The Crystal Structure of Di-π-allyl(dihydropentalenylene)dinickel

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The crystal structure of di-π-allyl(dihydropentalenylene)dinickel, $(C_8H_6)Ni_2(C_3H_5)_2$, has been determined from three-dimensional single-crystal X-ray photographic data. The crystal of this compound is composed of discrete molecular units in the monoclinic space group $P2_1/a$, with two molecules per unit cell with dimensions of $a=8.451\pm0.004$, $b=12.691\pm0.005$, $c=5.976\pm0.006$ Å, and $\beta=108.81\pm0.05°$. The calculated and observed densities are 1.650 and 1.60 g·cm^{-3} respectively. The structure was deduced from a sharpened Patterson synthesis and was refined by means of the least-squares method to the final R index of 0.121 for 1151 independent non-zero reflections. The molecule has a crystallographic center of symmetry; therefore, two nickel atoms which are complexed in a sandwich fashion between the dihydropentalenylene ring and the π-allyl group take a *trans* configuration. The distances of the nickel atom from the ring carbons range from 2.03 to 2.27 Å, the closest approach being to the three non-bridging atoms of the five-membered ring. The orientation of the π-allyl groups with respect to the nickel atom is similar to those found in other π-allyl complexes.

In the reaction of (dihydropentalenylene)dilithium with allyl metal chlorides, Miyake and Kanai have newly synthesized π-allyl-dihydropentalenylene complexes of nickel, chromium, and zirconium.[1] The NMR spectra of the nickel derivative in C_6D_6 and benzene indicate the presence of the π-allyl group and the dihydropentalenylene ring. In order to confirm the configuration of the complex, the measurement of the dipole moment was attempted; however, because of its small value ($\mu=0.65\pm0.5$ D in benzene at 30°C), no definite conclusion was obtained. Thus, it is not certain whether the complex has a *cis* or a *trans* configuration; therefore, a single-crystal X-ray structure analysis of the complex was carried out in order to determine the molecular configuration and the mode of coordination of the π-allyl groups to the nickel.

Experimental

Di-π-allyl(dihydropentalenylene)dinickel, $(C_8H_6)Ni_2(C_3H_5)_2$, was prepared by the reaction of (dihydropentalenylene)-dilithium and bis π-allyl nickel chloride. The complex was recrystallized from an ether solution as extremely air-sensitive, deep green monoclinic plates elongated in the *b* direction. For the crystallographic analysis, the crystals were sealed into thin-walled glass capillary tubes, under an argon atmosphere; therefore, no serious crystal decomposition was found during the collection of the intensity data. The unit-cell dimensions were obtained by the least-squares procedure from measurements on Weissenberg photographs around the *b* and *c* axes. The density was measured by flotation in an aqueous solution of zinc chloride at 25°C. The crystal data are summarized in Table 1.

TABLE 1. CRYSTAL DATA

Di-π-allyl(dihydropentalenylene)dinickel, $Ni_2C_{14}H_{16}$
Molecular weight: 301.6
Monoclinic
$a=8.451\pm0.004$Å
$b=12.691\pm0.005$
$c=5.976\pm0.006$
$\beta=108.81\pm0.05°$
$V=606.77$ Å^3
$D_m=1.60$ g·cm^{-3}, $D_x=1.650$ g·cm^{-3} for $Z=2$
Systematic absences, $h0l$ with $h=2n+1$
$0k0$ with $k=2n+1$
Space group C_{2h}^5—$P2_1/a$ (No. 14)
Linear absorption coefficient for Cu$K\alpha$: $\mu=48.9$ cm^{-1}

The three-dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with Ni-filtered Cu$K\alpha$ radiation. The multiple-film technique was used, and zero to seventh layers about the *b* axis and zero to fifth layers about the *c* axis were recorded. The intensities were estimated visually by comparison with a calibrated

TABLE 2. THE ATOMIC COORDINATES OF DI-π-ALLYL(DIHYDROPENTALENYLENE)DINICKEL, ALONG WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c
Ni	0.2400(2)	0.0447(2)	0.2436(4)
C (1)	0.0310(20)	0.0080(22)	−0.0969(22)
C (2)	0.1818(24)	−0.0534(24)	−0.0510(28)
C (3)	0.2015(26)	−0.1100(26)	0.1537(28)
C (4)	0.0828(24)	−0.0789(24)	0.2633(26)
C (5)	0.4234(30)	0.1453(30)	0.2298(34)
C (6)	0.3192(28)	0.1835(28)	0.3535(32)
C (7)	0.3078(34)	0.1255(32)	0.5489(34)

TABLE 3. THERMAL PARAMETERS (Å^2) IN THE FORM OF $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$ (each multiplied by 10^4, estimated standard deviations in parentheses)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	33(2)	10(1)	106(5)	−10(2)	16(5)	− 8(4)
C (1)	42(14)	8(5)	85(30)	−12(14)	−30(34)	− 7(22)
C (2)	22(16)	6(6)	85(38)	− 1(16)	26(40)	−20(27)
C (3)	24(17)	5(7)	69(39)	−18(17)	−60(42)	30(28)
C (4)	30(15)	3(6)	55(35)	−15(16)	−11(38)	2(25)
C (5)	46(21)	15(8)	152(49)	−40(22)	54(53)	−21(34)
C (6)	46(20)	3(7)	144(49)	2(19)	1(51)	−26(31)
C (7)	90(27)	15(8)	143(50)	−43(25)	119(61)	−55(35)

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1) A. Miyake and A. Kanai, *Angew. Chem.*, **83**, 851 (1971); *Angew. Chem. internat. Edit.*, **10**, 801 (1971).

TABLE 4. OBSERVED AND CALCULATED STRUCTURE FACTORS
The table gives h, k, $10\,|F_0|$, and $10F_c$ in blocks of constant l.

H	K	FO	FC
L = 0			
2	0	966	-1147
4	0	788	740
6	0	580	-499
8	0	117	133
10	0	109	-161
1	1	291	318
2	1	490	502
3	1	143	-121
4	1	118	-81
5	1	357	231
6	1	119	69
7	1	246	-243
9	1	155	196
10	1	116	-170
0	2	999	-1182
1	2	430	-555
2	2	525	-610
3	2	464	405
4	2	720	677
5	2	387	-326
6	2	510	-423
7	2	243	208
8	2	281	292
9	2	193	-216
10	2	184	-235
1	3	475	548
2	3	381	326
3	3	257	-173
4	3	66	57
5	3	298	218
6	3	25	-42
7	3	187	-177
8	3	40	61
10	3	145	-259
0	4	107	-26
1	4	310	-325
2	4	208	-145
3	4	694	711
4	4	474	376
5	4	603	-547
6	4	183	-146
7	4	457	457
8	4	268	286
9	4	357	-462
2	5	224	-182
3	5	317	225
4	5	191	158
5	5	72	20
6	5	268	-253
7	5	127	84
8	5	204	216
9	5	34	-16
0	6	42	-50
1	6	627	-687
2	6	232	202
3	6	741	721
5	6	606	-535
6	6	147	110
7	6	414	420
8	6	17	-7
9	6	290	-356
1	7	182	-123
2	7	88	-72
3	7	290	202
4	7	90	79
6	7	217	-212
7	7	236	245
8	7	172	206
9	7	58	-82
0	8	498	-367
1	8	743	-643
2	8	570	468
3	8	456	374
4	8	255	-212
5	8	529	-498
6	8	261	251
7	8	290	335
8	8	137	-166
1	9	79	28
2	9	104	-71
3	9	170	168
5	9	113	-111
6	9	38	-67
7	9	104	137
0	10	627	-505
1	10	257	-221
2	10	624	554
3	10	94	71
4	10	446	-393
5	10	269	-257
6	10	392	419
7	10	120	137
1	11	97	75
3	11	271	242
4	11	218	-190
5	11	201	-214
6	11	89	51
7	11	27	67
0	12	496	-475
1	12	91	72
2	12	586	632
3	12	113	-114
4	12	402	-425
5	12	121	144
6	12	192	245
1	13	74	72
3	13	90	100
4	13	85	-100
5	13	63	-90
0	14	271	-265
1	14	285	302
2	14	466	484
3	14	234	-280
4	14	190	-264
5	14	114	241
2	15	26	-27
3	15	55	75
0	16	62	88
1	16	164	287
L = 1			
2	0	82	6
4	0	361	294
6	0	164	-165
8	0	252	312
-2	0	232	193
-4	0	133	-124
-6	0	327	207
-8	0	424	-337
-10	0	172	188
0	1	335	-375
1	1	673	-92
2	1	200	168
3	1	487	476
4	1	153	-113
5	1	431	-366
6	1	125	113
7	1	408	431
8	1	84	-97
9	1	133	-187
-1	1	1218	1436
-2	1	318	328
-3	1	767	861
-4	1	290	-244
-5	1	740	892
-6	1	204	159
-7	1	534	-553
-8	1	71	-74
-9	1	143	147
-10	1	76	95
0	2	381	391
1	2	575	703
2	2	360	-275
3	2	257	-159
4	2	305	234
5	2	281	-217
6	2	51	-62
7	2	94	95
8	2	161	197
9	2	176	-211
-1	2	113	-88
-2	2	214	181
-3	2	292	220
-4	2	39	-56
-5	2	76	-72
-6	2	282	239
-7	2	205	-157
-8	2	306	-309
-9	2	25	-32
-10	2	54	83
0	3	357	-379
1	3	207	-214
2	3	560	604
3	3	697	729
4	3	654	-575
5	3	430	-379
6	3	409	362
7	3	394	408
8	3	266	-316
9	3	221	-260
-1	3	392	473
-2	3	449	516
-3	3	449	-438
-4	3	464	-426
-5	3	409	319
-6	3	380	326
-7	3	394	-360
-8	3	333	-336
-9	3	262	255
-10	3	256	308
0	4	338	278
1	4	40	3
2	4	152	94
3	4	304	230
4	4	22	19
5	4	338	-279
6	4	145	67
7	4	152	170
8	4	75	67
9	4	131	-179
-1	4	94	-86
-2	4	20	-26
-3	4	215	235
-4	4	156	87
-5	4	225	-200
-6	4	43	41
-7	4	132	116
-8	4	117	-104
-9	4	69	-98
0	5	551	-636
2	5	815	1001
3	5	430	335
4	5	799	-797
6	5	439	393
7	5	154	126
8	5	338	-360
9	5	97	-122
-1	5	229	171
-2	5	651	820
-3	5	140	-88
-4	5	550	522
-5	5	64	-34
-6	5	383	335
-7	5	33	-34
-8	5	455	-420
-9	5	54	60
-10	5	238	329
0	6	132	-27
1	6	181	-140
2	6	577	461
3	6	242	197
4	6	135	57
5	6	257	-230
6	6	121	107
7	6	239	259
8	6	56	-54
-1	6	63	-32
-2	6	134	-85
-3	6	100	77
-5	6	90	-89
-6	6	211	-167
-7	6	222	229
-8	6	161	149
-9	6	133	-169
0	7	787	-880
1	7	406	350
2	7	776	750
3	7	168	-126
4	7	504	-478
5	7	287	247
6	7	349	321
7	7	135	-121
8	7	193	-201
-1	7	242	-230
-2	7	657	748
-3	7	345	292
-4	7	505	-469
-5	7	238	-189
-6	7	433	422
-7	7	121	121
-8	7	266	-243
-9	7	110	-102
2	8	295	168
3	8	153	117
4	8	248	170
5	8	186	-171
6	8	82	113
-1	8	25	1
-2	8	168	98
-3	8	182	144
-4	8	287	-113
-5	8	182	144
-6	8	109	-125
-7	8	141	146
-8	8	157	157
-9	8	74	111
0	9	479	-433
1	9	655	545
2	9	314	249
3	9	301	-258
4	9	288	-248
5	9	388	405
6	9	414	357
-1	9	507	-433
-2	9	320	244
-3	9	468	432
-4	9	261	-237
-5	9	437	-410
-6	9	412	447
-7	9	301	279
-8	9	146	-164
2	10	75	83
4	10	30	-50
5	10	40	25
6	10	107	114
-1	10	94	-74
-2	10	168	111
-3	10	160	114
-4	10	187	184
-5	10	63	41
-6	10	183	-190
-8	10	65	105
0	11	43	58
1	11	493	465
2	11	54	-73
3	11	391	-322
5	11	468	454
6	11	42	65
-1	11	442	-400
-3	11	531	530
-5	11	391	-524
-6	11	109	105
-7	11	333	366
2	12	128	110
3	12	144	-147
4	12	138	-134
5	12	185	201
6	12	116	164
-2	12	43	40
-3	12	114	-107
-4	12	162	192
-5	12	264	231
-6	12	132	-157
0	13	246	297
1	13	405	390
2	13	182	-220
3	13	249	-329
4	13	173	212
5	13	183	228
-1	13	391	-411
-2	13	139	-113
-3	13	473	627
-4	13	179	188
-5	13	188	-355
-6	13	113	-153
2	14	51	88
-1	14	193	214
-2	14	31	33
-3	14	64	-72
0	15	336	416
1	15	229	268
2	15	251	-331
3	15	251	-234
-1	15	147	-161
-2	15	211	-286
-3	15	186	233
L = 2			
0	0	738	-940
2	0	688	656
4	0	407	-339
6	0	637	607
8	0	248	-202
-2	0	521	547
-4	0	771	-819
-6	0	727	723
-8	0	462	-455
-10	0	263	245
0	1	82	73
1	1	78	-84
2	1	196	-117
3	1	342	271
4	1	218	-143
5	1	114	-125
6	1	131	115
7	1	252	326
-1	1	89	71
-2	1	39	-22
-4	1	318	211
-5	1	140	-123
-7	1	127	124
-8	1	65	-20
-9	1	162	-284
-10	1	64	-76
0	2	534	-601
1	2	428	372
2	2	664	685
3	2	398	-305
4	2	476	-467
5	2	347	289
6	2	518	528
7	2	207	-228
8	2	213	-195
-1	2	361	-346
-2	2	447	480
-3	2	357	317
-4	2	37	-523
-5	2	328	-265
-6	2	481	438
-7	2	210	171
-8	2	467	-458
-9	2	137	-155
-10	2	250	237
0	3	2'2	-150
1	3	52	-1
2	3	121	-93
3	3	118	107
4	3	343	-272
5	3	165	75
6	3	168	152
7	3	176	215
8	3	21	-67
-1	3	191	-116
-2	3	127	73
-3	3	115	-84
-4	3	431	372
-5	3	49	-42
-6	3	186	-166
-7	3	75	71
-8	3	102	97
-9	3	107	-130
-10	3	121	-142
0	4	209	-196
1	4	646	636
2	4	525	460
3	4	763	-704
4	4	369	-278
5	4	481	426
6	4	258	247
7	4	267	-262
8	4	131	-145
-1	4	563	-613
-2	4	496	445
-3	4	647	732
-4	4	350	-290
-5	4	420	-362
-6	4	89	45
-7	4	359	336
-8	4	264	-264
-9	4	311	-344
-10	4	51	67
0	5	200	-125
1	5	426	326
2	5	356	262
3	5	156	-84
4	5	226	-186
5	5	85	40
6	5	166	154
7	5	126	111
8	5	99	-114
-1	5	180	-110
-2	5	46	18
-3	5	53	-17
-4	5	209	160
-5	5	57	-2
-6	5	241	-222
-7	5	265	-202
-8	5	121	206
-9	5	27	3
-10	5	93	-143
0	6	201	155
1	6	736	711
2	6	35	-34
3	6	559	-494
4	6	208	163
5	6	288	234
6	6	45	-22
7	6	175	-192
8	6	44	36
-1	6	762	-897
-2	6	32	-9
-3	6	857	1012
-5	6	583	-561
-6	6	184	-171
-7	6	403	403
-8	6	32	22
-9	6	251	-235
-10	6	103	-109
0	7	25	-18
1	7	140	96
2	7	220	172
3	7	153	76
4	7	192	-159
6	7	209	211
7	7	134	-154
-1	7	283	221
-3	7	35	43
-4	7	101	73
-5	7	223	-174
-6	7	101	-93
-7	7	169	-170
-8	7	155	161
-9	7	57	-31
0	8	523	422
1	8	628	565
2	8	321	-271
3	8	250	-208
4	8	343	325
5	8	310	275
6	8	177	-202
-1	8	671	-553
-2	8	446	-392
-3	8	575	451
-4	8	371	302
-5	8	541	-474
-6	8	352	-345
-7	8	330	354
-8	8	131	132
-9	8	114	-122
0	9	115	-70
1	9	161	-107
2	9	253	188
3	9	209	124
4	9	93	-90
5	9	175	182
-1	9	216	125
-2	9	32	19
-4	9	179	124
-5	9	111	-72
-6	9	99	-101
-8	9	162	170
0	10	583	450
1	10	290	225
2	10	481	-400
3	10	165	-135
4	10	510	527
5	10	341	324
6	10	392	-398
-1	10	34	-35
-2	10	358	-308
-3	10	34	-30
-4	10	318	307
-5	10	107	-106
-6	10	406	-420
-7	10	178	166
-8	10	216	247
0	11	181	124
	11	48	48
3	11	32	-54
4	11	165	154
5	11	210	252
-1	11	131	-118
-2	11	49	-34
-3	11	71	-72
-4	11	49	-71
-5	11	111	128
-6	11	83	63
-7	11	111	-132
0	12	334	329
1	12	107	-119
2	12	354	-370
3	12	82	72
4	12	463	509
-1	12	193	207
-2	12	387	-380
-3	12	46	-59
-4	12	337	354
-5	12	124	137
-6	12	332	-336
0	13	178	185
1	13	52	71
2	13	168	-172
4	13	212	253
-4	13	108	-124
-6	13	154	119
0	14	269	259
1	14	265	-266
2	14	240	-257
3	14	216	235
-1	14	352	384
-2	14	408	-437
-3	14	201	-223
-4	14	285	333
-5	14	213	279
-2	15	164	196
L = 3			
0	0	142	-121
2	0	310	230
4	0	229	-201
6	0	253	282
-2	0	83	-80
-4	0	73	-40
-6	0	141	-136
-10	0	165	-180
0	1	261	241
1	1	673	771
2	1	212	-168
3	1	449	-384
4	1	178	147
5	1	434	423
6	1	140	-141
7	1	188	-211
-1	1	765	-870
-2	1	210	-212
-3	1	437	451
-4	1	268	214
-5	1	619	-664
-6	1	170	-135
-7	1	331	309
-8	1	56	50
-9	1	262	-288
-10	1	30	-49
0	2	126	-107
1	2	205	-122
2	2	308	245
3	2	65	14
4	2	117	-107
5	2	188	190
6	2	205	210
-1	2	176	-134
-2	2	162	-113
-3	2	71	-25
-4	2	106	-57
-5	2	137	87
-6	2	243	-222
-7	2	49	42
-8	2	74	84
-9	2	117	131
-10	2	92	-116
0	3	503	450
1	3	472	447
2	3	510	-482
3	3	482	-455
4	3	502	466
5	3	374	361
6	3	250	-281
7	3	101	-117
-1	3	477	-466
-2	3	480	-483
-3	3	330	313
-4	3	423	424
-5	3	348	-306
-6	3	300	-265
-7	3	197	179
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0	4	170	105
1	4	129	114
2	4	47	44
3	4	53	-53
4	4	33	-38
5	4	117	112
6	4	206	196
7	4	44	-76
-1	4	257	-190
-2	4	341	-272
-3	4	130	70
-4	4	35	37
-5	4	163	128
-6	4	199	-175
-7	4	175	-165
-8	4	84	-58
-9	4	220	221
0	5	445	393
2	5	498	-426
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4	5	515	463
5	5	152	132
6	5	255	-251
7	5	44	-46
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-2	5	637	-671
-3	5	184	137
-4	5	656	627
-5	5	208	-154
-6	5	473	-458
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-9	5	139	-131
-10	5	229	-276
1	6	192	159
2	6	201	-176
3	6	165	-128
4	6	47	16
5	6	161	157
6	6	71	57
7	6	117	-150
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-2	6	35	-20
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-4	6	32	45
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-7	6	156	-154
-8	6	188	-181
-9	6	147	145
0	7	437	421
1	7	280	-225
2	7	286	-228
3	7	211	184
4	7	265	231
5	7	78	-70
6	7	252	-264
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-3	7	318	-250
-4	7	590	616
-5	7	118	95
-6	7	527	-585
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-8	7	421	387
-9	7	49	39
0	8	272	-173
1	8	191	157
2	8	165	-130
3	8	89	-89
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5	8	96	119
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-3	8	74	39
-4	8	190	-153
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-6	8	34	36
-7	8	48	-78
-8	8	48	-59
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2	9	319	-287
3	9	378	382
4	9	262	259
5	9	312	-285
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-2	9	178	-131
-3	9	403	-376
-4	9	262	208
-5	9	291	263
-6	9	280	-265
-7	9	284	-298
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3	10	93	30
4	10	291	246
5	10	106	-37
-1	10	35	37
-3	10	105	72
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-6	10	31	30
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0	13	180	-181
1	13	267	-256
2	13	193	196
3	13	255	332
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-3	13	470	-519
-4	13	150	-164
-5	13	215	204
-4	14	51	78
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-6	0	669	-735
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0	1	131	-69
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2	1	127	81
3	1	204	-191
4	1	132	147
5	1	95	112
6	1	117	-155
-1	1	168	-133
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0	2	474	444
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4	2	260	256
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0	3	59	-9
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3	3	143	-149
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-4	3	153	-119
-6	3	72	-37
-7	3	292	-255
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-10	3	103	126
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2	4	333	-323
3	4	501	561
4	4	267	280
5	4	326	-338
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2	5	116	-86
3	5	54	-50
4	5	152	140
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-6	5	66	58
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0	6	176	-164
1	6	373	-322
3	6	410	440
4	6	46	36
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-1	6	419	374
-2	6	47	2
-3	6	461	-398
-4	6	174	-126
-5	6	369	328
-7	6	394	-422
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-9	6	348	355
0	7	105	88
1	7	245	-246
2	7	120	-116
3	7	151	166
4	7	141	151
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-5	7	136	-112
-7	7	189	163
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2	8	202	202
3	8	215	230
4	8	164	-182
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-5	8	380	369
-6	8	213	190
-7	8	346	-309
-8	8	204	-177
1	9	197	-205
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-7	9	147	122
-8	9	58	-78
0	10	475	-518
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3	10	130	115
4	10	212	-293
-1	10	278	266
-2	10	370	349
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0	11	104	-75
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0	12	334	-338
1	12	116	137
2	12	185	224
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-4	0	83	-67
-8	0	118	-122
-10	0	84	108
0	1	118	-96
1	1	372	-385
2	1	133	107
3	1	130	147
4	1	101	-101
5	1	267	-330
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-6	1	123	144
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-9	1	263	294
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1	2	39	-66
2	2	158	-154
3	2	144	178
4	2	29	-10
5	2	204	-283
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-8	2	112	-105
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1	3	357	-363
2	3	319	342
3	3	232	229
4	3	235	-272
5	3	160	-203
-1	3	266	287
-2	3	323	388
-3	3	349	-409
-4	3	289	-308
-5	3	176	156
-6	3	180	176
-7	3	183	-204
-8	3	190	-210
-9	3	147	160
0	4	121	-72
1	4	88	-71
2	4	95	-95
3	4	129	145
4	4	12	15
5	4	136	-189
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-2	4	101	-85
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-5	4	110	-95
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0	5	360	-409
1	5	157	-144
2	5	322	405
3	5	125	104
4	5	269	-319
-1	5	49	36
-2	5	442	533
-3	5	212	-199
-4	5	312	-368
-5	5	30	-25
-6	5	194	192
-7	5	65	-46
-8	5	251	-270
-9	5	51	52
0	6	91	-73
1	6	132	-104
2	6	24	17
3	6	147	137
-1	6	45	30
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-3	6	95	-33
-4	6	197	-240
-5	6	35	-32
-6	6	34	-43
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-9	6	39	-56
0	7	300	-328
1	7	89	63
2	7	275	274
3	7	141	-129
4	7	138	-179
-1	7	221	-219
-2	7	301	320
-3	7	93	90
-4	7	286	-343
-5	7	173	-198
-6	7	261	295
-7	7	130	130
-8	7	209	-259
0	8	98	-114
1	8	107	-35
2	8	112	96
3	8	106	97
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-5	8	42	-38
-6	8	126	-87
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0	9	295	-279
1	9	246	236
2	9	185	160
-1	9	337	-337
-2	9	147	141
-3	9	252	221
-4	9	235	-232
-5	9	317	-347
-6	9	213	216
-7	9	190	225
0	10	118	-116
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-5	10	35	-33
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-4	0	206	-229
-6	0	293	282
-8	0	155	-153
0	1	115	-135
1	1	129	-145
2	1	44	63
3	1	43	34
-1	1	48	-33
-2	1	71	59
-3	1	49	-53
-4	1	95	77
-5	1	35	12
-6	1	51	-41
-7	1	48	64
-8	1	61	67
1	2	159	178
2	2	186	194
3	2	160	-168
-1	2	175	-188
-2	2	228	231
-3	2	175	190
-4	2	248	-262
-5	2	164	-166
-6	2	193	233
-7	2	110	106
-8	2	129	-152
0	3	140	-175
1	3	62	-85
2	3	41	74
-1	3	142	-106
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-3	3	32	-42
-4	3	76	41
-6	3	53	-49
-7	3	26	36
-8	3	99	98
0	4	204	-189
1	4	204	213
2	4	74	60
3	4	181	-234
-1	4	329	-366
-2	4	194	210
-3	4	356	413
-4	4	128	-203
-5	4	291	-279
-6	4	120	134
-7	4	213	231
-8	4	100	-122
0	5	86	-59
1	5	71	-100
2	5	56	59
-1	5	43	-24
-2	5	63	41
-3	5	86	50
-4	5	49	-31
-5	5	113	-94
-7	5	22	16
-8	5	43	43
1	6	127	160
2	6	69	68
-1	6	275	-267
-2	6	77	-54
-3	6	329	329
-5	6	316	-340
-7	6	244	315
0	7	91	-81
-1	7	78	49
-4	7	26	-25
-5	7	19	-32
-6	7	66	-58
-7	7	41	-29
L = 7			
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0	1	74	71
-1	1	255	-277
-2	1	80	-78
-3	1	211	235
-4	1	81	85
-5	1	218	-247
-6	1	66	-67
-7	1	139	195
0	2	50	-60
-1	2	108	-131
0	3	125	149
-1	3	183	-208
-2	3	188	-250
-3	3	199	221
-4	3	197	213
-5	3	117	-134
-6	3	144	-176
0	4	50	-95
-1	4	51	-62
-4	4	56	50
-5	4	36	32
-6	4	52	-49
-1	5	36	-42
-2	5	210	-247
-3	5	64	63
-2	6	41	39
-4	6	56	65

intensity scale. The usual Lorentz and polarization corrections were applied to 1151 independent intensities. The crystals used for the intensity measurement had dimensions of $0.12\times0.25\times0.15$ and $0.13\times0.15\times0.30$ mm for the *b*-axis and *c*-axis Weissenberg photographs respectively, which were cut out from large crystals. No absorption correction was made.

Structure Determination

Since the unit-cell contains two molecules with the space group of $P2_1/a$, it is necessary for each molecule to lie on a crystallographic center of symmetry. The position of the nickel atom was readily deduced from a three-dimensional sharpened Patterson synthesis. The carbon atoms were found on successive Fourier syntheses phased initially by the nickel atom. The inclusion of these atoms in the structure-factor calculations reduced the conventional agreement index, $R(=\sum||F_o|-|F_c||/\sum|F_o|)$, from 0.36 to 0.28. The structure thus obtained was refined by the isotropic least-squares method; the *R* index fell to 0.20 after a few cycles of this refinement. The structure was further refined by several cycles of positional and anisotropic thermal parameters refinement, which led to the final *R* index of 0.121 for all the non-zero reflections. A difference Fourier synthesis was then computed in an attempt to find the positions of the hydrogen atoms. Some peaks appeared at or near the expected positions, but not all the hydrogen atoms could be located. Thus, contributions from the hydrogen atoms are not included in the structure-factor calculations. Throughout the refinement of the structure, equal weights were employed for all the reflections, and the atomic scattering factors were adopted from the International Tables for X-ray Crystallography.[2] The main part of the calculations was performed on the IBM7040 and 360 computers, with the use of the ERFR2 program for Fourier synthesis[3] and the HBLS program for structure-factor and least-squares refinement calculations.[4] The positional and anisotropic thermal parameters,along with their estimated standard deviations, are listed in Tables 2 and 3 respectively. The final observed and calculated structure factors are given in Table 4.

Results and Discussion

The principal interatomic bond distances and angles, along with their estimated standard deviations, are listed in Tables 5 and 6. A perspective view of the molecule is shown in Fig. 1, along with the atomic levels. Figure 2 represents the front and side views of the asymmetric unit of the molecule in order to show the mode of coordination of carbon atoms to the nickel.

The molecule has a crystallographic center of symmetry; therefore, two nickel atoms take a *trans* configuration, with a nickel-nickel distance of 4.31 Å. The nickel atom is bonded to the carbon atoms of the dihydropentalenylene ring and of the π-allyl group in a sandwich fashion. The nickel-carbon distances for the five-membered ring range from 2.03 Å to 2.27 Å, the closest nickel-carbon approach being to the non-bridging atoms of the ring. The mean Ni–C distance of 2.146 Å and the perpendicular distance from the nickel atom to the best plane of the ring carbons of 1.75 Å can well be compared with the corresponding ones observed in $(\pi\text{-}C_5H_5)Ni(P(C_6H_5)_3)C_6H_5$,[5] $(\pi\text{-}C_5H_5)Ni(P(C_6H_5)_3)C_6F_5$,[6] and other π-cyclopentadienyl nickel

Table 5. Principal interatomic lengths along with their estimated standard deviations in parentheses

Bond	Length	Bond	Length
Ni–C(1)	2.27(3)Å	C(1)–C(2)	1.44(3)Å
Ni–C(2)	2.08(3)	C(2)–C(3)	1.38(3)
Ni–C(3)	2.03(3)	C(3)–C(4)	1.42(3)
Ni–C(4)	2.08(3)	C(4)–C(1′)	1.45(3)
Ni–C(1′)	2.27(3)	C(1′)–C(1)	1.43(3)
Ni–C(5)	2.03(4)	C(5)–C(6)	1.41(4)
Ni–C(6)	1.92(4)	C(6)–C(7)	1.41(4)
Ni–C(7)	2.01(4)		

Table 6. Principal bond angles along with their estimated standard deviations in parentheses

	Angle
C(1)–C(2)–C(3)	107.2(1.2)°
C(2)–C(3)–C(4)	111.3(1.2)
C(3)–C(4)–C(1′)	105.5(1.2)
C(4)–C(1′)–C(1)	107.9(1.2)
C(1′)–C(1)–C(2)	107.5(1.3)
C(5)–C(6)–C(7)	118.5(1.5)
C(5)–Ni–C(7)	73.5(1.1)

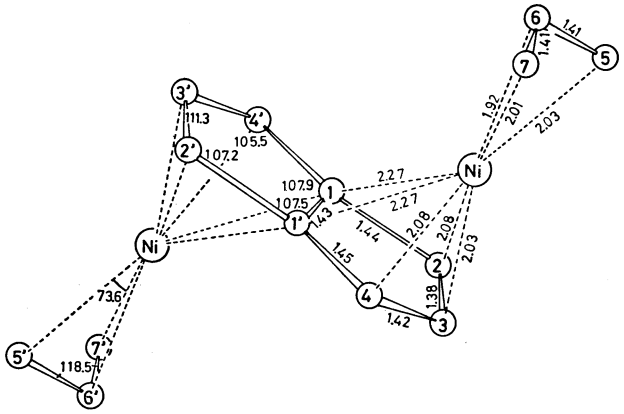

Fig. 1. A perspective view of the molecule.

2) "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham (1962).

3) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, ERFR2 Two and Three-Dimensional Crystallographic Fourier Summation Program, 1962.

4) T. Ashida, HBLS Universal Crystallographic Computation Program System (I) p. 65, The Crystallographic Society of Japan, 1967.

5) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.*, *A*, **1969**, 226.

6) M. R. Churchill and T. A. O'Brien, *ibid.*, *A*, **1968**, 2970.

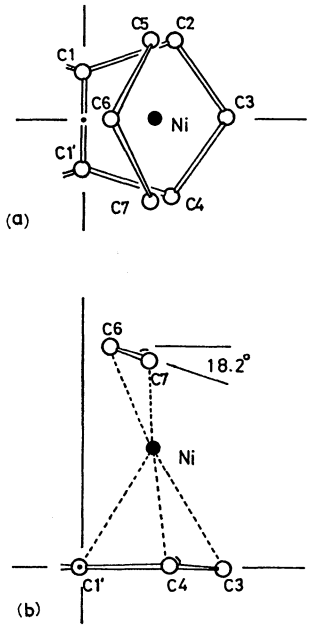

Fig. 2. (a) Front and (b) side views of the asymmetric unit of the molecule showing the mode of coordination of carbon atoms to the nickel. Center of symmetries are shown by dots.

complexes.[7-11] The dihydropentalenylene ring carbons are nearly coplanar. The best plane through the five-membered carbons of the ring is defined, with respect to the crystallographic axes, by this equation:

$$0.6605x + 1.1647y + 0.4975z = 0.0218.$$

The average displacement of atoms from the mean plane is 0.03 Å, with the maximum deviation of 0.05 Å for C(3). The mean carbon-carbon bond length of 1.424 Å, and the mean bond angle of 107.9° in the dihydropentalenylene ring, are comparable with those expected for the five-membered conjugated ring systems and are similar to the corresponding values found in π-cyclopentadienyl rings.[12]

As far as the allyl group is concerned, the mean distance of 1.99 Å of the carbon atoms of the π-allyl group from the nickel atom resembles those found in other allyl complexes of nickel[13-15] and palladium.[16-20]

The mean carbon-carbon bond length of 1.41 Å is within the range of those previously determined, and the bond angle of 118.5° is comparable with the values of 119.6° for dimeric 2-carboxyethyl-π-allylnickel bromide[13] and 118.9° for bis(1,2-diphenylphosphino)-

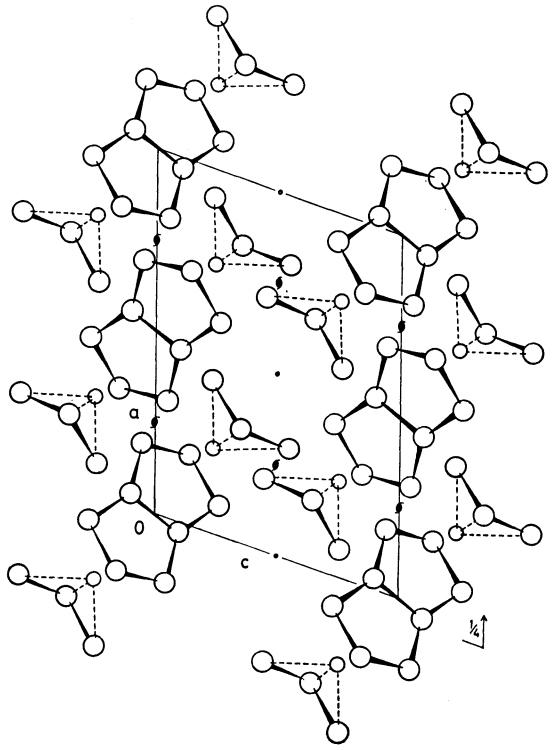

Fig. 3. The crystal structure projected along the *b* axis. Small and big circles represent nickel and carbon atoms, respectively.

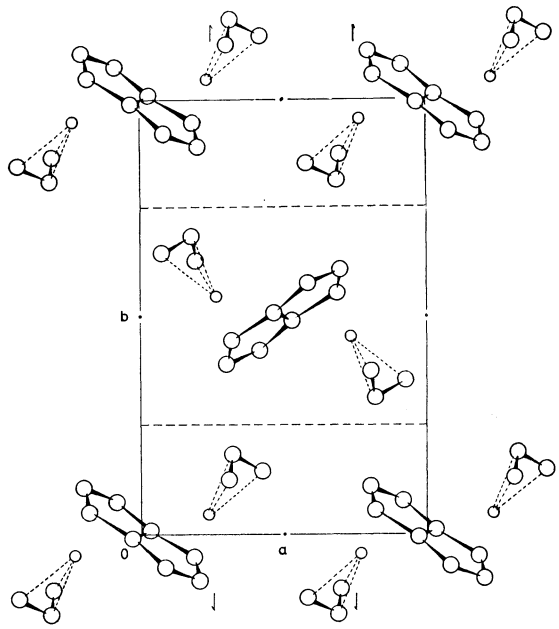

Fig. 4. The crystal structure projected along the *c* axis. Small and big circles represent nickel and carbon atoms, respectively.

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8) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc., A*, **1970**, 161.
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10) W. Oberhansli and L. F. Dahl, *Inorg. Chem.*, **4**, 150 (1965).
11) L. F. Dahl and C. H. Wei, *ibid.*, **2**, 713 (1963).
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13) M. R. Churchill and T. A. O'Brien, *Inorg. Chem.*, **6**, 1386 (1967).
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ethane-π-metallylnickel bromide.[14] The equation for the best plane containing the π-allyl carbon atoms is:

$$0.7066x + 0.6097y + 0.4419z = 4.2586.$$

The dihedral angle between this plane and that containing the carbon atoms of the dihydropentalenylene ring is 18.2° (Fig. 2), which is comparable with the corresponding value found in bis(cyclopentadienyl)-2,2'-bi-π-allyl-bis(nickel).[21]

The molecular arrangements in the crystal viewed along the *b* and *c* axes are illustrated in Figs. 3 and 4 respectively. The crystal is built up of individual molecules of $(C_8H_6)Ni_2(\pi\text{-}C_3H_5)_2$, with the adjacent molecules held together by van der Waals forces. All interatomic contacts less than 4.0 Å were calculated. There are no abnormally short distances.

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