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The Crystal and Molecular Structure of Diiodo[bis(*o*-methylthiophenyl)phenylphosphine]nickel(II), $Ni(C_{20}H_{19}PS_2)I_2$

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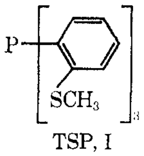
A three-dimensional X-ray structure determination of $Ni(DSP)I_2$ (DSP = bis(*o*-methylthiophenyl)phenylphosphine) is reported. The compound crystallizes in the space group D_{2h}^{15}-Pbca with eight formula units in a cell of dimensions a = 13.95 (2), b = 17.97 (2), and c = 18.12 (2) Å. The calculated density (1.95 g/cm^3) is in excellent agreement with the observed density of 1.95 ± 0.01 g/cm^3. Data were collected by the equiinclination Weissenberg technique and intensities were estimated visually. The structure has been refined by full-matrix least-squares methods to a final conventional R factor of 8.3% for 1100 observed reflections. The structure has discrete square-pyramidal $Ni(DSP)I_2$ molecules in which the phosphorus, one sulfur, and two iodine atoms form the basal plane and the other sulfur atom is the apex. This structure is unique among square-pyramidal complexes of the first transition series in that the central metal lies only slightly (0.09 Å) above the basal plane. The specific arrangement of donor atoms and the long Ni–S apical bond are interpreted in terms of maximum metal to ligand π-back-bonding and the *prolate* nature of the 3d-electron density along the z axis in a d^8 low-spin, square-pyramidal complex.

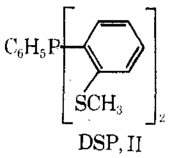
Introduction

As recently as 1964 only a few five-coordinate Ni(II) complexes were known,[1] and they all contained polydentate ligands with only arsenic or phosphorus donor atoms, which supposedly are capable of extensive π bonding. Since thioethers and selenoethers are generally thought to involve less π bonding than the corresponding phosphines and arsines, Meek and coworkers[2–6] prepared and investigated several series of tetradentate, tridentate, and bidentate ligands with $-SCH_3$ or $-SeCH_3$ groups to determine if these donor atoms could promote formation of low-spin, five-coordinate complexes.

These studies showed that the tetradentate ligands $P(o\text{-}C_6H_4SCH_3)_3$ (TSP, I)[2] and $P(o\text{-}C_6H_4SeCH_3)_3$ (TSeP)[3] form crystalline five-coordinate nickel(II) complexes of the types $Ni(Lig)X^+$ (X = I, Br, Cl, and NCS) and $Ni(Lig)L^{2+}$ (L = thiourea, ethylenethiourea, and triphenylphosphine). Both series of diamagnetic complexes were assigned trigonal-bipyramidal structures on the basis of the electronic spectral similarity with the known trigonal-bipyramidal nickel(II) complex, $[Ni(TAP)CN]ClO_4$ (TAP = $P[CH_2CH_2CH_2As(CH_3)_2]_3$).[7] The trigonal-bipyramidal structure of $[Ni(TSP)Cl]ClO_4$ has recently been confirmed by X-ray crystallography.[8]



TSP, I



DSP, II

Workman, *et al.*,[5] found that the similar tridentate ligand bis(*o*-methylthiophenyl)phenylphosphine (DSP, II) forms monomeric, five-coordinate $Ni(DSP)X_2$ complexes and that the electronic absorption spectra of the latter series are significantly different from those of the trigonal-bipyramidal $Ni(TSP)X^+$ series.[2] The other limiting five-coordinate geometry to consider is the square pyramid; however, the electronic spectra did not agree well with a simple one-electron, d-orbital energy diagram for a C_{4v} arrangement of donor atoms around nickel.[5] Especially since there was no known regular square-pyramidal nickel(II) complex with which one could compare the spectral assignment, we undertook an X-ray study on $Ni(DSP)I_2$ to verify the coordination number and to determine the stereochemistry around nickel. This paper reports the results of this study and confirms that $Ni(DSP)I_2$ exists as discrete square-pyramidal molecules in the crystal.

Determination of the Unit Cell and Collection of Intensity Data

The complex $Ni(DSP)I_2$ was prepared and recrystallized from dichloromethane as described previously.[5] The analyses (performed by Galbraith Laboratories, Knoxville, Tenn.) were consistent with this formulation, and the molecular weight data (calcd, 667; found 665) showed that the compound is monomeric in chloroform solutions. Opaque rods with the principal faces being {010}, {011}, {012}, and {110} were grown from dichloromethane. Preliminary precession photographs taken with Cu Kα radiation showed mmm symmetry with systematic absences: 0kl, $k \neq 2n$; h0l, $l \neq 2n$; hk0, $h \neq 2n$. These absences are consistent with the space group D_{2h}^{15}-Pbca.

The unit cell dimensions, obtained with Cu Kα (λ 1.5418 Å) and Mo Kα (λ 0.7107 Å) radiation at 22°, are a = 13.95 (2), b = 17.97 (2), and c = 18.12 (2) Å, where the errors are estimates from repeated measurements. The observed density, 1.95 ± 0.01 g/cm^3 (obtained by flotation in a methyl iodide–Freon 113 mixture), is in excellent agreement with the density of 1.95 g/cm^3 cal-

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[1] J. A. Ibers, *Ann. Rev. Phys.*, **16**, 380 (1965).
[2] G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965).
[3] G. Dyer and D. W. Meek, *ibid.*, **6**, 149 (1967).
[4] G. Dyer, M. O. Workman, and D. W. Meek, *ibid.*, **6**, 1404 (1967).
[5] M. O. Workman, G. Dyer, and D. W. Meek, *ibid.*, **6**, 1543 (1967).
[6] G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967).
[7] D. L. Stevenson and L. F. Dahl, *ibid.*, **89**, 3424 (1967).
[8] L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, **8**, 1072 (1969).

culated for a formula weight of 667, $Z = 8$, and a unit cell volume of 4542 Å^3.

A crystal of approximate dimensions of 0.32 × 0.15 × 0.21 mm was chosen for intensity measurements and was mounted on a glass fiber with the column length and the a axis parallel to the spindle axis of the instrument. The data (layers of $0kl$–$12kl$ inclusive) were collected on a Nonius integrating Weissenberg camera using Mo Kα, Zr-filtered radiation and the equiinclination technique. The intensities of 1597 independent, nonzero reflections were estimated visually and corrected for Lorentz and polarization effects. The linear absorption coefficient for Mo Kα radiation is 38.52 cm^{-1}, so a further correction was made for absorption.[9] The transmission coefficients were found to vary from 0.40 to 0.60.

Solution and Refinement of the Structure

With eight molecules per unit cell and no molecular symmetry imposed by the crystallographic symmetry, all atoms occupy general positions. The nickel and both iodine atoms were located from the three-dimensional map of the Patterson function. A subsequent least-squares refinement of these atomic positions followed by a difference Fourier synthesis disclosed the location of the other three donor atoms. At this stage the phosphorus atom could not be differentiated from the sulfur atoms. The positional parameters of all six heavy atoms were refined, and after a difference Fourier synthesis, most of the carbon atoms in the phenyl rings were located. From the nature of the ligand, the phosphorus atom could then be assigned.

The structure was then solved by conventional least-squares and Fourier calculations. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively. The atomic scattering factors used were those tabulated by Ibers[10] for S, P, and C, those of Cromer and Waber[11] for Ni and I, and those of Stewart, *et al.*,[12] for H. The effects of anomalous dispersion were included in the calculated structure factors.[13] The values of $\Delta f'$ and $\Delta f''$ for Ni, I, S, and P were those reported by Cromer.[14]

Five cycles of full-matrix, least-squares refinement of the atomic positions and individual isotropic thermal parameters for the 6 heavy atoms plus 17 of 18 phenyl carbon atoms converged to values of R_1 and R_2 of 17.0 and 19.6% where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (or weighted R factor) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ with unit weights on all reflections. Separate scale factors, determined by least-squares analysis, were applied to the 13 layers of data.

After the intensity data were corrected for absorption, additional refinements were carried out in which the three phenyl rings were treated as rigid groups. Only the most reliable reflections (1103 in number), *i.e.*, those with observed intensity (I_o) values larger than three times the minimum readable I_o values (5), were used in the final refinements along with the weighting scheme: $\sqrt{w} = 4.0F_o/I_o$ for $15 < I_o < 40$; $\sqrt{w} = 0.1F_o$ for $I_o > 40$. The 1597 observed intensity values ranged from 5 to 960. A difference Fourier map revealed the positions of the two methyl carbon atoms and gave evidence of anisotropic thermal motion in the regions of the nickel and iodine atoms. Thus all atoms in the structure except the hydrogens were located. A least-squares refinement still involving individual isotropic thermal parameters led to values of 15.4 and 18.6% for R_1 and R_2, respectively. A subsequent refinement in which anisotropic thermal parameters were assigned to the nickel and iodine atoms showed marked improvement with R_1 and R_2 values of 10.3 and 12.8%. At this point an examination of the calculated and observed structure amplitudes for intense reflections indicated that extinction effects were important. One additional cycle of least-squares refinement with a variable extinction coefficient led to values of 8.8 and 11.0% for R_1 and R_2. The positions of the 13 phenyl hydrogen atoms were then calculated (C–H = 1.084 Å)[15] and their contributions to F_c were included in subsequent calculations. One least-squares cycle led to values of 8.5 and 10.6% for R_1 and R_2, respectively. Three reflections, which were obvious indexing errors, were removed and a final full-matrix least-squares refinement with 1100 observed reflections, 82 variables, anisotropic thermal parameters for the nickel and iodine atoms, and a variable extinction coefficient produced values of 8.3 and 10.2% for R_1 and R_2. The value of the extinction coefficient on an absolute scale is $(6.0 \pm 0.6) \times 10^{-6}$. The shifts of the variable parameters in the final cycle were all less than one-sixth of their respective standard deviations. A final difference Fourier map revealed no spurious detail to which any chemical significance could be ascribed; the maximum residual was 0.85 e$^-$ Å^{-3}. On the same scale a carbon atom had a height of ~3.7 e$^-$ Å^{-3}.

The final values of F_o and F_c (in electrons) are given in Table I; only the 1100 reflections that were used in the last refinement are listed. The final positional, thermal, and group parameters, along with the associated standard deviations in these parameters, are presented in Table II. The positional parameters of the phenyl carbon atoms, which may be derived from the data in Table II, are presented in Table III.

Description of the Structure

The interatomic distances and angles of Ni(DSP)I$_2$ are given in Table IV, and the geometries of the inner

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(9) In addition to various Northwestern computing programs for the CDC 3400 and 6400 computers, the programs used in the refinement of this structure were local modifications of Burnham's GNABS absorption correction program, Busing and Levy's ORFFE function and error program, Johnson's ORTEP thermal ellipsoid plotting program, and Zalkin's FORDAP Fourier program.

(10) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

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

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

(13) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 787 (1964).

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

(15) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965, p S18s.

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $Ni(DSP)I_2$

K	L	FO	FC
***** H = 0 *****			
0	8	273	232
0	10	83	76
0	12	301	319
0	14	216	229
0	16	118	135
0	18	197	226
0	20	180	227
2	4	260	235
2	5	115	90
2	6	95	87
2	7	334	317
2	8	101	95
2	9	436	426
2	11	335	345
2	13	173	159
2	14	99	91
2	15	103	106
2	20	120	110
4	3	55	56
4	4	340	308
4	5	79	75
4	6	63	63
4	7	214	209
4	8	114	99
4	9	352	345
4	11	228	233
4	12	100	97
4	13	218	221
4	14	102	84
4	16	108	97
6	0	238	236
6	1	105	121
6	2	196	176
6	3	256	286
6	4	285	265
6	5	63	47
6	6	156	166
6	7	70	55
6	8	127	135
6	9	79	69
6	11	149	149
6	12	145	145
8	0	135	133
8	1	94	86
8	2	110	103
8	3	369	356
8	5	271	313
8	6	200	188
8	7	113	99
8	8	78	67
8	13	109	118
8	15	119	125
8	17	143	153
10	0	70	58
10	1	70	66
10	2	107	130
10	3	368	366
10	4	141	154
10	5	183	223
10	6	250	281
10	8	193	182
10	9	86	87
10	10	90	80
10	12	165	173
10	13	152	130
10	14	158	152
10	15	164	157
10	16	113	111
10	17	174	162
12	0	121	121
12	3	114	114
12	4	176	184
12	5	124	136
12	6	191	185
12	8	134	139
12	12	159	166
12	14	108	105
14	3	96	92
14	6	91	72
14	7	140	126
16	0	103	85
16	3	94	94
18	0	135	124
20	1	108	90
***** H = 1 *****			
0	8	479	432
0	10	598	570
0	12	244	238
0	14	99	73
0	16	157	171
1	5	289	237
1	6	138	140
1	8	174	174
1	12	92	74
1	14	125	121
1	16	106	92
2	5	84	45
2	6	78	69
2	7	268	260
2	8	250	260
2	9	80	54
2	10	153	143
2	11	117	92
2	12	131	137
2	13	184	162
2	14	100	74
2	17	110	141
2	19	117	125
3	4	268	282
3	5	252	256
3	6	84	69
3	7	225	229
3	8	175	180
3	9	126	137
3	10	139	134
3	11	125	98
3	13	138	127
3	15	104	94
3	16	107	106
4	2	115	125
4	3	270	287
4	4	53	52
4	5	86	82
4	6	124	124
4	7	105	112
4	8	108	98
4	9	78	52
4	10	83	62
5	2	73	69
5	3	112	105
5	4	151	183
5	5	121	141
5	6	147	152
5	7	147	176
5	8	118	124
5	9	97	95
5	10	111	112
5	12	142	138
6	1	77	86
6	2	151	149
6	4	154	159
6	5	78	83
6	6	67	46
6	7	95	77
6	8	159	153
6	9	117	106
6	12	114	99
6	13	130	127
6	14	150	139
7	1	315	330
7	2	85	80
7	3	60	41
7	4	84	79
7	5	101	89
7	6	85	81
7	7	151	162
7	8	113	119
7	10	84	79
7	12	87	64
7	13	97	84
8	1	92	87
8	4	98	107
8	5	234	281
8	7	194	208
8	8	78	68
8	11	130	120
8	13	163	183
8	15	120	105
9	1	161	148
9	2	75	66
9	3	117	140
9	4	70	56
9	5	102	102
9	8	81	62
9	10	109	88
10	1	101	90
10	2	130	145
10	4	265	328
10	5	235	267
10	6	87	91
10	7	175	215
10	8	103	101
10	10	111	109
10	11	87	84
10	13	125	120
10	16	113	111
11	1	109	106
11	8	127	104
12	2	130	139
12	3	79	79
12	4	179	198
12	5	82	96
12	10	95	91
12	14	109	90
13	2	82	86
13	8	114	103
13	10	141	119
13	12	104	86
15	1	100	80
16	8	102	81
***** H = 2 *****			
0	8	207	182
0	12	209	217
0	14	86	100
1	6	352	357
1	7	184	161
1	8	222	211
1	9	236	245
1	10	111	106
1	11	111	85
1	12	171	203
1	14	156	161
1	16	134	156
2	5	165	156
2	6	163	146
2	9	155	162
2	11	161	145
2	13	84	78
2	15	130	113
3	4	178	178
3	5	308	328
3	7	154	181
3	8	157	166
3	9	89	70
3	10	63	47
3	12	82	97
3	13	162	161
3	14	115	91
3	15	143	153
3	17	146	167
3	18	86	90
4	3	53	45
4	5	73	76
4	6	138	159
5	0	496	405
5	1	99	96
5	2	250	246
5	3	332	336
5	4	195	196
5	5	175	195
5	6	136	146
5	7	79	66
5	8	64	62
5	9	68	70
5	11	76	68
5	15	115	119
5	16	96	115
5	17	143	169
6	0	70	71
6	2	101	95
6	4	52	36
6	5	79	70
6	6	58	45
6	7	89	85
6	12	116	96
7	0	149	167
7	1	228	238
7	2	67	64
7	3	152	164
7	4	233	236
7	5	122	129
7	6	68	76
7	7	177	174
7	8	100	101
7	9	316	329
7	10	107	98
7	11	194	222
7	12	81	62
7	14	76	60
7	15	104	104
7	16	96	75
8	1	98	103
8	2	83	78
8	3	222	204
8	5	74	60
8	6	116	129
8	7	65	47
8	9	141	138
8	10	84	79
8	11	113	100
9	0	195	196
9	1	58	55
9	2	88	91
9	3	59	51
9	4	61	52
9	6	151	175
9	7	147	147
9	8	153	167
9	9	177	194
9	11	130	133
9	13	136	166
10	0	103	94
10	2	108	108
10	3	130	105
10	4	72	73
10	5	95	84
10	6	122	134
10	7	70	58
10	8	82	57
10	9	85	79
10	11	82	77
11	0	235	260
11	2	81	76
11	3	91	84
11	4	128	124
11	9	112	116
11	11	84	92
12	0	118	135
12	2	68	58
12	5	72	47
12	6	73	51
12	8	78	68
12	12	89	79
13	0	280	296
13	2	152	146
13	3	100	86
13	6	94	95
13	7	67	44
13	8	80	78
13	12	131	130
13	14	97	95
14	3	76	49
15	1	78	66
15	2	67	57
15	6	82	61
15	9	115	88
15	11	93	82
17	3	105	76
17	9	94	58
17	12	86	80
18	0	87	80
19	3	91	66
***** H = 3 *****			
0	10	89	98
0	12	155	168
0	14	131	131
0	16	99	116
1	6	198	162
1	8	100	100
1	9	93	90
1	10	130	124
1	14	112	117
1	16	94	105
2	5	286	232
2	7	140	127
2	8	128	114
2	10	162	140
2	11	83	86
2	12	96	96
2	13	100	98
3	4	511	317
3	5	338	286
3	6	44	45
3	7	200	189
3	8	268	227
3	9	111	108
3	10	157	172
3	11	89	100
3	12	66	74
3	13	137	146
3	15	123	130
3	16	153	166
4	2	243	234
4	3	79	75
4	4	318	279
4	5	157	153
4	9	62	43
4	10	66	55
4	14	108	107
4	15	88	71
4	16	128	130
5	1	184	184
5	2	154	151
5	3	36	32
5	4	102	115
5	5	289	282
5	7	296	303
5	8	150	165
5	9	141	149
5	10	183	187
5	11	115	102
5	12	130	130
5	13	166	169
5	15	99	114
6	1	202	196
6	2	51	53
6	5	95	101
6	6	94	93
6	7	156	159
6	8	196	216
6	10	170	187
6	11	99	109
6	12	158	166
6	13	137	139
6	15	118	102
7	1	343	342
7	2	89	98
7	4	89	87
7	5	93	93
7	6	85	90
7	7	220	243
7	8	90	98
7	9	114	114
7	11	68	64
7	13	138	142
7	14	95	96
8	1	203	196
8	2	59	48
8	3	76	81
8	4	51	59
8	5	101	103
8	7	95	88
8	8	111	113
8	10	97	92
8	17	97	88
8	19	86	77
9	1	178	180
9	2	88	103
9	3	96	109
9	4	120	116
9	5	55	51
9	6	62	62
9	7	72	79
9	8	102	110
9	10	120	124
9	12	68	69
9	16	90	87
10	1	99	98
10	2	50	56
10	3	94	86
10	5	95	81
10	8	152	154
11	1	133	128
11	7	69	66
11	8	118	110
11	10	86	68
11	11	85	73
11	12	92	95
12	4	67	40
12	7	80	84
12	8	92	90
13	2	157	163
13	4	87	95
13	5	71	70
13	8	95	103
13	10	154	161
13	12	87	89
14	1	86	83
14	4	88	90
14	8	79	71
15	1	112	101
15	2	75	69
15	4	129	131
15	8	82	63
16	1	77	65
16	5	85	69
16	7	93	85
17	1	68	55
17	2	67	50
17	5	69	63
17	7	71	62
***** H = 4 *****			
0	10	84	65
0	18	110	101
1	6	88	63
1	11	106	92
1	12	95	87
2	5	109	99
2	6	65	56
2	7	184	179
2	8	61	60
2	9	227	220
2	11	122	118
2	13	211	219
2	14	97	75
3	4	72	73
3	6	277	262
3	7	63	51
3	8	164	164
3	10	69	71
3	12	85	86
3	14	141	132
3	18	111	100
4	3	133	140
4	4	301	268
4	5	86	80
4	6	334	332
4	7	149	154
4	8	143	159
4	9	286	287
4	11	209	221
4	12	207	231
4	13	155	174
4	14	156	164
5	0	256	219
5	1	95	104
5	3	344	302
5	4	134	135
5	5	174	170
5	7	107	102
5	8	86	86
5	9	226	234
5	11	122	124
5	12	99	95
5	15	109	101
6	0	416	403
6	1	103	114
6	2	257	258
6	3	319	307
6	4	108	124
6	5	278	269
6	7	91	93
6	9	180	201
6	11	140	149
6	16	89	92
6	17	107	[illegible]
6	18	94	99
7	0	193	199
7	1	177	185
7	2	107	118
7	3	163	166
7	4	85	88
7	9	96	91
7	11	137	124
7	12	95	92
7	15	103	95
8	0	119	132
8	2	200	187
8	3	139	142
8	5	170	182
8	7	111	110
8	9	131	133
8	10	83	75
8	13	95	70
9	0	79	83
9	2	65	60
9	5	108	102
10	3	134	129
10	4	75	79
10	5	77	69
10	6	93	86
10	7	66	57
10	12	78	70
10	13	81	80
10	14	84	70
10	15	88	79
10	16	91	92
11	3	62	76
11	6	83	85
12	4	97	94
12	6	118	124
12	12	82	70
13	0	130	145
13	4	81	70
13	8	86	89
13	9	88	64
14	0	87	75
14	4	72	68
14	6	144	143
14	8	97	93
15	2	83	82
15	6	132	127
15	8	95	82
16	0	111	111
16	3	131	155
16	5	77	66
17	3	91	68
***** H = 5 *****			
0	8	286	263
0	10	261	241
0	12	229	229
1	5	228	208
1	6	152	133
1	7	119	100
1	8	126	113
1	10	107	105
1	12	143	143
1	14	109	103
2	4	101	101
2	5	146	126
2	6	81	69
2	7	75	67
2	8	194	180
2	10	193	187
2	12	107	122
3	4	169	169
3	5	273	255
3	6	72	69
3	7	132	120
3	8	127	132
3	9	116	106
3	10	86	84
3	11	85	75
3	13	100	90
4	2	206	224
4	3	94	108
4	4	372	338
4	6	69	58
4	7	176	183
4	10	183	177
4	13	145	145
4	14	105	106
4	16	96	107
5	1	186	190
5	2	236	219
5	3	180	192
5	4	122	135
5	5	93	90
5	6	129	136
5	7	61	64
5	8	102	107
5	11	135	121
5	13	100	104
5	14	129	140
6	1	253	246
6	4	61	56
6	5	215	230
6	7	232	266
6	8	139	160
6	9	101	100
6	10	91	89
6	11	147	157
6	12	95	91
6	13	150	184
6	15	109	92
7	2	109	114
7	3	94	102
7	5	58	64
7	6	61	60
7	8	157	159
7	10	208	211
7	12	113	111
8	2	106	92
8	4	69	51
8	5	157	155
8	9	95	111
8	10	119	116
8	12	91	86
8	13	101	108
9	1	173	162
9	3	70	50
9	5	74	75
9	7	90	98
10	4	155	170
10	5	126	134
10	7	88	89
10	10	79	78
11	2	77	72
11	3	83	82
11	4	80	64
11	6	89	79
11	8	76	67
11	10	81	77
12	2	100	99
12	4	135	138
12	10	83	77
13	1	113	124
13	2	79	88
13	8	95	86
14	2	110	112
14	4	122	116
14	8	92	79
15	8	95	84
***** H = 6 *****			
0	6	176	157
0	8	155	139
0	10	81	63
0	12	99	64
0	14	119	104
1	5	176	157
1	6	364	296
1	7	72	65
1	8	156	144
1	11	105	94
1	12	150	156
1	14	108	115
1	16	103	106
2	4	138	124
2	5	77	69
2	6	355	305
2	8	166	158
2	10	69	44
2	14	102	99
3	5	216	216
3	6	51	47
3	7	152	147
3	10	85	72
3	13	152	155
3	15	157	164
3	17	107	100
4	2	117	123
4	3	208	225
4	5	185	185
4	6	65	80
4	8	94	87
4	9	122	127
4	12	100	104
4	15	113	113
4	17	114	106
5	0	111	128
5	2	137	146
5	4	214	218
5	6	102	97
5	7	116	114
5	8	75	66
5	9	150	143
5	12	145	134
6	0	90	98
6	1	129	143
6	2	71	78
6	3	260	256
6	5	138	149
6	9	160	155
6	11	127	126
6	15	102	99
6	17	92	100
7	0	324	295
7	2	145	154
7	4	57	47
7	7	140	143
7	9	155	162
7	11	86	76
7	16	89	93
8	0	97	114
8	1	60	54
8	3	121	127
8	4	105	102
8	7	72	61
8	8	80	77
8	9	74	68
8	11	125	122
9	0	120	130
9	1	112	132
9	6	104	100
9	7	80	93
9	8	97	103
9	9	185	193
9	11	144	151
10	2	73	76
10	6	122	134
10	9	89	94
10	11	76	79
11	0	242	236
11	2	117	111
11	8	83	77
12	0	122	121
12	2	71	71
12	3	77	81
13	0	105	102
13	2	79	82
13	7	87	67
13	9	113	115
14	0	134	123
14	2	88	87
14	6	93	91
14	8	97	93
***** H = 7 *****			
0	6	182	160
0	8	209	202
0	10	96	91
0	14	160	155
1	5	134	139
1	6	94	95
1	7	136	122
1	10	146	141
1	14	101	95
1	16	138	129
2	4	217	197
2	5	80	76
2	6	110	98
2	7	108	92
2	16	124	114
3	5	302	286
3	7	141	128
3	9	131	126
3	11	154	152
3	13	195	187
3	15	95	86
4	3	83	87
4	5	194	196
4	6	73	66
4	7	185	186
4	8	89	87
4	9	71	58
4	0	145	138
4	3	99	98
5	1	53	43
5	4	51	48
5	8	119	120
5	9	71	75
6	1	84	80
6	4	63	51
6	5	67	69
6	6	105	106
6	7	64	74
6	8	131	143
6	9	102	100
6	10	137	146
6	12	119	109
7	1	175	191
7	2	72	85
7	5	60	57
7	7	164	185
7	8	128	145
8	1	182	204
8	2	85	90
8	3	113	108
9	1	221	251
9	2	73	69
9	4	64	70
9	7	136	152
9	8	74	87
9	11	83	81
9	13	105	106
10	1	95	102
10	3	83	80
10	5	69	53
10	8	76	68
11	2	131	129
11	4	82	68
11	8	135	133
11	10	134	149
11	12	105	103
12	1	82	84
12	10	109	116
13	1	74	75
13	2	95	91
13	7	98	84
13	8	100	94
***** H = 8 *****			
0	18	113	97
1	5	132	114
1	6	237	212
1	7	90	83
1	8	115	99
1	9	192	173
1	11	98	89
1	12	173	182
1	14	106	104
2	4	91	88
2	5	88	84
2	6	144	129
2	7	146	138
2	9	175	181
2	11	75	65
2	13	148	134
3	3	178	177
3	5	61	49
3	7	88	83
3	8	78	74
3	9	135	137
3	11	180	179
4	1	72	71
4	2	54	66
4	3	120	113
4	4	89	89
4	5	101	102
4	6	67	57
4	7	68	59
4	9	105	105
4	11	143	150
5	0	48	42
5	2	57	59
5	3	87	87
5	6	77	71
5	9	83	70
5	11	75	76
6	0	286	268
6	2	95	108
6	3	71	67
6	4	118	129
6	5	67	74
6	16	109	85
7	1	65	63
7	3	120	141
7	4	59	73
7	5	96	101
7	6	107	110
7	8	77	74
7	9	86	75
7	17	98	77
8	2	63	49
8	3	55	48
8	4	79	73
8	7	123	125
8	8	67	47
8	9	119	124
8	11	77	65
9	0	108	105
9	1	156	159
9	3	166	189
9	5	118	132
9	6	64	61
9	9	122	124
9	11	91	83
9	15	127	129
10	4	110	115
10	12	103	99
11	0	158	179
11	2	80	77
11	4	87	89
11	6	153	165
11	8	116	112
11	12	111	110
11	14	92	100
12	0	105	114
12	3	68	69
12	4	69	62
13	0	70	55
13	1	70	55
13	6	88	83
13	8	79	67
***** H = 9 *****			
0	8	219	205
0	10	96	92
0	12	80	86
0	16	111	100
1	7	131	108
1	8	241	235
1	10	270	273
1	11	91	78
1	12	155	156
1	13	81	58
2	7	92	78
2	10	72	64
2	12	78	70
3	3	144	169
3	5	63	54
4	2	70	65
4	4	128	144
4	9	86	76
4	10	73	61
4	13	83	59
5	1	109	122
5	2	65	66
5	3	91	94
5	4	101	113
5	6	110	108
5	8	81	69
5	10	71	57
5	12	78	69
6	1	51	48
6	2	61	54
6	3	66	71
6	4	51	52
6	5	124	129
6	7	127	140
6	8	83	73
6	10	71	63
7	2	95	101
7	4	95	95
7	5	73	66
7	6	90	77
7	7	94	90
7	10	72	52
7	14	87	82
8	4	90	89
9	1	86	87
9	3	92	86
9	5	166	191
9	7	179	187
9	11	95	89
9	13	123	129
10	2	78	69
10	4	95	86
10	10	77	47
11	2	134	148
11	4	172	162
11	6	85	78
11	14	91	89
12	4	89	88
***** H = 10 *****			
0	6	168	172
0	8	124	101
1	4	76	62
1	7	116	109
1	9	152	141
1	11	125	100
2	4	119	123
2	6	147	141
2	8	143	126
2	12	77	77
3	3	69	65
3	7	143	141
3	9	131	172
3	11	112	108
3	13	81	81
4	0	102	127
4	1	162	170
4	2	78	79
4	3	109	111
4	5	87	72
4	7	58	42
4	8	62	54
4	12	78	62
4	15	102	102
5	0	86	93
5	2	78	85
5	4	96	89
5	5	60	47
5	12	78	75
6	0	45	34
6	2	107	116
6	3	143	160
6	5	118	122
6	9	109	109
6	17	96	86
7	3	67	71
7	4	91	89
7	6	117	117
7	7	64	65
7	8	65	67
8	3	109	124
8	6	111	117
8	9	90	82
8	11	119	116
9	1	66	62
9	3	139	157
9	5	122	142
10	0	62	72
10	2	78	64
10	11	79	64
11	4	84	88
11	6	121	120
11	12	84	89
12	0	68	68
12	2	104	96
14	0	98	85
14	6	77	70
***** H = 11 *****			
0	6	132	143
0	8	78	63
0	10	98	88
0	16	96	97
1	7	63	57
1	8	67	61
2	4	174	167
2	5	81	81
2	6	89	79
2	7	89	88
2	10	99	80
2	14	104	94
3	4	47	43
3	5	68	56
3	10	88	71
4	3	95	103
4	5	141	144
4	7	142	140
4	8	87	82
4	9	102	87
4	10	108	107
4	13	102	102
5	1	65	64
5	5	93	87
5	7	63	58
5	8	97	94
5	13	88	71
6	1	77	77
6	5	97	101
6	6	80	80
6	7	129	151
6	8	107	116
6	10	88	84
7	1	62	55
7	2	54	48
7	4	97	100
7	7	87	73
8	1	151	168
8	3	59	68
8	4	109	116
9	5	87	82
10	1	75	78
11	4	71	65
***** H = 12 *****			
0	16	96	92
2	5	57	59
2	6	102	91
2	7	72	66
2	8	96	79
2	9	120	129
2	11	79	76
2	12	108	86
3	5	53	43
3	6	83	73
3	8	87	65
3	11	104	92
3	12	84	82
4	3	105	124
4	5	96	79
4	7	73	54
5	1	59	59
5	3	113	127
5	5	73	63
5	6	86	83
5	7	64	54
5	9	121	109
5	11	115	112
6	0	93	106
6	2	79	93
6	3	83	89
6	4	72	76
6	9	73	77
7	0	112	118
7	2	97	93
7	5	88	81
8	6	87	92
8	9	99	103
9	0	61	46
9	7	72	58
12	0	72	68
12	3	74	70
13	6	81	76

TABLE II

FINAL ATOMIC, THERMAL, AND GROUP PARAMETERS FOR $Ni(DSP)I_2$

Atom[a]	x	y	z	$10^4\beta_{11}$ or B	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
I_1	0.34515 (18)	0.21113 (13)	0.07498 (13)	53 (4)[b]	36 (1)	20 (1)	−15 (1)	−3 (1)	7 (1)
I_2	0.11774 (19)	0.16544 (17)	−0.02403 (14)	44 (4)[b]	70 (1)	24 (1)	−11 (1)	−11 (1)	20 (1)
Ni	0.21947 (28)	0.11105 (21)	0.08097 (23)	32 (4)[b]	29 (2)	11 (1)	−3 (2)	−2 (2)	−1 (1)
S_1	0.14040 (60)	0.16026 (48)	0.21362 (50)	3.30 (22)[c]					
S_2	0.12094 (60)	0.01627 (42)	0.08228 (48)	2.85 (20)[c]					
P	0.30411 (56)	0.05690 (44)	0.16193 (47)	2.03 (20)[c]					
C_1	0.1121 (40)	0.2605 (24)	0.2054 (27)	7.2 (12)[c]					
C_2	0.1579 (33)	−0.0459 (22)	0.0031 (22)	5.3 (9)[c]					

Group[d]	x_c	y_c	z_c	δ	ϵ	η	Group B[e]
Ph_1	0.3288 (10)	0.1504 (6)	0.3126 (7)	−1.999 (13)	−2.975 (11)	2.100 (12)	2.49 (30)
Ph_2	0.3208 (11)	0.4197 (8)	0.2213 (8)	−1.318 (18)	2.290 (13)	0.472 (20)	3.55 (33)
Ph_3	0.5021 (13)	−0.0142 (8)	0.1037 (8)	−0.519 (13)	−2.932 (13)	−0.422 (16)	3.80 (35)

[a] x, y, and z are the fractional coordinates. The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The standard deviations of the least significant digits reported are given in parentheses. [b] The $10^4\beta_{11}$ values for the three atoms that were refined with anisotropic thermal parameters. The root-mean-square amplitudes of vibration along the principal thermal ellipsoid axes 1, 2, and 3, respectively, are: I_1, 0.1696 (47), 0.1966 (69), 0.2769 (43); I_2, 0.1531 (56), 0.2094 (78), 0.3623 (38); Ni, 0.1306 (87), 0.177 (12), 0.2202 (66). [c] Isotropic temperature factor in Å², with the corresponding standard deviations in parentheses. [d] x_c, y_c, and z_c are the fractional coordinates of the center of the group. The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the group with a fixed external coordinate system are those described previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). [e] Group B is the isotropic thermal parameter for the entire phenyl group.

coordination sphere and of the complete molecule are illustrated in Figures 1 and 2, respectively. Two significant points are readily apparent. First, the structure consists of discrete square-pyramidal $Ni(DSP)I_2$ molecules in which the phosphorus, one sulfur, and two iodine atoms form the basal plane and the second sulfur donor is the apex atom. Second, the apical nickel–sulfur bond is significantly longer (0.60 (1) Å) than the one in the basal plane.

The nickel atom is displaced 0.09 Å toward the apex

TABLE III

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a,b]

	x	y	z
		Ph_1	
C_1	0.3208 (15)	0.1101 (10)	0.2469 (9)
C_2	0.2470 (11)	0.1579 (11)	0.2686 (10)
C_3	0.2550 (13)	0.1982 (10)	0.3343 (11)
C_4	0.3367 (16)	0.1908 (10)	0.3782 (9)
C_5	0.4105 (12)	0.1430 (11)	0.3565 (10)
C_6	0.4026 (13)	0.1027 (11)	0.2909 (11)
		Ph_2[c]	
C_1	0.2347 (21)	−0.0199 (14)	0.1982 (13)
C_2	0.2622 (14)	−0.0612 (15)	0.2600 (12)
C_3	0.2067 (19)	−0.1216 (10)	0.2831 (10)
C_4	0.1237 (21)	−0.1407 (14)	0.2444 (12)
C_5	0.0961 (15)	−0.0994 (15)	0.1826 (12)
C_6	0.1516 (19)	−0.0390 (10)	0.1595 (10)
		Ph_3	
C_1	0.4185 (14)	0.0152 (13)	0.1347 (14)
C_2	0.4183 (15)	−0.0567 (12)	0.1053 (13)
C_3	0.5018 (18)	−0.0861 (9)	0.0744 (13)
C_4	0.5856 (15)	−0.0436 (13)	0.0728 (14)
C_5	0.5859 (14)	0.0283 (12)	0.1022 (14)
C_6	0.5024 (17)	0.0577 (9)	0.1331 (13)

[a] See Figure 2 for the numbering scheme of the atoms. [b] The estimated standard deviations are derived from those of the group parameters. Intra-ring C–C distance is 1.397 Å. [c] The parameters for the C atoms of Ph_2 given here are related to those which may be derived from the data of Table II by the transformation $^1/_2 - x, {}^1/_2 + y, z$.

sulfur atom from the best least-squares plane through the other four donor atoms. The equation for the basal plane through I_1, I_2, S_2, and P is $7.28x - 8.92y - 12.57z = -0.31$ (orthorhombic coordinates) and the deviations of these four atoms from the plane are 0.001 (2), −0.002 (3), 0.016 (8), and −0.015 (8) Å, respectively.

The apical sulfur atom is distorted somewhat from its idealized square-pyramidal apex position, owing to the short bridging distance of the *o*-phenylene linkage. The I_2–Ni–S_1 and the S_1–Ni–P angles of 107.4 (3) and 76.7 (3)°, respectively, show that the S_1 atom is pulled toward the phosphorus position, as compared with an apex position perpendicular to the basal plane.

The orientations of the thermal ellipsoids for the nickel and iodine atoms are illustrated in Figure 1, and the root-mean-square amplitudes of vibration along the principal axes are given in Table II, footnote *b*. If a correction for the effects of independent thermal motion is applied, the difference between the Ni–I_1 and Ni–I_2 bond lengths remains essentially the same as given in Table III.

The possibility that an *o*-hydrogen atom of the ligand may occupy the sixth coordination site of the complex must be examined. Such an effect has been demonstrated in the cases of $Ru(P(C_6H_5)_3)_3Cl_2$[16] and polymeric $Pd(PC_6H_5(CH_3)_2)_2I_2$.[17] In the case of Ni(DSP)I_2, no phenyl or methyl hydrogen atoms are closer to nickel than 3.5 Å so a hydrogen atom does not block the sixth coordination position.

Discussion

Insofar as we are aware, Ni(DSP)I_2 is the only square-pyramidal complex of the first transition series that has the metal atom so close to the basal plane. Generally the central metal atom is 0.2–0.4 Å above the basal plane,[18] even in those complexes where conjugation within the ligand imposes a square-pyramidal structure on the metal ion. Even in the simple $Ni(CN)_5^{3-}$ ion, for example, the nickel atom is 0.34 Å above the plane of the four carbon atoms.[19] In Ni(DSP)I_2, we believe that ligand-field stabilization energy[20] favors the square-pyramidal geometry over a trigonal-bipyramidal one and that π back-bonding is an important contribution for the metal being located only slightly above the basal plane of donor atoms.

TABLE IV

BOND LENGTHS AND ANGLES IN Ni(DSP)I_2

Atoms	Length, Å	Atoms	Angle, deg	Atoms	Angle, deg
Ni–I_1	2.514 (5)	I_1–Ni–I_2	94.7 (2)	Ni–S_1–R_1C_2	98.3 (8)
Ni–I_2	2.567 (5)	I_1–Ni–P	88.3 (3)	Ni–S_2–R_2C_6	107.1 (8)
Ni–S_1	2.789 (10)	I_1–Ni–S_1	94.9 (2)	C_1–S_1–R_1C_2	104.2 (18)
Ni–S_2	2.189 (9)	I_1–Ni–S_2	174.3 (3)	C_2–S_2–R_2C_6	101.7 (18)
Ni–P	2.120 (9)	I_2–Ni–S_1	107.4 (2)	Ni–P–R_2C_1	107.7 (8)
S_1–C_1	1.85 (5)	I_2–Ni–S_2	87.6 (3)	Ni–P–R_1C_1	114.5 (8)
S_1–R_1C_2	1.79 (4)	I_2–Ni–P	174.7 (3)	Ni–P–R_3C_1	119.1 (8)
S_2–C_2	1.89 (4)	S_1–Ni–S_2	89.4 (3)	R_1C_1–P–R_3C_1	109.3 (12)
S_2–R_2C_6	1.77 (4)	S_1–Ni–P	76.7 (3)	R_2C_1–P–R_3C_1	104.6 (12)
P–R_1C_1[a]	1.83 (4)	S_2–Ni–P	89.1 (3)	R_1C_1–P–R_2C_1	99.3 (12)
P–R_2C_1	1.81 (4)	Ni–S_1–C_1	108.9 (15)		
P–R_3C_1	1.83 (4)	Ni–S_2–C_2	106.3 (14)		

[a] R_1 is ring 1; Ph_1 in Figure 2.

A square pyramid with the central metal in the basal plane represents the best geometry for efficient π back-bonding from the metal d orbitals in five-coordinate complexes.[21] That is, the three orbitals (d_{xy}, d_{xz}, and d_{yz}) are fully available for π bonding in the plane and out of the plane, just as they are in a square-planar complex. A distorted pyramid (with the central atom above the plane) is less efficient because the d_{xz} and d_{yz} orbitals

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(16) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

(17) N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Commun.*, 237 (1965); N. A. Bailey and R. Mason, *J. Chem. Soc., A*, 2594 (1968).

(18) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

(19) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

(20) This idea was originally published by F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958.

(21) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).

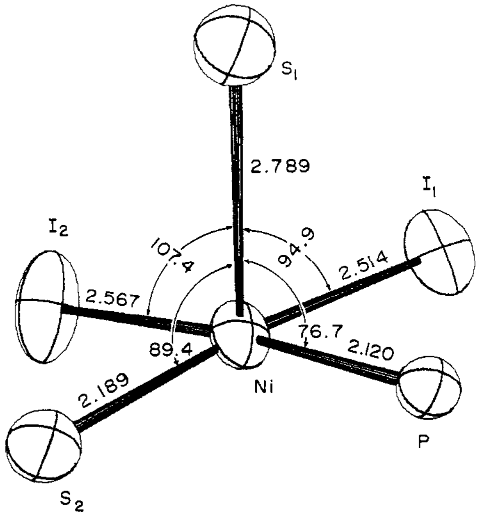

Figure 1.—The arrangement of atoms in the inner coordination sphere of $Ni(DSP)I_2$.

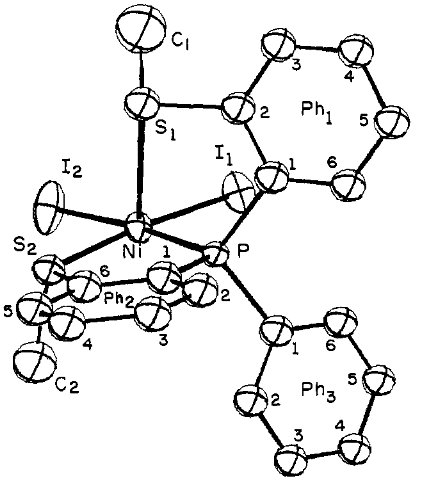

Figure 2.—The geometry of the complete five-coordinate $Ni(DSP)I_2$ molecule.

become partially σ^*, so the number of filled orbitals available for π bonding is less than 3. Although all five donor atoms of $Ni(DSP)I_2$ potentially may function as π acceptors, only the Ni–P bond distance is significantly shorter than the sum of the appropriate covalent radii. The present structure, in which the metal atom is located close to the basal plane of the square pyramid, may be rationalized on the basis of maximum nickel to phosphorus π back-bonding.

The phosphorus–nickel bond length (2.120 (9) Å) is considerably shorter than the sum of the covalent radii (2.26 (1) Å).[22–25] The P–Ni values of 2.26 Å in $Ni(P(C_2H_5)_3)_2Br_2$[25] and 2.179 (3)[26] and 2.175 (4) Å[27] in $Ni(P(C_2H_5)_3)_2(C{\equiv}CC_6H_5)_2$ have been reported. Thus, the nickel–phosphorus bond length in $Ni(DSP)I_2$ is significantly shorter than in any of these examples, and we take it as evidence for considerable π bonding between nickel and the phosphorus atom of DSP. Additional support for strong Ni–P π bonding may be deduced from the Ni–I bond length of the iodide that is *trans* to phosphorus. The Ni–I_2 distance is 0.053 (7) Å longer than for the iodide that is *trans* to the thioether group. The Ni–I_1 and Ni–S_2 bond lengths are comparable with the single-bond values.[28,29] All bond lengths (*e.g.*, P–C and S–C) angles in the tridentate ligand appear normal (Table IV).

The relative importance of π bonding by thioether groups is difficult to assess directly because of the paucity of data on Ni–SR_2 (R = aryl or alkyl) bond lengths. If one makes the reasonable assumption that the bonds in the basal plane of $Ni(DSP)I_2$ approximate those in a similar square-planar complex, then the observed Ni–S_2 bond length (2.189 (9) Å) is only slightly shorter than the sum of the covalent radii (2.20 (1) Å).[22,24] The value of 2.189 (9) Å also is longer than the distances of 2.101 (2), 2.146 (1), and 2.165 (5) Å found in the square-planar 1,2-dithiolato complexes of $Ni(S_2C_2(C_6H_5)_2)_2$,[30] $Ni(S_2C_2(CN)_2)_2^-$,[31] and $Ni(S_2C_2(CN)_2)_2^{2-}$,[32] respectively, where the sulfur atoms formally are mercaptide donors and where extensive π-bonding interactions between nickel and sulfur are thought to exist. Very recently, Haugen and Eisenberg found that the three equatorial Ni–S distances in the trigonal-bipyramidal $[Ni(TSP)Cl]ClO_4$ complex averaged 2.267 (7) Å.[8] This value is 0.078 (12) Å longer than we observed for the Ni–S_2 bond of $Ni(DSP)I_2$, but *these two distances are totally consistent* when one recalls that the bonding radius of low-spin, trigonal-bipyramidal nickel(II) in the xy plane (*i.e.*, equatorial bonds) is 0.08 Å larger than it is along the basal plane (xy plane) of a square pyramid.[19] We conclude, therefore, that the π bonding between nickel and the thioether groups in $Ni(DSP)I_2$ is insignificant compared with the phosphorus–nickel π interactions.[29]

The long apical bond (2.789 (10) Å) (along the z axis) and the difference (0.60 (1) Å) between it and the Ni–S_2 bond in the basal plane are similar to the distances observed with the few other square-pyramidal, strong-field d^8 complexes. The bond distances in Table

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[22] The value of 2.26 Å is calculated from the covalent radius of Ni(II) in square-planar complexes (1.16 Å)[23] and the single-bond radius of P (1.10 Å).[24] Using Pauling's octahedral value for Ni(II) (1.39 Å)[24] the bond length would be 2.49 Å. Although the value of about 2.49 Å appears reasonable for *high-spin*, six-coordinate complexes, the Ni–P distance in low-spin, four-coordinate complexes according to Pauling should be 2.30 Å and is found to be in the range 2.1–2.3 Å, *e.g.*, 2.26 Å in $Ni(P(C_2H_5)_3)_2Br_2$.[25]

[23] B. T. Kilbourn and H. M. Powell are quoted as giving 1.16 Å as the correct Ni(II) radius in square-planar complexes: see G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc., A*, 1750 (1967).

[24] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

[25] V. Scatturin and A. Turco, *J. Inorg. Nucl. Chem.*, **8**, 447 (1958).

[26] W. A. Spofford, III, P. D. Carfagna, and E. L. Amma, *Inorg. Chem.*, **6**, 1553 (1967); the original P–Ni distance was corrected: *ibid.*, **7**, 2677 (1968).

[27] G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc., A*, 1750 (1967).

[28] The nickel–iodine distances are even slightly longer than the equatorial Ni–I distance of 2.49 (2) Å in $Ni(P(C_6H_5)_2H)_3I_2$: J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966). Using the covalent radius value of 1.16 Å for Ni(II)[23] and the value of 1.33 Å for I,[24] the calculated Ni–I distance is 2.49 Å.

[29] If π bonding to a thioether donor were important, one would expect it to be even more significant in a palladium(II) complex. However, the Pd–S bond length in $[Pd(S(CH_3)_2)Br_2]_2$ is 2.30 ± 0.02 Å, which is only slightly shorter than the sum of the covalent radii (2.36 Å): D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc., A*, 1852 (1968).

[30] D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966).

[31] C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966).

[32] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).

TABLE V

COMPARISON OF APICAL AND BASAL METAL–LIGAND BOND DISTANCES IN SQUARE-PYRAMIDAL COMPLEXES

Complex	M–L$_{basal}$	Dist, Å	M–L$_{apical}$	Dist, Å	Δ, Å	Ref
$Ni(DSP)I_2$	Ni–S	2.189	Ni–S	2.789	0.60	This work
$Ni(CN)_5^{3-}$	Ni–C	1.86	Ni–C	2.17	0.31	19
$Ni(tas)Br_2$[a]	Ni–Br	2.37	Ni–Br	2.69	0.32	33
$Ni(\pi\text{-}CH_2C(CH_3)CH_2)(diphos)Br$[b]	. . .	. . .	Ni–Br	2.67	0.37[c]	34
$Ni(C_{15}H_{22}N_4)Br_2 \cdot H_2O$[d]	. . .	. . .	Ni–Br	2.79	0.49[c]	35
$Ni(PNP)Br_2$[e]	Ni–Br	2.33	Ni–Br	2.70	0.37	36
$[Ni(diars)(triars)](ClO_4)_2$[f]	Ni–As	2.29	Ni–As	2.39	0.10	37
$Pd(C_{14}H_{13}P)_3Br_2$[g]	Pd–Br	2.52	Pd–Br	2.93	0.41	38
$Pd(TPAS)Cl^+$[h]	Pd–As	~2.36[i]	Pd–As	2.86	0.50	39
$[Pd(PC_6H_5(CH_3)_2)_2I_2]_n$	Pd–I	2.63	Pd–I	3.28	0.65	17

[a] tas = bis(3-dimethylarsinopropyl)methylarsine; the structure may be viewed as intermediate between a regular square pyramid and a trigonal bipyramid. [b] diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, and π-$CH_2C(CH_3)CH_2$ is the π-bonded methallyl group. [c] Since there is only one Ni–Br bond in this complex, Δ was determined from a calculated Ni–Br$_{basal}$ distance of 2.30 Å (Ni radius = 1.16 Å and Br radius = 1.14 Å).[23] [d] $C_{15}H_{22}N_4$ is the tetradentate macrocycle 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),-2,11,13,15-pentaene; only one of the bromides is coordinated to nickel. [e] PNP is the tridentate ligand $HN[CH_2CH_2P(C_6H_5)_2]_2$. [f] diars = *o*-phenylenebis(dimethylarsine); triars = bis(*o*-dimethylarsinophenyl)methylarsine. [g] $C_{14}H_{13}P$ = 2-phenylisophosphindoline. [h] TPAS = the tetraarsine ligand *o*-phenylenebis(*o*-dimethylarsinophenyl)methylarsine. [i] The Pd–As distance is the average of three values.[39]

V[17,19,33–39] illustrate the long apical bond generally observed in such complexes. The 3d-electron density distribution is a *prolate* spheroid along the z axis for a diamagnetic, square-pyramidal d^8 complex, since the d_{z^2} orbital will contain two electrons and the $d_{x^2-y^2}$ orbital (in the basal plane) will be empty. The filled d_{z^2} orbital is pointed at the apical ligand and electron–electron repulsion between the filled d_{z^2} orbital and the electron pair of the donor will lead to a much longer metal–ligand distance than for an analogous bond in the basal plane.

The specific arrangement of the ligand in $Ni(DSP)I_2$ may also be a consequence of the long apical bond. If phosphorus had been the apex atom and if we still allow for a long apical bond, the necessarily equal Ni–S bond lengths and the short *o*-phenylene linkages would have pulled the phosphorus atom strongly over to one side of a square pyramid. Consequently, the σ-bonding contribution of an apical phosphorus atom would have been minimized. One additional factor may also influence the stereochemistry of the tridentate ligand in $Ni(DSP)I_2$. The benzene ring of the ligand can accept d-electron density into its vacant π^* orbitals effectively only if the ring lies in the basal plane. Thus, the observed structure, in which one phenyl ring, four donor atoms, and the central metal all lie nearly in the basal plane of a square pyramid, facilitates maximum π bonding between nickel and the ligand.

This structure determination emphasizes the importance of ligand-field stabilization energy for the d^8 electron configuration, where it is greater for a square pyramid than for a trigonal bipyramid. Also, the more subtle effects of the planar *o*-phenylene connecting linkage and π back-bonding to donor atoms in the basal plane are illustrated by the unusual situation that the metal is located nearly in the base of the square pyramid.

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(33) G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1962).

(34) M. R. Churchill and T. A. O'Brien, *Chem. Commun.*, 246 (1968).

(35) E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, **7**, 2312 (1968).

(36) P. L. Orioli and L. Sacconi, *Chem. Commun.*, 1310 (1968).

(37) B. Bosnich, R. S. Nyholm, P. J. Pauling, and M. L. Tobe, *J. Am. Chem. Soc.*, **90**, 4741 (1968).

(38) J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *J. Chem. Soc.*, 1803 (1964).

(39) T. L. Blundell and H. M. Powell, *ibid.*, *A*, 1650 (1967).