Table VI

Angular Distortions of $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$ and $Ni(CN)_5^{3-}$ from Idealized Five-Coordinate Geometries

	Angles, deg			
Atoms	Trigonal bipyramid	$Ni(CN)_2$-$(P(C_6H_5)$-$(OC_2H_5)_2)_3$	$Ni(CN)_5^{3-}$	Tetragonal[a] pyramid
P_1–Ni–P_2[b]	120	113.0[c]	107.4	100
P_1–Ni–P_3	120	113.5	111.5	100
P_2–Ni–P_3	120	133.5	141.2	160
C_1–Ni–C_2	180	170.8	172.8	180
P_1–Ni–C_1	90	93.4	92.3	100
P_1–Ni–C_2	90	95.7	94.4	100
P_2–Ni–C_1	90	89.8	89.3	88
P_2–Ni–C_2	90	88.7	91.3	88
P_3–Ni–C_1	90	87.4	89.5	88
P_3–Ni–C_2	90	87.0	85.6	88

[a] These angles represent the average values for the tetragonal pyramid formed by $Ni(CN)_5^{3-}$, in which the Ni atom lies 0.34 Å above the plane of the four C atoms and 0.55 Å above the plane of the four N atoms.[9] These values appear to be normal for tetragonal pyramids involving first-row transition metals, in which the metal atom has been found to lie 0.3–0.6 Å above the tetragonal plane: see, for example, B. F. Hoskins, R. L. Martin, and A. H. White, *Nature,* **211**, 627 (1966). A purely electrostatic model with five equivalent ligands gives an L(apical)–M–L (basal) angle of 104°: J. Zemann, *Z. Anorg. Allgem. Chem.*, **324**, 241 (1963). [b] Or the corresponding C–Ni–C angle for the $Ni(CN)_5^{3-}$ ion. [c] The standard deviations of these angles range from 0.2 to 0.8°.

and the indirect evidence again indicates a trigonal-bipyramidal structure with axial cyanide groups. We feel that this fact, coupled with the close similarities between this compound and the $Ni(CN)_5^{3-}$ ion, tend to preclude such an argument based on steric grounds alone.

It is of interest to view this intermediate structure in relation to the infrared evidence and other similar structures. Although the symmetry of the inner coordination sphere in this case is halfway between the D_{3h} of a trigonal bipyramid and C_{2v} of a tetragonal pyramid, the infrared spectrum of the crystalline solid still exhibits a single C–N stretching frequency. This is, of course, one of the many examples of the ineffectiveness of band counting in the determination of important deviations from idealized symmetries. Moreover, it is just these small differences, inaccessible by nondiffraction means, that often present the clues to changes in chemical bonding on change of ligands. Clearly it is necessary to examine other $Ni(CN)_2(PR_3)_3$ structures in an attempt to understand possible causes for the distortion from idealized geometry observed here. The following paper discusses the structure of $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$.

Acknowledgments.—We are indebted to Drs. E. A. Rick and R. L. Pruett for supplying the crystals. J. K. S. gratefully acknowledges the support of the National Science Foundation through a predoctoral fellowship. We thank the National Science Foundation for its support of this work.

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

The Crystal and Molecular Structure of Dicyanotris(phenyldimethylphosphine)nickel(II), $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$

By JUDITH K. STALICK and JAMES A. IBERS

Received November 25, 1968

The crystal and molecular structure of dicyanotris(phenyldimethylphosphine)nickel(II), $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final R factor on F of 4.9%. The material crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system, with two molecules in a cell of dimensions a = 8.907 (8), b = 16.292 (15), c = 9.876 (9) Å, α = 97° 58 (1)′, β = 102° 40 (1)′, and γ = 86° 40 (1)′. (Reduced cell: a = 8.907, b = 16.292, c = 17.842 Å, α = 146° 46′, β = 93° 55′, and γ = 93° 20′.) The observed and calculated densities are 1.26 ± 0.01 and 1.260 g/cm³, respectively. The inner coordination about the Ni is trigonal bipyramidal with the two cyanides at the apices and the three phosphines in the basal plane. There is a slight but significant distortion toward a tetragonal-pyramidal geometry, which is discussed in relation to the far more distorted structure of $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$. The Ni–P bond lengths are 2.261 (3), 2.223 (3), and 2.223 (3) Å, and the Ni–C distances are 1.84 (1) and 1.86 (1) Å.

Introduction

In the preceding paper[1] the structure of $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$ was described. It was found that the geometry about the Ni atom is a highly distorted trigonal bipyramid, with a distortion remarkably similar to that found for one of the $Ni(CN)_5^{3-}$ ions in $[Cr(NH_2CH_2CH_2NH_2)_3][Ni(CN)_5]\cdot1.5H_2O$.[2] This paper describes the structure of $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$. Both $P(C_6H_5)(OC_2H_5)_2$ and $P(C_6H_5)(CH_3)_2$ should have similar steric requirements, but the latter phosphine is more basic and hence capable of transferring more electrons to the $Ni(CN)_2$ system. Thus any differences be-

---

[1] J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1084 (1969).

[2] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 1362 (1968).

tween the two $Ni(CN)_2(PR_3)_3$ structures should result from the effects of electronic changes to a far greater extent than from the effects of steric changes.

Collection and Reduction of the Intensity Data

Dark red-orange crystals of $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$ were prepared by Dr. E. Alyea and were kindly supplied by Professor D. W. Meek.[3] The material was recrystallized from benzene, yielding a few many-faceted crystals. A crystal of approximate dimensions 0.20 × 0.15 × 0.25 mm was attached to the end of a small glass fiber and mounted on a eucentric goniometer head. Preliminary precession photographs did not indicate any special symmetry or systematic absences, and a unit cell was defined assigning the b^* reciprocal lattice vector along the direction of the spindle axis. A Delaunay reduction failed to indicate any hidden symmetry, indicating space groups C_i^1-$P\bar{1}$ or C_1^1-$P1$ of the triclinic system. A convenient choice of a cell was made, with cell parameters as determined from diffractometer measurements using Mo Kα radiation (λ 0.7093 Å) of $a = 8.907$ (8), $b = 16.292$ (15), $c = 9.876$ (9) Å, $\alpha = 97° 58 (1)'$, $\beta = 102° 40 (1)'$, and $\gamma = 86° 40 (1)'$ (at 22°). The corresponding reduced cell parameters are $a = 8.907$, $b = 16.292$, $c = 17.842$ Å, $\alpha = 146° 46'$, $\beta = 93° 55'$, and $\gamma = 93° 20'$. The reduced cell was not used because of the inconveniently large value for α. The calculated density of 1.260 g/cm^3 for two molecules per cell agrees well with the experimental value of 1.26 ± 0.01 g/cm^3 obtained by flotation in n-C_7H_{16}–CF_2ClCCl_2F solution.

The cell parameters and orientation angles for the Picker four-circle automatic diffractometer were determined from a least-squares refinement of the setting angles of 16 carefully centered reflections as previously described.[4] Mo Kα radiation was used for data collection. The diffracted beams were filtered through a 3.0-mil Nb foil, and the intensities were collected by the θ–2θ scan technique at a takeoff angle of 1.2°. A scan range of 0.4° on the low-angle side of the Kα_1 peak to 0.4° on the high-angle side of the Kα_2 peak was found to be sufficient for all reflections; this gives an indication of the low mosaic spread of the crystal. The scan rate was 1.0°/min. Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The counter was placed 29 cm from the crystal and had an aperture of 7.0 × 7.0 mm.

A unique data set having $2\theta \leq 36°$ was initially collected. The intensities of four reflections at different positions in reciprocal space were monitored as standards after every 250 reflections had been collected, and each of these standards remained constant within experimental error throughout the data collection process. A second shell for $36° < 2\theta \leq 37°$ showed little intensity. In all, 2076 reflections were observed. The crystal was carefully measured by means of a micrometer eyepiece in preparation for the application of an absorption correction, and the 14 faces of the forms $\{100\}$, $\{010\}$, $\{001\}$, $\{110\}$, $\{1\bar{1}0\}$, $\{01\bar{1}\}$, and $\{1\bar{1}\bar{1}\}$ and the face $(\bar{1}\bar{1}1)$ were identified with the aid of an optical goniometer.

The data were corrected for background and standard deviations were assigned as previously described.[4] A value of 0.04 was assigned for p, and a later statistical analysis of the discrepancy factors indicated that this choice was reasonable. The data were also corrected for Lorentz and polarization effects at this time. Of the 2076 reflections, 1802 were greater than one standard deviation above background. Only the 1556 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$ were used in the solution and refinement of the structure.

Solution and Refinement of the Structure

A three-dimensional Patterson map was computed[5] which readily yielded the positions of the Ni and three P atoms and the two CN groups. Two cycles of least-squares refinement assuming the centric space group $P\bar{1}$ resulted in discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ of 32.3 and 39.9%, respectively, where the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In this and succeeding refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The atomic scattering factors for Ni, P, N, and C were those tabulated by Ibers,[6] and those of Stewart, *et al.*,[7] were used for H. The values given by Cromer[8] for $\Delta f'$ and $\Delta f''$ were used for the anomalous scattering by Ni and P.[9] A difference Fourier map gave the positions of the remaining 24 nonhydrogen atoms. Two cycles of least-squares refinement assigning isotropic temperature factors to all atoms and treating the phenyl rings as rigid groups[10] of known geometry and dimensions with a single group thermal parameter lowered the R_1 and R_2 values to 10.3 and 12.4%.

The intensities were then corrected for absorption, using a calculated absorption coefficient of 8.88 cm^{-1} for Mo radiation. The corresponding transmission factors ranged from 0.80 to 0.92. One cycle of least-squares refinement allowing the Ni and P atoms to vibrate anisotropically and assigning individual temperature factors to the C atoms of the phenyl rings was followed by the inclusion of the structure factor contributions of the phenyl group H atoms (C–H = 1.0 Å) added as fixed contributions to the calculated structure factors. The R_1 and R_2 values dropped to 7.7 and 9.8%, respectively. Next, anisotropic vibrations were permitted for all nongroup atoms. Two full cycles of refinement resulted in values for R_1 and R_2 of 6.4 and 7.8%. A difference Fourier map yielded the positions of the 18 H atoms associated with the methyl groups. There was no evidence of rotational disorder. The H

---

(3) D. W. Meek and E. Alyea, unpublished results.

(4) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(5) Programs used in this refinement included local modifications of Zalkin's FORDAP Fourier program, Hamilton's GONO9 absorption correction program, the Busing–Levy ORFLS least-squares and ORFFE error function programs, and Johnson's ORTEP plotting program.

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

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

(8) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(9) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(10) S. J. La Placa and J. A. Ibers, *ibid.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) (IN ELECTRONS) FOR $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$

K	L	FO	FC
***** H = 0 *****			
0	0		5534
0	2	237	236
0	3	342	310
0	4	336	298
0	5	350	339
0	6	145	141
0	7	210	216
0	8	151	127
1	-7	217	221
1	-6	179	168
1	-5	192	190
1	-4	293	275
1	-3	354	344
1	-2	462	445
1	-1	588	571
1	0	100	91
1	1	753	737
1	4	87	56
1	5	184	208
1	6	397	404
1	7	94	96
2	-8	163	175
2	-7	124	129
2	-6	361	359
2	-5	90	86
2	-4	166	170
2	-3	393	371
2	-2	553	556
2	-1	683	681
2	0	808	788
2	1	755	769
2	2	439	433
2	3	256	236
2	4	174	190
2	5	279	294
2	6	156	154
2	7	252	267
2	8	206	188
3	-8	172	153
3	-7	202	211
3	-5	116	140
3	-4	126	123
3	-3	561	582
3	-2	581	564
3	-1	60	55
3	0	330	334
3	1	391	379
3	2	63	45
3	3	160	167
3	4	168	178
3	5	332	322
3	6	402	401
3	7	224	240
4	-8	228	218
4	-7	209	215
4	-6	216	229
4	-5	109	83
4	-4	501	487
4	-3	330	317
4	-2	396	379
4	-1	930	904
4	0	331	312
4	1	287	278
4	2	160	153
4	3	476	476
4	4	95	109
4	5	225	229
4	7	271	272
5	-7	126	119
5	-6	81	43
5	-5	222	208
5	-4	149	161
5	-3	130	110
5	-2	471	456
5	-1	619	619
5	0	272	281
5	1	608	593
5	2	204	211
5	3	102	88
5	4	389	391
5	6	175	171
5	7	81	76
6	-8	156	151
6	-4	334	347
6	-3	1042	1050
6	-2	299	291
6	-1	163	151
6	0	84	81
6	1	127	137
6	2	55	30
6	3	557	536
6	4	363	343
6	5	162	164
7	-7	118	122
7	-6	91	84
7	-5	324	312
7	-4	588	585
7	-3	142	115
7	-2	420	432
7	-1	354	334
7	0	255	245
7	1	132	142
7	2	218	236
7	3	362	364
7	4	73	79
8	-6	136	120
8	-4	429	406
8	-3	803	815
8	-1	232	228
8	0	159	153
8	1	149	164
8	2	121	128
8	3	201	183
8	4	239	238
8	5	215	216
8	6	116	98
9	-6	245	230
9	-4	198	211
9	-3	81	66
9	-2	312	303
9	0	129	129
9	1	103	102
9	2	486	501
9	3	442	452
9	4	119	97
9	6	119	102
10	-3	378	374
10	-1	279	275
10	0	229	224
10	1	244	255
10	2	241	255
10	4	231	222
10	5	140	118
11	-5	121	139
11	-4	150	153
11	-3	133	133
11	1	139	144
11	2	233	225
11	3	290	275
12	-5	182	165
12	-4	127	131
12	-2	165	152
12	-1	192	171
12	0	250	254
12	1	74	50
12	2	90	81
13	-4	112	130
13	-3	164	168
13	-1	309	310
14	-3	116	119
14	-2	134	129
14	-1	155	129
14	0	153	143
14	1	106	100
***** H = 1 *****			
-14	0	276	273
-14	1	124	135
-14	2	120	108
-13	-1	165	179
-13	0	129	116
-13	1	158	147
-13	3	155	142
-12	-3	174	169
-12	-2	103	104
-12	0	94	107
-12	2	182	186
-12	3	189	196
-12	4	106	119
-12	5	159	191
-11	-4	158	173
-11	-2	105	109
-11	-1	215	214
-11	0	253	258
-11	2	115	106
-11	6	138	130
-10	-4	270	275
-10	-3	407	424
-10	-2	132	127
-10	-1	111	136
-10	0	80	81
-10	1	191	196
-10	2	82	69
-10	3	154	147
-10	4	80	89
-10	5	209	197
-10	6	119	85
-9	-6	125	118
-9	-5	240	254
-9	-4	206	194
-9	-2	112	104
-9	-1	233	242
-9	0	219	216
-9	1	69	74
-9	2	479	492
-9	3	392	389
-9	4	73	84
-9	5	90	88
-9	7	94	77
-8	-4	258	242
-8	-3	319	329
-8	-2	238	245
-8	-1	105	101
-8	0	473	443
-8	1	177	197
-8	2	245	224
-8	3	159	163
-8	4	429	408
-8	5	280	277
-8	6	164	156
-7	-6	116	139
-7	-5	216	194
-7	-4	293	303
-7	-2	66	66
-7	-1	91	101
-7	0	72	77
-7	1	257	245
-7	2	650	631
-7	3	626	655
-7	4	92	89
-7	5	81	75
-7	6	77	70
-7	7	113	102
-6	-6	159	170
-6	-5	212	202
-6	-4	83	82
-6	-3	472	487
-6	-2	207	207
-6	-1	477	492
-6	0	195	201
-6	1	239	248
-6	2	260	276
-6	3	194	185
-6	4	339	347
-6	5	204	197
-5	-7	76	59
-5	-6	89	83
-5	-5	142	145
-5	-4	249	261
-5	-3	65	55
-5	-2	425	384
-5	-1	71	48
-5	0	145	138
-5	1	105	109
-5	2	573	584
-5	3	831	846
-5	4	56	44
-5	5	243	241
-5	6	118	157
-5	7	262	260
-4	-8	107	95
-4	-7	301	292
-4	-6	279	291
-4	-5	242	264
-4	-4	172	158
-4	-3	146	158
-4	-2	320	291
-4	0	141	142
-4	1	367	378
-4	2	683	676
-4	3	172	170
-4	6	139	143
-4	7	133	137
-4	8	223	227
-3	-8	268	274
-3	-7	189	214
-3	-6	183	199
-3	-5	145	130
-3	-4	105	90
-3	-3	178	187
-3	-2	327	338
-3	-1	407	409
-3	0	53	40
-3	1	774	763
-3	2	797	800
-3	3	651	632
-3	4	179	149
-3	5	254	250
-3	6	205	209
-3	7	112	107
-3	6	105	102
-2	-7	261	263
-2	-6	215	210
-2	-5	202	194
-2	-4	209	224
-2	-3	649	660
-2	-2	366	355
-2	-1	317	316
-2	0	80	80
-2	1	349	322
-2	2	1123	1166
-2	4	127	135
-2	5	84	97
-2	6	172	178
-1	-8	216	212
-1	-7	191	198
-1	-6	196	188
-1	-5	296	296
-1	-4	457	444
-1	-3	281	298
-1	-2	56	57
-1	-1	1826	1921
-1	0	1049	1046
-1	1	316	299
-1	2	1003	991
-1	3	364	375
-1	4	158	151
-1	5	200	166
-1	6	132	157
-1	7	86	74
-1	8	83	70
0	-8	157	136
0	-6	259	232
0	-5	138	149
0	-4	111	121
0	-3	422	424
0	-2	435	458
0	-1	653	645
0	0	682	640
0	1	674	665
0	2	133	119
0	3	217	237
0	5	431	429
0	6	229	217
0	8	78	77
1	-8	105	108
1	-7	256	266
1	-5	443	441
1	-3	114	132
1	-2	668	663
1	-1	794	795
1	0	760	724
1	1	325	343
1	2	629	624
1	4	359	341
1	6	310	288
1	7	169	188
1	8	140	148
2	-8	199	188
2	-6	143	159
2	-4	338	344
2	-3	299	291
2	-2	333	322
2	-1	396	402
2	0	308	292
2	1	664	659
2	2	472	466
2	3	92	91
2	4	168	177
2	5	615	610
2	6	281	288
3	-8	135	124
3	-7	122	136
3	-6	148	120
3	-5	205	216
3	-4	63	52
3	-3	413	379
3	-2	1096	1083
3	-1	345	321
3	0	641	627
3	1	1143	1163
3	2	676	682
3	3	56	24
3	4	231	223
3	6	357	355
3	7	224	220
4	-8	169	171
4	-6	410	386
4	-5	144	154
4	-4	124	102
4	-3	249	256
4	-2	473	470
4	-1	826	822
4	0	194	193
4	1	138	142
4	2	407	388
4	3	378	350
4	5	277	293
4	6	237	226
5	-5	270	263
5	-4	526	521
5	-3	549	556
5	-1	536	499
5	0	792	783
5	1	69	87
5	2	476	468
5	3	272	273
5	4	122	137
5	5	110	105
6	-6	356	367
6	-5	659	655
6	-4	115	103
6	-3	523	532
6	-2	337	341
6	-1	575	566
6	0	147	165
6	2	424	444
6	3	231	221
7	-8	109	96
7	-7	117	88
7	-5	308	322
7	-4	814	801
7	-2	281	276
7	-1	295	313
7	0	524	509
7	1	181	189
7	2	197	208
7	3	214	214
7	4	160	160
7	5	200	187
8	-7	156	142
8	-6	300	280
8	-5	174	188
8	-4	202	189
8	-3	338	347
8	-2	376	383
8	1	235	241
8	2	652	641
8	3	285	271
8	4	137	147
8	6	140	149
9	-6	146	127
9	-5	124	113
9	-4	128	141
9	-3	398	379
9	-2	314	307
9	-1	223	237
9	0	230	244
9	1	326	308
9	3	216	210
9	4	157	147
10	-5	117	113
10	-4	247	262
10	-2	246	264
10	-1	77	68
10	1	202	201
10	2	384	383
10	3	150	142
10	4	159	172
10	5	126	119
11	-6	195	192
11	-5	209	205
11	-3	196	191
11	-2	165	176
11	-1	337	326
11	1	199	198
11	3	196	199
12	-5	111	127
12	-4	210	213
12	-2	366	335
12	-1	202	203
12	1	85	94
12	2	79	83
13	-3	155	165
13	-2	109	88
13	-1	139	110
13	0	111	102
13	2	129	110
14	-3	123	110
14	-2	157	163
14	-1	353	344
14	0	154	155
***** H = 2 *****			
-13	-2	114	104
-13	-1	114	115
-13	0	153	140
-13	1	138	143
-13	2	233	229
-13	3	104	96
-12	-2	128	113
-12	-1	191	202
-12	1	103	122
-11	-4	246	270
-11	-3	138	118
-11	-2	91	80
-11	-1	69	75
-11	0	145	147
-11	1	59	14
-11	2	249	243
-11	5	122	116
-10	-5	234	218
-10	-3	87	80
-10	-2	152	160
-10	-1	214	222
-10	0	88	95
-10	1	269	263
-10	2	317	336
-10	4	214	204
-9	-5	97	91
-9	-4	305	305
-9	-3	137	121
-9	-2	55	1
-9	-1	190	182
-9	0	367	371
-9	1	307	310
-9	3	130	103
-9	4	182	181
-9	5	213	212
-8	-6	136	125
-8	-5	227	222
-8	-4	131	145
-8	-3	96	101
-8	-2	123	117
-8	-1	218	220
-8	0	190	179
-8	1	429	415
-8	2	462	478
-8	3	300	299
-8	4	72	49
-8	5	107	105
-8	6	119	129
-7	-6	143	131
-7	-4	292	277
-7	-2	461	479
-7	-1	280	279
-7	0	417	455
-7	1	449	429
-7	3	335	352
-7	4	300	291
-7	5	115	106
-7	7	159	161
-6	-6	90	90
-6	-5	289	305
-6	-4	158	128
-6	-3	209	194
-6	-2	204	207
-6	-1	143	128
-6	0	143	122
-6	1	199	187
-6	2	442	449
-6	4	172	169
-6	5	179	211
-6	6	210	200
-6	7	183	190
-5	-7	159	166
-5	-6	251	258
-5	-5	178	167
-5	-4	86	86
-5	-3	159	156
-5	-1	344	337
-5	1	99	115
-5	2	164	162
-5	3	57	30
-5	4	281	292
-5	6	230	229
-5	7	246	243
-4	-8	174	199
-4	-6	133	120
-4	-4	181	195
-4	-2	628	643
-4	-1	729	739
-4	0	161	145
-4	1	173	192
-4	2	305	305
-4	3	149	155
-4	4	174	168
-4	5	308	334
-4	6	161	149
-4	7	81	87
-3	-8	101	90
-3	-7	318	303
-3	-6	167	170
-3	-5	191	185
-3	-4	314	296
-3	-3	652	628
-3	-2	308	319
-3	-1	205	196
-3	0	167	169
-3	1	363	360
-3	2	470	466
-3	3	478	513
-3	4	237	235
-3	6	75	64
-2	-8	178	174
-2	-6	176	167
-2	-5	139	161
-2	-4	343	348
-2	-3	191	176
-2	-2	423	414
-2	-1	539	545
-2	1	705	690
-2	2	342	314
-2	3	388	384
-2	4	536	531
-2	5	102	95
-2	7	131	113
-1	-7	204	206
-1	-6	79	90
-1	-5	189	177
-1	-4	436	452
-1	-3	780	770
-1	-2	328	316
-1	-1	138	145
-1	0	320	336
-1	2	187	201
-1	3	136	113
-1	4	644	638
-1	5	326	320
-1	6	107	128
-1	7	93	80
0	-8	198	214
0	-7	71	48
0	-6	389	407
0	-4	80	79
0	-3	57	46
0	-2	497	472
0	-1	242	259
0	0	111	119
0	1	333	363
0	2	537	517
0	3	377	369
0	4	306	316
0	5	220	216
0	6	119	118
0	7	115	133
1	-7	125	122
1	-6	65	43
1	-5	165	153
1	-4	555	545
1	-3	521	538
1	-2	356	374
1	-1	122	121
1	0	345	326
1	1	982	980
1	2	175	166
1	3	185	186
1	4	583	585
1	5	428	434
1	6	76	82
2	-8	105	109
2	-5	188	185
2	-2	197	195
2	-1	310	295
2	0	944	927
2	1	605	602
2	2	835	844
2	3	614	590
2	4	181	186
2	5	241	249
2	6	170	181
3	-7	265	255
3	-6	257	268
3	-5	157	156
3	-3	335	322
3	-2	459	458
3	-1	71	67
3	0	634	631
3	1	948	950
3	3	248	254
3	4	152	160
3	5	405	366
3	7	140	134
4	-8	90	78
4	-7	128	137
4	-6	280	282
4	-5	435	479
4	-4	501	514
4	-3	471	434
4	-2	154	167
4	-1	426	422
4	0	90	91
4	1	412	433
4	2	114	110
4	4	204	197
4	6	82	62
5	-7	360	374
5	-6	575	567
5	-5	366	356
5	-4	206	191
5	-2	386	362
5	-1	387	389
5	0	468	464
5	1	623	661
5	2	234	238
6	-7	115	97
6	-6	140	154
6	-5	738	705
6	-4	255	254
6	-3	152	123
6	-2	333	301
6	-1	873	850
6	0	490	517
6	2	105	61
6	4	243	246
6	5	85	95
7	-7	317	303
7	-6	412	420
7	-5	85	80
7	-4	194	204
7	-3	212	208
7	-2	70	57
7	-1	220	215
7	0	327	328
7	1	902	886
7	2	465	491
7	3	105	119
7	4	82	80
7	5	173	192
8	-6	106	130
8	-4	226	225
8	-3	194	177
8	-2	299	311
8	-1	352	377
8	0	474	447
8	2	69	61
8	4	106	109
8	5	105	98
9	-6	73	61
9	-5	160	167
9	-3	288	309
9	-2	180	171
9	-1	89	93
9	0	282	265
9	1	499	493
9	2	352	361
9	3	118	135
9	4	227	216
9	5	120	103
10	-7	141	135
10	-6	339	319
10	-4	103	108
10	-3	104	93
10	-2	284	278
10	-1	223	223
10	0	210	205
10	1	168	172
10	2	235	236
11	-6	119	114
11	-5	150	147
11	-3	360	350
11	-2	323	325
11	0	113	96
11	2	110	104
11	3	192	189
11	4	142	131
12	-5	95	90
12	-4	243	238
12	-3	97	123
12	-2	117	120
12	-1	187	197
12	1	101	88
12	2	89	56
12	3	135	129
13	-3	239	253
13	-2	378	379
13	-1	239	226
13	1	105	111
13	2	92	84
14	-3	271	271
14	0	106	102
***** H = 3 *****			
-13	0	190	194
-13	1	99	96
-12	-3	104	84
-12	-1	162	158
-12	1	164	180
-11	-3	100	96
-11	-2	171	166
-11	0	114	107
-11	1	278	293
-11	2	122	134
-11	3	88	94
-11	4	77	78
-10	-5	109	97
-10	-4	104	107
-10	-1	207	204
-10	0	240	246
-10	4	133	136
-9	-5	94	77
-9	-4	76	73
-9	-3	174	165
-9	-2	222	206
-9	-1	111	117
-9	0	289	301
-9	1	428	423
-9	2	314	317
-9	3	141	121
-9	5	98	118
-8	-5	78	77
-8	-4	118	146
-8	-2	121	125
-8	-1	338	364
-8	0	580	597
-8	1	105	110
-8	2	178	164
-8	4	105	104
-8	6	139	136
-7	-6	196	200
-7	-5	137	119
-7	-4	153	143
-7	-3	245	242
-7	-2	131	155
-7	-1	125	91
-7	0	117	114
-7	1	593	600
-7	2	104	102
-7	3	169	184
-7	4	96	94
-7	5	229	220
-7	6	265	256
-6	-6	236	252
-6	-5	114	89
-6	-4	217	245
-6	-3	163	166
-6	-2	185	178
-6	0	242	274
-6	1	76	71
-6	2	274	283
-6	3	100	91
-6	4	84	86
-6	5	137	151
-6	6	236	223
-5	-5	279	314
-5	-3	336	354
-5	-2	433	420
-5	-1	110	130
-5	0	104	79
-5	1	83	77
-5	3	141	172
-5	4	254	261
-5	5	404	381
-5	6	156	156
-4	-7	75	66
-4	-4	453	452
-4	-3	209	231
-4	-1	65	67
-4	0	63	63
-4	1	467	475
-4	2	121	113
-4	3	220	217
-4	6	145	133
-4	7	151	130
-3	-6	143	156
-3	-5	295	280
-3	-3	430	394
-3	-2	539	564
-3	-1	395	383
-3	0	239	246
-3	2	335	345
-3	3	246	245
-3	4	267	285
-3	6	201	191
-2	-7	123	115
-2	-5	290	273
-2	-4	556	543
-2	-3	443	428
-2	-2	92	113
-2	-1	340	317
-2	0	193	207
-2	1	230	226
-2	2	128	147
-2	3	678	705
-2	4	508	490
-2	6	148	165
-1	-7	190	216
-1	-6	246	233
-1	-4	234	229
-1	-3	207	221
-1	-2	1036	1032
-1	-1	254	231
-1	0	302	288
-1	1	212	203
-1	2	203	226
-1	3	507	527
-1	5	189	187
-1	7	108	100
0	-8	86	94
0	-7	161	157
0	-6	89	77
0	-5	311	328
0	-4	342	332
0	-3	589	591
0	-2	148	154
0	-1	397	403
0	0	103	104
0	1	178	174
0	2	101	125
0	3	540	521
0	4	680	697
1	-7	139	143
1	-6	173	176
1	-5	213	202
1	-2	461	458
1	0	220	220
1	1	503	508
1	2	937	933
1	3	386	408
1	6	76	36
1	7	88	97
2	-8	151	129
2	-7	315	313
2	-6	180	183
2	-4	401	397
2	-3	213	213
2	-2	147	148
2	-1	68	82
2	0	272	245
2	1	270	266
2	2	255	249
2	3	312	336
2	4	382	376
2	6	164	155
2	7	84	75
3	-8	212	215
3	-7	114	111
3	-6	323	335
3	-5	244	252
3	-4	488	466
3	-3	371	387
3	-2	78	89
3	-1	117	106
3	0	191	183
3	1	379	382
3	2	265	280
3	3	194	185
3	4	78	74
3	5	113	102
4	-8	236	228
4	-7	440	454
4	-6	307	316
4	-5	84	81
4	-4	124	131
4	-3	120	102
4	-2	93	90
4	-1	394	394
4	0	236	222
4	1	161	154
4	4	138	130
4	6	164	159
5	-8	172	185
5	-6	330	335
5	-5	408	386
5	-4	202	210
5	-3	369	340
5	-2	171	181
5	-1	439	465
5	1	255	258
5	2	68	65
5	3	213	222
5	4	80	86
6	-8	141	147
6	-7	385	373
6	-6	191	212
6	-5	121	107
6	-4	294	286
6	-2	159	171
6	0	854	842
6	1	648	632
6	3	159	128
6	6	143	107
7	-8	88	103
7	-7	198	199
7	-6	83	85
7	-5	158	182
7	-4	93	92
7	-3	238	239
7	-2	190	182
7	-1	681	682
7	0	362	368
7	1	217	204
7	2	113	115
7	3	191	194
7	5	140	160
8	-6	117	105
8	-5	138	136
8	-4	337	355
8	-3	179	171
8	-1	287	273
8	0	708	700
8	1	539	556
8	3	138	122
8	4	139	141
8	5	138	125
9	-7	238	227
9	-6	159	141
9	-5	159	133
9	-4	157	140
9	-3	169	213
9	-2	289	302
9	-1	345	343
9	0	164	169
9	1	164	161
9	2	125	114
9	4	85	72
10	-4	261	251
10	-3	158	156
10	1	247	248
10	2	284	286
10	3	232	239
10	4	100	94
11	-5	243	239
11	-4	209	212
11	-3	87	69
11	-1	149	144
11	0	117	126
11	1	116	115
11	2	107	108
11	3	140	118
12	-5	91	86
12	-4	143	156
12	-3	304	306
12	-2	270	259
12	0	118	115
12	2	81	78
13	-4	403	387
13	-3	173	168
13	-1	108	93
13	0	156	144
***** H = 4 *****			
-12	-1	95	85
-12	0	153	150
-12	1	137	150
-11	-2	88	89
-11	-1	212	212
-11	0	112	81
-11	3	115	125
-10	-3	125	99
-10	-2	169	191
-10	-1	118	118
-10	0	315	331
-10	1	200	188
-10	2	109	94
-9	-2	294	296
-9	-1	409	420
-9	0	127	119
-9	2	76	80
-9	3	127	127
-8	-5	118	121
-8	-4	71	63
-8	-3	228	269
-8	-2	168	127
-8	-1	63	98
-8	0	351	350
-8	1	219	228
-8	2	148	169
-8	4	134	140
-8	5	211	218
-7	-5	182	203
-7	-3	93	101
-7	-2	120	96
-7	-1	315	324
-7	0	228	226
-7	1	251	250
-7	2	114	111
-7	3	78	86
-7	4	141	157
-6	-6	93	86
-6	-4	312	341
-6	-3	137	134
-6	-2	128	159
-6	-1	102	81
-6	0	77	100
-6	1	224	221
-6	2	170	183
-6	3	245	243
-6	4	236	218
-6	5	248	264
-5	-5	256	247
-5	-4	277	284
-5	-2	137	130
-5	0	277	273
-5	1	103	78
-5	2	284	276
-5	4	97	114
-5	5	74	86
-5	6	234	237
-4	-5	122	94
-4	-4	279	242
-4	-3	372	385
-4	-2	173	181
-4	-1	293	282
-4	1	337	323
-4	2	112	103
-4	3	237	258
-4	5	145	174
-4	6	95	113
-3	-5	466	490
-3	-4	613	649
-3	-3	130	98
-3	-2	85	101
-3	-1	162	169
-3	0	607	606
-3	1	115	92
-3	2	254	227
-3	3	242	252
-3	5	183	196
-2	-7	110	86
-2	-6	207	211
-2	-5	228	229
-2	-4	136	142
-2	-3	605	578
-2	-2	231	234
-2	-1	223	230
-2	0	78	76
-2	1	279	303
-2	2	377	374
-2	3	106	102
-2	4	175	171
-2	6	107	104
-1	-6	119	120
-1	-5	323	309
-1	-4	468	469
-1	-3	260	291
-1	-2	504	540
-1	-1	100	89
-1	0	170	177
-1	1	191	171
-1	2	277	274
-1	3	496	490
-1	4	235	248
0	-8	134	118
0	-7	171	177
0	-6	243	257
0	-5	250	239
0	-3	231	228
0	-2	245	232
0	-1	392	360
0	0	283	282
0	1	315	284
0	2	405	421
0	3	141	146
0	4	139	153
0	5	103	94
0	6	114	100
1	-8	171	182
1	-7	136	125
1	-6	63	48
1	-5	139	138
1	-4	69	88
1	-1	240	250
1	0	122	120
1	2	175	195
1	3	407	400
1	4	91	84
1	5	170	167
1	6	86	100
2	-7	227	217
2	-6	211	207
2	-5	261	264
2	-4	333	334
2	-3	54	53
2	-2	319	319
2	-1	245	242
2	0	319	315
2	1	180	218
2	2	143	152
2	3	111	102
2	4	232	224
2	5	152	163
3	-8	331	319
3	-7	275	300
3	-3	160	167
3	-2	340	318
3	-1	333	319
3	0	68	102
3	1	201	205
3	3	319	308
3	5	199	208
3	6	145	151
4	-8	99	92
4	-7	196	183
4	-6	242	226
4	-5	290	285
4	-4	185	186
4	-3	215	240
4	-2	502	519
4	0	110	90
4	2	217	228
4	4	186	189
4	5	79	76
5	-8	268	263
5	-7	309	313
5	-5	224	224
5	-4	185	183
5	-3	80	106
5	-1	348	364
5	0	419	391
5	1	134	147
5	3	91	106
5	4	96	88
5	5	98	97
6	-8	185	175
6	-7	96	97
6	-6	280	267
6	-4	113	125
6	-3	285	281
6	-2	621	619
6	-1	597	576
6	1	260	265
6	2	143	156
6	3	178	188
6	5	137	148
7	-7	160	161
7	-5	401	414
7	-4	271	289
7	-3	232	210
7	-1	320	303
7	0	478	491
7	1	79	100
7	2	63	11
7	4	187	185
8	-7	110	77
8	-6	130	107
8	-5	83	86
8	-4	193	187
8	-3	282	270
8	-2	491	475
8	-1	166	172
8	1	285	296
8	2	187	191
8	3	132	157
9	-5	198	179
9	-4	239	222
9	0	226	227
9	1	121	98
9	2	334	340
9	3	84	83
10	-6	198	201
10	-5	258	260
10	-1	191	189
10	1	202	214
10	2	171	160
11	-4	152	139
11	-3	97	109
11	-2	195	189
11	-1	114	123
11	2	170	183
12	-4	252	244
12	-1	123	112
12	1	121	119
***** H = 5 *****			
-10	-2	270	274
-10	-1	142	132
-10	2	124	134
-9	-3	172	169
-9	-1	186	159
-9	0	120	137
-9	3	95	90
-8	-3	72	37
-8	-2	275	291
-8	-1	219	206
-8	1	85	73
-8	2	127	132
-8	3	222	238
-7	-5	187	195
-7	-3	105	84
-7	-2	198	225
-7	-1	105	113
-7	0	173	149
-7	1	74	68
-7	2	153	162
-7	3	83	99
-7	4	210	196
-6	-6	118	117
-6	-5	131	110
-6	-2	164	165
-6	-1	205	206
-6	1	248	248
-6	2	190	200
-6	3	182	185
-5	-4	190	181
-5	-3	244	265
-5	-2	200	173
-5	0	231	228
-5	2	210	213
-5	4	88	65
-5	5	120	106
-4	-6	162	166
-4	-5	372	420
-4	-4	214	199
-4	-1	326	356
-4	1	280	282
-4	2	106	92
-4	4	102	71
-4	5	77	60
-3	-7	81	82
-3	-6	132	143
-3	-4	261	251
-3	-3	218	226
-3	-1	116	109
-3	0	266	290
-3	1	318	307
-3	4	159	169
-2	-6	174	190
-2	-5	406	409
-2	-4	230	227
-2	-3	207	226
-2	-2	187	173
-2	-1	173	164
-2	0	352	365
-2	1	241	253
-2	2	297	289
-2	3	195	212
-2	4	153	145
-1	-6	124	108
-1	-4	192	176
-1	-3	154	160
-1	-2	167	182
-1	-1	162	163
-1	0	287	276
-1	1	480	479
-1	2	231	233
0	-5	284	292
0	-4	79	66
0	-3	182	189
0	-2	234	219
0	-1	284	315
0	0	147	159
0	1	159	161
0	2	345	370
0	3	209	206
0	4	104	97
0	5	120	115
1	-6	156	165
1	-5	187	169
1	-3	223	222
1	-2	135	131
1	-1	270	275
1	0	190	183
1	1	244	255
1	2	138	107
1	3	188	173
1	4	220	214
1	5	81	100
2	-5	124	111
2	-4	271	286
2	-3	126	145
2	-2	465	467
2	-1	251	253
2	0	281	278
2	2	137	125
2	4	161	131
2	5	153	154
3	-7	132	138
3	-6	177	198
3	-5	209	203
3	-4	128	141
3	-3	433	410
3	-2	187	190
3	-1	89	99
3	0	132	111
3	2	125	129
3	3	191	196
3	4	197	205
4	-6	127	125
4	-5	186	187
4	-4	251	249
4	-3	97	103
4	-2	315	334
4	-1	378	360
4	0	187	183
4	1	202	235
4	3	186	193
4	4	96	86
5	-7	286	267
5	-6	81	80
5	-5	74	67
5	-4	78	82
5	-3	573	588
5	-2	526	526
5	-1	133	148
5	1	75	90
5	2	169	199
5	4	187	205
6	-6	305	323
6	-5	171	188
6	-4	199	187
6	-3	325	332
6	-2	110	94
6	-1	276	281
6	0	167	176
6	3	229	240
7	-6	206	197
7	-5	84	80
7	-4	186	201
7	-3	391	380
7	-2	325	328
7	0	97	118
7	1	191	192
7	2	178	164
8	-5	281	267
8	-3	93	111
8	-1	132	107
8	1	208	186
8	2	191	199
8	3	254	252
9	-6	182	195
9	-2	110	100
9	0	247	263
9	1	238	225
10	-3	94	87
10	-2	135	129
10	1	191	199
11	-4	110	107
11	0	132	132
***** H = 6 *****			
-8	-3	165	176
-8	-1	173	146
-7	-2	182	185
-7	0	188	190
-7	1	188	191
-7	2	170	180
-6	-4	96	118
-6	-3	126	91
-6	-1	182	166
-6	3	111	99
-5	-5	109	110
-5	-2	147	156
-5	0	231	237
-5	1	154	120
-5	2	109	131
-4	-6	77	69
-4	-4	81	57
-4	-3	110	103
-4	-1	185	183
-4	0	243	247
-4	3	128	136
-3	-6	209	209
-3	-3	142	147
-3	-2	191	183
-3	-1	222	232
-3	1	218	224
-3	2	107	73
-3	3	123	135
-2	-4	134	152
-2	-3	95	102
-2	-1	188	181
-2	0	407	402
-2	1	268	264
-1	-5	72	34
-1	-4	194	220
-1	-3	248	222
-1	-2	299	318
-1	-1	278	271
-1	1	283	289
-1	2	280	293
0	-6	155	155
0	-4	250	248
0	-3	97	117
0	-1	147	141
0	0	422	410
0	1	193	203
0	2	162	160
0	3	112	90
1	-5	183	199
1	-4	92	95
1	-3	299	324
1	-2	169	129
1	-1	223	224
1	1	217	212
1	3	102	101
1	4	95	110
2	-6	157	136
2	-4	352	348
2	-3	202	212
2	1	85	86
2	2	102	89
2	3	157	162
2	4	96	66
3	-6	96	93
3	-5	313	311
3	-4	109	100
3	-3	190	200
3	-2	143	116
3	-1	113	108
3	0	168	191
3	1	106	101
3	2	122	132
4	-4	360	357
4	-3	448	452
4	-2	100	90
4	-1	147	162
4	0	92	95
4	1	134	142
4	2	97	92
4	3	205	205
5	-6	162	161
5	-5	139	145
5	-4	354	373
5	-2	214	238
5	-1	111	123
5	2	154	154
5	3	145	158
6	-5	122	142
6	-4	152	148
6	-3	413	407
6	-2	103	126
6	-1	135	164
6	0	120	117
6	1	135	120
6	2	111	122
7	-6	198	203
7	-5	165	174
7	-4	105	116
7	-2	240	231
7	0	126	111
7	1	140	158
7	2	248	242
8	-4	79	78
8	-3	112	111
8	-1	241	221
8	0	195	193
8	1	98	97
9	-4	80	71
9	-2	100	108
9	-1	147	159
9	0	98	103
10	-1	95	85
***** H = 7 *****			
-6	-1	117	116
-5	-1	227	226
-4	-2	155	150
-4	0	143	145
-3	-2	123	108
-3	-1	300	298
-3	0	236	232
-3	1	84	70
-2	-5	81	109
-2	-4	88	63
-2	-3	181	184
-2	-2	261	275
-2	-1	97	67
-2	0	98	71
-2	1	172	161
-1	-5	126	120
-1	-4	99	119
-1	-2	110	121
-1	-1	300	302
-1	0	208	223
-1	2	91	83
0	-5	80	86
0	-4	141	156
0	-3	138	128
0	-2	186	187
0	-1	81	78
0	0	151	163
0	1	79	63
0	2	81	71
1	-5	176	161
1	-4	207	221
1	1	99	97
1	2	172	152
2	-4	122	101
2	-1	116	110
3	-5	174	161
3	-4	396	397
3	-3	86	63
3	-2	134	143
3	-1	89	100
3	0	187	196
4	-5	192	222
4	-3	164	170
4	-1	142	132
4	1	163	161
5	-5	127	116
5	-4	367	351
5	-3	249	265
5	-2	139	145
5	-1	155	166
5	0	175	152
5	1	158	163
6	-3	194	179
6	-2	159	158
7	-2	186	179
7	-1	179	184

TABLE II

FINAL ATOMIC AND GROUP PARAMETERS FOR $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.16510 (12)[b]	0.25920 (7)	−0.13657 (11)	0.01529 (22)	0.00361 (6)	0.01259 (19)	−0.00110 (8)	0.00422 (15)	0.00174 (8)
P_1	0.13354 (31)	0.13346 (16)	−0.08585 (29)	0.02131 (53)	0.00479 (14)	0.01755 (45)	−0.00360 (22)	−0.00074 (38)	0.00407 (20)
P_2	0.36419 (28)	0.33129 (15)	0.00091 (26)	0.01771 (47)	0.00404 (13)	0.01365 (39)	−0.00230 (19)	0.00252 (34)	0.00189 (18)
P_3	0.02584 (28)	0.32073 (16)	−0.31209 (28)	0.01569 (46)	0.00480 (13)	0.01667 (44)	0.00006 (20)	0.00305 (36)	0.00307 (20)
N_1	0.3571 (11)	0.1820 (6)	−0.3353 (10)	0.0326 (22)	0.0085 (6)	0.0217 (17)	0.0045 (9)	0.0137 (17)	0.0016 (8)
N_2	−0.0461 (12)	0.3302 (7)	0.0511 (12)	0.0306 (23)	0.0159 (10)	0.0283 (21)	0.0008 (12)	0.0208 (19)	−0.0019 (11)
C_1	0.2843 (11)	0.2116 (6)	−0.2579 (10)	0.0181 (19)	0.0052 (5)	0.0115 (15)	0.0014 (8)	0.0043 (14)	0.0016 (7)
C_2	0.0340 (12)	0.3042 (6)	−0.0209 (11)	0.0221 (22)	0.0071 (7)	0.0161 (18)	−0.0015 (9)	0.0075 (16)	0.0005 (8)
C_3	0.0892 (16)	0.1266 (7)	0.0820 (10)	0.0614 (37)	0.0095 (8)	0.0121 (15)	−0.0162 (15)	−0.0012 (19)	0.0040 (9)
C_4	0.2939 (12)	0.0621 (6)	−0.0820 (16)	0.0223 (22)	0.0051 (6)	0.0596 (38)	−0.0006 (9)	−0.0100 (23)	0.0096 (12)
C_5	0.3142 (12)	0.4303 (6)	0.0947 (11)	0.0292 (22)	0.0036 (5)	0.0226 (18)	−0.0006 (8)	−0.0035 (16)	0.0001 (8)
C_6	0.5093 (11)	0.3602 (7)	−0.0840 (11)	0.0211 (19)	0.0105 (8)	0.0224 (19)	−0.0083 (10)	0.0017 (15)	0.0072 (10)
C_7	−0.1641 (11)	0.3639 (7)	−0.2954 (12)	0.0158 (18)	0.0111 (8)	0.0318 (24)	0.0050 (10)	0.0077 (17)	0.0099 (11)
C_8	−0.0169 (12)	0.2560 (6)	−0.4798 (10)	0.0284 (21)	0.0067 (6)	0.0153 (16)	−0.0059 (9)	−0.0040 (15)	0.0018 (8)

Group	x_c[c]	y_c	z_c	δ	ϵ	η	B_1	B_2	B_3	B_4	B_5	B_6
Ring 1	−0.1503 (5)	0.0416 (3)	−0.2965 (4)	0.839 (5)	−2.567 (4)	0.589 (5)	4.4 (2)	5.6 (2)	7.1 (3)	7.5 (3)	7.6 (3)	6.6 (3)
Ring 2	0.5356 (5)	0.2238 (2)	0.2416 (5)	1.384 (5)	−2.413 (4)	−0.960 (5)	4.0 (2)	5.8 (2)	7.6 (3)	6.9 (3)	7.0 (3)	5.6 (2)
Ring 3	0.2120 (4)	0.4729 (3)	−0.3608 (4)	0.715 (6)	−2.316 (4)	2.795 (5)	4.5 (2)	6.1 (2)	7.1 (3)	7.0 (3)	6.7 (2)	5.6 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. [b] The standard deviations of the least significant figures are given in parentheses. [c] The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the ring with a fixed external coordinate system have been defined in previous papers.[10] B_i is the isotropic thermal parameter (in Å^2) of atom i in a given ring.

atom coordinates were idealized to fit best the known geometry (C–H = 1.09 Å, H–C–H = 109° 28′) and were added as additional fixed contributions to the calculated structure factors. There was an immediate drop in the values of R_1 and R_2 to 5.9 and 7.1%, and two cycles of least-squares refinement resulted in final values of R_1 = 4.9% and R_2 = 6.0% for the 1556 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$.

An analysis of the weighting scheme applied showed no systematic variations of R_2 with the magnitude of F_o or $\lambda^{-1} \sin \theta$. The error in an observation of unit weight was 1.76. This rather high value indicates that the values for $\sigma(I)$ assigned to all reflections were probably underestimated, although the relative weights are acceptable. A final difference Fourier map computed using all 1954 reflections above background ($F_o^2 \geq \sigma(F_o^2)$) contained no peak higher than 0.74 e$^-$/Å^3, compared with an average value of 2.75 e$^-$/Å^3 for a C atom. There was no evidence for extinction.

Table I presents the values of $10|F_o|$ and $10|F_c|$ (in electrons) obtained from the final refinement. The positional, thermal, and group parameters are presented in Table II, along with the corresponding standard deviations in these parameters as estimated from the inverse matrix. Table III gives the positional parameters of the group carbon atoms which may be derived from the data in Table II.

The orientations of the thermal ellipsoids are indicated in the figures. The anisotropy is especially evident for the N atoms, which are vibrating perpendicular to the C–N bonds, and for the methyl carbon atoms.

Description of the Structure

The crystal structure consists of discrete monomeric molecular units. The closest Ni–Ni distance is 8.42 Å. All intermolecular contacts appear to be normal, with the closest approaches between hydrogen atoms of two adjacent molecules being 2.40 and 2.45 Å, respectively. Figure 1 shows a stereoscopic view of the molecular structure. Interatomic distances and angles and their standard deviations as computed from the final parameters and the correlation matrix are presented in Table IV. It can be seen that the molecular geometry is essentially trigonal bipyramidal, with cyanide groups axial and the phosphine ligands occupying the equatorial plane. Although no symmetry is imposed upon the molecule, it very nearly possesses a threefold rotation axis, as shown in Figure 2. There is, however, a slight but significant distortion from the idealized trigonal-bipyramidal geometry; this distortion is again in the direction of a tetragonal-pyramidal configuration, as for $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$, but much less pronounced. Figure 3 shows the inner coordination sphere

TABLE III

DERIVED PARAMETERS FOR GROUP CARBON ATOMS

	x	y	z
		Ring 1	
C_1[a]	−0.0253 (6)[b]	0.0809 (5)	−0.2059 (6)
C_2	−0.0012 (6)	0.0128 (4)	−0.3014 (7)
C_3	−0.1262 (8)	−0.0265 (3)	−0.3919 (6)
C_4	−0.2754 (7)	0.0023 (5)	−0.3870 (7)
C_5	−0.2995 (5)	0.0704 (5)	−0.2916 (8)
C_6	−0.1744 (8)	0.1097 (3)	−0.2010 (6)
		Ring 2	
C_1	0.4668 (9)	0.2744 (4)	0.1412 (6)
C_2	0.6029 (7)	0.2304 (3)	0.1292 (6)
C_3	0.6717 (7)	0.1798 (5)	0.2295 (8)
C_4	0.6044 (9)	0.1733 (5)	0.3419 (7)
C_5	0.4683 (8)	0.2172 (4)	0.3540 (6)
C_6	0.3995 (6)	0.2678 (5)	0.2537 (7)
		Ring 3	
C_1	0.1244 (10)	0.4083 (4)	−0.3451 (7)
C_2	0.2298 (9)	0.3942 (3)	−0.4315 (7)
C_3	0.3174 (6)	0.4588 (5)	−0.4473 (6)
C_4	0.2996 (11)	0.5376 (4)	−0.3766 (8)
C_5	0.1942 (10)	0.5517 (3)	−0.2901 (7)
C_6	0.1066 (6)	0.4870 (4)	−0.2744 (6)

[a] The rings are numbered so that C_1 is attached to P; C_4 is *para* to C_1. [b] Estimated standard deviations are derived from those of the group parameters. Intra-ring distances are fixed (C–C = 1.392 Å).

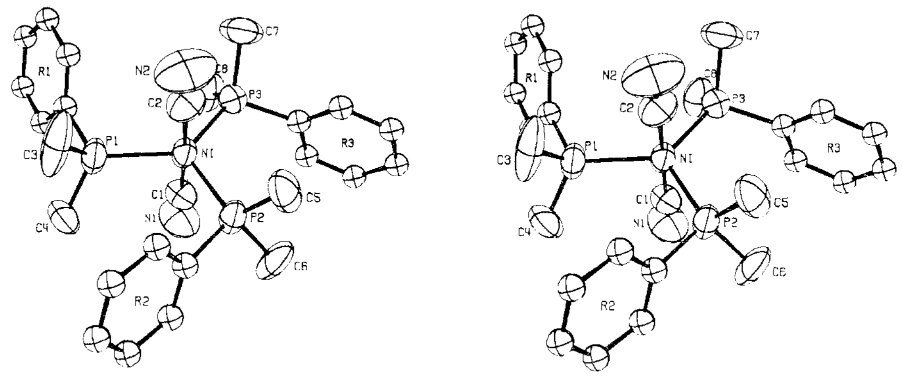

Figure 1.—Stereoscopic view of $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$.

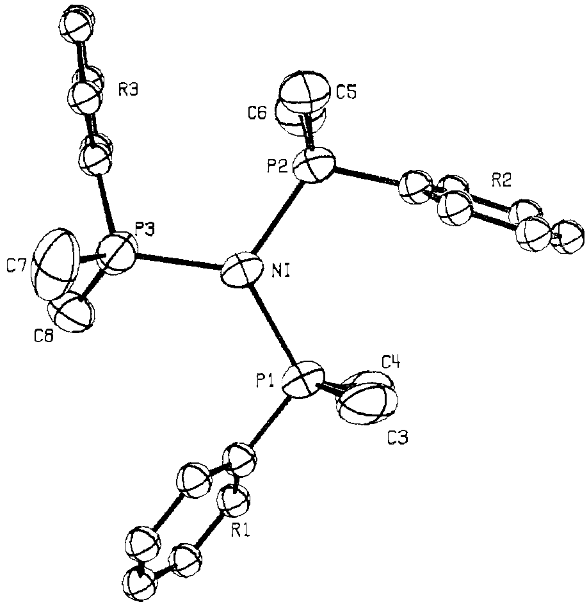

Figure 2.—Equatorial plane of $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$.

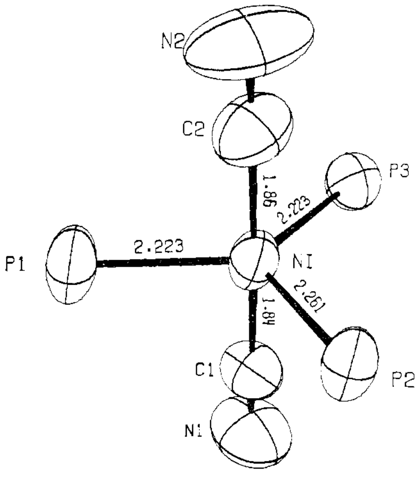

Figure 3.—Inner coordination sphere of $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$.

about the Ni atom; selected bond lengths are also presented. Again one of the Ni–P bonds in the equatorial plane is longer than the other two, and the angle opposite this long bond has expanded somewhat; the $Ni-P_2$ bond of 2.261 (3) Å is significantly longer than the other two distances of 2.223 (3) and 2.223 (3) Å, and the P_1-Ni-P_3 angle is 127.0 (1)° instead of 120°. The

Table IV

Selected Distances (Å) and Angles (deg)

Atoms	Distance	Atoms	Angle
$Ni-P_1$	2.223 (3)	C_1-Ni-P_1	88.6 (3)
$Ni-P_2$	2.261 (3)	C_1-Ni-P_2	92.4 (3)
$Ni-P_3$	2.223 (3)	C_1-Ni-P_3	87.8 (3)
$Ni-C_1$	1.836 (11)	C_2-Ni-P_1	90.0 (3)
$Ni-C_2$	1.860 (12)	C_2-Ni-P_2	91.1 (3)
C_1-N_1	1.146 (9)	C_2-Ni-P_3	90.5 (3)
C_2-N_2	1.140 (10)	$Ni-P_1-C_3$	117.3 (4)
P_1-C_3	1.806 (10)	$Ni-P_1-C_4$	116.7 (4)
P_1-C_4	1.786 (11)	$Ni-P_2-C_5$	116.1 (3)
P_2-C_5	1.828 (10)	$Ni-P_2-C_6$	116.7 (4)
P_2-C_6	1.803 (9)	$Ni-P_3-C_7$	118.2 (4)
P_3-C_7	1.826 (9)	$Ni-P_3-C_8$	115.3 (3)
P_3-C_8	1.813 (10)	$Ni-P_1-R_1C_1$	112.6 (3)
$P_1-R_1C_1$[a]	1.807 (6)	$Ni-P_2-R_2C_1$	111.6 (3)
$P_2-R_2C_1$	1.821 (7)	$Ni-P_3-R_3C_1$	111.6 (3)
$P_3-R_3C_1$	1.819 (9)	$C_3-P_1-C_4$	100.8 (7)
		$C_3-P_1-R_1C_1$	102.3 (5)
Atoms	Angle	$C_4-P_1-R_1C_1$	105.3 (4)
P_1-Ni-P_2	116.75 (11)	$C_5-P_2-C_6$	102.3 (5)
P_1-Ni-P_3	127.01 (11)	$C_5-P_2-R_2C_1$	103.1 (4)
P_2-Ni-P_3	116.21 (11)	$C_6-P_2-R_2C_1$	105.6 (4)
C_1-Ni-C_2	176.5 (4)	$C_7-P_3-C_8$	102.2 (5)
$Ni-C_1-N_1$	179.0 (9)	$C_7-P_3-R_3C_1$	103.8 (5)
$Ni-C_2-N_2$	178.5 (11)	$C_8-P_3-R_3C_1$	104.3 (4)

[a] R_iC_1 refers to carbon atom 1 on phenyl ring *i*.

cyanide groups are also bent away from this long bond, with a C–Ni–C angle of 176.5 (4)°. Thus the $Ni(CN)_2(P(C_6H_5)(CH_3)_2)_3$ molecule exhibits the same type of distortions from a trigonal bipyramid as does $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$, but all of the distortions are decreased in magnitude. Table V summarizes these distortions along with those for the $Ni(CN)_5^{3-}$ ion.

The Ni atom lies nearly on the plane of the three P atoms; the greatest distance of a P atom from the best weighted least-squares plane through these four atoms is 0.018 (3) Å for P_1. Both of the Ni–C–N linkages are essentially linear, with an average C–N distance of 1.14 Å. The P–C distances and C–P–C angles are within the range reported for phosphine complexes of transition metals. The average $P-CH_3$ distance is 1.81 Å. If the six $P-CH_3$ bonds are assumed to be equivalent, the standard deviation of a given distance from the mean is 0.016 Å, while the computed standard deviations range from 0.009 to 0.011 Å; hence the error in these bond lengths may have been slightly underesti-

TABLE V

DISTORTIONS OF $Ni(CN)_2X_3$ COMPLEXES FROM A TRIGONAL-BIPYRAMIDAL GEOMETRY

	X			
	CN^-	$P(C_6H_5)(OC_2H_5)_2$	$P(C_6H_5)(CH_3)_2$	Trigonal bipyramid
		Angle,[a] deg		
X_1–Ni–X_2	107.4 (5)	113.0 (2)	116.8 (1)	120
X_1–Ni–X_3	111.5 (5)	113.5 (2)	116.2 (1)	120
X_2–Ni–X_3	141.2 (5)	133.5 (2)	127.0 (1)	120
C_1–Ni–C_2	172.8 (5)	170.8 (8)	176.5 (4)	180
X_1–Ni–C_1	92.3 (5)	93.4 (5)	92.4 (3)	90
X_1–Ni–C_2	94.4 (5)	95.7 (6)	91.1 (3)	90
X_2–Ni–C_1	89.3 (5)	89.8 (6)	88.6 (3)	90
X_2–Ni–C_2	91.3 (5)	88.7 (5)	90.0 (3)	90
X_3–Ni–C_1	89.5 (4)	87.4 (5)	87.8 (3)	90
X_3–Ni–C_2	85.6 (4)	87.0 (5)	90.5 (3)	90
		Distance, Å		
Ni–X_1	1.992 (14)	2.289 (5)	2.261 (3)	
Ni–X_2	1.913 (13)	2.205 (6)	2.223 (3)	
Ni–X_3	1.902 (13)	2.189 (6)	2.223 (3)	

[a] The three X ligands lie in the equatorial plane, with Ni–X_1 being the longest bond in each case.

mated. However, the distortions of the molecule remain highly significant.

The derived bond distances can be corrected for the effects of thermal motion,[11] the most reasonable assumption appearing to be that of a "riding" model. The calculated bond lengths increase slightly; for example, the Ni–P_3 distance increases from 2.223 to 2.231 Å, but the relative differences in bond lengths remain essentially the same.

The variation in Ni–P bond lengths is similar to that cited in the preceding paper, but less extreme: the values of 2.223, 2.223, and 2.261 Å can be compared with those of 2.189, 2.205, and 2.289 Å in $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$. The average Ni–C distance of 1.85 Å, however, is closer to the axial Ni–C bond length in $Ni(CN)_5^{3-}$ of 1.84 Å than to the 1.88 Å in $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$. This seems to be a consequence of the more idealized geometry: the C–P nonbonded interactions in the two $Ni(CN)_2(PR_3)_3$ complexes are approximately the same, but the less distorted trigonal bipyramid permits shorter Ni–C bonds while keeping the same C–P interactions.

At this time the trends away from an idealized trigonal-bipyramidal configuration toward a tetragonal-pyramidal configuration displayed in Table V are difficult to interpret. Thus although the basic properties of various phosphines have been determined by indirect means,[12] there appears to be no definitive information on where one might place CN^- in this scheme. If indeed one is seeing the effects of decreasing σ donation in approaching the tetragonal pyramid, then one could conclude that CN^- has decreased σ-donation character over the phosphite ligand. In fact, comparative studies of $Ni(CN)_2(PR_3)_3$ systems may provide a sensitive and direct measure of such donating properties. Nevertheless, there are obvious steric factors in these systems: steric factors must be the reason that the compound $Ni(CN)_2(P(C_6H_5)_3)_3$ is not formed, since $P(C_6H_5)_3$ is less basic than $P(C_6H_5)(CH_3)_2$ but more basic than $P(C_6H_5)(OC_2H_5)_3$.

Further chemical and structural studies are in progress which may provide additional insight into the factors involved in the determination of the distortions of related five-coordinate complexes of Ni(II).

Acknowledgments.—We are indebted to Dr. E. Alyea and Professor D. W. Meek for supplying the crystals and for helpful conversations. J. K. S. gratefully acknowledges the support of the National Science Foundation through a predoctoral fellowship. We thank the National Science Foundation for its support of this work.

---

[11] W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

[12] W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
LOUISIANA STATE UNIVERSITY IN NEW ORLEANS, LAKEFRONT, NEW ORLEANS, LOUISIANA 70122

Preparation and Spectral Studies of a Series of Rhodium(III)–Acetonitrile Complexes

BY BASIL D. CATSIKIS AND MARY L. GOOD

Received October 31, 1968

A series of rhodium(III)–acetonitrile complexes of the general formula $RhCl_m(CH_3CN)_n^{3-m}$ have been prepared and characterized by their visible, infrared (4000–70 cm^{-1}), and proton nmr spectra. The preparation of the *trans*-$RhCl_4(CH_3CN)_2^-$ is reported for the first time. The configurations of the two geometrical isomers of the complex $RhCl_3(CH_3CN)_3$ are elucidated on the basis of their proton nmr spectra. The visible and far-infrared spectra of these rhodium(III) acetonitrile complexes are quite similar to those exhibited by the analogous rhodium(III) pyridine complexes, thus indicating the considerable strength of acetonitrile as a ligand for second-row transition metals.

Introduction

The reactions between transition metal halides and various nitriles and the characterization of the resulting metal complexes have attracted a great deal of attention.[1] However, there is relatively little known about nitrile complexes of rhodium(III), although Lebedinskii and Fedorov[2] have reported the synthesis of the species

---

[1] R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965), and the references quoted therein.

[2] V. V. Lebedinskii and I. A. Fedorov, *Ann. Inst. Platine* (U.S.S.R.), **12**, 87 (1935).