ten-second stationary-background counts were taken at both extremes of the scan range. Crystal and electronic stabilities were monitored by three standards. These standards, which showed a uniform decrease of 2% during data collection, were used to place all intensities on a common scale. Cu Kα radiation, obtained by passing the primary beam through 0.35 mil of nickel foil, was employed for data collection. The pulse height analyzer was set for approximately a 90% window when centered on the Cu Kα peak. Nine reflections whose intensities exceeded the linear response range of the scintillation counter were remeasured by reducing the current on the X-ray tube.

All of the 3365 independent reflections for $2\theta \leq 100°$ ($(\sin \theta)/\lambda \leq 0.50$) were measured. These intensities were reduced to values of F^2 by correction for background, Lorentz, and polarization effects. Standard deviations of the intensities were computed using the formula

$$\sigma(I) = [C + 0.25(t_S/t_B)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where I is the net intensity, C is the total integrated scan count obtained in time t_S, t_B is the time required for each background count B_1 and B_2, and p is a factor introduced to account for random fluctuations which occur during data collection. For this structure, p was chosen to be 0.03. The 2361 reflections for which $I > 2.0\sigma(I)$ were classified as observed and used in the solution and refinement of the structure. For this complex the linear absorption coefficient of Cu Kα radiation is 19.2 cm^{-1}. The crystal studied had transmission coefficients which ranged from approximately 0.91 to 0.83 and no absorption corrections were made.

Solution and Refinement of the Structure

Application of the standard heavy-atom techniques including a three-dimensional Patterson function located the nickel and chlorine atoms. Least-squares refinement of the structure factors phased on these two atoms gave an R_1 of 0.468 and R_2 of 0.570. The residuals throughout the text are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ with the weight $w = 4F_o^2/\sigma^2(F_o^2)$. The function minimized by the full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors used for the neutral light atoms except hydrogen were those of Ibers.[9] The hydrogen and nickel atom scattering factors were those of Stewart, *et al.*,[10] and Cromer and Waber,[11] respectively. The values of the nickel and chlorine scattering factors were corrected for the real and imaginary components of anomalous dispersion using the tabulation of Cromer.[12]

Fourier and least-squares methods located the remaining nonhydrogen atoms and yielded R_1 = 0.113 and R_2 = 0.143 when all atoms were assumed to vibrate isotropically. When the nickel, chlorine, three cyclopropenyl carbon, and two coordinated nitrogen atoms were assigned anisotropic temperature factors, the residuals fell to an R_1 of 9.7% and an R_2 of 10.9%. Examination of a difference Fourier map phased on these structure factors showed 16 peaks of density 0.56–0.20 e$^-$/Å^3 ($\sigma(\Delta\rho)$ = 0.06 e$^-$/Å^3) in reasonable locations for hydrogen atoms. Also noted on this map were six peaks (0.76–0.51 e$^-$/Å^3) at positions which were staggered with respect to the atoms in the pyridine of crystallization. These peaks and the high thermal parameters for the atoms in this group suggest disorder or severe thermal librational motion for the pyridine ring.

A model composed of two staggered six-membered carbon atom rings with partial occupancy factors was chosen to represent the pyridine of crystallization in the final cycles of least-squares refinement. All parameters were varied except the occupancy factors which were readjusted by hand after each cycle subject to the two constraints: (1) that the sum of the two ring occupancy factors must equal unity and (2) that the average temperature factors of the atoms in each ring must be identical. During this final stage of refinement hydrogen atom coordinates were varied but their thermal parameters were fixed at a value for B of 6 Å^2. Convergence occurred for a $^{55}/_{45}$ disorder of the pyridine ring. The final values of R_1 and R_2 were 0.081 and 0.086, respectively.

During the final cycle of least-squares refinement the largest change in a nonhydrogen atom parameter was 0.98σ (y coordinate of atom C(12)) and the average change was 0.05σ. The three highest peaks (0.79–0.71 e$^-$/Å^3 or about one-fifth the height of a typical carbon atom) on a final-difference Fourier map were in the vicinity of atoms C(12) and C(13). A final structure factor calculation for the 1004 unobserved reflections showed two reflections for which $|F_c|$ was greater than twice the minimum observable. The major programs used in the elucidation of this structure were Prewitt's SFLS-5 for structure factor and full-matrix least-squares refinenent calculations, Zalkin's FORDAP for Patterson and Fourier synthesis, and Johnson's ORTEP for pictorial representation.

The positional and thermal parameters obtained in the last cycle of least-squares refinement are given in Table I.[13]

Description of the Structure

The crystal structure is made up of discrete molecular units of $(\pi\text{-}C_3(C_6H_5)_3)NiCl(py)_2$ and pyridine. A projection of the molecule on the plane of the cyclopropenyl ring is shown in Figure 1 while Figures 2 and 3 give projections of the crystal packing down the crystallographic b^* and c^* axes, respectively. The bond distances and angles obtained from the final cycle of least-squares refinement are given in Table II.

The nickel atom is surrounded in a distorted tetrahedral fashion by a chlorine atom, two nitrogen atoms of the coordinated pyridine molecules, and the cyclopropenyl ring. The angles around the nickel atom range from 96.1 (2) to 125.5 (2)° with an average value of 108.7°. (These angles were calculated with reference to a Ni–R(3) vector where R(3) is a point in the center of the three-membered ring.)

An average Ni–C(ring) distance of 1.941 (5) Å was determined for this complex which may be compared with the average Ni–C-(cyclopropenyl ring) distance of 1.961 (4) Å found in $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$. See Table III. Apparently the electronic

---

[8] L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **15**, 983 (1962).

[9] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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

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

[13] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE I

Final Positional and Thermal Parameters[a]

Atom	*x*	*y*	*z*	*B*, $Å^2$
Ni	0.17039 (10)	0.05531 (12)	0.22525 (7)	3.38[b]
Cl	0.1521 (2)	0.2608 (2)	0.1810 (1)	4.46[b]
C(10)	0.3106 (6)	0.0453 (7)	0.3164 (5)	3.35[b]
C(11)	0.3722 (7)	0.1235 (8)	0.3854 (5)	3.69 (18)
C(12)	0.3897 (11)	0.0828 (14)	0.4520 (9)	9.31 (40)
C(13)	0.4413 (12)	0.3249 (15)	0.0171 (8)	10.32 (41)
C(14)	0.4832 (8)	0.2168 (10)	0.0157 (6)	5.79 (24)
C(15)	0.4710 (8)	0.3152 (10)	0.4528 (6)	6.35 (26)
C(16)	0.4180 (8)	0.2334 (11)	0.3895 (6)	5.67 (25)
C(20)	0.7271 (6)	0.4201 (8)	0.2124 (5)	3.47[b]
C(21)	0.7364 (6)	0.2924 (8)	0.1920 (5)	3.54 (18)
C(22)	0.7310 (7)	0.1868 (10)	0.2256 (6)	4.85 (22)
C(23)	0.7380 (8)	0.0645 (11)	0.2028 (6)	5.92 (25)
C(24)	0.7485 (8)	0.0483 (10)	0.1489 (6)	6.21 (25)
C(25)	0.7555 (8)	0.1527 (10)	0.1156 (6)	5.63 (24)
C(26)	0.7490 (7)	0.2772 (9)	0.1365 (5)	4.33 (20)
C(30)	0.6967 (6)	0.4986 (8)	0.2462 (5)	3.44[b]
C(31)	0.3537 (6)	0.0062 (8)	0.2194 (5)	3.42 (18)
C(32)	0.6304 (8)	0.3987 (10)	0.3076 (6)	5.20 (24)
C(33)	0.5833 (9)	0.4104 (12)	0.3421 (7)	6.58 (30)
C(34)	0.4539 (9)	0.0236 (12)	0.1571 (6)	6.61 (27)
C(35)	0.4377 (8)	0.1336 (10)	0.1817 (6)	6.01 (25)
C(36)	0.3861 (8)	0.1190 (10)	0.2125 (6)	4.87 (23)
N(4)	0.0972 (5)	0.0791 (6)	0.2708 (4)	3.74[b]
C(41)	0.1153 (8)	0.1846 (10)	0.3100 (5)	4.69 (22)
C(42)	0.0798 (9)	0.1958 (11)	0.3533 (7)	6.27 (27)
C(43)	0.0275 (8)	0.0978 (10)	0.3548 (6)	6.02 (25)
C(44)	0.9897 (8)	0.4928 (11)	0.1851 (6)	5.53 (24)
C(45)	0.9531 (7)	0.4847 (9)	0.2265 (5)	4.18 (20)
N(5)	0.9525 (5)	0.4828 (6)	0.3756 (3)	3.21[b]
C(51)	0.9543 (8)	0.0358 (9)	0.0864 (5)	4.31 (21)
C(52)	0.1335 (8)	0.4920 (10)	0.4852 (6)	5.53 (25)
C(53)	0.1244 (8)	0.1095 (10)	0.0183 (6)	5.24 (23)
C(54)	0.0292 (8)	0.3357 (10)	0.4803 (6)	4.67 (22)
C(55)	0.9450 (7)	0.3819 (9)	0.4096 (5)	3.82 (19)
C(60)[c]	0.755 (5)	0.157 (5)	0.474 (3)	11.1 (21)
C(61)	0.670 (3)	0.090 (3)	0.431 (3)	7.2 (8)
C(62)	0.663 (3)	0.001 (3	0.379 (2)	7.0 (8)
C(63)	0.238 (5)	0.482 (4)	0.109 (3)	8.7 (12)
C(64)	0.857 (3)	0.052 (4)	0.450 (3)	8.4 (9)
C(65)	0.843 (3)	0.132 (3)	0.492 (2)	6.2 (7)
C(60A)[c]	0.717 (5)	0.121 (5)	0.464 (3)	6.6 (10)
C(61A)	0.660 (3)	0.046 (6)	0.396 (3)	8.8 (13)
C(62A)	0.282 (4)	0.482 (3)	0.124 (2)	5.9 (9)
C(63A)	0.817 (4)	0.016 (4)	0.419 (3)	6.5 (9)
C(64A)	0.862 (4)	0.100 (6)	0.480 (3)	10.5 (21)
C(65A)	0.791 (4)	0.149 (3)	0.496 (2)	5.3 (9)
H(12)[d]	0.340 (7)	0.134 (8)	0.434 (5)	6.0[e]
H(16)	0.392 (6)	0.266 (8)	0.344 (5)	6.0
H(22)	0.729 (6)	0.202 (8)	0.268 (5)	6.0
H(23)	0.727 (6)	0.014 (8)	0.230 (5)	6.0
H(32)	0.658 (6)	0.320 (8)	0.313 (5)	6.0
H(33)	0.549 (7)	0.346 (9)	0.326 (5)	6.0
H(34)	0.481 (6)	0.023 (8)	0.126 (5)	6.0
H(36)	0.376 (6)	0.189 (8)	0.226 (5)	6.0
H(41)	0.162 (6)	0.255 (8)	0.314 (4)	6.0
H(42)	0.125 (6)	0.264 (8)	0.389 (5)	6.0
H(44)	0.016 (6)	0.406 (8)	0.192 (5)	6.0
H(45)	0.961 (6)	0.407 (8)	0.253 (5)	6.0
H(51)	0.952 (6)	0.117 (8)	0.104 (5)	6.0
H(52)	0.811 (7)	0.456 (8)	0.493 (5)	6.0
H(54)	0.005 (6)	0.262 (8)	0.492 (5)	6.0
H(55)	0.875 (7)	0.349 (8)	0.378 (5)	6.0

Anisotropic Temperature Factors[f] ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	58.6 (11)	73.4 (15)	29.4 (6)	−5.8 (11)	29.2 (7)	−7.9 (8)
Cl	92.5 (21)	73.2 (25)	43.9 (11)	1.6 (18)	47.4 (13)	−0.6 (13)
C(10)	63.2 (68)	49.1 (89)	34.0 (37)	−18.8 (64)	31.5 (44)	−7.8 (50)
C(20)	51.9 (66)	64.5 (97)	32.9 (38)	0.1 (62)	25.6 (45)	2.6 (48)
C(30)	55.3 (69)	72.7 (88)	31.4 (38)	−3.4 (63)	28.3 (47)	−2.9 (47)
N(4)	72.6 (58)	68.7 (77)	36.3 (31)	−7.1 (56)	38.0 (38)	−7.3 (40)
N(5)	50.4 (54)	79.9 (79)	23.2 (26)	−2.5 (52)	22.1 (34)	0.4 (36)

[a] Numbers in parentheses are esd's in the last figure quoted.
[b] Equivalent isotropic *B*'s.
[c] One atom in the C(60) series and the C(60A) series is, in fact, a nitrogen atom.
[d] Hydrogen atoms have the same numbers as the carbon atoms to which they are bonded.
[e] Hydrogen atom temperature factors fixed at 6.0 $Å^2$.
[f] Anisotropic temperature factors are of the form: $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

demands of two pyridines and a chlorine are approximately equivalent to that of a cyclopentadienyl ring. For nickel derivatives of this type there is a decrease in the average Ni–C-

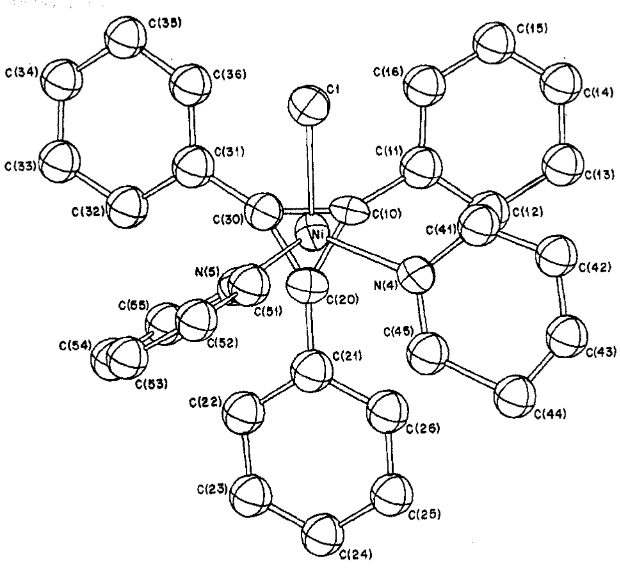

Figure 1.—A molecule of $(\pi\text{-}C_3(C_6H_5)_3Ni)Cl(py)_2$ projected on the plane of the cyclopropenyl ring. The 50% probability ellipsoids are given for atoms refined anisotropically; the ellipsoids of atoms refined isotropically are fixed at 4.0 $Å^2$.

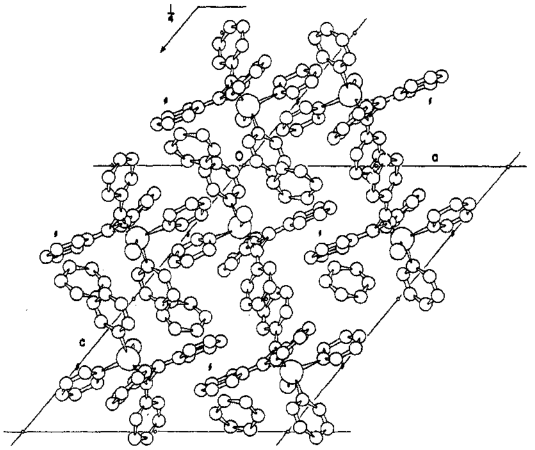

Figure 2.—Molecular packing of $[(\pi\text{-}C_3(C_6H_5)_3)NiCl(py)_2]\cdot py$ projected on the crystallographic *ac* plane.

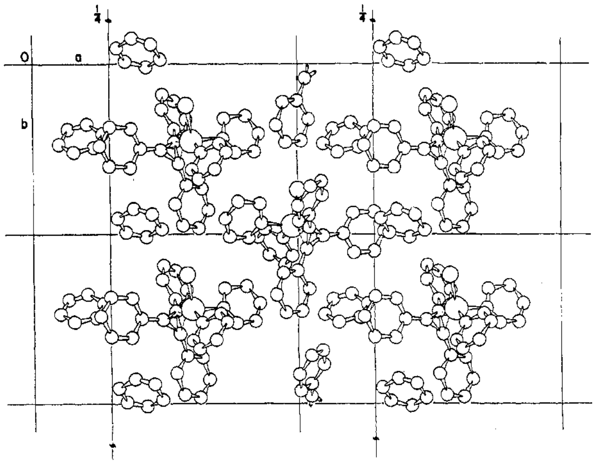

Figure 3.—Molecular packing of $[(\pi\text{-}C_3(C_6H_5)_3)NiCl(py)_2]\cdot py$ projected on the crystallographic *ab* plane.

(ring) distances as the size of the 5-membered carbocyclic ring is reduced, *viz.*, Ni–C(π-C_5H_5), 2.125 Å,[14a] Ni–C(π-$C_4(CH_3)_4$),

---

(14) (a) R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 1504 (1971); (b) M. D. Rausch, R. M. Tuggle and D. L. Weaver, *J. Amer. Chem. Soc.*, **92**, 4981 (1970).

TABLE II

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES[a]

Bond Distances, Å

Ni–Cl	2.322 (3)	C(11)–C(12)	1.40 (2)
Ni–N(4)	2.037 (7)	C(12)–C(13)	1.50 (2)
Ni–N(5)	2.011 (6)	C(13)–C(14)	1.35 (2)
Ni–R(3)[b]	1.759	C(14)–C(15)	1.34 (2)
Ni–C(10)	1.896 (8)	C(15)–C(16)	1.40 (2)
Ni–C(20)	1.968 (8)	C(16)–C(11)	1.36 (1)
Ni–C(30)	1.958 (8)	C(21)–C(22)	1.38 (1)
Wtd av of 3 Ni–C	1.941 (5)	C(22)–C(23)	1.42 (2)
C(10)–C(20)	1.429 (11)	C(23)–C(24)	1.34 (2)
C(20–C(30)	1.414 (11)	C(24)–C(25)	1.38 (1)
C(30–C(10)	1.422 (11)	C(25)–C(26)	1.42 (1)
Wtd av of 3 C–C	1.421 (7)	C(26)–C(21)	1.40 (1)
C(10)–C(11)	1.459 (12)	C(31)–C(32)	1.39 (1)
C(20)–C(21)	1.461 (12)	C(32)–C(33)	1.41 (2)
C(30)–C(31)	1.456 (11)	C(33)–C(34)	1.35 (2)
Wtd av of 3 C–C	1.459 (7)	C(34)–C(35)	1.38 (2)
N(4)–C(41)	1.33 (1)	C(35)–C(36)	1.41 (1)
C(41)–C(42)	1.42 (1)	C(35)–C(31)	1.35 (1)
C(42)–C(43)	1.36 (2)	Wtd av of 18 phenyl C–C	1.387 (4)
C(43)–C(44)	1.34 (2)		
C(44)–C(45)	1.40 (1)	C(60)–C(61)[c]	1.30 (7)
C(45)–N(4)	1.32 (1)	C(61)–C(62)	1.45 (5)
N(5)–C(51)	1.33 (1)	C(62)–C(63)	1.49 (7)
C(51)–C(52)	1.40 (1)	C(63)–C(64)	1.46 (7)
C(52)–C(53)	1.37 (1)	C(64)–C(65)	1.37 (5)
C(53)–C(54)	1.36 (1)	C(65)–C(60)	1.29 (7)
C(54)–C(55)	1.38 (1)	Wtd av of 6 C–C	1.39 (3)
C(55)–N(5)	1.36 (1)	C(60A)–C(61A)[c]	1.42 (8)
		C(61A)–C(62A)	1.47 (7)
		C(62A)–C(63A)	1.32 (7)
		C(63A)–C(64A)	1.38 (8)
		C(64A)–C(65A)	1.52 (8)
		C(65A)–C(60A)	1.00 (8)
		Wtd av of 6 C–C	1.35 (3)

Angles, Deg

Cl–Ni–R(3)	118.6 (2)	C(13)–C(14)–C(15)	120.2 (10)
Cl–Ni–N(4)	98.2 (2)	C(14)–C(15)–C(16)	119.8 (10)
Cl–Ni–(5)	96.1 (2)	C(14)–C(15)–C(16)	119.8 (10)
R(3)–Ni–N(4)	116.4 (3)	C(15)–C(16)–C(11)	124.0 (10)
R(3)–Ni–N(5)	125.5 (2)	C(16)–C(11)–C(12)	117.4 (10)
N(4)–Ni–N(5)	96.5 (2)	C(16)–C(11)–C(10)	122.7 (8)
C(30)–C(10)–C(20)	59.5 (5)	C(20)–C(21)–C(22)	121.0 (7)
C(10)–C(20)–C(30)	60.0 (6)	C(21)–C(22)–C(23)	119.1 (9)
C(20)–C(30)–C(10)	60.5 (6)	C(22)–C(23)–C(24)	122.0 (10)
C(30)–C(10)–C(11)	144.4 (7)	C(23)–C(24)–C(25)	119.6 (10)
C(20)–C(10)–C(11)	144.7 (8)	C(24)–C(25)–C(26)	120.6 (9)
C(10)–C(20)–C(21)	144.2 (8)	C(25)–C(26)–C(21)	119.1 (8)
C(30)–C(20)–C(21)	148.4 (8)	C(26)–C(21)–C(22)	119.6 (8)
C(20)–C(30)–C(31)	146.8 (8)	C(26)–C(21)–C(20)	119.3 (8)
C(10)–C(30)–C(31)	142.1 (8)	N(4)–C(41)–C(42)	120.3 (9)
C(30)–C(31)–C(32)	121.3 (8)	C(41)–C(42)–C(43)	119.9 (10)
C(31)–C(32)–C(33)	119.6 (9)	C(42)–C(43)–C(44)	118.7 (10)
C(32)–C(33)–C(34)	120.0 (10)	C(43)–C(44)–C(45)	119.9 (10)
C(33)–C(34)–C(35)	122.1 (10)	C(44)–C(45)–N(4)	122.4 (9)
C(34)–C(35)–C(36)	115.9 (9)	C(45)–N(4)–C(41)	118.9 (8)
C(35)–C(36)–C(31)	124.1 (9)	N(5)–C(51)–C(52)	122.9 (9)
C(36)–C(31)–C(32)	117.9 (8)	C(51)–C(52)–C(53)	119.5 (10)
C(36)–C(31)–C(30)	120.7 (8)	C(52)–C(53)–C(54)	118.3 (10)
C(10)–C(11)–C(12)	119.8 (9)	C(53)–C(54)–C(55)	120.0 (9)
C(11)–C(12)–C(13)	116.9 (12)	C(54)–C(55)–N(5)	122.6 (8)
C(12)–C(13)–C(14)	120.7 (13)	C(55)–N(5)–C(51)	116.7 (7)

Angles of Tilt of Phenyl Groups, Deg

[C(11), . . . , C(16)][d,e]	19.4	[C(31), . . . , C(36)]	20.2
[C(21), . . . , C(26)]	16.7		

Angles of Twist of Phenyl Groups, Deg

[C(11), . . . , C(16)][d,f]	8.4	[C(31), . . . , C(36)]	−18.9
[C(21), . . . , C(26)]	13.4		

[a] Figures in parentheses are the estimated standard deviations in the last figure quoted. [b] R(3) is a point at the center of the cyclopropenyl ring. [c] One atom in the C(60) series and in the C(60A) series is, in fact, a nitrogen atom. [d] [C(11), . . . , C(16)] refers to the phenyl group containing carbon atoms C(11) through C(16). [e] The tilt angle is the supplement of the average of the R(3)–C(10)–C(11) and R(3)–C(10)–C(14) angles. The other two tilt angles are similarly defined. [f] The twist angle is the complement of the dihedral angle between the [C(11), . . . , C(16)] plane and the [Ni, R(3), C(10), C(11), C(14)] plane. The two remaining twist angles are similarly defined.

TABLE III

COMPARISON OF STRUCTURAL DATA FOR TRIPHENYLCYCLOPROPENYL DERIVATIVES[a]

	$(C_3(C_6H_5)_3)$-(ClO_4)[b]	$[(\pi\text{-}C_3(C_6H_5)_3)$-$NiCl(py)_2]\cdot py$[c]	$(\pi\text{-}C_5H_5)Ni$-$(\pi\text{-}C_3(C_6H_5)_3)$[d]
M–C (av), Å	. . .	1.941 (5)	1.961 (4)
M–C (range), Å	. . .	1.896–1.968	1.953–1.968
M–C_3 ring (⊥), Å	. . .	1.759	1.779
Cyclopropenyl C–C (av), Å	1.373 (5)	1.421 (7)	1.428 (5)
Exocyclic C–C (av), Å	1.436 (5)	1.459 (7)	1.452 (4)
Tilt angles,[e] deg	0.0	19.4	20.1
	1.1	16.7	19.2
	0.8	20.2	19.7
Twist angles,[e] deg	7.6	8.4	19.9
	21.2	13.4	20.1
	12.1	−18.9	23.5

[a] The esd's are given in parentheses. [b] M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966). [c] This work. [d] R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 1504 (1971). [e] The tilt and twist angles are defined in Table II.

2.019 Å,[14a] and Ni–C(π-$C_3(C_6H_5)_3$), 1.950 Å.[14b] However, perpendicular Ni–ring distances remain relatively constant despite ring size; the range for all nickel complexes of π-ring systems is about 1.72–1.78 Å.[14a] An angle of 3.6° was found between the Ni–ring center vector and the normal to the cyclopropenyl ring. This finite angle results from the fact that one of the Ni–C(ring) distances is significantly shorter than the other two. No chemical significance in terms of localized bonding to the C_3 ring is attached to the unequal Ni–C(ring) distances, particularly in view of the equality of the three C–C distances within this ring (*vide infra*).

The average Ni–N(py) bond length is 2.024 (5) Å and the Ni–Cl distance is 2.322 (3) Å. An internally consistent value of about 1.34 Å for the tetrahedral Ni(0) covalent radius can be obtained from these bond lengths since none of the bonds should be effected by appreciable multiple character. Other pyridine complexes such as *trans*-$Co(acac)_2(py)_2$[15] and *trans*-$Ni(acac)_2(py)_2$,[16] where acac is the acetylacetonate anion, similarly show no evidence of significant metal–pyridine π bonding.

Table III gives a comparison of some pertinent bond distances and angles for $C_3(C_6H_5)_3^+$ and two nickel complexes of this ligand. Carbon–carbon distances in the C_3 ring are all equal (within 1σ) to an average value of 1.421 (7) Å for the present complex which is significantly longer than that found in the free ligand.[17] This lengthening is characteristic of metal π complexes of aromatic ligands.[18] Inspection of Table III also shows that the average exocyclic C–C bond distance is essentially equal for the two nickel complexes and $C_3(C_6H_5)_3^+$. All of these lengths are shorter than the value of 1.48 Å expected for a C(sp^2)–C(sp^2) single bond. A contraction of this type results from an increase in s character of the orbitals directed toward the phenyl groups as the exocyclic angles become greater than 120°. Conjugation between the C_3 ring and the phenyl groups may also contribute to these shortened bond lengths.

The phenyl groups are tipped out of the plane away from the nickel atom by about 19°. These groups are also twisted (not all in the same sense) about the cyclopropenyl–phenyl bonds by ~14°. Departures from planarity of this type, which are due to a combination of hybridization and steric effects, have also been observed in similar compounds such as (π-$C_4(C_6H_5)_4$)Fe-$(CO)_3$.[19] Within the phenyl groups, the geometry is that normally observed.

It is interesting to note the different attitudes assumed by the coordinated pyridine molecules with respect to a plane parallel to the cyclopropenyl ring; the two pyridine rings are parallel and perpendicular, respectively, to this plane. These two orientations are presumably positions of minimum intramolecular repulsion between the pyridine and phenyl groups. Distances in the coordinated pyridine rings are equal within experimental error to those previously determined in two pyridine adducts.[15,16] The disordered pyridine of crystallization is reasonably planar and Table IV gives some pertinent weighted least-squares planes.

Most of the closest intermolecular distances result from approach of the two coordinated pyridine molecules which are

---

(15) R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

(16) R. C. Elder, *ibid.*, **7**, 2316 (1968).

(17) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

(18) P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 1 (1967).

(19) R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, **18**, 614 (1965).

Table IV

Weighted[a] Least-Squares Planes in the Form: $AX + BY + CZ + D = 0^b$

Plane	Atoms	A	B	C	D
1	C(10), C(20), C(30)	0.6815	−0.3550	0.6399	−3.8069
2	C(11), . . ., C(16)[c]	0.8065	−0.4689	0.3601	−2.3998
3	C(21), . . ., C(26)	0.7002	−0.0150	0.7138	−3.8595
4	C(31), . . ., C(36)	0.4046	−0.1454	0.9029	−4.5464
5	N(4), . . ., C(45)	0.4657	−0.3795	0.7995	−2.4214
6	N(5), . . ., C(55)	−0.6406	−0.6200	0.4531	−1.7214
7	C(60), . . ., C(65)	−0.1982	−0.7217	0.6632	−3.2552
8	C(60A), . . ., C(65A)	−0.1892	−0.7770	0.6004	−2.8165
9	C(60), . . ., C(65A)	−0.1851	−0.7488	0.6364	−3.1270

Distances of Atoms from Mean Planes, Å

Plane	
2	C(11), −0.029; C(12), 0.063; C(13), −0.041; C(14), −0.008; C(15), −0.004; (16), 0.019
3	C(21), 0.004; C(22), −0.001; C(23), −0.006; C(24), 0.010; C(25), −0.005; C(26), −0.001
4	C(31), 0.009; C(32), 0.010; C(33), −0.036; C(34), 0.032; C(35), 0.000; C(36), −0.015
5	N(4), −0.003; C(41), 0.002; C(42), 0.000; C(43), 0.001; C(44), −0.005; C(45), 0.006
6	N(5), 0.001; C(51), −0.002; C(52), 0.000; C(53), 0.004; C(54), −0.004; C(55), 0.002
7	C(60), −0.109; C(61), 0.051; C(62), 0.009; C(63), 0.000; C(64), 0.012; C(65), 0.037
8	C(60A), 0.041; C(61A), −0.054; C(62A), 0.027; C(63A), 0.005; C(64A), −0.030; C(65A), 0.011
9	C(60), −0.172; C(61), 0.017; C(62), 0.033; C(63), 0.043; C(64), 0.017; C(65), −0.010
	C(60A), 0.080; C(61A), −0.080; C(62A), −0.025; C(63A), −0.006; C(64A), 0.022; C(65A), 0.082

Dihedral Angles, Deg

Planes	Angle	Planes	Angle
1,2	18.8	1,4	25.2
1,3	20.1	7,8	4.8

[a] Atoms are weighted by the reciprocals of their variances. [b] The direction cosines were computed in an orthogonal coordinate system in which X, Y, and Z are parallel to a, b, and c^*, respectively. [c] C(11), . . ., C(16) refers to the plane of the phenyl group containing atoms C(11) through C(16). Other planes are similarly defined.

related to one another by a center of symmetry. A perpendicular interplanar distance of 3.44 Å was found for these two aromatic rings.

Discussion

(π-$C_3(C_6H_5)_3$)NiCl(py)$_2$ is diamagnetic and can be approximately described as a tetrahedral complex of Ni(0) where the cyclopropenyl ring occupies one coordination position. With the four ligands each donating a pair of electrons the complex attains the expected rare gas configuration. Qualitatively the nickel–ring bonding can be envisioned as arising from the overlap of an sp^3 hybridized orbital on the metal and the lowest energy a$_1$ combination (C_{3v} localized symmetry) of pπ orbitals which is localized largely on the three C_3 ring carbon atoms. A pathway for nickel→ring back-bonding is provided by the e combination of pπ orbitals on the cyclopropenyl ring. However, there is no experimental evidence for an appreciable metal to ring bonding interaction of the latter type (*vide infra*).

Use of this model aids in understanding the electronic spectrum of the complex given in Figure 4. Comparison of this spectrum with that of uncomplexed pyridine and $C_3(C_6H_5)_3^+$ shows that it is a composite of the two free-ligand absorptions and one additional lower energy band at ~29,000 cm^{-1} (ϵ 2300). This new peak is assigned to the metal to ligand transitions d(e, t$_2$) → $\pi^*(C_3(C_6H_5)_3^+)$. Splitting of the e and t$_2$ levels is presumably small and not resolved in the spectrum. As expected, the $\pi \rightarrow \pi^*$ transition in the coordinated pyridine[20] is unchanged from that of the free ligand. It is, however, perhaps surprising that there is no appreciable alteration in the spectrum of the bonded cyclopropenyl group. Two reports in the literature support this observation. First, the lowest energy a$_1$ combination of pπ orbitals[21] on the ring which is presumed to be responsible for the principal bonding interaction in the nickel complex is not involved in the $\pi \rightarrow \pi^*$ transition observed in the spectrum. Second, the electronic spectrum of the $C_3(C_6H_5)_3^+$ cation has essentially the same bands as its covalent derivatives[1] such as 1,2,3-triphenylcyclopropenyl methyl ether.

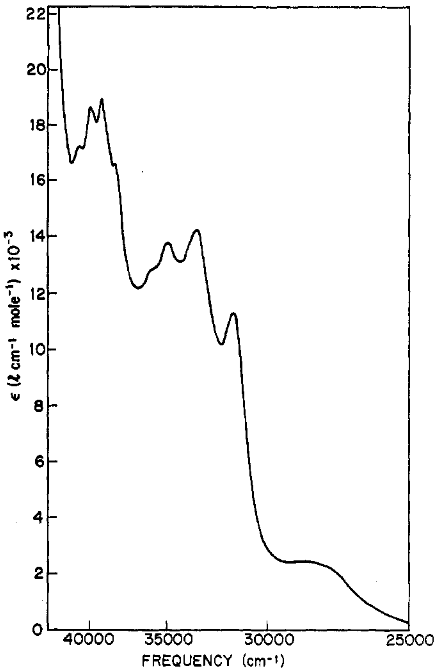

Figure 4.—The electronic spectrum of (π-$C_3(C_6H_5)_3$)NiCl(py)$_2$.

Further support for these spectral assignments and the bonding description comes from the following considerations. (1) Electronic spectra of the approximately tetrahedral nickel complexes[22] Ni(PC$_6$H$_5$(OR)$_2$)$_4$, where R = methyl or ethyl, exhibit a lower energy band in addition to those of the free ligand and this absorption has been assigned to nickel → π^*(ligand) transitions. (2) Semiempirical molecular orbital calculations[23] indicate that there is little d-orbital contribution to the π bonding in Ni(CO)$_4$. Indeed, Shriner and Brown concluded that there is considerably less net π bonding in Ni(CO)$_4$ than in Cr(CO)$_6$ or Fe(CO)$_5$. Furthermore, photoelectron spectroscopy results[24] for Ni(CO)$_4$ and Ni(PF$_3$)$_4$ give a separation of about 1 eV for the e and t$_2$ levels. In (π-$C_3(C_6H_5)_3$)NiCl(py)$_2$ where there is less π bonding this splitting should be diminished which is consistent with these levels not being resolved in the electronic spectrum.

Acknowledgments.—The work was generously supported by the National Science Foundation (Grant No. GP-8371). R. M. T. acknowledges with gratitude the receipt of an NDEA fellowship, 1966–1969.

---

(20) H. H. Schmidtke in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience, New York, N. Y., 1968, p 145.

(21) R. Basu and S. K. Bose, *Theor. Chim. Acta*, **4**, 94 (1966).

(22) A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chim. Acta*, **3**, 8 (1969).

(23) A. F. Schreiner and T. L. Brown, *J. Amer. Chem. Soc.*, **90**, 3366 (1968).

(24) J. C. Green, D. I. King, and J. H. D. Eland, *Chem. Commun.*, 1121 (1970).