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The Crystal and Molecular Structure of *trans*-Bis(diphenyl-*o*-selenolatophenylphosphine)nickel(II)

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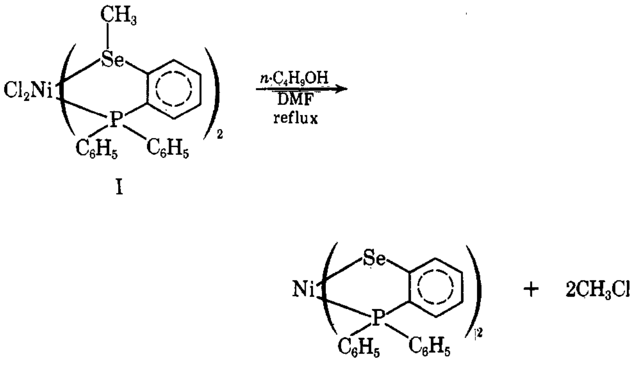
The crystal and molecular structure of the Se-demethylation product *trans*-bis(diphenyl-*o*-selenolatophenylphosphine)-nickel(II) has been determined from three-dimensional single-crystal X-ray data collected by counter θ–2θ scans. The structure has been refined by least-squares methods to a conventional R factor of 0.048 for 1247 statistically reliable reflections. The complex crystallizes in space group $P2_1/c$ of the monoclinic system in a unit cell of dimensions a = 9.85 (1), b = 13.17 (1), c = 12.56 (1) Å, β = 113.7 (1)°, and V = 1492 Å^3. The experimental density is 1.61 ± 0.03 g/cm^3; the calculated value is 1.59 g/cm^3 for Z = 2. The coordination geometry of the complex is essentially square planar with a trans arrangement of selenium and phosphorus donor atoms. The Ni–P bond length is 2.177 (3) Å and the Ni–Se bond length is 2.280 (3) Å. The intraligand Se–Ni–P bond angle is 88.4 (1)°. On the basis of the Ni–Se bond length and other structural parameters, no firm conclusions can be drawn concerning the question of whether or not multiple-bond character in the Ni–Se bond exists.

Introduction

Recently, Meek[2] has reported the facile demethylation of complex I[3] by refluxing the complex in 1-butanol–dimethylformamide solutions for approximately 15 min. The resultant green diamagnetic solid is proposed by Meek to be the complex *trans*-bis(diphenyl-*o*-selenolatophenylphosphine)nickel(II), II, hereafter Ni(sep)$_2$, on the basis of molecular weight determinations and spectral data. The trans arrangement of donor atoms was suggested, presumably because of steric factors. In the same communication, Meek also reports the synthesis of a complex which analyzes chemically as the Pd analog of II, but which has properties suggestive of a polymeric structure. Similar demethylation reactions have also been reported by Livingstone and coworkers[4,5] for related systems containing coordinated methylthio ether functions and a number of demethylation schemes have been proposed. A complete structure determination of II, which is presented herein, was undertaken in order to verify Meek's structural proposal and to gain structural information on the coordinating properties of the selenolate donor atom.



I

II

Collection and Reduction of the X-Ray Data

A generous sample of the Ni(sep)$_2$ complex, II, was kindly supplied to us by Professor Devon Meek and green crystals suitable for single-crystal X-ray work were grown from a chloroform–1-butanol solution. The crystals grew as parallelpipeds with the {100} and {011} faces showing development. Preliminary precession photographs indicated that the crystals belong to the monoclinic system. The final cell dimensions which were obtained after a least-squares refinement (*vide infra*) are a = 9.85 (1), b = 13.17 (1), c = 12.51 (1) Å, β = 113.7 (1)°, and V = 1492 Å^3. The observed extinctions, $h0l$ for l odd and $0k0$ for k odd, uniquely determine the space group as $P2_1/c$. The observed density of 1.61 ± 0.03 g/cm^3 obtained by the flotation method in bromoform–carbon tetrachloride solution agrees well with the value of 1.59 g/cm^3 calculated for two molecules per unit cell. Hence, the Ni(sep)$_2$ complex is crystallographically required to possess a center of symmetry.

Intensity data were collected from a single crystal of approximate dimensions 0.27 × 0.27 × 0.10 mm (approximately parallel to b, c, and a, respectively) which was mounted on a glass fiber parallel to the a axis and placed on a Picker four-circle automated diffractometer. The mosaic spread of the crystal was determined from open-counter, narrow-source scans through several strong reflections and found to have an average value of 0.6°.[6] Fifteen reflections of both general and special classes were centered in the counter aperture by varying χ, ϕ, and 2θ in conjunction with the left–right and top–bottom balancing features of the variable receiving aperture. The settings for these reflections formed the basis for a least-squares refinement of the

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[2] D. W. Meek, *Inorg. Nucl. Chem. Lett.*, **5**, 235 (1969).

[3] M. O. Workman, G. Dyer and D. W. Meek, *Inorg. Chem.*, **6**, 1543 (1967).

[4] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Nature* (*London*), **211**, 519 (1966).

[5] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, **6**, 652 (1967).

[6] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS ($\times 10^4$) FOR *trans*-BIS(DIPHENYL-*o*-SELENOLATOPHENYLPHOSPHINE)NICKEL(II)

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	62 (2)	49 (1)	50 (2)	−13 (2)	29 (2)	−8 (2)
Se	−2345 (1)	−75 (1)	−68 (1)	73 (1)	91 (1)	85 (1)	−30 (1)	47 (1)	−34 (1)
P	649 (3)	863 (2)	1608 (2)	58 (4)	45 (2)	50 (3)	−7 (2)	27 (2)	−8 (2)
C(1)	−999 (10)	1349 (7)	1782 (8)	80 (15)	41 (8)	50 (10)	14 (9)	36 (10)	10 (7)
C(2)	−2287 (10)	886 (8)	1084 (8)	61 (14)	48 (8)	56 (10)	−9 (9)	23 (10)	13 (8)
C(3)	−3569 (10)	1107 (8)	1269 (9)	88 (16)	56 (9)	67 (11)	7 (9)	44 (11)	5 (8)
C(4)	−3512 (14)	1814 (9)	2078 (11)	131 (23)	65 (11)	83 (15)	30 (12)	58 (16)	25 (10)
C(5)	−2179 (14)	2315 (9)	2770 (10)	167 (22)	64 (10)	69 (13)	47 (12)	65 (14)	11 (9)
C(6)	−922 (11)	2069 (8)	2610 (8)	109 (17)	51 (9)	36 (9)	12 (10)	30 (11)	1 (8)
C(7)	3417 (13)	3768 (9)	2095 (12)	151 (20)	49 (9)	134 (15)	−25 (11)	108 (16)	−24 (10)
C(8)	3587 (13)	3198 (10)	3051 (11)	123 (21)	80 (12)	104 (16)	−37 (13)	69 (15)	−49 (11)
C(9)	2800 (12)	2295 (9)	2930 (9)	100 (17)	63 (10)	70 (12)	−13 (11)	41 (12)	−5 (8)
C(10)	1871 (10)	1959 (8)	1843 (9)	71 (15)	34 (8)	60 (11)	3 (9)	35 (11)	−6 (8)
C(11)	1754 (11)	2535 (8)	882 (9)	96 (16)	58 (9)	70 (11)	9 (10)	45 (11)	7 (8)
C(12)	2521 (13)	3434 (9)	1031 (10)	145 (19)	53 (10)	85 (13)	−17 (11)	71 (13)	6 (9)
C(13)	772 (10)	−319 (8)	3504 (9)	98 (15)	54 (10)	67 (11)	−2 (9)	38 (11)	11 (8)
C(14)	1539 (9)	71 (8)	2875 (7)	90 (13)	33 (7)	46 (8)	−17 (11)	30 (8)	7 (8)
C(15)	3023 (10)	−198 (9)	3230 (8)	90 (14)	62 (10)	63 (10)	0 (10)	31 (10)	12 (9)
C(16)	3705 (11)	−829 (9)	4167 (10)	108 (18)	66 (10)	78 (12)	11 (11)	32 (12)	3 (9)
C(17)	2943 (13)	−1176 (8)	4813 (9)	155 (20)	45 (9)	73 (11)	3 (10)	36 (13)	6 (8)
C(18)	1452 (12)	−920 (9)	4442 (10)	117 (18)	76 (10)	77 (12)	−10 (12)	56 (12)	10 (10)

[a] x, y, and z represent fractional coordinates. The standard deviations of the least significant figure are given in parentheses in this and all succeeding tables. [b] The thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}k + 2\beta_{13}h)]$.

unit cell parameters and the orientation angles using our PICKLST program.[7]

Data were collected at ambient room temperature using Zr-filtered Mo Kα radiation (λ 0.7107 Å). A takeoff angle of 2.0° was used for the data collection with a counter opening of 6 × 6 mm. Data were collected using the θ–2θ scan technique over a range from -0.90 to $+1.05°$ of the calculated 2θ value of the reflection with a scan rate of 1°/min. Allowance was made in the scan range for the separation of the Mo Kα doublet at higher 2θ angles. Stationary-counter, stationary-crystal background counts of 10-sec duration were collected at both ends of the 2θ scan range for each reflection. The maximum 2θ value for reflections which were measured was 45°. Pulse height analysis designed to accept 90% of the diffracted Mo Kα radiation was employed, and no attenuation was found to be necessary. The intensities of three standard reflections were measured after every 100 reflections and showed no significant change during the data collection. The greatest single deviation of any of the standard reflections from its respective mean was 2.3%.

The intensities of 2068 independent reflections were measured, and these were then corrected for the usual Lorentz and polarization factors to yield a set of $F_o{}^2$ values where F_o is the observed structure factor amplitude. Of the 2068 independent reflections measured, 1247 were assumed to be statistically reliable, having intensities greater than their estimated standard deviations (*vide infra*). The data were then corrected for absorption using W. C. Hamilton's GONO9 absorption program. The linear absorption coefficient for Ni(sep)$_2$ is 33.8 cm^{-1}, and for this crystal, the transmission coefficients range from 0.68 to 0.76.

Solution and Refinement of the Structure

With two molecules per unit cell, the position of the nickel atom is fixed at a center of symmetry which was chosen as the origin. A difference Fourier map based on phases obtained solely from the Ni atom contribution revealed the position of selenium and phosphorus atoms. The positional parameters of the selenium and phosphorus atoms along with the single scale factor and an overall temperature factor were refined through two cycles of least-squares refinement. A second difference Fourier map, based on the contributions of the Ni, P, and Se atoms, revealed the positions of the carbon atoms.

The trial structure was refined using a least-squares procedure. The function minimized was $\Sigma w(F_o - F_o)^2$ where the weights w were assigned as $4F_o{}^2/\sigma^2(F_o{}^2)$ and the standard deviations were estimated from counting statistics according to the formula

$$\sigma(F^2) = \frac{1}{TLp}\left(C + \frac{1}{2}\left(\frac{t_c}{t_b}\right)^2(B_1 + B_2) + (0.03I)^2\right)^{1/2}$$

where Lp is the Lorentz–polarization factor, T is the transmission coefficient, C is the total integrated count obtained in time t_o, B_1 and B_2 are the background counts, each obtained in time t_b, and I is the net integrated count. The nickel, phosphorus, selenium, and carbon atom scattering factors used were those tabulated by Cromer and Waber[8] and the hydrogen atom scattering factor was that of Stewart, *et al.*[9] The effects of anomalous scattering were included in the

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(7) The programs used in this study were our PICKLST refinement and setting program and local versions of W. C. Hamilton's GONO9 absorption program, the Busing–Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the Busing–Martin–Levy ORFFE function and error program, and C. K. Johnson's ORTEP plotting program.

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

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

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS × 10) FOR *trans*-BIS(DIPHENYL-*o*-SELENOLATOPHENYLPHOSPHINE)NICKEL(II)

H	K	FOBS	FCAL
******L= 0******			
1	0	1489	1354
2	0	1669	1628
3	0	573	533
4	0	777	795
5	0	453	456
6	0	397	405
7	0	536	538
8	0	386	372
9	0	312	319
1	1	88	91
2	1	102	82
3	1	274	258
5	1	134	142
6	1	119	128
7	1	175	175
8	1	151	130
9	1	137	64
0	2	1605	1602
1	2	877	832
3	2	355	324
4	2	1067	1066
5	2	497	491
6	2	337	359
7	2	154	134
8	2	440	461
9	2	363	382
0	3	425	430
1	3	549	513
2	3	321	325
3	3	223	215
4	3	206	207
5	3	278	259
8	3	205	194
9	3	141	121
0	4	1109	1101
1	4	766	752
2	4	647	632
3	4	290	281
4	4	1190	1200
5	4	725	715
7	4	140	163
8	4	430	423
9	4	371	359
2	5	291	291
0	6	673	696
1	6	106	112
2	6	458	441
3	6	206	199
4	6	751	753
5	6	453	445
7	6	183	162
9	6	534	535
1	7	316	315
3	7	401	400
4	7	453	465
5	7	149	106
7	7	168	140
8	7	179	174
0	8	889	912
1	8	342	319
2	8	400	392
4	8	644	635
5	8	288	278
7	8	165	153
8	8	351	344
1	9	193	178
2	9	166	158
3	9	358	369
4	9	404	405
5	9	157	159
7	9	147	127
0	10	834	841
1	10	319	319
2	10	129	76
3	10	205	185
4	10	340	322
5	10	227	235
3	11	162	155
4	11	274	273
0	12	490	432
1	12	254	261
4	12	313	295
5	12	220	215
2	13	155	130
0	14	244	190
1	14	176	174
******L= 1******			
-9	1	398	399
-8	1	660	664
-7	1	197	212
-6	1	451	433
-5	1	1072	1064
-4	1	1675	1592
-3	1	346	339
-2	1	346	331
-1	1	1073	997
0	1	1543	1494
1	1	619	598
2	1	990	933
4	1	1063	1033
5	1	575	558
6	1	389	391
7	1	413	417
8	1	325	309
9	1	557	537
-8	2	179	195
-7	2	339	328
-6	2	307	301
-5	2	144	134
-4	2	205	160
-3	2	469	444
-1	2	455	436
0	2	541	559
1	2	866	847
2	2	469	451
3	2	186	147
6	2	156	139
9	2	166	137
-9	3	532	529
-8	3	440	432
-7	3	135	129
-6	3	308	311
-5	3	497	497
-4	3	1778	1740
-3	3	484	458
-2	3	935	940
-1	3	1387	1391
0	3	1394	1446
1	3	397	374
2	3	574	573
3	3	144	120
4	3	973	976
5	3	722	723
6	3	293	252
8	3	624	619
9	3	338	336
-6	4	231	229
-1	4	327	337
0	4	294	277
1	4	438	453
2	4	471	400
3	4	153	144
4	4	237	187
5	4	170	150
7	4	149	147
8	4	152	125
-9	5	436	437
-8	5	611	621
-7	5	134	122
-6	5	164	184
-5	5	432	433
-4	5	565	570
-3	5	355	365
-2	5	585	619
-1	5	482	457
0	5	1135	1155
2	5	446	433
3	5	514	522
4	5	1027	1039
5	5	722	737
6	5	139	138
8	5	439	433
-8	6	244	232
-7	6	150	137
-6	6	141	129
-4	6	213	206
-2	6	315	331
-1	6	318	335
0	6	230	158
1	6	226	225
2	6	146	97
3	6	179	171
4	6	129	111
6	6	243	266
-9	7	494	499
-7	7	133	30
-6	7	171	144
-5	7	354	376
-4	7	353	369
-2	7	138	220
-1	7	226	201
0	7	715	708
1	7	299	303
2	7	194	172
3	7	310	307
4	7	761	762
5	7	512	493
8	7	399	406
-8	8	327	337
-7	8	231	241
-3	8	192	172
-1	8	342	320
0	8	548	539
1	8	173	142
3	8	401	412
4	8	316	349
5	8	156	134
6	8	260	273
-6	9	199	187
-5	9	331	339
-4	9	520	534
-2	9	152	100
-1	9	391	397
0	9	557	549
1	9	170	192
2	9	129	63
3	9	165	193
4	9	535	589
5	9	325	304
7	9	143	75
-7	10	195	164
-4	10	165	133
-3	10	192	200
-1	10	192	215
3	10	365	366
4	10	162	171
5	10	162	127
-5	11	255	261
-4	11	480	459
-3	11	304	315
-1	11	373	379
0	11	526	525
1	11	133	118
2	11	302	291
4	11	360	354
-1	12	188	167
1	12	165	174
3	12	143	133
-4	13	355	375
-3	13	249	242
-1	13	246	246
0	13	272	257
1	13	154	116
0	14	150	57
1	14	150	99
******L= 2******			
-9	0	435	438
-8	0	797	818
-7	0	264	280
-5	0	1441	1447
-4	0	1511	1473
-3	0	478	406
-2	0	224	176
0	0	443	468
1	0	650	645
2	0	1147	1174
4	0	1348	1340
5	0	373	364
6	0	362	346
8	0	532	514
-3	1	212	170
-2	1	700	595
-1	1	438	440
0	1	1042	1090
1	1	205	214
2	1	244	227
4	1	283	280
7	1	268	256
8	1	226	207
-9	2	654	658
-8	2	673	656
-7	2	306	305
-6	2	312	309
-5	2	1070	1039
-4	2	1709	1634
-3	2	366	356
-2	2	1199	1167
0	2	1963	2012
1	2	872	842
2	2	485	506
3	2	105	98
4	2	832	839
5	2	456	448
6	2	311	284
8	2	546	526
-10	3	171	193
-7	3	236	244
-6	3	286	275
-5	3	325	327
-4	3	112	79
-3	3	872	864
-2	3	201	226
-1	3	646	656
0	3	1273	1289
1	3	164	111
4	3	244	283
5	3	151	144
6	3	270	261
7	3	310	323
-9	4	585	604
-8	4	415	404
-7	4	353	364
-6	4	184	173
-5	4	439	440
-4	4	512	501
-3	4	192	163
-1	4	671	686
0	4	794	847
1	4	270	301
3	4	311	329
4	4	1065	1088
5	4	705	719
6	4	249	256
8	4	453	456
-6	5	161	170
-3	5	285	261
-2	5	252	224
-1	5	135	144
0	5	115	82
1	5	388	395
2	5	207	201
3	5	292	277
4	5	270	276
6	5	128	132
8	5	249	259
-9	6	511	523
-8	6	326	345
-7	6	315	324
-6	6	460	466
-5	6	406	408
-4	6	821	834
-3	6	236	220
-2	6	473	471
-1	6	556	569
0	6	740	759
1	6	468	467
2	6	125	98
3	6	594	599
4	6	1214	1216
5	6	414	403
6	6	295	280
8	6	296	288
-9	7	151	149
-7	7	202	194
-5	7	215	192
-1	7	411	414
0	7	325	335
1	7	258	277
3	7	146	151
4	7	213	211
5	7	126	99
-8	8	269	274
-5	8	310	317
-4	8	468	489
-2	8	307	303
-1	8	325	319
0	8	770	785
1	8	294	298
3	8	301	297
4	8	650	651
5	8	327	314
6	8	155	174
-8	9	243	226
-7	9	167	154
-5	9	224	205
-2	9	268	287
-1	9	395	406
0	9	166	199
1	9	162	159
2	9	164	162
4	9	178	185
6	9	256	256
-6	10	129	36
-5	10	404	420
-4	10	613	616
-3	10	265	299
0	10	373	367
1	10	185	191
2	10	271	233
4	10	326	292
-5	11	180	151
-3	11	143	93
-1	11	148	126
-5	12	320	320
-4	12	374	397
-3	12	193	186
-1	12	222	186
0	12	337	317
2	12	158	180
4	12	148	83
-3	13	236	217
0	13	151	130
******L= 3******			
-9	1	665	681
-8	1	655	659
-5	1	773	756
-4	1	1687	1618
-3	1	440	402
-2	1	903	886
-1	1	503	494
0	1	1055	1138
1	1	221	194
2	1	569	599
3	1	120	104
4	1	885	889
5	1	543	559
6	1	131	96
8	1	503	498
-10	2	212	228
-6	2	294	279
-5	2	402	386
-4	2	176	172
-3	2	670	627
-2	2	505	500
-1	2	647	627
0	2	374	364
1	2	209	221
2	2	243	232
3	2	184	196
4	2	117	134
5	2	161	163
7	2	160	185
-9	3	511	518
-8	3	534	529
-7	3	306	314
-5	3	963	959
-4	3	777	736
-2	3	586	594
-1	3	593	593
0	3	2202	2235
1	3	630	640
2	3	498	500
3	3	458	469
4	3	757	773
5	3	236	231
6	3	197	162
8	3	317	312
-10	4	201	166
-6	4	236	240
-5	4	230	233
-4	4	856	859
-3	4	445	430
0	4	321	273
1	4	190	184
2	4	194	206
3	4	357	400
4	4	368	379
5	4	228	236
-9	5	325	321
-8	5	171	142
-7	5	311	311
-6	5	331	348
-5	5	459	464
-4	5	1053	1027
-3	5	157	153
-2	5	315	318
-1	5	959	965
0	5	1771	1791
1	5	813	800
2	5	222	202
3	5	336	327
4	5	741	741
6	5	424	426
-7	6	174	169
-5	6	172	162
-4	6	346	343
-3	6	213	173
-1	6	163	142
0	6	333	367
1	6	184	226
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3	0	324	341
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3	10	155	143
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3	9	237	222
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3	1	192	232
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6	1	163	141
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3	3	143	115
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-3	2	204	201
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4	2	154	150
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0	3	684	691
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2	3	225	210
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0	9	221	186
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-2	0	534	543
0	0	533	550
2	0	252	276
-6	1	191	181
-4	1	123	92
-3	1	264	265
-1	1	290	304
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-5	2	498	506
-4	2	470	461
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-1	2	344	371
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1	2	217	195
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-5	3	240	251
-4	3	257	242
1	3	156	150
2	3	200	178
-9	4	289	261
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-2	4	144	140
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-7	6	199	185
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-1	8	328	334
0	8	350	314
-5	9	260	232
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-3	8	165	170
******L= 12******			
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-2	5	156	118
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-4	6	351	346
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-5	2	224	212
-4	2	219	206
-3	2	169	148
-5	3	491	460
-4	3	280	261

calculated structure factors with values of $\Delta f'$ and $\Delta f''$ for Ni, P, and Se taken from Cromer's tabulation.[10]

Two cycles of full-matrix least-squares refinement of atomic positional and isotropic thermal parameters for all 21 nonhydrogen atoms and the single scale factor converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.130 and a weighted R factor ($R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$) of 0.109. The nickel, selenium, and phosphorus atoms were then allowed to vibrate according to an anisotropic model while all other atoms were restricted to the isotropic thermal model. Two cycles of least-squares refinement of the 97 scale, positional, and thermal parameters yielded values of R and R' of 0.063 and 0.057, respectively. A difference Fourier based on this refinement allowed us to determine the hydrogen atom positions, and their contributions to the calculated structure factors were included as fixed contributions in all subsequent calculations. The isotropic thermal parameter of each hydrogen atom was estimated as equal to the isotropic thermal parameter of the carbon atom to which it is bonded. Two additional cycles of least-squares refinement, including the hydrogen atom contributions, converged to an R factor of 0.054 and a weighted R factor R' of 0.047. An additional refinement was then carried out in which all nonhydrogen atoms were allowed to vibrate according to an anisotropic model. This final refinement of 187 parameters converged to R and R' values of 0.048 and 0.042, respectively, for 1247 statistically reliable reflections. The complete anisotropic thermal model represents a significant improvement (at the 0.5% significance level) over the partial anisotropic thermal model according to Hamilton's R-factor test.[11] The final difference Fourier map showed no

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[10] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[11] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

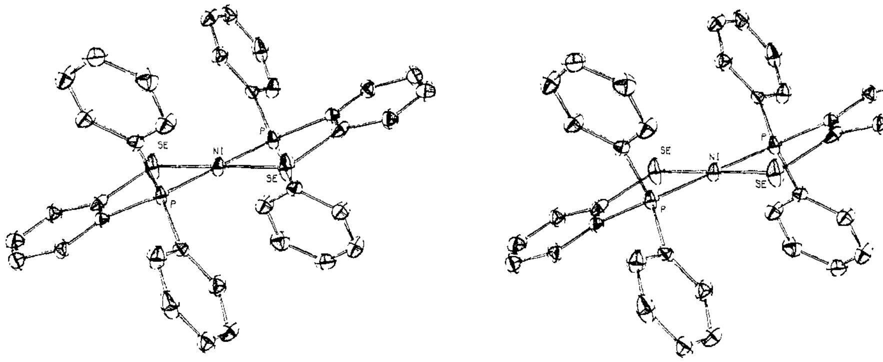

Figure 1.—A stereoscopic view of the Ni(sep)$_2$ molecule. The thermal ellipsoids have been scaled to 30% probability distributions.

peaks above 0.6 e$^-$/Å^3 or about 15% of the height of a carbon atom in this structure. The parameters obtained in this anisotropic refinement are taken as the final parameters for the structure and are given in Table I along with their estimated standard deviations as obtained from the inverse matrix. The F_o and $|F_c|$ values (in electrons × 10) for the 1247 reflections included in the final refinement are tabulated in Table II, and the unrefined hydrogen atom parameters are presented in Table III.

TABLE III

HYDROGEN POSITIONAL AND ISOTROPIC THERMAL PARAMETERS

Atom[a]	x(×10^4)	y(×10^4)	z(×10^4)	B, Å^2
H(3)	−4556	752	769	3.0
H(4)	−4449	1982	2155	3.7
H(5)	−2248	2832	3336	4.0
H(6)	89	2415	3165	2.9
H(7)	3969	4434	2177	4.0
H(8)	4279	3455	3835	4.4
H(9)	2927	1838	3636	3.8
H(11)	1009	2278	29	3.4
H(12)	2417	3887	324	3.7
H(13)	−333	−137	3256	3.1
H(15)	3625	76	2787	3.5
H(16)	4778	−1033	4389	3.7
H(17)	3437	−1625	5506	4.0
H(18)	854	−1185	4883	4.1

[a] The number for each hydrogen is the same as the carbon to which it is bonded.

TABLE IV

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES[a]

Atoms	Length, Å	Atoms	Angle, deg
Ni–Se	2.280 (3)	Se–Ni–P	88.42 (8)
Ni–P	2.177 (3)	Ni–Se–C(2)	102.8 (3)
P–C(1)	1.838 (9)	Ni–P–C(1)	110.3 (3)
P–C(10)	1.826 (10)	Ni–P–C(10)	119.4 (3)
P–C(14)	1.808 (10)	Ni–P–C(14)	111.9 (3)
Se–C(2)	1.906 (10)	P–C(1)–C(2)	114.0 (7)
C(1)–C(2)	1.36 (1)	P–C(10)–C(11)	118.1 (8)
C(2)–C(3)	1.40 (1)	P–C(14)–C(13)	122.0 (7)
C(3)–C(4)	1.36 (1)	Se–C(2)–C(1)	121.4 (7)
C(4)–C(5)	1.41 (2)	C(1)–C(2)–C(3)	117.9 (10)
C(5)–C(6)	1.37 (1)	C(2)–C(3)–C(4)	119.7 (10)
C(6)–C(1)	1.39 (1)	C(3)–C(4)–C(5)	121.9 (11)
C(7)–C(8)	1.37 (1)	C(4)–C(5)–C(6)	118.0 (11)
C(8)–C(9)	1.39 (1)	C(5)–C(6)–C(1)	119.4 (10)
C(9)–C(10)	1.38 (1)	C(6)–C(1)–C(2)	123.0 (9)
C(10)–C(11)	1.39 (1)	C(7)–C(8)–C(9)	120.3 (11)
C(11)–C(12)	1.38 (1)	C(8)–C(9)–C(10)	120.2 (11)
C(12)–C(7)	1.34 (1)	C(9)–C(10)–C(11)	118.4 (10)
C(13)–C(14)	1.39 (1)	C(11)–C(12)–C(7)	121.4 (11)
C(14)–C(15)	1.39 (1)	C(12)–C(7)–C(8)	119.5 (11)
C(15)–C(16)	1.37 (1)	C(13)–C(14)–C(15)	117.7 (9)
C(16)–C(17)	1.39 (1)	C(14)–C(15)–C(16)	121.1 (9)
C(17)–C(18)	1.39 (1)	C(15)–C(16)–C(17)	120.5 (10)
C(18)–C(13)	1.35 (1)	C(16)–C(17)–C(18)	118.1 (11)
		C(17)–C(18)–C(13)	121.4 (10)
		C(18)–C(13)–C(14)	121.2 (9)
		C(10)–P–C(1)	105.2 (5)
		C(10)–P–C(14)	105.0 (4)
		C(1)–P–C(14)	103.6 (4)

[a] The carbon atoms are numbered in the following manner. Carbon atoms C(1)–C(6) comprise the bridging phenyl ring while C(7)–C(12) and C(13)–C(18) make up the two other phenyl rings.

Description of the Structure

The Ni(sep)$_2$ complex is crystallographically required to be centrosymmetric and the coordination geometry about the nickel atom is essentially square planar with a trans arrangement of donor atoms. Figure 1 gives a stereoscopic view of an isolated molecule of Ni(sep)$_2$, and Table IV presents all important intramolecular distances and angles. The Ni–Se bond length is 2.280 (3) Å and the Ni–P bond distance is 2.177 (3) Å. Although the coordination geometry is crystallographically required to be planar, the principal plane of the Ni(sep)$_2$ molecule which includes the bridging *o*-phenylene rings as well as the Ni, Se, and P atoms deviates significantly from planarity. The slight chair conformation of the atoms comprising the principal plane of the molecule can be seen in Figure 1. The Ni atom thus lies significantly out of the least-squares plane through Se, P, and the bridging phenyl ring carbon atoms by 0.365 Å. The equation of that plane is $1.47x + 9.82y - 8.22z = -0.364$, in monoclinic coordinates, with none of the included atoms exhibiting a significant deviation from it. Least-squares planes through the phenyl rings and other important parts of the structure, along with deviations of the atoms from their respective planes, are presented in Table V.

To within experimental limits, the phenyl rings in this structure exhibit D_{6h} symmetry. The phenyl ring carbon–carbon distances range from 1.34 (1) to 1.41 (1) Å with an average value of 1.379 (18) Å. While some of the differences between carbon–carbon ring distances appear to be statistically significant, there is no systematic ordering of the distances within each phenyl ring. We therefore take these differences as

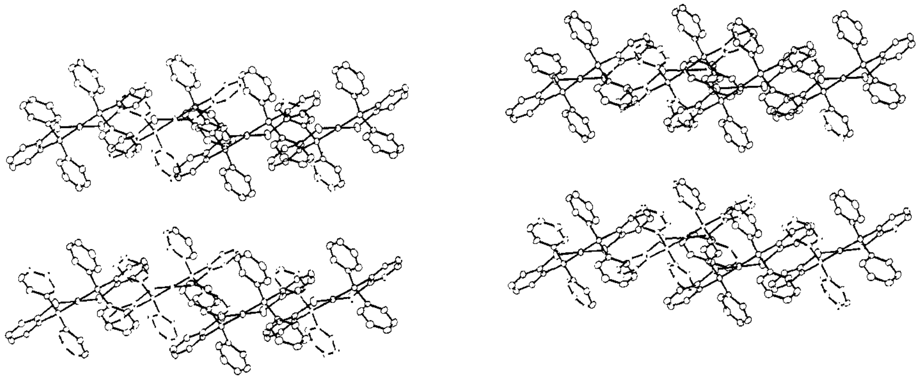

Figure 2.—A stereoscopic view of the packing of the Ni(sep)$_2$ molecules. The *b* axis is approximately vertical.

TABLE V

SELECTED LEAST-SQUARES PLANES[a]

Atom	Distance, Å	Atom	Distance, Å
a. Plane through Phenyl Ring 1 $-0.751x - 9.57y + 8.23z = 0.237$			
C(1)	0.012 (9)	C(4)	0.000 (11)
C(2)	−0.021 (9)	C(5)	−0.010 (10)
C(3)	0.016 (10)	C(6)	0.000 (9)
b. Plane through Phenyl Ring 2 $8.51x - 6.56y - 5.18z = -0.639$			
C(7)	−0.010 (10)	C(10)	−0.008 (9)
C(8)	0.014 (11)	C(11)	0.011 (9)
C(9)	−0.000 (10)	C(12)	−0.003 (10)
c. Plane through Phenyl Ring 3 $0.30x + 10.60y + 6.65z = 2.026$			
C(13)	−0.009 (10)	C(16)	−0.021 (12)
C(14)	0.009 (10)	C(17)	0.018 (11)
C(15)	0.004 (11)	C(18)	−0.003 (11)
d. Plane through Se, P, and Phenyl Ring 1 $1.47x + 9.82y - 8.22z = -0.364$			
Se	0.002 (1)	C(4)	−0.077 (11)
P	−0.014 (3)	C(5)	0.041 (10)
C(1)	0.078 (9)	C(6)	0.116 (10)
C(2)	0.007 (9)	Ni	0.364
C(3)	−0.116 (10)		

[a] The least-squares planes were calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14,** 185 (1961), using the variance–covariance matrix. The equations of the planes are given in monoclinic coordinates.

being indicative of random errors in the intensity data and possible limitations in our calculated model, and not as evidence for the significant dominance of any one resonance structure and the localization of π-electron density within the phenyl rings. The C–C distance of the bridging carbon atoms in the chelate ring is 1.36 (1) Å.

The crystal structure of the complex consists of the packing of discrete, monomeric Ni(sep)$_2$ molecules. A stereoscopic view of the packing is presented in Figure 2. All intermolecular contacts are normal and the closest Ni–Ni distance is 9.10 Å.

Discussion

The structural results reported here confirm Meek's proposal of a monomeric square-planar demethylation product. The Ni–P bond length of 2.177 (3) Å is significantly shorter than the sum of the covalent radii (2.28 Å) and can be taken as evidence of significant metal→ligand π bonding in this d^8 complex. The value of 2.177 (3) Å is comparable to the values of 2.179 (3)[12] and 2.175 (4) Å[13] reported for Ni((C$_2$H$_5$)$_3$P)$_2$(C≡CC$_6$H$_5$)$_2$. These values are also significantly shorter than the 2.26 (1) Å value reported for Ni((C$_2$H$_5$)$_3$P)$_2$Br$_2$[14] and the value of 2.251 (3) Å reported for NiBr$_2$(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$ in the structure of NiBr$_3$(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$·0.5NiBr$_2$(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$·C$_6$H$_6$[15] but are significantly longer than the 2.120 (9) Å Ni–P bond distance reported for the square-pyramidal complex Ni((C$_6$H$_5$)(*o*-C$_6$H$_4$SCH$_3$)$_2$P)I$_2$.[16] The extreme shortness of the Ni–P bond length in the last structure appears to be related to the presence of the negligible π-accepting ability of the iodide ligand in the position trans to phosphorus.[16]

An evaluation of the π bonding between the nickel and selenium atoms is much more difficult to assess because of the paucity of structural work on complexes possessing selenium donor ligands. The Ni–Se bond distance of 2.280 (3) Å is significantly, but not drastically, shorter than either the 2.35 Å sum of the covalent radii[17] or the revised 2.317 (1) Å distance found by Bonamico and Dessy for the planar Ni(Se$_2$CN(C$_2$H$_5$)$_2$)$_2$ complex.[18] Clearly, no definite conclusions concerning the existence of π bonding between the nickel and selenium atoms can be reached on the basis of the observed Ni–Se bond distance alone. A comparison of the Se–C bond distance of 1.905 (10) Å with other Se–C distances in the literature leads us to the conclusion that a limited amount of Se–C multiple bonding probably does exist in the present complex. Although the value is close to the 1.91 Å sum of covalent

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[12] W. A. Spofford, III, P. D. Carfagna, and E. L. Amma, *Inorg. Chem.*, **6**, 1553 (1967), as corrected: *ibid.*, **7**, 2677 (1968).

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

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

[15] D. W. Meek, E. C. Alyea, J. K. Stalick, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 4920 (1969).

[16] D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **8**, 1915 (1969).

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

[18] M. Bonamico and G. Dessy, *Chem. Commun.*, 1114 (1967). Professor Bonamico has kindly informed us that the values appearing in the aforementioned communication were incorrect and that the diselenocarbamate ligands coordinate in a symmetrical manner as in the bis-dithiocarbamate complexes of Ni(II). The values quoted by us for the Ni–Se and Se–C distances are the corrected ones. We thank Professor Bonamico for calling the error in their communication to our attention.

radii,[17] it is possibly significantly shorter than the values of 2.01 (3) and 1.98 (3) Å observed in the saturated heterocycles $S(C_2H_4)_2SeBr_2$[19] and $O(C_2H_4)_2SeICl$[20] in which no π bonding exists. In addition, the 1.905 (10) Å value is not significantly longer than the average Se–C distance of 1.87 (1) Å in the $Ni(Se_2CN(C_2H_5)_2)_2$ complex[18] or the corresponding value of 1.86 (1) Å found in the trigonal prismatic diselenolene complex $Mo(Se_2C_2(CF_3)_2)_3$[21] in which some π delocalization over the chelate ring is presumed to exist. However, the fact that some Se–C multiple-bond character may exist in the present structure must not be interpreted to mean that any significant π bonding between the Ni and Se atoms occurs in this complex. Further structural studies seem necessary before definite conclusions concerning the bonding in selenium donor chelates can be unequivocally established.

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[19] L. Battelle, C. Knobler, and J. D. McCullough, *Inorg. Chem.*, **6**, 958 (1967).

[20] C. Knobler and J. D. McCullough, *ibid.*, **7**, 365 (1968).

[21] C. G. Pierpont and R. Eisenberg, submitted for publication in *J. Chem. Soc. A*.

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The Crystal and Molecular Structure of Isothiocyanatothiocyanato-(1-diphenylphosphino-3-dimethylaminopropane)palladium(II)

BY G. R. CLARK AND GUS J. PALENIK*

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The orange compound $Pd[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2](SCN)(NCS)$ is monoclinic, with cell parameters $a = 11.684 \pm 0.003$, $b = 12.961 \pm 0.004$, $c = 14.641 \pm 0.003$ Å, and $\beta = 110.04 \pm 0.01°$. The space group is $P2_1/c$ with four molecules per unit cell, $d_c = 1.578 \pm 0.002$ g/cm³ and $d_m = 1.567 \pm 0.005$ g/cm³. Diffractometer data were collected for Cu Kα radiation and the structure has been refined by least-squares methods with anisotropic thermal parameters to a final R of 0.041 for 2716 observed reflections. The palladium atom is four-coordinated in a square-planar arrangement. The donor atoms are the phosphorus and nitrogen atoms of the organic ligand and one nitrogen and one sulfur atom from each thiocyanate group. They are arranged with the isothiocyanate linkage trans to the phosphorus atom and the thiocyanate linkage trans to the amine nitrogen atom. Bond distances about the palladium atom show a shortening (Pd–P = 2.243 ± 0.002 Å; Pd–S = 2.295 ± 0.002 Å) and a lengthening (Pd–N(ligand) = 2.147 ± 0.006 Å; Pd–N(NCS) = 2.063 ± 0.007 Å) consistent with a trans effect.

Introduction

The subtle factors influencing the formation of inorganic linkage isomers and particularly those involving the thiocyanate group[1] are of recent interest. A few compounds have been prepared which are reported to contain both metal–NCS and metal–SCN bonds (nonbridging) in the same molecule.[2–5] The evidence for these linkage isomers has been based entirely on physical measurements in solution. However, the interpretation of the spectral data has not been conclusive since the C–N or C–S stretching frequencies may be masked by broad bands from other ligands[3] or they may coincide with intense overtones from the N–C–S deformation mode.[6]

Only three X-ray structural studies have been reported on compounds postulated to have S- and N-bonded thiocyanate groups. The compound Pd(4,7-diphenylphen)$(SCN)_2$ was amorphous.[2] One ionic and one nitrogen-bonded thiocyanate group was found in $[Cu(N(CH_2CH_2NH_2)_3)(NCS)](NCS)$[7,8] and bridging –N–C–S– groups were found in bis(ethylenethiourea)-cadmium thiocyanate.[9]

The compound $Pd[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$(SCN)(NCS) was also believed to exhibit mixed bonding in the solid state[10] and we undertook an X-ray examination of this compound to provide structural evidence for this hypothesis. A preliminary report of our results has appeared recently.[11]

Experimental Section

Orange, polyhedral crystals of the complex were kindly supplied by Professor D. W. Meek. Preliminary Weissenberg and precession photographs indicated that the crystals were mono-

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[1] For reviews of the properties of these compounds see J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).

[2] I. Bertini and A. Sabatini, *Inorg. Chem.*, **5**, 1025 (1966).

[3] P. Nicpon and D. W. Meek, *ibid.*, **6**, 145 (1967).

[4] G. C. Kulasingam and W. R. McWhinnie, *Chem. Ind.* (*London*), 2200 (1966).

[5] A. J. Carty and A. Efraty, *Can. J. Chem.*, **47**, 2573 (1969).

[6] L. H. Jones, *J. Chem. Phys.*, **28**, 1234 (1958).

[7] K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966).

[8] P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, **89**, 724 (1967).

[9] L. Cavalca, M. Nardelli, and G. Fava, *Acta Crystallogr.*, **13**, 125 (1960).

[10] D. W. Meek, P. E. Nicpon, and V. I. Meek, unpublished results.

[11] G. R. Clark, G. J. Palenik, and D. W. Meek, *J. Amer. Chem. Soc.*, **92**, 1077 (1970).