The dimensions of the tetraphenylborate anion are shown in Table VI. Its structure and position relative to one of its cation neighbors is shown in Figure 2.

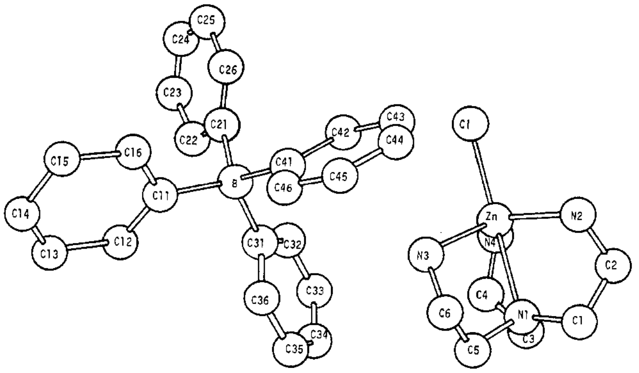


Figure 2.—Structure of the anion and its relation to one of its cation neighbors.

The molecular packing can be described in terms of a distorted sodium chloride type structure. The positions of the bulky anions are near a cubic closest packing based on a pseudocubic pseudocell with axes a, $b + c/2$, $b - c/2$. The cations are in octahedral holes in this anion packing, as in the sodium chloride structure, with atoms N1 close to the centers of the holes. The closest approach of the two ions is a distance of 2.56 Å between a carbon atom (C43) of the anion and a hydrogen atom (H1N3) of the cation.

Table VII shows the interatomic distances to hydrogen in this structure. The average N–H bond distance is 0.85 Å, and the average C–H distance is 0.95 Å. As is generally the case in X-ray structure determinations involving hydrogen, these distances between the centers of gravity of electron clouds tend to be shorter by about 0.1 Å from the generally accepted values for the internuclear distances.

CONTRIBUTION FROM THE LABORATORIO DI TEORIA E STRUTTURA ELETTRONICA E COMPORTAMENTO SPETTROCHIMICO DEI COMPOSTI DI COORDINAZIONE DEL C.N.R., ISTITUTO DI CHIMICA GENERALE ED INORGANICA, UNIVERSITÁ DEGLI STUDI, ROME, ITALY

The Crystal and Molecular Structure of the Adduct of Bis(diphenyldithiophosphinato)nickel(II) with Pyridine

BY P. PORTA,* A. SGAMELLOTTI, AND N. VINCIGUERRA

Received December 18, 1969

The crystal structure of the adduct of bis(diphenyldithiophosphinato)nickel(II) with pyridine, $Ni[S_2P(C_6H_5)_2]_2 \cdot 2py$, has been determined by three-dimensional single-crystal X-ray analysis. Fourier methods were applied and the positional and isotropic thermal parameters of the atoms were refined by least-squares methods on three-dimensional photographic data. The compound forms monoclinic crystals, space group $P2_1/c$, with two molecules in the unit cell, whose dimensions, determined using zinc oxide as the standard, are $a = 12.38 \pm 0.02$ Å, $b = 8.98 \pm 0.01$ Å, $c = 15.97 \pm 0.02$ Å, and $\beta = 106.95 \pm 0.08°$. The measured density (by flotation) is 1.394 ± 0.006 g/cm^3 while that calculated for two formula units is 1.399 ± 0.008 g/cm^3. The nickel atom lies at a center of symmetry on the plane formed by the four sulfur atoms and completes its coordination sphere with the nitrogen atoms of two pyridine molecules. The average Ni–S distance is 2.50 (2) Å and the Ni–N bond length is 2.08 (1) Å. The final R factor is 0.104 for 1220 independent nonzero reflections. The correlation between Ni–S distances and the variations in the chelate rings are given and discussed for the tetracoordinated pyridine-free compound and the present octahedral pyridine adduct. The optical spectra are also given and discussed.

Introduction

Syntheses and spectral investigations of nickel complexes with molecules containing two sulfur atoms which may act as chelating ligands are at present being carried out in this laboratory. The crystal structure of the planar bis(diphenyldithiophosphinato)nickel(II) compound, $Ni[S_2P(C_6H_5)_2]_2$, hereafter $Ni(dtpi)_2$, has already been determined,[1] and it was thought interesting to carry out a single-crystal three-dimensional X-ray structure determination of the adduct of the above compound with two molecules of pyridine.

The purpose of this work was mainly to evaluate, with sufficient accuracy, the actual Ni–S bond distances and to compare them with the corresponding ones of the tetracoordinated chelate. Moreover, it would be interesting to observe the possible changes in the structure of the metal chelate caused by the completion of the coordination sphere of the metal atom with solvent molecules such as pyridine.

Experimental Section

Preparation of the Compound.—$Ni(dtpi)_2$ was prepared as described by Kuchen, *et al.*[2] Subsequently, green, prismatic crystals of bis(diphenyldithiophosphinato)nickel(II)–2-pyridine, $Ni[S_2P(C_6H_5)_2]_2 \cdot 2C_5H_5N$ (hereafter called $Ni(dtpi)_2 \cdot 2py$) were obtained by addition of pyridine to a solution of $Ni(dtpi)_2$ in toluene. The crystals, when exposed to air, slowly reverted to the original violet pyridine-free compound with loss of pyridine. In order to prevent decomposition, the crystals were enclosed in

---

* To whom correspondence should be addressed at Università di Roma, Istituto di Chimica Generale ed Inorganica, Rome, Italy.

[1] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, **7**, 2625 (1968).

[2] W. Kuchen, J. Metten, and A. Jadat, *Chem. Ber.*, **97**, 2306 (1964).

Lindemann capillaries with a thin layer of paraffin, during X-ray data collection.

Crystallographic Data.—The following cell diminsions were determined, by superimposing zinc oxide lines (ZnO annealed at 1200°; $a = 3.24968$ (5) and $c = 5.2060$ (3) Å at 21°; a Charles-Supper back-reflection symmetrical focusing camera of 12-cm diameter was used)[3] on zero-layer Weissenberg photographs about the b and c axes and using an improved version of Christ's method:[4] $a = 12.38 \pm 0.02$ Å, $b = 8.98 \pm 0.01$ Å, $c = 15.97 \pm 0.02$ Å, $\beta = 106.95 \pm 0.08°$. The data were taken using nickel-filtered Cu Kα radiation (λ 1.5418 Å, 21°) and the errors of the cell parameters are average standard deviations.

The volume of the unit cell is 1698 Å^3. The calculated density for two formula units of the compound (formula weight 715.54) is 1.399 ± 0.008 g/cm^3 and the value measured by flotation in a mixture of toluene and carbon tetrachloride is 1.394 ± 0.006 g/cm^3. (These numbers were evaluated from the deviations observed on three independent measurements.) It should be added that the measurements of the density were carried out as rapidly as possible since, as mentioned above, this compound decomposes in air. However, it was observed during the measurements that the crystals were still the color of Ni(dtpi)$_2$·2py.

Systematic absences, as determined from precession ($0kl$ and $1kl$) and Weissenberg ($h0l$, $h1l$, $hk0$, and $hk1$) photographs, were as follows: $0k0$ when k is odd, $h0l$ when l is odd. The crystals thus belong to the monoclinic system, space group $P2_1/c$-$C_{2h}{}^5$. The unit cell contains two molecules and each molecule is crystallographically required to be centrosymmetric with the nickel atom in the special position (0, 0, 0). For Cu Kα radiation the linear absorption coefficient is $\mu = 40.7$ cm^{-1} (approximate limits of $\mu R = 0.06$–0.08).

Collection of X-Ray Data.—Intensity photographs were taken from a prismatic crystal about 0.015 × 0.02 × 0.03 mm in size (the elongation is on the b axis) at room temperature (about 21°) and with nickel-filtered Cu Kα radiation (λ 1.5418 Å). The X-ray intensities of 1220 independent nonzero reflections were estimated visually, with the aid of a calibrated strip, from sets of multiple-film equiinclination Weissenberg photographs taken about the b (seven layers) and c (three layers) axes. They were corrected for Lorentz and polarization factors and for spot size on the upper layers (according to Phillips),[5] and placed on a common scale by the method of Hamilton, Rollett, and Sparks.[6] No absorption or extinction corrections were applied.

Structure Determination and Refinement.—As mentioned above, the origin of the cell was chosen as coincident with the nickel position at 0, 0, 0. The approximate positions of two sulfur atoms, one phosphorus atom, and the nitrogen atom of the pyridine adduct were found from a three-dimensional Patterson synthesis. The positions of all carbon atoms belonging to the phenyl and pyridine groups were determined from Fourier syntheses. The positional and isotropic temperature factors of each nonhydrogen atom were then refined by a least-squares method. After six cycles an R value of 0.11 was obtained. Following the introduction of hydrogen atoms in planar positions with C–H bond lengths of 1.09 Å and some additional least-squares cycles in which only the positional and isotropic thermal parameters of nonhydrogen atoms were refined, the R value was 0.104. All hydrogen atoms were given a fixed isotropic thermal parameter B of 8.0 Å^2.

A further cycle of refinement indicated no shifts greater than 25% of the corresponding standard deviations; thus refinement was considered to be complete at the above value of R.

The refinement employed the block-diagonal approximation and included observed reflections only. The quantity minimized was $R' = \Sigma w(|F_o| - |F_c|)^2$, where the weighting factor $w = \{a + bk|F_o| + c(kF_o)^2\}^{-1}$, with $a = 15$, $b = 1.0$, and $c = 0.004$.

The positional parameters of hydrogen atoms, calculated from the final positions of the carbons and numbered by reference to their respective carbon atoms, are given in Table I. The final atomic coordinates (Å) and the thermal parameters for nonhydrogen atoms with their standard deviations[7] are reported in Table II. Table III shows the complete list of observed and calculated structure amplitudes; the F_c values have been calculated from the parameters of Table II and include the contributions of hydrogen atoms (Table I).

TABLE I

CALCULATED COORDINATES (×10^4) FOR HYDROGEN ATOMS

Atoms	X	Y	Z
H(2)	4773	1635	444
H(3)	6607	488	1354
H(4)	6508	−1658	2315
H(5)	4666	−2393	2574
H(6)	2914	−969	1799
H(8)	3572	3786	1170
H(9)	3923	6283	533
H(10)	3265	6589	−1125
H(11)	2324	4614	−2057
H(12)	1908	2168	−1452
H(13)	−675	3269	102
H(14)	−1413	5407	−866
H(15)	−1277	5166	−2437
H(16)	−886	2783	−2997
H(17)	−357	595	−1967

TABLE II

FINAL ATOMIC COORDINATES (×10^4) AND ISOTROPIC THERMAL PARAMETERS WITH ESD'S OF NONHYDROGEN ATOMS

Atoms	X	Y	Z	B, Å^2
Ni	0	0	0	1.88 (7)
S(1)	1676 (3)	−372 (5)	−530 (2)	2.42 (11)
S(2)	1386 (3)	1584 (5)	1120 (2)	2.51 (10)
P	2411 (3)	1126 (5)	381 (2)	2.12 (9)
N	−475 (9)	1796 (15)	−854 (7)	2.95 (24)
C(1)	3745 (11)	348 (19)	1069 (8)	2.59 (26)
C(2)	4770 (14)	766 (23)	935 (11)	4.22 (37)
C(3)	5790 (15)	103 (24)	1416 (12)	5.05 (41)
C(4)	5725 (15)	−1055 (25)	1969 (12)	5.16 (42)
C(5)	4693 (16)	−1473 (25)	2118 (12)	5.62 (45)
C(6)	3719 (14)	−710 (23)	1670 (11)	4.34 (38)
C(7)	2728 (12)	2787 (21)	−97 (9)	3.25 (30)
C(8)	3284 (15)	3975 (24)	456 (11)	4.86 (40)
C(9)	3482 (18)	5353 (28)	105 (14)	6.69 (54)
C(10)	3121 (16)	5532 (26)	−827 (13)	5.87 (49)
C(11)	2591 (18)	4443 (26)	−1346 (13)	6.20 (50)
C(12)	2364 (14)	3046 (23)	−1007 (10)	4.22 (37)
C(13)	−759 (11)	3146 (20)	−596 (9)	3.13 (30)
C(14)	−1119 (13)	4380 (22)	−1111 (10)	4.17 (37)
C(15)	−1098 (16)	4201 (25)	−2001 (12)	5.45 (45)
C(16)	−855 (14)	2907 (23)	−2304 (11)	4.41 (37)
C(17)	−546 (13)	1668 (22)	−1719 (10)	3.81 (34)

The atomic scattering factors of Hanson and coworkers[8] were used for Ni, S, C, N, and H, those of Ni being corrected for the real part of anomalous dispersion ($\Delta f' = -3.2$);[9] scattering factors of Cromer and Waber[10] were used for phosphorus.

A difference Fourier synthesis, calculated with the use of the final parameters, confirmed the correctness of the structure since at the sites of all atoms the value of $\Delta\rho$ was approximately zero

---

(3) A. Cimino, G. Mazzone, and P. Porta, *Z. Phys. Chem. (Frankfurt am Main)*, **41**, 154 (1964).

(4) G. Mazzone, A. Vaciago, and M. Bonamico, *Ric. Sci.*, **33**, 1113 (1963).

(5) D. C. Phillips, *Acta Crystallogr.*, **9**, 819 (1956).

(6) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *ibid.*, **18**, 129 (1965).

(7) D. W. J. Cruickshank, *ibid.*, **2**, 65 (1949).

(8) H. P. Hanson, F. Herman, J. D. Lea, and S. Skilman, *ibid.*, **17**, 1040 (1964).

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

(10) D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	$\lvert F_o\rvert$	F_c
0	2	0	124.6	123.2
0	6	0	40.5	41.1
0	1	1	120.1	137.4
0	2	1	32.6	-33.0
0	3	1	16.0	20.5
0	4	1	12.2	-11.8
0	5	1	15.0	15.0
0	6	1	18.0	-22.4
0	7	1	55.3	52.5
0	0	2	164.7	153.9
0	1	2	16.2	14.9
0	2	2	75.6	81.5
0	3	2	41.1	-46.0
0	4	2	23.7	32.6
0	6	2	25.5	22.0
0	2	3	110.5	-115.7
0	3	3	74.7	75.0
0	4	3	18.2	-21.3
0	0	4	21.6	-16.3
0	1	4	76.4	-81.9
0	3	4	120.1	-124.0
0	4	4	33.0	34.6
0	5	4	27.3	-20.8
0	1	5	21.6	23.2
0	2	5	40.5	-42.2
0	3	5	42.7	39.1
0	4	5	12.1	-18.2
0	0	6	21.7	-16.9
0	1	6	25.5	25.6
0	2	6	41.2	40.4
0	3	6	43.1	-38.0
0	4	6	25.7	25.2
0	5	6	45.4	-37.4
0	1	7	11.9	9.5
0	2	7	22.7	21.8
0	3	7	18.1	15.5
0	4	7	27.8	-28.0
0	5	7	26.8	20.6
0	0	8	14.1	12.6
0	1	8	23.8	-22.2
0	3	8	20.1	-17.4
0	4	8	29.8	30.4
0	6	8	26.9	29.6
0	2	9	37.5	-39.6
0	3	9	15.3	-14.2
0	5	9	24.1	19.2
0	0	10	33.5	27.8
0	1	10	28.6	-28.5
0	4	10	15.3	10.6
0	5	10	42.8	32.5
0	2	11	38.1	-39.5
0	5	11	26.7	21.5
0	0	12	25.4	-20.9
0	1	12	19.7	-13.3
0	4	12	36.5	37.3
0	5	12	29.9	24.8
0	1	13	18.6	-13.7
0	3	13	22.0	33.4
0	0	14	20.0	-21.2
0	1	14	20.6	18.5
0	4	14	30.4	36.8
0	2	15	21.8	27.8
0	3	15	24.9	25.2
0	1	16	22.0	20.5
0	3	16	20.6	17.2
0	4	16	16.8	19.9
0	2	17	16.6	18.3
0	0	18	20.6	27.5
0	1	19	15.9	17.0
1	1	0	64.4	-66.6
1	2	0	33.2	-33.9
1	4	0	19.2	28.7
1	5	0	49.2	63.0
1	6	0	39.0	38.5
1	1	1	32.7	32.0
1	1	-1	79.2	76.4
1	2	1	100.8	-105.2
1	3	1	46.6	47.8
1	3	-1	22.4	-23.4
1	5	1	40.7	42.8
1	5	-1	37.5	40.8
1	6	1	41.1	50.1
1	6	-1	35.7	44.2
1	0	2	23.0	19.9
1	0	-2	127.2	117.8
1	1	2	36.5	-37.8
1	1	-2	78.9	-88.2
1	2	2	65.0	69.2
1	2	-2	9.5	11.8
1	4	2	68.2	82.8
1	4	-2	30.7	-39.1
1	5	2	46.0	47.2
1	5	-2	16.5	11.8
1	6	2	27.5	27.7
1	6	-2	42.6	45.0
1	1	3	85.2	83.9
1	1	-3	142.6	153.6
1	2	-3	15.4	-15.5
1	3	3	159.0	148.2
1	3	-3	15.2	14.9
1	4	3	14.2	-12.6
1	4	-3	10.7	-11.2
1	5	3	23.8	22.5
1	6	3	22.5	21.1
1	6	-3	21.0	22.2
1	0	4	22.3	16.2
1	0	-4	40.2	34.7
1	1	4	43.7	40.0
1	1	-4	11.3	-9.8
1	2	4	98.7	98.6
1	2	-4	48.6	53.7
1	3	-4	14.7	-15.7
1	4	4	100.5	110.0
1	5	4	13.2	-14.4
1	1	5	69.6	61.6
1	1	-5	12.7	-13.8
1	2	-5	32.4	28.9
1	3	5	117.2	102.2
1	3	-5	65.9	63.6
1	4	5	16.0	-14.1
1	4	-5	9.2	-10.6
1	5	5	57.4	50.5
1	5	-5	12.3	-7.0
1	0	6	17.9	-15.1
1	1	6	12.0	9.2
1	1	-6	13.2	-13.3
1	2	6	54.5	47.7
1	2	-6	34.6	28.5
1	3	6	21.0	-21.3
1	3	-6	37.3	32.3
1	4	6	48.1	49.7
1	4	-6	10.8	-11.8
1	5	6	54.5	-45.5
1	6	6	24.9	30.9
1	1	7	59.0	56.9
1	1	-7	7.7	2.6
1	4	7	36.3	-36.5
1	4	-7	32.7	33.2
1	5	7	63.2	48.1
1	5	-7	23.9	-20.9
1	0	8	14.8	15.9
1	0	-8	25.6	18.8
1	1	8	34.8	-33.9
1	1	-8	32.8	-29.3
1	3	8	19.1	-17.4
1	3	-8	11.0	8.3
1	4	8	28.8	25.6
1	4	-8	29.9	-30.8
1	5	8	51.0	-37.9
1	2	9	30.0	-27.8
1	2	-9	23.0	-23.7
1	3	9	19.3	13.1
1	3	-9	16.8	-14.0
1	4	9	12.9	-10.8
1	4	-9	31.7	-26.9
1	5	9	34.9	40.9
1	0	10	19.3	-16.2
1	0	-10	54.4	49.1
1	1	10	34.9	-32.1
1	2	-10	18.4	17.0
1	3	10	14.4	13.2
1	3	-10	19.6	12.5
1	4	10	22.1	24.7
1	4	-10	15.1	-10.6
1	5	-10	38.2	-32.3
1	1	11	17.5	-11.5
1	1	-11	39.2	36.9
1	2	-11	28.9	27.9
1	3	-11	25.7	-21.0
1	4	-11	46.5	-40.5
1	5	-11	51.7	40.8
1	0	12	22.9	-24.9
1	0	-12	54.4	-44.3
1	1	-12	32.6	32.5
1	2	12	20.2	-20.4
1	2	-12	31.1	30.8
1	3	12	35.8	29.0
1	5	-12	45.2	-39.5
1	1	13	18.7	-13.6
1	1	-13	34.9	38.3
1	2	13	41.5	41.3
1	2	-13	20.3	15.2
1	3	13	25.4	21.0
1	3	-13	28.3	24.9
1	5	-13	32.2	19.8
1	1	14	30.2	31.0
1	2	-14	35.1	35.0
1	3	14	17.5	18.5
1	4	-14	28.9	33.0
1	5	-14	22.9	-15.7
1	2	15	24.5	29.3
1	3	-15	41.1	41.7
1	0	16	28.1	36.1
1	2	-16	24.9	22.8
1	4	-16	22.7	24.6
1	1	17	17.6	20.7
1	3	-17	20.3	20.3
1	1	18	16.9	25.3
1	0	-18	12.0	12.9
1	4	-18	9.4	12.6
1	5	-18	9.5	11.5
1	1	19	9.2	10.8
2	0	0	11.4	-14.2
2	1	0	33.7	37.4
2	3	0	16.3	19.6
2	4	0	25.9	33.4
2	5	0	41.8	50.6
2	6	0	40.1	44.6
2	1	1	74.6	81.5
2	1	-1	17.0	19.0
2	2	1	18.7	18.0
2	2	-1	68.0	-76.7
2	3	1	66.8	79.8
2	3	-1	18.1	-17.6
2	4	1	24.2	31.3
2	4	-1	40.7	58.4
2	5	1	46.9	51.5
2	5	-1	54.1	60.4
2	6	1	30.1	28.4
2	6	-1	38.0	39.9
2	0	2	161.5	-150.8
2	0	-2	17.0	-13.9
2	1	2	38.8	38.2
2	1	-2	45.3	-50.1
2	2	2	73.0	71.7
2	2	-2	15.2	-16.6
2	3	2	30.4	32.2
2	3	-2	17.3	-15.3
2	4	2	73.1	85.2
2	4	-2	16.1	15.0
2	5	-2	33.6	39.1
2	6	-2	59.8	65.2
2	1	-3	55.5	-56.5
2	2	3	57.4	56.4
2	2	-3	13.1	9.4
2	3	3	119.2	119.0
2	3	-3	33.9	-36.3
2	4	3	12.7	12.5
2	4	-3	40.2	41.1
2	5	3	46.4	42.1
2	5	-3	48.0	44.8
2	6	3	21.7	20.2
2	0	4	52.8	50.5
2	0	-4	36.8	-23.7
2	1	4	56.4	60.4
2	1	-4	37.2	34.2
2	2	4	74.2	69.7
2	2	-4	36.8	-33.2
2	3	4	33.6	27.3
2	3	-4	49.4	-44.1
2	4	4	49.4	53.3
2	4	-4	17.5	16.3
2	5	4	22.4	-17.5
2	5	-4	40.2	-32.5
2	6	4	20.1	23.0
2	6	-4	41.9	41.7
2	1	5	53.5	52.2
2	1	-5	21.5	-21.0
2	2	5	38.9	36.7
2	3	5	37.8	31.0
2	3	-5	26.1	26.1
2	4	-5	37.9	-43.2
2	5	5	68.7	60.9
2	6	5	24.6	-26.2
2	0	6	63.8	67.7
2	0	-6	45.2	-35.4
2	1	6	38.7	44.0
2	1	-6	57.6	-60.3
2	2	6	66.1	67.2
2	2	-6	20.0	22.3
2	3	6	41.9	34.8
2	3	-6	76.2	-71.7
2	4	6	25.1	23.9
2	4	-6	27.5	30.7
2	5	6	34.9	-25.7
2	5	-6	44.4	-34.4
2	6	6	38.9	47.6
2	1	7	42.0	47.7
2	1	-7	30.9	29.9
2	2	7	16.4	18.3
2	2	-7	58.4	-52.1
2	3	7	24.9	19.4
2	3	-7	78.1	72.7
2	4	-7	46.4	-48.5
2	5	7	54.0	43.5
2	5	-7	24.7	18.9
2	0	8	60.9	62.9
2	0	-8	49.1	-36.9
2	1	8	22.4	-22.6
2	1	-8	46.3	-47.6
2	2	8	53.2	52.4
2	2	-8	60.6	54.9
2	3	-8	53.4	-47.6
2	4	8	12.7	13.4
2	4	-8	34.9	37.3
2	5	-8	19.2	15.0
2	1	9	34.0	35.8
2	1	-9	72.2	76.7
2	2	-9	51.9	-48.6
2	3	-9	48.3	36.8
2	4	9	32.1	31.9
2	5	-9	17.5	11.0
2	0	10	29.1	29.2
2	0	-10	100.3	78.2
2	1	10	17.1	-13.1
2	1	-10	19.6	-20.1
2	2	10	38.1	41.5
2	2	-10	52.0	50.7
2	3	-10	21.0	-16.3
2	1	11	26.9	29.1
2	1	-11	78.9	73.8
2	2	11	26.0	22.2
2	3	-11	20.5	-18.5
2	4	11	18.2	-17.0
2	5	-11	28.7	19.1
2	0	12	23.3	21.6
2	0	-12	108.5	77.4
2	1	-12	9.6	13.0
2	2	12	20.4	18.4
2	2	-12	30.2	30.5
2	3	-12	29.6	-26.6
2	5	12	35.2	-33.2
2	5	-12	24.5	-19.3
2	1	13	20.6	22.0
2	1	-13	52.4	52.7
2	2	-13	20.2	18.5
2	4	13	26.2	-28.1
2	0	14	24.9	25.9
2	0	-14	49.0	40.7
2	1	-14	20.5	22.6
2	2	-14	22.5	21.2
2	4	14	17.3	-17.7
2	5	14	18.4	-20.5
2	5	-14	20.8	-12.6
2	1	-15	23.6	29.6
2	2	-15	20.3	15.8
2	3	-15	34.8	32.1
2	4	-15	13.2	11.3
2	0	-16	10.6	15.0
2	1	-16	11.4	12.0
2	2	-16	27.4	28.7
2	3	-16	16.4	14.1
2	3	-17	18.2	20.0
2	3	-18	11.0	12.3
2	5	-18	10.4	15.3
3	1	0	115.6	118.4
3	2	0	24.6	27.2
3	3	0	11.5	13.1
3	4	0	31.8	42.9
3	1	1	16.5	-16.8
3	1	-1	100.9	-98.7
3	2	1	42.2	49.2
3	2	-1	60.8	-69.4
3	3	1	39.9	46.1
3	3	-1	11.0	12.6
3	4	1	13.8	17.5
3	5	1	16.7	17.6
3	5	-1	31.6	31.0
3	6	1	23.8	-26.8
3	6	-1	39.1	-43.2
3	0	2	70.1	-68.5
3	0	-2	160.4	170.9
3	1	2	52.1	70.1
3	1	-2	21.8	-17.4
3	2	2	30.0	28.7
3	3	2	22.4	24.2
3	4	2	18.2	21.7
3	4	-2	17.4	20.0
3	5	2	31.5	-28.7
3	6	-2	32.5	36.2
3	1	-3	42.1	-41.4
3	2	3	110.6	114.0
3	2	-3	53.2	-52.5
3	4	3	30.8	28.9
3	4	-3	23.5	20.3
3	5	-3	43.7	40.1
3	6	-3	30.7	-32.5
3	0	4	53.8	48.4
3	0	-4	79.6	66.6
3	1	4	56.1	56.6
3	2	4	23.8	23.9
3	3	4	17.1	18.4
3	3	-4	15.2	-14.3
3	4	4	10.5	-12.4
3	4	-4	38.0	41.0
3	5	-4	26.2	-22.5
3	6	-4	49.4	53.3
3	1	5	60.6	64.0
3	1	-5	30.9	26.3
3	2	5	37.2	39.5
3	2	-5	14.0	15.3
3	3	5	31.8	-28.4
3	3	-5	69.3	61.3
3	4	5	32.2	32.2
3	4	-5	36.1	-39.1
3	5	-5	34.9	32.4
3	6	-5	25.9	-27.9
3	0	6	103.8	108.5
3	0	-6	42.3	34.1
3	1	6	13.7	-12.5
3	1	-6	29.5	21.5
3	2	6	48.9	48.5
3	2	-6	31.1	30.4
3	3	6	28.2	27.3
3	3	-6	21.4	15.5
3	4	6	13.7	-12.7
3	4	-6	61.6	69.1
3	5	6	51.5	46.6
3	5	-6	47.2	-39.5
3	6	-6	29.8	33.7
3	1	7	70.3	74.8
3	1	-7	29.3	28.2
3	2	-7	14.2	10.3
3	3	7	17.0	16.8
3	3	-7	80.6	75.0
3	4	7	36.2	36.1
3	4	-7	44.2	-40.1
3	5	-7	45.8	38.9
3	0	8	79.3	82.4
3	0	-8	43.8	-38.5
3	1	8	15.8	-14.9
3	1	-8	18.1	-15.8
3	2	8	54.2	53.6
3	2	-8	66.2	62.7
3	3	-8	31.4	-28.2
3	4	8	22.9	24.8
3	4	-8	67.5	76.8
3	5	8	42.9	43.0
3	1	9	55.5	53.3
3	1	-9	14.5	14.6
3	2	9	33.7	-37.3
3	2	-9	51.0	-44.4
3	3	9	48.2	46.8
3	3	-9	89.9	79.0
3	5	-9	28.7	23.2
3	0	10	30.3	30.8
3	0	-10	25.1	19.2
3	1	10	17.7	-10.2
3	1	-10	23.8	-20.2
3	2	10	37.5	43.1
3	2	-10	53.2	46.5
3	3	10	25.0	-21.8
3	3	-10	29.8	-23.4
3	4	10	25.8	27.3
3	4	-10	62.6	66.4
3	5	-10	27.9	23.0
3	1	11	43.2	42.9
3	1	-11	38.8	37.2
3	2	-11	27.4	-25.0
3	3	11	20.1	19.3
3	3	-11	29.0	22.7
3	4	11	23.0	-25.5
3	5	-11	34.2	34.6
3	6	-11	26.5	31.4
3	0	12	32.3	36.2
3	0	-12	81.3	77.2
3	1	-12	9.6	-11.8
3	2	-12	30.2	29.4
3	3	12	24.5	-23.4
3	3	-12	21.4	-15.8
3	4	-12	19.8	17.5
3	5	12	20.6	-21.4
3	5	-12	28.9	22.7
3	1	13	13.2	12.9
3	1	-13	52.9	45.1
3	4	13	13.1	-16.4
3	0	-14	48.4	43.4
3	2	15	21.8	-26.0
3	1	16	14.6	-15.2
3	2	17	13.4	-20.4
3	3	17	10.4	10.7
3	0	18	11.7	-15.5
3	4	-19	7.1	7.8
4	0	0	16.6	-14.1
4	1	0	58.2	67.5
4	2	0	17.9	-14.8
4	5	0	31.2	-33.8
4	1	1	18.9	18.4
4	1	-1	49.2	59.8
4	2	1	30.7	35.4
4	2	-1	11.8	-9.7
4	3	-1	42.1	45.4
4	4	1	40.3	-50.4
4	4	-1	14.3	-14.1
4	5	1	24.9	-26.4
4	5	-1	16.8	-19.4
4	6	1	23.5	-27.1
4	6	-1	35.6	-40.9
4	0	-2	137.1	128.4
4	1	2	21.9	24.3
4	1	-2	43.2	-45.6
4	2	-2	20.4	18.6
4	3	2	22.0	-26.2
4	4	-2	18.0	19.8
4	5	2	40.8	-40.6
4	1	3	44.8	49.3
4	1	-3	110.0	111.9
4	2	3	23.2	-17.5
4	2	-3	17.3	-16.8
4	3	3	13.6	-16.8
4	3	-3	45.8	47.9
4	4	3	11.6	-12.6
4	5	3	15.6	-16.8
4	5	-3	32.1	30.5
4	6	-3	30.2	-33.1
4	0	4	61.5	60.1
4	0	-4	96.5	104.4
4	1	4	19.5	-19.9
4	1	-4	33.1	-39.6
4	2	4	15.5	14.2
4	2	-4	33.9	34.3
4	3	4	13.6	-12.6
4	4	4	19.1	-19.9
4	4	-4	11.3	16.3
4	5	4	25.0	20.6
4	6	-4	38.0	44.8
4	1	5	48.4	55.2
4	1	-5	75.6	81.0
4	2	5	24.3	-25.7
4	2	-5	23.3	21.1
4	3	5	28.0	-27.1
4	3	-5	40.3	34.9
4	4	5	19.6	19.0
4	5	5	17.1	17.6
4	5	-5	40.9	37.5
4	6	-5	28.4	-35.2
4	0	-6	105.2	109.3
4	1	6	51.7	-57.1
4	1	-6	33.4	31.3
4	2	-6	37.7	39.5
4	3	-6	42.5	39.3
4	4	6	15.4	17.2
4	4	-6	24.2	27.6
4	5	6	32.6	30.9
4	5	-6	31.2	-28.9
4	6	-6	29.5	33.4
4	1	7	11.2	-7.1
4	1	-7	35.6	30.8
4	2	7	30.5	-33.7
4	2	-7	69.1	69.7
4	3	7	35.1	35.2
4	3	-7	58.4	52.7
4	5	-7	47.2	36.9
4	6	7	30.0	35.8
4	0	-8	37.0	33.6
4	1	8	26.1	-29.4
4	1	-8	30.9	27.4
4	2	-8	68.3	62.3
4	3	-8	30.6	27.8
4	4	8	27.4	31.9
4	4	-8	50.0	48.7
4	5	8	37.7	34.0
4	5	-8	19.7	-18.1
4	1	9	8.1	12.9
4	2	9	19.6	-14.3
4	2	-9	32.5	30.3
4	3	9	38.1	39.7
4	3	-9	89.9	85.2
4	4	-9	14.9	12.8
4	5	-9	23.0	20.8
4	0	10	21.2	17.4
4	0	-10	18.1	-15.9
4	2	-10	34.4	31.1
4	3	-10	40.3	33.2
4	4	10	21.5	27.1
4	4	-10	53.2	59.2
4	5	-10	29.1	21.3
4	1	11	20.5	26.4
4	2	11	20.5	19.5
4	3	11	29.8	32.5
4	3	-11	53.7	44.8
4	5	-11	23.0	21.2
4	0	12	26.8	34.7
4	1	12	16.7	15.5
4	3	-12	32.0	29.2
4	4	12	21.7	26.2
4	4	-12	18.1	18.6
4	5	-12	42.4	29.0
4	1	13	18.1	18.3
4	3	13	21.9	21.6
4	3	-13	15.5	-15.8
4	5	13	24.8	24.7
4	5	-13	45.7	34.4
4	0	14	23.1	23.0
4	2	14	19.0	19.3
4	4	14	12.7	18.1
4	5	-14	14.7	11.5
4	3	15	16.1	18.3
4	4	-15	10.9	-2.7
4	5	15	12.8	14.0
4	5	-15	25.8	21.6
4	0	-18	18.1	-18.9
4	3	-18	14.7	-15.3
4	2	-19	18.0	-20.5
4	1	-20	15.8	-16.4
5	1	0	13.1	12.3
5	2	0	58.5	65.1
5	3	0	56.4	-59.1
5	4	0	32.1	39.2
5	5	0	59.8	-61.8
5	1	1	61.0	71.0
5	1	-1	105.2	109.2
5	2	1	13.3	11.6
5	2	-1	25.8	-27.6
5	3	1	45.3	46.4
5	3	-1	47.6	52.2
5	4	1	44.7	-51.4
5	4	-1	43.6	-50.0
5	5	1	27.3	25.2
5	5	-1	21.4	19.4
5	6	-1	23.5	22.4
5	0	2	52.0	52.1
5	0	-2	30.4	28.3
5	1	2	24.5	-23.9
5	1	-2	34.5	-38.1
5	2	2	29.3	35.5
5	2	-2	32.8	36.2
5	3	2	27.1	-27.9
5	3	-2	18.4	-18.4
5	4	2	16.6	21.0
5	4	-2	26.7	30.3
5	5	2	33.0	-30.1
5	1	-3	52.9	69.1
5	2	3	48.7	-58.1
5	2	-3	45.9	-55.0
5	3	-3	19.6	22.9
5	4	3	15.2	-19.5
5	4	-3	21.1	24.6
5	5	3	35.0	34.1
5	5	-3	17.5	12.4
5	6	-3	23.0	-20.7
5	0	-4	91.9	86.3
5	1	4	24.8	-31.0
5	1	-4	34.3	-41.2
5	2	-4	77.7	89.8
5	3	4	17.3	-18.8
5	3	-4	14.2	-8.4
5	5	-4	35.6	33.6
5	1	5	20.3	-28.2
5	1	-5	89.7	106.9
5	2	5	49.4	-54.2
5	2	-5	18.3	-20.5
5	4	-5	45.2	46.1
5	5	5	27.5	24.0
5	0	6	39.4	-41.2
5	0	-6	143.6	161.1
5	1	6	37.5	-42.2
5	2	-6	47.8	48.8
5	4	6	22.4	24.2
5	6	-6	26.2	35.1
5	1	7	27.2	-31.8
5	1	-7	72.0	69.9
5	2	-7	41.5	42.0
5	3	7	32.9	33.2
5	4	-7	19.4	19.7
5	5	7	23.1	19.7
5	0	8	25.0	-24.7
5	0	-8	47.3	39.5
5	1	-8	23.4	19.3
5	2	-8	24.2	24.6
5	3	8	15.2	15.4
5	3	-8	37.4	34.0
5	4	8	24.9	30.6
5	1	-9	23.0	23.8
5	2	9	30.7	33.8
5	2	-9	69.3	75.2
5	3	9	17.9	17.1
5	3	-9	31.4	33.0
5	4	-9	14.9	16.7
5	5	9	30.5	29.0
5	0	-10	52.4	-38.5
5	1	-10	28.1	26.6
5	2	-10	12.8	7.6
5	3	-10	43.0	35.8
5	4	10	17.0	18.1
5	1	11	29.7	31.0
5	2	-11	33.0	29.6
5	3	-11	30.8	25.1
5	5	11	19.6	18.5
5	0	12	24.7	28.7
5	0	-12	32.8	-27.7
5	3	-12	17.6	17.3
5	3	-13	17.9	-11.9
5	4	13	14.5	15.6
5	5	-13	32.2	26.6
5	2	14	16.5	15.8
5	4	14	11.1	14.3
5	3	15	16.7	17.8
5	5	-15	27.2	23.0
5	2	16	14.0	15.3
5	5	-16	23.8	-19.4
5	3	-17	13.0	12.2
5	5	-17	22.3	22.4
5	1	-18	16.7	12.1
5	3	-19	21.9	26.9
5	2	-20	12.3	13.9
6	1	0	31.3	34.0
6	2	0	56.7	65.7
6	3	0	12.1	-11.1
6	4	0	31.9	41.3
6	5	0	27.3	-23.7
6	1	1	23.0	23.2
6	1	-1	46.1	53.3
6	2	1	27.9	30.4
6	2	-1	18.8	19.4
6	3	1	19.8	18.9
6	3	-1	52.4	48.3
6	4	-1	13.2	-13.7
6	5	1	63.2	56.9
6	5	-1	60.8	55.5
6	0	2	43.2	47.4
6	0	-2	50.6	53.1
6	1	2	23.1	-24.3
6	1	-2	47.9	62.5
6	2	2	41.2	45.0
6	2	-2	64.7	78.8
6	3	2	27.8	-26.2
6	4	2	28.9	31.1
6	4	-2	54.9	66.2
6	1	3	16.3	15.8
6	1	-3	10.1	10.6
6	2	3	28.7	-28.0
6	2	-3	43.2	-53.0
6	3	3	29.8	31.9
6	3	-3	52.7	55.7
6	5	3	46.0	37.7
6	5	-3	51.6	48.7
6	0	-4	23.0	22.7
6	1	4	25.3	-27.2
6	1	-4	17.2	-16.1
6	2	4	41.2	42.6
6	2	-4	50.0	55.7
6	4	4	30.9	36.6
6	4	-4	40.7	49.5
6	5	-4	54.3	56.9
6	2	-5	61.6	-69.5
6	3	5	39.2	39.8
6	3	-5	23.5	25.2
6	4	-5	47.9	57.6
6	5	5	24.1	23.8
6	5	-5	23.8	22.0
6	6	-5	29.9	38.1
6	0	6	19.8	-22.3
6	0	-6	29.2	25.0
6	1	-6	7.7	-11.3
6	2	-6	15.9	-13.3
6	4	6	27.2	30.7
6	5	-6	54.2	51.8
6	6	-6	23.6	24.8
6	1	-7	26.9	23.7
6	2	7	20.8	16.6
6	2	-7	28.5	-28.4
6	3	7	23.4	23.1
6	3	-7	21.3	-22.7
6	6	7	27.7	-35.0
6	6	-7	23.9	25.1
6	0	8	17.4	-15.2
6	0	-8	56.7	52.8
6	1	8	21.8	25.2
6	1	-8	19.3	-18.0
6	4	-8	29.7	-33.4
6	5	8	26.3	-20.8
6	1	-9	24.9	22.5
6	2	9	24.3	26.9
6	3	9	17.9	-18.8
6	3	-9	18.2	-15.9
6	4	-9	17.2	-18.6
6	0	10	21.9	25.6
6	1	-10	9.2	10.5
6	2	-10	20.5	16.0
6	3	-10	19.8	-21.6
6	5	-10	24.3	-17.9
6	2	-11	21.3	20.2
6	3	11	14.5	-17.9
6	3	-11	20.4	23.9
6	4	-11	14.0	-17.9
6	0	12	14.4	15.5
6	0	-12	17.1	8.8
6	1	-12	9.9	12.1
6	2	-12	26.9	27.9
6	1	-13	22.0	20.1
6	0	-14	34.5	33.2
6	3	-14	21.8	-14.2
6	1	15	9.9	12.4
6	1	-15	22.0	21.1
6	3	15	9.7	10.9
6	0	-16	37.2	35.6
6	1	-17	21.1	25.1
6	0	-18	26.1	27.0
6	2	-18	16.4	16.8
6	4	-18	16.1	7.5
6	1	-19	18.9	15.6
6	3	-19	15.1	17.2
6	2	-20	11.5	15.7
7	0	0	25.1	25.4
7	1	0	34.8	38.9
7	2	0	30.1	32.1
7	3	0	21.8	20.2
7	4	0	20.6	22.5
7	1	1	37.1	36.0
7	1	-1	38.3	36.2
7	2	1	25.5	29.3
7	2	-1	54.7	57.3
7	3	1	30.3	25.5
7	4	1	21.0	21.1
7	5	1	39.0	30.3
7	5	-1	45.5	37.0
7	0	2	38.5	41.8
7	1	-2	55.4	60.5
7	2	2	37.5	41.2
7	2	-2	16.3	-15.4
7	3	2	28.9	25.8
7	3	-2	19.8	15.7
7	4	2	27.9	32.3
7	4	-2	29.0	33.6
7	5	2	33.5	30.4
7	6	-2	23.8	26.1
7	1	3	48.1	52.4
7	2	-3	29.2	32.2
7	3	3	37.1	35.7
7	3	-3	44.9	44.8
7	4	3	26.2	27.8
7	5	-3	28.6	24.0
7	0	4	31.9	30.8
7	0	-4	34.0	-39.4
7	2	4	42.3	42.2
7	3	4	19.0	15.4
7	3	-4	18.4	14.3
7	4	4	26.5	26.4
7	4	-4	31.3	38.9
7	1	5	37.2	41.3
7	2	5	26.2	26.6
7	3	5	41.4	44.7
7	3	-5	46.4	47.9
7	4	-5	17.8	17.8
7	5	-5	24.1	21.7
7	0	6	34.3	42.5
7	0	-6	15.8	-15.4
7	1	-6	22.4	-23.7
7	2	6	21.0	20.8
7	3	-6	11.0	-9.7
7	4	6	16.3	16.4
7	4	-6	26.1	31.3
7	5	6	32.6	-25.2
7	5	-6	25.5	24.8
7	1	7	30.0	37.9
7	1	-7	15.4	-19.2
7	2	-7	41.0	-44.9
7	3	7	15.6	15.8
7	3	-7	18.7	17.8
7	4	7	22.9	-18.5
7	5	-7	32.6	32.3
7	0	8	46.9	42.7
7	0	-8	17.0	19.3
7	1	-8	26.1	-26.2
7	3	8	17.9	-14.0
7	5	8	20.5	-19.7
7	6	-8	26.5	31.0
7	1	9	28.8	31.8
7	2	-9	18.7	-15.1
7	3	9	19.5	-18.5
7	5	-9	30.7	27.3
7	0	10	26.1	27.2
7	0	-10	20.1	17.2
7	3	10	16.6	-14.9
7	3	-10	34.5	-33.7
7	4	10	12.4	-16.8
7	5	-10	28.9	-25.6
7	2	11	19.2	-20.0
7	2	-11	21.8	-18.9
7	3	-11	26.6	25.6
7	4	-11	36.4	-42.3
7	3	12	11.9	-11.2
7	3	-12	25.4	-25.9
7	4	-12	23.0	26.8
7	5	-12	26.3	-22.2
7	1	-13	22.2	20.8
7	2	13	16.4	-16.9
7	2	-13	23.4	-22.5
7	3	-13	42.3	39.3
7	4	-13	35.7	-37.1
7	0	-14	47.0	36.1
7	2	-14	28.7	30.5
7	1	-15	42.7	44.2
7	2	-15	22.6	-22.6
7	3	-15	18.9	18.1
7	0	-16	54.8	51.4
7	1	-16	17.5	-22.1
7	2	-16	20.5	21.5
7	1	-17	29.0	35.0
7	0	-18	21.1	26.5
7	1	-19	12.0	17.3
7	2	-19	12.3	15.2
8	0	0	48.0	45.9
8	1	0	12.6	-9.8
8	2	0	20.9	20.7
8	3	0	21.1	18.8
8	1	1	39.2	33.8
8	1	-1	27.7	30.4
8	2	-1	46.1	49.9
8	3	-1	24.5	-22.5
8	4	1	24.3	23.6
8	4	-1	15.4	16.6
8	0	2	47.9	45.3
8	0	-2	14.9	11.3
8	1	-2	38.3	39.0
8	2	2	33.6	35.7
8	2	-2	22.7	-25.2
8	3	2	26.4	24.1
8	3	-2	22.9	19.3
8	5	2	38.7	33.7
8	5	-2	29.2	-28.2
8	1	3	35.1	35.6
8	1	-3	17.3	20.6
8	2	-3	53.1	57.8
8	3	3	30.3	27.5
8	3	-3	21.4	-20.7
8	0	4	24.2	18.3
8	0	-4	16.7	-20.4
8	1	-4	10.0	10.0
8	2	4	32.1	30.8
8	3	-4	24.9	23.8
8	4	4	18.2	15.5
8	5	-4	30.1	-26.2
8	1	5	23.4	25.4
8	1	-5	17.6	-14.9
8	2	-5	13.9	14.7
8	3	5	25.4	23.7
8	3	-5	16.3	16.5
8	4	5	19.1	-16.4
8	0	6	57.9	54.0
8	0	-6	29.8	-33.5
8	2	-6	21.6	24.3
8	4	-6	28.0	34.0
8	5	-6	24.1	-21.0
8	1	7	30.1	30.0
8	3	-7	19.7	23.2
8	0	8	46.5	50.4
8	0	-8	26.7	33.2
8	1	8	16.6	-12.0
8	1	-8	23.2	-23.3
8	4	-8	16.0	19.0
8	1	-9	19.2	20.4
8	2	9	21.1	-16.8
8	2	-9	17.5	-16.9
8	3	-9	19.5	16.4
8	5	9	17.0	14.9
8	5	-9	33.7	31.4
8	0	10	19.9	24.2
8	0	-10	32.9	31.4
8	1	10	16.9	-14.0
8	2	-10	20.0	22.6
8	3	10	21.2	-20.4
8	4	10	14.8	14.9
8	4	-10	24.4	27.7
8	1	-11	27.3	27.9
8	2	11	19.3	-21.8
8	2	-11	22.3	25.4
8	3	11	17.7	17.9
8	3	-11	47.0	48.2
8	5	-11	30.4	27.0
8	0	12	11.4	-14.8
8	0	-12	17.8	14.9
8	2	-12	21.5	19.3
8	3	12	11.9	-12.5
8	4	12	11.1	13.4
8	4	-12	28.9	34.9
8	5	-12	19.6	-17.0
8	2	-13	18.3	17.6
8	3	-13	39.7	37.3
8	4	-13	20.0	-24.0
8	5	-13	21.2	22.7
8	2	-14	23.7	20.4
8	4	-14	21.2	25.7
8	3	-15	21.6	22.5
8	5	-15	17.1	20.4
8	1	-16	18.6	-20.7
8	5	-16	14.9	16.9
8	0	-18	18.1	17.9
8	1	-19	11.1	14.0
9	1	0	37.3	-36.7
9	3	0	17.5	-15.3
9	1	1	31.1	-37.7
9	1	-1	22.0	19.0
9	2	1	28.0	-29.2
9	2	-1	16.2	-17.7
9	3	-1	21.3	-22.6
9	0	2	37.6	-35.5
9	0	-2	46.1	49.1
9	1	2	21.6	-22.6
9	1	-2	12.2	-13.9
9	2	-2	17.2	20.5
9	3	-2	32.3	-28.8
9	4	-2	22.8	-22.9
9	5	2	26.5	22.8
9	1	-3	43.3	45.7
9	2	-3	17.1	-15.4
9	3	3	18.0	15.2
9	3	-3	25.8	-24.9
9	4	-3	32.4	-34.3
9	0	-4	38.6	42.5
9	1	-4	17.2	17.8
9	2	-4	34.2	26.7
9	5	-4	30.9	-26.8
9	1	5	11.9	15.7
9	1	-5	27.9	31.7
9	2	5	20.5	16.0
9	2	-5	14.9	7.0
9	3	5	19.9	18.9
9	4	-5	17.0	-20.5
9	5	5	24.7	20.0
9	0	6	17.6	16.5
9	0	-6	23.2	19.3
9	1	-6	20.8	24.1
9	2	-6	35.6	39.9
9	4	6	16.1	19.0
9	1	7	14.1	18.8
9	1	-7	31.7	35.8
9	2	-7	15.2	-11.4
9	3	-7	31.7	30.4
9	5	7	25.2	27.5
9	0	8	18.6	14.9
9	0	-8	24.6	29.5
9	2	-8	30.7	30.9
9	4	-8	20.7	22.2
9	1	-9	33.7	36.1
9	3	-9	24.5	22.9
9	5	9	20.8	15.5
9	0	-10	39.3	44.8
9	2	10	15.6	15.6
9	2	-10	25.8	29.1
9	4	10	17.6	19.8
9	1	-11	31.3	30.9
9	2	-11	18.4	16.0
9	3	11	23.5	21.4
9	4	-11	13.9	13.8
9	0	12	15.2	-12.3
9	0	-12	21.9	26.6
9	2	-12	19.4	18.8
9	1	-13	16.6	15.6
9	2	-13	34.8	41.6
9	1	-14	21.4	26.1
9	2	-14	19.5	19.5
9	3	-14	16.5	18.4
9	4	-14	15.9	18.5
9	2	-15	19.4	20.9
9	3	-15	14.5	15.8
9	0	-16	17.4	-16.2
9	4	-16	11.6	16.6
9	1	-17	15.9	-16.1
9	3	-17	10.7	8.2
9	0	-18	16.6	-16.5
9	1	-19	6.8	-7.9
10	0	0	32.9	-31.4
10	1	0	27.8	-25.5
10	2	0	20.4	14.7
10	3	0	15.6	-14.7
10	4	0	26.9	28.1
10	1	-1	20.2	-18.1
10	2	-1	24.0	-22.4
10	3	1	37.2	34.7
10	3	-1	22.9	17.9
10	5	-1	26.3	23.7
10	3	-2	28.3	-27.3
10	1	-3	29.2	28.9
10	2	3	20.5	19.6
10	2	-3	19.1	-19.7
10	3	3	17.7	14.7
10	5	-3	28.7	22.8
10	0	-4	50.8	51.8
10	3	-4	29.7	-34.3
10	1	-5	48.5	49.0
10	3	-5	21.9	20.9
10	4	-5	23.7	-21.6
10	5	-5	24.2	23.7
10	0	-6	34.6	33.7
10	2	-6	35.0	33.5
10	3	-6	25.3	-27.1
10	4	-6	22.3	21.2
10	1	-7	34.9	41.4
10	3	-7	35.8	39.6
10	4	7	18.8	18.8
10	0	-8	33.0	38.8
10	2	-8	27.4	27.0
10	3	8	13.6	13.8
10	1	-9	26.5	28.2
10	3	9	16.8	12.1
10	3	-9	20.1	18.3
10	4	9	10.2	13.7
10	4	-9	22.0	19.9
10	0	-10	30.9	35.9
10	2	10	19.9	15.4
10	2	-10	20.5	26.0
10	3	10	11.5	12.9
10	5	-10	34.5	32.3
10	1	-11	13.3	14.4
10	4	-11	23.2	26.4
10	0	-12	25.1	28.1
10	2	-13	17.4	18.4
10	1	-14	19.0	22.9
10	2	-15	19.0	16.9
10	1	-16	16.6	13.3
11	2	0	20.4	21.8
11	3	0	12.5	9.1
11	4	0	30.1	32.6
11	1	-1	13.3	12.3
11	3	1	31.3	26.7
11	3	-1	46.7	41.6
11	4	1	15.2	-15.8
11	0	-2	19.8	18.5
11	2	-2	35.5	34.0
11	4	-2	35.5	35.7
11	5	2	24.4	-20.5
11	1	-3	23.8	22.9
11	3	-3	34.7	27.6
11	5	-3	28.2	24.0
11	2	4	25.3	25.8
11	0	-4	21.5	26.1
11	4	-4	29.0	30.1
11	1	-5	20.6	19.8
11	5	-5	31.0	24.6
11	0	6	15.3	17.2
11	4	-6	15.9	16.6
11	4	7	9.7	12.4
11	5	-7	20.3	18.3
11	4	-8	23.4	27.0
11	3	-9	24.0	20.3
11	4	-10	12.9	14.1
11	5	-10	19.9	17.1
11	2	-11	23.3	-26.5
11	1	-12	17.8	-16.4
11	0	-14	17.4	18.6
11	1	-15	10.6	8.4
11	4	-15	12.6	-16.1
11	0	-16	14.5	16.2
11	1	-17	8.1	8.1
11	3	-17	8.4	8.1
11	2	-18	8.1	11.8
12	0	0	22.8	23.3
12	2	0	23.7	19.1
12	3	0	14.2	13.5
12	1	1	31.6	28.0
12	2	-1	19.6	18.3
12	3	-1	33.5	30.2
12	0	2	42.9	39.5
12	2	-2	21.7	25.8
12	3	-2	22.4	19.8
12	4	-2	15.6	13.4
12	1	3	26.6	29.2
12	3	-3	19.1	13.6
12	0	4	31.0	31.5
12	0	-4	19.8	21.5
12	3	-4	21.0	17.2
12	1	5	15.8	14.6
12	1	-5	13.1	13.2
12	2	5	17.2	-17.8
12	5	-5	18.7	16.1
12	3	6	14.0	-12.3
12	3	-6	21.8	22.3
12	2	-7	23.5	23.8
12	5	-7	20.4	21.3
12	0	-8	19.5	-16.4
12	1	-8	20.0	20.4
12	3	-8	16.7	14.7
12	0	-10	30.6	-35.2
12	4	-10	13.6	15.1
12	1	-11	18.8	-21.6
12	3	-11	15.3	14.5
12	0	-12	19.4	-18.5
12	4	-12	14.2	16.9
12	2	-13	16.5	-14.7
12	3	-14	12.3	-12.6
12	4	-15	8.6	-11.6
12	0	-16	15.1	16.5
12	3	-16	10.0	-11.8
13	0	0	19.1	19.6
13	1	1	23.1	24.3
13	0	2	31.5	27.7
13	2	2	17.0	12.7
13	1	3	16.3	16.9
13	2	3	15.7	-13.7
13	4	3	7.6	5.7
13	0	4	12.2	9.3
13	2	5	13.7	-14.6
13	4	-6	13.1	-15.4
13	3	-7	17.9	-16.2
13	5	-8	15.8	-15.0
13	3	-11	20.0	14.8
13	2	-12	16.7	18.7
13	4	-12	12.0	14.5
13	3	-13	16.9	18.1
13	4	-14	9.2	12.7
13	1	-15	10.4	10.4
13	0	-16	11.5	11.5
14	3	-4	14.5	-14.9
14	2	-5	15.1	-12.5
14	1	-6	15.1	-15.3
14	3	-6	14.6	-14.7
14	1	-7	15.0	12.7
14	2	-7	13.2	-13.4
14	0	-8	26.6	28.2
14	1	-9	23.1	22.2
14	0	-10	24.0	26.6
14	1	-11	19.2	19.6
14	0	-12	11.6	12.9
14	2	-12	14.4	18.5
14	1	-13	13.4	10.8
14	3	-13	14.8	18.0
14	0	-14	9.6	10.6
14	2	-14	9.9	12.8
15	3	-3	8.4	10.1
15	3	-5	18.5	18.1
15	1	-6	12.0	-11.2
15	2	-7	10.8	-15.8
15	3	-7	12.8	11.9
15	1	-8	12.6	-12.2
15	1	-9	13.0	15.7
15	0	-10	15.9	16.4
15	1	-11	15.4	16.5

and never exceeded the uncertainty in the electron density ($\sigma(\rho) = 0.18\ e^-/Å^3$) calculated for the whole structure.

Computing Methods.—Calculations were performed on the IBM 7040 computer of Rome University. Programs used for data reduction, interlayer scaling, Fourier synthesis, interatomic distances, and bond angles with standard deviations were kindly provided by A. Domenicano and A. Vaciago. Structure factors and least-squares cycles of refinements were calculated by means of programs written by V. Albano, A. Domenicano, and A. Vaciago. The least-squares planes were determined by a program written by S. Chu and following the method developed by Schomaker, *et al.*[11] The equation of the plane is of the form $Ax + By + Cz = D$, where x, y, and z correspond to the crystallographic axes.

Optical Spectra.—The optical spectra, both reflectance and solution, were run with a Beckman DK 1-A spectrophotometer. They were performed on the present compound, $Ni(dtpi)_2 \cdot 2py$, and on the bis-pyridine adduct of bis(*O,O′*-diethyldithiophosphato)nickel(II), a compound whose X-ray structure analysis has been carried out by Ooi and Fernando[12] and hereafter called $Ni(dtp)_2 \cdot 2py$. MgO was used as reference for the powder reflectance spectra, and a toluene solution at 10^{-2} *M* concentration for both compounds was used for the solution spectra.

The optical spectra (both reflectance and solution) of the pseudooctahedral adduct of $Ni(dtpi)_2$ with pyridine show two broad bands centered around 8.8 (1) and 14.3 (1) kK, respectively. However, from the reflectance spectra a clear splitting of these two bands has been observed following the pattern typical of high-spin pseudooctahedral Ni(II) complexes, with distinct splitting of tetragonal components. In fact, the first broad band ($\tilde{\nu}_1$ at 8.8 kK) can be resolved into two components at 7.9 and 8.9 kK due to the $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow a^3E_g$ transitions, respectively (in the point group D_{4h}), and the second band ($\tilde{\nu}_2$ at 14.3 kK) into two components at 13.2 ($^3B_{1g} \rightarrow b^3E_g$) and at 14.8 kK ($^3B_{1g} \rightarrow {}^3A_{2g}$). The position of the highest frequency band ($\tilde{\nu}_3$) is very uncertain since it is obscured by the tail of a charge-transfer band, but it probably occurs at a frequency higher than 22 kK.

The analogous $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$ bands for $Ni(dtp)_2 \cdot 2py$ are centered at 9.3 (1), 14.6 (1) (both not resolved), and about 22.2 kK, respectively.

Results and Discussion

The calculated values of the bond distances and bond angles with their esd's[13] are given in Table IV and are also shown in Figure 1, which also indicates the numbering of atoms. The projection of the structure along the *a* axis is shown in Figure 2.

---

[11] V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959).

[12] S. Ooi and Q. Fernando, *Inorg. Chem.*, **6**, 1558 (1967).

[13] D. W. J. Cruickshank and A. P. Robertson, *Acta Crystallogr.*, **6**, 698 (1953).

TABLE IV

BOND DISTANCES AND ANGLES WITH THEIR ESD'S

Distances, Å		Angles, deg	
Ni-S(1)	2.482 (4)	S(1)-Ni-S(2)	81.6 (2)
Ni-S(2)	2.523 (3)	Ni-S(1)-P	84.8 (2)
Ni-N	2.083 (13)	Ni-S(2)-P	83.3 (2)
P-S(1)	1.993 (6)	S(1)-Ni-N	89.2 (4)
P-S(2)	2.013 (6)	S(2)-Ni-N	91.9 (3)
P-C(1)	1.83 (1)	P-Ni-N	87.0 (3)
P-C(7)	1.77 (2)	S(1)-P-S(2)	109.5 (3)
C(1)-C(2)	1.41 (2)	S(1)-P-C(1)	108.7 (6)
C(1)-C(6)	1.37 (3)	S(1)-P-C(7)	111.5 (5)
C(2)-C(3)	1.43 (3)	S(2)-P-C(1)	109.7 (5)
C(3)-C(4)	1.40 (3)	S(2)-P-C(7)	109.8 (6)
C(4)-C(5)	1.44 (3)	C(1)-P-C(7)	107.7 (7)
C(5)-C(6)	1.41 (3)	P-C(1)-C(2)	119 (1)
C(7)-C(8)	1.43 (3)	P-C(1)-C(6)	119 (1)
C(7)-C(12)	1.42 (2)	P-C(7)-C(8)	119 (1)
C(8)-C(9)	1.45 (3)	P-C(7)-C(12)	122 (1)
C(9)-C(10)	1.45 (3)	C(1)-C(2)-C(3)	120 (2)
C(10)-C(11)	1.34 (3)	C(2)-C(3)-C(4)	118 (2)
C(11)-C(12)	1.44 (3)	C(3)-C(4)-C(5)	122 (2)
N-C(13)	1.37 (2)	C(4)-C(5)-C(6)	118 (2)
N-C(17)	1.37 (2)	C(5)-C(6)-C(1)	121 (2)
C(13)-C(14)	1.39 (3)	C(6)-C(1)-C(2)	122 (1)
C(14)-C(15)	1.45 (3)	C(7)-C(8)-C(9)	121 (2)
C(15)-C(16)	1.35 (3)	C(8)-C(9)-C(10)	117 (2)
C(16)-C(17)	1.44 (3)	C(9)-C(10)-C(11)	122 (2)
		C(10)-C(11)-C(12)	122 (2)
		C(11)-C(12)-C(7)	119 (2)
		C(12)-C(7)-C(8)	119 (2)
		Ni-N-C(13)	122 (1)
		Ni-N-C(17)	121 (1)
		N-C(13)-C(14)	127 (1)
		N-C(17)-C(16)	121 (2)
		C(13)-N-C(17)	117 (1)
		C(13)-C(14)-C(15)	113 (2)
		C(14)-C(15)-C(16)	123 (2)
		C(15)-C(16)-C(17)	119 (2)

TABLE V

Deviations from Planes through Groups of Atoms, Å

Plane I		Plane II		Plane III		Plane IV	
Ni	0.045	C(1)	−0.017	C(7)	0.007	N	0.011
S(1)	−0.060	C(2)	−0.017	C(8)	0.001	C(13)	0.020
S(2)	−0.059	C(3)	0.035	C(9)	−0.006	C(14)	−0.038
P	0.074	C(4)	−0.021	C(10)	0.003	C(15)	0.030
		C(5)	−0.012	C(11)	0.005	C(16)	−0.001
		C(6)	0.032	C(12)	−0.010	C(17)	−0.021

Equations of Planes in the Form $Ax + By + Cz = D$, Referred to the Crystallographic Axes x, y, z with All Weights Equal to 1

Plane	Equation
I	$-0.145x + 0.781y + 0.539z = -0.045$
II	$-0.079x + 0.678y + 0.722z = 1.095$
III	$0.938x - 0.342y - 0.334z = 2.359$
IV	$0.930x + 0.290y - 0.056z = -0.017$

Dihedral Angles between Planes, Deg

I-II = 84.5
I-III = 68.6
I-IV = 87.4
II-III = 69.4
II-IV = 73.3
III-IV = 40.6

The nickel atom is surrounded by a slightly distorted octahedron; in fact, by symmetry the four sulfur atoms from the two dtpi$^-$ ligands and the nickel atom define a plane, and nickel completes its coordination sphere with the nitrogen atoms of two pyridine molecules.

Table V reports the calculation of the least-squares planes referring to the Ni–S(1)–S(2)–P plane and to those of the phenyl and pyridine groups. The maximum deviation of an atom from the plane formed by Ni, 2 S, and P is 0.07 Å and the dihedral angle between this plane and the plane formed by the pyridine molecule is 87°.

A list of some chelate distances and angles found in the structures of bis(diphenyldithiophosphinato)nickel(II), labeled Ni(dtpi)$_2$, of the present compound (Ni(dtpi)$_2$·2py), of bis(*O,O′*-diethyldithiophosphato)nickel(II), hereafter called Ni(dtp)$_2$,[14] and of the bis-pyridine adduct of Ni(dtp)$_2$[12] is reported in Table VI for a useful comparison between these similar structures.

As shown in the table, in the formation of the bis-pyridine adduct of Ni(dtpi)$_2$ some variations have been observed. Particularly the nickel–sulfur bond distance increases and significant changes in the bond angles within the chelate ring occur. In fact in Ni(dtpi)$_2$ the average nickel–sulfur bond length is 2.24 (1) Å, while in the hexacoordinated Ni(dtpi)$_2$·2py the same distance is increased to an average value of 2.50 (2) Å, in agreement with that found for other octahedral nickel(II) complexes where the nickel–sulfur bond lengths range from 2.4 to 2.6 Å.[15,16]

Variations of the bond angles in the chelate ring have also been observed in Ni(dtpi)$_2$ and Ni(dtpi)$_2$·2py: the S–Ni–S angle decreases from 88.3 (2)° in the square-planar complex to 81.6 (2)° in the pyridine adduct, while the S–P–S angle increases from 101.3 (3) to 109.5 (3)°.

These variations of the structural parameters are very similar to those found by Fernando and coworkers in Ni(dtp)$_2$[14] and in Ni(dtp)$_2$.2py,[12] as shown in Table VI, and have been interpreted on the basis of a simple electrostatic model.[12] We think, however, that the two variations, *i.e.*, increase in the Ni–S bond distances and variations of bond angles in the chelate ring, are strictly correlated; the longer Ni–S distance in the adduct and the consequent decrease of the S–Ni–S angle (only partially compensated by an increase of the

[14] Q. Fernando and C. D. Green, *J. Inorg. Nucl. Chem.*, **29**, 647 (1967).

[15] M. Nardelli, A. Braibanti, and G. Fava, *Gazz. Chim. Ital.*, **87**, 1209 (1957).

[16] A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

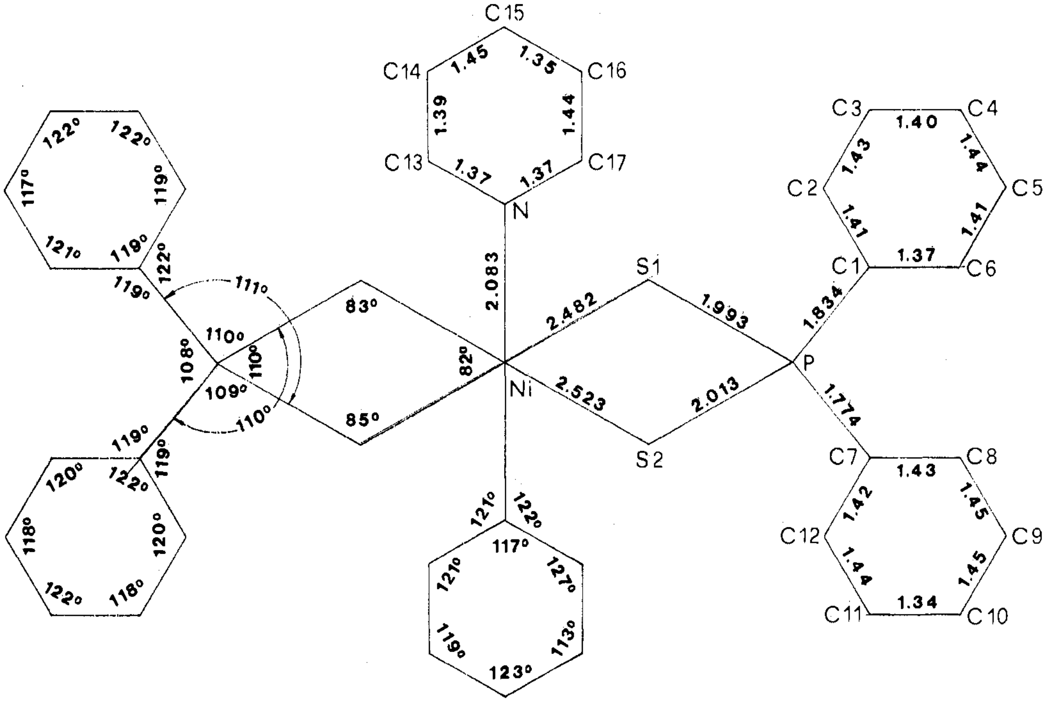


Figure 1.—Schematic representation of the molecule with bond lengths (Å) and bond angles (deg).

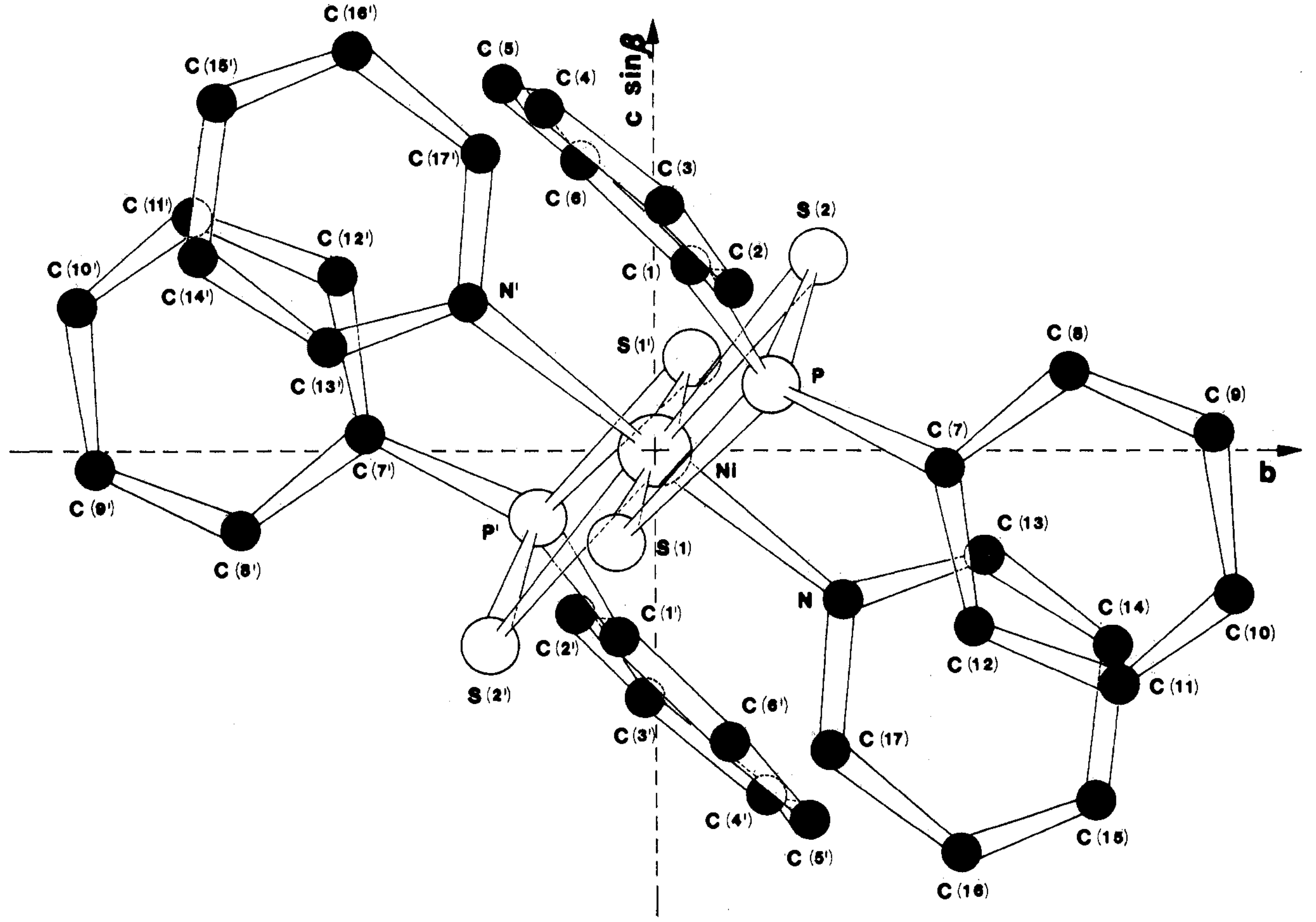


Figure 2.—[100] projection of the molecule.

S–P–S angle) is probably due mainly to an increase of the effective radius of the nickel atom, resulting from the occupation of the t_{2g}^* antibonding orbitals in the octahedral complexes.

Other structural parameters, such as the average values of S–P, P–C, and C–C (of the phenyl groups) bond distances and the average Ni–S–P, S–P–C, C–P–C, and C–C–C bond angles, have been observed to

TABLE VI

COMPARISON OF AVERAGE VALUES OF SOME DISTANCES AND ANGLES IN SIMILAR STRUCTURES OF COMPLEXES OF NICKEL(II) WITH SULFUR LIGANDS

	Ni(dtpi)$_2$[a]	Ni(dtpi)$_2$·2py[b]	Ni(dtp)$_2$·2py[c]	Ni(dtp)$_2$[d]
		Distances,[e] Å		
Ni-S	2.24 (1)	2.50 (2)	2.49 (2)	2.21 (1)
Ni–N		2.08 (1)	2.11 (1)	
S–P	2.01 (1)	2.00 (2)	1.98 (2)	1.97 (2)
N–C		1.37 (2)	1.36 (4)	
C–C (py)		1.40 (5)	1.38 (9)	
C-C (phenyl)	1.38 (4)	1.41 (7)		
P–C	1.78 (3)	1.80 (4)		
P–O			1.58 (2)	1.63 (9)
O-C			1.47 (5)	1.51 (8)
C-C (ethyl)			1.47 (5)	1.60 (10)
		Angles,[e] Deg		
S-Ni-S	88.3 (2)	81.6 (2)	81.7 (1)	88
S-P-S	101.3 (3)	109.5 (3)	110.4 (3)	103
Ni–S–P	85.2 (5)	84 (1)	84 (1)	85 (1)
S–Ni–N		90 (1)	90.4 (6)	
C–N-C		117 (1)	117 (1)	
N-C–C		124 (3)	123 (2)	
C–C–C (py)		118 (5)	118 (3)	
C–C–C (phenyl)	120 (3)	120 (2)		
S–P–C	112 (1)	110 (2)		
C–P–C	107 (1)	108 (1)		

[a] Bis(diphenyldithiophosphinato)nickel(II), Ni[$S_2P(C_6H_5)_2$]$_2$.[1] [b] Bis-pyridine adduct of bis(diphenyldithiophosphinato)nickel(II), Ni[$S_2P(C_6H_5)_2$]$_2$·$2C_5H_5N$ (present work). [c] Bis-pyridine adduct of bis(*O,O'*-diethyldithiophosphato)nickel(II), Ni[$S_2P(OC_2H_5)_2$]$_2$·$2C_5H_5N$.[12] [d] Bis(*O,O'*-diethyldithiophosphato)nickel(II), Ni[$S_2P(OC_2H_5)_2$]$_2$.[14] [e] Except for Ni-N, S-Ni-S, S–P–S, C–N–C, and C–P–C values, other numbers correspond to the average value (plus its associated rms deviation) of several bonds.

be unchanged, within experimental error, in Ni(dtpi)$_2$ and Ni(dtpi)$_2$·2py as shown in Table VI. This behavior is similar to that found by Fernando and coworkers in Ni(dtp)$_2$ and Ni(dtp)$_2$·2py (see Table VI).

The bond distances and angles related to the pyridine group in Ni(dtpi)$_2$·2py, *i.e.*, the average values of Ni–N, N–C, and C–C distances and S–Ni–N, C–N–C, N–C–C, and C–C–C angles, agree well, within experimental error, with the corresponding parameters found in Ni(dtp)$_2$·2py, as shown in Table VI.

Thus, as found in the strictly related structures of Ni(dtpi)$_2$ and Ni(dtp)$_2$ and of Ni(dtpi)$_2$·2py and Ni(dtp)$_2$·2py, the replacement of a POC_2H_5 with a PC_6H_5 group has no significant effect on bond distances and angles, and the variations on some structural parameters in the formation of the corresponding pyridine adducts from the two square-planar complexes are similar, within experimental error.

It should be added that all van der Waals contacts less than 4.5 Å were calculated at the end of the structure analysis of Ni(dtpi)$_2$·2py and the closest approach to the nickel atom from any other atom of a neighboring molecule is 3.7 Å.

As shown in Table VI the Ni–S distances do not appear to be significantly different in Ni(dtpi)$_2$·2py and Ni(dtp)$_2$·2py. However, from the results of the optical spectra performed on the two adducts it is evident that the relative positions in the spectrochemical series (as indicated by the energy of the $\bar{\nu}_1$ transitions, centered at 9.3 and 8.8 kK for Ni(dtp)$_2$·2py and Ni(dtpi)$_2$·2py, respectively) are dtp$^-$ > dtpi$^-$.

The results of the optical spectra for the two adducts were further analyzed assuming both a crystal field and a tetragonal perturbation model (using the method described by Lever).[17] In both cases it is found that $\Delta(\mathrm{dtp}^-) > \Delta(\mathrm{dtpi}^-)$. The latter method gives the values $Dq_\mathrm{S} = 0.81$ (2) kK (for Ni(dtpi)$_2$·2py) and $Dq_\mathrm{S} = 0.88$ (2) kK (for Ni(dtp)$_2$·2py), where Dq_S is the ligand field strength of the equatorial ligands, *i.e.*, sulfur, and assuming an axial ligand field strength $Dq_\mathrm{N} = 1.02$ kK as suggested by Lever.[17]

Thus both experimental results and calculations indicate that the relative positions in the spectrochemical series, previously found for the analogous square-planar complexes,[1] are the same in the pyridine adducts. It is thus plausible that similar electronic effects may be responsible for the spectrochemical sequences in both cases (square-planar and pseudooctahedral complexes), despite the different degree of occupation of the σ-antibonding orbitals and hence the different Ni–S bond lengths between the spin-paired square-planar and the spin-free pseudooctahedral structures.

A correlation between spectrochemical position of the sulfur ligands with variations of their effective charge, π-bonding effects, and repulsion between nonbonding electron pairs, that is, between spectrochemical position and electronic structure, has been established by Jørgensen.[18] On the basis of his suggestions (since, as found in the square-planar complexes,[1] $\Delta(\mathrm{dtp}^-) > \Delta(\mathrm{dtpi}^-)$, it may be concluded that dtpi$^-$ is a better π-donor ligand than dtp$^-$ even in the pyridine adducts.

Given the uncertainty of the position of the bands due to the $\bar{\nu}_3$ transitions, we believe that nephelauxetic effects cannot be discussed with sufficient accuracy.

(17) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).

(18) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

As mentioned above the Ni–S distances are equal, within experimental error, in Ni$(dtpi)_2\cdot$2py and Ni$(dtp)_2\cdot$2py, while a significant difference has been observed on the two adducts from both optical spectra and calculations. This leads to the conclusion that the position in the spectrochemical series is a more sensitive indication of variations in the electronic structures of sulfur-containing ligands than differences in the metal–sulfur bond lengths. In our opinion, the similarity of Ni–S distances in the two structures may be ascribed to the smallness of the variation of the electronic effects with respect to the experimental standard deviations.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA 16802

The Crystal and Molecular Structure of the Tetrahedrally Coordinated Complex Dibromo[*cis-endo-N,N′*-di(4-methylbenzylidene)-*meso*-2,3-butanediamine]nickel(II)

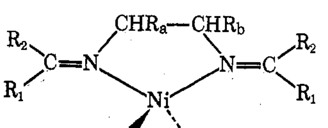
BY DONALD L. JOHNSTON,[1] WAYNE L. ROHRBAUGH, AND WILLIAM DEW. HORROCKS, JR.*

Received August 6, 1970

The crystal structure of Ni$[C_{20}H_{24}N_2]Br_2$ where $C_{20}H_{24}N_2$ is the bidentate imine ligand formed in the Schiff base reaction of 4-methylbenzaldehyde with *meso*-2,3-butanediamine has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter methods. The structure has been refined by full-matrix least-squares method to a conventional R factor of 0.065 and a weighted R factor of 0.059 based on 1273 reflections for which $I_{obsd} > \sigma(I)$. The compound crystallized in the monoclinic space group Cc with cell constants a = 15.584 (3) Å, b = 11.325 (3) Å, c = 14.135 (4) Å, and β = 122.53 (1)°. The density calculated for z = 4 is 1.6132 g/cm³ while the observed density is 1.60 (2) g/cm³. The structure consists of discrete molecules in which the coordination polyhedron about the nickel is a highly distorted tetrahedron with Br–Ni–Br and N–Ni–N angles of 138.8 (1) and 85.0 (7)°, respectively. The average Ni–Br distance is 2.359 (4) Å and the average Ni–N distance is 1.96 (2) Å. The tolyl groups are cis-endo with respect to the nickel atom and the aliphatic chain is puckered in the *gauche* configuration with one axial and one equatorial methyl substituent.

Introduction

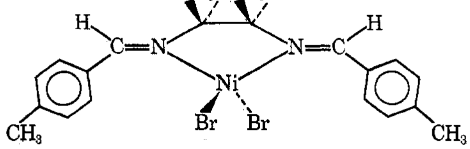
A recent series of pmr investigations[2-4] in these laboratories of paramagnetic Schiff base complexes of type **1** sought to establish, among other things, a criterion of stereochemistry based on the observed aryl proton isotropic nmr shift behavior. For complexes synthesized from benzaldehyde derivatives (B; R_1 = aryl, R_2 = H) the aryl proton resonances exhibit the ortho, meta, para alternation of shifts generally ascribed to the π-spin delocalization, while those derived from acetophenones (Ap; R_1 = CH_3, R_2 = aryl) show a shift behavior ascribable to σ-spin delocalization in the aryl moiety. The complexes prepared from benzophenone derivatives (Bp; R_1 = R_2 = aryl) exhibit aryl proton nmr spectra corresponding to a superposition of those of the B and Ap complexes, indicating magnetic inequivalence of the aryl groups with one showing σ- and the other π-type delocalization.



1, $R_1, R_2 = H, CH_3$, aryl
$R_a, R_b = H, CH_3$
X = halogen

It was argued at the time[3] that a steric interaction between the endo aryl groups (R_1 in **1**) and the coordinated halogen atoms would probably prevent their becoming coplanar with the Ni—N=C moiety and hence that σ-spin delocalization behavior would occur for such endo aryl groups. On the other hand, it was thought that an exo-situated aryl group (R_2) might be reasonably free of steric restraint and could conjugate with the imino π system, resulting in a predominant π-delocalization pattern. The present structural investigation on a B derivative, R_1 = tolyl, R_2 = H, was carried out to test this hypothesis and to put the pmr assignments on a firm basis.

Another structural feature of interest in the complex chosen for study, dibromo[*cis-endo-N,N′*-di(4-methylbenzylidene)-*meso*-2,3-butanediamine]nickel(II), **2**, lies in the geometry of the 2,3-butanediamine (bn) chelate ring. Fairly large differences in isotropic shifts were observed for the bn ring methyl resonances between meso and racemic forms of this complex.[2] For a puck-



2

---

[1] Petroleum Research Fund predoctoral fellow, 1969–1970.

[2] I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *Chem. Commun.*, 1471 (1969).

[3] I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 693, 698 (1970).

[4] D. L. Johnston, I. Bertini, and W. DeW. Horrocks, Jr., *ibid.*, in press.