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The Crystal and Molecular Structure of Bis(diphenyldithiophosphinato)nickel(II)

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The crystal structure of bis(diphenyldithiophosphinato)nickel(II), $Ni[S_2P(C_6H_5)_2]_2$, has been determined by 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 C2/c, with four molecules in the unit cell whose dimensions, determined using zinc oxide as the standard, are $a = 13.28$, $b = 11.55$, $c = 17.00$ Å, and $\beta = 103° 43'$. The measured density (by flotation method) is 1.473 g/cm^3 while that calculated for four formula units of $Ni[S_2P(C_6H_5)_2]_2$ is 1.461 g/cm^3. The molecule itself is centrosymmetric and each nickel atom lies at a center of symmetry with two ligand molecules coordinated in a plane which passes through the sulfur atoms (Ni–S bond lengths equal to 2.234–2.242 Å). The final R factor is 0.114 for 864 observed reflections. The correlation between Ni–S distances in certain square-planar complexes and the corresponding ligand field strengths, as deduced from optical spectra, is given and discussed.

Introduction

The interest in complexes of nickel with molecules containing two sulfur atoms and being able to act as chelating ligands is reflected in the numerous and recent literature references concerning their chemical[1] and crystallographic properties.[2-9]

During a systematic study of the relationship among magnetic and chemical properties and optical spectra of metal–sulfur adducts that has been undertaken in this laboratory, it was thought interesting to determine the crystal structures of some compounds.

The present paper shows the results of a three-dimensional single-crystal X-ray analysis of the bis(diphenyldithiophosphinato)nickel(II) complex, $Ni[S_2P(C_6H_5)_2]_2$. It should be pointed out that the purpose of this work was mainly to discover the environment of the metal atom rather than the details of the phenyl groups and to determine with sufficient accuracy the Ni–S bond distances. For this reason the discussion focuses on the correlation between the Ni–S distance and ligand field strength of particular ligands in tetragonal complexes.

Experimental Section

Preparation of Compound.—Bis(diphenyldithiophosphinato)nickel, $Ni[S_2P(C_6H_5)_2]_2$, was prepared as described by Kuchen, *et al.*,[10] and crystals suitable for X-ray analysis were obtained by recrystallization from ethyl alcohol as violet monoclinic prisms.

Crystallographic Data.—The cell dimensions were determined by superimposing zinc oxide lines (ZnO treated at 1200°, $a = 3.24968$ and $c = 5.2060$ Å at 21°)[11] on zero-layer Weissenberg photographs about the a and b axes and using an improved version of Christ's method:[12] $a = 13.28 \pm 0.01$, $b = 11.55 \pm 0.01$ $c = 17.00 \pm 0.01$ Å, $\beta = 103° 43' \pm 5'$ with Cu Kα radiation (λ 1.5418 Å, 21°). The errors of the cell parameters were evaluated from the sums of the average standard deviations in the measurements of the cell constants of $Ni[S_2P(C_6H_5)_2]_2$ and ZnO. The volume of the unit cell is 2533 Å^3. If it contains four formula units of the compound (formula weight 557.34), the calculated density is 1.461 g/cm^3; the value measured by flotation method in a mixture of toluene and carbon tetrachloride is 1.473 ± 0.005 g/cm^3 (these numbers were evaluated from the deviations observed on three independent measurements). $F(000)$ is 1144. Systematic absences, as determined from precession ($hk0$ and $hk1$) and Weissenberg ($h0l$, $h1l$, $0kl$, and $1kl$) photographs were as follows: hkl when $h + k$ is odd, $h0l$ when l is odd (and h is odd), $0k0$ when k is odd; the two space groups consistent with such absences are the centrosymmetric C2/c and the noncentrosymmetric monoclinic Cc. In view of the fact that no statistical methods could be applied in this case and that the external habit of the crystal did not permit us to distinguish between these two alternatives, C2/c was adopted initially because the absence of any piezoelectric effect indicated centrosymmetry, a choice which was subsequently confirmed by structure analysis. In fact, structure factor calculations and isotropic least-squares refinements were performed for both space groups; these calculations gave virtually the same value of refinement, but the shifts from the centrosymmetrical positions calculated with the Cc space group were not significant with respect to the standard deviations. Thus, the absence of piezoelectric effect and the fact that deviations from centrosymmetry, if any, are minute would seem to indicate that the molecules can be satisfactorily treated as being of a C2/c space group. For Cu Kα radiation the linear absorption coefficient $\mu = 52.5$ cm^{-1} (approximate limits of $\mu R = 0.08$–0.11).

Collection of X-Ray Data.—Intensity photographs were taken from a prismatic crystal about 0.03 × 0.04 × 0.07 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). Using a Nonius integrating Weissenberg camera and the multiple-film technique, eight layers of intensity photographs about the b axis, $h0l$ through $h7l$, and five layers about the a axis, $0kl$ through $4kl$, were collected with a total of 864 independent reflections. The X-ray intensities were estimated visually with the aid of a calibration strip, corrected for Lorentz-polarization factors and for spot size of the upper layers (according to Phillips[13]), and placed on a common scale by the method of Hamilton, Rollett,

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and Sparks.[14] No correction for absorption or extinction was applied.

Structure Determination and Refinement.—Since there are four molecules per unit cell (in the space group C2/c) it was assumed that the molecule must occupy one of the special positions, all of which are centers of symmetry, and the molecule itself must have a center of symmetry. The interpretation of a three-dimensional Patterson synthesis showed that the major peaks observed were consistent with all of the homogeneous vectors referring to the special nickel positions, *i.e.*, 0, 0, 0; $^1/_2$, $^1/_2$, 0; 0, 0, $^1/_2$; and $^1/_2$, $^1/_2$, $^1/_2$. The origin of the cell was then chosen as coincident with the nickel position at 0, 0, 0. From the same three-dimensional Patterson synthesis, peaks consistent with a square-planar Ni–S_2–P configuration were found and the approximate positions of the two sulfur and the phosphorus atoms were estimated. The coordinates of these four atoms (assigning a half-weight to nickel) were used for a structure factor calculation, which gave a reliability index R of 0.36. The positions of all carbon atoms belonging to the phenyl groups were taken after two successive three-dimensional difference Fourier syntheses and R was reduced to 0.29. It was thus confirmed from Patterson and Fourier maps that half a nickel atom and one ligand molecule constitute the asymmetric unit. The structure was then refined by a least-squares method for the positional parameters and isotropic temperature factors of each atom and by introducing into the calculation all atoms but hydrogens; after several cycles an R value of 0.128 was obtained. The introduction of hydrogen atoms in planar positions calculated to make the C–H bond lengths 1.09 Å and several more isotropic least-squares cycles to refine only the positional and thermal parameters of nonhydrogen atoms gave the final reliability index $R = 0.114$. A further cycle of refinement indicated no shifts greater than 20% of corresponding standard deviations; this refinement was considered to be sufficiently complete at the above value of R. The refinement employed the block-diagonal approximation and was applied on observed reflections only. All reflections were given unit weight and the quantity minimized was $R' = \Sigma w \cdot (|F_o| - |F_c|)^2$, where the weighting factor $w = \{a + bk|F_o| + c(kF_o)^2\}^{-1}$, with $a = 15$, $b = 1.0$, and $c = 0.0045$. The positional parameters of hydrogen atoms, calculated from the final positions of the carbons and numbered by reference to their respective carbon atoms, and their assumed isotropic temperature factors are given in Table I. The final atomic coordinates (in Å) and the isotropic thermal parameters of nonhydrogen atoms with their standard deviations[15,16] 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).

The atomic scattering factors of Hanson and coworkers[17] were used for Ni, S, C, and H, those of Ni being corrected for the real part of anomalous dispersion ($\Delta f' = -3.2$);[18] scattering factors of Cromer, *et al.*,[19] 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 and certainly never exceeded the value of the electron density esd ($\sigma(\rho) = 0.2$ e/Å^3) calculated for the whole structure.

Table I

Calculated Coordinates ($\times 10^4$) and Assumed Isotropic Temperature Factors for Hydrogen Atoms

Atoms	X	Y	Z	B, Å^2
H(2)	2304	3467	960	8.0
H(3)	3850	4027	2011	8.0
H(4)	4270	3006	3308	8.0
H(5)	2984	1596	3630	8.0
H(6)	1292	1142	2619	8.0
H(8)	−1443	2592	17	8.0
H(9)	−2718	4278	−6	8.0
H(10)	−1983	6091	713	8.0
H(11)	−581	5849	1920	8.0
H(12)	779	4271	1840	8.0

Table II

Final Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters with Esd's of Nonhydrogen Atoms

Atoms	X	Y	Z	B, Å^2	$\sigma(B)$, Å
Ni	0000	0000	0000	2.56	0.08
S(1)	−202 (4)	613 (5)	1197 (3)	3.56	0.10
S(2)	788 (4)	1684 (5)	−124 (3)	3.41	0.09
P	519 (4)	2057 (4)	970 (3)	2.58	0.09
C(1)	1700 (15)	2312 (16)	1709 (10)	2.76	0.35
C(2)	2432 (16)	3077 (18)	1563 (12)	3.78	0.43
C(3)	3322 (20)	3350 (22)	2141 (14)	5.14	0.53
C(4)	3532 (24)	2827 (27)	2860 (17)	7.41	0.76
C(5)	2815 (31)	2003 (34)	3029 (22)	9.45	1.16
C(6)	1863 (23)	1765 (26)	2467 (17)	6.96	0.72
C(7)	−266 (18)	3308 (20)	945 (13)	4.49	0.47
C(8)	−1214 (24)	3332 (26)	431 (18)	7.62	0.78
C(9)	−1918 (27)	4315 (33)	385 (20)	9.69	0.98
C(10)	−1569 (24)	5254 (28)	841 (16)	7.39	0.77
C(11)	−714 (33)	5205 (40)	1411 (25)	9.86	1.28
C(12)	−11 (26)	4238 (32)	1433 (20)	9.47	0.95

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 Domenicano and Vaciago. Structure factors and least-squares cycles of refinements were calculated by means of programs written by Albano, Domenicano, and Vaciago. The least-squares planes were determined by a program written by Chu and adapted to the method developed by Shomaker, *et al.*,[20] the equation of the plane being of the form $Ax + By + Cz = D$, which corresponds to the crystallographic axes.

Optical Spectra.—All optical spectra, both reflectance and solution, were run with a Beckman DK 1-A spectrophotometer. Magnesium oxide was used as reference for the reflectance spectra and toluene was used as solvent for the solution spectra taken here.

Discussion

The bond lengths and angles with their esd's[21] are given in Table IV and are also shown in Figure 1, where the numbering of all atoms but hydrogens is included. All intermolecular contacts of less than 4.0 Å were calculated and the closest approach to the nickel atom from any other atom of neighboring molecules was found to involve hydrogen atoms only and to be greater than 3.6 Å. The projection of the structure along the [100] direction is shown in Figure 2.

The nickel and four sulfur atoms of the ligand molecules are in a square-planar configuration since Ni occupies a special position in the space group C2/c and thus is constrained by crystallographic requirements to be strictly planar. This is confirmed by a calculation of the Ni–S(1)–S(2)–P least-squares plane whose results are shown in Table V. The maximum deviation of an atom from this plane (I) is 0.0007 Å.

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TABLE III
OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	$|F_o|$	F_c
2	0	0	225.4	244.8
4	0	0	172.9	139.9
6	0	0	92.1	91.9
12	0	0	42.1	47.1
1	1	0	139.1	157.9
3	1	0	156.8	174.3
5	1	0	59.4	73.9
7	1	0	42.5	51.2
9	1	0	31.8	30.6
11	1	0	29.0	39.9
0	2	0	76.4	-79.8
2	2	0	151.0	161.9
4	2	0	120.7	130.5
6	2	0	179.2	132.9
8	2	0	101.0	115.2
10	2	0	82.5	83.4
1	3	0	68.3	-67.4
3	3	0	131.2	151.1
5	3	0	139.4	134.4
7	3	0	142.5	132.3
9	3	0	140.9	123.1
0	4	0	102.5	95.2
2	4	0	54.4	56.6
4	4	0	47.3	60.2
6	4	0	79.5	75.0
8	4	0	35.9	30.0
1	5	0	140.6	145.5
3	5	0	62.2	54.8
5	5	0	35.9	26.4
0	6	0	117.3	129.6
2	6	0	49.7	44.9
6	6	0	[illegible]	-34.4
1	7	0	43.0	-36.3
5	7	0	25.7	7.1
9	7	0	66.7	49.1
11	7	0	55.0	44.3
0	8	0	86.9	-96.3
2	8	0	32.3	-30.3
0	12	0	19.1	22.5
1	1	1	136.8	-157.8
3	1	1	151.2	-182.4
3	1	-1	13.2	-14.0
5	1	1	123.7	-132.6
5	1	-1	44.5	-48.1
9	1	1	52.8	65.2
9	1	-1	25.6	30.4
11	1	1	54.5	68.6
11	1	-1	43.3	50.6
13	1	1	24.2	29.3
0	2	1	10.1	-21.4
2	2	1	147.5	-163.3
2	2	-1	109.7	-101.9
4	2	1	89.2	-102.8
4	2	-1	47.8	-40.5
6	2	1	23.2	-29.2
8	2	1	59.1	52.0
10	2	1	39.0	45.4
10	2	-1	31.1	48.8
12	2	1	32.7	36.1
1	3	-1	94.2	90.0
3	3	1	23.7	-21.9
3	3	-1	105.6	88.7
5	3	1	29.9	27.1
5	3	-1	119.9	111.7
7	3	-1	108.0	102.1
9	3	-1	64.7	67.9
0	4	1	47.7	-45.1
2	4	1	117.1	115.9
2	4	-1	169.6	182.6
4	4	1	125.7	127.0
4	4	-1	170.9	162.4
6	4	1	50.0	46.9
6	4	-1	99.2	96.7
8	4	-1	85.5	81.1
1	5	1	30.3	-27.9
1	5	-1	79.9	77.9
3	5	-1	59.4	71.1
5	5	-1	89.9	90.0
0	6	1	72.0	-72.8
2	6	1	70.6	-72.6
2	6	-1	41.6	32.4
4	6	1	50.1	-51.3
6	6	1	48.2	-41.8
8	6	-1	45.4	-22.0
1	7	1	59.1	-48.4
3	7	1	85.3	-76.4
5	7	1	56.8	-42.2
5	7	-1	35.9	-18.2
9	7	-1	57.7	41.2
11	7	1	42.0	40.4
1	9	1	37.8	34.9
1	9	-1	35.8	-26.4
3	9	1	41.1	37.7
1	13	1	29.1	16.4
1	13	-1	27.6	-27.7
0	0	2	135.8	154.9
2	0	2	236.5	276.6
2	0	-2	196.2	208.8
4	0	2	67.4	75.1
4	0	-2	27.0	22.3
4	0	2	40.1	-40.0
6	0	-2	32.6	-29.3
8	0	2	41.5	37.6
10	0	2	63.3	75.4
12	0	2	57.6	79.6
14	0	2	48.4	71.0
1	1	2	64.2	74.5
1	1	-2	154.0	147.6
3	1	2	125.1	141.9
3	1	-2	218.9	229.5
5	1	2	46.9	57.7
5	1	-2	19.3	-19.4
7	1	2	53.8	67.2
11	1	2	48.4	59.8
13	1	2	44.0	56.4
0	2	2	115.7	127.0
2	2	2	67.9	72.1
2	2	-2	192.6	-220.1
4	2	2	99.0	115.6
4	2	-2	44.0	38.0
6	2	2	198.1	211.3
6	2	-2	57.5	51.4
8	2	2	102.8	116.7
10	2	2	32.2	44.3
12	2	-2	34.9	30.7
1	3	-2	79.6	84.4
3	3	2	93.7	93.7
3	3	-2	83.0	-79.2
5	3	2	153.6	162.7
5	3	-2	76.1	79.4
7	3	2	155.2	180.4
7	3	-2	70.0	68.4
9	3	2	76.0	75.4
0	4	2	25.3	25.7
2	4	2	23.6	21.5
2	4	-2	97.3	101.2
4	4	2	62.8	64.2
4	4	-2	120.8	91.4
6	4	2	55.4	48.1
6	4	-2	100.6	104.9
8	4	-2	64.4	63.1
1	5	2	64.7	69.9
1	5	-2	115.6	108.3
3	5	-2	208.1	201.8
5	5	-2	64.4	59.8
7	5	2	89.9	-73.7
7	5	-2	59.7	54.5
0	6	2	101.6	110.4
2	6	2	130.7	140.2
2	6	-2	82.5	91.9
4	6	-2	33.5	29.5
6	6	2	41.7	-31.5
6	6	-2	27.9	16.6
8	6	-2	45.2	27.[illegible]
10	6	-2	52.9	55.3
12	6	-2	45.5	46.5
1	7	2	54.8	58.6
1	7	-2	42.6	35.8
3	7	2	42.9	49.8
5	7	-2	41.5	23.2
7	7	2	42.7	34.8
9	7	-2	60.4	54.6
11	7	-2	75.0	69.5
4	8	2	49.7	47.4
4	8	-2	45.2	43.0
1	9	-2	40.4	35.7
3	9	-2	71.2	61.2
2	10	-2	51.4	58.0
4	10	-2	78.9	69.7
1	11	2	42.1	45.6
1	11	-2	28.3	25.0
0	12	2	34.6	32.2
2	12	2	38.3	44.7
3	13	2	29.9	30.7
1	1	3	123.2	-136.6
1	1	-3	188.5	212.5
3	1	3	125.3	-140.3
3	1	-3	31.0	-16.4
5	1	3	66.1	-75.3
5	1	-3	17.5	-18.1
7	1	-3	26.2	28.0
9	1	3	47.1	58.5
11	1	3	32.8	32.8
11	1	-3	41.8	-47.9
0	2	3	16.0	-12.5
2	2	3	133.8	-144.3
2	2	-3	15.4	-23.3
4	2	3	89.1	-100.7
4	2	-3	83.7	-77.2
6	2	3	30.5	-33.2
8	2	3	29.3	29.1
10	2	3	32.6	29.6
1	3	-3	11.2	8.6
3	3	3	54.9	-55.1
3	3	-3	34.5	35.6
5	3	3	66.5	-73.4
5	3	-3	46.0	32.8
7	3	3	59.8	-70.2
9	3	3	56.9	-64.2
0	4	3	62.0	-56.1
2	4	-3	40.8	32.9
4	4	-3	86.3	80.2
6	4	3	69.8	-74.9
6	4	-3	30.1	-21.7
8	4	3	99.2	-104.4
10	4	3	60.5	-71.4
12	4	3	34.0	-39.4
1	5	3	20.9	-19.6
1	5	-3	76.4	81.5
3	5	-3	106.5	92.2
5	5	-3	45.4	45.0
9	5	3	70.7	-54.4
0	6	3	89.0	-94.4
2	6	3	78.6	-86.4
2	6	-3	77.3	79.1
4	6	3	34.1	-31.7
8	6	-3	45.2	-23.2
10	6	-3	52.9	-50.0
12	6	-3	40.9	-28.4
1	7	3	39.4	-45.6
1	7	-3	22.1	22.1
3	7	3	76.3	-78.8
5	7	3	50.7	-35.8
7	7	-3	36.4	21.9
0	8	3	46.1	44.0
2	8	-3	74.3	-80.3
4	8	3	35.0	-29.1
4	8	-3	56.1	-45.3
1	9	3	48.6	42.2
1	9	-3	48.3	-47.2
2	10	-3	35.5	33.7
4	10	3	38.2	35.4
3	11	3	26.7	26.7
3	11	-3	36.5	30.0
4	12	3	31.1	22.0
1	13	3	30.6	25.6
1	13	-3	32.4	-37.8
3	13	-3	35.0	-34.1
0	0	4	12.0	-12.8
2	0	4	12.1	3.2
2	0	-4	192.1	-223.1
4	0	4	158.3	-169.7
4	0	-4	41.2	-39.2
10	0	4	57.9	63.3
10	0	-4	66.5	70.4
12	0	4	47.5	64.7
12	0	-4	51.0	46.9
14	0	4	36.5	58.0
1	1	4	15.3	15.0
1	1	-4	[illegible]	170.3
3	1	4	17.5	15.1
3	1	-4	17.6	-20.9
5	1	4	27.3	16.7
7	1	-4	26.5	24.9
9	1	-4	25.6	34.0
11	1	4	29.2	38.6
11	1	-4	40.6	43.2
13	1	4	28.7	35.9
13	1	-4	32.2	37.1
0	2	4	33.1	-34.0
2	2	-4	32.0	33.0
4	2	4	95.5	102.1
4	2	-4	53.8	59.5
6	2	4	38.9	46.7
8	2	4	33.7	33.8
1	3	4	34.4	33.0
1	3	-4	37.2	-36.0
3	3	4	77.6	70.9
3	3	-4	84.5	74.2
5	3	4	86.9	89.8
7	3	4	62.6	69.2
7	3	-4	49.0	47.5
9	3	4	36.2	39.8
0	4	4	30.5	-21.5
2	4	4	47.3	50.8
2	4	-4	38.5	28.7
4	4	-4	161.2	153.5
6	4	4	52.7	50.5
6	4	-4	113.3	101.7
8	4	4	74.2	74.8
8	4	-4	60.7	64.5
10	4	-4	51.0	48.5
1	5	4	61.4	57.5
1	5	-4	136.7	137.1
3	5	4	21.0	22.9
3	5	-4	46.2	38.9
5	5	-4	98.8	104.8
7	5	-4	82.1	65.2
9	5	-4	97.2	80.4
0	6	4	129.9	145.8
2	6	4	99.2	108.5
2	6	-4	93.5	106.0
4	6	4	66.8	69.8
4	6	-4	24.6	11.9
6	6	4	39.5	27.3
6	6	-4	40.2	44.5
8	6	-4	40.6	35.5
10	6	4	33.3	40.4
10	6	-4	48.3	43.8
12	6	-4	45.8	48.2
1	7	4	130.5	146.3
1	7	-4	133.9	141.6
3	7	4	100.9	102.0
3	7	-4	84.2	81.6
5	7	4	93.0	95.8
0	8	4	78.1	74.7
2	8	4	80.6	89.6
2	8	-4	86.8	89.1
4	8	4	80.7	90.8
4	8	-4	101.7	97.1
3	9	-4	65.8	69.8
2	10	-4	51.2	44.9
4	10	-4	72.5	65.2
1	11	4	40.7	43.2
1	11	-4	54.0	62.2
3	11	4	43.1	36.0
0	12	4	50.7	60.1
2	12	4	45.4	52.3
4	12	4	33.1	33.8
1	1	5	31.7	33.0
1	1	-5	38.6	-36.5
3	1	-5	51.7	-52.4
9	1	-5	25.8	37.0
11	1	-5	20.4	-15.6
13	1	-5	56.1	-69.7
0	2	5	59.2	63.2
2	2	5	23.3	-20.2
2	2	-5	137.1	-118.3
4	2	5	25.9	-19.4
4	2	-5	29.4	36.7
8	2	-5	32.2	31.3
14	2	-5	25.9	-39.5
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1	3	-5	65.2	-63.0
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5	3	5	46.1	-43.0
5	3	-5	114.3	-103.5
7	3	-5	75.0	-72.5
9	3	-5	58.1	-59.3
0	4	5	26.4	21.0
2	4	5	24.6	-11.4
4	4	-5	136.2	-123.1
6	4	5	52.9	-47.0
6	4	-5	96.2	-79.9
8	4	5	64.0	-58.2
8	4	-5	108.1	-100.9
10	4	5	36.2	-49.1
10	4	-5	64.3	-60.1
14	4	5	10.3	4.1
1	5	5	85.1	77.4
3	5	5	70.5	55.0
3	5	-5	32.2	30.4
5	5	5	54.4	44.3
7	5	-5	74.9	-63.8
9	5	-5	75.0	-53.6
0	6	5	25.5	19.6
2	6	5	37.0	39.7
4	6	5	44.9	39.6
4	6	-5	35.0	41.9
6	6	5	49.8	38.8
12	6	-5	40.8	-33.6
1	7	-5	31.8	-24.0
3	7	-5	55.1	-52.3
2	8	5	32.6	-33.8
2	8	-5	85.9	-78.1
4	8	5	48.5	-45.5
4	8	-5	64.8	-54.8
2	10	-5	38.5	52.4
4	10	5	39.3	32.9
4	10	-5	28.3	39.3
1	11	-5	45.3	48.6
3	11	5	36.8	32.5
3	11	-5	63.3	66.6
1	13	5	19.9	-16.2
3	13	5	28.5	-30.3
0	0	6	61.9	77.1
2	0	6	50.3	68.4
2	0	-6	23.4	-23.9
4	0	6	48.1	32.9
6	0	6	28.0	-25.3
8	0	-6	108.5	108.0
10	0	-6	122.5	134.8
12	0	6	30.1	28.9
12	0	-6	106.7	126.8
14	0	-6	50.8	62.8
1	1	6	62.8	54.8
1	1	-6	77.3	73.0
3	1	6	51.6	45.8
3	1	-6	35.3	15.4
5	1	6	23.1	13.9
5	1	-6	39.1	32.4
7	1	-6	71.7	77.0
9	1	-6	70.9	81.0
11	1	-6	75.3	86.0
13	1	-6	47.5	59.4
0	2	6	49.7	56.5
2	2	6	80.4	82.6
2	2	-6	156.2	181.2
4	2	-6	179.6	195.2
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8	2	-6	44.2	47.3
1	3	-6	66.6	54.1
3	3	-6	94.7	42.9
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5	3	-6	176.3	161.3
7	3	-6	121.4	112.0
0	4	6	42.2	33.9
2	4	6	24.7	-19.3
2	4	-6	47.3	60.2
4	4	6	71.2	63.1
4	4	-6	66.9	49.5
6	4	6	74.3	78.5
6	4	-6	71.7	68.8
8	4	6	57.6	49.5
8	4	-6	57.1	50.5
10	4	6	39.9	35.4
10	4	-6	40.1	31.6
1	5	6	71.2	65.5
1	5	-6	29.5	30.7
3	5	6	79.4	70.1
5	5	6	90.5	72.1
7	5	6	88.2	76.0
9	5	-6	61.8	55.4
11	5	-6	71.1	61.1
0	6	6	67.0	59.3
2	6	6	104.9	105.1
2	6	-6	33.5	27.1
4	6	6	60.6	53.9
6	6	-6	47.0	-37.3
10	6	-6	30.6	30.5
12	6	-6	32.0	28.2
1	7	6	107.4	117.3
1	7	-6	89.9	89.7
3	7	6	75.6	77.2
3	7	-6	79.1	74.0
5	7	-6	35.8	29.9
0	8	6	50.2	47.2
2	8	6	33.8	38.6
2	8	-6	63.5	68.6
4	8	6	38.1	39.6
4	8	-6	44.4	41.1
4	10	6	44.4	47.1
1	11	6	36.7	37.8
1	11	-6	25.3	28.0
3	11	6	34.3	41.4
0	12	6	42.9	50.4
2	12	6	33.7	44.4
2	12	-6	28.6	36.6
1	1	7	67.0	69.1
1	1	-7	161.6	-165.5
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3	1	-7	98.7	-110.7
5	1	-7	23.1	-22.1
7	1	-7	95.6	107.2
9	1	-7	51.3	57.8
11	1	-7	32.5	38.9
0	2	7	128.8	138.0
2	2	7	40.8	39.7
2	2	-7	77.1	-66.1
4	2	-7	48.5	-31.0
6	2	-7	49.3	45.8
8	2	-7	65.4	67.1
10	2	-7	39.0	45.7
1	3	7	36.2	42.7
1	3	-7	29.4	19.6
3	3	-7	42.4	-39.2
5	3	-7	56.7	-44.0
7	3	7	35.6	45.9
7	3	-7	54.2	-45.8
0	4	7	15.8	-15.8
2	4	7	26.6	24.1
4	4	7	71.4	74.9
6	4	7	60.1	64.3
6	4	-7	91.4	-91.8
8	4	-7	74.8	-71.5
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1	5	7	30.9	25.7
3	5	7	98.8	96.0
5	5	7	66.0	63.2
11	5	-7	31.7	19.1
0	6	7	80.0	80.8
2	6	7	65.2	63.7
2	6	-7	54.1	-56.8
4	6	7	62.4	64.0
6	6	-7	38.8	42.9
8	6	-7	37.8	24.2
10	6	-7	43.2	38.2
1	7	7	44.3	43.2
1	7	-7	65.1	-65.9
3	7	-7	57.1	-44.4
5	7	-7	59.6	-41.1
7	7	-7	50.1	46.3
2	8	7	41.1	-38.6
4	8	7	58.4	-53.9
1	9	7	33.6	-32.2
1	9	-7	43.9	44.4
4	10	7	26.6	22.9
1	13	7	17.2	-24.5
3	13	7	27.7	-35.4
0	0	8	148.2	172.6
2	0	8	197.[illegible]	225.6
2	0	-8	125.4	130.2
4	0	8	142.7	172.7
6	0	8	45.7	43.1
8	0	-8	65.7	65.7
10	0	-8	73.9	80.9
12	0	-8	61.9	70.4
14	0	-8	69.9	63.2
1	1	8	139.3	164.9
1	1	-8	139.6	142.8
3	1	8	89.6	107.1
3	1	-8	64.8	70.6
5	1	8	69.4	82.7
5	1	-8	56.8	61.2
7	1	8	31.7	33.3
7	1	-8	53.4	55.9
9	1	-8	40.9	49.7
11	1	-8	46.3	59.4
13	1	-8	34.6	35.3
0	2	8	93.9	87.1
2	2	8	20.5	28.1
2	2	-8	115.8	135.7
4	2	8	24.0	20.5
4	2	-8	171.1	173.3
6	2	8	44.2	52.0
6	2	-8	141.4	125.9
8	2	8	40.3	42.2
8	2	-8	88.3	92.3
1	3	-8	44.4	44.8
3	3	-8	175.2	138.2
5	3	-8	202.9	209.8
7	3	8	48.3	61.4
7	3	-8	179.8	121.[illegible]
9	3	-8	43.2	44.9
2	4	8	58.6	49.0
2	4	-8	60.1	55.9
4	4	8	71.5	66.3
4	4	-8	41.0	36.6
6	4	8	58.7	52.1
6	4	-8	34.7	23.0
8	4	8	44.6	45.8
8	4	-8	38.1	29.8
1	5	8	82.1	90.8
1	5	-8	21.8	20.6
3	5	8	77.6	74.8
5	5	8	63.5	69.4
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0	6	8	99.7	55.[illegible]
2	6	8	48.8	43.7
4	6	8	32.6	27.5
4	6	-8	33.9	-37.2
10	6	-8	43.0	38.7
12	6	-8	44.0	38.1
1	7	-8	30.2	22.1
0	8	8	31.5	-27.3
2	8	8	36.[illegible]	-34.9
4	8	8	28.3	-13.2
1	1	9	43.9	37.1
1	1	-9	59.9	-55.6
3	1	9	17.3	-23.8
3	1	-9	136.7	-134.9
5	1	9	60.2	-66.3
7	1	9	27.2	-37.1
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9	1	-9	75.7	86.0
11	1	-9	37.4	37.9
0	2	9	36.0	39.6
2	2	9	18.9	-23.2
2	2	-9	50.4	-43.5
4	2	9	44.6	-46.6
6	2	9	47.0	-51.3
6	2	-9	40.8	39.4
8	2	-9	62.1	55.2
10	2	-9	53.7	56.0
1	3	9	66.5	-70.4
1	3	-9	44.7	47.4
3	3	-9	76.6	84.9
5	3	9	21.5	30.3
5	3	-9	77.6	92.0
7	3	-9	33.2	37.5
0	4	9	68.2	-65.4
2	4	-9	116.8	116.3
4	4	9	60.2	53.1
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1	5	-9	70.0	79.8
1	5	-9	73.5	75.2
[illegible]	6	9	32.8	29.3
8	6	-9	42.7	39.5
10	6	-9	42.7	39.6
12	6	-9	30.4	34.7
1	7	-9	40.1	-43.7
3	7	-9	60.0	-57.0
5	7	9	36.6	-19.1
7	7	-9	39.3	29.3
9	7	-9	51.3	41.6
2	8	9	25.8	-23.3
0	0	10	151.7	147.1
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2	0	-10	77.3	78.1
4	0	10	63.5	87.4
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6	0	-10	37.2	-35.9
8	0	-10	32.5	-30.3
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1	1	-10	81.4	88.2
3	1	10	86.1	95.2
3	1	-10	31.8	33.5
5	1	10	44.0	53.0
7	1	10	32.8	38.9
2	2	-10	29.4	20.0
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8	2	10	56.1	69.0
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10	2	10	45.1	58.6
1	3	10	27.7	-22.8
3	3	-10	79.9	85.7
5	3	10	46.2	53.8
5	3	-10	96.4	110.9
7	3	10	43.3	60.2
7	3	-10	80.4	75.2
9	3	10	54.4	65.4
0	4	10	44.3	47.8
2	4	10	33.3	31.6
2	4	-10	47.5	57.7
4	4	-10	61.1	53.8
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1	5	10	79.2	90.8
1	5	-10	61.1	72.6
3	5	10	66.8	65.1
3	5	-10	32.7	36.5
0	6	10	57.8	61.0
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2	6	-10	41.1	41.6
4	6	10	28.4	31.1
6	6	-10	47.1	29.3
8	6	-10	43.2	37.6
10	6	-10	50.9	49.9
7	7	-10	63.4	55.2
9	7	-10	72.7	61.6
11	7	-10	65.5	58.6
13	7	-10	39.3	35.0
2	8	10	29.6	-30.8
4	8	-10	48.8	48.4
3	9	-10	51.4	55.3
2	10	-10	33.7	41.7
4	10	-10	26.1	22.0
1	1	-11	43.2	-44.9
3	1	11	98.7	-105.1
5	1	11	35.4	-49.7
2	2	11	44.4	-49.1
4	2	11	90.8	-94.6
6	2	11	36.8	-46.4
1	3	11	37.0	-22.0
1	3	-11	47.3	41.4
3	3	-11	32.6	29.0
5	3	-11	47.2	49.1
7	3	-11	35.4	38.2
0	4	11	58.8	-56.2
2	4	-11	88.9	93.2
4	4	11	38.9	35.5
4	4	-11	58.1	48.3
6	4	-11	57.6	64.2
1	5	11	47.4	-59.9
1	5	-11	46.1	49.1
3	5	-11	37.2	41.3
2	6	11	49.7	-54.7
4	6	11	56.6	-60.1
6	6	-11	47.9	-39.8
3	7	11	45.5	-39.7
5	7	11	42.8	-35.3
7	7	-11	40.8	28.8
0	8	11	36.8	28.8
2	8	11	38.5	24.2
2	12	11	21.9	16.0
0	0	12	59.4	59.5
2	0	12	39.3	31.2
6	0	12	29.8	-24.9
8	0	12	32.2	-31.2
0	2	12	34.9	-31.3
6	2	12	39.9	44.5
8	2	12	41.9	48.3
1	3	-12	20.0	-15.7
5	3	-12	21.5	26.1
7	3	12	49.3	56.7
9	3	12	35.5	46.0
0	4	12	37.1	42.7
2	4	-12	54.8	49.4
4	4	-12	58.6	60.3
6	4	-12	62.5	66.9
1	5	12	51.3	56.6
1	5	-12	66.2	76.0
3	5	12	27.7	34.0
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5	5	-12	76.8	56.5
0	6	12	63.8	67.1
2	6	12	66.0	71.5
2	6	-12	37.6	43.7
4	6	12	49.9	51.9
4	6	-12	32.6	31.3
8	6	-12	47.8	41.0
10	6	-12	44.7	43.6
12	6	-12	33.6	25.8
1	7	12	57.8	46.4
3	7	12	61.9	57.7
3	7	-12	25.3	19.1
5	7	12	40.6	42.1
9	7	-12	68.8	52.1
11	7	-12	50.7	44.2
13	7	-12	42.7	32.0
0	8	12	34.1	26.8
2	8	-12	36.0	36.0
4	8	-12	43.2	34.1
1	9	-12	42.0	48.9
3	9	-12	60.6	68.7
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2	10	-12	45.0	48.1
4	10	-12	50.9	60.4
1	1	13	52.6	-49.4
5	1	13	41.2	-37.1
2	2	-13	39.7	-31.7
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6	2	13	31.6	-26.5
1	3	13	40.5	40.2
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3	3	-13	39.3	-30.7
5	3	-13	22.2	-30.9
7	3	-13	36.9	-27.2
0	4	13	27.1	24.7
4	4	-13	34.0	-20.0
6	4	-13	60.3	-45.7
7	5	-13	71.1	-57.1
0	6	13	28.6	-30.2
2	6	13	16.3	-14.7
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10	6	-13	42.7	-37.7
12	6	-13	34.8	-25.8
1	7	-13	27.3	-23.0
13	7	-13	33.2	-21.4
0	8	13	44.1	42.0
2	8	13	38.6	19.2
2	8	-13	33.7	-37.8
2	10	-13	23.0	27.3
1	11	13	11.7	-22.7
1	11	-13	23.0	30.8
3	11	-13	26.4	30.3
6	0	-14	33.1	46.0
8	0	-14	67.2	84.4
10	0	-14	58.4	66.1
12	0	-14	39.6	46.9
13	1	-14	22.7	28.3
0	2	14	39.9	36.1
2	2	-14	30.6	30.8
4	2	-14	42.7	39.2
1	3	-14	33.2	30.3
3	3	-14	48.8	43.9
5	3	-14	45.2	40.4
2	4	-14	44.5	38.3
4	4	-14	61.1	49.6
6	4	-14	44.6	44.4
0	6	14	44.5	42.2
2	6	14	47.9	46.3
4	6	14	39.8	34.5
1	7	14	77.4	59.5
1	7	-14	38.2	38.1
3	7	14	59.8	57.4
5	7	14	33.4	39.7
2	8	-14	34.2	31.6
4	8	-14	25.3	19.6
3	9	-14	33.1	38.5
1	1	15	46.7	41.7
1	1	-15	27.4	-14.3
7	1	-15	40.9	32.0
9	1	-15	36.0	16.8
11	1	-15	36.4	-33.4
0	2	15	59.1	50.2
2	2	15	29.4	28.0
2	2	-15	23.5	-16.8
1	3	15	21.3	10.4
1	3	-15	40.4	-43.4
3	3	-15	49.9	-40.3
5	3	-15	41.3	-30.0
2	4	-15	36.3	-39.7
4	4	-15	58.6	-47.0
6	4	-15	54.1	-48.4
8	4	-15	42.4	-40.2
3	5	15	37.8	30.8
2	6	15	30.5	23.4
4	6	15	27.1	29.0
1	7	15	22.4	18.4
2	8	-15	31.6	-32.4
0	10	15	21.4	-23.6
2	10	-15	21.7	25.4
4	10	-15	11.5	10.4
2	0	16	42.3	53.6
4	0	16	36.2	34.0
6	0	16	25.0	28.8
6	0	-16	33.1	31.1
8	0	-16	53.4	55.9
10	0	-16	91.2	93.6
12	0	-16	40.4	45.5
1	1	16	48.0	46.8
1	1	-16	38.1	37.1
3	1	16	37.0	39.9
5	1	16	26.9	28.2
5	1	-16	29.1	38.4
7	1	-16	32.0	44.9
11	1	-16	29.3	38.2
0	2	16	59.3	64.3
2	2	16	31.5	27.4
2	2	-16	74.6	76.7
4	2	16	28.4	22.4
4	2	-16	71.4	67.7
6	2	-16	52.7	45.5
1	3	16	25.1	16.6
1	3	-16	56.2	61.8
3	3	-16	71.7	69.0
5	3	-16	59.0	51.4
4	4	-16	40.7	32.2
6	4	-16	42.5	26.4
2	6	16	20.6	19.4
4	6	16	29.5	17.9
4	6	-16	32.8	-23.8
1	7	16	20.1	21.4
1	1	17	27.4	37.3
1	1	-17	40.6	-38.7
5	1	-17	28.2	40.3
7	1	-17	37.5	43.4
9	1	-17	38.0	34.5
11	1	-17	13.2	8.3
2	2	17	26.2	22.6
6	2	-17	47.5	46.8
8	2	-17	44.0	44.9
1	3	17	20.1	-14.7
0	4	17	42.5	-30.8
2	4	17	31.6	-26.8
2	4	-17	38.8	33.6
1	5	17	19.4	-13.2
2	6	17	25.7	10.4
2	0	18	46.6	47.9
4	0	18	44.0	56.6
4	0	-18	30.7	-32.1
1	1	18	30.1	36.1
1	1	-18	36.0	24.5
3	1	18	32.4	39.9
9	1	-18	14.1	10.7
2	2	-18	37.7	44.7
4	2	-18	50.8	54.7
3	3	-18	59.1	60.6
5	3	-18	42.6	47.9
3	5	18	23.5	30.1
1	1	-19	31.6	-34.1
1	3	-19	23.8	27.4
3	3	-19	26.3	29.1
0	4	19	42.7	-39.9
2	4	19	24.8	-22.7
2	4	-19	32.8	40.7
2	0	20	22.7	29.4
4	0	-20	21.9	-14.2
6	0	-20	21.1	-23.6

TABLE IV
BOND DISTANCES AND ANGLES WITH THEIR ESD'S

Distances, Å	
Ni–S(1)	2.234 (5)
Ni–S(2)	2.242 (6)
P–S(1)	2.006 (8)
P–S(2)	2.022 (8)
P–C(1)	1.786 (17)
P–C(7)	1.776 (24)
Angles	
S(1)–Ni–S(2)	88° 18′ (12′)
Ni–S(1)–P	85° 32′ (15′)
Ni–S(2)–P	84° 50′ (15′)
S(1)–P–S(2)	101° 18′ (18′)
S(1)–P–C(1)	112° 24′ (39′)
S(1)–P–C(7)	112° 08′ (51′)
S(2)–P–C(1)	111° 24′ (43′)
S(2)–P–C(7)	112° 28′ (47′)
C(1)–P–C(7)	107° 10′ (56′)

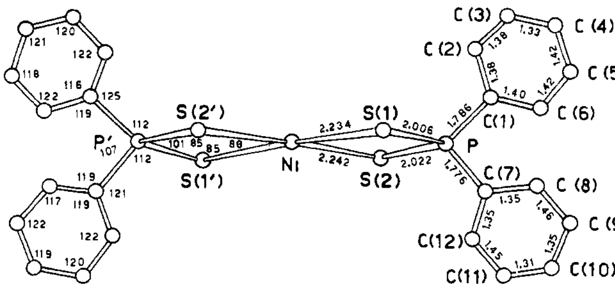

Figure 1.—Schematic representation of the molecule with bond lengths (Å) and bond angles (deg).

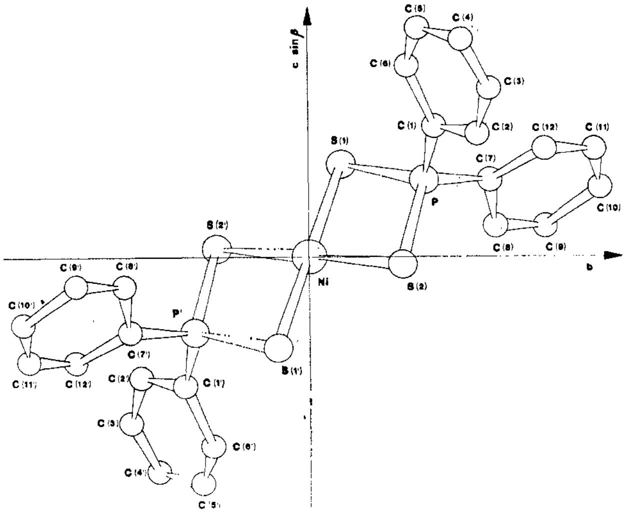

Figure 2.—[100] projection of the molecule.

The Ni–S(1) and Ni–S(2) distances (2.234 and 2.242 Å, respectively) are to be regarded as equal, the statistical errors being, respectively, 0.005 and 0.006 Å; the two sulfur atoms of the dithiophosphinato ligand are therefore equivalent with respect to the Ni atom. The mean Ni–S distance (2.238 ± 0.004 Å) agrees fairly well with similar lengths reported for other structures, such as nickel(II) xanthate[4] and bis(diethyldithiophosphato)nickel(II),[8] and it is well within the range 2.1–2.3 Å found in many square-planar nickel(II) complexes.

The difference in the Ni–S bond lengths found in square-planar nickel complexes is closely related to the

Table V

Deviations from Planes through Groups of Atoms, Å

Plane I		Plane II		Plane III	
Ni	−0.00057	C(1)	−0.0041	C(7)	−0.0247
S(1)	0.00065	C(2)	−0.0187	C(8)	0.0123
S(2)	0.00064	C(3)	0.0197	C(9)	0.0345
P	−0.00071	C(4)	0.0029	C(10)	−0.0705
		C(5)	−0.0255	C(11)	0.0553
		C(6)	0.0258	C(12)	−0.0068

Equations of Planes ($Ax + By + Cz = D$) Which Refer to the Crystallographic Axes

Plane	Equation
I	$0.798x - 0.402y + 0.246z = 0.00057$
II	$-0.566x + 0.742y + 0.482z = 2.10838$
III	$-0.598x - 0.417y + 0.806z = -0.06365$

Dihedral Angles between Planes

I to II = 53° 49′; I to III = 89° 49′; II to III = 74° 6′

Table VI

Ni–S Distances (Å) in Planar Four-Membered-Ring Ni(II) Complexes and First-Band Maxima (kK) as Determined by Uv Spectra

Compound	$\bar{\nu}_1{}^a$	$\bar{\nu}_1{}^b$	Ni–S distance[c]	Ref
Bis(diphenyldithiophosphinato)nickel(II)	13.9	14.1	2.238 ± 4	Present work
Bis(diethyldithiophosphato)nickel(II)	14.5[d]	14.9	2.233 ± 4	McConnell and Kastalsky[8]
Bis(ethylxanthate)nickel(II)	15.5[d]	16.0	2.235 ± 6	Franzini[4]
Bis(dithiocarbamate)nickel(II)	15.6[d]	...	2.215 ± 9	Gasparri, Nardelli, and Villa[3]
Bis(diethyldithiocarbamate)nickel(II)	15.8[d]	16.0	2.201 ± 6	Vaciago, Zambonelli, Bonamico, Dessy, and Mariani[2]
Bis(dibutyldithiocarbamate)nickel(II)	16.1	16.4	2.198 ± 12	Arcovito, Colapietro, Torelli, and Vaciago[e]
Bis(dipropyldithiocarbamate)nickel(II)	16.3	16.0	2.203 ± 6	Peyronel and Pignedoli[9]

[a] From solution spectra. [b] From reflectance spectra. [c] Average value between the different Ni–S bond lengths in the molecule with the estimated errors. [d] Data reported by Jørgensen, 1962. The other data are from our experiments. [e] Personal communication.

corresponding ligand field strength, as indicated by the energy of the $\bar{\nu}_1$ transition. According to current views,[22] the particular spectrochemical position of a sulfur-containing ligand can be related to the particular electronic situation for a sulfur atom in a given ligand. This effect can be expressed as any of three approaches or as a combination of any or all of these. They are: (a) the difference between the σ-antibonding effect (which is probably relatively insensitive to change of ligand) and the π-antiboding effect; (b) the availability of the lone pairs of the sulfur atom [obviously, the greater the availability (*i.e.*, the smaller the C–S or P–S bond order) the greater will be the difference stated in (a)]; and (c) an increase of effective negative charge on sulfur (again an increase will be reflected in a larger coordinative π-antibonding effect).

Whichever of the three aspects of the bond structure is considered (increased π antibonding, increased repulsion among nonbonding lone pairs, or an increase of the effective charge which is reflected in a larger radius of the sulfur atom), it can be inferred that an increase of the metal–sulfur distance should correspond to a decrease of the ligand field strength and equally to a decrease of $\bar{\nu}_1$.

In order to confirm this correlation we have examined some complexes containing Ni–S bonds with the nickel atom in a square-planar configuration. The experimental data for the optical spectra and the Ni–S bond lengths, some of which were obtained from this investigation, are reported in Table VI.

The optical spectrum of bis(diphenyldithiophosphinato)nickel(II) has not previously been reported in the literature, except for a preliminary communication,[23] where the first spin-allowed d–d band was observed at 14.3 kK. A careful reexamination showed that this band occurs at 13.9 kK in toluene solution (14.1 kK in the reflectance spectrum); indeed, the diphenyldithiophosphinato ligand is remarkable for its extremely low spectrochemical position. The frequencies of $\bar{\nu}_1$ are quite similar in solution and in reflectance spectra; however, there is usually a small hypsochromatic shift in the latter case. Figure 3 reports data from solution spectra.

From the values shown in Table VI and in Figure 3 it can be seen that a relationship indeed exists between the two experimental parameters ($\bar{\nu}_1$ and Ni–S distance); moreover, a correlation can be seen between either of these two experimental quantities and the features of the electronic structure described above.

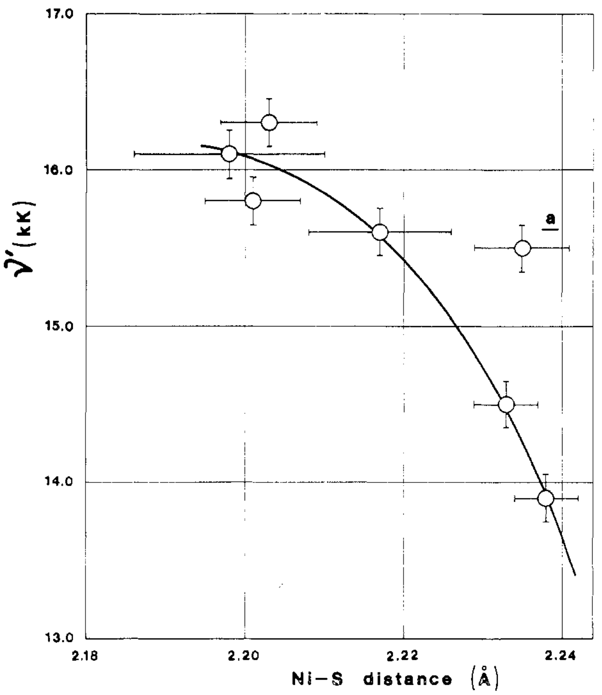

Figure 3.—First-band maxima (kK) *vs.* average values of Ni–S bond lengths for planar four-membered-ring Ni(II) complexes. Point a refers to bis(diethyldithioxanthate)nickel(II) which behaves anomalously (see text).

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[22] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

[23] V. Caglioti, G. Sartori, C. Furlani, E. Cervone, and P. Cancellieri, Proceedings of the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, 1966.

Perhaps the most useful correlation can be made with the negative charge of the sulfur atom. This might account also for the spectrochemical difference between bis(diethyldithiophosphato)nickel(II)[8] and bis(diphenyldithiophosphinato)nickel(II) since, in the former compound, one has the inductive effect of the oxygen which draws electrons from the sulfur atom. The only compound whose data do not fit the curve of Figure 3 well is bis(diethyldithioxanthate)nickel(II);[4] it should also be noted that the same compound behaves anomalously in that it has an unusually low spectrochemical position.

The C(1) and C(7) carbon atoms of the two phenyl groups bonded to the phosphorus atom (whose distances from the sulfur atoms are in agreement with the values reported in the literature for other similar compounds[8]) are in such position as to form with the sulfur atoms the slightly distorted tetrahedral configuration around phosphorus.

As reported in Table V other least-squares planes were calculated and these pass precisely through the carbon atoms of the phenyl groups, which are approximately planar. The maximum deviations from the planes are 0.026 and 0.07 Å for planes II and III, respectively. The standard deviations for the carbon parameters (Table II) are naturally higher than those of the heavier atoms, but, even so, the bond angles and distances within the phenyl groups are reasonable with an average C–C bond length of 1.38 ± 0.04 Å and bond angles equal to 120 ± 3°.

The dihedral angles (Table V) between planes I, II, and III are: 53° 49′ (between I and II), 89° 49′ (between I and III), and 74° 6′ (between II and III).

It is worth noting that very recently a paper[24] reported preliminary data of the crystal structure determination of a compound very similar to ours, the only difference being that the phenyl groups are methyl substituted. The configuration around the nickel atom in this compound has been found to be planar also and the average bond lengths and angles are in good agreement with those reported here.

(24) P. E. Jones, G. B. Ansell, and L. Katz, *Chem. Commun.*, **2**, 78 (1968)

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY,
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The Crystal and Molecular Structure of Tetraphenylarsonium Triiodo(triphenylphosphine)nickelate(II), $[(C_6H_5)_4As][Ni(C_6H_5)_3PI_3]$[1a]

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The structure of tetraphenylarsonium triiodo(triphenylphosphine)nickelate(II), $[(C_6H_5)_4As][Ni(C_6H_5)_3PI_3]$, has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, space group I2/c, with $a = 33.971 \pm 0.004$, $b = 14.992 \pm 0.002$, $c = 16.253 \pm 0.004$ Å, and $\beta = 92.06 \pm 0.05°$. For $Z = 8$ the measured and calculated densities are 1.73 ± 0.02 and 1.745 g/cm³, respectively. Counter data were collected for 2548 independent reflections by the stationary-crystal, stationary-counter technique. The structure was refined by least-squares methods to a conventional R value of 0.082. The pseudo-tetrahedral anion has approximately C_{3v} symmetry, excluding the phenyl groups, with an average Ni–I distance of 2.55 Å and an Ni–P distance of 2.28 Å. The tetraphenylarsonium ion is unremarkable (almost exactly tetrahedral angles at the arsenic atom) and possesses no over-all symmetry. Four nearest neighbor cations approach a given anion to within 6.6–8.0 Å (Ni–As distance). The proximity and mode of counterion approach is compared with earlier solution-state estimates based on pmr data.

Introduction

Not long ago in one of these laboratories it was discovered[2,3] that large proton chemical shifts occur for diamagnetic cations in the presence of certain paramagnetic anions as a result of a dipolar nucleus–unpaired electron interaction between ions in an ion pair. The phenomenon was first observed[2] in chloroform solutions of the tetra-*n*-butylammonium salts of the pseudo-tetrahedral anions $M(C_6H_5)_3PI_3^-$, M = Co, Ni. Such dipolar shifts (resonance frequency displacements from their diamagnetic positions) will generally occur when one of the ions in the ion pair exhibits significant magnetic anisotropy and there is a preferred relative orientation of the partners. Since the original discovery, such shifts have been observed[4-6] in a number of other systems where they are also related to ion association. The magnitude of the dipolar shift of a

(1) (a) This work was done at the Lawrence Radiation Laboratory and the University of California under the auspices of the U. S. Atomic Energy Commission and was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF 49-(638)-1492 and by the National Science Foundation through Grant GP 6321. (b) Princeton University. (c) University of California. (d) Lawrence Radiation Laboratory.

(2) G. N. LaMar, *J. Chem. Phys.*, **41**, 2992 (1964).

(3) G. N. LaMar, *ibid.*, **43**, 235 (1965).

(4) D. W. Larsen and A. C. Wahl, *Inorg. Chem.*, **4**, 1281 (1965).

(5) W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchison, and G. N. LaMar, *J. Am. Chem. Soc.*, **88**, 2436 (1966).

(6) G. N. LaMar, R. H. Fischer, and W. D. Horrocks, Jr., *Inorg. Chem.*, **6**, 1798 (1967).